

Purification Procedure for Single-Walled Nanotubes

K. Tohji,* H. Takahashi, Y. Shinoda, N. Shimizu, B. Jeyadevan, and I. Matsuoka

Department of Geoscience and Technology, Tohoku University, Sendai, 980-77, Japan

Y. Saito

Department of Electrical and Electronic Engineering, Mie University, Tsu 514, Japan

A. Kasuya, S. Ito, and Y. Nishina

Institute for Materials Research, Tohoku University, Sendai, 980-77, Japan

Received: September 19, 1996; In Final Form: December 5, 1996[®]

A purification procedure for single-walled nanotubes is presented in this report. A novel purification method that incorporates the hydrothermal treatment along with other treatments such as extraction of fullerenes and oxidation and dissolution of metal particles is used in this study. The effects of each treatment in the purification process is also discussed by characterizing the intermediate products using X-ray diffraction, Raman spectroscopy, scanning electron microscopy, and transmission electron microscopy.

Introduction

Since the discovery of single-walled nanotubes (SWNTs),^{1–3} various methods for their synthesis and possible characterization have been hotly pursued.^{4–16} Parallel to these efforts, theoreticians have introduced a new coordinate system to define their chiral crystallography, while others have predicted them to be one-dimensional conductors or semiconductors.^{17,18} Recently, SWNTs have been successfully synthesized in large quantities using composite consumable carbon electrodes mixed with several metallic species, predominantly transition metals such as Ni, Fe, and Co.^{5,6,8,16} The SWNTs synthesized by this method coexist with metals and various forms of carbon and other such impurities, resulting in a serious impediment to detailed characterization of the nanotubes and assessment of their potential utility.

In our previous report,¹⁹ we briefly presented the novel purification method for SWNTs incorporating the hydrothermal treatment along with other treatments for the extraction of fullerene and oxidation and dissolution of metal particles. As a result, at least 20 mg of SWNTs with 95 wt % purity is obtained from 1 g of raw soot. In the hydrothermal treatment (hydrothermally initiated dynamic extraction method or HIDE),^{20,21} it is believed that H₂O molecules break the network between SWNTs and amorphous carbon and metal particles and makes a valuable contribution to the overall performance of the purification process. The byproducts that coexist with SWNTs in the soot are removed at each step of the purification process. In this report, the purification procedure for SWNTs is presented and the effects of each treatment in the purification process is discussed by characterizing the intermediate products using X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

Experimental Section

Preparation of SWNTs. The method employed to synthesis SWNTs is the same as that employed to synthesize for

nanocapsules stuffed with metal crystallites.^{22–24} Packed graphite rods containing a mixture of Fe and Ni powders of 99.9% purity (Wako Chemical Co. Ltd., Japan) were used as the anode of DC arc discharge. The mixing ratio of Ni, Fe, and graphite powder for efficient production of SWNTs was roughly 1:1:3 by weight. Total metal content in the anode is approximately 6 at. %. A hole of 3.2 mm diameter and 50 mm in depth was drilled out from a graphite rod (99.998% purity, 100 mm long and 6 mm in diameter) supplied from Toshiba Ceramics Co. Ltd., Japan, and filled with a mixture of metal and graphite powders. A pure graphite rod of 10 mm in diameter was used as cathode. The arc discharge was carried out under a He atmosphere of 100 Torr. The discharge current was 70 A, and during the discharge, the gap between the electrodes was maintained at about 1 mm by manually advancing the consumed anode.

Purification of SWNTs. The soot produced by DC arc discharge was retrieved from the upper wall of the arc discharge chamber and homogenized. In the HIDE treatment, used as the initial step of the purification process, 100 mg of the soot containing SWNTs was introduced into a flask with a reflux attachment together with 50 mL of distilled water and was heated at 373 K for 12 h. The soot was disintegrated to submicron-sized particles. The processed soot was filtered and dried at 333 K for 12 h. Then, fullerenes were washed out using toluene in a Soxhlet. The residual soot was heated at 743 K for 20 min. In the final step of the purification process, the soot was treated in 6 M hydrochloric acid and almost all the metal complexes were washed out.

Evaluation of the Purification Procedure and Characterization of Purified SWNTs. The purification procedure of SWNTs was probed by SEM and XRD. The purified SWNTs were characterized by TEM and Raman scattering and their surface areas were measured by BET method. The intermediate product at each purification step was dispersed in ethanol, sonicated for 5 min, deposited on a sample stage, and observed in a SEM operated at 5 keV. XRD patterns were taken by a powder X-ray diffractometer with a Cu K α X-ray source. For TEM observation, the sample was ultrasonically dispersed in ethanol and the suspension was dropped onto a microgrid. The Raman scattering measurements were carried out at room

* Author to whom correspondence should be addressed. E-mail: tohji@ni4.earth.tohoku.ac.jp.

[®] Abstract published in *Advance ACS Abstracts*, February 1, 1997.

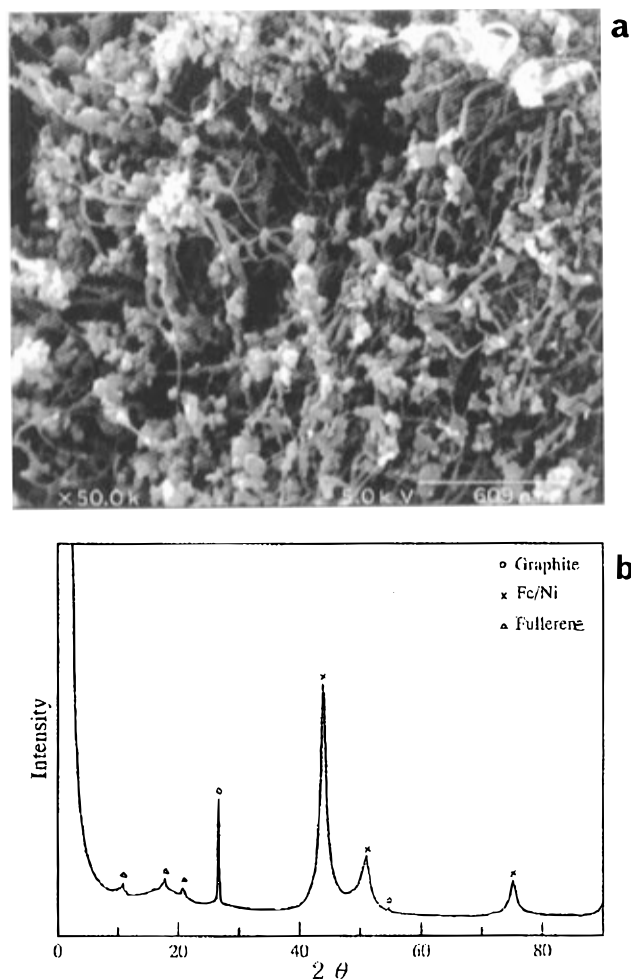


Figure 1. (Top) SEM photograph and (bottom) XRD profile of the raw soot.

temperature using Ar ion laser (488.0 nm) in a backscattering configuration. The surface area of SWNTs was obtained from the N_2 gas adsorption isotherm equilibrium proposed by Langmuir. The amount of residual metals in the purified SWNTs was also estimated by chemical analysis using the inductively coupled plasma method (ICP).

Results and Discussion

Purification Procedure for SWNTs. In the raw soot produced by arc discharge, SWNTs coexist with many byproducts such as metal particles, fullerenes, and amorphous carbon.^{5,6,8} Therefore, SWNTs have to be separated step by step in the purification processes.

Figure 1 shows the SEM photograph and XRD profile of the raw soot. Under the present preparative conditions, the SWNTs are efficiently grown and coexist with many byproducts as seen in Figure 1a. Furthermore, the SWNTs and metal particles are surrounded by carbon materials such as amorphous carbon and fullerenes. XRD pattern in Figure 1b shows the presence of C_{60} , graphite, and metal particles.

Figure 2a shows a SEM photograph of the soot treated by the HIDE method. The SWNTs certainly look much more slender in comparison to those observed in Figure 1a. The XRD profile of Figure 2b does not show any change, except for the decrease in the intensity of the 002 peak of graphite compared to that of the 002 peak in Figure 1b. This suggests that the graphite particles and amorphous carbon adsorbed on SWNTs were partly removed as a result of the HIDE treatment.

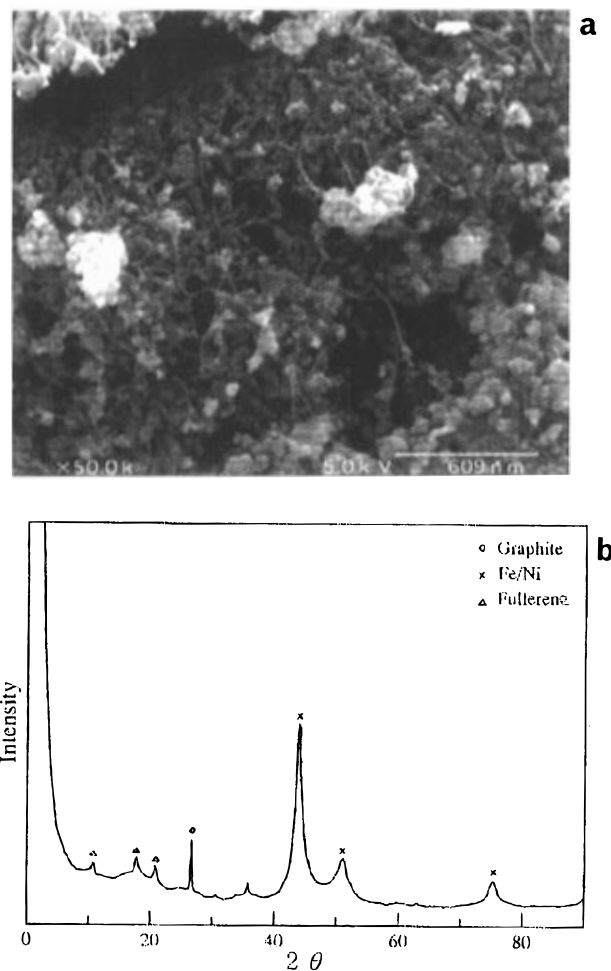


Figure 2. (Top) SEM photograph and (bottom) XRD profile of hydrothermally treated soot.

The soot used in these experiments contained about 10 wt % of fullerene. It is well-known that fullerenes can be extracted with organic solvent such as toluene, benzene, or CS_2 . It has been confirmed that fullerenes are freed from the soot and extracted easily in toluene in a Soxhlet by carrying out the HIDE treatment prior to the extraction by organic solvent.^{20,21} During Soxhlet extraction, in addition to the dissolution of fullerenes in toluene, the hydrophobic graphite particles are dispersed and removed from the soot.

After the above treatments, the residual soot was left only with SWNTs and metal particles wrapped with a thick amorphous carbon layer. The metal particles barely dissolved in acid. Therefore, the residual soot was baked at 743 K in air for 20 min to remove the amorphous carbon particles and the graphitic layer around the metal particles and to make them dissolve easily in acid. As a result of baking, the weight of the soot decreased by about 40%. Figures 3b,c are the expanded portions of the left and right part of Figure 3a. As seen in Figure 3, SWNTs and metal particles formed into separate aggregates during the course of baking. The XRD profile of the baked soot shown in Figure 4 suggests that the metal particles changed to their oxides NiO and $\alpha-Fe_2O_3$. At the same time, remaining amorphous carbon in the soot was burned out. It is believed that, as a result of transformation of metal alloy into metal oxides and the removal of amorphous carbon, SWNTs and metal particles are isolated from each other and form separate aggregates. However, the increase in the intensity of the graphite peak at 002 is believed due to the increase in the ratio of the graphite particles in the sample as the result of the

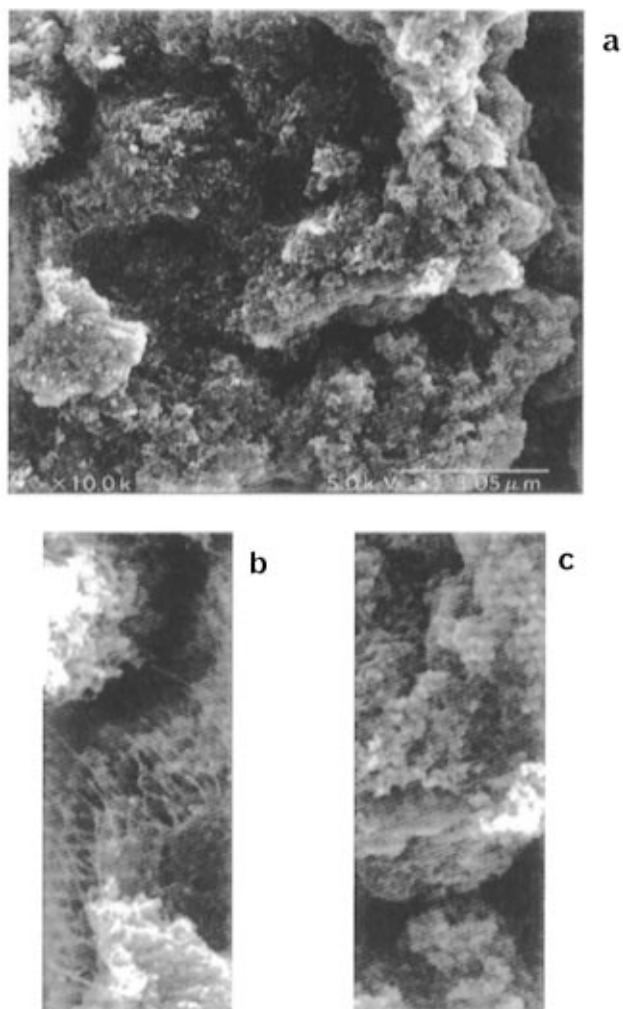


Figure 3. (Top) SEM photograph of the soot that has been hydrothermally treated, toluene extracted, and baked at 743 K. (Bottom left) and (bottom right) are the expanded portions of the left and right side of (top), respectively.

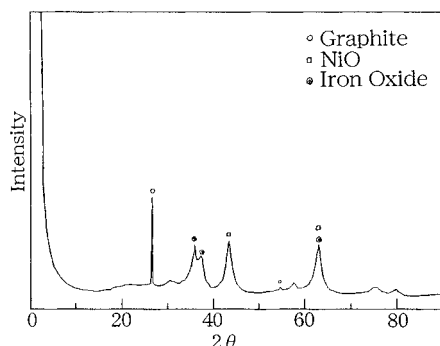


Figure 4. X-ray diffraction profile of the soot used in Figure 3.

elimination of amorphous carbon on the baking treatment. This problem is overcome by repeating the HIDE treatment and by washing with toluene. With the final treatment using 6 M hydrochloric acid, almost all the metal particles which formed into separate aggregates are washed out.

Purity of Separated SWNTs. Figures 5a,b show that high purity SWNTs are separated in large quantities. However, if we carefully observe the SEM photographs, we could find white dots of about 20 nm in diameter. To investigate this in detail, the sample used for the SEM observation was checked by high resolution TEM measurements. Figure 6a shows the TEM photograph of the portion where many metal particles exist. From the photograph, it can be seen that the particles are

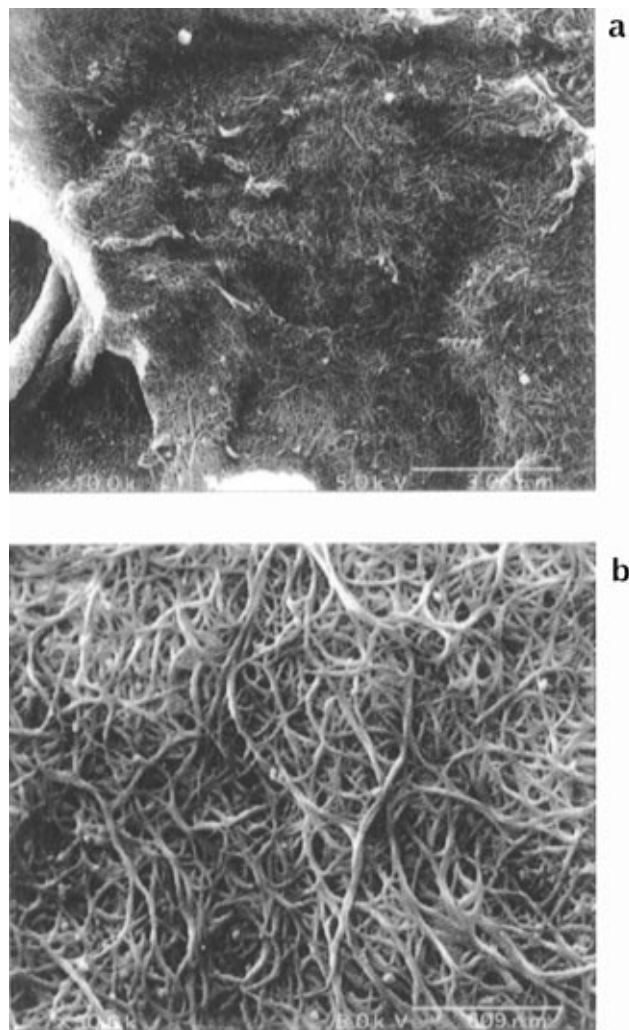


Figure 5. SEM photographs of the purified SWNTs observed under different magnifications.

nanocapsules wrapped in graphitic carbon layers. However, almost all the nanocapsules observed in Figure 6a were empty and free of metal particles. In the final product, metallic alloy particles that are perfectly covered with the graphitic layers and protected from dissolution on acid are present in very small quantities. The Ni and Fe metal concentrations in the separated SWNTs, estimated using ICP, were 2.3 and 2.5 wt %, respectively. Therefore, the purity of the separated SWNTs in this experiment is about 95 wt % while not taking the empty capsules with graphitic layers into account. Therefore, to obtain purity of over 99 wt %, these SWNTs were sonicated in water until nanocapsules were eliminated from the sample.

As seen in the TEM photograph in our previous report,¹⁹ the other forms carbon materials were completely removed from the SWNTs. This was further confirmed by carrying out Raman scattering on a bulk sample of SWNTs. The SWNTs show multiple split Raman peaks of crystalline graphite centered at 1580 cm^{-1} because of their cylindrical symmetry.²⁵ Kasuya et al. have reported that the scattering wavenumber would directly provide information on SWNTs such as the tube diameter and the carbon network.^{26,27} As stated in our previous report,¹⁹ the Raman scattering from the purified SWNTs shows multiple split peaks (1570 and 1590 cm^{-1}) which are five times more intensive than those of the SWNTs in the raw soot without any change in their position and intensity ratios. From the results of Raman scattering measurements, the following can be said: (a) only trace amounts of carbon material other than SWNTs are present



Figure 6. (a) TEM photograph of the metal particles encapsulated within the graphitic layers, which are present as impurities in the purified SWNTs. (b) A magnified portion of nanoparticles in (a).

in the final product and (b) the SWNTs have not suffered significant damage in the course of the purification procedure used.

The measurement of a specific surface area also confirms the purify of separated SWMTs. The specific surface areas of purified SWNTs, of raw soot containing SWNTs, and of fullerene soot made from pure graphite rod were 550, 170, and 110 m²/g, respectively. For fullerene soot, the estimated average particle size assuming the density of the soot to be 2.3 g/cm³, was 25 nm in diameter. However, the calculated average diameter of the purified SWNTs, assuming a density of 1.5 g/cm³, was about 5 nm. This value suggests that SWNTs are contained in bundles with each made up of a few SWNTs as seen in the TEM photograph of Figure 6b.

Effects of Hydrothermal Treatment on the Purification of SWNTs. A portion of Figure 6a, in which many metal particles exist, is magnified and shown in Figure 6b. There are many nanocapsules that have received damage on the graphitic layers (for example, A in Figure 6b). Especially, the graphitic layers of some empty capsules are completely destroyed (for example, B in Figure 6b). The graphitic layers of nanocapsules are made up of small domains of graphitic carbon sheets stacked parallel to the surface of the core metal particles. Hence, the graphitic sheets of the nanocapsules, for the most part, have defects and dislocations, in contrast to the SWNTs.²⁸ Therefore, it is believed that the reaction of H₂O with the carbon breaks the graphitic layers that wrap the metal particles. Consequently, incorporating the HIDE treatment in the purification procedure makes possible the exposure and dissolution of the encapsulated metal particles to hydrochloric acid in the final step of the treatment.

The application of the baking technique²⁹ was not successful on the purification of SWNTs,¹⁰ even though the purification of multiwalled nanotubes is possible. In the case of the baking method, graphite particles, nanocapsules, and amorphous carbon adsorbed on the SWNTs are not removed from the soot. In contrast, we believe that, during the HIDE treatment, water molecules break the network between SWNTs and amorphous carbon and metal particles and also attack the graphitic layer

encapsulating the metal particles. Consequently, almost all graphite nanoparticles and nanocapsules are washed out from the soot.

Acknowledgment. This work was supported in part by a grant-in-aid for New Program No. 03NP0301 from the Ministry of Education, Science, Culture and Sports of Japan and by Izumi Science and Technology Foundation.

References and Notes

- (1) Iijima, S.; Ichihashi, T. *Nature* **1993**, *363*, 603.
- (2) Bethune, D. S.; Kiang, C.-H.; de Vries, M. S.; Gorman, G.; Savoy, R.; Vazquez, J.; Beyers, R. *Nature* **1993**, *363*, 605.
- (3) Saito, Y.; Yoshikawa, M.; Okuda, T.; Fujimoto, M.; Sumiyama, K.; Suzuki, K.; Kasuya, A.; Nishina, Y. *J. Phys. Chem. Solids* **1993**, *54*, 1849.
- (4) Subramoney, S.; Ruoff, R. S.; Lorents, D. C.; Malhotra, R. *Nature* **1993**, *366*, 637.
- (5) Seraphin, S.; Zhou, D. *Appl. Phys. Lett.* **1994**, *64*, 2087.
- (6) Zhou, D.; Seraphin, S.; Wang, S. *Appl. Phys. Lett.* **1994**, *65*, 1593.
- (7) Saito, Y. *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1994; Vol. 1, p 1419.
- (8) Seraphin, S. *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1994; Vol. 1, p 1443.
- (9) Lin, X.; Wang, X. K.; Chang, R. P. H.; Ketterson, J. B.; Dravid, V. P. *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1994; Vol. 1, p 1478.
- (10) Bethune, D. S.; Kiang, C.-H.; Goddard, W. A., III; Salem, J. R.; Beyer, R. *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1994; Vol. 1, p 1487.
- (11) Subramoney, S.; Kavelaar, P. V.; Ruoff, R. S.; Lorents, D. C.; Malhotra, R. *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1994; Vol. 1, p 1498.
- (12) Kiang, C.-H.; Goddard, W. A., III; Boyers, R.; Bethune, D. S. *Carbon* **1995**, *33*, 903.
- (13) Saito, Y.; Okuda, M.; Fujimoto, N.; Yoshikawa, T.; Tomita, M.; Hayashi, T. *Jpn. J. Appl. Phys., Part 1* **1994**, *33*, L526.
- (14) Saito, Y.; Kawabata, K.; Okuda, M. *J. Phys. Chem.* **1995**, *99*, 16076.
- (15) Saito, Y.; Nishikubo, K. *J. Phys. Chem. Solids* **1996**, *57*, 243.
- (16) Thess, A.; Lee, R.; Nikolaev, P.; Dai, H.; Petit, P.; Robert, J.; Xu, C.; Lee, H. Y.; Kim, S. G.; Rinzler, A. G.; Colbert, D. T.; Scuseria, G. E.; Tomanek, D.; Fischer, J. E.; Smalley, R. E. *Science* **1996**, *273*, 483.

- (17) White, C. T.; Robertson, D. H.; Mintmire, J. W. *Phys. Rev. B: Condens. Matter* **1993**, 47, 5485.
- (18) Saito, R.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. *Mater. Sci. Eng., B* **1993**, 19, 185.
- (19) Tohji, K.; Goto, T.; Takahashi, H.; Shinoda, Y.; Shimizu, N.; Jeyadevan, B.; Matsuoka, I.; Saito, Y.; Kasuya, A.; Ohsuna, T.; Hiraga, K.; Nishina, Y. *Nature* **1996**, 383, 679.
- (20) Takahashi, H.; Akiyama, Y.; Goto, T.; Jeyadevan, B.; Tohji, K.; Matsuoka, I. *Mater. Sci. Eng. A* **1996**, 217/218, 42.
- (21) Takahashi, H.; Jeyadevan, B.; Tohji, K.; Matsuoka, I.; Kasuya, A.; Nishina, Y.; Nirasawa, T. *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1996; Vol. 3, p 72.
- (22) Ruoff, R. S.; Lorents, D. C.; Chan, B.; Malhotra, R.; Sabramoney, S.; *Science* **1993**, 259, 346.
- (23) Tomita, M.; Saito, Y.; Hayashi, T. *Jpn. J. Appl. Phys., Part 1* **1993**, 32, L280.
- (24) Saito, Y.; Okuda, M.; Yoshikawa, T.; Kasuya, A.; Nishina, Y. *J. Phys. Chem.* **1994**, 98, 6696.
- (25) Holden, J. M.; Zhou, P.; Bi, X.-X.; Eklund, P. C.; Bandow, S.; Jishi, R. A.; Chowdhury, K. D.; Dresselhaus, G.; Dresselhaus, M. S. *Chem. Phys. Lett.* **1994**, 220, 186.
- (26) Kasuya, A.; Saito, Y.; Sasaki, Y.; Fukushima, M.; Maeda, T.; Horie, C.; Nishina, Y. *J. Mater. Sci. Eng., A* **1996**, 217/218, 46.
- (27) Takahashi, H.; Sugano, M.; Kasuya, A.; Saito, Y.; Koyama, T.; Nishina, Y. *J. Mater. Sci. Eng., A* **1996**, 217/218, 48.
- (28) Saito, Y. *Carbon* **1995**, 33, 979.
- (29) Ebbesen, T. W.; Ajayan, P. M.; Hiura, H.; Tanigaki, K. *Nature* **1994**, 367, 519.