Purification and characterization of zeolite-supported single-walled carbon nanotubes catalytically synthesized from ethanol

Hideyuki Igarashi,[a] Hiroto Murakami,[a] Yoichi Murakami,[b]
Shigeo Maruyama,[b] Naotoshi Nakashima[a,]*

[a] *Department of Materials Science, Graduate School of Science and Technology, Nagasaki University, Bunkyo, Nagasaki 852-8521, Japan*

[b] *Department of Mechanical Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan*

Received 10 February 2004; in final form 12 May 2004

Abstract

Nearly complete removal of zeolite particles and Fe/Co catalysts from raw single-walled carbon nanotubes (SWNTs) produced by chemical vapor deposition was achieved by oxidation of raw material at 240 or 340 ˚C and treatment with 1 % aqueous solution of hydrofluoric acid. The yields of SWNTs were estimated to be ≈95% and the purities of SWNTs thus obtained were more than 95 %, as characterized by thermo-gravimetric (TG) analysis. Raman spectra of the purified SWNTs were essentially identical with those of the corresponding raw samples. The raw and purified SWNTs were also characterized by EDX spectroscopy and transmission electron

microscopy (TEM).

* Corresponding author. Present address: Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki, Fukuoka 812-8581, Japan FAX: +81-92-642- 3602. e-mail: nakashima-tcm@mbox.nc.kyushu-u.ac.jp (N. Nakashima).

1. Introduction

Since the first finding in 1991 [1], studies of carbon nanotubes have been developed in wide fields of science and technology. The samples have been synthesized by laser ablation, arc-discharge and chemical vapor deposition (CVD) [2,3]. Catalytic CVD (CCVD) has been developed in recent several years for large-scale production and controlled synthesis of single-walled carbon nanotubes (SWNTs) [4,5]. Shinohara et al. reported large-scale production of quasi-aligned multi-walled carbon nanotube bundles on zeolite by CCVD, in which acetylene was used as the carbon source to produce nanotubes by catalytic decomposition [6]. High-quality SWNTs were produced by Maruyama et al. on zeolite from alcohol by CCVD, where oxygen radical generated from alcohol was suggested to contribute production of SWNTs by attacking carbon impurities such as amorphous carbon [7,8]. CCVD synthesis and purification of SWNTs have also been reported on aerosol-supported catalyst (by Liu et al. [9]) or from

CO disproportionation over Co-Mo catalyst using silica support (Resasco et al. [10,11]).

The target of our present research is a suitable process for removal of zeolite and catalyst from raw SWNTs synthesized by CCVD using ethanol. Previous studies of this method [7,8] have indicated that it can provide high-quality SWNTs, i.e., those containing hardly any amorphous carbon or multi-walled carbon nanotubes, for wide use as functional materials in science and engineering. Combinations of two main conditions were tested in the present study on the procedures for purification of the samples: (a) treatment with hydrofluoric acid (HF) and (b) oxidation by heating. The SWNTs thus obtained were characterized by TG analysis, Raman spectra, TEM and EDX-SEM. We have found that a suitable combination can produce SWNTs with sufficient thermal stability and appreciable purity.

2. Experimental

The synthetic procedure of zeolite supported-SWNTs from alcohol has been described in detail [7,8]. Ethanol containing 1.0 g of Y-type zeolite (Tosoh Co., HSZ-390HUA) and 2.5 wt % of metals from either iron acetate (78 mg) or cobalt

acetate tetrahydrate (106 mg) were sonicated for 10 min and then dried at 80 ˚C to obtain zeolite-supported catalyst. The catalyst (50 mg) on a quartz boat was placed in a quartz tube (i.d. 28 mm) inside an electric furnace. After evacuating the air, Ar gas (40 kPa) was introduced and heated to 800 ˚C. Then Ar gas was evacuated and ethanol gas (0.67 kPa) was introduced for 15 min, 1 h, and 2 h to produce raw-SWNTs-**1**, -**2**, and -**3**, respectively. The SWNTs were heated to oxidize the catalyst metals, and the samples (12 mg) thus obtained were placed in a 1 vol % (0.45 M) aqueous solution of HF (9 ml) to remove metal particles and zeolite, followed by drying to get purified SWNTs.

The following three procedures were examined to reach higher purity from the raw SWNTs: i) HF treatment only (method 1), ii) oxidation (heating) and then HF treatment (method 2), and iii) oxidation (heating) and then HF treatment followed by further oxidation (method 3). The details are described in Section 3.

For characterization of the products thus obtained, TG curves (10 ˚C/min), Raman spectra (excitation at 514.5 nm with an Ar ion laser), transmission electron microscopic (TEM) images, and EDX spectra were measured with Shimadzu TGA-50H, Renishaw Ramanscope System 1000, JEOL JEM-100S, and HITACHI S-2250N equipped with

Horiba EMAX-5770Q, respectively.

3. Results and discussion

3.1. Purification by methods 1 and 2

Figure 1 shows the TG curves of three raw samples synthesized by the present method. The weight-loss at 500-800 ˚C for raw-SWNTs-**1**, -**2,** and -**3** were 7.9, 12.1, and 15.4 wt %, respectively. Since HF aqueous solutions are known to dissolve zeolite and metal oxides, we first added raw SWNTs-**1** in HF aqueous solutions (1-10wt%) and shook it with a vortex mixer for 5-360min (method 1). The SWNTs were collected with a filter (Millipore GTTP, pore size 200nm), thoroughly rinsed with water to remove HF and then dried in vacuum. The obtained samples were characterized by the TG analysis and Raman spectra. Although the Raman spectra of these samples were almost identical with that of the raw SWNTs (data not shown), their TG curves showed that weight-loss had started at 240˚C and that ≈30 wt% of the samples corresponding to metal particles remained after heating at 800 ˚C. We then tested method 2, where raw SWNTs were heated to either 240˚C or 340˚C for 1.5 hr in humid argon containing 20% oxygen gas

and then treated with the same procedure as method 1. By this treatment the remaining metal particles decreased to ≈6% after heating to 800 ˚C, while the weight-loss started at 240 ˚C. The Raman spectra of these samples were almost identical with that of the raw SWNTs (data not shown).

All the data described above indicate that both methods 1 and 2 are insufficient to purify raw SWNTs. It is suggested that the low temperature stability of the SWNTs obtained by methods 1 and 2 is due to the adsorption of amorphous carbons and/or acids onto SWNT surfaces. On this viewpoint, we have modified method 2 to method 3 by adding further oxidation procedure.

3.2. Purification by method 3

Raw SWNTs-**1** were heated either at 240 ˚C for 18 h or at 340 ˚C for 1.5 h in humid argon containing 20% oxygen gas to oxidize the reduced metal catalysts to give SWNTs-**1**[240(18h)] and SWNTs-**1**[340(1.5h)], respectively. The corresponding samples were also obtained for SWNTs-**2** and –**3**. Although heating at 350 ˚C for 1.5 h was reported to decompose SWNTs (so-called HiPco, CNI) [12], both heating conditions gave essentially identical results with our samples. This is ascribable to the

higher thermal stability of our SWNTs than that of HiPco. Each sample obtained was placed in a 1vol% HF aqueous solution in a polypropylene plastic vessel and was shaken with a vortex mixer at 300 rpm for 30min. The same treatment was carried out for 24h to examine the effect of HF on the nanotubes. The original zeolite itself readily dissolves in a 1vol % HF solution without treatment with a vortex mixer, but in this case dissolution of zeolite from the raw samples required the above treatment.

After this treatment with HF, the SWNTs were collected by a filter (Millipore GTTP; pore size, 200 nm), and then washed with pure water. The SWNTs thus obtained were dried in vacuum for 3h at room temperature and then heated at 120 ˚C or 350 ˚C for 1h in humid argon containing 20% oxygen gas to obtain SWNTs-**1**[240(18h)-120], SWNTs-**1**[240(18h)-350], SWNTs-**1**[340(1.5h)-120], and SWNTs-**1**[340(1.5h)-350], respectively. Similar treatments were conducted for SWNTs-**2**[240(18h)], SWNTs-**2**[340(18h)], SWNTs-**3**[240(18h)] and SWNTs-**3**[340(1.5h)]. SWNTs with higher purity were obtained by these treatments from the corresponding raw materials with ≈95 yield (average).

Typical TG curves of SWNTs-**1**[340(1.5h)-120] and SWNTs-**1**[340(1.5h)-350] are

shown in Fig. 2. It is evident that the thermal stability of the latter sample is much higher than that of the former. The lower stability of the former is probably due to the acids remaining on the nanotube surfaces. The purities of the SWNTs-**1**[340(1.5h)-350] were estimated from the TG curves to be ≈ 99 %. The purities of SWNTs-**1**[240(18h)-350], SWNTs-**2**[240(18h)-350], SWNTs-**2**[340(1.5h)-350], SWNTs-**3**[240(18h)-350], and SWNTs-**3**[340(1.5h)-350] estimated from the corresponding TG curves were 95-97%.

The Raman spectra of raw SWNTs-**1**[240(18h)-350] and SWNTs-**1**[340(1.5h)-350] are shown in Fig. 3. The G-bands near 1590 cm^{-1} and the radial breathing mode (RBM) at 150-270 cm^{-1} for the raw and purified SWNTs appear at the same wavenumbers, indicating that the chemical damage by HF on the nanotubes was negligible. The purified SWNTs prepared by the HF treatment for a longer time gave essentially the same Raman spectra (data not shown). The diameters of the purified SWNTs-**1**[240(18h)-350] estimated from the peaks of RBM using the relationship, $d = 223.5/(\nu - 12.5)$ [13], were 0.88 and 1.33 nm, which are nearly identical to the reported values. SWNTs-**1**[340(1.5h)-350] also gave nearly identical data.

Typical TEM images of the raw and purified SWNTs are shown in Fig. 4, in which the black-colored particles observed in the left panel is the image of the zeolite used as catalyst support. Bundle-structured nanotubes are observed in the right panel, but no evident traces of zeolite, amorphous carbon, carbon nanoparticles or metal particles are observed.

The EDX spectra of the SWNT samples produced by the present procedure gave direct evidence for their purity. As shown in Fig. 5, the peaks of Si ($K_\alpha 1$=1.74 eV), Fe ($K_\alpha 1$=6.40 eV), and Co ($K_\alpha 1$=6.92 eV) observed for the raw SWNTs were very small or essentially absent in the purified nanotubes.

4. Concluding remarks

We have presented a procedure for removal of zeolite particles and Fe/Co catalysts in the SWNTs synthesized by CCVD using ethanol. The purities of the SWNTs produced after repeated oxidation with HF treatment were estimated to exceed 95%. For SWNTs-**1**[340(1.5h)-350], the purity was $\approx$ 99 %. This method is expected to be applicable for purification of SWNTs synthesized by CCVD techniques with different

experimental conditions.

References

[1] S. Iijima, Nature 354 (1991) 56.

[2] P.J.F. Harris, Carbon Nanotubes and Related Structures, Cambridge University Press, Cambridge, 1999.

[3] K. Tanaka, T. Yamabe, K. Fukui, (Eds.), The Science and Technology of Carbon Nanotubes, Elsevier, Oxford (1999).

[4] M.J. Bronikowski, P.A. Willis, D.T. Colbert, K.A. Smith, R.E. Smalley, J. Vac. Sci. Technol. A 19 (2001) 1800.

[5] Y. Zhang, A. Chang, J. Cao, Q. Wang, W. Kim, Y. Li, N. Morris, E. Yenilmez, J. Kong, H. Dai, Appl. Phys. Lett. 79 (2001) 3155.

[6] K. Mukhopadhyay, A. Kosho, T. Sugai, N. Tanaka, H. Shinohara, Z. Konya, J.B. Nagy, Chem. Phys. Lett. 303 (1999) 117.

[7] S. Maruyama, R. Kojima, Y. Miyauchi, S. Chiashi, M. Kohno, Chem. Phys. Lett., 360 (2002) 229.

[8] Y. Murakami, Y. Miyauchi, S. Chiashi, and S. Maruyama, Chem. Phys. Lett. 374 (2003) 53.

[9] B. Zeng, Y. Li, J. Liu, Appl. Phys. A 74 (2002) 345.

[10] W.E. Alvarez, F. Pompeo, J.E. Herrera, L. Balzano, D.E. Resasco, Chem. Mater. 14 (2002) 1854.

[11] S.M. Bachilo, L. Balzano, J.E. Herrera, F. Pompeo, D.E. Resasco, R.B. Weisman, J. Am. Chem. Soc. 125 (2003) 11186.

[12] I.W. Chiang, B.E. Brinson, A.Y. Huang, P.A. Willis, M.J. Bronikowski, J.L. Margrave, R.E. Smalley, R.H. Hauge, J. Phys. Chem. B, 105 (2001) 8297.

[13] S.M. Bachilo, M.S. Strano, C. Kittrell, R.H. Hauge, R.E. Smalley, R.B. Weisman, Science, 298 (2002) 2361.

Figure captions

Fig. 1. TG curves of raw SWNTs synthesized at 800 ˚C for (a) 15min, (b) 60 min and (c) 120 min.

Fig. 2. Typical TG curves of (a) SWNTs-**1**[340(1.5h)-120] and (b)

SWNTs-**1**[340(1.5h)-350].

Fig. 3. Raman spectra of purified SWNTs-**1[**240(18h)-350] (A and B), SWNTs-**1 [**340(1.5h)-350] (C and D), and the corresponding raw SWNTs.

Fig. 4. TEM images of (left) raw SWNTs and (right) SWNTs-**1**[340(1.5h)-350].

Fig.5. Typical EDX spectra of (A) raw and (B) purified SWNTs-**1**[240(18h)-350].

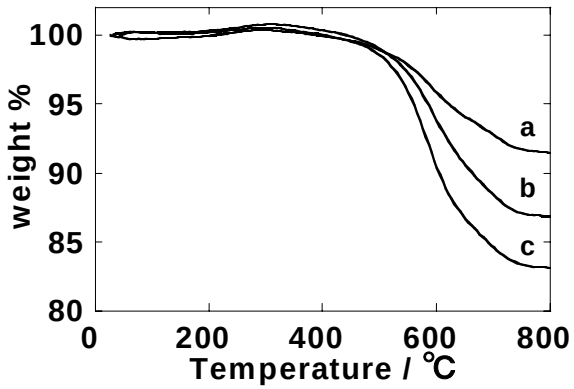

Fig. 1. Igarashi et al.

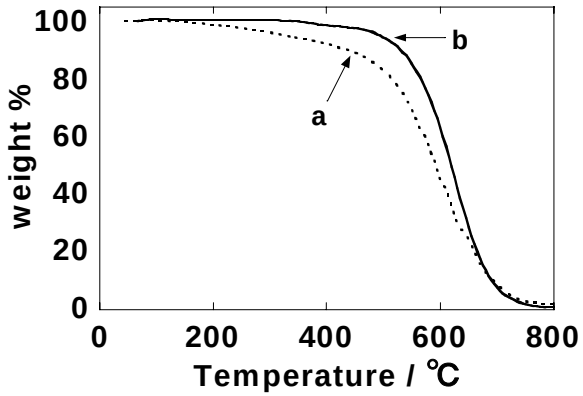

Fig. 2. Igarashi et al.

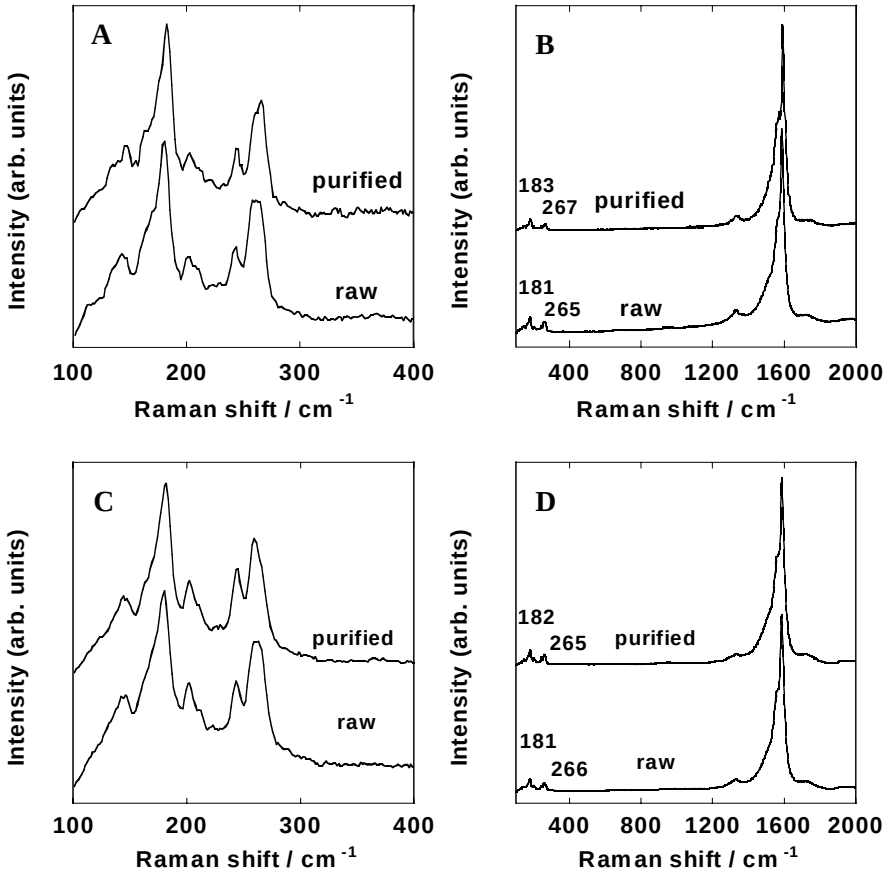

Fig. 3. Igarashi et al.

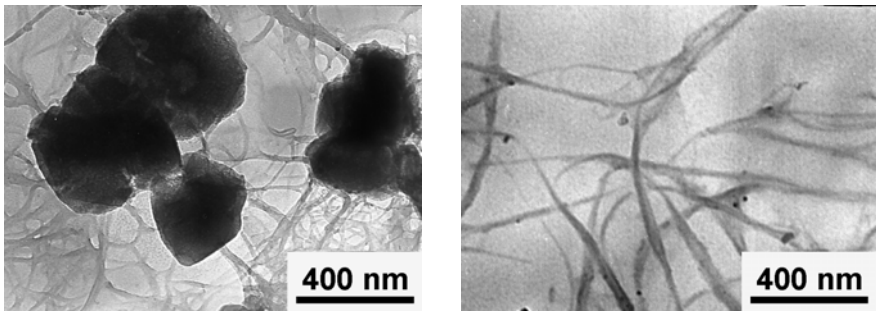

Fig. 4. Igarashi et al.

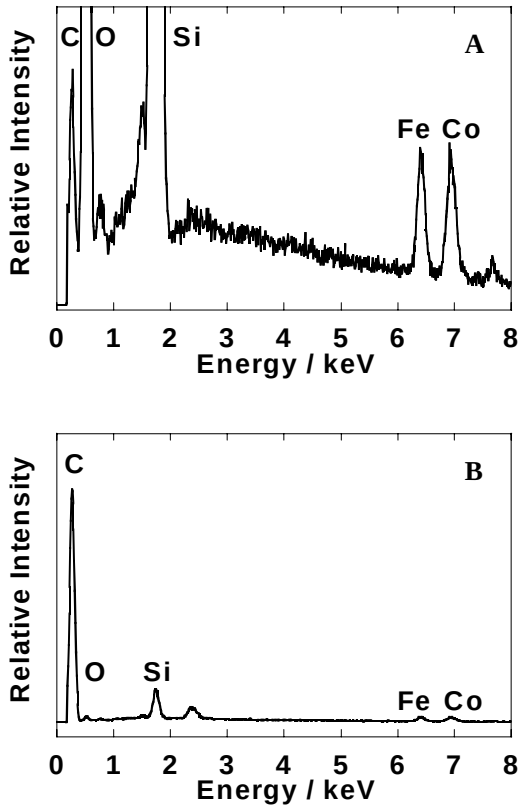

Fig. 5. Igarashi et al.