직경이 제어된 단일벽 탄소나토튜브의 촉매성장

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Catalytic Growth of Diameter Controlled Single Walled Carbon Nanotubes

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Abstract

Single wall carbon nanotubes (SWNTs) were successfully produced by catalytic thermal decomposition of C_2H_2 at 800 ℃ over magnesia supported Co-Mo catalysts in a tubular flow reactor under an atmosphere of hydrogen flow. The loading amount of metals on magnesia support varies from 5 to 40 wt% with a 1:1 wt ratio of the two metals. Raman spectroscopy was exclusively used to characterize the growth of SWNTs. From radial breathing mode (RBM) frequencies of Raman spectrum it was revealed that bundle type SWNTs were grown with diameters ranging from 0.78 to 2.07 nm and SWNTs with thinner diameter become abundant for the catalysts having lower metal loading. Good quality and high density SWNTs was grown at the catalyst loading weight of 20 to 30 %. Using these high performance bimetallic supported catalysts it is assumed that scale-up production method of SWNTs can be readily achieved with low cost.

Introduction

Single-walled carbon nanotubes (SWNTs) offer great promise for use functional molecular scale devices because of their remarkable mechanical and electrical properties [1]. It is well established that the electron and phonon nanotube properties are significantly dependent on their symmetry and diameter. Since control of the nanotubes diameter can be an important issue for different applications of these materials, study of the influence of the catalyst on the diameter distribution in the SWNT sample is an important step for improving the synthesis of SWNTs for specific applications. In the growth of SWNTs, several methods have been employed such as laser vaporization [2], arc discharge [3], and chemical vapor deposition (CVD) [4-7]. Laser vaporization and arc discharge methods are advantageous for growth the high-quality SWNTs, but are difficult to control the structure of the CNTs during the growth because of high-growth temperature. On the other hand, CVD method is one of the promising candidates for producing SWNTs for industrial applications, because it is suitable for mass production and has potential of growth control by engineering the catalyst. Several successful experiments on CVD of SWNTs have reported through catalytic decomposition of CO, benzene and hydrocarbons. However, the catalyst productivity of the method is low. Recently, reported literature [7] observed very high productivity of SWNTs from the decomposition of methane over $Mo_{0.05}Co_{0.05}Mg_{0.9}O$ catalyst at 1000 ℃. In the current contribution we report a method that afford good quality SWNTs with higher output ratio (~ 300 %) from the decomposition of

acetylene over Co-Mo catalyst supported on MgO at a moderate temperature.

Experimental

Bimetallic Co-Mo catalysts were prepared through impregnation method described elsewhere [8] by using required amount of $Co(NO_3)_2.6H_2O$, $(NH_4)_6Mo_7O_{24}.4H_2O$ and MgO. The loading amount of the metals on magnesia support varies from 5 to 40 wt% with a 1:1 wt ratio of the two metals. The growth of CNTs was carried out in a horizontal tubular reactor at 800 ℃ by flowing C_2H_2/H_2 (10/100 sccm). Carbon yields over the catalysts for 30 min growth time were investigated. The structure and morphology of CNTs were determined by using scanning electron microscopy (SEM) and FT-Raman spectroscopy.

Results and Discussion

Table 1 presents the deposited carbon yield with metal wt% over the catalysts for 30 min growth time. Carbon yield (deposited carbon during reaction) is defined as the mass increase divided by the original catalyst mass. Table 1 indicates that catalyst loading with 20 - 40 weight percent showed the better performance for carbon deposition.

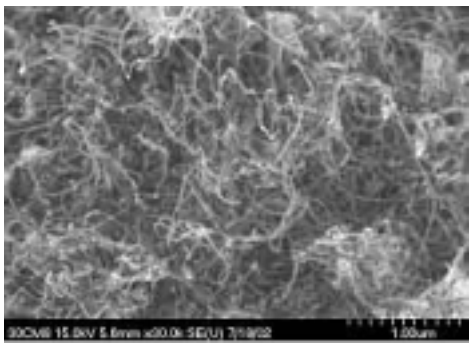

Figure 1: SEM micrograph for CNTs grown over 30 wt% metals loaded catalyst.

Table 1: Deposited CNTs yield (%) as a function of metals loading in the catalysts.

Metal wt%	Carbon Yield (%)
5	6.06
10	27.08
20	105.85
30	216.96
40	336.51

Figure 1 represents the SEM image of CNTs grown for 30 min at 800 ℃ by C_2H_2/H_2 (10/100 sccm) over 30 wt% metals loaded catalyst. According to the electron microscopic observations, every catalyst particle is covered by carbon nanotubes of regular diameter. The average value of the outer diameter is approximately 10-20 nm. The average length, between two entanglement points, is at the micron scale, but it was impossible to follow individual filament as both ends were not observed together. From SEM view it is not clear whether the CNTs are MWNTs or bundle type SWNTs.

Figure 2 shows the Thermal Gravimetric Analysis (TGA) curves for CNTs grown over 20 wt% Co-Mo. The TGA was measured under the flow of 100 sccm Ar : O_2 (92 : 8 v/v) mixed gas, varying temperature from room temperature to 1000 ℃ with a heating rate of 5 ℃/min. The weight loss is due to the combustion of carbons in the grown samples by O_2. The residual weight at high temperatures is due to metal

oxides produced from the catalyst. The weight loss is very small below 400 ℃ and one step large weight loss commences at around 400 ℃ and ends at around 600 ℃ (Fig. 2). Tang et al. and Kitiyanan et al. reported that the oxidative temperatures were around 330 ℃ for amorphous carbon, 500 - 600 ℃ for SWNT, and 700 ℃ for MWNT, respectively [7,9]. The TGA curves of our grown CNTs over the catalysts are very similar to those of SWNTs observed in the above literatures. The inset on the right top of Fig. 2 shows differential thermal analysis (DTA) curves for the grown CNTs. The DTA curves show three stepwise burning temperatures at ~ 200, 500, and 930 ℃ and more than 90 % weight losses were observed at the temperature range of 400 - 600 ℃. Based on the TGA and DTA analyses, it is concluded that our grown CNTs are primarily SWNTs.

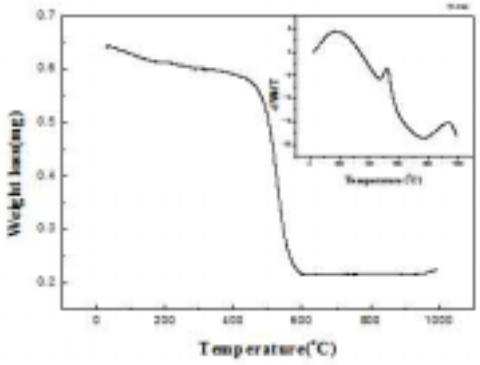

Figure 2: TGA and DTA (inset) graphs for CNTs grown over 20 wt% metals loaded catalyst.

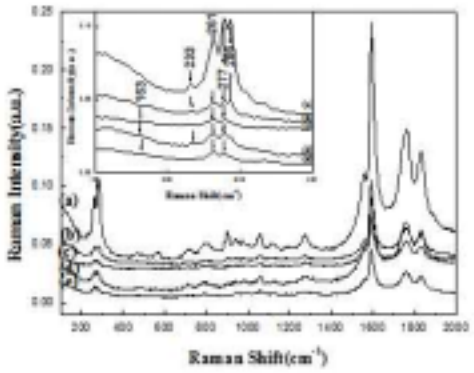

Figure 3: Raman spectra for CNTs grown over (a) 5 (b) 10 (c) 20 (d) 30 (e) 40 wt% metals loaded catalysts, respectively. RBM peaks distribution show in the inset of the figure.

To confirm the presence of SWNT in our grown samples, Raman measurements were conducted at room temperature using an excitation wavelength of 1064 nm (Nd : YAG laser) for the CNTs shown in SEM figure 1. The Raman scattering peak positions (Fig. 3) at low frequency region ($\omega \leq 500$ cm^{-1}) for SWNTs are strongly tube diameter dependence [10]. In figure 3 Raman peak at 262 cm^{-1} in the radial breathing mode (RBM) region (A_{1g} and E_{1g} symmetry) is an indication of formation of SWNTs and diameter of the tube is 0.85 nm [10]. Raman observation proposes that the tubes observed in SEM are composed of bundle type SWNTs. The bundle type SWNTs was further confirmed by TEM observation. The high frequency group of bands consists of three resolved peaks at 1593, 1757 and 1835 cm^{-1}; frequency peak at 1757 cm^{-1} results due to the second-order Raman process involving the combination of the RBM and the tangential mode (G-line) at 1593 cm^{-1}, which strongly supports the growth of SWNTs. The peak at 1593 cm^{-1} seems to appear due to the C-C stretching Raman active E_g modes, indicating the formation of graphitic sheets and unresolved shoulder triplet peaks (A_{1g}, E_{1g}, E_{2g}) at 1535, 1550 and 1562 cm^{-1} have been confirmed

from the theoretical calculations for SWNTs [10]. Peak at 1283 cm^{-1} (D_1 band) indicated the polycrystalline graphitic carbon materials.

The intense RBM peaks at 286, 277 and 261 cm^{-1} for SWNTs grown over 5 and 10 wt% metals loaded catalysts (Fig. 3 inset) indicating that the sample abundant with tubes having diameters ranging from 0.78 to 0.86 nm. But for the higher metal loaded catalysts the RBM peak at 286 cm^{-1} was disappeared and more RBM peaks were observed at lower wave number which were the measure of the tubes with thicker diameters. Thus by changing the metal loading in the catalysts we avail to control the diameter of the SWNTs.

Conclusions

It is concluded that large amount of SWNTs could be produced successfully by rapid thermal chemical vapor deposition (RTCVD) method from catalytic decomposition of C_2H_2 at 800 ℃ in H_2 atmosphere. It was also established, how to control the growth density and diameter of SWNTs by varying the metal loading in the catalyst. It was observed that more than 20 wt% metals loaded Co-Mo binary system with 1 : 1 wt ratio of the two metals produced high performance selective catalysts in order to grow large amount of SWNTs, 336.51 yield % of good quality SWNTs was achieved over 40 wt% metals loaded Co-Mo catalyst. Diameter of the SWNTs ranges from 0.78 to 2.07 nm and thinner tubes become abundant for the catalyst having lower metal loading.

Acknowledgement

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