行政院國家科學委員會專題研究計畫　成果報告

微波輔助奈米碳管之純化與分析

計畫類別：個別型計畫
計畫編號：NSC94-2113-M-009-020-
執行期間：94 年 08 月 01 日至 95 年 07 月 31 日
執行單位：國立交通大學奈米科技研究所

計畫主持人：柯富祥

報告類型：精簡報告
報告附件：出席國際會議研究心得報告及發表論文
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中　華　民　國 95 年 7 月 31 日

行政院國家科學委員會補助專題研究計畫期中進度報告

微波輔助奈米碳管之純化與分析

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成果報告類型(依經費核定清單規定繳交)：☑精簡報告　□完整報告

本成果報告包括以下應繳交之附件：

□赴國外出差或研習心得報告一份

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☑出席國際學術會議心得報告及發表之論文各一份

□國際合作研究計畫國外研究報告書一份

執行單位：交通大學 奈米科技研究所

中文摘要

我們發展以 5 毫升硝酸為主的微波輔助法，來純化多壁奈米碳管內的非晶碳、碳奈米微粒及金屬等缺陷雜質。最佳的微波純化條件是 160℃下維持 30 分鐘，電子顯微鏡影像驗證雜質可以有效分離而碳管仍保持完整。相對的，若是微波溫度提高到 180℃，純化溶液的氧化能力會過強而致使碳管被分解。碳管的拉曼光譜之 G 帶與 D 帶之比率亦指出 160℃的反應溫度是最適宜的，DTG 熱分析結果亦證明本微波法對於碳管之純化相當有效。另者，感應耦合電漿光譜儀亦證明碳管上的金屬雜質已經被完全純化。

關鍵字：奈米碳管、電子顯微鏡、拉曼光譜、缺陷

Abstract

We demonstrate that microwave-assisted heating in 5mL 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 ^{o}C for 30min 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 ^{o}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 ^{o}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.

Keywords: Carbon nanotubes; Electron microscopy, Raman spectroscopy; Defects

Introduction

Multi-walled carbon nanotubes (MWNTs) have been attracting considerable attention not only because of their unique physical properties but because of their potential use in various applications [1-4]. These applications includes high mechanical strength, and unusual electronic properties, such as field emission displays, capability for the storage of large amount of hydrogen, high modulus, and structural diversities that make it possible for the band gap engineering. Most of the widely used nanotube synthesis methods such as the arc discharge method [5], the laser ablation [6] and the chemical vapor deposition [7]. However, the unwanted impurities may be included in the MWNTs during synthesis. These impurities are ascribed to polyaromatic carbon shells, amorphous carbon, fullerenes or remains of the primary materials which are graphite flakes from the arc electrodes or laser target, catalyst crystals. These impurities are a handicap for further applications, therefore, it is inevitable to develop a purification method for MWNTs.

Various methods for purifying carbon nanotubes have been reported, including chemical oxidation [8], thermal oxidation [9-11], filtration [12], and chromatography [13-14]. These methods can be divided into two groups, namely 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, reliable control over amenable temperatures and pressures. Despite the versatility of microwave techniques, they have not been used previously to purify carbon nanotubes with nitric acid.

In this paper, we propose a new microwave purification method for isolating pristine carbon nanotubes by nitric acid under pressurized condition. We have used a gravimetric method, based on weighing residual solid samples, to evaluate the defect removal efficiency at various heating temperatures by nitric acid. Prior to verification by SEM, we evaluate the effects of different temperatures on the samples by Raman spectroscopy and thermogravimetric analysis. Furthermore, we also studied the efficiency of this process toward the removal of metal defects from the samples.

Experimental

Microwave purification of the nanotube samples (50 mg) using chemical reagents (5ml) was accomplished by placing them in closed vessels inside a commercial 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. The 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 m1, 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 alternative method 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 solution, of analytical or higher grades, was obtained from E. Merck (Darmstadt, Germany). A Model-AT201 analytical balance (readability = 0.01 mg), obtained from Mettler–Toledo (Switzerland), was used to measure sample weights. MWNTs (outer diameter: 50–100 nm, inner diameter: 20–40 nm, 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 $M\Omega cm^{-1}$) was used throughout these experiments. The morphology of the MWNTs was characterized by field-emission scanning electron microscopy (SEM, Hitachi S-4000, Tokyo, Japan). 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 characterized by inductively coupled plasma optical emission spectroscopy (Perkin–Elmer Optima 3000, Norwalk, CT, USA). The schematic diagram of experimental flow is listed in Fig. 1.

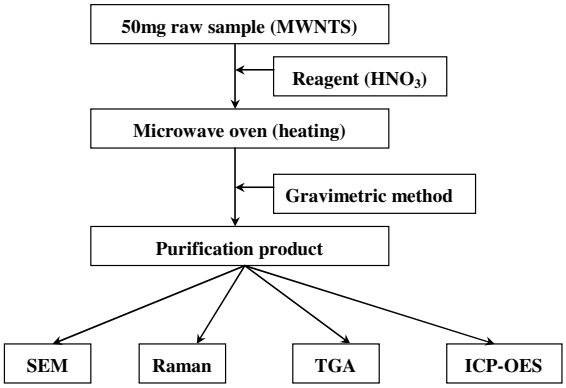


Fig 1. The schematic diagram of microwave-assisted purification processes.

Results and discussion

In the purification, the use of nitric acid has some efficiency on dissolving the impurities from the MWNTs [15]. However, it requires a couple days to purify the MWNTs under open reactor. We propose the closed-vessel system to purify MWNTs with nitric acid in microwave system, and suggest the gravimetric method can be used to evaluate the removal efficiency on impurities. In closed-vessel microwave apparatus, the high temperature will evaporate the purification reagents to sustain high pressure condition. In this work, the boiling point of nitric acid is 122°C. The nitric acid vaporizes and refluxes in the closed vessel as if the purification temperature is elevated to higher than the boiling point. The MWNTs are the high strength materials, but the amorphous carbon ascribed to impurity can be destroyed. Figure 2 illustrates the purification efficiency 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 ranging

120-180 °C and then remained constant (38%) at up to 180 °C. The oxidation power of the nitric acid is the influencing parameter for microwave-assisted purification, especially at the reaction temperature higher than boiling point. This observation implies that the oxidizing power of nitric acid toward the decomposition of such defects as amorphous carbon and metal particles is only effective as if the acid vaporized. The purpose of the purification method, however, was aimed only at the decomposition of defects; the higher reaction temperature may also destroy the nanotubes. Thus, more evidence is required to elucidate the effectiveness of this method at a suitable purification temperature.

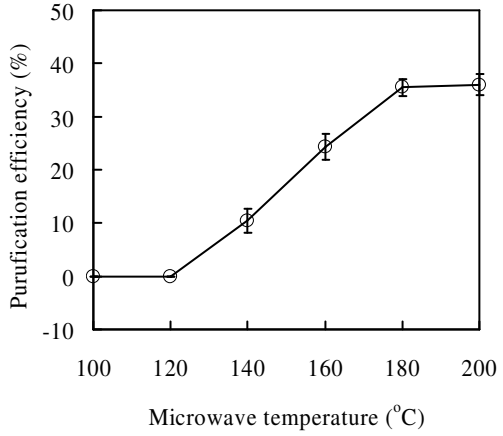
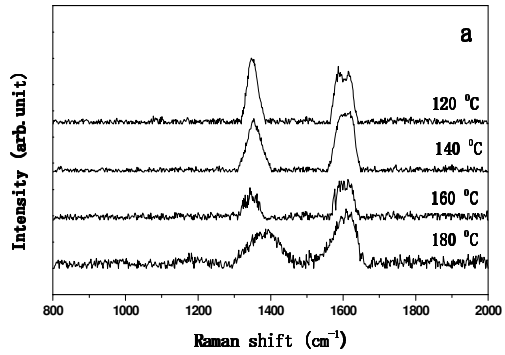


Fig 2. The effects of reaction temperature on the defect removal efficiency of the nanotubes by nitric acid, as measured by the gravimetric method.

We employed Raman spectroscopy to evaluate the microwave-assisted purification of nanotube samples at various temperatures. The spectrum presented in Figure 3a is composed of two characteristic peaks for the pristine nanotubes. The peak near 1280 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 graphite 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 carbon-containing defects. Purification of the nanotubes under 120 °C, the intensity of the G band is lower than that of the D band. This finding suggests that a large number of defects exist in the original samples. In order to minimize the experimental error, we plotted the ratio of the G (1590 cm^{-1}) and D (1280 cm^{-1}) bands at various purification temperatures. Figure 3b indicates that the ratio increases abruptly from 0.91 at 120 °C to 1.52 at 160 °C, and then decreases at 180 °C. This observation clearly supports the assumption that purification at 180 °C simultaneously destroys both the nanotubes and the defects. In addition, purification at 160 °C reaches the maximal ratio of the two bands. This finding indicates that 160 °C is the most suitable temperature for removing the defects and ensuring that the nanotubes remain intact by microwave-assisted purification.



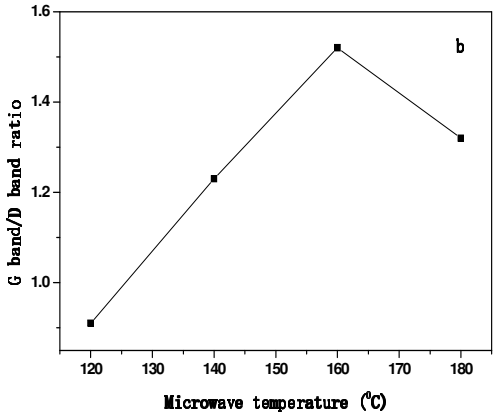
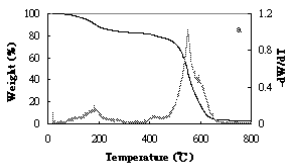


Fig 3. (a) The Raman spectra of the raw MWNTs sample purified with nitric acid at different microwave purification temperatures, and (b) Ratios of the G and D bands in the Raman spectra of the nanotubes purified at various temperatures.

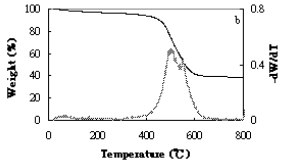
Figure 4 displays the effect of the purification temperature on the weight loss and plots of derivative

thermogravimetric analysis curves as a function of temperature. We see from the derivative thermogravimetry that prior to purification the sample undergoes two significant weight losses at 190 and 550 °C, whereas the samples after purification with nitric acid exhibit only one significant weight loss temperature. What causes the different behavior? As Figure 4a illustrates, the first weight loss arises from the combustion of carbonaceous defects in air at ca. 190 °C. As the temperature of the thermogravimetric analysis system exceeds 400 °C, the nanotube samples begin to decompose in the air. The nanotubes samples do not fully evaporate until the temperature reaches 650 °C. Obviously, the broad peak in the derivative thermogravimetry plot in Figure 4b to 4d originates from the partial and unsymmetrical decomposition of the nanotubes in the presence of nitric acid.

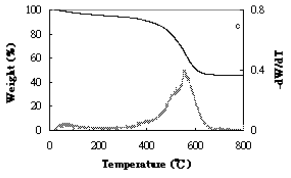
(a)



(b)



(c)



(d)

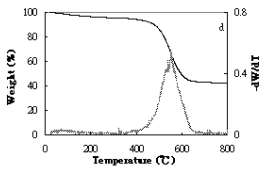
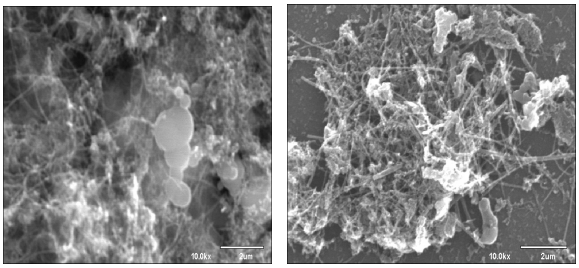


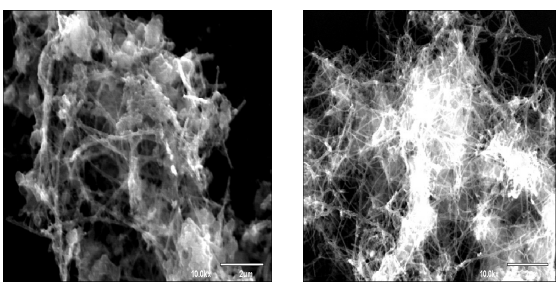
Fig 4. TGA graphs of the raw MWNTs sample purified with nitric acid at different microwave temperatures: (a) raw sample, (b)140 ^{o}C, (c)160 ^{o}C and (d)180 ^{o}C.

The nanotubes samples were purified in closed vessels by microwave-assisted heating in the presence of nitric acid (5 mL). Figure 5 illustrates the SEM images of nanotubes after purification at various temperatures. In Figure 5a, the raw sample contains not only bundles of aligned carbon nanotubes, but also a significant amount 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 the percentage of nanotubes in the raw sample to be ca. 30%. Most of the nanotubes are several-to-tens-of-microns long. When the purification temperature was increased to 120 ^{o}C, the impurities that previously had been attached to the nanotubes gradually detach and dissolve into the purification solution. As the purification is elevated to 140 ^{o}C, the purification efficiency is increased. Figure 5d indicates convincingly that microwave heating at 160 °C can remove most of the defects (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 defects are fully removed when the purification temperature is elevated to 180 °C, as the SEM image in Figure 5e illustrates, but the density and diameters of these nanotubes have reduced.

(a) (b)



(c) (d)



(e)

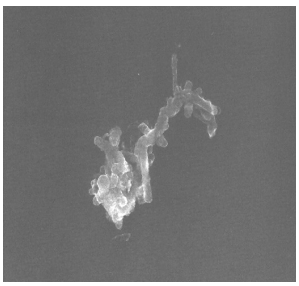


Fig 5. The SEM image (scale bar = 2μm) of the raw MWNTs sample purified with nitric acid at different microwave purification temperatures: (a) raw sample, (b) 120 °C, (c) 140 °C, (d) 160 °C, and (e) 180 °C.

The metal defects in the raw sample, which originate from the synthetic process, must also be removed during the purification process. In this study, we analyzed metal impurities, such as Fe, Co, and Ni, using an optical emission spectrometer. We detected and counted 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 could not be determined because their concentrations in the raw sample were lower than the detection limit. Thus, iron is the only metal element that we observed in the pristine sample. Figure 6 depicts the iron concentration after purification at various temperatures. We found that the iron concentration (n=3) decreases gradually as the purification temperature was increased from 100 to 160 °C, and then it levels off at ca. 0.19 ppm. The relative standard deviation for iron measurements is controlled within 14%. This observation clearly indicates that this metal catalyst can be effectively removed at temperatures above 160 °C.

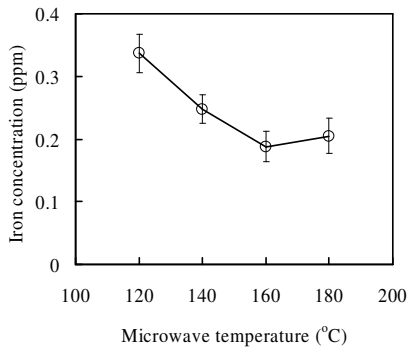


Fig 6. Iron concentration in nanotube samples that had been purified with nitric acid at different microwave temperatures.

Table 1 lists a comparison of this new microwave-assisted purification technique with other methods described in the literature with respect to purification temperatures, times, and reagents. The microwave-assisted purification technique by nitric acid has the advantage of a low thermal budget and is more timesaving than the more-classical thermal purification method. The chemical purification techniques operate at either room temperature or the boiling point of the purification chemicals. Clearly, the chemical purification technique conducted at room temperature requires the lowest thermal budget, but it requires at least a day to undertake it. Hence, the approach meets a purification throughput obstacle that our microwave technique does not. The microwave-assisted method with nitric acid that we have developed is very suitable for purifying nanotubes from organic and inorganic defects on the basis of a consideration of thermal and time parameters.

Table 1. Comparison of traditional purification methods and microwave-assisted purification method

	Temperature	Time	Reagent	Reference
Thermal purification	500 - 800 °C	40-60 min	O_2 or Air	[16]
Chemical agent purification[a]	(1) Room temperature	(1) 1-3 days	H_2O_2, HNO_3, HCl	[17-18]
	(2) Near boiling point	(2) 5-7 hours	H_2SO_4	[19]
Microwave-assisted purification	120 - 180 °C	30 min	HNO_3	

a: The boiling points are 114, 122, 110, and 340 °C for H_2O_2, HNO_3, HCl, and H_2SO_4, respectively.

Conclusions

We have successfully developed a microwave-assisted method to purify MWNTs by only 5mL nitric acid. The advantages of this technique are its minimal thermal budget, short operation time, and the use of a simple and low-volume reagent. We conclude, after gravimetric and thermogravimetric analyses, and Raman and optical emission spectroscopic studies, that heating by microwave at a temperature of 160 °C for 30 min is suitable for the purification of raw samples of nanotubes from amorphous carbon and iron defects. Lower temperatures (< 160 °C) reduce the efficiency of defect removal, while temperatures that are too high (e.g., 180 °C) cause decomposition of the nanotubes' walls. In addition, we have verified these observations by viewing SEM images of the nanotubes obtained

after purification at various temperatures.

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計畫成果自評

本年度研究已經成功的開發奈米碳管及其雜質的分析技術，應用到微波輔助純化法上。研究中應用重量分析法、電子顯微鏡分析法、拉曼光譜法、熱分析法及感應耦合電漿光譜法等，成功的找到微波最適操作參數，並且能夠解釋缺陷之分離條件與機構。本年度的成果符合目標，已經有成果發表在SCI級的期刊上，同時本計畫亦培養分析化學應用在奈米材料領域的研究人員。