촉매제어를 통한 촉매화학기상증착법으로 성장시킨 탄소나노튜브의 특성분석

김종식, 김관하, 김창일*
중앙대학교 전자전기공학부

The charateristics of grown carbon nanotubes by controlled catalyst preparation at the catalytic chemical vapor deposition

Jong-Sik Kim, Gwan-Ha Kim, and Chang-Il Kim*
School of Electrical and Electronic Engineering

Abstract - Carbon nanotubes (CNTs) with few defects and very small amount of amorphous carbon coating have been synthesized by catalytic decomposition of acetylene in H_2 over well-dispersed metal particles supported on MgO. The yield, quality and diameters of CNTs were obtained by control of catalyst metal compositions to be used. The optimization condition of carbon nanotubes with high yield is when Co and Mo are in a 1:1 ratio and Fe metal contents to Co is increased on magnesium oxide support. It is also found that the diameter of the as-prepared CNTs can be controlled mainly by adjusting the molar ratio of Fe-Mo, Co-Fe, and Co-Mo versus the MgO support. Our results indicated that desired diameter distribution of CNTs is obtained by choosing or combining the catalyst to be employed.

1. Introduction

CNTs have been extensively studied with a great deal of interest at a very rapid rate in the last decade due to their unique electronic and extraordinary mechanical properties. Until now, the synthesis of high-quality CNTs in various forms has been widely grown and studied by many research teams using various methods. Among others, the CVD process is particularly considered to be the most promising technique and very sensitive to the operation conditions for producing high quality nanotuebes at large scale because synthetic parameters which control the physical structure of CNTs are easily adjustable. This technique has been used for years to synthesize carbon fibers since Endo et al.[1] confirmed the presence of carbon nanotubes during the synthesis of vapor grown carbon fibers. After then, recent several studies[2-5] have demonstrated that the catalytic method could be a possibility for the selectively grown CNTs on various catalysts and support materials and high-quality of carbon nanotubes at a very low cost.

In addition to obtain controlled or optimized for various applications of CNTs, it is necessary to attain the controlled growth of the CNTs with a uniform diameter should be obtained. However, the choice of the catalysts as one of the most important parameters for controlled synthesis of CNTs has been considered lower than others. In this work, we investigated the factors affecting the catalyst and growth temperature on the CVD nucleation, growth and structural type of CNTs while using acetylene (C_2H_2) as the carbon feed source. We used the magnesium oxide support material known to be easily removed by a simple acidic treatment and transition metals including Fe, Co and a binary mixture Co-Fe as the catalyst for CNTs growth. To increase the production and improve the quality of CNTs, Mo as additives was used to dilute the catalyst.

2. Experimental details

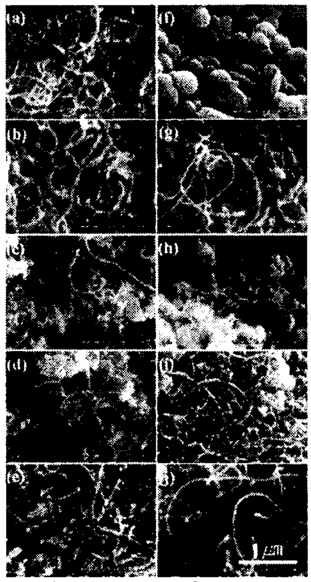
The supported catalysts were prepared by the impregnation method with magnesium oxide powder and an aqueous solution of the transition metal salts or an aqueous mixture solution of different transition metals (using different molar ratio between catalyst metals as shown in table 1), following by sonication for 1 h. The content of the metals was 5 wt% for all of the catalysts. After then, the catalyst was dried overnight at 130℃ in an oven and calcining at 400℃ for 4 h.

The synthesis of carbon nanotubes was carried out in a quartz tube reactor placed in a horizontal furnace with temperature controller. The quartz reactor has 23 mm of inner diameter and 240 mm of the tube length. In each synthesis process, 100 mg of catalyst powder was placed in a ceramic boat at the center of quartz tube. The synthesis process includes the following temperature cycle; (1) Argon stream up to the 1000℃ of reaction temperature. (2) During 1 h of reaction time, three gaseous stream of reacting gas (acethylene) and reduction gas (hydrogen) and carrier gas (argon) were passed over the catalyst, and set to 50, 25 and 1000 ml/min, respectively. (3) Argon stream down to room temperature.

The morphology and the structure of the as-synthesized carbon materials were characterized by field emission scanning electron microscope and Raman scattering. Raman spectroscopy with an Nd:YAG laser with an excitation wavelength of 1064 nm was employed to demonstrate the diameter distribution of carbon nanotubes. Powder X-ray diffraction patterns of the synthesized carbon nanotubes were perfomed with a rotating anode and Cu-Kα radiation to understand the influence of the catalyst composite condition.

3. Results and discussion

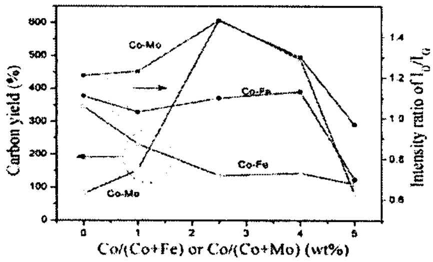
We have studied the effect of catalyst types on the grown of nanotubes. The carbon nanotubes were grown at 800℃ for 1 h under a flow of $C_2H_2/H_2/Ar$.



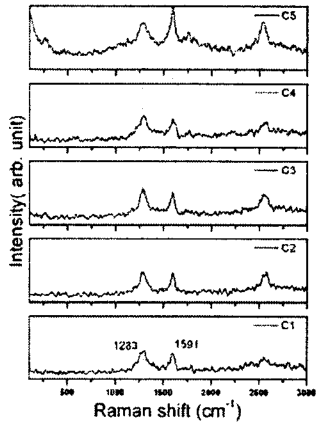
<Figure 1> The SEM images of the carbon nanotubes synthesized using the different catalyst molar ratio. ((a)~(e)=C1~C5, (f)~(j)=C6~C10)

Figure 1 shows the SEM images of the carbon nanotubes synthesized according to the Co-Fe or Co-Mo catalyst molar ratio, respectively. SEM observation of the composite powders revealed that the materials dominantly consisted of a high or low density of CNTs bundles with lengths of up to several micrometers in all samples except for the sixth sample. CNTs bundles with a maximum diameter close to 50 nm could be mainly detected. Residual catalyst metals or carbon material having other morphology was also observed.

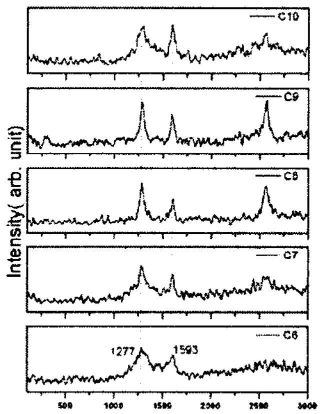
Figure 2 shows the carbon deposit or carbon yield and intensity ratio of I_D/I_G on the grown carbon nanotubes according to the addition of the content amount of Co to the catalyst transmit metal Fe and Mo. We found that carbon yield or product mass was increased with the increase of the content amount of Fe compared to Co and with the increase of the content amount of Mo which is up to the content of Co as equal as possible. It is proved that the carbon production yield and the diameter of CNTs are possible to obtain controllably according to control of catalyst composition. When Mo was added to Co, aromatic species of synergism between Co and Mo makes the combination of the two metals effective on Co sites[6]. As it is called, the addition of appropriate amount of the molybdenum to Co on MgO support is thus critical for the controlled synthesis of carbon nanotubes. The increase of carbon deposit is extremely important when Co and Mo are in a 1:1 ratio. But, with the higher molar ratio of Mo/Co, the further MWNTs were formed.



<Figure 2> The yield of carbon and intensity ratio of I_D/I_G with the addition of Co to Fe or Mo



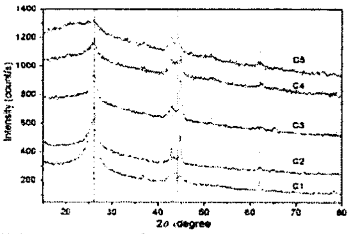
<Figure 3> The Raman scattering spectra of the carbon nanotubes synthesized using the Co-Fe/MgO catalyst



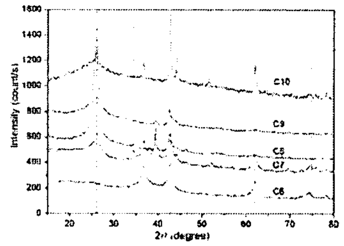
<Figure 4> The Raman scattering spectra of the carbon nanotubes synthesized using the Co-Mo/MgO catalyst

Figure 3 and 4 were shown the Raman spectra from nanotubes grown as a function of Co/Fe and Co/Mo molar ratio. The two main features in the Raman spectra are the D and G peaks at about 1280 and 1590 cm^{-1} and the corresponding second order peaks at around 2570 cm^{-1}, which is related to the properties of disorder carbon. In addition, the peak at 1564 cm^{-1} which is appearing at the left shoulder of the peak at 1590 cm^{-1} is the characteristics of the Raman spectrum for SWNTs. D-band peak was shown weak or strong in the all samples of as-synthesized carbon materials. The relatively strong D-band demonstrates that the as-grown samples contain large amount of amorphous carbon materials, revealing that rather low-purity carbon nanotubes are synthesized in our experimental procedure. But, the absence of asymmetry on the right side of the G^* band at around 2690 cm^{-1} indicates the presence of SWNTs with only very few MWNTs.

Figure 5 and 6 shows the XRD patterns of the carbon nanotubes synthesized at various Co/Fe and Co/Mo molar ratio, respectively. The comparison of these patterns of the separated CNTs samples indicates only small differences with the grown CNTs and gives important information about their composition. C(002) which is a wide peak around 2Θ = 25 ° arises form the presence of CNTs its width can be related to the mean number of walls is detected in all samples except for the six samples(C6). With the increase of the content amount of Co, this peak is clearly decreased. This peak is clearly narrower for sample C1, which could be interpreted as the signature of CNTs with more concentric wall.



<Figure 5> XRD patterns of the carbon nanotubes synthesized using the Co-Fe/MgO catalyst.



<Figure 6> XRD patterns of the carbon nanotubes synthesized using the Co-Mo/MgO catalyst.

According to these results, their quality of as-prepared carbon nanotubes is considerd as good experimental results. The high yield of SWNTs on Mo or Fe-doped Co/MgO catalyst is attributed to the increase of Co sites suitable for the growth of SWNTs and the promotion effect of Mo or Fe on the intermediate aromatic specie

4. Conclusion

We investigated the influence of catalyst preparation conditions for the synthesis of CNTs by catalytic CVD. We found that the type and the diameter of synthesized CNTs and the quality of CNTs substantially depend on the content amount of the catalyst composition. First, in the case of the use of iron alone, it can give a higher carbon production but lower quality nanotubes. With the increase of the addition of Fe to Co, production mass is decreased but higher quality of nanotubes. Second, molybdenum alone is inactive in the production of nanotubes by the decomposition of acetylene and no carbon nanotubes were grown. With the increase of the addition of Mo to Co, production mass and the quality of CNTs were increased. As a result, it is obvious that it is possible to grown CNTs with the production and desired diameter distribution of CNTs by choosing or combining the catalyst to be employed.

[Reference]

[1] M. Endo, K. Takeuchi, S. Igarashi, K. Kobori, M. Shiraishi, and H. W. Kroto, "The production and structure of pyrolytic carbon nanotubes (PCNTs)", J. Phys. Chem. Solids, Vol. 54, pp. 1841-1848., 1993.

[2] H. Dai, A. G. Rinzler, P. Nikolaev, A. Thess, D. T. Colbert, and R. E. Smalley, "Single-wall nanotubes produced by metal-catalyzed disproportionation of carbon monoxide", Chem. Phys. Lett., Vol. 260, pp. 471-475, 1996.

[3] Y. Yonglai, X. Hengyong, and L. Wenzhao,"Morphology observation of carbon deposition by CH4 decomposition over Ni-based catalysts", Nanotechnology, Vol. 16, pp. 129-132, 2005.

[4] H. Kathyayini, I. Willems, A. Fonseca, J. B. Nagy, and N. Nagaraju, "Catalytic materials based on aluminium hydroxide, for the large scale production of bundles of multi-walled (MWNT) carbon nanotubes", Cata. Comm., Vol. 7, pp. 140-147, 2006.

[5] E. Flahaut, C. Laurent,and A. Peigney, "Catalytic CVD synthesis of double and triple-walled carbon nanotubes by the control of the catalyst preparation", Carbon, Vol. 43, pp. 375-383, 2005.

[6] A. M. Cassell, J. A. Raymakers, J. Kong, and H. Dai, "Large Scale CVD Synthesis of Single-Walled Carbon Nanotubes", J. Phys. Chem. B., Vol. 103, pp. 6484-6492, 1999.