

Effect of Mo in Co–Mo/MgO catalysts on the synthesis yield and structure of carbon nanotubes

Masataka BABA, Hideaki SANOK*, Guo-Bin ZHENG*[†] and Yasuo UCHIYAMA*

Graduate School of Science and Technology, Nagasaki University, 1-14, Bunkyo-machi, Nagasaki 852-8521

*Department of Materials Science and Engineering, Faculty of Engineering, Nagasaki University, 1-14, Bunkyo-machi, Nagasaki 852-8521

Carbon nanotubes (CNTs) were synthesized at 650–770°C using Co/MgO and Co–Mo/MgO as catalysts and ethylene as carbon source. The dependence of the carbon yield on Mo amount in catalyst, synthesis temperature and time were investigated, and the structures of CNTs were characterized using FESEM, TEM, and Raman spectroscopy. It was found that CNTs with “bamboo-like” structure were synthesized using Co–Mo/MgO catalysts, in contrast to typical multi-walled carbon nanotubes with hollow inner tube obtained from Co/MgO catalyst. Addition of 5–10% Mo in catalysts resulted in the highest carbon yield, e.g. 5500% for 60 min synthesis, which is about 20 times higher than that of Co/MgO. The addition of Mo also extended the lifespan of catalyst for the growth of CNTs. TEM observation showed that the growth of CNTs was in a root-growth mode. The structure of CNTs obtained from Co–Mo/MgO catalysts was explained based on the growth mechanism of CNTs.

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1. Introduction

Carbon nanotubes (CNTs) are expected to have a wide range of applications due to their excellent mechanical properties, electrical properties and long aspect ratio.¹⁾ Catalytic CVD is regarded as an effective method to produce CNTs at a large scale.²⁾ For the applications such as composites and electrodes, the synthesis technology with high efficiency and low cost is still to be developed.

In CVD synthesis of CNTs, Fe, Co, Ni supported on oxides such as Al₂O₃, SiO₂ and MgO are usually used as catalysts.^{3)–5)} After synthesis of CNTs, removal of the catalyst is required. From the viewpoint of easiness and cost to purify the CNTs products, MgO is considered to be a good supporter for catalyst,^{6)–10)} since MgO can be easily dissolved in dilute HCl solution, while the removal of Al₂O₃ or SiO₂ requires HF, much more toxic than HCl.

The structure and carbon yield of CNTs were dependent upon the catalyst type and catalyst size as well as temperature. Especially, the catalyst size has a direct relation to the diameter of synthesized CNTs. The formation of solid solution of CoO and MgO was a good way to control the size of catalyst because the reduction of solid solution resulted in the precipitation of nano-size Co particles on the surface of MgO.^{8)–10)} It was also found that Mo addition in Fe, Co, Ni, has a significant effect to improve the carbon yield, though Mo alone did not have a catalytic effect to grow CNTs.^{11)–19)}

Besides the effect to carbon yield, Mo addition in Co/MgO has also effect on the structure of CNTs. The mechanism of Mo effect on the structure and carbon yield has not been fully understood. In this study, we synthesize CNTs at temperature between 650 to 770°C using CoO–MoO₃/MgO catalyst with Mo/Co per-

centage of 1% to 20%, and investigate the effect of Mo on the carbon yield and structure of CNTs, and explore the mechanism of Mo addition effect.

2. Experimental procedure

2.1 Preparation of catalysts

The catalyst precursors CoO–MoO₃/MgO were prepared by sol–gel method. Co(CH₃COO)₂·4H₂O, Mg(CH₃COO)₂·4H₂O and (NH₃)₆Mo₇O₂₄·4H₂O were mixed in a citric acid aqueous solution with the molar ratio of Co/Mo/Mg shown in **Table 1**. The solution was then stirred and gelled at 60°C. After being dried at 110°C for 2 d, the dried gels were calcined at 700°C for 5 h in air to obtain CoO–MoO₃/MgO catalysts. As a comparison, CoO/MgO was also prepared in the same method.

2.2 Synthesis of CNTs

Syntheses of CNTs were carried out by using CVD method. A mullite boat (50 mm long and 40 mm wide) loaded with 50 mg of catalyst powders was set in tubular reactor (50 mm in diameter and 1000 mm in length). After the reactor was heated to synthesis temperature in N₂ of 150 ml·min⁻¹, the catalysts were reduced in H₂ of 30 ml·min⁻¹ for 30 min. Subsequently,

Table 1. Molar Ratio of Elements in CoO–MoO₃/MgO Catalysts

Catalyst name	Molar ratio			CNT name
	Co	Mo	Mg	
Co	1	0	1	CNT–Co
CM1	0.99	0.01	1	CNT–CM1
CM5	0.95	0.05	1	CNT–CM5
CM10	0.9	0.1	1	CNT–CM10
CM20	0.8	0.2	1	CNT–CM20

[†] Corresponding author: G.-B. Zheng; E-mail: gbzheng@nagasaki-u.ac.jp

C_2H_4 was introduced to the reactor, and CNTs were synthesized at 650–770°C for 30–120 min, respectively. The names of catalysts and CNTs are shown in Table 1.

2.3 The evaluation method

The carbon yield was calculated by using the following equation.

$$\text{Carbon yield}(\%) = \left(\frac{M_{\text{Total}} - M_{\text{Cat}}}{M_{\text{CoO}} + M_{\text{MoO}_3}} \right) \times 100 \quad (1)$$

where M_{Total} , M_{Cat} , M_{CoO} and M_{MoO_3} stand for the total mass of final catalyst and product, the initial mass of catalyst, the mass of CoO in catalyst and the mass of MoO₃ in catalyst, respectively.

The structure and morphology of CNTs were observed by transmission electron microscopy (TEM, JEOL Ltd., JEM-2010UHL) and field emission scanning electron microscopy (FE-SEM, JEOL Ltd., JSM-7500F). The CNTs were also characterized using Raman spectroscopy with an excitation wavelength of 532.15 nm.

3. Results

3.1 Carbon yield of CNTs

Figure 1 shows carbon yield of CNT-CM20 synthesized for 30 min at different temperature. The carbon yield was about 1000% at 650°C, increased with synthesis temperature, peaked at 750°C and decreased beyond 750°C. In general, reaction rate increases with temperature, but in the case of the CNT growth, the nucleation number of CNTs also contributes to the carbon yield. Higher temperature resulted in the aggregation of catalyst particles and thus decreased the nucleation number for CNT growth. Therefore, an optimum temperature range existed for the growth of CNTs.

Figure 2 shows the relation of carbon yield with synthesis time at 750°C. For Co catalyst, the carbon yield increased slightly beyond 30 min, suggesting that the growth of CNTs almost stopped at 30 min. For CM20 catalyst, the carbon yield reached 2000% for 30 min, and then increased with synthesis time. However, the increasing rate of carbon yield of CM20 was lower after 30 min than that before 30 min. For CM10 catalyst, the carbon yield increased very rapidly even to 2 h, indicating the catalyst still kept its activity for long time. CM5 catalyst showed similar behavior to CM10.

Figure 3 shows the relation of carbon yield with Mo amount in the catalysts used for the synthesis of CNTs. The addition of 1 mol% Mo increased slightly the carbon yield, but addition of 5 mol%, 10 mol%, or 20 mol% Mo dramatically increased the carbon yield. In particular, the 5% and 10% addition increased the carbon yield by 20 times in comparison to the Co/MgO catalyst for 60 min synthesis. In the viewpoint of carbon yield, the optimum catalyst composition is CM10 and CM5.

3.2 Microstructure of CNTs

Figures 4A, B shows the FESEM images of as-synthesized CNTs by using Co/MgO catalyst. It was found that the product consisted of small aggregates with size of several micrometers. These aggregates formed probably from the CNTs growing from same catalyst precursor particles, on which small metallic particles precipitated by reduction in H₂. Some CNTs grew very long, so the aggregates further assembled to larger aggregates. Fig. 4B shows that CNTs are relatively straight with diameter of tens of nanometers. The TEM images in Fig. 4C, D shows the tubular structure of CNTs. From Fig. 4C, it can be seen that the

graphenes were parallel to the axis direction with about 10 layers of graphenes. Some fluctuation of CNTs structure could be observed, which was very difficult to avoid in CVD method. Fig. 4D showed that the structure of CNTs was relatively uniform. As

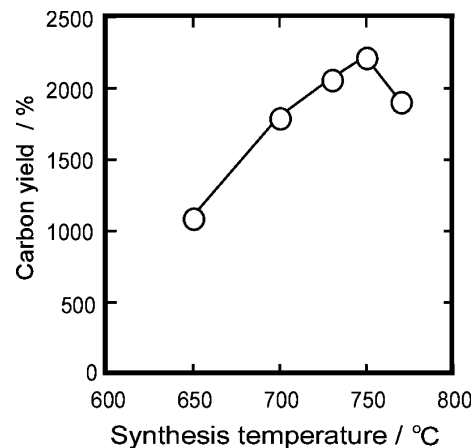


Fig. 1. Relation of carbon yield of CNT-CM20 (Mo/Co ratio 2:8 in the catalyst) with synthesis temperature.

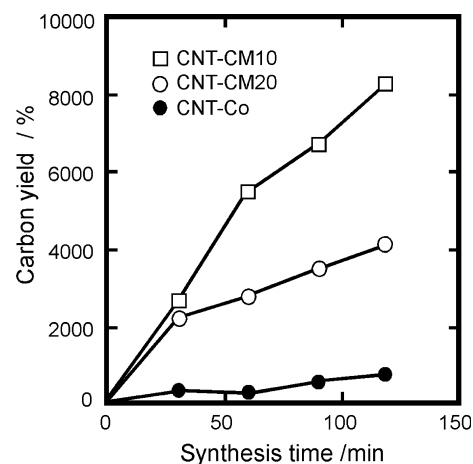


Fig. 2. Relation of carbon yield of CNT-Co, CNT-CM10, CNT-CM20 with synthesis time at the synthesis temperature of 750°C.

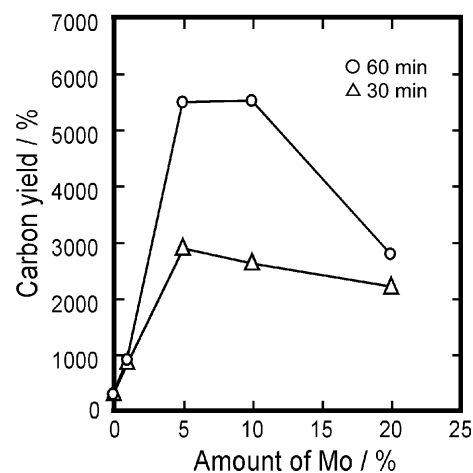


Fig. 3. Relation of carbon yield with Mo amount in catalyst at the synthesis temperature of 750°C for 30 min and 60 min.

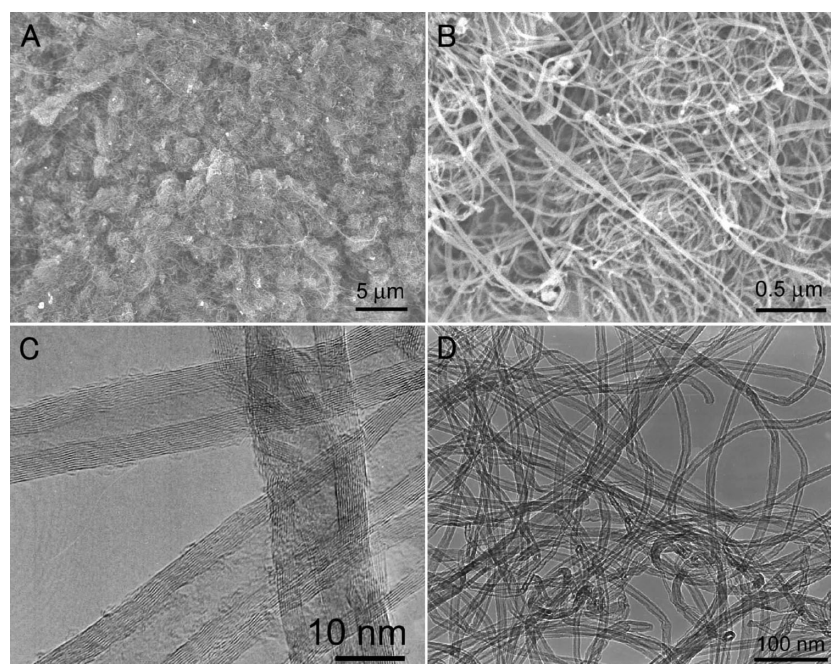


Fig. 4. FESEM images (A, B) and TEM images (C, D) of CNT–Co synthesized at 750°C. The as-synthesized CNTs contain about 25% catalyst residue.

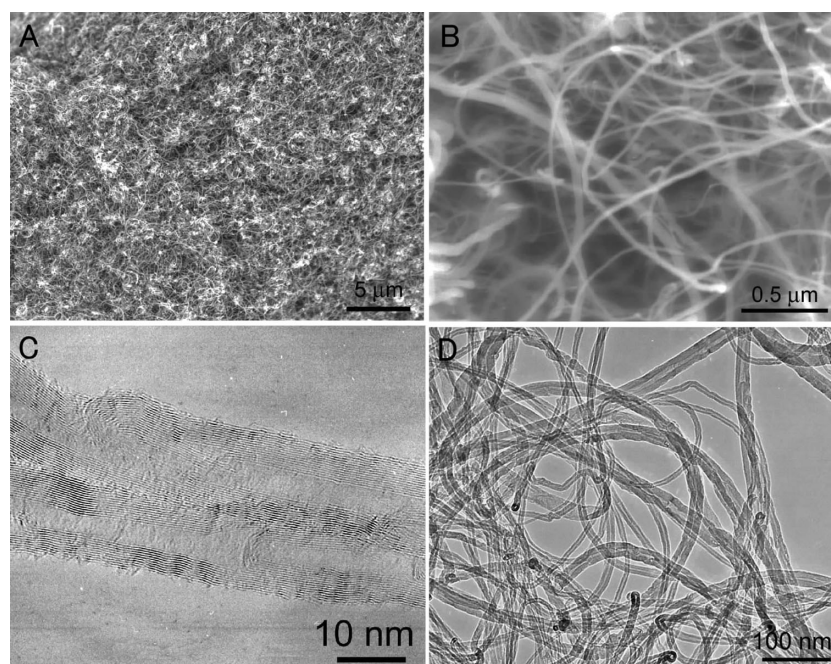


Fig. 5. FESEM images (A, B) and TEM images (C, D) of CNT–CM20 synthesized at 750°C. The as-synthesized CNTs contain less than 5% catalyst residue depending on the synthesis time.

described as later, the growth of CNTs is in root-mode, the catalyst particles were aggregated and wrapped by CNTs and scarcely appeared in the images, although there are about 25 mass% catalyst residue in the product.

Figure 5 shows the microstructure of CNTs obtained from CM20. Similar morphology was obtained, but the CNTs showed relatively curved in comparison to those synthesized from Co/MgO. Fig. 5C shows a typical CNT structure obtained. Though graphenes in walls were also parallel to CNT axis, they showed

more fluctuation in structure than those by Co/MgO. Instead of hollow tube structure, the CNTs showed a “bamboo-like” structure. Fig. 5D shows that the CNTs had a broader distribution in size and structure in comparison to those in Fig. 4.

The outer and inner diameters of CNTs were measured and shown in **Fig. 6** in relation to synthesis temperature. It can be seen that both the inner and outer diameter of CNTs increased with increasing the synthesis temperature. At high temperature, the metallic particles tended to condense to larger particles, thus

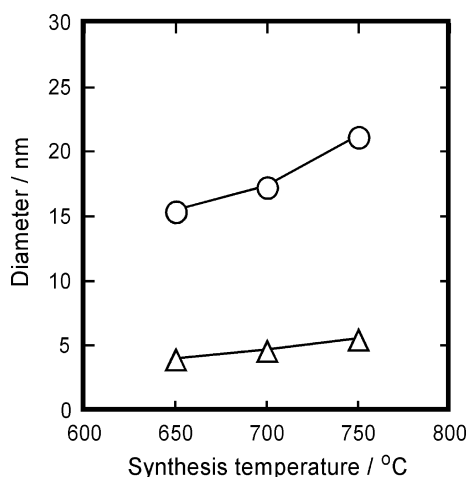


Fig. 6. Relation of outer and inner diameter of CNT-CM20 with synthesis temperature.

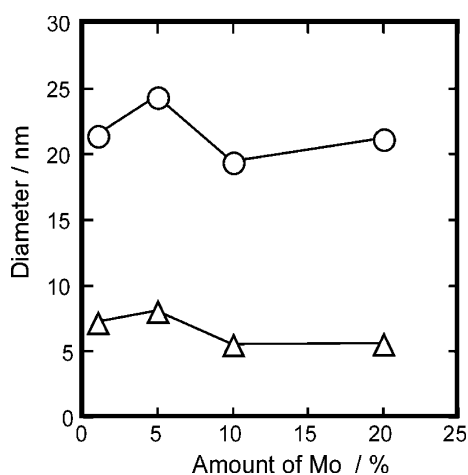


Fig. 7. Relation of outer and inner diameter of CNTs with Mo amount in catalyst at synthesis temperature of 750°C.

resulting in thicker nanotubes.

Figure 7 shows the relation of the outer and inner diameter with Mo amount in catalyst. The CNTs by CM5 showed slightly larger diameter than those obtained from other catalysts in catalyst.

3.3 Raman spectra

Figure 8 shows the Raman spectra of CNTs obtained from different catalysts. They showed typical peaks of carbon, the D band at 1380 cm^{-1} , which is attributed to the disorder carbon, and the G band at 1580 cm^{-1} representing the tangential C-C stretching mode of graphite. Table 2 shows the I_D/I_G ratio, the ratio of the intensity of D band and G band, which can express the disorder in CNTs. With increasing synthesis temperature, the I_D/I_G ratio of CNT-CM20 showed a slightly decreasing tendency. In general, higher temperature resulted in more ordered graphite structure. The Mo content in catalyst ratio showed no apparent effect on the I_D/I_G ratio.

4. Discussion

The growth of CNTs is generally explained using dissolving-diffusion-precipitation model.²⁰⁾ Carbon source molecules such

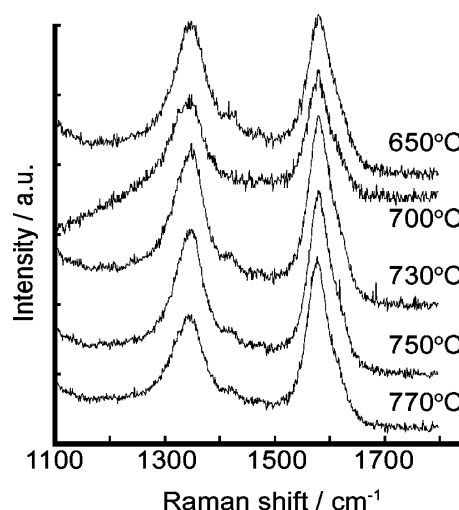


Fig. 8. Raman spectra of CNT-CM20 synthesized at different temperature.

Table 2. I_D/I_G Ratio of Raman Spectra of CNTs

Catalyst name	Synthesis temperature (°C)	I_D/I_G
CM20	650	0.95
CM20	700	0.77
CM20	730	0.85
CM20	750	0.80
CM20	770	0.62
CM10	750	0.70
CM5	750	0.62
CM1	750	0.72
Co	750	0.89

as C_2H_4 are absorbed on the surface of metallic catalyst particles, and decompose to carbon, which is dissolved in the catalyst particles. The carbon atoms diffuse by surface route or bulk route and precipitate in the opposite side of catalyst to form carbon nanotubes.

It has been reported there are two modes of growth, the tip mode and root mode.²¹⁾ In the tip-mode, catalyst particle locates at the top of CNTs, and is raised with the growth of CNTs. On the other hand, in the root mode, catalyst particle stays on the surface of substrate. In the observation of CNTs, almost no catalyst particles are found at the tip of CNTs, suggesting that the growth was in a root mode.

The growth mode depends on the interaction between catalyst particles and the support. If the interaction between catalyst particle and support is weak, the catalyst particles can be easily raised, and a tip mode dominates. On contrary, if the interaction between catalyst particle and support is strong, the catalyst particles are difficult to be raised, and a root mode dominates. The root mode in the present case is probably due to the strong interaction between the Co-Mo particles with MgO. The catalyst in this study was precipitated from reduction of $\text{CoO-MoO}_3/\text{MgO}$ by hydrogen. The reduction occurred just on the surface of the $\text{CoO-MoO}_3/\text{MgO}$ solid solution, thus it is reasonable that the interaction between the precipitated CoMo particles and support

oxide particles was very strong.

From the structure of CNTs, we could infer the growth process of CNTs. At initial stage of CNT growth when the graphenes precipitated from the catalysts, the subsequently precipitated graphenes will become smaller, due to the limitation of the outer graphenes. In this way, with the precipitation of graphene layers, the stress around the particles will transform catalyst particles to long conical or cylindrical shape. After the initial transformation, the Co catalyst particles will keep a relatively stable shape since no graphene precipitated from the base surface of particles and thus no stress further on the particles.

For Co–Mo catalyst, the strong interaction between graphene and Co–Mo made the particles transform further to thin long conical shape. At a certain length, the surface tension of the particle will pull the particles back and change to a more round shape. The graphenes were then precipitated again and the transformation of particles occurred again. This process could go on repeatedly, resulting in the bamboo-like shape. The shrinking of Co–Mo back to the round shape rapidly occurred, disturbing the growth of CNTs abruptly and resulting in the discontinuous growth of graphenes in the outer layers of CNTs.

5. Conclusions

Addition of Mo in Co/MgO catalyst affected dramatically the carbon yield and structure of CNTs synthesized by CVD method. The structure of CNTs was “bamboo-like” structure without continuous hollow tube, while those synthesized by Co/MgO showed a typical MWNT structure. 5–10% Mo addition showed high yield of carbon, e.g. 5500% for 60 min synthesis, and extended lifespan of the catalysts.

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