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# New Synthesis of High-Quality Double-Walled Carbon Nanotubes by High-Temperature Pulsed Arc Discharge

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## ABSTRACT

Novel syntheses of high-quality double-walled carbon nanotubes (DWNTs) have been realized by the high-temperature pulsed arc discharge method with Y/Ni alloy catalysts at 1250 °C. The optimum conditions of the DWNT synthesis are almost the same as those of single-walled carbon nanotubes (SWNTs), indicating that the growth processes of DWNTs and SWNTs are closely related to each other. High-resolution TEM and Raman spectroscopy have revealed that the present DWNTs have an inner and an outer diameter of 0.8–1.2 and 1.6–2.0 nm, respectively, which correspond to the smallest diameters and the narrowest diameter distribution of mass produced DWNTs ever reported. The purification of the so-produced DWNTs can be achieved by oxidation in air at 500 °C as a result of the remarkable chemical resistance of the current DWNTs compared with that of SWNTs.

Carbon nanotubes (CNTs) have attracted much interest in nanoscale science and technology,[1] providing such promising materials as molecular electronic devices,[2] high-strength mechanical materials,[3] hydrogen gas storage materials,[4] and field-emission tips.[5] These fundamental studies and engineering applications are mainly performed on single-walled carbon nanotubes (SWNTs), whereas applications of multiwalled carbon nanotubes (MWNTs) have been relatively limited because of their low structural uniformity. Double-walled carbon nanotubes (DWNTs) are unique MWNTs in this respect, having the thinnest graphite layer structure with excellent graphitization as reported in SWNTs. In this sense, DWNTs are ideal MWNTs with the thinnest graphite layer structures.

DWNTs have been produced by several methods such as the electric steady arc discharge method,[6,7] the catalytic chemical vapor deposition (CCVD) method,[8] and a method utilizing fusion reactions of fullerenes in nanotubes (the so-called "nanopeapods").[9] The DWNTs produced by these methods, except for the peapod method, usually provide DWNTs with large diameter distributions (from 2 to 5 nm for outer diameters).[6−8] Because the novel properties of CNTs such as quantum mechanical effects should be enhanced with narrower tube diameters, thinner DWNTs can offer intriguing device applications in nanoelectronics. The recent utilization of DWNTs for field-electron emitters[10] actually has shown that DWNTs and SWNTs have similar threshold voltages, but DWNTs have much longer lifetimes than SWNTs. In addition, chemical functionalization on the surface of DWNTs may lead to novel CNT materials while maintaining inner tube intact.

Here, we report a high-yield synthetic method and purification of thin DWNTs with an inner and an outer diameter of 0.8−1.2 and 1.6−2.0 nm, respectively.

The present DWNTs were produced by utilizing and modifying the so-called a high-temperature pulsed arc discharge technique,[11−13] which is equipped with a DC pulsed arc discharge mechanism inside a high-temperature (1000−1400 °C) furnace. In previous studies,[11−13] we have produced SWNTs with this method and have shown that the synthesis of SWNTs is widely controlled by the pulsed arc width (microseconds to seconds), the furnace temperature, and catalytic metals. The pulsed arc discharge method is also known to produce fullerenes, another type of novel nanocarbon material.[11−13]

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The experimental setup of the high-temperature pulsed arc discharge system has been described elsewhere.[11−13] Briefly, the apparatus consists of a furnace (ISUZU KRO-12K), a quartz tube ($\phi$ 25 mm), graphite electrodes, a water-cooled trap, and a homemade pulsed HV power supply capable of providing 1.5 kV and 100 A. The electrodes of graphite doped with catalytic metal atoms (Ni/Co 0.7/0.7 at. % and Y/Ni 1.0/4.2 at. %: Toyo Tanso Co. Ltd.) were located at the center of the furnace. The pulsed arc discharges (600 $\mu$s, 40−60 A, and 50 Hz) were generated between the electrodes, which vaporized the cathode in high-temperature Ar buffer gas (1000−1400 °C).[11−13] The vapor from the cathode was annealed in the buffer gas and was converted into soot containing DWNTs.

The crude DWNTs containing SWNTs, fullerenes, and amorphous carbon materials were subjected to purification. The fullerenes in the crude DWNTs were washed out with carbon disulfide. The subsequent ultrasonication in concentrated HCl solution removed the catalytic metals from DWNTs. This procedure prevented the degradation of DWNTs induced by the following oxidation. The sonicated DWNTs were rinsed with distilled water and were oxidized in air at 200 °C for a day. The sample was again sonicated in concentrated HCl and rinsed with distilled water. Finally, oxidation in air at 500 °C for 1 or 2 h eliminated SWNTs from residual amorphous carbon particles in the sample.

The raw and the purified samples were characterized by SEM (SEM: JEOL JSM-6340F), TEM (TEM: JEOL JEM-2010F), and Raman spectroscopy (Jobin Yvon HR-800). The Raman measurements were performed on the wide (100−2000 cm$^{-1}$) and the radial breathing mode (RBM: 100−300 cm$^{-1}$) regions in a micro-Raman mode where excitation lasers (HeNe: 632.8 nm, Ar$^+$: 488.0, and 514.5 nm) were employed ($\phi \approx \mu$m).

TEM images in Figure 1a show that DWNTs are produced above 1200 °C with Y/Ni catalysts, which have been known to produce only SWNTs. Importantly, DWNTs have been produced at temperatures above 1200 °C while maintaining other conditions the same. This temperature dependence is also confirmed by Raman spectroscopy obtained with excitation at 632.8 nm (cf. Figure 1b), where peaks at 214 and 136 cm$^{-1}$ correspond to the inner and the outer diameters of DWNTs of 1.15 and 1.83 nm, respectively. The diameter evaluation is made from the well-known relation $d = 248/\omega_r$, where $d$ is diameter of the tube in nm and $\omega_r$ is the frequency of the breathing mode in cm$^{-1}$.[14] The results show that the DWNT synthesis can be carried out with the conditions that are almost the same as those of SWNTs except for temperature. Also, the present DWNT synthesis does not require additional sulfur catalyst and hydrogen buffer gas, which are necessary for the reported steady-arc synthesis of DWNTs.[6,7]

The RBM Raman spectra (cf. Figure 1b) reveal that the average diameter of SWNTs increases as the temperature increases below 1200 °C. The spectral feature suddenly changes at 1200 °C, suggesting that DWNTs are synthesized when the temperature is high enough to produce thick SWNTs with some critical tube diameters. The same
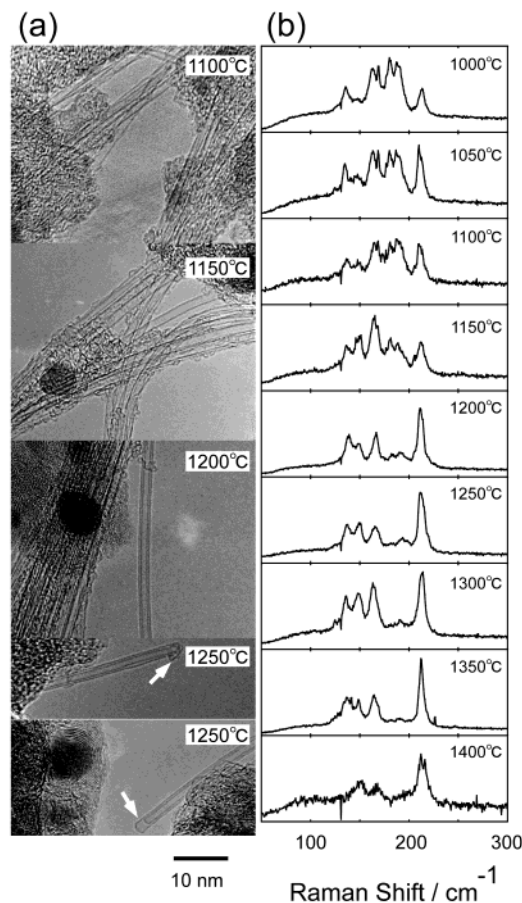


**Figure 1.** (a) Temperature dependence of TEM images and (b) Raman spectra of products by high-temperature pulsed arc discharge. The TEM images show that DWNTs are produced only at temperatures above 1200 °C. This temperature threshold is confirmed by the Raman spectra obtained with excitation at 632.8 nm. Peaks at 214 and 136 cm$^{-1}$ corresponding to inner and outer diameters of DWNTs of 1.15 and 1.83 nm, respectively, are enhanced at the higher temperature. Doubly capped structures of the ends of DWNTs are marked by arrows in the TEM images at 1250 °C.

temperature threshold for DWNTs is also observed in Raman spectra obtained with excitation at 514.5 nm. Such temperature thresholds for DWNTs are also seen in the CCVD synthesis of DWNTs.[8] Although the DWNTs are produced in the temperature range between 1200 and 1350 °C, the yields of DWNTs together with that of SWNTs are reduced at 1400 °C. This temperature dependence is similar to that of SWNTs produced by the laser furnace method.[15] These results strongly suggest that the growth of the present DWNTs is closely related to that of SWNTs. Statistical analyses of diameters from TEM images also support this suggestion of the growth processes (cf. Figure 5).

TEM images show that the ends of DWNTs have doubly capped structures (cf. Figure 1a at 1250 °C). These structures have also been observed in the CNT samples obtained by other methods.[6−8] Because the capped structures have been known as important candidates for the precursors of SWNTs,[16] these doubly capped structures can also be the precursors of DWNTs. Most of the interlayer distances of these cap areas are similar to those of MWNTs, but some DWNTs show
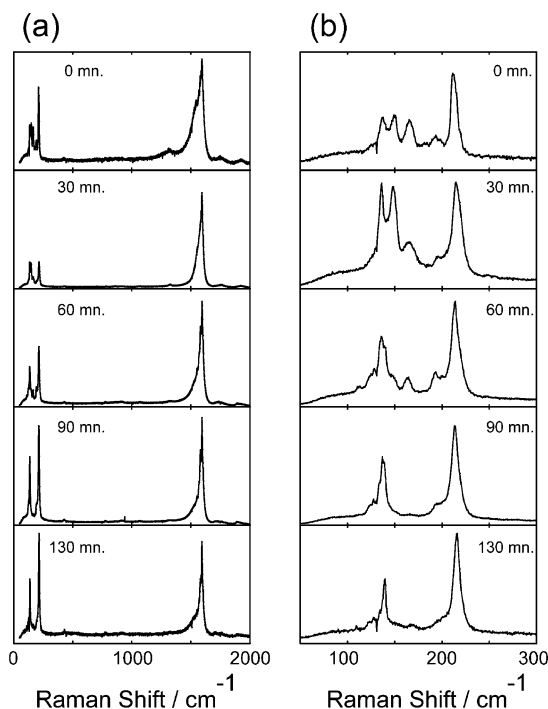
**Figure 2.** Raman spectra of the DWNTs after purification in air at 500 °C with excitation at 632.8 nm. All of the spectra (a) show that the graphitization of DWNTs is improved as purification proceeds with the optimum reaction duration of 90 min. The intensity ratios between G and D bands and the total scattering intensity are enhanced by an order of magnitude from those of the crude DWNTs. Breathing modes of the Raman spectra (b) show that peaks at 214 and 136 cm$^{-1}$ are particularly enhanced with the purification.



**Figure 3.** Raman spectra of the purified DWNTs with excitation at 632.8 nm. The inset shows the breathing modes at 214 and 136 cm$^{-1}$ corresponding to inner and outer layers of the DWNTs.

much wider interlayer spacing. Interestingly, all DWNTs have been produced with Ni/Co catalysts over the whole temperature range and the arc pulse width range studied (300 $\mu$s$-$100 ms and 1000$-$1400 °C). This is due to the fact that Ni/Co catalysts tend to produce much narrower SWNTs than the Y/Ni case in the pulsed arc discharge.[11-13]

On the basis of these results on the temperature and the catalysts' dependence on the DWNTs synthesis, outer layers and outer caps play crucial roles in the early growth of DWNTs. Virtually no DWNTs are produced when outer tubes are not thick enough to encapsulate SWNTs with the usual diameters.

Figure 2 shows the Raman spectra of crude and purified (oxidized in air at 500 °C) DWNTs. By purification, intensity ratios between G and D bands and the total intensity of the Raman spectra increased substantially by an order of magnitude (cf. Figure 2a). The Raman spectra in the breathing-mode area (cf. Figure 2b) show that peaks at 214 and 136 cm$^{-1}$ are particularly enhanced as the purification proceeds. The presence of the salient peaks due to RBM indicates the improved purity and quality of the present DWNTs. The corresponding TEM observations also show that DWNTs are purified with very small amounts of SWNTs and amorphous carbon materials. Figure 3 shows the Raman spectra of the purified DWNTs.

The purification is confirmed by the typical TEM observation of the purified DWNTs as shown in Figure 4. Most of
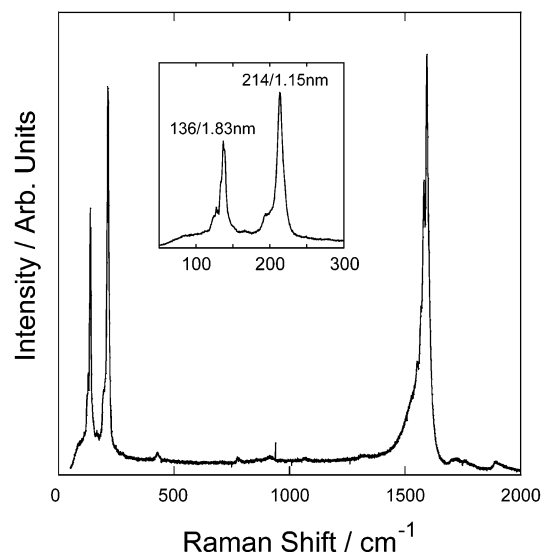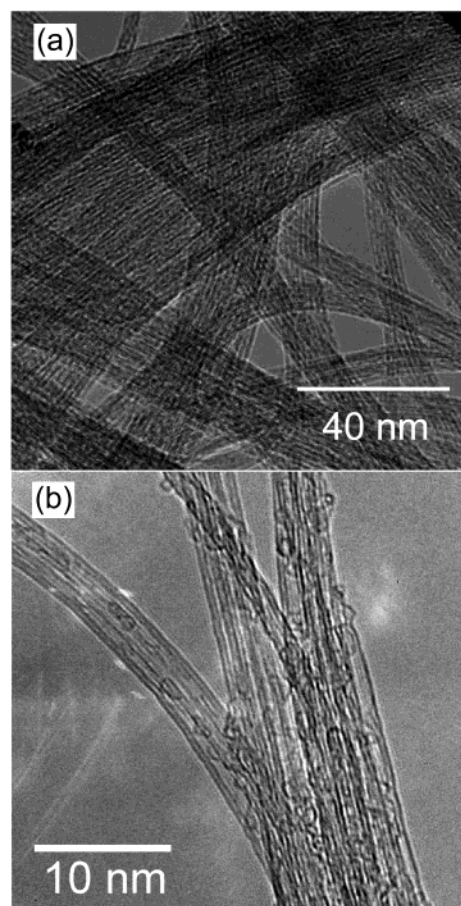


**Figure 4.** TEM images of (a) bundles and (b) individual purified DWNTs produced by the pulsed arc discharge method.

the SWNTs and amorphous carbon are removed from the sample. The abundance of DWNTs among all carbon nanotubes (DWNTs/(DWNTs + SWNTs)) is evaluated from these TEM images, which show a substantial increase in the purity from ca. 20% (23/(23 + 88)) to 90% (104/(104 +
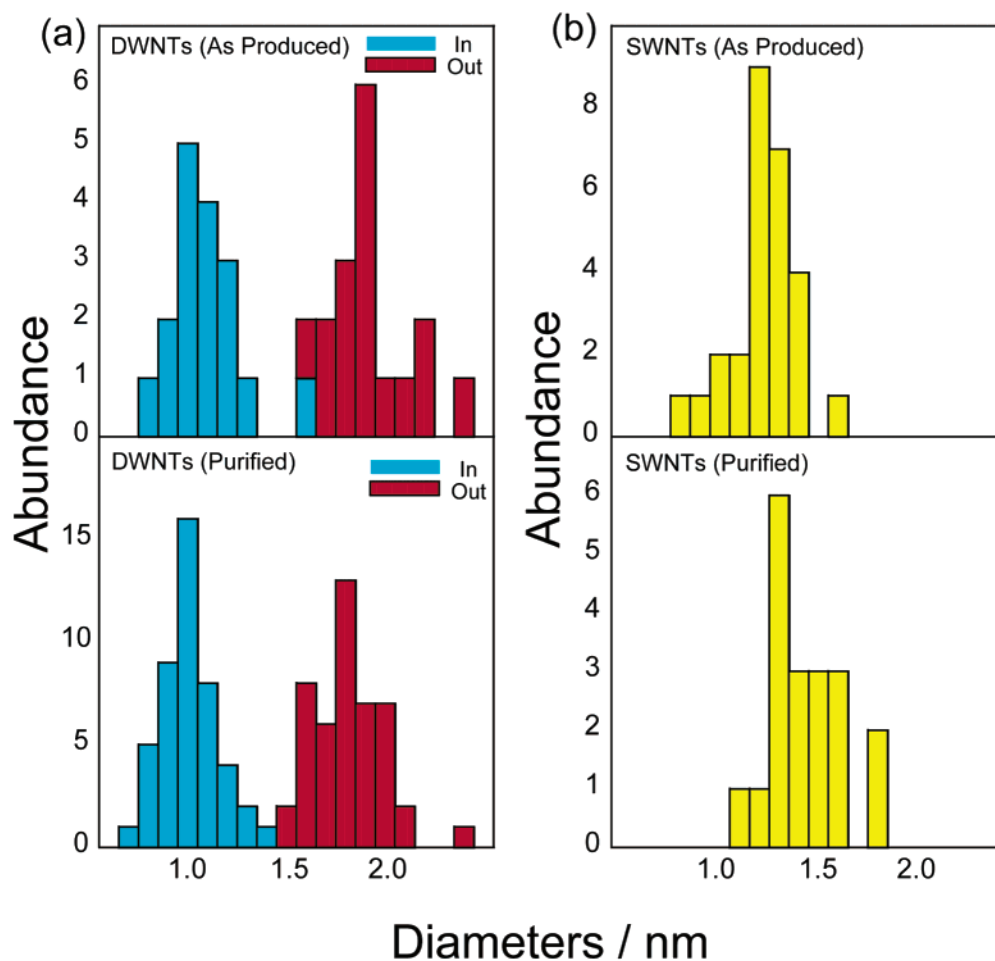
**Figure 5.** Diameter distributions of (a) DWNTS and (b) SWNTs before (upper panels) and after (lower panels) the purification.

14)). Statistical analyses on the abundance of DWNTs and SWNTs before and after the purification are shown in Figure 5. The diameter distribution of DWNTs shows that inner and outer diameters are 0.8–1.2 nm and 1.6–2.0 nm with peaks at 1.0 and 1.8 nm, respectively (cf. Figure 5a). The distribution does not change significantly but slightly shifts to the narrower side through the purification. This diameter distribution is consistent with the Raman spectroscopy measurements (cf. Figure 3). Diameters of SWNTs, however, are distributed from 1.2 to 1.6 nm with the most abundant diameter of 1.4 nm (cf. Figure 5b), which falls between 1.0 and 1.8 nm of the inner and outer diameters of DWNTs, respectively.

The preferential formation of SWNTs and DWNTs seems to be related to the diameters of the nanotubes.[7] The results suggest that thicker nanotubes are necessary to form DWNTs. This tendency is supported by the temperature dependence (cf. Figure 1), where the average diameters and the abundance of DWNTs increase as the furnace temperature increases.[15] Furthermore, the average diameter distributions of SWNTs become narrower after the purification (cf. Figure 5b). The narrowing of the diameter distribution of SWNTs in purification has been reported in other SWNT samples produced by the laser vaporization and the HiPco methods,[17] revealing that the thinner SWNTs are more reactive than the thicker SWNTs.

Because the crude samples contain SWNTs having diameters similar to those of DWNTs (around 2 nm), the chemical resistance of DWNTs cannot originate from the large diameters themselves but may be related to the quality of the CNT structures: better graphitization and the presence of interaction between the inner and the outer tube layers.[18] Bernholc and co-workers have pointed out that the edge of DWNTs can form so-called "lip–lip bonds" across the tube layers,[18] which may minimize dangling bonds and defects at the end brought about by the oxidation. In fact, we have found such TEM images in some of the heavily oxidized DWNTs. These unique properties of DWNTs allow us to purify the present DWNTs and may be one of the main causes for the much longer observed lifetimes than those of SWNTs as field electron emitters as mentioned earlier.[10] These DWNTs have the smallest diameters and the narrowest diameter distribution so far reported for macroscopically produced DWNTs.[6-8] The observed interlayer distance is 0.36–0.40 nm, which is much larger than that of graphite (0.335 nm). Similar results were reported previously for DWNTs obtained by the steady arc method and the peapod method.[6-9] Such large interlayer distances of DWNTs seem to be independent of the production methods employed.

Theoretical considerations of Raman spectroscopy on nanotubes[19] suggest that the peaks at 214 (inner) and 136 (outer) cm$^{-1}$ (cf. Figure 3) correspond to metallic and

semiconducting SWNTs, respectively. The present DWNTs can thus be viewed as the narrowest "nanocoaxial cable" ever made. Further studies are now in progress on these high-quality DWNTs such as mechanical properties, peapods synthesis, and various transport properties.

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NL034183+