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Catalyst effect on carbon nanotubes synthesized by thermal chemical vapor deposition

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Abstract

The catalyst effect on the synthesis of carbon nanotubes (CNTs) using thermal chemical vapor deposition (CVD) was investigated. The respective growth rate of CNTs shows that the performance of catalysts is in the order of nickel (Ni) > cobalt (Co) > iron (Fe). The average diameter of CNTs follows the sequence of Fe, Co, and Ni catalysts. The structure of CNTs reveals almost same morphology regardless of catalyst but the crystallinity of CNTs is largely dependent on catalyst. The crystallinity of CNTs synthesized from Fe catalyst is higher than that from Ni or Co catalyst. The results indicate that the growth rate, the diameter, and the crystallinity can be manipulated by the selection of the catalyst. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Synthesis of carbon nanotubes (CNTs) has been extensively investigated by a number of research groups, since the first observation in 1991 [1]. Various synthetic methods such as arc discharge [2], laser vaporization [3], pyrolysis [4,5], plasma-enhanced [6,7] or thermal chemical vapor deposition (CVD) [8,9] have been developed for the production of CNTs. Recently, the synthesis of CNTs using CVD method has attracted much attentions because of many advantages such as high

purity, high yield, controlled growth, and vertical alignment.

The most effective catalysts for the CVD growth of CNTs are known to be iron (Fe), cobalt (Co), and nickel (Ni). The peculiar ability of these metals was suggested to relate to the catalytic activity for the decomposition of carbon precursors, the formation of meta-stable carbides, the diffusion of carbons, and the formation of graphitic sheets, etc. [10,11]. Despite tremendous progress in synthesizing CNTs, the systematic study of the catalyst effect on the CNT growth is still not much reported yet. Recently, Ren and coworkers [12] reported effect of catalyst on the growth of aligned carbon nanotubes using plasma-enhanced hot filament CVD system. Exact understanding of the catalyst activity would lead eventually a controlled

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growth of CNTs, which is prerequisite for various potential applications.

In this work, we studied the effect of Fe, Co, and Ni catalysts on the CNTs synthesized by thermal CVD of acetylene (C_2H_2) gas. The CNTs were grown on three different catalyst particles under the same conditions. The nanometer sized catalyst particles were formed by ammonia pretreatment [13]. The growth rate and structure of CNTs were fully optimized. The configuration and crystallinity of CNTs grown on Fe, Co, and Ni catalyst particles were investigated using scanning electron microscopy, transmission electron microscopy, thermogravimetric analysis, and Raman spectroscopy. We observed that the growth and crystallinity of CNTs depend on the catalyst species, providing a manipulation of CNT growth according to the catalyst.

2. Experimental

The 20 mm \times 30 mm size p-type plane silicon (100) substrates with a resistivity of 15 Ω cm were thermally oxidized. The thickness of silicon oxide (SiO_2) layer was estimated approximately as 300 nm. A 50 nm-thick Fe (or Co, Ni) film was thermally deposited on the SiO_2 substrate using a thermal evaporator under a pressure of 10^{-6} Torr. The catalyst deposited substrates were loaded on a quartz boat. Argon (Ar) was flowed into a quartz CVD reactor in order to prevent the oxidation of catalyst metal while raising the temperature. The catalyst films were pretreated by ammonia (NH_3) gas with a flow rate of 100 sccm for 20 min at 750–950 $^{\circ}C$ in order to form the nanometer sized catalyst particles on the substrates. The catalyst films were etched by introducing NH_3 gas into the quartz reactor at 750–950 $^{\circ}C$ and were easily agglomerated on the substrates, resulting in nanometer sized particles. The Fe catalyst particles generally had a larger diameter and a broader size distribution compared with Co or Ni catalyst particles. For the condition of NH_3 treatment at 950 $^{\circ}C$, the diameter of Fe, Co, and Ni catalyst particles was in the range of 150–190, 130–150, and 120–130 nm, respectively. After formation of nanometer sized catalyst particles, the CNTs were

sequentially grown using C_2H_2 with a flow rate of 30 sccm for 10 min at the same temperature. After finishing the CNT growth, the reactor was cooled down to room temperature under Ar ambient. The CNTs grown on catalyst particles were examined by a scanning electron microscopy (SEM) (Hitachi S-800, 30 kV) to measure the length, the diameter, and the uniformity. A transmission electron microscopy (TEM) (Philips CM20T, 200 kV) was used to investigate the structure and crystallinity. A thermogravimetric analysis (TGA) system (TA instrument TGA 2050) has been used for the temperature-programmed oxidation at a constant heating rate of 10 $^{\circ}C/min$ under air ambient, in order to measure the degree of crystalline perfection. A Raman spectrometer (Renishaw micro-Raman 2000) was also used to identify the crystallinity of CNTs. The 632.8 nm line of a He–Ne laser was used for excitation.

3. Results and discussion

Fig. 1 shows SEM images of the CNTs grown on catalyst particles formed on the SiO_2 substrates using thermal CVD of acetylene for 10 min at 950 $^{\circ}C$. The length of vertically aligned CNTs is 10, 17, and 20 μm for Fe, Co, and Ni catalyst deposited substrates, respectively. The average diameter of CNTs grown on Fe, Co, and Ni catalysts is 130, 110, and 100 nm, respectively. The density of CNTs is about $\sim 4 \times 10^9$, $\sim 4 \times 10^9$, and $\sim 2 \times 10^9$ cm^{-2} for Fe, Co, and Ni catalysts. These results are summarized in Table 1, showing that the growth rate, diameter, and density of CNTs are dependent on the catalyst.

From several experimental runs, the average growth rate of CNTs on Fe, Co, and Ni catalysts is measured as 1 ± 0.2 , 1.7 ± 0.3 , and 2 ± 0.3 $\mu m/min$, respectively. The maximum growth rate can be achieved when the Ni catalyst is used. The Fe catalyst renders the lowest growth rate among three catalysts. The growth rate is almost constant during the growth time 30 min but it decreases significantly after about 40 min as the carbonaceous particles cover the surface of metal particles. The growth rate mainly depend on the diffusion rate of carbons. We already reported that the

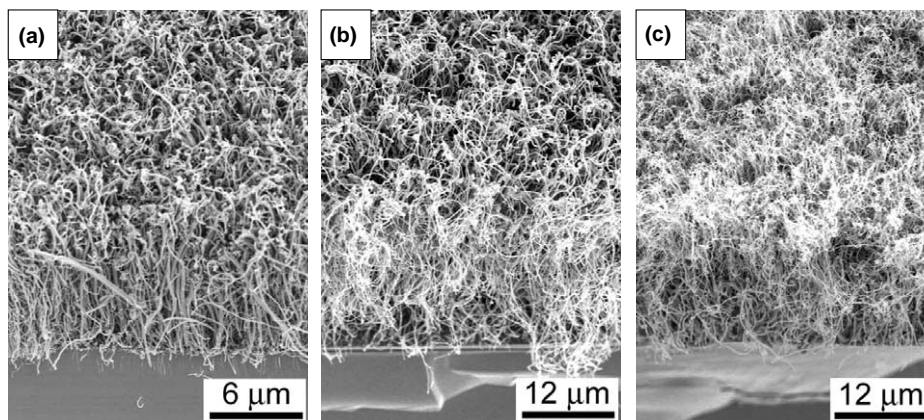


Fig. 1. SEM micrographs for the vertically aligned CNTs grown on (a) Fe, (b) Co, and (c) Ni catalyst particles deposited SiO₂ substrate, under the condition that C₂H₂ flows with a rate of 30 sccm for 10 min at 950 °C.

Table 1

The growth rate, diameter, and density of CNTs grown on Fe, Co, and Ni catalysts using thermal CVD of C₂H₂ at 950 °C

Catalyst type	Growth rate (μm/min)	Diameter distribution (nm)	Averaged diameter (nm)	Density (cm ⁻²)
Fe	1 ± 0.2	80–200	130	4 × 10 ⁹
Co	1.7 ± 0.3	80–130	110	4 × 10 ⁹
Ni	2 ± 0.3	90–110	100	2 × 10 ⁹

growth rate of CNTs on the Fe catalyst increased by a factor of 4 as the temperature increased from 750 to 950 °C [14]. In our experiment, the growth rate increases as the growth temperature increases regardless of catalyst.

To understand the catalyst effect on the growth rate of CNTs, we evaluated a correlation between the diffusion rate of carbon and the relative growth rate of CNT according to the catalysts at 950 °C. In bulk Fe, Co, and Ni metals, the diffusion coefficient of carbon is 1.1×10^{-7} , 8×10^{-8} , and 1.6×10^{-7} cm² s⁻¹ at 950 °C, respectively [15]. Since the diffusion rate is usually proportional to the diffusion coefficient, the diffusion rate of carbon would follow the order Ni > Fe > Co. The growth rate of CNTs between Ni and Co catalysts is consistent with the diffusion rate in bulk Ni and Co metals. While the growth rate of CNTs reveals inverse sequence from the diffusion coefficients between Fe and Co catalysts. This result can be explained by the size effect of catalyst particles on the CNT 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. In this work, the size of Co catalyst particle is smaller than that of Fe catalyst particle. We suggest that the size effect of catalyst particles would be another factor to determine the growth rate of CNTs beside the diffusion rate of carbon. Bower et al. [16] also reported the inverse dependence of growth rate on the diameter of catalyst particles for the growth of CNTs on Co catalyst using plasma-enhanced CVD.

In our result, the CNTs grown on Fe catalyst have a larger diameter and a broad diameter distribution compared with Co or Ni catalyst. We could find that the Fe catalyst particles had the largest diameter and the broadest size distribution among the three catalysts (Fe > Co > Ni) before the CNT growth. The lower density of CNTs grown on Ni catalysts is rationalized by the easy agglomeration of the small sized Ni particles compared with Fe or Co particles.

We measured TEM images of the CNTs to investigate the structure dependence on the three catalysts. Figs. 2a–c show TEM images of the CNTs grown on Fe, Ni, and Co catalysts, respectively. The CNTs exhibit exclusively a multi-walled bamboo-like structure for all three catalysts. The CNTs have a closed tip without encapsulated catalyst particle and compartment layers with a curvature oriented to the closed tip. The high-resolution TEM (HRTEM) images were obtained to elucidate the catalyst effect on the crystallinity of CNTs. Figs. 2d–f show the HRTEM images for the wall of CNTs grown on Fe, Ni, and Co catalysts. The left and top of the images correspond to the outside of the wall and the tip of a nanotube, respectively. The graphitic sheets are separated by ~ 0.34 nm and are tilted with a few degree angles toward the tube axis [17].

The outer graphitic sheets of CNTs are less crystalline compared with the inner graphitic sheets for all three catalysts. The graphitic sheets of the CNT grown on Fe catalyst reveal highly ordered crystalline structure. The CNT grown on Ni catalyst has a little lower degree of crystalline perfection than that of Fe catalyst. On the other hand, the CNT grown on Co catalyst shows that the graphitic sheets are waved over a short range and thus are more defective structure compared with Fe or Ni catalysts. The HRTEM images reveal that the crystallinity of CNTs follows a sequence of $\text{Fe} > \text{Ni} > \text{Co}$.

TEM is one of the most powerful methods for the evaluation of the crystallinity of CNTs. However, it does not provide the overall information about the structure of the entire CNTs. The use of TGA and Raman spectroscopy compensates such

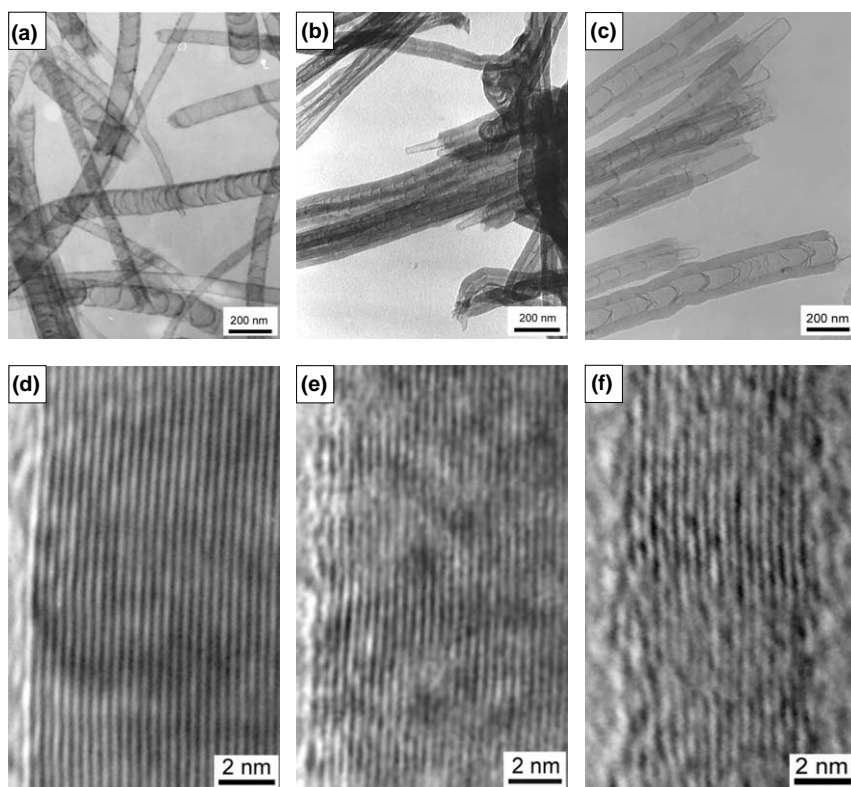


Fig. 2. TEM images for the bamboo-like structured CNTs grown on (a) Fe, (b) Ni, and (c) Co catalysts, showing the closed tip without encapsulated catalyst particles and the compartment layers with a curvature directed to the tip. HRTEM images for the graphitic sheets of CNTs grown on (d) Fe, (e) Ni, and (f) Co catalysts.

shortcoming of TEM. The temperature-programmed oxidation technique allows one to ascertain the relative amounts of defective and crystalline constituents in the CNTs grown on Fe, Ni, and Co catalysts. Less ordered crystalline CNTs will react preferentially with the oxidant and lose weight at a lower temperature compared with more highly crystalline CNTs. Fig. 3 is a plot for the weight loss in % vs. the oxidation temperature, measured by heating up the CNTs in a TGA. The weight loss curve between 200 and 800 °C is plotted by adjusting about 100% for the weight loss at 800 °C, in which the actual weight is presumably the weight of catalyst (usually 10% of total weight). The CNTs grown on Fe, Ni, and Co catalysts start to gasify at approximately 550, 550, and 500 °C, respectively. For pure graphite, the onset of gasification is observed at 700 °C under the same experimental conditions. The respective weight loss is measured in the range of 550–680, 550–650, and 500–620 °C for the CNTs grown on Fe, Ni, and Co catalysts, respectively. The TGA data indicate that the crystallinity of the CNTs grown on Fe catalyst is a little better than that of CNTs grown on Ni catalyst, but the CNTs grown on Co catalyst exhibit much less crystallinity compared with Fe or Ni catalyst.

Fig. 4 shows Raman spectra for the CNTs grown on Fe, Ni, and Co catalysts. All spectra show mainly two Raman bands at $\sim 1335 \text{ cm}^{-1}$ (D band) and $\sim 1580 \text{ cm}^{-1}$ (G band). The G band indicates original graphite features but the D band

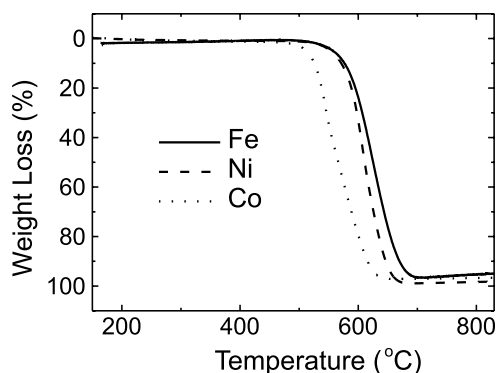


Fig. 3. TGA data of the weight loss in % vs. the oxidation temperature for the CNTs grown on Fe, Ni, and Co catalysts.

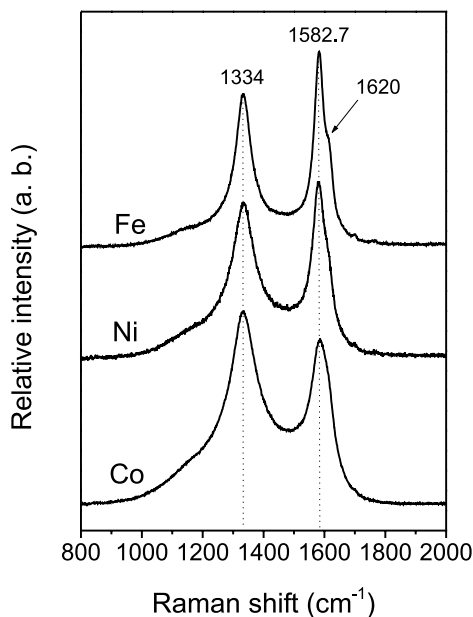


Fig. 4. Raman spectrum for the CNTs grown on Fe, Ni, and Co catalysts.

has been explained as disorder features of graphitic sheets [18,19]. In the spectrum of CNTs grown on Fe and Ni catalysts, the D' band at $\sim 1620 \text{ cm}^{-1}$ appears as a small bump of G band. However, for the CNTs grown on Co catalyst, the D' and D bands become stronger and broader. As a result, the D' band is completely overlapped with G band, showing a converged peak whose position is at a higher wave number than that of G band by $\sim 10 \text{ cm}^{-1}$. The linear relation between the inverse of the in-plane crystallite dimension and the intensity ratio of D band to G band ($I(D)/I(G)$) were noted [18]. In Fig. 4, the value of $I(D)/I(G)$ for the CNTs grown on Fe, Ni, and Co catalysts is 0.8, 0.9, and 1.2, respectively. It reveals that the degree of crystalline perfection of the CNTs grown on Fe or Ni catalyst is higher than that of CNTs grown on Co catalyst, which is very consistent with the HRTEM images and TGA data. Recently, Ren and coworkers [12] also reported that the CNTs grown on Ni catalyst using hot filament plasma CVD exhibited a higher degree of crystalline perfection than that of CNTs grown on Co catalyst. From above results, we suggest that the crystallographic characteristics of catalyst particle

play an important role in governing the crystallinity of CNTs, but further extensive studies are necessary to provide a definite evidence for such possibility.

In summary, we have studied the catalyst effect on the growth and structure of the CNTs using thermal CVD. The growth rate of CNTs indicates that the performance of catalyst follows in the order of Ni > Co > Fe. The size effect of catalyst particle would be another factor to determine the growth rate of CNT even though the growth rate mainly depend on the diffusion rate of carbon at the catalyst particle. The bamboo-like structured CNTs are exclusively produced irrespective to the catalyst. The CNTs grown on Fe catalyst reveals the best crystallinity among the three catalysts. On the other hand, the CNTs grown on Co catalyst exhibit much lower degree of crystalline character compared with Fe or Ni catalyst. We demonstrate that the growth rate, the diameter, and the crystallinity of CNTs can be manipulated by selecting the catalysts.

Acknowledgements

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