Purification of multi-walled carbon nanotubes through microwave heating of nitric acid in a closed vessel

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Abstract

We demonstrate that microwave-assisted heating in 5 mL of nitric acid eliminates impurities, such as amorphous carbon, carbon nanoparticles, and metals, from multi-walled carbon nanotubes (MWNTs). Heating the closed reaction vessel under microwave irradiation at 160 °C for 30 min is a very effective means of purifying the MWNTs. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images confirm that these reaction conditions are beneficial for removing the impurities and ensuring that the MWNTs remain intact. In contrast, a purification temperature of 180 °C provides too strongly oxidizing conditions that destroy the MWNTs. The ratio of the G and D bands in the Raman spectra also confirms that a temperature of 160 °C is optimal. The defect peak that we observed in the differential thermogravimetry (DTG) analysis of the raw material was not present after microwave purification. The presence of metal impurities in the MWNTs can be reduced significantly when using this method.
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1. Introduction

Multi-walled carbon nanotubes (MWNTs) have been attracting considerable attention not only because of their unique physical properties but also because of their potential for use in various applications [1–4]. These characteristics include their high mechanical strength and unusual electronic properties, which make them useful for field emission displays, their capability to store a large amount of hydrogen, their high modulus, and their structural diversities, which make band gap engineering possible. The most widely used nanotube synthesis methods are arc discharging [5], laser ablation [6], and chemical vapor deposition [7]. Unfortunately,

unwanted impurities may be included in the MWNTs during their synthesis. These impurities include polyaromatic carbon shells, amorphous carbon, fullerenes, and the remains of primary materials, such as graphite flakes from the arc electrodes, the laser target, or the catalyst crystals. The presence of these impurities handicap the development of further applications of MWNTs and, therefore, it is inevitable to develop suitable purification methods.

Various methods have been reported for purifying carbon nanotubes, such as chemical oxidation [8], thermal oxidation [9–11], filtration [12], and chromatography [13,14]. These methods can be divided into two groups: destructive and nondestructive. These techniques, however, are time-consuming and have high thermal budgets. Recently, microwave-assisted heating has received much attention because of its high sample throughput, small reagent volumes, and reliable control

over amenable temperatures and pressures. Despite the versatility of microwave techniques, they have not been used previously to purify carbon nanotubes in the presence of nitric acid.

In this paper, we propose a microwave purification method for isolating pristine carbon nanotubes by the use of nitric acid under pressurized condition. We have used a gravimetric method, based upon the weighing of residual solid samples, to evaluate the defect removal efficiency of nitric acid at various heating temperatures. Prior to verifying the purity of the samples by Raman spectroscopy and differential thermogravimetry, we evaluated the effects that different temperatures have on purification by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Furthermore, we have also studied the efficiency of this process toward the removal of metal defects from the samples.

2. Experimental

Microwave purification of the nanotube samples (50 mg) using chemical reagents (5 mL) was accomplished by placing them in closed vessels inside a commercial microwave oven. The microwave device (Model MARS-5, CEM, Matthews, NC, USA) was equipped with a Teflon-coated cavity and a removable 14-position sample carousel. The oven had a variable power range (up to 1200 W) that was adjustable in 1% increments. The existing turntable was rotated for homogeneous heating. A pressure line (ESP-1500 Plus) was installed with a transducer to allow monitoring of the pressure at up to 100 bar; the pressure limit was set at 350 psi. An optical fiber monitored and controlled the purification temperature at up to 300 °C using a feedback system (EST-300 Plus). The sample was purified in a vessel (HP-500 Plus; volume: 100 mL; maximum operating pressure: 500 psi; maximum operating temperature: 260 °C) consisting of a chemically resistant inner liner (Teflon PFA), which contains and isolates the sample solution, and a high-strength outer pressure vessel body (advanced composite material). A special cap (Autovent Plus) was used to protect the purification vessel from excessive pressure; the vessel was immediately resealed to prevent the loss of any sample. An empirical estimation for evaluating the purification efficiency was to weigh the total dry residual solid before and after sample purification and complete evaporation of the reagent.

Nitric acid solutions, of analytical or higher grades, were obtained from E. Merck (Darmstadt, Germany). A Model-AT201 analytical balance (readability: 0.01 mg), obtained from Mettler–Toledo (Switzerland), was used to measure the samples' weights. MWNTs (outer diameter: 50–100 nm; inner diameter: 20–40 nm;
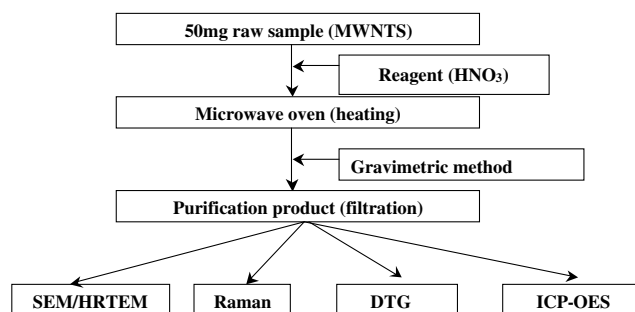

Fig. 1. A schematic diagram of the microwave-assisted purification process.

length: 2–20 μm) were purchased from the Chinese Academy of Sciences (China); a weighed sample (50 mg) was used for each run. De-ionized water (>18 MΩ cm^{-1}) was used throughout these experiments. The MWNT sample obtained after microwave-assisted purification was dried and then the product was collected. The morphology of the MWNTs was characterized by field emission SEM (Hitachi S-4000, Tokyo, Japan). A portion of the sample was dispersed in acetone under mild sonication. The sample solution was dipped onto a 200-mesh Cu grid. The morphology of this sample was also characterized by field emission TEM (JEM-2010F, JEOL) using an accelerating voltage of 200 keV. The TEM was equipped with an energy dispersive X-ray (EDX) elemental analysis tool. Raman spectroscopy (Ranishaw System 1000) and thermogravimetric analysis (Thermal Analyzer, Seiko SSC-5000, Chiba, Japan) instruments were used to characterize the MWNTs during the purification processes. The presence of metal defects was confirmed by the use of inductively coupled plasma optical emission spectroscopy (Perkin–Elmer Optima 3000, Norwalk, CT, USA). A schematic diagram of the experimental set-up is provided in Fig. 1.

3. Results and discussion

Conventionally, the use of nitric acid is somewhat efficient for dissolving the impurities from MWNTs [15], but a couple days are required to purify the MWNTs in an open reactor. We propose the use of a closed-vessel system to purify MWNTs in the presence of nitric acid in a microwave system, and suggest that the gravimetric method can be used to estimate the efficiency of the removal of the impurities. In a closed-vessel microwave apparatus, a high temperature will cause evaporation of the purification reagent, which produces high-pressure conditions. In this work, we used nitric acid, whose boiling point is 122 °C. The nitric acid vaporizes and refluxes in the closed vessel as if the puri-
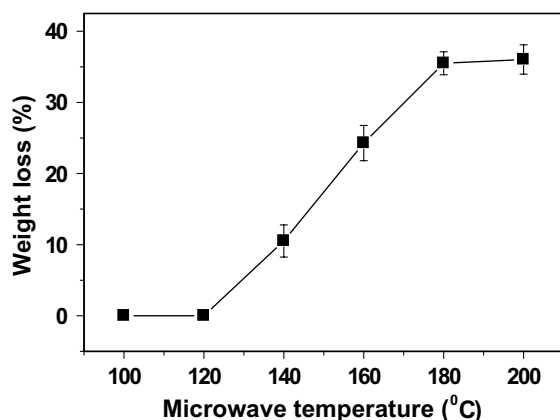
Fig. 2. The effect that reaction temperature has on the weight loss of nanotubes in the presence of nitric acid, as measured using the gravimetric method.

fication temperature were elevated above the boiling point. The MWNTs are high-strength materials, but amorphous carbon and metal impurities can be dissolved. Fig. 2 illustrates the weight loss of three replicates at various microwave purification temperatures. The reaction temperatures below 120 °C had no effect on the nanotubes' purity, but the efficiency of purification increased linearly with the temperature in the range 120–180 °C and then it remained constant (38%) above 180 °C. The oxidation power of the nitric acid is the influencing parameter for microwave-assisted purification, especially at reaction temperatures above its boiling point. Our observations imply that the oxidizing power of nitric acid toward the decomposition of such defects as amorphous carbon and metal particles is effective only if the acid is vaporized in a closed vessel. The purpose of this purification method, however, is to decompose the defects; higher reaction temperatures may destroy the nanotubes as well. Thus, more evidence is required to elucidate the effectiveness of this method and to determine a suitable purification temperature.

The nanotubes samples were purified in closed vessels by effecting microwave-assisted heating in the presence of nitric acid (5 mL). Fig. 3 illustrates SEM images of the nanotubes after purification at various temperatures. In Fig. 3a, we observe that the raw sample contains not only bundles of aligned carbon nanotubes but also significant amounts of amorphous carbon and metal particles entangled with them. Defect formation has been suggested to result possibly from variations in the deposition process arising from an inhomogeneous distribution of catalyst. From the SEM images, we estimate that the percentage of nanotubes in the raw sample is ca. 30%. Most of the nanotubes are several to tens-of-microns long. When the purification temperature was increased to 120 °C (see Fig. 3b), the impurities that were previously attached to the nanotubes gradually began to

detach and dissolve into the purification solution. The purification efficiency increased when the temperature was elevated to 140 °C (see Fig. 3c). Fig. 3d indicates convincingly that microwave heating at 160 °C does remove most of the impurities (such as amorphous carbon, carbon nanoparticles, and metal catalysts) from the nanotubes; the diameters and shapes of the nanotubes remain the same as those in the image of the raw sample. The SEM image in Fig. 3e illustrates that the impurities were fully removed when the purification temperature was elevated to 180 °C, but both the density and diameters of these nanotubes were reduced.

To identify in more detail the morphologies of the carbon nanotubes obtained under the different conditions, we obtained high-resolution transmission electron microscopy (HRTEM) images (Fig. 4). Under low-temperature microwave heating conditions, ca. 140 °C, most of the nanotubes remained encapsulated with impurities present in the end cap. We attribute this finding to the fact that nitric acid at low temperature does not possess sufficient oxidation power. In Fig. 4b, we observe that most of the impurities have been removed because a suitable oxidation temperature was applied. In addition, the end caps had opened because their constituent five- and/or seven-membered rings are less stable structures than are the six-membered rings of the nanotubes. Fig. 4c indicates that when the temperature of the microwave oven was increased to 180 °C, the surface of the nanotubes gradually decomposed under the more highly oxidative conditions. The surfaces of the nanotubes were not smooth: laminated structures appeared. These findings indicate clearly that the nanotubes' surfaces decompose at temperatures of 180 °C or above.

We employed Raman spectroscopy to evaluate the microwave-assisted purification of nanotube samples at various temperatures. The spectrum presented in Fig. 5a displays the two peaks that are characteristic of pristine nanotubes. The peak near 1350 cm^{-1}, the so-called D band, indicates disordered sp^2-hybridized carbon atoms. In contrast, the peak near 1590 cm^{-1} is the so-called G band and is related to the graphitic E_{2g} symmetry of the interlayer mode. This mode reflects the structural integrity of the sp^2-hybridized carbon atoms of the nanotubes. Together, these bands can be used to evaluate the extent of any carbon-containing defects. To determine the efficiency of purification, we plotted the ratio of the G (1590 cm^{-1}) and D (1350 cm^{-1}) bands after purification at various temperatures. Fig. 5b indicates that the ratio increases abruptly from 4.85 at 120 °C to 6.75 at 160 °C, and then it decreases at 180 °C. These findings clearly support our earlier observation that purification at 180 °C simultaneously destroys both the nanotubes and the defects. In addition, because purification at 160 °C gave the maximum value of the ratio of the two bands, we believe that this temperature is the most suitable one for removing the
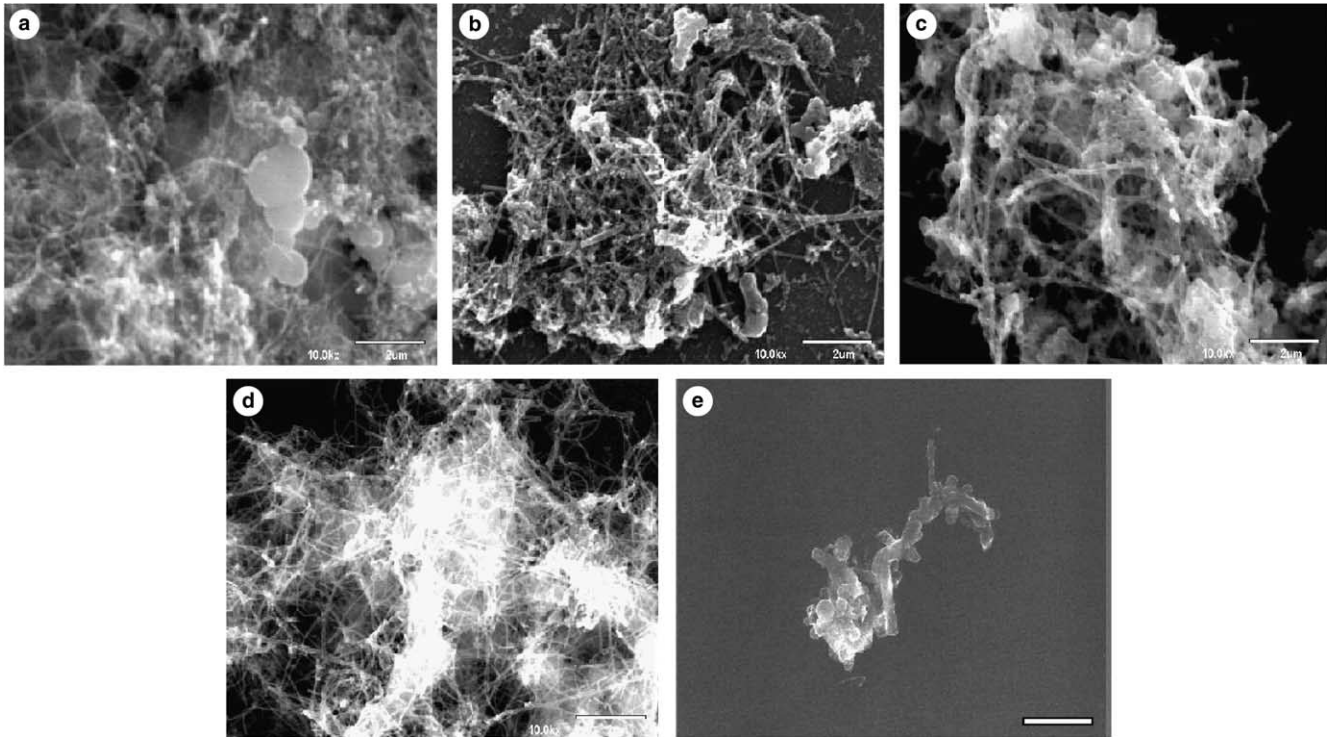
Fig. 3. SEM images (scale bar = 2 μm) of the raw MWNTs and samples purified in a microwave oven using nitric acid at different temperatures. (a) Raw sample, (b) 120 °C, (c) 140 °C, (d) 160 °C, and (e) 180 °C.
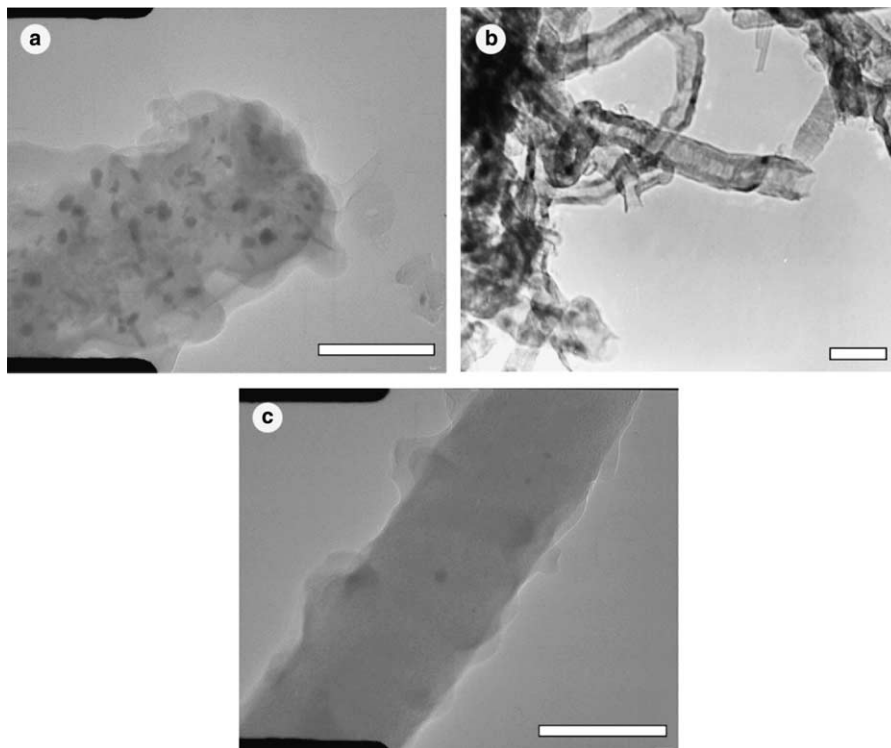

Fig. 4. TEM images (scale bar = 50 nm) of the MWNTs purified in a microwave oven in the presence of nitric acid at different purification temperatures. (a) 140 °C, (b) 160 °C, and (c) 180 °C.

defects and ensuring that the nanotubes remain intact during the microwave-assisted purification process.

Differential thermogravimetry (DTG) can identify the status of defects such as amorphous carbon and car-
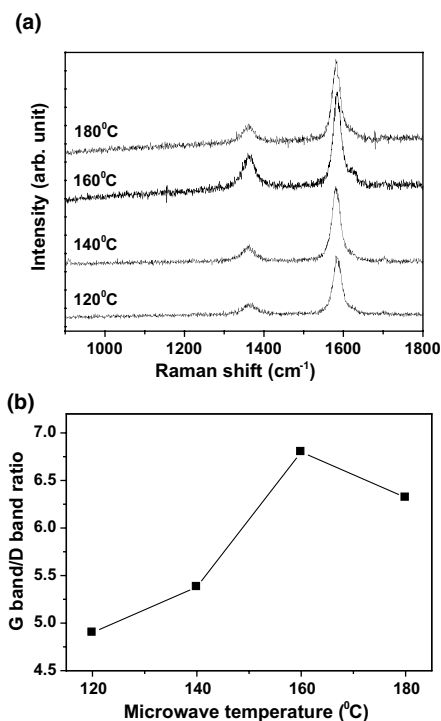
(a)

(b)

Fig. 5. (a) Raman spectra of the MWNTs samples purified in a microwave oven using nitric acid at different purification temperatures, (b) ratios of the intensities of the G and D bands in the Raman spectra of nanotubes purified at various temperatures.

bon nanoparticles (CNPs) at different purification temperatures [16]. The broad peak we observe in Fig. 6a, which contains a shoulder peak at ca. 600 °C, may suggest that carbon nanoparticles (CNPs) coexist with the MWNTs. Fig. 6a also illustrates that the first weight loss arises from the combustion of carbonaceous impurities in air at ca. 190 °C. When the temperature exceeds 400 °C, the samples begin to decompose in the air, but, at temperatures up to 700 °C, the oxidation of the

MWNTs in air is not effective for removal of the defects. The DTG analysis presented in Fig. 6 demonstrates that, without microwave purification, the sample undergoes two significant weight losses—at ca. 190 °C (a small peak) and 550 °C (a broad peak)—whereas the samples obtained after microwave purification with nitric acid exhibit only one significant weight-loss temperature. In addition, the major thermal decomposition temperature of the MWNTs occurs at ca. 550 °C.

Metal impurities in the raw sample, which originate from the synthetic procedures, must also be removed during the purification process. In this study, we have analyzed these metal impurities, such as Fe, Co, and Ni, using an optical emission spectrometer by detecting and counting the specific emission lines of the metals (Fe: 259.9 nm; Co: 228.6 nm; Ni: 231.6 nm). The abundances of Co and Ni were not determined because their concentrations in the raw sample were lower than the detection limit. Thus, iron was the only metallic element that we could observe in the pristine sample. The iron concentration in the untreated MWNTs was ca. 3 µg/g. The iron impurity in the MWNTs could not be easily removed by merely heating in air because of the high boiling points of iron and iron oxide (>1000 °C). The microwave-assisted purification in acid solution is superior for the removal of these metal impurities. Fig. 7a depicts the iron concentration after purification at

(a)

(b)

Fig. 7. (a) Concentrations of iron in the nanotube samples purified using nitric acid at different temperatures, (b) the EDX spectra of the untreated and purified MWNTs.
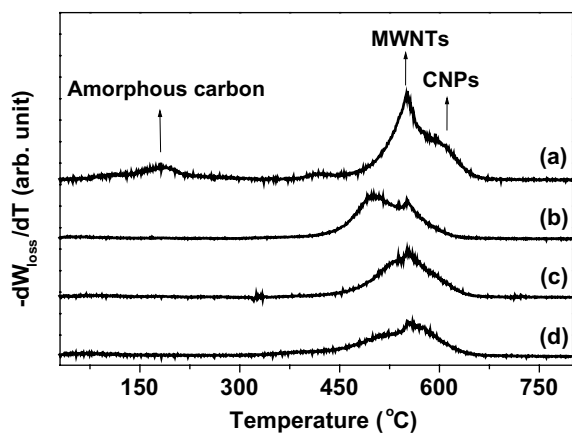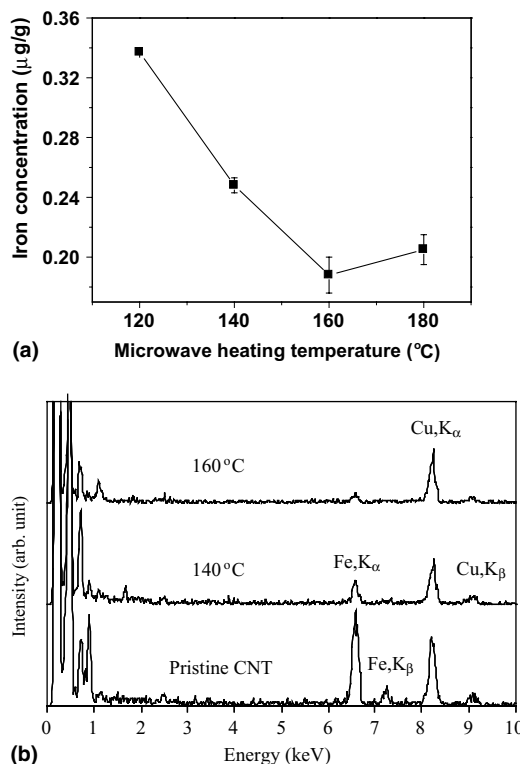

Fig. 6. DTG analyses of the raw MWNTs and samples purified in a microwave oven using nitric acid at different temperatures. (a) Raw sample, (b) 140 °C, (c) 160 °C, and (d) 180 °C.

Table 1
Comparisons of traditional purification methods and the new microwave-assisted purification method

	Temperature	Time	Reagent	Reference
Thermal purification	500–800 °C	40–60 min	O_2 or air	[17]
Chemical agent purification[a]	(1) Room temperature	(1) 1–3 days	H_2O_2, HNO_3, HCl	[18,19]
	(2) Near boiling point	(2) 5–7 h	H_2SO_4	[20]
Microwave-assisted purification	120–180 °C	30 min	HNO_3	This paper

[a] The boiling points of H_2O_2, HNO_3, HCl, and H_2SO_4 solutions are 114 °C, 122 °C, 110 °C, and 340 °C, respectively.

various temperatures. We find that the iron concentration ($n = 3$) decreases gradually as the purification temperature is increased from 100 to 160 °C, and then it levels off at ca. 0.19 µg/g. The relative standard deviation of the iron concentration is controlled to within 14%. These observations indicate clearly that this metal catalyst can be removed effectively at temperatures >160 °C.

We have also used the TEM EDX method to analyze the metal impurities. Fig. 7b illustrates that both Fe and Cu peaks can be observed. The K_α and K_β peaks for Cu are present at 8.20 keV and 9.06 keV; we attribute their existence to the use of a Cu grid when preparing the samples. The intense peak at 8.2 keV can be normalized to the same value for evaluating the efficiency of iron purification. The iron peaks that appear at 6.58 keV and 7.26 keV suggest that Fe is the only impurity in the MWNT samples. The iron peaks (K_α and K_β) decrease upon increasing the purification temperature of nitric acid. We determined that the most-suitable temperature for the removal of iron from the MWNTs is 160 °C; this conclusion is consistent with that we determined from the optical emission spectrometry studies. In addition, we identify the peaks at 0.22 keV and 0.46 keV in Fig. 7b as those for C (K_α) and O (K_β), respectively. We attribute the peak representing carbon as arising from the MWNTs; the oxygen peak suggests that some of the carbon atoms in the outer or inner shell have been oxidized during the purification process.

In Table 1 we compare our new microwave-assisted purification technique with other methods that have been described in the literature [17–20] with respect to their purification temperatures, times, and reagents. The microwave-assisted purification technique using nitric acid has the advantages of a low thermal budget and shorter reaction time when compared with the more-classical thermal purification method. The chemical purification techniques operate at either room temperature or at the boiling point of the purification chemicals. Clearly, the chemical purification technique conducted at room temperature requires the lowest thermal budget, but it takes at least a day to complete. Hence, this approach encounters a purification throughput obstacle that our microwave technique does not. Our microwave-assisted method using nitric acid is very suitable for separating the nanotubes from organic and inor-ganic impurities when consideration both thermal and time parameters.

4. Conclusions

We have developed a microwave-assisted method to successfully purify MWNTs in the presence of only 5 mL of nitric acid. The advantages of this technique are its minimal thermal budget, short operation time, and the use of a simple reagent in low volume. We conclude, from gravimetric and thermogravimetric analyses and spectroscopic studies, that conditions of heating in a microwave oven at a temperature of 160 °C for 30 min are suitable for the purification of raw samples of nanotubes from its amorphous carbon and iron impurities. Temperatures lower than 160 °C reduce the efficiency of defect removal and temperatures that are too high (e.g., 180 °C) cause decomposition of the nanotubes. We have verified these observations by viewing SEM and TEM images of the nanotubes obtained after purification at various temperatures.

Acknowledgments

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