

Diameter Enlargement of Single-Wall Carbon Nanotubes by Oxidation

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The diameter of high-pressure CO (HiPco) single-wall carbon nanotubes (SWNTs) has been enlarged by treating them with nitric acid and oxygen, and the diameter enlargement is related to the nitric acid refluxing time. Raman spectra (exciting wavelength 488 nm) and transmission electron microscopy showed that the 0.8–1.2 nm diameter distribution of HiPco SWNTs could be narrowed to one centered around 1.2 nm when the nitric acid treatment time was 1 h. Significantly, SWNTs of 1.37–2.4 nm in diameter were discovered when the nitric acid treatment lasted more than 2 h.

1. Introduction

Since their discovery in 1993,¹ single-wall carbon nanotubes (SWNTs) have attracted much interest because of the potential applications due to their unusual structures and properties.² The properties of SWNTs are determined by such structural characteristics as diameters and chiralities. However, SWNTs obtained by laser ablation,^{3,4} arc discharge,⁵ and chemical vapor deposition (CVD)^{6,7} always are mixtures with different diameters and chiralities. Therefore, it is very necessary to study how to control the diameter of SWNTs from as-grown SWNTs.

When SWNTs are heated in air or oxygen, those with smaller diameters are burned before those with larger ones,⁸ and this makes it possible to narrow their diameter distribution.⁹ On the other hand, the coalescence of two adjacent tubes was useful to enlarge the diameters of SWNTs. It has been reported that heat-treating SWNTs at 1400–2000 °C in H₂¹⁰ or argon¹¹ or under a vacuum^{12,13} results in SWNTs with larger diameters.

Recently, we used the oxidation of nitric acid to treat HiPco SWNTs, which was formed by using a high-pressure CO (HiPco) process with Fe(CO)₅ at about 1000 °C.⁷ We expected that the diameter distribution of SWNTs could be controlled through nitric acid treatment assisted with oxygen treatment. Our experimental results showed that the diameter distribution was narrowed. Moreover, the diameter of SWNTs could be enlarged when the nitric acid treatment time was more than 2 h, even at temperatures as low as 500 °C. In the present report, we show these interesting experimental results and discuss the coalescence of SWNTs that occurred at lower temperature assisted by oxidation.

2. Experimental Section

HiPco SWNTs, purchased from Carbon Nanotechnologies Inc., were refluxed in 70% nitric acid at 130 °C for 1–4 h. After acid treatment, the suspension was centrifuged, rinsed with water to neutralize, and freeze-dried. The dried samples were

further heat-treated in oxygen (250 Torr, 20 min) at 350–550 °C or under vacuum at 500–1200 °C. Raman spectrum (excitation wavelength 488 nm, measuring area $\approx 100 \mu\text{m}^2$) and transmission electron microscopy (TEM) were used to analyze the structure change of SWNTs after nitric acid and oxygen treatments. Samples treated with nitric acid but not with oxygen were also measured by thermogravimetric analysis (TGA) (TA Instruments 2950) and TG–mass spectrometry. TGA was carried out at temperatures from room temperature to 1000 °C with a heating rate of 5 °C/min, and the flowing gas was 1% O₂ and 99% argon. TG–mass spectrometry was carried out in the same temperature range but with a heating rate of 10 °C/min and with 100% argon as the flowing gas.

3. Results

3.1. Effect of Nitric Acid Treatment on SWNTs. It is well-known that nitric acid treatment can damage SWNTs and form functional groups such as -COOH, COO, and -CO on their wall.¹⁴ Three kinds of samples were prepared by treating HiPco SWNTs with nitric acid for 1, 2, and 4 h. For convenience, they are referred to here as HiPco(HNO₃, 1 h), HiPco(HNO₃, 2 h), and HiPco(HNO₃, 4 h). The structural changes of these three samples were investigated by Raman spectroscopy (Figure 1). The Raman spectra of the original HiPco SWNTs (Figure 1a) show radial breathing modes (RBM) with peaks at 300, 255, 240, and 201 cm⁻¹. These peaks indicate the existence of nanotubes with diameters of 0.8, 0.95, 1.0, and 1.2 nm.¹⁵ The spectra for HiPco(HNO₃, 1 h) (Figure 1b) show no RBM peaks at 300, 255, or 240 cm⁻¹, indicating that the tubes with diameters of 0.8, 0.95, and 1.0 nm had disappeared. Nevertheless, the two small peaks at 224 and 201 cm⁻¹ corresponding to diameters of 1.1 and 1.2 nm, remained. Figure 1 spectra c and d show that the RBM peaks almost disappeared when the samples were treated for 2 or 4 h. In addition, the intensity of the peak at about 1350 cm⁻¹, which corresponds to the disordered carbon,¹⁵ was greatly increased, and the tangential mode peak at about 1562 cm⁻¹, which is the characteristic peak of SWNTs,¹⁵ could not be found. This indicated that nitric acid treatment destroyed the SWNTs and resulted in highly disordered carbon. Such damage became more severe with increases in the nitric acid treatment time.

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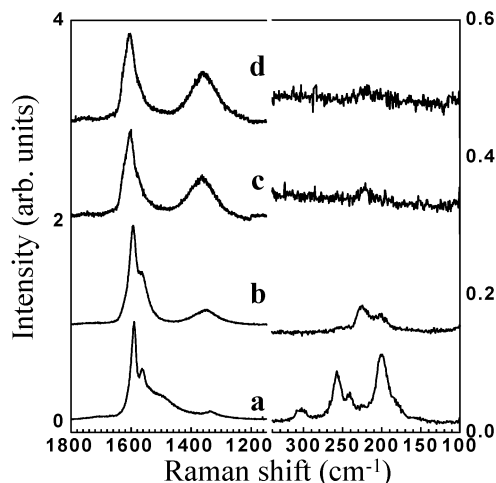


Figure 1. Raman spectra of (a) original HiPco SWNTs and HiPco SWNTs treated with nitric acid for (b) 1 h, (c) 2 h, and (d) 4 h.

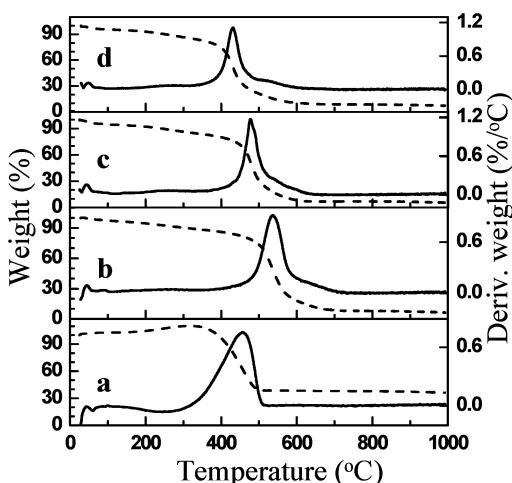


Figure 2. TGA results for (a) original HiPco SWNTs and HiPco SWNTs treated with nitric acid for (b) 1 h, (c) 2 h, and (d) 4 h. The broken lines are weight-temperature curves, and the solid lines show temperature derivatives of the weights.

The stabilities of SWNTs in the three samples were investigated by using TGA and TG-mass spectroscopy. The TGA results are shown in Figure 2. The weight-loss curve of the original HiPco SWNTs (Figure 2a) and its derivative curve indicated that SWNT combustion occurred in the range of 300–500 °C. The derivative peak on the weight-loss curve is at 465 °C. The weight-loss curve for HiPco(HNO₃, 1 h) shows that combustion occurred in the range from 400 to 690 °C, and its derivative peak curve was at about 550 °C (Figure 2b), which is about 90 °C higher than that of original HiPco SWNTs because of the decrease of metal (Fe) content from 40 to 7 wt %. When the nitric acid treatment time lasted 2 and 4 h, however, the combustion of SWNTs occurred at the lower temperature ranges of 380–620 °C (Figure 2c) and 350–550 °C (Figure 2d), and the respective peaks in the derivative curves were at about 480 and 420 °C. These results indicated that the stability of SWNTs decreased with increasing nitric acid treatment time.

TG-mass spectroscopy was used to investigate the amount of functional groups formed by nitric acid treatment by measuring the released gases from samples. The results showed that CO and CO₂ contents of the exit gases from HiPco(HNO₃, 1 h) were about 13.44 and 16.23 wt %, whereas they were 0 and 4.97 wt % in the exit gases from the original HiPco SWNTs

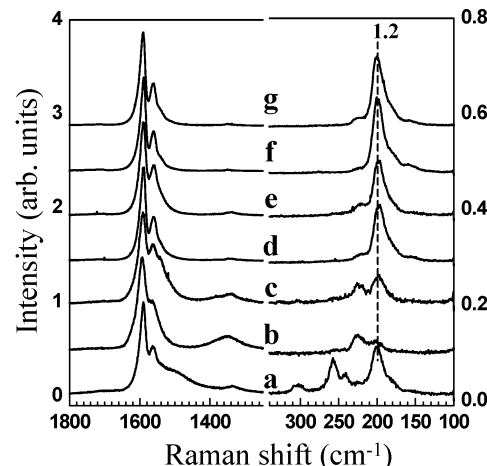


Figure 3. Raman spectra of (a) original HiPco SWNTs, (b) HiPco(HNO₃, 1 h), and HiPco(HNO₃, 1 h) treated with oxygen (250 Torr) for 20 min at (c) 350, (d) 400, (e) 420, (f) 500, and (g) 550 °C.

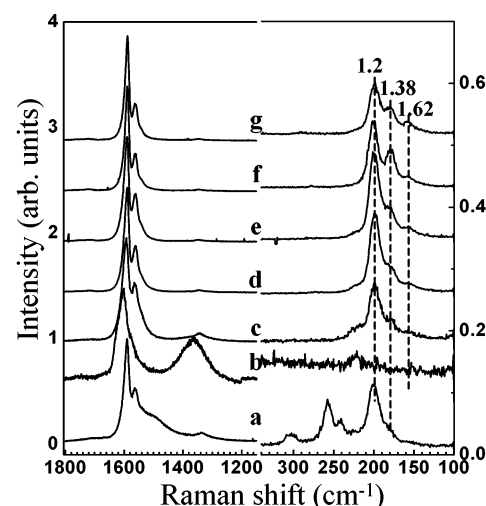


Figure 4. Raman spectra of (a) original HiPco SWNTs, (b) HiPco(HNO₃, 2 h), and HiPco(HNO₃, 2 h) treated with oxygen (250 Torr) for 20 min at (c) 350, (d) 400, (e) 420, (f) 500, and (g) 550 °C.

(Table 1). This means that about 12% of the C atoms in the HiPco SWNTs had been reacted with functional groups such as COOH and COO after nitric acid treatment for 1 h.

The disordered carbon and oxygenated functional groups caused by nitric acid treatment were removed by further treating the SWNTs in oxygen (250 Torr) for 20 min at temperatures from 350 to 550 °C and under vacuum at 500–1200 °C.

3.2. Effect of Oxygen Treatment on HiPco SWNTs Treated with Nitric Acid. When the temperature of oxygen treatment was higher than 350 °C, the Raman spectra of three samples (Figures 3c–g, 4c–g, and 5c–g) all showed the characteristic peaks of SWNTs at about 1591 and 1567 cm⁻¹ and also showed RBM peaks. When the temperature of oxygen treatment was higher than 400 °C, the peak at 1350 cm⁻¹, corresponding to disordered carbon, in the Raman spectra of all three samples almost disappeared (Figures 3d–g, 4d–g, and 5d–g). However, the RBM peaks of HiPco(HNO₃, 1 h) differed from those of HiPco(HNO₃, 2 h) and HiPco(HNO₃, 4 h) when the oxygen treatment temperature was 400–550 °C. There was only one RBM peak corresponding to diameter about 1.2 nm in the Raman spectra of HiPco(HNO₃, 1 h) (Figure 3d–g) and there were three RBM peaks in the spectra of HiPco(HNO₃, 2 h) (Figure 4d–g) and HiPco(HNO₃, 4 h) (Figure 5d–g), corresponding to diameters of 1.2, 1.38, and 1.56 nm. The

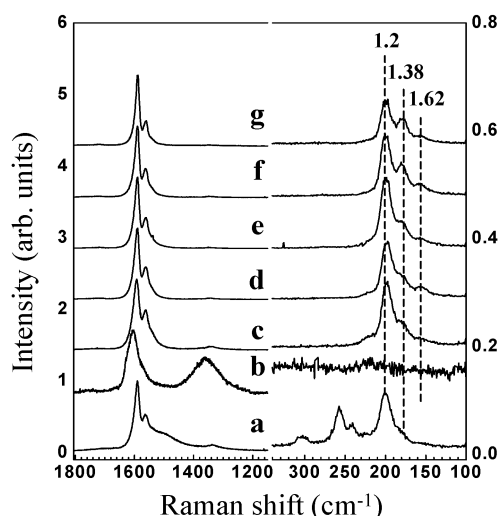


Figure 5. Raman spectra of (a) original HiPco SWNTs, (b) HiPco-(HNO₃, 4 h), and HiPco(HNO₃, 4 h) treated with oxygen (250 Torr) for 20 min at (c) 350, (d) 400, (e) 420, (f) 500, and (g) 550 °C.

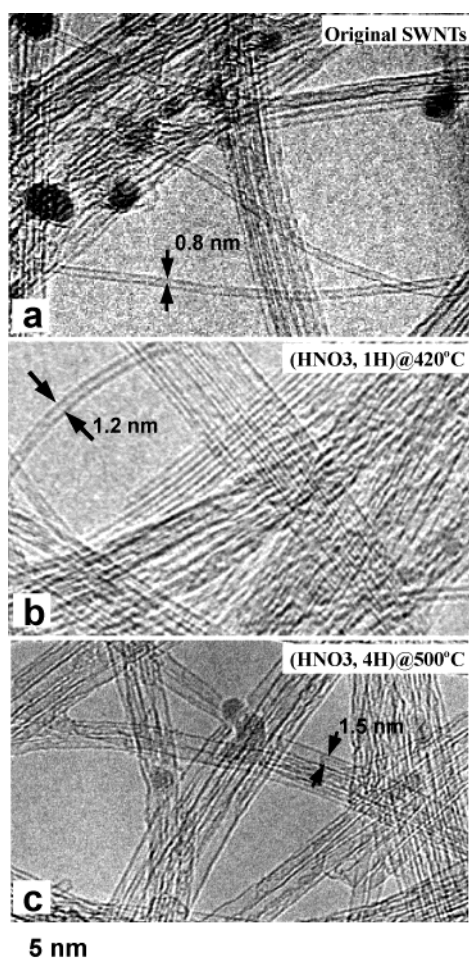


Figure 6. TEM images of (a) original HiPco SWNTs, (b) HiPco(HNO₃, 1 h) treated with oxygen at 420 °C for 20 min, and (c) HiPco(HNO₃, 4 h) treated with oxygen at 500 °C for 20 min.

SWNTs with 1.38 and 1.56 nm diameters were newly appeared because their peaks were not detected in the Raman spectra of the original HiPco SWNTs. Therefore, the oxidation might have enhanced the polymerization or coalescence of SWNTs at lower energies and/or temperatures, due to the facile formation of vacancies and interstitials.¹²

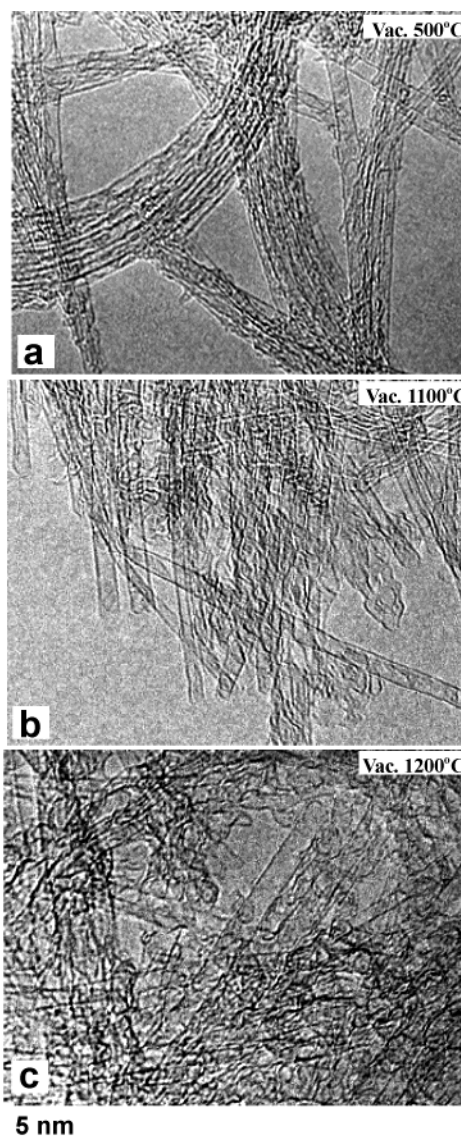


Figure 7. TEM images of HiPco(HNO₃, 4 h) treated in a vacuum for 2 h at (a) 500, (b) 1100, and (c) 1200 °C.

Estimation from careful observation of TEM images indicated that the diameters of the original HiPco SWNTs (Figure 6a) were distributed between 0.8 and 1.2 nm. The TEM image (Figure 6b) for HiPco(HNO₃, 1 h) treated with oxygen at 420 °C showed that the metal particles were largely reduced, and the diameters of SWNTs were almost all in the range of 1.1–1.2 nm. This indicated that nitric acid treatment is useful not only for removing impurities from SWNTs but also for narrowing the distribution of their diameters. There were a lot of SWNTs with diameters between 1.4 and 1.6 nm and a few of them with diameters greater than 2 nm in HiPco(HNO₃, 2 h) and HiPco(HNO₃, 4 h) treated with oxygen at 500 °C. A typical TEM image of HiPco(HNO₃, 4 h) treated with oxygen at 500 °C is shown in Figure 6c. Because nitric acid treatment cannot remove impurities of metal completely [TGA result of HiPco(HNO₃, 4 h) (Figure 1d) showed that about 7 wt % metal impurities were left after TGA treatment], some round shape impurities on the SWNT wall due to the residual metals were found in Figure 6c.

3.3. Effect of Heat Treatment on HiPco SWNTs Treated with Nitric Acid. HiPco(HNO₃, 4 h) was also treated under a vacuum of 10⁻⁶ Torr at 500, 800, 1100, and 1200 °C in order

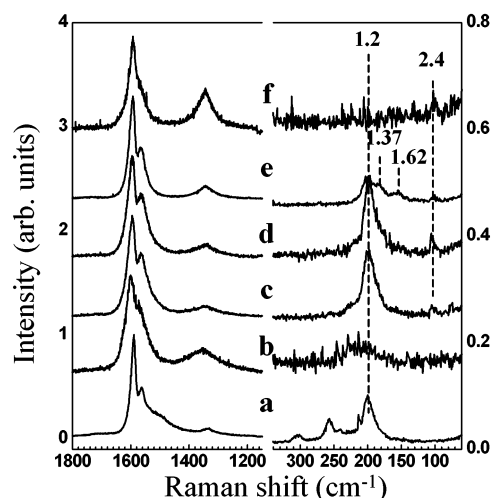


Figure 8. Raman spectra of (a) original HiPco SWNTs and HiPco-(HNO₃, 4 h) treated in a vacuum for 2 h at (b) 500, (c) 800, (d) 1000, (e) 1100, and (f) 1200 °C.

to remove the oxygenated groups formed by nitric acid treatment and study the structure change of HiPco SWNTs after heat treatment

When HiPco(HNO₃, 4 h) was heat-treated under vacuum at 500 °C, a large portion of it was converted to disordered carbon or polymerized carbon materials (not shown) and only a few SWNTs were evident in TEM images. This indicated again that nitric acid treatment damaged the SWNTs severely. Some of the SWNTs that could be distinguished, however, had diameters of 1.6–2.4 nm (Figure 7a). When the temperature of heat treatment was 1100 °C, the amount of disordered carbon decreased and most of the SWNTs had larger diameters between 1.6 and 2.8 nm (Figure 7b). When the heat-treatment temperature was 1200 °C, there were a lot of irregular tubes and pieces of them and there were some SWNTs with diameters between 2.0 and 2.8 nm (Figure 7c).

The Raman spectra of HiPco(HNO₃, 4 h) treated at 500 °C (Figure 8b) showed that the peak corresponding to disordered carbon was still large and the RBM peak at about 200 cm⁻¹ was weak and broad. When the heat-treatment temperatures were 800 and 1000 °C, there was one strong peak at 201 cm⁻¹ and a weak peak at 105 cm⁻¹, corresponding to SWNTs with diameters of about 1.2 and 2.36 nm, respectively (Figure 8c,d). The SWNTs with a diameter of 2.36 nm could be thought of as coalescence products of SWNTs 1.2 nm in diameter. Because the Raman exciting wavelength used here was 488 nm, it is very difficult to detect diameters greater than 1.7 nm.^{16,17} We should note that the lower intensity of peak at 105 cm⁻¹ did not indicate the lower amount of SWNTs with about 2.36 nm. The Raman spectra of HiPco(HNO₃, 4 h) treated at 1100 °C (Figure 8e) showed that there were four peaks corresponding to diameters about 1.2, 1.37, 1.6, and 2.4 nm. When the heat-treatment temperature was 1200 °C, only the weak peak for 2.4 nm SWNTs was left (Figure 8f).

The above results indicate that the coalescence of SWNTs also occurred during the heat treatment of HiPco(HNO₃, 4 h) under vacuum at 800–1200 °C. This temperature is lowered by 600 °C compared with the coalescence temperature of HiPco SWNTs untreated with nitric acid.¹³

4. Discussion

Our results indicate that oxidation with nitric acid and oxygen not only removes the impurities from SWNTs but also narrows

TABLE 1: TG–Mass Spectroscopy Results for Original HiPco SWNTs before and after Treatment with Nitric Acid for 1 h

	amount of gases released during heating from 25 to 1000 °C (wt %)					
	H ₂ O	CO	NO	CO ₂	organic	total
original HiPco	1.01			4.97		5.97
treated HiPco	4.47	13.47	0.98	16.23	0.04	35.19

the distribution of their diameters (Figures 1b and 6b). This confirms earlier findings that SWNTs with smaller diameters are oxidized more easily than those with larger diameters.^{8,9} Moreover, the longer time of nitric acid treatment helped enlarge diameter of SWNTs to 1.37–2.4 nm at a low temperature following heat treatment in oxygen or under vacuum (Figures 6c and 7a,b). When the treatment with nitric acid lasted for 4 h, the coalescence of HiPco SWNTs could occur at 400–550 °C in oxygen or at 800–1200 °C under vacuum.

The coalescence of SWNTs had been reported to occur only when SWNTs were annealed at high temperatures (1500–2400 °C) in the presence of H₂¹⁰ or under vacuum.¹³ It is very interesting that nitric acid treatment enables it to occur at a lower temperature. The zipperlike mechanism proposed by Terrones et al.¹² might be useful to explain the coalescence of SWNTs in this study. The difference between our study and the previous reports is that we produced defects by nitric acid treatment rather than by electron irradiation¹² or high-temperature treatment.¹³ The nitric acid treatment destroyed the SWNTs and chemically modified them with many functional groups such as carbonyl and carboxyl groups (Figure 1 and Table 1). These functional groups may help the tubes interact with each other. After such functional groups were removed by oxygen treatment or heat treatment under vacuum, many defects such as vacancies, interstices, and dangling bonds would be produced on the walls of SWNTs. Then some of them (possibly tubes with the same chiralities) might reconstruct into new tubes with larger diameters, polymerize as disordered carbon, or burn off. It has been reported that the fullerene C₆₀ could be polymerized by oxidation of ozone at temperatures of only 300–600 °C.¹⁸ A recent study showed that the coalescence of fullerene inside SWNTs can be triggered by the formation of vacancies or defects.¹⁹ Therefore, the oxidation may have enhanced the polymerization or coalescence of SWNTs.

In addition, after nitric acid treatment, the coalescence of HiPco SWNTs during oxygen treatment occurred at lower temperatures (400–550 °C), and the enlarged SWNTs were 1.37–1.56 nm in diameter, smaller than those coalescing during heat treatment under vacuum. The reason might be that disordered carbon and part of the SWNTs burned during the oxygen treatment. This combustion released heat and caused the local temperature to rise rapidly. The burning of part of SWNTs thus might lead to coalesced SWNTs with smaller diameters. The heat of combustion obstructed the merging of adjacent tubes, with many defects such as vacancies, interstices, and dangling bonds, into a new large one. As a result, the coalescence of SWNTs occurred at a lower temperature relative to that of heat treatment.

However, when the as-grown SWNTs obtained by laser ablation were treated with nitric acid as the same way we treated HiPco SWNTs, we did not observe coalescence. This is probably because the SWNTs obtained by laser ablation, unlike the HiPco SWNTs, did not contain many functional group after nitric acid treatment for 1–8 h. It has been reported that the SWNTs obtained by laser ablation might be transformed into multiwall carbon nanotubes and onionlike structures by nitric acid

treatment for 20 h.²⁰ We therefore think that the damaging of SWNTs by oxidation is the key factor causing the coalescence of SWNTs at a lower temperature.

5. Conclusions

Our study on the nitric acid treatment of HiPco SWNTs has revealed the following two important facts related to controlling the diameter of SWNTs.

1. The diameter distribution of SWNTs could be narrowed from one ranging from 0.8 to 1.2 nm to one centered around 1.2 nm when the nitric acid treatment time was about 1 h. This confirmed the result of a previous study showing that SWNTs with smaller diameters burned more easily than ones with larger diameters.

2. More important is that the oxidation of nitric acid enlarged the diameter of SWNTs assisted with oxidation or heat treatment under vacuum at a temperature lower than it had so far been reported for enlargement. The diameter enlargement is related to the nitric acid refluxing time. Raman spectra (exciting wavelength 488 nm) and transmission electron microscopy also showed the SWNTs with diameters as large as 1.37–2.4 nm were formed when the nitric acid treatment lasted more than 2 h.

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