

Catalytic Growth and Properties of Carbon Nanotubes from Fe-Mo/MgO by Chemical Vapor Deposition

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Carbon nanotubes (CNTs) are largely synthesized on Fe catalysts by catalytic chemical vapor deposition. The various shapes and compositions of these nanostructure CNTs were obtained by controlled parameters such as the reaction temperature, gas-mixing ratio. The influence of these parameters is investigated, together with observations of the produced materials after the purification processes. A diameter of CNTs, range from 2 to 10 nm, closely correlated with the size of the catalyst particle found attached to the tube end. The yield of CNTs was estimated to be 88.5 % and the purities of CNTs thus obtained were more than 80 %. The experimental results were documented with field emission scanning electron microscopy and raman spectroscopy and transmission electron microscopy, both before and after the purification.

Keywords : Carbon nanotubes, Growth, High density, Catalytic CVD

1. INTRODUCTION

The remarkable physical, chemical and electrical properties of CNTs make them attractive possibilities for many microelectronic application areas and nanoscale devices. Since the CNTs were firstly discovered in 1991, extensive interests were focused on the fabrication of CNTs. In recent several years, due to its low cost and large-scale production capacity, the catalytic decomposition of hydrocarbon has become one of the most important synthesis methods than arc discharge, laser ablation and chemical vapor deposition (CVD) for carbon micro- and nano-structures. Dai[1] first synthesized CNTs by CVD on a Mo/Al₂O₃ catalyst with CO as the carbon feedstock, but the yield was very low. Recently, several studies [2-6] have demonstrated that the catalytic method could be a possibility for the selective and controlled grown CNTs on various catalysts and support materials and high-quality of CNTs at relatively low cost. All of those literatures indicated that the yield and quality of CNTs are very sensitive to catalyst preparation.

In general, silicon oxide, magnesia and alumina have all been employed as supporting materials. These materials were easily aggregated and the effective catalyst area was decreased, leading to a decrease in the yield. We also employed PEG 200 among the organic

additives such as citric acid and poly-(ethylene glycol) for solving the upper problems. In fact, it is the most effective as a dispersant at improving the yield of CNTs due to the effect of additives on the specific surface area of the catalyst[7]. The CNTs were extracted by dissolution of MgO and part of the Fe catalyst in the PEG 200 aqueous solution. In addition, MgO presents the advantage over the supports such as alumina, spinel, and silica that it can be readily dissolved in acids. Therefore, the produced CNTs can be removed easily from support by a simple acidic treatment to obtain a sample containing high yields of CNTs (70-80 %).

In this work, we reported an improved CVD method for preparation of CNTs with high productivity using a novel aerogel supported Fe-Mo/MgO catalyst. High qualities of CNTs can be synthesized by catalytic decomposition of methane and acetylene over well-dispersed metal particles supported on MgO. In order to achieve the highest yield and quality and the highest purity of CNTs, we investigated in detail the effect on the growth temperature and reaction gas among the many growth parameters. Moreover, we adopt a purification process to raw CNTs synthesized by CVD. The yield, the quality and the quantity of CNTs have been investigated by Raman spectroscopy, field-emission scanning electron microscopy and TEM, both before and after the purification.

2. EXPERIMENTAL

2.1 Catalyst preparation

The Fe/Mo/MgO catalysts were prepared by a wet mechanical mixing and combustion method[8]. The weighted amounts of compounds $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (99.0 %, Samchun), $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (98.0 %, Samchun), and $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (99.99 %, Aldrich) were dissolved in the minimum amount polyethylene glycol 200 (PEG 200) to yield the molar ratios as in Fe: Mo: MgO=1:0.05:13 were mixed together. Then the above solution were transferred to a quartz boat, and directly brought into a furnace, heated to 550 °C, where it ignited and stayed on furnace for about 15 min. The boat was taken out and cooled to room temperature. The catalyst prepared this way is in the form of very fine powder with surface areas $\sim 600 \text{ m}^2/\text{g}$. The powder was calcined at 500 °C in air for 30 min before used for carbon nanotubes growth.

2.2 Carbon nanotube growth

The synthesis of CNTs was carried out in a simple CVD setup made of a horizontal quartz tube furnace and gas flow control system. In a typical growth experiment is as follow: 200 mg catalyst power was uniformly put into an alumina boat inside a quartz tube, and when the furnace reached the reaction temperature, 800 °C to 1000 °C, the quartz boat was inserted into the center of reactor while the nitrogen as the protective gas flow was maintained for 5 min. Subsequently, a mixture of $\text{CH}_4:\text{H}_2=75/300$ or $\text{C}_2\text{H}_2/\text{N}_2/\text{H}_2=50/1000/25$ or $\text{C}_2\text{H}_2/\text{N}_2=50/1000$ was introduced. The growth reaction was maintained for 30 min. After methane and hydrogen flow was turn off and nitrogen flow turn on and temperature reduced to room temperature. The black materials were then weighted and characterized.

2.3 Carbon nanotube purification

In order to eliminate the metallic catalysts and the amorphous carbon, we adopt the following purification procedures to as-grown products synthesized by above catalytic CVD. The purification procedure of as-grown products is as follows; the sample was refluxed in 30 % nitric acid at 100 °C for 12 h. The sample was washed thoroughly with deionized water, the as-grown products were immersed in 6 M hydrochloric acid for 24 h. These two processes were repeated several times until the color of acid was unchanged, respectively. The sample was washed thoroughly with deionized water. After rinsing and drying, the black sediment was finally obtained.

2.4 Characterization

As-prepared samples were characterized by field emission scanning electron microscope (FESEM) [JEOL, JSM-6700F]. Raman spectroscopy [Burker, RFS 100/S] which was equipped with an Nd:YAG laser with an excitation wavelength of 1064 nm was used to demonstrate

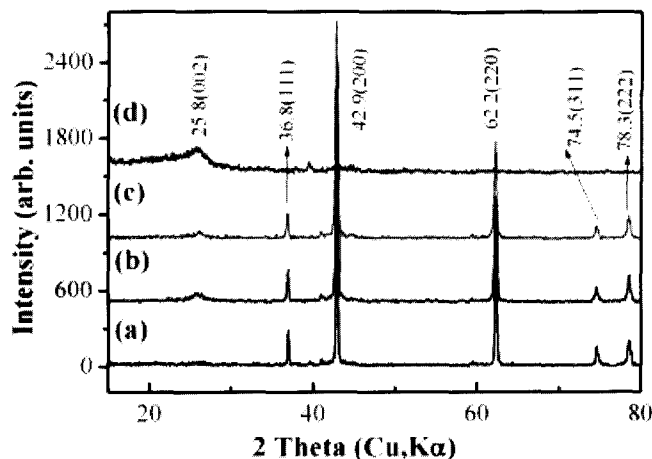


Fig. 1. XRD pattern of as-synthesized carbon nanotubes (a) at 1000 °C, (b) at 900 °C, (c) at 800 °C, and (d) the purified carbon nanotubes.

the diameter distribution of CNTs. This material was sonicated with methanol, and a drop place on a holey carbon grid for observation in the transmission electron microscope (TEM). Thermogravimetric analysis (TGA) [TA Instrument, TGA2050] was used to investigate weight change and the content of carbon in the sample.

3. RESULTS AND DISCUSSION

Figure 1 is shown the XRD pattern for as-synthesized and purified samples. The difference between the as-synthesized and the purified CNTs has been investigated. As shown in Fig. 1(a)-(c), it was shown the diffraction peak of CNTs, graphite, and metal particles. A sharp diffraction peak at $2\theta = 25.8^\circ$ with a d-value of 0.345 nm is from graphite. The peak at $2\theta = 36.8, 42.9, 62.2, 74.5$ and 78.3 corresponds to MgO. Unfortunately, unwanted impurities may be included in the CNTs during their synthesis. These impurities include amorphous carbon, fullerenes, and the remains of primary materials. The XRD profile is shown Fig. 1(d) corresponds to the sample of CNTs after purification process. It presents some change, the catalyst peaks nearly disappeared after acid treatment but a small quantity of peaks still remained. It was considered due to graphite layers which have resistance to the HNO_3 acid; therefore, a small amount of encapsulated carbon coexists in the samples.

Figure 2(a)-(c) is shown the typical FESEM images of the as-synthesized carbon materials produced by catalytic reaction of CH_4 over Fe-Mo/MgO catalyst at a growth temperature range, from 800 °C to 1000 °C. Synthesized carbon filaments are mostly intricate and

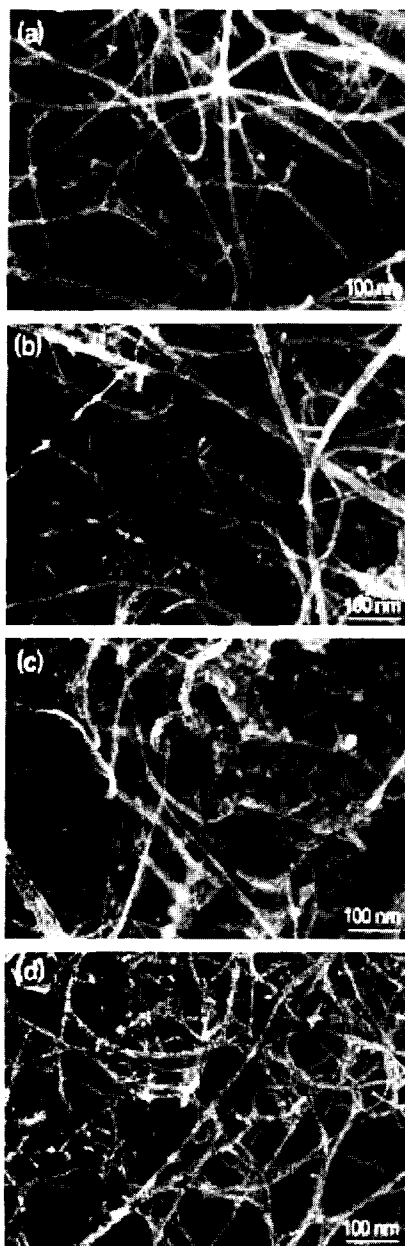


Fig. 2. FESEM images of grown CNTs (a) at 1000 °C, (b) at 900 °C, (c) at 800 °C, and (d) the purified carbon nanotubes.

bundle up together. As shown in the SEM images, we could find the effect of the growth temperature on the structure of CNTs. In a reaction temperature range of 900–1000 °C, the morphology of the as-synthesized CNTs was almost similar, while the yield of CNTs was slightly increased with increasing reaction temperature. However, the yield of CNTs rapidly decreases and amorphous carbon materials were appeared in the carbon product when the reaction temperature was 800 °C. To quantify the yield, we conducted the weight gain measurement. For a 30 min growth experiment, the yield of CNTs defined as the weight gain ratio of the produced

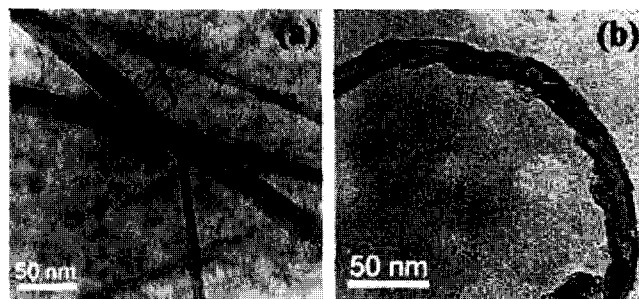


Fig. 3. TEM images of carbon nanotubes grown at 1000 °C for 30 min under a flow of $\text{CH}_4/\text{H}_2/\text{N}_2$ (a) body, and (b) tip, respectively.

carbon bundles to the starting catalyst materials including support materials was about 108.28 %, 96.9 %, and 88.5 % in a reaction temperature at 1000 °C, 900 °C, and 800 °C, indicating a high yield of carbon filament, respectively. FESEM images of purified CNTs (see in Fig. 1(d)) indicated that most of amorphous carbon was dramatically decreased during purification process and the yield of CNTs was increased significantly. As a result of purification process, the weight of the soot sample was reduced to about 10 wt.% of the original sample and the yield of 96.6 wt.% of as-grown samples.

TEM was employed to further characterize the tubular structure of the nanotubes grown using catalytic CVD. Figure 3 shows cross-sectional TEM (200 kV, CM-20) images of carbon nanotubes grown at 1000 °C for 30 min under a flow of $\text{CH}_4/\text{H}_2/\text{N}_2$. The nanotubes (Fig. 3(a)) exhibit exclusively a multi-walled bamboo-like structure with a central hollow region. The closed tips (Fig. 3(b)) are encapsulated catalytic particles and the curvature of compartment layer is oriented toward the closed tip. The tip growth model is adequate to describe these results. The catalytic particles are attached to the tips of nanotubes.

Figure 4 is the high-resolution TEM (HRTEM, 300kV, JEM-3000F) result showing the interior, wall structures (Fig. 4(a)) and tip (Fig. 4(b)) of nanotubes grown at 1000 °C for 30 min under a flow of $\text{CH}_4/\text{H}_2/\text{N}_2$. The fringes in a multi-wall are individual cylindrical graphitic layers. The lined part is nearly 3.06 nm and this has 9 graphitic walls. As can be seen in Fig. 4(a), the nanotubes have outer diameters of about 10 nm and inner diameters of 2–3 nm. This is clearly consistent with the fact that the graphite spacing is $c/2 = 0.34$ nm. High resolution TEM of purified CNTs indicated that even after HNO_3 and HCl treatments the tubes existed in the form of bundles. General quality of the tubes was found to be good, however, with a very few defects. The tube surfaces were not found to be associated with any amorphous carbon. In general, the number of walls of the tubes was 2–25 with an average outer and inner diameter of 4.8–10.1 nm, respectively.

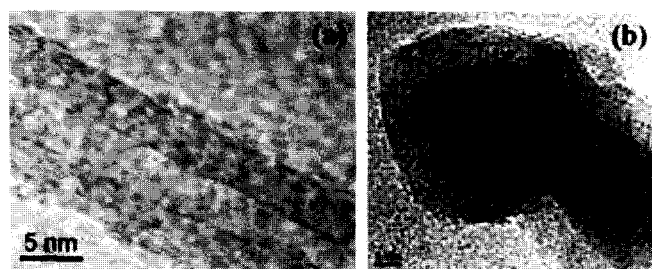


Fig. 4. HRTEM images of carbon nanotubes grown at 1000 °C for 30 min under a flow of CH₄/H₂/N₂ (a) body, and (b) tip, respectively.

The Raman scattering spectra of the synthesized and the purified CNTs are shown in Fig. 5. The difference in microstructure between the as-synthesized CNTs and the purified CNTs has been further investigated by raman spectroscopy. The spectrum corresponds to a typical raman spectrum of the as-grown materials produced at three different growth temperatures and the purified CNTs, respectively. The G-band (observed at 1590 cm⁻¹) is the strongest peak. This very narrow and strong peak associated with the G-band indicating that structural defects along the tube wall are low. The peak associated with the D-band (1276 cm⁻¹) is related to the level of disorder carbon. Its strength can be either identified with wall disorder or with the presence of carbon coating the outside of tubular bundles. The low I_D/I_G values indicate that the CNTs have a perfect graphite structure. The relatively weak D-band compare to G-band demonstrates that the as-synthesized samples contain small amount of amorphous carbon materials, revealing that high-purity CNTs are synthesized in our method. As shown in Fig. 5(a), several peaks are observed in the spectrum: 104-264 cm⁻¹. These peaks are presented the radial breathing mode (RBM) in the 50-300 cm⁻¹ range, which is well known to be strongly dependent on the diameters of CNTs. We used the equation as follows: ω (cm⁻¹) = 12.5 + 223.5/d (nm) can be used to calculate the CNT diameters because the as-synthesized CNTs are packed into a bundle due to van der Waals interaction. According to this formula, the RBM peaks corresponding to the CNTs with inner diameters of from 0.41 to 1.13 nm were calculated. Fig. 5(d) is shown the Raman spectra of purified CNTs. The intensities of the disorder line (so called D-band) were relatively decreased compare to the as-grown CNTs (as shown Fig. 5(a)), while it appears that the RBM mode was changed. Through the reference[9] it is possible to assign an individual RBM mode in the Raman spectra to a particular E₁₁ band gap energy.

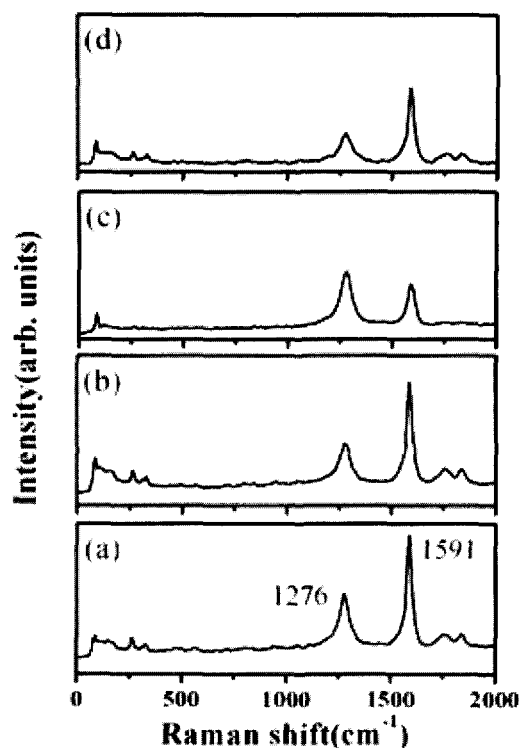


Fig. 5. Raman spectrum of as-synthesized carbon nanotubes (a) at 1000 °C, (b) at 900 °C, (c) at 800 °C, and (d) the purified carbon nanotubes.

Figure 6 is shown the TGA graphs of the as-prepared products and the purified samples. Thermogravimetric analysis was performed in an oxidation environment to evaluate the resistance of different carbon materials toward oxidization. The sample was oxidized at temperature of 450-600 °C. The maximum oxidation rate of the as-synthesized sample is found at around 590 °C, while for the purified sample the maximum rates appear almost identically at 530 °C. When the oxidation is carried out up to 1000 °C, an interesting phenomenon is noticeable for carbon materials. According to the literature[10], around 330 °C is a temperature to burn out amorphous carbon, 500-600 °C is for SWNTs, and 700 °C is for MWNTs. Therefore, our results can be a promising way to large-scale the synthesis of carbon nanotubes. Moreover, it is well known that DTG (Derivative TG) is a common method for quantitative analysis, the content of carbon materials corresponding to its peak area in DTG. Thus, it can be calculated that the yield of nanotubes is 85 % in the raw produced with Fe-Mo as catalyst. From above these results, our results show a promising technique for large-scale synthesis of carbon nanotubes which is relatively simple and effective.

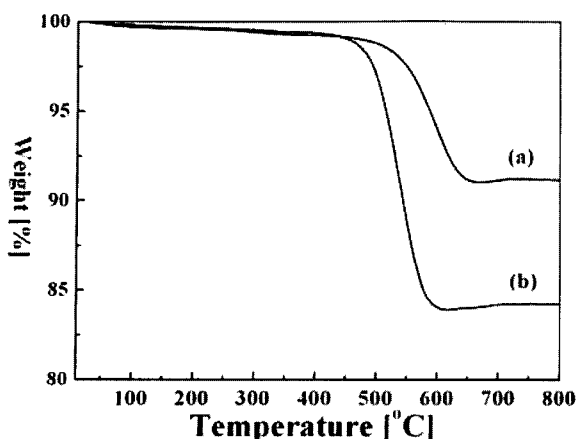


Fig. 6. Typical TGA curves for (a) the synthesized carbon nanotubes at 1000 °C and (b) the purified carbon nanotubes.

4. CONCLUSION

In this paper, we have shown that the large-scale production of CNTs is possible by catalytic chemical vapor deposition method similar to the two techniques, arc discharge and laser evaporation. Indeed, the method using catalytic decomposition of methane over well-dispersed metal particles supported on MgO at 1000 °C has been adapted to produce large quantities of CNTs. we have successfully produced CNTs by catalytic decomposition of CH₄ over Fe particles dispersed on porous MgO nanoparticles in high yield of above 88.5 %. The inner diameters of CNTs are in the range of 2-3 nm and outer diameters of about 10 nm. The yield of CNTs was slightly increased with increasing reaction temperature, but the yield of CNTs rapidly decreases and amorphous carbon materials were appeared in the carbon product when the reaction temperature was 800 °C. The synthesis yield was estimated for removal of support by a simple purification process. The purities of the CNTs produced were estimated approximately to be of the order of 83 %. In the near future, these needs to be investigated and the purification of CNTs produced will be optimized to obtain pure CNTs in large quantities. And other reaction conditions of CNTs production, i.e., increasing (until 1200 °C) and decreasing the reaction temperature, under CH₄/H₂, will be further investigated to improve the quantity and enhance the yield of CNTs.

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