Room Temperature Purification of Few-Walled Carbon Nanotubes with High Yield

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ABSTRACT Purification of high-quality few-walled carbon nanotubes (fWNTs) was developed by slow but selective oxidation in hydrogen peroxide (H_2O_2) at room temperature. The purity, nanotubes' structure, and thermal stability of purified fWNTs were characterized by transmission electron microscopy (TEM), Raman spectroscopy, and thermogravimetric analysis (TGA), respectively. The results showed that fWNTs could be selectively purified by prolonging the stirring time in 30 wt % H_2O_2 solution. Highly purified fWNTs were obtained, having a high G/D ratio in Raman spectra and good thermal stability indicating the good quality of the purified fWNTs. The approach provides a simple low cost method for purification that also has higher nanotube yield than other purification methods.

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Discovery of carbon nanotubes (CNTs) offers a great promise to new applications by taking advantage of their exceptional mechanical and electronic properties in combination with superb nanostructural characteristics.[1−3] Such applications include transistor,[4] field emission,[5,6] super capacitor,[7,8] and photovoltaic[9,10] devices. Recently, synthesis of few-walled CNTs (fWNTs)[11] has particularly distinguished them from single-walled CNTs (SWNT) and multiwalled CNTs (MWNT). As an intermediate between SWNT and MWNT, fWNTs which typically have 2−6 layers display the appropriate combination of structural perfection and remarkable electronic properties, which indicate their potential in field emission and nanocomposite applications.

Despite the synthesis of high-quality fWNTs by chemical vapor deposition (CVD),[12,13] it remains both important and challenging to purify raw fWNTs samples because carbonaceous impurities produced at high growth temperatures[14] prevent comprehensive and accurate understanding of the performance of these nanotubes. Several approaches have been attempted to remove these impurities, such as gas phase reaction,[15−17] acid oxidation,[18−20] electrochemical oxidation,[21] filtration,[22] and chromatography;[23] however, no method produces both high yields and scalability. For large-scale purification, gas phase oxidation is very attractive since it is simple to scale up and low in cost. However, the yield is usually low, especially when dealing with large amounts of samples. The main reason for low yields is the similar reactivity of CNTs and carbonaceous impurities.[19] Large portions of nanotubes are burned away during the purification process.[16,17] Furthermore, it is extremely difficult to purify large amounts of sample using such a method since the reaction conditions (temperature and surrounding gas composition) are not uniform throughout the samples. Conditions that can purify the nanotubes on the sample surface will leave nanotubes at the inner parts of the sample unpurified. Other purification methods also have their limitations. Filtration assisted by sonication and chromatography are available merely for small-scale samples. Strong acid purification works effectively on the oxidation of impurities but inevitably results in shortened CNTs due to the lack of selectivity between the nanotubes and the impurities.[24] Severe damage to the remaining walls decreases the quality of purified CNT's, although some structure can be recovered by annealing.[15]

Compared to the strong oxidation in acid, H_2O_2 treatment is a milder oxidation method,[25−28] and CNTs can be purified by H_2O_2 under neutral conditions. However, the purification of CNTs with different amounts of carbon impurities and catalyst metals by H_2O_2 solution was not investigated systematically. Most reactions stud-

ied thus were carried out in boiling H_2O_2 for quick purification.[29] However, the selectivity at such conditions is still not optimized, resulting in the sacrifice of a significant amount of carbon nanotubes in order to reach high purity. In this study, we sacrificed the reaction time for more selectivity and higher yield by carrying out the reaction in a homogeneous H_2O_2 solution at room temperature under constant stirring. Different degrees of purified fWNTs were obtained by stirring in H_2O_2 for different lengths of time. The results show that impurities in raw nanotubes can be removed by a short acid treatment combined with a long, slow oxidation in H_2O_2 at room temperature. The selectivity and yield are significantly improved. Purified fWNTs with good quality and high yield were achieved through a relatively simple procedure in this study.

RESULTS AND DISCUSSION

Figure 1 shows TEM images of (a) as-grown fWNTs and purified fWNTs by stirring in H_2O_2 solution at room temperature for (b) 1 h, (c) 1 day, (d) 3 days, and (e) 7 days. In addition to the bundle of nanotubes, the dark spots are thought to be carbonaceous nanoparticles, amorphous carbon, and catalyst metal particles[24] produced at high growth temperature. This group of impurities also was identified as bright areas in the SEM image (see Supporting Information). Moreover, the metals are mainly embedded in larger carbon agglomerations attached on the nanotubes.

The carbon impurities and catalyst metals in raw samples can be removed by mild oxidation in uniform H_2O_2 at room temperature over a long period of time. Figure 1b shows unremarkable changes from the raw sample, indicating that 1 h oxidation is insufficient. In contrast, the decrease of the amount of carbonaceous impurities, as indicated by gray and black groups, was observed on the surface of the bundle of nanotubes in Figure 1c. This is a result of this sample's long oxidation time of 1 day based on the fact that amorphous carbon can be etched away selectively faster than nanotubes. Thus the key to producing high-quality purified fWNTs with high yield is stirring oxidation time in H_2O_2. Figure 1d shows that a large amount of carbon impurities were removed by stirring in a uniform H_2O_2 solution for 3 days; however, some carbonaceous nanoparticles were left in the bundle of nanotubes. Highly purified fWNTs, essentially free of carbon impurities and metals, were obtained by stirring in a H_2O_2 solution for 7 days (Figure 1e). The corresponding SEM image (see Supporting Information) also shows a large amount of bundled and purified fWNTs.
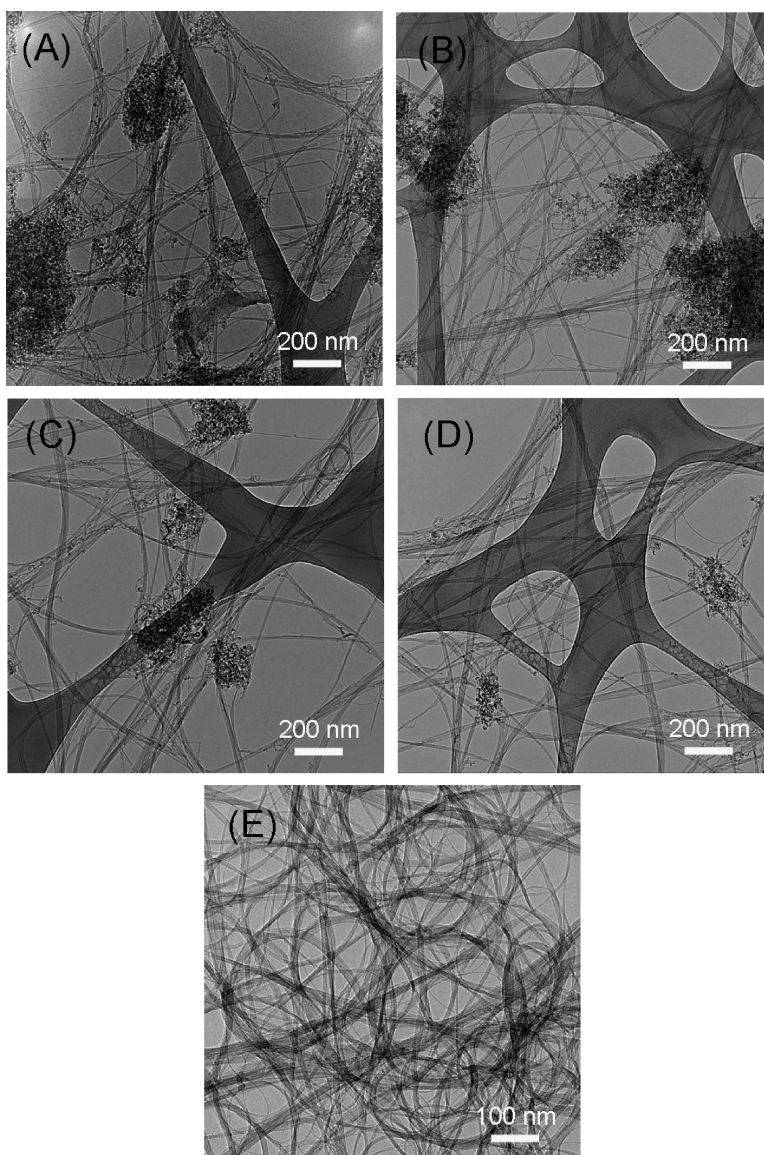

Figure 1. TEM images of (a) raw fWNT sample, purified fWNTs by stirring in H_2O_2 solution for (b) 1 h, (c) 1 day, (d) 3 days, and (e) 7 days.

The major problem with the purification of CNTs by gas reaction is the loss of a large amount of nanotubes due to high temperature oxidation. Table 1 compares the yield of fWNTs purified by refluxing and slow oxidation in H_2O_2 at room temperature and gas oxidation. Weight loss and yield were both determined accurately after drying the final samples at 90 °C overnight. Apparently, the yield of H_2O_2 purification is much higher than that of gas oxidation. Moreover, purified fWNTs

TABLE 1. Yield of fWNTs Purified by Refluxing and Slow Oxidation in Uniform H_2O_2 at Room Temperature and Gas Oxidation

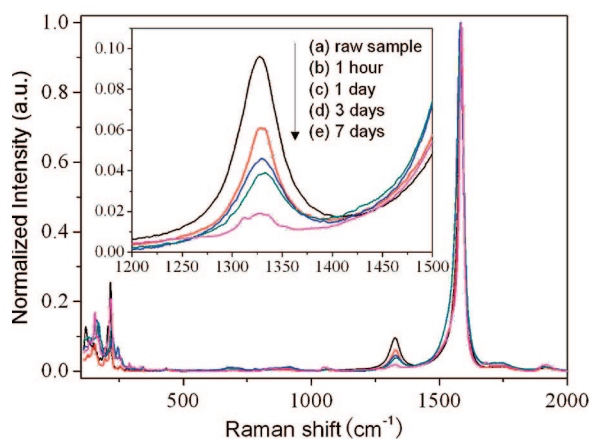| yield = final product/catalyst for raw sample			
method	temperature	stirring time	yield
gas oxidation	525 °C		2.5%
H_2O_2 purification	reflux	8 h	3.0%
H_2O_2 purification	room temperature	7 days	10.8%

Figure 2. Raman spectroscopy of (a) raw fWNT sample, purified fWNTs by stirring in H$_2$O$_2$ solution for (b) 1 h, (c) 1 day, (d) 3 days, and (e) 7 days. Inset shows the expanded Raman spectra.

with higher yields, up to 10.8%, indicate the oxidative selectivity of room temperature stirring in H$_2$O$_2$ over a long period of time. The selective oxidation of room temperature treatment was confirmed by refluxing in uniform H$_2$O$_2$ for different lengths of time (see Supporting Information). Purification by refluxing in H$_2$O$_2$ for 8 h (conditions that yield nanotubes with purity similar to that of the 7 day room temperature stirring) with a low yield of 3% indicates inefficient selectivity due to strong oxidation at boiling temperature.

Raman spectroscopy was employed to identify changes in raw and purified fWNTs in Figure 2. Typical Raman spectra of fWNTs are composed of two characteristic regions. In the low frequency range of 120−300 cm^{-1}, several bands in radial breathing modes (RBM) originated from a small amount of SWNT and the inner and outer wall of the double-wall carbon nanotubes (DWNT)[30,31] in the fWNTs sample (see Supporting Information). This feature is quite distinct from that of MWNTs, which shows no low frequency modes. Another region in high frequency displays two characteristic bands, D-band
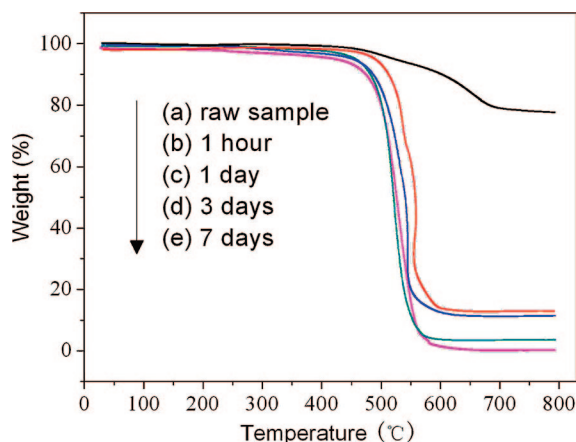

Figure 3. TGA graphs of (a) raw fWNT sample, purified fWNTs by stirring in H$_2$O$_2$ solution for (b) 1 h, (c) 1 day, (d) 3 days, and (e) 7 days.

TABLE 2. G/D Ratio of Raman Spectroscopy for the Raw Sample and Different Degrees of Purified fWNTs

stirring time	raw sample	purified fWNTs			
		1 h	1 day	3 days	7 days
G/D ratio	10.4	16.3	21.8	26	52.3

(1330 cm^{-1}) and G-band (1585 cm^{-1}), which are related to the graphite in-plane vibration with an E$_{2g}$ symmetry intralayer mode[32] and the defect on the nanotubes and amorphous carbon, respectively.[33] Therefore, the relative intensity of the D-band is proportional to the amount of defects and non-nanotube carbon impurities in the fWNTs sample. The inset of Figure 2 shows that the intensity of the D-band decreased dramatically with the increase of stirring time in H$_2$O$_2$ solution due to the preferential removal of amorphous carbon.[34,35] Table 2 shows changes in the calculated G/D ratio of the raw sample and fWNTs with different degrees of purification. It is noted that the G/D ratio changes with stirring time of fWNTs in H$_2$O$_2$ solution. Previous studies reported that H$_2$O$_2$ primarily attacked the nanotube ends rather than the defects on the nanotubes.[29] In other words, few defects were generated on the side wall of fWNTs except at the ends. The electrical properties of CNTs, the valence (V) to conduction (C) electronic transition, can be characterized by UV−vis−NIR absorption spectra (see Supporting Information). This spectra indicate E$_{11}$ (V1→C1) transitions from roughly 1000 to 1300 nm with the maximum at 1150 as well as E$_{22}$ (V2→C2) transition. The electrical properties of fWNTs appear unchanged as indicated by the similarity in the bands in both regions. The result indicates that the slow, selective oxidation in H$_2$O$_2$ did not affect the electrical structure of fWNTs. Thus the increase of G/D ratio is essentially assigned to the reduction in the amount of carbon impurities in the sample. The G/D band of purified fWNTs is almost five times larger than that of the raw sample. Purified fWNTs exhibit superior electrical performance than MWNT purified by H$_2$O$_2$ solutions at 65 °C for 6 days.[29] These results indicate the great promise of fWNT incorporation in nanoelectronic devices.

TGA provides a straightforward characterization method with which the thermal stability of fWNTs can be measured and quantitative calculation of catalysts can be made. The weight loss during heat treatment is due to the burning of carbonaceous impurities and amorphous carbon, leaving only the catalyst as the residue. Figure 3 shows the TGA trace of the raw sample and fWNTs by stirring in a H$_2$O$_2$ solution for (b) 1 h, (c) 1 day, (d) 3 day, and (e) 7 days in air atmosphere. The corresponding TGA data are also shown in Figure 4. Raw fWNTs show the fastest decomposition at 600 °C, with 77.66 wt % final resi-

TABLE 3. Weight of Residue for the Raw Sample and Different Degrees of Purified fWNTs Based on TGA

	raw sample	purified fWNTs			
stirring time		1 h	1 day	3 days	7 days
residue weight	77.66%	12.91%	11.34%	3.52%	0.16%

due attributed to a considerable amount of catalyst. In contrast, purified fWNTs with less residue exhibit the highest decomposition rate at round 530−550 °C. According to Figures 3 and 4, purified fWNTs produced by stirring at different times show similar monotonically decreasing curves with increasing temperature, only varying by residue weight. It is believed that the thermal stability of fWNTs depends on the defects on the side walls and impurities in the sample. With the reduced amount of impurities, the high quality of fWNTs with few defects contributes to the high thermal stability, which is consistent with the analysis of Raman and UV−vis−NIR absorption spectroscopy. Table 3 displays the weight of the residue of fWNTs from different stirring times in H_2O_2 solutions at room temperature. The decreased weight of catalyst indicates the improvement of purified fWNTs. This is evidence that the purification in H_2O_2 can selectively oxidize the metals within carbon nanoparticles, allowing oxidized metals to be dissolved away by HCl treatment. Quantitatively characterization of TGA with Raman spectroscopy indicates that high purity fWNTs can be achieved by slow selective oxidation in H_2O_2 solutions.
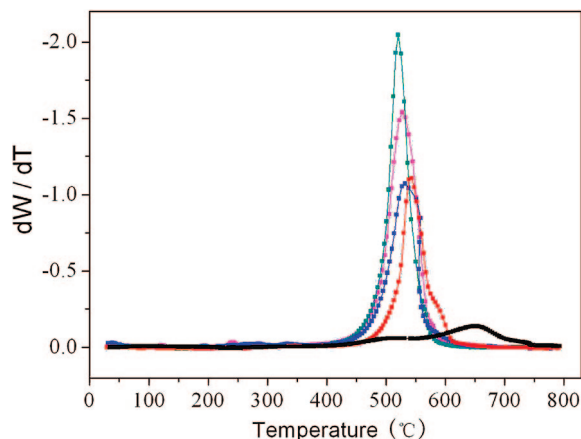

Figure 4. Corresponding differentiated TGA curve.

CONCLUSIONS

We defined an effective three-step purification process of which the key step is stirring in H_2O_2 solution assisted by ultrasonication at room temperature. The slow, selective oxidation over a long time results in the enhancement of purification. Highly purified fWNTs were obtained by stirring in 30 wt % H_2O_2 solution at room temperature for 7 days followed by HCl treatment. TEM images show purified fWNTs free of carbon impurities and catalyst metals. The high quality of purified fWNTs was determined by the high G/D ratio and good thermal stability as shown in Raman spectroscopy and TGA, respectively. The optimum purification provided a total yield of 10% with fewer defects on the nanotubes.

METHODS

Raw fWNTs used in this research were synthesized by the reported method.[12] Highly purified fWNTs were obtained by a three-step purification in which the key oxidation step is stirring in a H_2O_2 solution. As-grown fWNT samples first were refluxed in a concentrated HCl solution for 1 h in order to remove the exposed metal catalyst and MgO support. After washing with distilled water and ethanol several times and drying at 90 °C overnight, the black product was immersed into 30 wt % H_2O_2 solution by ultrasonication in order to separate the nanotubes. The dispersed fWNTs were then stirred in an H_2O_2 solution for up to 7 days in order to discover the optimal time for the purification. The suspension was filtered and washed with distilled water and ethanol, which left a black buckypaper. This buckypaper was refluxed in concentrated HCl again for 1 h to remove the remaining metal catalysts. Highly purified fWNTs were obtained after filtration and drying.

The purity of purified fWNTs was evaluated by transmission electron microscopy (TEM, FEI Tecnai). Raman spectroscopy was performed on a Horiba Jobin Yvon LabRam ARAMIS instrument operated at 630 nm to confirm the existence of graphitized carbon nanotubes and to investigate the degree of purification. The weight loss on heating in air was determined by thermogravimetric analysis (TGA, Model 2960 from Thermal Instruments).

Supporting Information Available: The morphologies of raw fWNT samples and purified fWNTs were documented by scanning electron microscopy (SEM, FEI XL30). The purity of fWNTs purified by refluxing in H_2O_2 for different lengths of time was evaluated by TEM (FEI Tecnai). SWNTs and DWNTs in purified fWNT samples were observed by TEM (FEI Tecnai). UV−vis−NIR absorption spectra (Shimadzu UV-3600) were measured by ultrasonicating fWNTs in 0.1 wt % SC solution. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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