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Atsuto Okamoto [a], Tomoju Kawakubo [b], Tatsuki Hiraoka [b], Toshiya Okazaki [b], Toshiki Sugai [b] & Hisanori Shinohara [b]

[a] Toyota Central R&D Labs., Inc., Nagakute, Aichi, 480-1192, Japan

[b] Department of Chemistry, Nagoya University, Nagoya, 464-8602, Japan

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# SYNTHESIS AND CHARACTERIZATION OF MULTI- AND SINGLE-WALL CARBON NANOTUBES BY THE CATALYTIC VAPOR DEPOSITION METHOD

*Atsuto Okamoto**
*Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan*

*Tomoju Kawakubo, Tatsuki Hiraoka, Toshiya Okazaki, Toshiki Sugai, and Hisanori Shinohara*
*Department of Chemistry, Nagoya University, Nagoya 464-8602, Japan*

*Carbon nanotubes (CNTs) have been synthesized by catalytic decomposition of acetylene (catalytic chemical vapor deposition, the so-called CCVD method) over well dispersed metal particles (cobalt and iron) embedded in supports such as commercially available zeolites and folded sheets mesoporous material (FSM) at temperature above 600°C. A few individual single-wall carbon nanotubes (SWNTs) and bundles of SWNTs are observed in pristine soot synthesized with FSM supports at 900°C, whereas no SWNTs but only multi-wall CNTs (MWNTs) are observed in pristine soot synthesized at less than 800°C. The observed temperature dependence is similar to the synthetic result obtained with zeolites supports. The yield of CNTs (both SWNTs and MWNTs) is higher with Zeolite supports than with FSM. Transmission electron microscopy and Raman spectroscopy also revealed that surface pores of support materials could act as an excellent growth sites for SWNTs.*

*Keywords*: Carbon nanotube; CCVD; FSM; Zeolite; surface pore

## 1. INTRODUCTION

The mass-fabrication of structure-controlled carbon nanotubes (CNTs) at low cost is increasingly necessary in view of various applications such as electric devices, composites, nano-reactors [1], and energy storage. Catalytic pyrolysis of hydrocarbons (catalytic chemical vapor deposition,

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*Corresponding author. E-mail address: okamoto@mosk.tytlabs.co.jp

the so-called CCVD method [2–4]) is one of the most promising techniques for this purpose. We have already reported the synthesis of quasi-aligned multi-wall CNTs (MWNTs) by the pyrolysis of acetylene ($C_2H_2$) over well-dispersed metal particles embedded in commercially available zeolite at a lower temperature (600–700°C) [3,4]. Recently, the synthetic results of single-wall CNTs (SWNTs) by CVD techniques were reported [5–7]. The synthesis of SWNTs seems to be related to the very small size of the catalyst particles in these papers. It is, therefore, very important to control the catalyst size during the growth above 800°C. A zeolite material with sub-nano-size pores and a folded mesoporous material (FSM) [8] with nano-size pores were expected to be suitable for the stability of small size catalysts at the synthesis temperatures utilized.

In this paper, we report the synthesis and characterization of CNTs obtained by catalytic decomposition of $C_2H_2$ over well-dispersed metal catalysts embedded in supports. The effects of reaction temperature and types of supports such as commercially available zeolite and unavailable FSM produced by Toyota CRDL on SWNTs synthesis are also presented.

## 2. EXPERIMENTAL

CNTs were synthesized by means of the catalytic decomposition of $C_2H_2$ over supported Co and Fe catalysts in the temperature range of 600–900°C. In this work, a commercially available zeolite (Y-type zeolite from Tosoh Corporation) and FSM produced by Toyota CRDL were applied as support materials of catalysts. The catalyst preparation was carried out using the impregnation method as described in Ref. [3,4]. The solution of Co-acetate (2.5 wt%) and Fe-acetate (2.5 wt%) were used in the preparation. The catalysts mixture was sprayed over the quartz boat and was placed in the central position of the furnace. It was then annealed for 30 min at 600°C and heated to growth temperature of 600°C to 900°C under Ar at a flow rate of a 250 ml/min. $C_2H_2$ was passed through the furnace at the rate of 10 ml/min for 30 min while Ar gas flow was maintained at 250 ml/min flow rate. After the reaction, the furnace was cooled down to the room temperature by the passage of Ar gas (250 ml/min). The pristine soot was then collected as a black power from the quartz boat.

The pristine all soot were characterized by transmission electron microscopy (TEM) and Raman spectroscopy. TEM observations were done with a JEOL JEM-2000EX at 200 kV. Raman measurements have been carried out at room temperature by using a Jobin Yvon T-64000 spectrometer. The 514.5 nm (2.41 eV) line of an Ar ion laser was used for excitation.

## 3. RESULTS AND DISCUSSION

Figure 1 shows typical TEM images of pristine soot synthesized by using suitable zeolite supports. As shown in insets of Figure 1b, bundles of SWNTs were observed in pristine soot synthesized at temperatures above 800°C. In contrast, we have found no SWNTs (but only MWNTs) in soot synthesized at temperature lower than 800°C (Fig. 1a). On the other hand, as shown in Figure 2b, a few individual SWNTs and bundles of SWNTs were observed in pristine soot synthesized with FSM supports at 900°C. No SWNTs, however, were synthesized in soot synthesized at temperatures lower than 800°C (Fig. 2a). The observed temperature dependence is similar to the result obtained with zeolites supports as mentioned above. The yield of CNTs (both SWNTs and MWNTs) was also higher with Zeolite

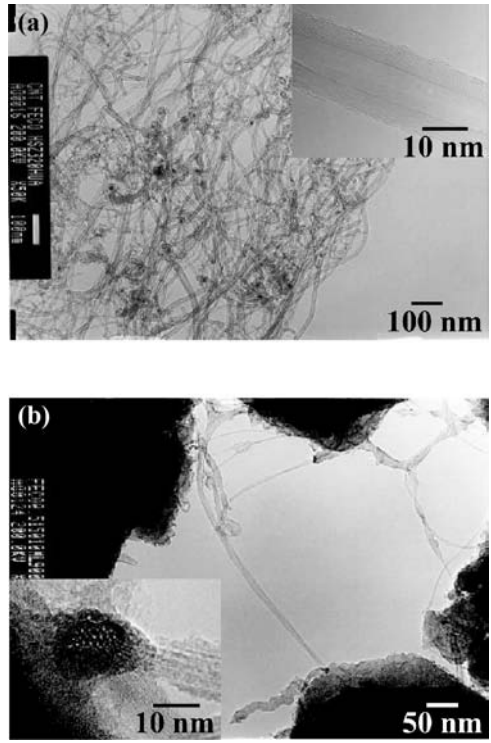


**FIGURE 1** TEM images of the pristine soot: (a) multi-wall carbon nanotubes synthesized with Fe/Co/zeolite (HSZ-320NAA) catalyst at 600°C, (a) single-wall carbon nanotubes synthesized with Fe/Co/zeolite (HSZ-390HUA) at 900°C. The insets show high-resolution TEM images of each sample.

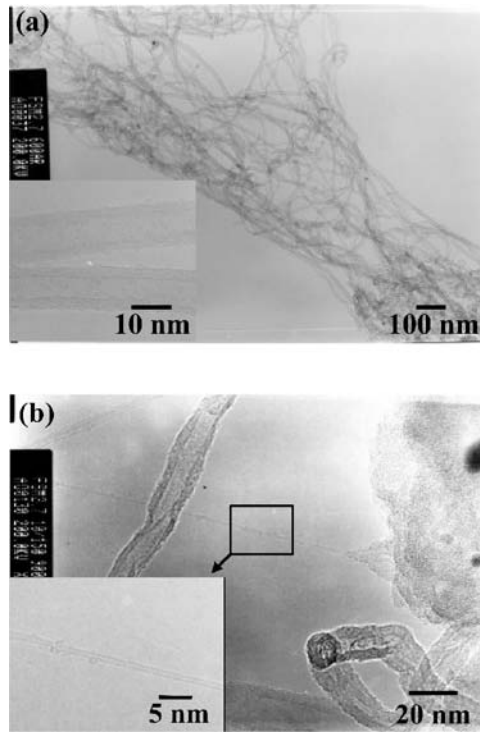


**FIGURE 2** TEM images of the pristine soot synthesized with Fe/Co/FSM catalyst: (a) multi-wall carbon nanotubes synthesized at 600°C, (a) single-wall and multi-wall carbon nanotubes synthesized at 900°C. The insets show high resolution TEM image of each sample.

supports than with FSM. In both cases, some amorphous carbon materials were observed on the external wall and the root of the CNTs. Evidently, removing these amorphous carbon materials in the growth process is essential for the fabrication of structure-controlled CNTs at low cost. Further studies in this regard are underway.

Figure 3 shows typical Raman spectra of the pristine soot synthesized with the zeolite support at 800°C and 900°C. From Raman spectra for radial breathing modes (RBM) of SWNTs it can be stated that the SWNTs synthesized by the CCVD method have comparatively thinner diameter than those produced by both laser furnace and arc discharge methods, as shown in insets of Figure 3. Examination of a temperature dependence of the RBM of SWNTs synthesized by the CCVD method revealed that the tube diameter decreased as the reaction temperature decreased. The temperature

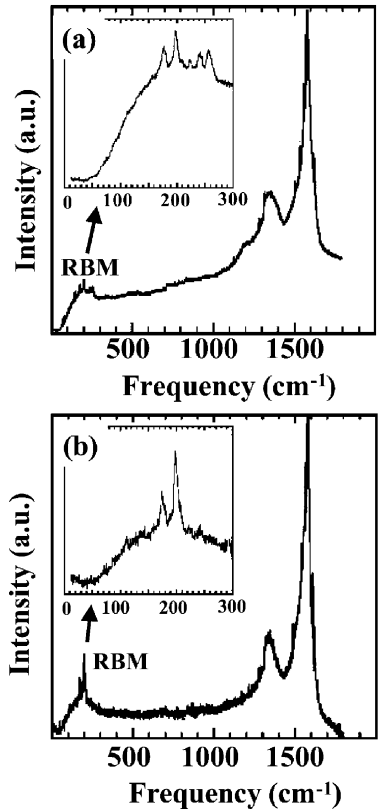


**FIGURE 3** Raman spectra for the pristine soot synthesized with Fe/Co/zeolite (HSZ-390HUA) catalyst: (a) at 800°C, (b) at 900°C. The insets show the nanotube radial breathing modes.

dependence of the tube diameter is similar to that reported by Bandow *et al.* in the laser furnace experiment [9].

In contrast, SWNTs in the range from ~0.7 nm to 3 nm in diameter were observed in TEM images although we could not obtain a Raman spectrum from the pristine soot synthesized with a FSM support at 900°C because of a low yield. According to an estimation based on Ref. [10], the diameter of SWNTs in the pristine soot synthesized with zeolite support at 800°C is in the range of 0.95–1.42 nm. This is indicative of the fact that some SWNTs synthesized in soot have a diameter distribution equivalent to the pore size of the zeolite (~0.8 nm) and of the FSM (2.7 nm). Evidently, surface pores of the catalyst supports can act as an excellent growth site for SWNTs.

## 4. CONCLUSION

We have synthesized carbon nanotubes *via* catalytic decomposition of hydrocarbons by the so-called CCVD method over well-dispersed metal catalysts embedded in supports such as commercially available zeolites and folded sheets mesoporous material at temperatures above 600°C. Transmission electron microscopy and Raman spectroscopy of the pristine soot synthesized also revealed that surface pores of the catalyst supports could act as an excellent growth site for single-wall carbon nanotubes. Although the carbon nanotubes obtained have been affected by growth conditions such as support materials (type of zeolites and folded sheets mesoporous material) and reaction temperature, the overall synthesis procedure of single-wall carbon nanotubes is similar to that of multi-wall carbon nanotubes. The CCVD method described herein may be useful for bulk-production of both multi- and single-wall carbon nanotubes.

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