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Effects of Catalyst on Carbon Nanotubes Synthesized by Thermal Chemical Vapor Deposition Method

Udomdej Pakdee[1,a*], Santipab Srabua[1,b] ,Aphichard Phongphala[1,c], and Chatchai Pawong[1,d]

[1]Rajamangala University of Technology Krungthep, Bangkok 10120, Thailand

[a]udomdej.p@rmutk.ac.th, [b]santipab.s@rmutk.ac.th, [c]aphichard.p@rmutk.ac.th,

[d]chutchai.p@rmutk.ac.th

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Abstract. The effects of cobalt, nickel and iron catalyst on carbon nanotubes (CNTs) were examined with scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffractrometer (XRD) and Fourier transform Raman spectrometer (FT-Raman). The samples were prepared by the thermal chemical vapor deposition (CVD) method at 780 ^{o}C under pressure of acetylene gas (C_2H_2) at 0.5 bar. The average diameter of CNTs grown on Co, Fe and Ni catalyst obtained from SEM image is 100, 90, 70 nm, respectively. The crystallinity and the yield of CNTs synthesized from Ni catalyst were higher than that from Fe or Co catalyst. The Raman peak of radial breathing mode (RBM) region and the TEM images highlighted the hollow tubes of the CNTs. The results indicated that the diameter, the yield and the crystallinity for synthesis of carbon nanotubes were manipulated by the selection of the catalyst.

Introduction

Multi-walled carbon nanotubes (MWCNTs) present exceptional physical properties that make them suitable for many applications in electronics [2], medicine [5] and polymers [6]. There are many techniques for synthesizing either the single-walled or multi-walled CNTs. Of the techniques available, chemical vapor deposition (CVD) has demonstrated several advantages in growing the carbon nanotubes. For example, it is able to fabricate not only aligned but also single-walled or multi-walled CNTs by using different hydrocarbon gases. For a number of gaseous environments of different chemical compositions and concentrations, the growth conditions include a variety of temperatures and pressures ranging from 650 to 1000 ^{o}C, or higher and several tens of millitorr to one atmosphere. CNTs can be grown on most substrates such as silicon, alumina or aluminosilicates, as long as the temperature is sustained in growth. This paper reports the initial research of CNTs growth on nickel, iron and cobalt by using thermal CVD method.

Experimental Procedure

A 20 nm-thick Fe (or Co, Ni) film was thermally deposited on the SiO_2 substrate using the sputtering method. The samples were placed in a stainless steel chamber, with pressure less than 10^{-3} bar acheived using a rotary pump. The Fe, Co and Ni samples were then placed separately into a CVD chamber with a pressure of 10^{-3} bar. Helium gas (He) was fed into the chamber with flow rate of 30 standard cubic centimeters per minute (sccm) while waiting for the chamber to heat up to 780 ^{o}C to prevent the oxidation of catalyst metal. After that hydrogen gas (H_2) was fed with a flow rate of 200 sccm for 30 minutes and acetylene gas (C_2H_2) was fed with flow rate of 150 sccm for 30 minutes. The CNTs were synthesized in this step at 780 ^{o}C and a pressure of 0.5 bar. The CNTs were examined with scanning electron microscopy, transmission electron microscopy, Raman spectrometer and X-ray diffractrometer. Figure 1 shows the schematic diagram of thermal CVD apparatus.

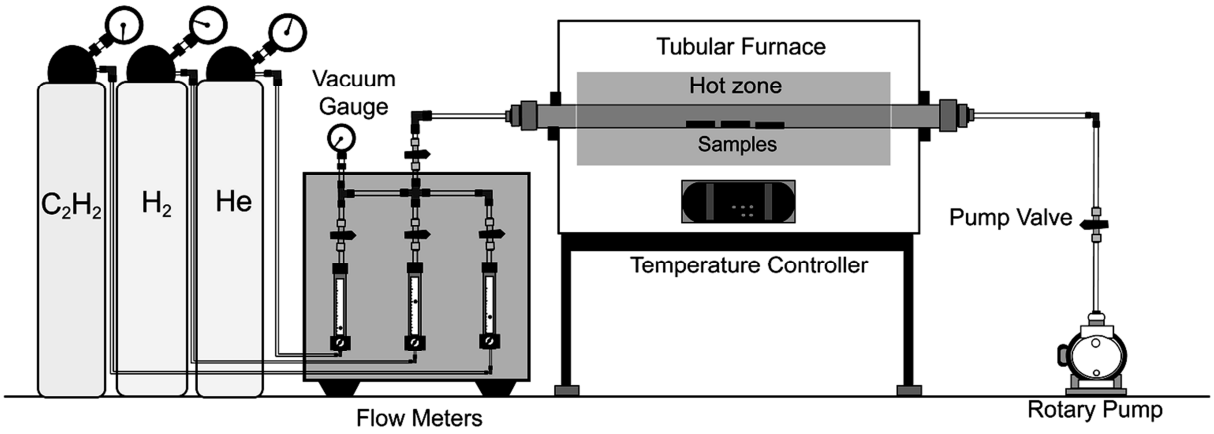

Fig.1. The schematic diagram of thermal CVD apparatus.

Results and Discussion

Fig. 2 shows SEM images and schematic diagrams of the CNTs grown on a thin catalytic film using thermal CVD of acetylene for 30 minutes at 780 ^{0}C in pressure of 0.5 bar. The average diameter of CNTs grown on Co, Ni, and Fe catalysts was 100, 70, and 90 nm, respectively.

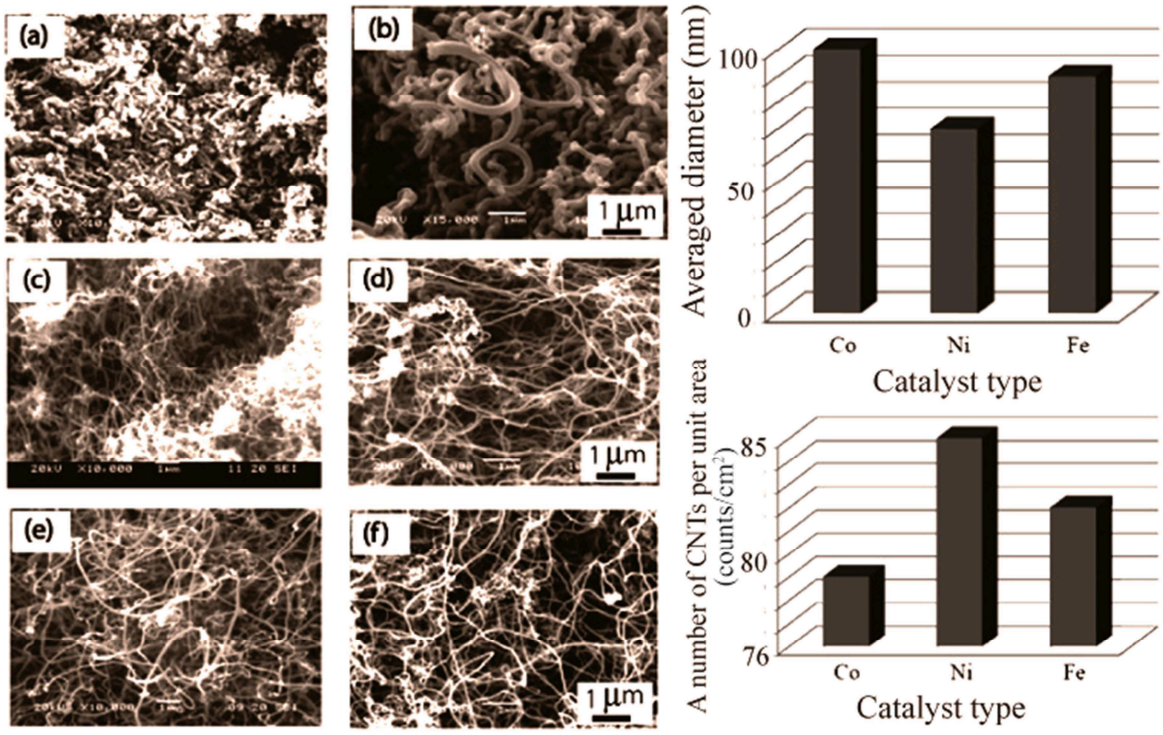

Fig. 2. SEM images and schematic diagrams of the CNTs grown on thin Co film (a)-(b), thin Ni film (c)-(d), and thin Fe film (e)-(f).

The results show the CNTs grown on Co catalyst had a larger diameter and a wider diameter distribution when compared with Fe or Ni catalyst. To understand the catalyst effect on the growth of CNTs, a correlation between the diffusion rate of carbon and the relative growth rate of CNT according to the catalyst was evaluated. In bulk Ni, Fe, and Co metals, the diffusion coefficient of carbon is 1.6×10^{-7} cm^2 s^{-1}, 1.1×10^{-7} cm^2 s^{-1} , and 0.8×10^{-7} cm^2 s^{-1} , respectively. Since the diffusion rate is usually proportional to the diffusion coefficient, the diffusion rate of carbon would follow the order Ni > Fe > Co. This result can be explained by the size effect of catalyst particles on the CNTs growth.

As the size of catalyst particle decreases, carbons adsorbed at the catalyst surface can arrive at the growth site at a shorter time, resulting in an increasing growth rate of CNTs. The size of Ni catalyst particle is smaller than that of Fe and Co catalyst particles. It was found that the Co catalyst particles had the largest diameter and the broadest size distribution among the three catalysts (Co > Fe > Ni).

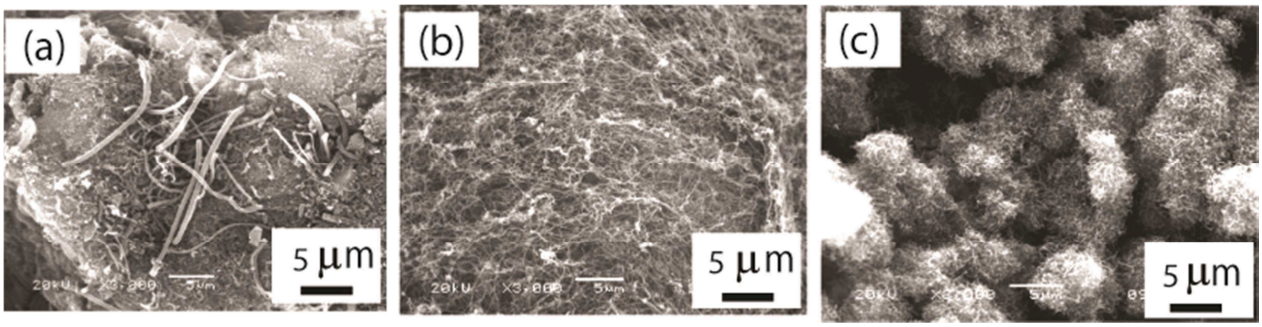

Fig. 3. SEM images for the yield of CNTs grown on thin Co (a), Ni (b), and Fe (c).

Fig. 3 shows SEM images for the yield of CNTs grown on thin Co, Ni, and Fe. With the bundles of CNTs , nanotubes with very big diameter (around 100 nm) are mostly shown in Fig. 3 (a). This result can be explained by the catalytic effect on the yield of CNTs growth. The highest yield of CNTs was obtained on Ni catalyst. The yield would follow the order Ni > Fe > Co. These clearly demonstrate that the use of catalyst became the important role as a promoter for high yield CNTs synthesis.

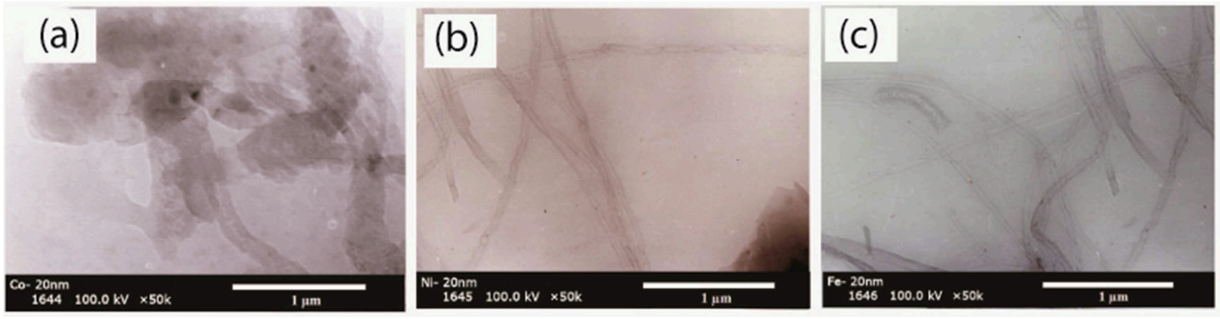

Fig. 4. TEM images for the structured CNTs grown on (a) Co, (b) Ni, and (c) Fe catalysts.

Fig. 4 shows TEM images of CNTs grown on Co, Ni, and Fe catalysts. The samples exhibit exclusively a multiwalled structure for all three catalysts. The average d_{002} inter-shell spacing of 0.3350 nm is estimated from the position of the (002) diffraction by applying the Bragg equation. This is an indication that the straight nanotubes and amorphous carbon are all involved in the carbon products and contributes to the diffraction intensity of the (002) peak. This is due to the fact that the diffraction is treated as the flat parallel layers instead of parallel cylindrical shells of varying curvature. The (002) peak of CNTs/Ni was higher than the (002) peak of CNTs/Fe and CNTs/Co. This result shows that The crystallinity of CNTs on nickel catalyst is higher than that on iron and on cobalt catalyst. Raman spectroscopy analyses performed on the carbon structures shown in Fig. 5 (b) confirms that they are of MWCNTs nature. Fig. 5 (b) shows Raman spectra are presented two broad and quite intense peaks about 1274 and 1591 cm^{-1}. The former band corresponds to the defect-induced Raman band and is known as the defect mode or D-band associated with the disordered of graphite or diamond-like carbon. The latter peak, also referred as G-band, represents the mode of graphite and is related to the vibration of C–C bonded in a two-dimensional hexagonal lattice of a graphite layer. The presence of a stronger D-peak as compared to G-peak in the samples show that CNTs possess a significant amount of defect and impurities. Strong peaks at 169 cm^{-1} are shown in our samples. These observed breathing modes suggest that the diameters exist in the samples. In Table. 1, the value of I(D)/I(G) for the CNTs grown on Co, Ni, and Fe catalysts is 1.44, 1.26, and 1.33, respectively. It reveals that the degree of crystalline perfection of the CNTs grown on Ni or Fe catalyst is higher than that of CNTs grown on Co catalyst.

Table 1. Raman parameters of CNTs grown on Co, Ni, and Fe catalysts

Samples	Raman Shift (cm^{-1})			Intensity (counts)			I(D)/I(G)
	RBM	D-mode	G-mode	RBM	D-mode	G-mode	
CNTs/Co	169	1277	1591	0.040745	0.203275	0.141024	1.44
CNTs/Ni	169	1276	1590	0.039768	0.435376	0.345563	1.26
CNTs/Fe	169	1274	1591	0.040006	0.270056	0.202298	1.33

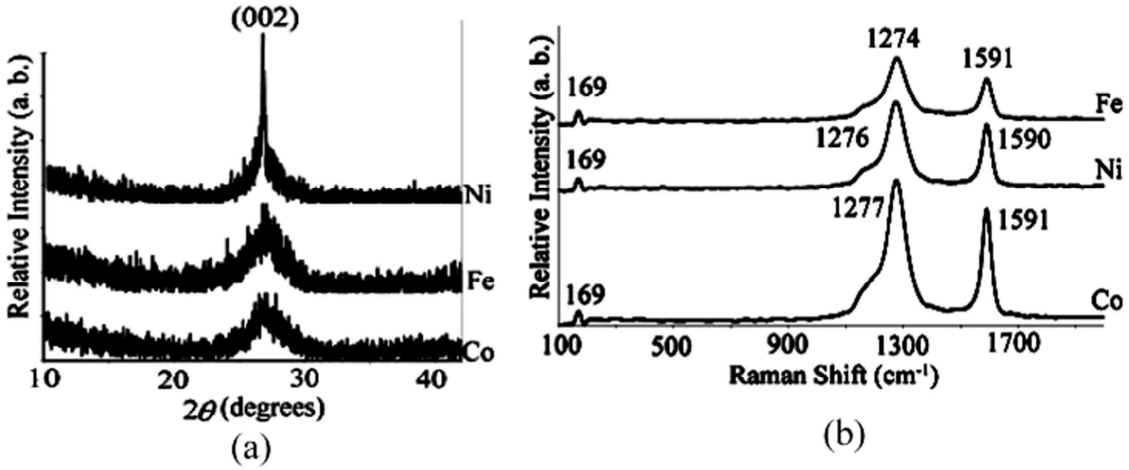

Fig. 5. XRD patterns (a) and Raman spectrum (b) of CNTs grown on Co, Ni, and Fe catalysts.

Summary

The study of the catalyst effect on structure of CNTs by thermal CVD method was found that the catalyst effect on the growth and structure of CNTs using thermal CVD. The largest diameter of CNTs was synthesized on Co catalyst. It had been known that the high-yielded synthesis of CNTs using Ni catalyst. The CNTs grown on Ni catalyst revealed the best crytallinity among the three catalysts. On the other hand, the CNTs grown on Co catalyst exhibited much lower degree of crystalline character compared with Fe or Ni catalyst.

Acknowledgements

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