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Diameter Enlargement of HiPco Single-Wall Carbon Nanotubes by Heat Treatment

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ABSTRACT

The diameters of HiPco single-wall carbon nanotubes were increased by heat treatments. The original diameters estimated from Raman spectra were in the range of 0.79 to 1.2 nm; they increased with the heat-treatment temperature, reaching about 1.47 nm after 1800 °C heat treatment. Thermogravimetric analyses showed that the burning temperature of the HiPco tubes rose by about 350 °C after 1800 °C heat treatment, and the metal content, which was about 30% in the original HiPco, decreased to about 2% after heat treatment at 1800 °C.

Introduction. The single-wall carbon nanotube (SWNT)[1] has a cylindrical structure made of a single graphene sheet with a diameter of about 1 nm. Its formation is easy,[2−5] and a large quantity of SWNTs of high purity can be obtained by degradation of high-pressure CO with $Fe(CO)_5$ at about 1000 °C.[6]

There have been demands for structural control of SWNTs, and better methods of controlling the diameter and chirality have been sought. Although chirality control is difficult, partial success in diameter control has been achieved by controlling the furnace temperature[7,8] or choosing the metal catalysts[9] in the laser ablation process. On the other hand, it is reported that the diameter can be enlarged locally by coalescing two or more SWNTs with an electron beam,[10] which suggests that diameter enlargement might be possible by applying heat treatment to SWNTs. This report shows that the thermal enlargement of SWNT diameters is possible for the HiPco tubes.

The HiPco tubes were purchased from Carbon Nanotechnologies Inc., and used without any purification. Heat treatment (HT) was carried out in a vacuum of 10^{-6} Torr for 5 h in the temperature range from 1000 to 2000 °C. The structure of the heat-treated HiPco tubes was analyzed by Raman spectra (excitation wavelength: 488 nm, measuring area: about 100 μm^2), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA). The chemical stability of SWNTs and the amount of Fe were analyzed by TGA performed in oxygen atmosphere (1% oxygen, 99% argon) with a temperature increase rate of 5 °C/min from 30 to 1000 °C.

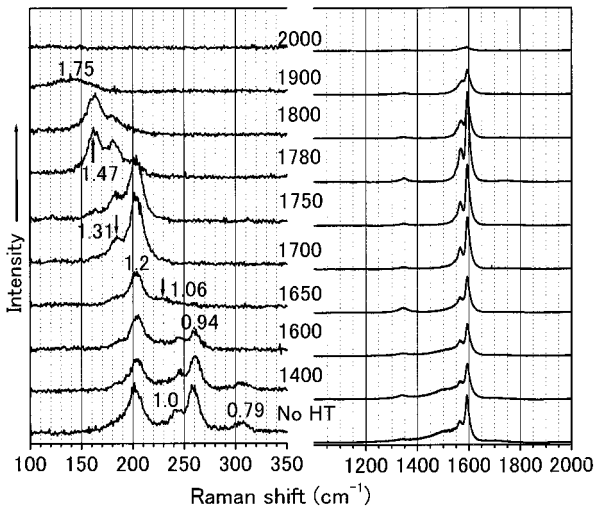

Figure 1. Raman spectra of pristine HiPco sample and samples heat-treated at various temperatures. Heat-treatment temperatures (°C) and diameters (nm) estimated from the peak position of the radial breathing modes are indicated.

The Raman spectra of the heat-treated HiPco samples are shown in Figure 1. The SWNT diameters estimated from the radial breathing modes[11] appearing at 100 to 350 nm are indicated at each peak position. The estimated diameters of the pristine tubes became larger as the HT temperature increased. The peaks corresponding to diameters of 1.31,

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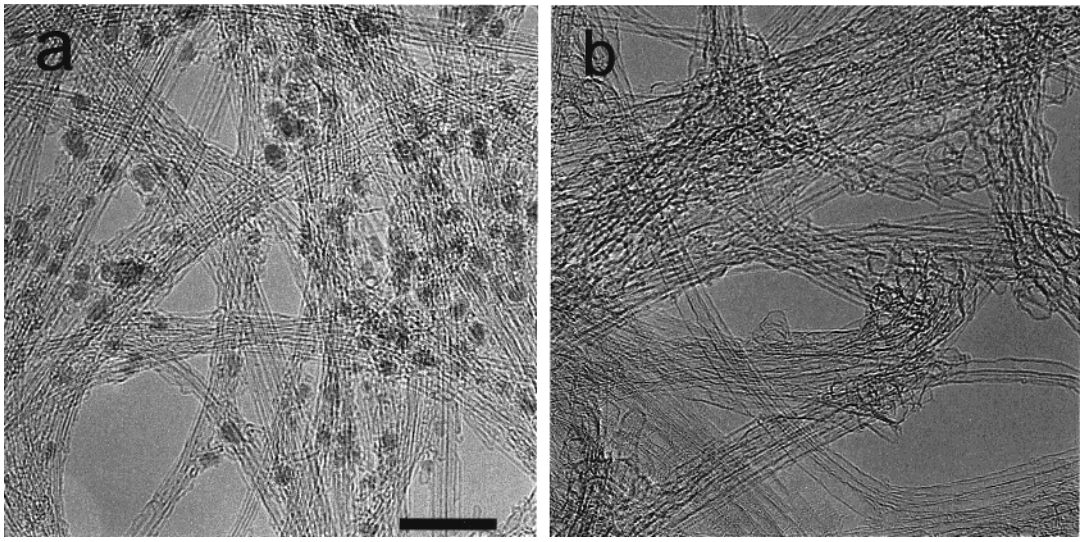

Figure 2. Transmission electron microscope images of (a) a pristine HiPco sample and (b) one heat treated at 1780 °C taken with the same magnification. The black bar in (a) corresponds to about 10 nm.

1.47, and 1.75 nm were not obvious in the spectrum of the pristine tubes, indicating that the small-diameter nanotubes disappeared and changed into larger ones. The tangential modes of the SWNTs showed peaks at about 1570 and 1592 cm^{-1}.[11] The intensity of the Fano line shape originating from metallic nanotubes at 1500-cm^{-1} decreased as the HT temperature increased and was almost insignificant after 1700 °C HT, which is consistent with the disappearance of high-frequency radial breathing modes, since thin metallic nanotubes have optical transition around 2.54 eV (488 nm).[12] The broad peaks centered at about 1350 cm^{-1} in Figure 1 indicate that the HiPco sample also contained carbon with disordered structures[13] or that SWNTs themselves have incomplete hexagon networks.[14] The intensity of the 1350-cm^{-1} peak relative to that of the tangential-mode peaks did not show any systematic changes for heat treatment at various temperatures. This might mean that the1350-cm^{-1} peak was probably due to the carbon with disordered structure that did not homogeneously distribute in the HiPco sample. After the 1900 and 2000 °C HT, the peaks that were characteristics of SWNTs became weak.

TEM observation revealed that the diameters of SWNTs in the pristine HiPco sample (Figure 2a) increased after HT, for example, 1780 °C HT (Figure 2b). A few fragments of the disordered carbon existed in the pristine sample, and polyhedron-like structures were seen after 1780 °C HT. Spherical particles of Fe or Fe−C contained in the pristine sample disappeared, and a small number of large Fe or Fe−C particles remained after HT. It is difficult to judge whether the thickness of the nanotube rope was changed by the heat treatment or not because it ranged widely from that of a single SWNT to several tens of nanometers.

To study the stability of SWNTs and the quantity of residual Fe after HT, we performed TGA in oxygen atmosphere. The burnoff temperature of the pristine HiPco sample was 480 °C, which increased to 600 °C after 1400 °C HT, followed by 750 °C after 1600 °C HT, 800 °C after 1800 °C HT, and 860 °C after 2000 °C HT. When the measurement finished at 1000 °C, iron oxide remained. Assuming that the iron oxide was Fe_2O_3, the quantity of Fe was estimated, and then the percentage of Fe in the HiPco sample before the heat treatment was calculated. The pristine HiPco contained about 30 wt % of Fe, which decreased as the HT temperature increased: 7 wt % after1400 °C HT, 5 wt % after 1600 °C HT, 2 wt % after 1800 and 2000 °C HT.

Discussion. The diameter of SWNTs in HiPco can be enlarged by heat treatment in a vacuum. The enlarged diameters do not coincide with any additions of the diameters of thin tubes, so the enlargement is not due to the coalescence of the thin tubes. It is not clear how the diameter enlargement occurred. The diameter might increase as a result of by the self-reconstruction accompanying the increase of the chiral indexes. The residual oxygen gas in the vacuum chamber and Fe might catalyze the diameter enlargement.

When we heat treated SWNTs with diameter of about 1.33 and 1.47 nm formed by pulsed Nd:YAG laser ablation (details of the formation conditions are given in ref 13), the population of the former tubes relative to that of the latter decreased as the HT temperature increased, and when it was about 1800 and 2000 °C, a few SWNTs with diameters of about 1.53 and 1.75 nm appeared. The diameter enlargement of the SWNTs formed by laser ablation showed a similar tendency to the HiPco tubes.

This study found the phenomenon of diameter enlargement; in other words, it presents a new diameter-control method for SWNTs. However, the mechanism is unclear. To clarify the mechanism, precise studies, both experimental and theoretical, will be necessary.

References

(1) Iijima, S.; Ichihashi, T. *Nature* **1993**, *363*, 603.
(2) Guo, T.; Nikolaev, P.; Thess, A.; Colbert, D. T.; Smalley, R. E. *Chem. Phys. Lett.* **1995**, *243*, 49.
(3) Journet, C.; Maser, W. K.; Bernier, P.; Loiseau, A.; Chapelle, M. L.; Lefrant, S.; Deniard, P.; Lee, R.; Fisher, J. E. *Nature* **1997**, *388*, 756.

(4) Colomer, J.-F.; Stephan, C.; Lefrant, S.; Tendeloo, G. V., Eiliams, U.; Konya, Z.; Fonseca, A.; Laurent, Ch., Nagy, J. B. *Chem Phys. Lett.* **2000**, *317*, 83.
(5) Su, M.; Zheng, B.; Liu, J. *Chem. Phys. Lett.* **2000**, *322*, 321.
(6) Nikolaev, P.; Bronikowski, M. J.; Bradley, R. K.; Rohmund, F.; Colbert, D. T.; Smith K. A.; Smalley R. E. *Chem. Phys. Lett.* **1999**, *313*, 91.
(7) Bandow, S.; Asaka, S.; Saito, Y.; Rao, A. M.; Grigorian, L.; Richter, E.; Eklund, P. C. *Phys. Rev. Lett.* **1998**, *80*, 3779.
(8) Yudasaka, M.; Ichihashi, T.; Iijima, S. *J. Phys. Chem. B* **1998**, *102*, 10201.
(9) Kataura, H.; Kumazawa, Y.; Maniwa, Y.; Otsuka, Y.; Sen R.; Suzuki, Y.; Achiba, *Carbon* **2000**, *38*, 1691.
(10) Terrones, M.; Terrones, H.; Bamhart, F.; Chalier, J.-C.; Ajayan, P. M. *Science* **2000**, *288*, 1226.
(11) Rao, A. M.; Richter, E.; Bandow, S.; Chase, B.; Eklund, P. C.; Williams, K. A.; Fang, S.; Subbaswamy, K. R.; Menon, M.; Thess, A.; Smalley, R. E.; Dresselhaus, G.; Dresselhaus, M. S. *Science* **1997**, *275*, 187.
(12) Kataura, H.; Kumazawa, Y.; Maniwa, Y.; Umezu, I.; Suzuki, S.; Ohtsuka, Y.; Achiba, Y. *Synth. Met.* **1999**, *103*, 2555.
(13) Kinoshita, K. *Carbon, Electrochemical and Physicochemical Properties*, 3rd ed.; John Wiley & Sons: New York, 1988; Chapter 2.2.
(14) Duesberg, G. S.; Ioa, I.; Burghard, M.; Syassen, K.; Roth, S. *Phys. Rev. Lett.* **2000**, *85*, 5436.
(15) Yudasaka, M.; Komatsu, T.; Ichihashi, T.; Achiba Y.; Iijima, S. *J. Phys. Chem. B* **1998**, *102*, 4892.

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