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Microwave digestion and acidic treatment procedures for the purification of multi-walled carbon nanotubes

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Abstract

Multi-walled carbon nanotubes (MWCNTs) synthesized by thermal chemical vapor deposition have been successfully purified by using efficient microwave digestion method. Recently, various purification methods have been provided to eliminate metal catalysts and most were acid treatment procedures that take long time and damage the structure of nanotubes. Comparing to these methods, microwave digestion takes a tremendous advantage because the acid in this approach can absorb microwave energy rapidly and dissolve metal efficiently without damaging the wall structure and the processing time could be the shortest. The ability of microwave digestion method was studied by various experimental parameters. The efficient purification proceeded for 90 min and at 210 °C with 5 M nitric acid treatment in the microwave digestion system to dissolve the metal catalyst. High-resolution transition electron microscopy and Raman spectra were used to characterize the specimen. Purities were characterized by thermogravimetric analysis (TGA). Results showed that the amount of catalyst decreased with increasing acid treatment time and concentration. Purity of MWCNTs achieved as high as about 99.9%. This study presents a highly efficient purification method for carbon nanotubes with high purity and no structure destruction. In addition, carbon nanotubes synthesized by various methods were also purified and the results were comprehensively discussed.
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1. Introduction

Since the first discovery of carbon nanotubes (CNTs) by Iijima [1], there has been increasing scientific and technologic interest in their properties and applications. Numerous studies have been reported because of their unique physical properties, such as mechanical and electrical properties. Carbon nanotubes may have exceptional strength and stiffness along with high thermal and electrical conductivity. These properties with their low density have attracted much attention for fundamental scientific studies in the fields of nano-structure, fullerene science, physics, chemistry, and material science.

Recently, various beneficial applications, such as field emission displays, nanoscale electronic devices, diodes, transistors, sensors, composite polymers, artificial muscles, mechanical reinforcements, capacitors, and hydrogen storage [2–16], have already been represented.

However, the as-prepared carbon nanotubes usually contain not only CNTs but also other carbonaceous and transition metal particles. The presence of impurities may significantly influence the properties of CNTs and the behavior of any device built from these materials. Carbonaceous particles, including amorphous carbon particles, fullerenes and nanocrystalline polyaromatic shells, can be eliminated by gas phase oxidation [17] or thermal annealing in air or oxygen atmosphere [18]. These purification processes are based on the phenomenon that the oxidation temperature of carbonaceous particles is different from that

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of CNTs in air or oxygen. On the other hand, transition metal catalysts encapsulated in wall structure could affect the performance of many practical applications.

There have been many efforts on eliminating the metal catalyst. Bandow et al. [19] investigated a purification method of microfiltration which could separate carbon nanospheres, metal nanoparticles, polyaromatic carbons and fullerenes from the single-walled carbon nanotubes (SWNTs) fraction. Shelimov et al. [20] also proposed a purification method of SWNTs by ultrasonically assisted filtration. These methods were based on physical phenomena. On the other hand, many studies have focused on chemical oxidation. Chiang et al. [21] reported a purification strategy based on oxidizing Fe and then dissolving the oxide. Ando et al. [22] proposed that the multi-walled carbon nanotubes (MWCNTs) were ground, boiled with H_2O_2 and then refluxed in a mixture of sulfuric acid and nitric acid in the ratio of 3:1. Chen et al. [23] reported a three-step purification process of MWCNTs. The sample was stirred in nitric acid and refluxed and then suspended and refluxed in HCl solution. After acid treatment, MWCNTs were calcined in static air at 510 °C. However, these methods were either time consuming or defect inducing. During the purification process, carbon nanotubes were even cut into short pieces by long acid treatment time or ultrasonication.

In our previous work, we have successfully investigated a high efficiency and nondestructive purification method of MWCNTs by using microwave digestion system [24]. The microwave-assisted digestion system (Milestone Microwave Labstation ETHOSD) has dual magnetrons (1600 W) with rotating mode stirrer and can create a homogeneous microwave field with no hot or cold spots that might cause incomplete digestions. The advantages of this method are high temperature, closed vessel, and acid digestion prepared samples in shorter time than other methods, less acid consumed and volatile elements available. In application, microwave sample preparation has been widely used for trace and ultra-trace metal analysis, such as atomic absorption spectrometry (AA), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma–mass spectrometry (ICP-MS).

Although a chemical reagent can adsorb energy rapidly and eliminate metal catalyst efficiently in this method, the amount of residual metal catalyst in our previous study was still high (5%). The reason might be that the length of electron cyclotron resonance chemical vapor deposition (ECRCVD)-synthesized carbon nanotubes was shorter than that synthesized by arc discharge or thermal CVD, and the weight ratio of metal catalyst/carbon nanotubes reached 30%. In this paper, as-prepared commercial multi-walled carbon nanotubes synthesized by thermal CVD were purified by microwave-assisted digestion method with nitric acid. The length of thermal CVD-synthesized carbon nanotubes were longer; and these nanotubes were gathered in higher purity regions of the substrate. Therefore, the

weight ratio of catalyst/nanotubes was lower, and carbon nanotubes of high purity were obtained with nitric acid treatment assisted by microwave. Although chemical reagents, such as H_2SO_4, HNO_3, and HCl, can absorb microwave energy rapidly and dissolve metals, nitric acid was applied in this work according to the Environment Protection Agency recommendation that nitric acid can solubilize heavy metals and has been widely applied in leaching sediment soils and sludge.

Purification efficiencies at various acid concentrations, processing time and ultrasonication time were evaluated by thermogravimetric analysis (TGA), based on weighing the amount of residual sample weight. Morphology of purified carbon nanotubes was evaluated by scanning electron microscopy (SEM) and wall structure was observed by high-resolution transmission electron microscopy (HRTEM). We evaluated the effects of acid concentration and processing time on the MWCNTs by Raman spectroscopy. Furthermore, purification efficiency of MWCNTs by different synthesized methods was also discussed.

2. Experiments

In the experiment of group A, as-prepared multi-walled carbon nanotubes (diameter: 40–60 nm) were dispersed in 25 ml deionized water with ultrasonic agitation for 1, 2, and 3 h. The weight of each sample was 0.6 g. After sonication, each sample was dried and then divided into three parts for microwave purification of 30, 60, and 90 min in 1 M nitric acid and the weight of each part became 0.2 g. Procedures were the same for group B and group C, but different in acid concentration. Group B was purified by microwave-assisted purification with 3 M nitric acid and group C with 5 M nitric acid as shown in Table 1.

In purification, samples were placed in 100 ml TFM (thermally resistant form of Teflon by Milestone) vessels filled with nitric acid and then put on the sample rotor made of Teflon and available for 12 vessels. The power of microwave was set at 100 W. At the first step, temperature ramped up from room temperature to 210 °C in 30 min. The temperature was controlled by temperature control system (ATC-400CE) which allows continuous monitoring and ±1 °C control of the internal temperature in a standard Milestone reference vessel. The maximum operating tem-

Table 1
Experiment condition of nitric acid concentration, sonication time, and microwave-assisted purification time

Experiment groups	Group A	Group B	Group C
Concentration of nitric acid	1 M	3 M	5 M
Sonication time	1 h, 2 h, 3 h		
Microwave-assisted acid-treatment time	30, 60, 90 min		
Microwave power	100 W		
Temperature	210 °C		

perature of the ATC-400CE is 300 °C. The second step was carried out isothermally at 210 °C for 30, 60, and 90 min, respectively. After digestion, the suspension was filtered with 0.1 μm PTFE (poly-(tetrafluoroethylene)) membrane in deionized water. After rinsing with alcohol and vacuum drying for 8 h, there appeared a black thin mat.

The morphology of MWCNTs and the wall structure of nanotubes, before and after purification, were observed by high-resolution transmission electron microscopy (HRTEM, Philips TECNAI 20). The amount of metal catalyst in the raw sample and purified sample was estimated by thermogravimetric analysis (TGA, Perkin Elmer 1020 Series TGA 7) with the heating rate of 20 °C/min from 30 °C to 900 °C at the air flow rate of 10 sccm. The bonding structure of carbon nanotubes in raw and purified samples was analyzed by Raman spectroscopy at 514.5 nm Ar$^+$-laser (Renishaw system 200).

3. Results and discussion

Fig. 1 is an HRTEM image of the tubes' tip. As shown in Fig. 1, the catalysts embedded in the tip of MWCNTs were removed. Obviously, the closed tube tip was opened by acid treatment in microwave digestion method. It seems that closed tip was opened first and then the metal catalyst was eliminated by nitric acid. In this high-resolution TEM image, it also shows that the wall structure of tubes was not damaged by acid treatment.

Fig. 2 shows the effect of acid concentration on purification ability for different processing time. The amount of residual catalyst was measured by TGA and this is an effective way to evaluate the key features of purification process. By observing the behavior of weight–
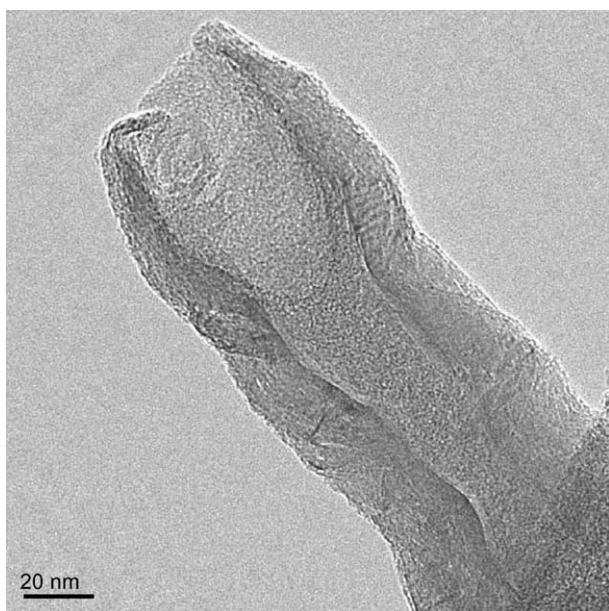

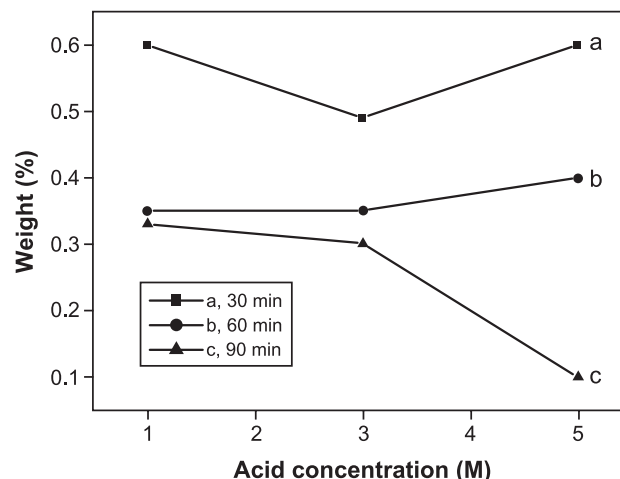Fig. 1. HRTEM image of acid-treated MWCNTs.

Fig. 2. The effect of acid concentration on purification ability for different processing times.

temperature curve, by-products during acid treatment such as carbonaceous matter could appear in as-purified samples [25]. Curves a and b show that the purification ability of shorter microwave-digestion time is not strong enough no matter how high the acid concentration is. However, curve c shows that the catalyst elimination ability increases with increasing the acid concentration for 90 min treatment. This result could be that the tube-opening process needs time to occur. Once in excess of the critical time, the metal could be etched away quickly. In this experiment, it might be an appropriate parameter of purifying carbon nanotubes with 5 M nitric acid and 90 min.

Fig. 3 shows the effect of ultrasonication time on purification efficiency of 5 M nitric acid under various treatment times. In curves d and e, the increase of sonication time results in the decrease of residual metal amount. In samples with 60 min purification treatments, the catalyst amount measured by TGA decreases from 0.49% to 0.31% with increasing the treatment time from 1 h to 3 h. It seems that the ultrasonic treatment could make the raw sample more dispersed and enhance the ability of acid treatment. However, the experiment for the acid treatment time of 90 min (curve f) reveals almost the same amount of residual catalyst. The results could be that the time of acid treatment might dominate the efficiency of purification process and did not need long sonication time, which might induce the defect of the tube's wall [20].

Fig. 4 shows the result of TGA analysis of raw and purified samples. In Fig. 4a, the TGA analysis shows that the content of metal catalyst in the raw sample was 1.34%. The early slight weight gain in the raw sample might be due to the oxidation of metal catalysts. In the raw sample, the weight starts to reduce near 515 °C and MWCNTs completely evaporate above 712 °C. The decomposition temperature at 673 °C is defined as the inflection point during oxidation of the tubes [25]. Different from the raw sample, the weight loss of purified MWCNTs by burn-off starts from 550 °C and completely burn out near 758 °C, as
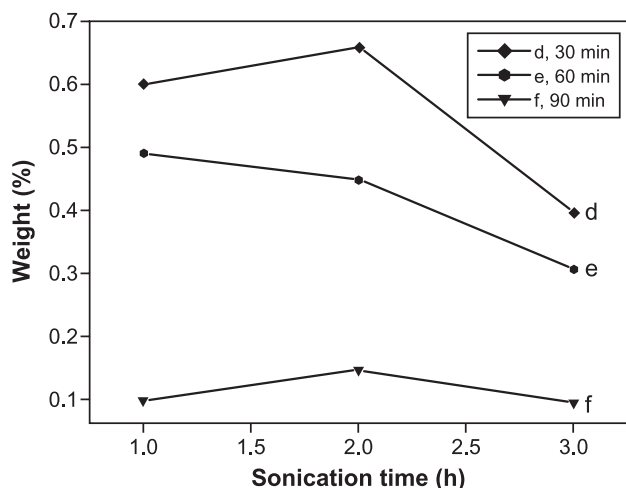
Fig. 3. The effect of ultrasonication time on purification efficiency.

shown in Fig. 4b. The amount of residual catalyst dropped to 0.1 wt.% in purified sample of group C for 90 min purification. The decomposition temperature in this purified sample was 703 °C, which was slightly higher than that in the raw sample. This result reveals that residual metal
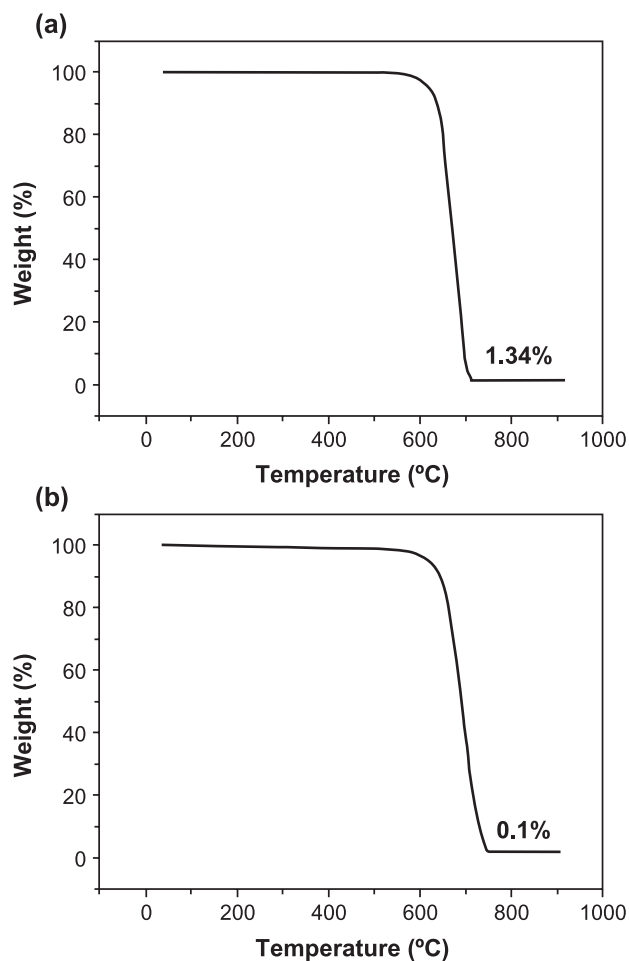

Fig. 4. (a) The TGA analysis of raw sample. (b) The TGA analysis of purified sample.

embedded in raw samples acted as oxidation site and initiated oxidation reactions [26]. It was also reported that the metal impurities in the sample would lower the decomposition temperature and increase the decomposition rate [26]. The purified sample is thermally more stable towards oxidative destruction than the raw MWCNTs. In Fig. 4a and b, evidently there are no other separate regimes except the main combustion regime. This points out that microwave digestion method does not introduce carboxyl, aldehyde and other oxygen-containing functional groups on the surface of the non-nanotube carbonaceous fractions. These groups, by report, were extremely hygroscopic and reactive towards oxidation.

Fig. 5 reported the catalyst contents after purification with 5 M acid for various treatment times. The amount of catalyst decreases from 1.34% to 0.6% at the processing time of 30 min and 0.49% at 60 min treatment. After treated for 90 min, the total amount of catalyst dropped to 0.1%. This result clearly indicated that nitric acid could eliminate more catalyst under sufficient treatment time. The purity of purified MWCNTs could reach 99.9% only in 90 min acid processing time without damaging the wall structure.

The Raman spectroscopy of raw and purified samples in Fig. 6 is composed of two characteristic peaks for the nanotubes. The G band near 1580 cm^{-1} is related to the graphite E_{2g} symmetry of the interlayer mode, which reflects the structural intensity of the sp^2-hybridized carbon atoms of the nanotubes. Another peak at 1350 cm^{-1}, the D band, indicates disordered carbon atoms. The extent of defect in carbon nanotubes can be evaluated with these two peaks. The result of Raman analysis shows that ratios of I_D/I_G before and after purification are almost the same. This means that the bonding structure of tubes wall was not damaged by microwave-assisted purification method. Some studies [18,26] have suggested that the I_D/I_G ratio would increase after purification, because of the improvement in nanotube content by eliminating amorphous carbon. In this study the amount of carbonaceous materials was low (<3%) and the
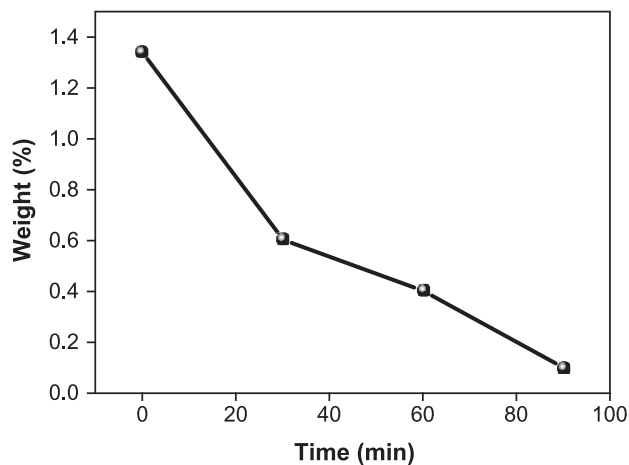

Fig. 5. The catalyst content of purified sample for various treatment times with 5 M nitric acid.
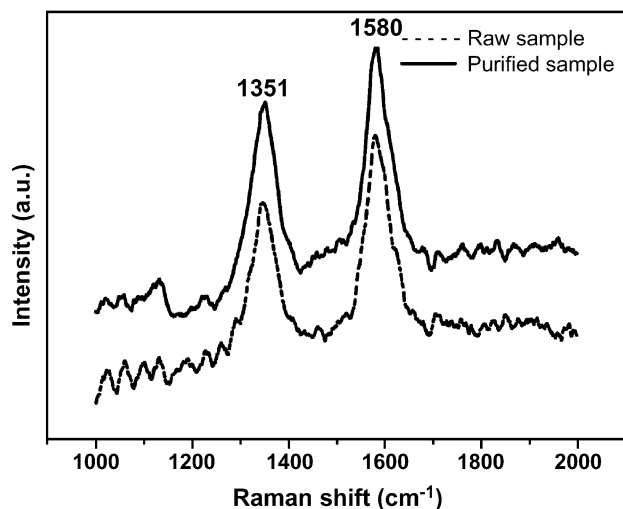
Fig. 6. The Raman analysis of raw and purified sample.

purification process did not damage the bonds, so the Raman curves of raw and purified sample are almost the same.

A lot of research has been reported to obtain purified carbon nanotubes. Ando et al. [22] reported that the MWCNTs were ground and boiled with 20% H_2O_2 in a reflux condenser for 45 h. Then the residual material was refluxed for 24 h in a mixture of sulfuric acid (96%) and nitric acid (61%) with the ratio of 3:1. Chen et al. [23] proposed that the MWCNTs were stirred in 3 M nitric acid and refluxed in 5 M HCl solution for 6 h at 120 °C. After acid treatment, the samples were calcined in static air at 510 °C with the reaction time of about 60 min. Moon et al. reported a two-step process of thermal annealing in air acid treatment to purify single-walled carbon nanotubes. In this study, the acid treatment with HCl for 24 h was to etch away the metal catalyst [25]. Evidently most acid treatment methods removed metal catalyst for more than 24 h. It was reported that the carbon nanotubes would break into short pieces for too long acid treatment time [26]. This is because that oxygen-containing mineral acid, HNO_3, for example, are known to be very efficient in dissolving metal particles and such polyaromatic solids as graphite or amorphous carbon. However, in the microwave digestion system, nitric acid can rapidly absorb microwave energy without agitation in solution. Owing to the high efficiency of heat adsorption and no agitation, the processing time of microwave digestion method to dissolve catalyst in MWCNTs can be reduced to 2 h and metals could be eliminated from MWCNTs rapidly without destruction in the wall structure.

In addition to the acid treatment, Shelimov et al. [20] also proposed a method of ultrasonically assisted filtration. In this method, sample sonication during filtration prevents filter contamination and provides a fine nanotube–nanoparticle suspension through the purification process. The process generates SWNTs material with purity of more than 90%. Although this method could separates coexisting carbon nanospheres, metal nanoparticles, polyaromatic

carbons, and fullerenes from the carbon nanotubes fraction, metal catalysts embedded in the tip and wall structure could not be eliminated by this method. One advantage of microwave digestion method was that the embedded metal catalyst would be eliminated and the purity of carbon nanotubes could be higher.

Another purification method to eliminate metal catalyst was proposed by Chiang et al. [21]. This method suggests a purification strategy based on oxidizing Fe and then dissolving the oxide. Raw material was heated in static air at 200 °C for 24 h and followed by sonication in concentrated HCl (37%) in an 80 °C water bath for 15 min. Although the HCl treatment time was 15 min, the total purification time was obviously more than 24 h. In this report, the total acid treatment time was below 2 h. It was apparent that microwave digestion could effectively eliminate the catalyst from carbon nanotubes and would not introduce structure defect.

4. Conclusion

In our previous work, we successfully developed a high efficient and damage-free microwave digestion method. The advantages of this method are highly efficient, easy to operate, short in time, free of damage on CNTs and little consumed reagents. However, the residual catalyst of ECR-synthesized MWCNTs after purification was still high, because of the catalyst content in the raw sample was too high. In this work, we studied the efficiency of purification on MWCNTs synthesized by thermal chemical vapor deposition with different parameters by using TGA, SEM, TEM, and Raman spectroscopy and indented to get high-purity MWCNTs. The results show that the purification efficiency increases with increasing acid treatment time. The amount of residual catalyst in purified sample was reduced to 0.1% after digestion for 90 min at 210 °C. In conclusion, microwave digestion method may have great potential in mass purification. High quality and large amount of purified CNTs would be applied to more intrinsic studies and industrial applications.

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