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Effect of Metal Catalysts on Synthesis of Carbon Nanomaterials by Alcohol Catalytic Chemical Vapor Deposition

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Abstract. Carbon nanomaterials (CNMs) were synthesized by alcohol catalytic chemical vapor deposition (CVD) at atmospheric pressure using different metal catalysts (Ni, Co and Fe) at a growth temperature of 700°C. Ni and Fe acted as active catalysts for multi-walled carbon nanotubes (MWNTs) growth, while Co acted as an active catalyst for bamboo-like MWNTs and carbon nanofibers (CNFs) growth. The CNMs synthesized from Ni catalyst showed the highest crystallinity with a small amount of by-products. These results imply that metal catalyst is a key parameter to the structure, morphology and crystallinity of CNMs. The different effects of metal catalysts on the growth of CNMs can be explained in terms of the difference in the change in Gibbs free energy of metal carbide formation.

Keywords: Carbon nanomaterials, multi-walled carbon nanotubes, carbon nanofibers, alcohol catalytic chemical vapor deposition.

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1. Introduction

Carbon nanomaterials (CNMs) such as fullerenes [1], carbon nanotubes (CNTs) [2-3], carbon nanofibers (CNFs) [4] and graphene [5] have attracted great attention due to their excellent structural, electronic, thermal and mechanical properties. Especially, CNTs have been extensively studied for their potential applications of nanotechnology. To produce such CNMs, chemical vapor deposition (CVD) has been considered as a promising method for mass production with controlled diameter, purity, quantity and orientation [6].

One of the key parameters for CVD method is metal catalyst. There have been several reports on the effects of the metal catalysts on the synthesis of CNMs using methane [7], ethylene [8] and acetylene [9] as carbon sources. It was found that the structure, morphology and crystallinity of CNMs depend crucially on the selection of metal catalyst. Recently, a simple and safe technique for producing high quality CNTs has been proposed. It entails a low-temperature alcohol catalytic CVD method using ethanol (C_2H_5OH) as a carbon source [10]. However, the relationship between the obtained structure of CNMs and the metal catalyst type has not been fully explored.

In this work, the effects of metal catalysts on the synthesis of CNMs by alcohol catalytic CVD were investigated. Ni, Co and Fe were employed as metal catalyst. The morphology, structure and crystallinity of CNMs synthesized from these metal catalysts were characterized.

2. Experimental

An electron-beam evaporator was used to sequentially deposit an under layer (Al (5 nm)/Cr (2 nm)) and a metal catalyst layer (Ni, Co or Fe (5 nm)) on Si substrate. The deposited substrates were then annealed in a quartz tube at 700°C for 60 min under a flow of Ar gas at a flow rate of 500 sccm. Then, ethanol vapor was introduced by bubbling Ar gas through ethanol at a flow rate of 800 sccm. The CVD growth was carried out for 20 min at atmospheric pressure. After that, the synthesized material was cooled down to room temperature under Ar gas at a flow rate of 500 sccm. The morphology, structure and crystallinity of the obtained CNMs were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy.

3. Results and Discussion

3.1. CNMs Characterization

Figures 1(a)-1(c) and Figs. 1(d)-1(f) show SEM and TEM images of CNMs synthesized from Ni, Co and Fe catalysts, respectively. Tubular structures were synthesized in all cases, but their morphologies and structures were different. The SEM images shows that the CNMs grown from Ni and Co catalysts had a relatively high density of tubular structures covered wholly on the surface of substrates (Figs. 1(a) and 1(b)), while the CNMs grown from Fe had a low density with a mixture of long-straight and shortly random CNMs (Fig. 1(c)). The TEM images, clearly show that the structures of CNMs grown from different metal catalysts were completely different. The CNMs grown from Ni catalyst shows graphene planes aligning paralleling to each other and to the axis of the tubular structure, indicating multi-walled carbon nanotube (MWNT) structure (Fig. 1(d)). For the CNMs grown from Co catalysts, their graphene planes are parallel to each other but made an angle with the axis of the tube with bamboo compartments along the tube, indicating bamboo like-MWNT structure (Fig. 1(e)). CNFs were also mixed in the CNMs grown from Co catalyst. For the CNM grown from Fe catalyst, their graphene planes are parallel to each other, indicating MWNT structure. The average diameters of the synthesized CNMs from Ni, Co and Fe catalysts were approximately 9.35±4.29, 30.20±12.18 and 43.67±18.70 nm, respectively. From the TEM images at low magnification (Fig. 1(g) and 1(h)), two types of CNMs were observed. One was CNMs without metal catalyst at the tube end. The other was CNMs with clusters of metal catalyst (dark contrast in TEM image) encapsulated at the tube end. This implies that the growth of the synthesized CNMs was based on both the base growth [11] and the tip growth [12] mechanisms, respectively. Moreover, as can be seen in the TEM images at low magnification, the CNMs grown from Ni catalyst showed a higher density of a relatively uniform diameter of MWNTs with a small amount of by-products, when compared to those grown from Co catalyst.
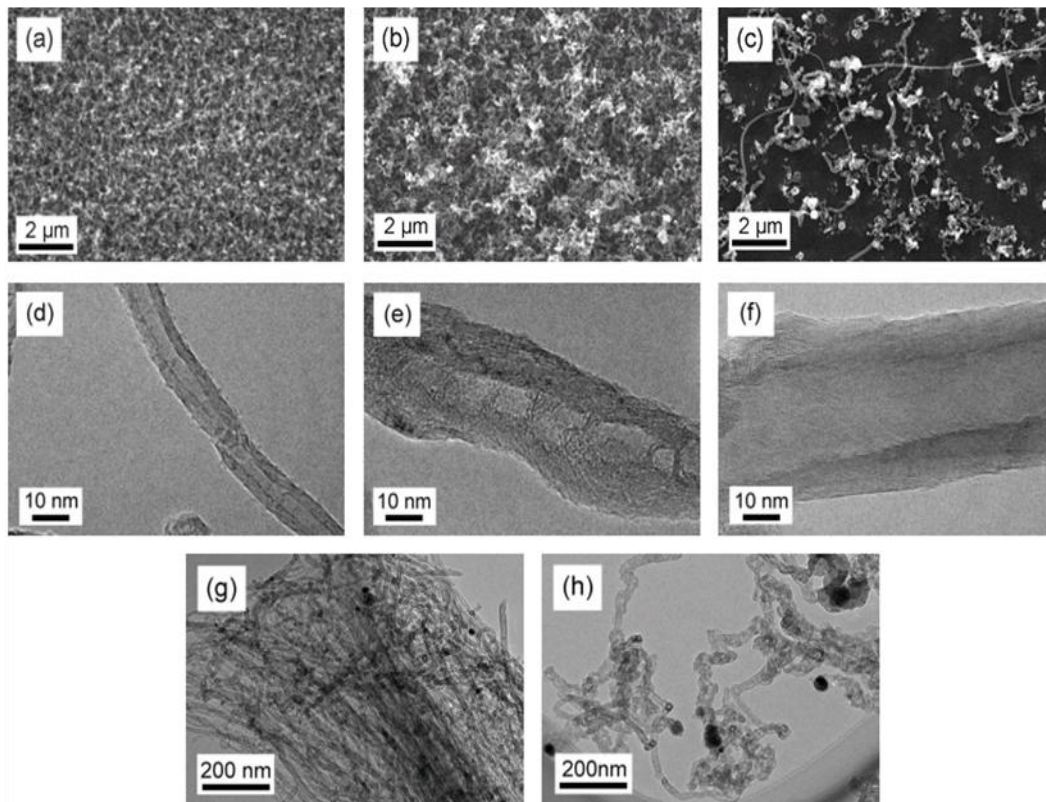
Fig. 1.   SEM and TEM images of CNMs synthesized from different metal catalysts; (a), (d) Ni (b), (e) Co and (c), (f) Fe. TEM images at low magnification of CNMs synthesized from (g) Ni and (h) Co.

Next, Raman spectroscopy was utilized to characterize the structure, purity and crystallinity of the synthesized CNMs. Ar ion laser with a wavelength of 532 nm (2.33eV) was used as the excitation light. All spectra showed mainly two bands at ~1340 cm^{-1} (D-band disorder carbon) and ~1590 cm^{-1} (G-band graphitic structure), corresponding to MWNT structure. Furthermore, the small peaks at ~2700 cm^{-1} (G´ band) were also observed in every sample. This spectrum indicates the overtone or second order of D band, which originates from the two phonon double resonance Raman process [13]. The intensity ratio between G (I_G) band and D (I_D) band, (I_G/I_D) is an indication of the crystallinity of CNMs. The I_G/I_D ratio of the CNMs synthesized from Ni, Co and Fe were 0.73, 0.44 and 0.49, respectively. Hence, it can be concluded that the CNMs synthesized from Ni catalyst had the highest crystallinity.
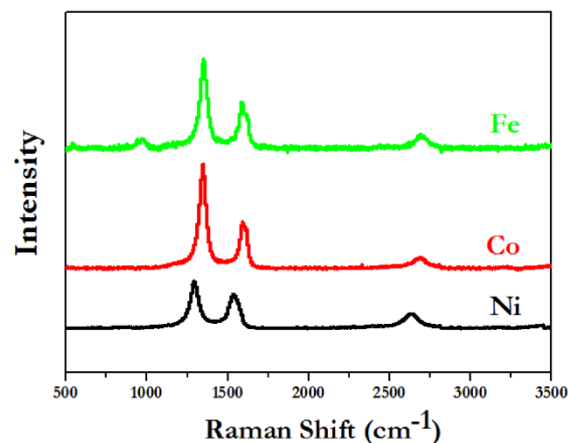

Fig. 2.   Raman Spectra of synthesized CNMs from different metal catalysts.

The obtained results, indicate that the morphology of CNMs strongly depended on the selection of metal catalyst. At the growth temperature of 700°C, Ni catalyst afforded a high density growth of a uniform diameter of MWNTs with a small amount of by-products, while Co catalyst afforded a high density growth of a mixture of bamboo-like MWNTs and CNFs. Fe catalyst afforded a growth of MWNTs at low density.

3.2. Discussion of Effect of Metal Catalyst on Morphology of CNMs

In order to understand the effect of Ni catalyst on high yield growth of CNMs, the growth mechanism of CNMs is explained based on the thermodynamics of carbon-metal reaction. The possible growth model of CNMs is as follows: carbon source decomposes and dissolves forming metal carbides on the surface of metal catalyst nanoparticles: additional carbon atoms precipitate and get extracted easily from the metal carbides, leading to formation of CNMs [14]. The direction of the reaction can be considered thermodynamically by the change in Gibbs free energy (ΔG). The reaction proceeds forward when ΔG value is less than zero or negative value ($\Delta G<0$). A previous study has reported that the ΔG of ethanol decomposition at a reaction temperature of 700°C, as shown in Eq. (1), is less than zero [15].

$$C_2H_5OH \rightarrow 2C(s) + 2H_2 + H_2O \qquad (1)$$
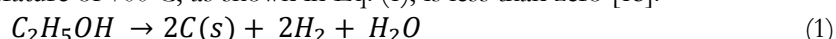
For the carburization of decomposed carbon source by metal catalyst, the reaction can be expressed as Eq. (2) bellow [14-15].

$$C_2H_5OH + M \rightarrow MC_2 + 2H_2 + H_2O \qquad (2)$$
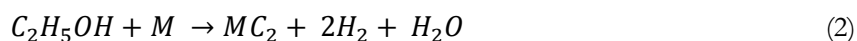
where M denotes a metal catalyst and MC_2 denotes metal carbide.

ΔG of carburization reaction of different metal catalysts under acetylene (C_2H_2) system has been reported in several studies. The magnitude of ΔG of Ni, Co and Fe catalysts were in the following order: Fe<Co<Ni [14]. For the C_2H_2OH system, we assumed that ΔG behaves like the C_2H_2 system. That is why the Ni catalyst with the highest magnitude of ΔG gave the highest yield of CNMs, while the Fe catalyst with the lowest magnitude of ΔG gave the lowest yield of CNMs. However, a more accurate determination of the ΔG for the ethanol system is needed and will be addressed in future work.

4. Conclusion

CNMs were successfully synthesized by alcohol catalytic CVD at 700°C using from three different metal catalysts using ethanol as a carbon source. Ni and Fe were shown to be active catalysts for MWNTs growth, while Co acted as an active catalyst for bamboo-like MWNTs and CNFs. Ni catalyst afforded the highest yield and crystallinity, while Fe catalyst afforded the lowest. The average diameter of CNMs synthesized from each catalyst was in the following order: Ni<Co<Fe. The relationship between CNMs yield and metal catalyst type can be explained by the change in Gibbs free energy. We conclude that the desired yield, diameter, structure, morphology and crystallinity of CNMs can be controlled by judicious selection of appropriate metal catalyst.

Acknowledgement

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