

Purification of multi-walled carbon nanotubes by microwave digestion method

Chieng-Ming Chen^a, Mi Chen^{b,*}, Fang-Chin Leu^b, Shu-Yu Hsu^b, Sheng-Chuan Wang^b,
Shih-Chen Shi^a, Chia-Fu Chen^a

^aDepartment of Materials Science and Engineering, National Chiao-Tung University, Hsinchu 30049, Taiwan, ROC

^bDepartment of Chemical Engineering, Minghsin University of Science and Technology, 1 Hsin-Hsing Road, Hsinfong, Hsinchu 304, Taiwan, ROC

Abstract

Here developed is an efficient method for purification of multi-walled carbon nanotubes synthesized by electron cyclotron resonance chemical vapor deposition (ECRCVD). Carbon nanotubes may find their limited use for some applications as they contain a small fraction of metal catalysts in the tubes and tend to have defects along the graphene tube wall. Defects within the multi-walled carbon nanotubes would reduce electrical and structure properties. A two-step acidic treatment in microwave digestion system is used to dissolve metal catalysts. HNO₃ or HCl can rapidly absorb microwave heat and energy and completely dissolve metal, which reside in carbon nanotubes without damage. The processing time of the two-step microwave-assisted and acid-treated time to dissolve metal in the MWCNTs is below 1 h. After purification, the amount of residual catalyst metals in samples is estimated by using the thermogravimetric analysis (TGA). The results show that a high-yield of multi-walled carbon nanotubes with approximately 5% of metal is obtained.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Nanotubes and fullerenes; Purification; Multi-walled carbon nanotubes; Microwave digestion

1. Introduction

Since carbon nanotubes (CNTs) were discovered [1], relevant research fever and developments of commercial applications such as hydrogen storage, atomic force microscope probe, microelectronic transistor, electrical field emitter of flat panel display and scanning tunneling microscope tip have been stimulated tremendously. High-quality and well-aligned carbon nanotubes are essential to the potential applications in the field of microelectronic industries.

Many kinds of synthetic techniques have been developed, such as laser ablation, plasma-enhanced chemical vapor deposition, arc discharge, pyrolysis and thermal chemical vapor deposition [2–7]. Transition metal (e.g. Fe, Co, Ni) particles are known to be catalysts for vapor grown carbon nanotube synthesis, in which hydrocarbons (e.g. CH₄, C₆H₆) are used as gas source. Metal catalysts are generally necessary to activate carbon

nanotube growth. Carbon nanotubes may find their limited use for some applications as they contain a small fraction of metal catalyst in the tubes and tend to have defects along the graphene tube wall. Defects within the multi-walled carbon nanotubes would reduce electrical and structure properties.

Recently, many purified methods have been investigated and have been used successfully to remove impurities from carbon soot [8–13]. One of the efficient purification methods reported by Tsang et al. [14] was oxidation in air at 750 °C. Due to the small difference in reactivity between multi-walled carbon nanotubes (MWCNTs) and carbon nanoparticles, pure MWCNTs were obtained after prolonged oxidation. Many following up researchers [15–17] adopted thermal annealing and similar thermal oxidation method to purify CNTs but with low yield.

Shelimov et al. [18] proposed a method to purify single walled carbon nanotubes by ultrasonically-assisted filtration. Amorphous carbon, crystalline carbon impurities and metal particles are removed from single walled carbon nanotube samples by ultrasonically-assist-

*Corresponding author. Tel.: +886-3-5593142x3339; fax: +886-3-5595142.

E-mail address: chenmi@must.edu.tw (M. Chen).

ed microfiltration. The process generates SWNT material with purity above 90% and yields of 30–70%. A two-step process of thermal annealing in air and acid treatment, proposed by Moon et al. [19], was used to purify single walled carbon nanotubes. Their result showed that the reproducible optimal purification process provided a total yield of approximately 25–30 wt.% with transition metals less than 1%. Zhang et al. [20] investigated the effect of PMMA and MCB on the purification and cutting of SWCNTs by thermogravimetric analyses. Chattopadhyay et al. [21] proposed a method of complete elimination of metal catalysts from single walled carbon nanotubes. Chen et al. [22] investigated a three-step purification of MWCNTs by which the raw material can be purified completely without damage. Various acids such as HF, H₂SO₄, HNO₃ and HCl have been used to remove metal catalysts mostly. These processes involved repeated steps of filtering and ultra-sonication in acid solution. However, while metals are dissolved into solution, CNTs are cut into small length and even cause destruction. Walls of CNTs are always damaged by strong acid.

In this work, a microwave-assisted digestion system was used to dissolve the metal catalyst. Inorganic acids such as H₂SO₄, HNO₃ and HCl can rapidly absorb microwave heat and energy and completely dissolve metals that residue in carbon nanotubes. Since Environmental Protection Agency (EPA) recommended the microwave-assisted method with nitric acid [23], this leaching procedure of metals has been widely applied in sediments soils and sludge. Nitric acid is strong enough to solubilize metals from material.

In closed microwave digestion system, metal catalysts are dissolved in acid solution rapidly without agitation. Therefore, lower concentration of acids and acid immersing time are available to completely retain walls of carbon nanotubes.

After purification, morphology of carbon nanotubes and degree of purification are evaluated by SEM and TEM. The amount of residual catalyst metals in the samples is estimated by using the thermogravimetric analysis (TGA). A high-yield and no destructive multi-walled carbon nanotubes in high purity are obtained. Metal content is under 5 wt.%.

2. Experiments

2.1. Synthesis of MWCNTs

The Co catalyst nanoparticles were deposited on p-type Si (111) wafer by sputtering method. Co catalyst was 7.5 nm in thickness. Experiments took place by electron cyclotron resonance chemical vapor deposition (ECRCVD). Mixture of CH₄ and H₂ was used as sources gas. Gas flow rates of CH₄ and H₂ were 18 sccm and 2 sccm, respectively. Power was set at 800 W. The reaction

temperature was 600 °C. After deposition, a scanning electron microscope (Hitachi S-4700I) was used to examine the morphology of MWCNTs. A high resolution transmission electron microscope (Philips Tecnai-20) was then used to investigate the microstructure of MWCNTs.

2.2. Purification procedure of MWCNTs

An acidic treatment in microwave digestion system (Milestone Microwave Labstation ETHOSD) was used to dissolve the metal catalysts. In this procedure, raw sample of MWCNTs were placed in a 100 ml Pyrex digestion tube. The first digestion step run at 210 °C for 20 min with a 1:1 mixture of 5 M HNO₃ and 5 M HCl. The microwave power was set at 100 W. The second digestion step was carried out at 210 °C for 30 min. After digestion, the suspension was filtered with 0.1 μm PTFE (poly-(tetrafluoroethylene)) membrane in deionized water. After rinsing with alcohol and drying the sample, a black thin mat composed of MWCNTs was obtained.

2.3. Characterization of the MWCNTs

After purification, the morphology of MWCNTs and the degree of purification were observed by TEM. The amount of residual catalyst metals in the samples were estimated with thermogravimetric analysis (TGA) by using a thermal analysis system of Perkin Elmer 1020 Series TGA 7 with a rate of 20 °C/min from 30 to 900 °C at the air flow rate of 10 sccm. Acid treated MWCNTs were oxidized by air at the temperature determined by TGA for 45 min.

3. Results and discussion

Fig. 1 shows a low magnification TEM image of raw carbon nanotubes. In this image, there appeared impurities such as amorphous carbons, graphite and metals in multi-walled carbon nanotubes. Metal particles were evident embedded in the tip or in tube core of MWCNTs. Many bundles with a diameter ranging from 10 to 30 nm can be observed in the TEM image.

3.1. Acidic treatment

Fig. 2 shows a low magnification TEM image of MWCNTs after purification by microwave digestion. It indicated that most of the metal particles were removed. The structure and wall of MWCNTs were no destruction. It is well known that HNO₃ is very efficient in solving metal particles and HCl is good in solving metal oxide. Amorphous carbon can be removed by nitric acid because it is a strong oxidant. However, in the microwave system, inorganic acid such as HNO₃ and HCl

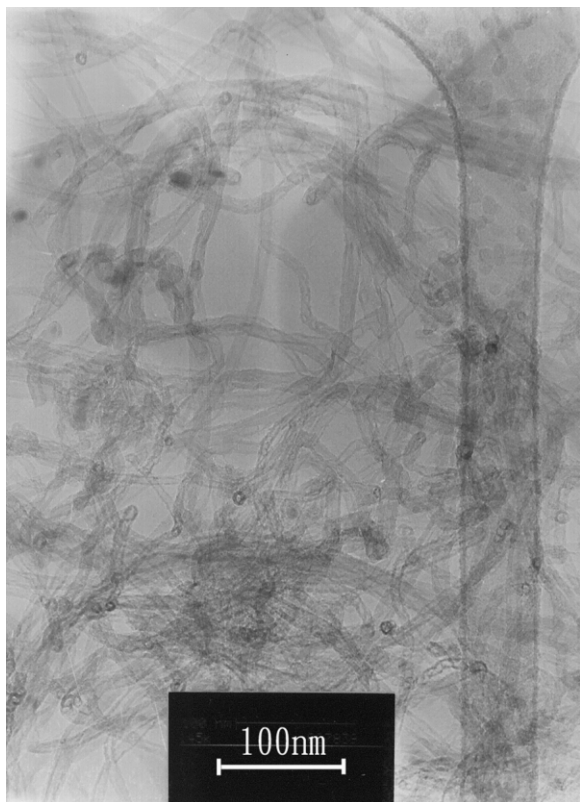


Fig. 1. Low magnification TEM image of raw sample.

rapidly absorbed microwave heat and energy without agitation and rapidly dissolved metals. The processing time of the two-step microwave-assisted and acid treated approach to dissolve metals in the MWCNTs was less than 1 h. In a microwave digestion system without agitation, heat was absorbed rapidly so that metal catalysts could be eliminated from MWCNTs rapidly with no damage.

Chen et al. [22] reported a three-step non-destructive purification of MWCNTs by which the raw material can be purified completely without damage. However, their procedure crude stirred in 3 M nitric acid and refluxed for 24 h at 60 °C, and then was suspended and refluxed in 5 M HCl solution for 6 h at 120 °C. The total acid treatment processing time was above 30 h. Moon et al. [19] proposed a two-step process of thermal annealing in air and acid treatment to purify single walled carbon nanotubes. This purification process used an acid treatment with HCl for 24 h to etch away the catalytic metals and obtained SWCNTs with metals less than 1%. Kajiura et al. [24] reported a three-step purification process consisting of soft oxidation with 2.8 N HNO₃ for 6–24 h, air oxidation for 10 min at 550 °C and a high-temperature vacuum treatment for 3 h at 1600 °C. After the final step, approximately 20% of the weight of the initial raw soot remained and the final product contained metals less than 1%. Most purification meth-

ods removed metal catalysts with acid for more than 24 h. Nitric acid treatment for too long a time will break down the CNTs to small pieces [19].

Fig. 3 shows a TEM image of acid treated MWCNTs. It indicates the open end of MWCNTs, revealing that the cap is etched off and the wall of the graphite structure is not damaged. The diameter of tube is approximately 20 nm. So, lower concentration of acids and acid immersing time are available to completely retain wall of carbon nanotubes.

In this research, microwave-assisted digestion system was used to dissolve metal catalysts. The total acid treatment time of the two-step digestion system was below 1 h. So, microwave digestion is an effective and fast method to remove metal particles from carbon nanotubes.

3.2. Thermogravimetric analysis

The purpose of the combustion of acid treated samples is to purify CNTs according to the oxidation temperature difference between non-carbon nanotubes and CNTs. The burning temperature of CNTs is related to pre-treatment process and graphitization degree, so there is no general combustion temperature of CNTs. TGA is an

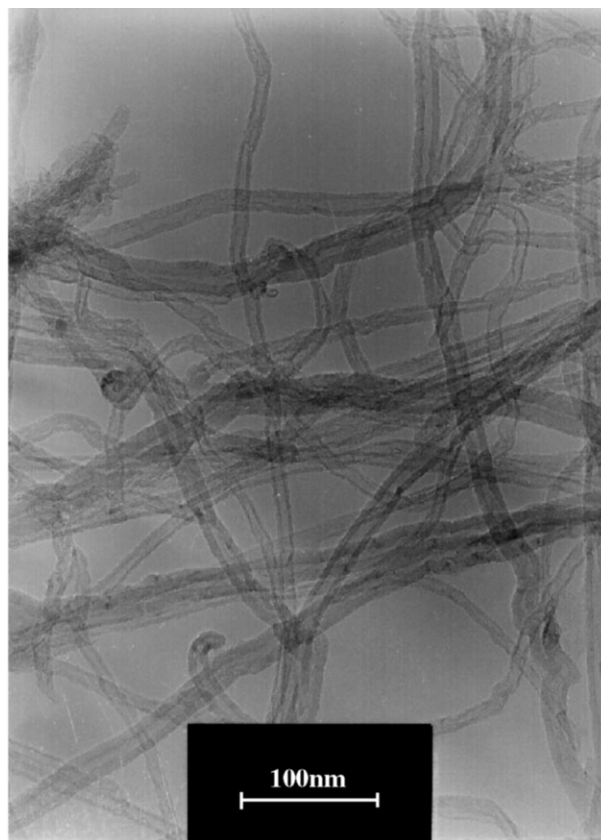


Fig. 2. Low magnification TEM image of MWCNTs after purification by microwave digestion.

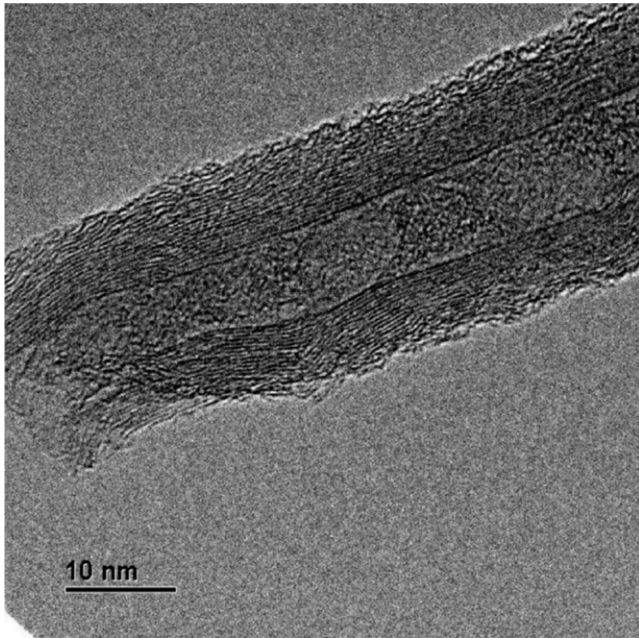


Fig. 3. HRTEM image of acid treated MWCNTs.

effective method to detect the combustion temperature in air.

Fig. 4 shows TGA graphs of raw samples and purified MWCNTs. Fig. 4a shows the TGA of raw samples and indicates that the weight starts to reduce near 410 °C. The MWCNTs are completely evaporated at 730 °C. The remaining materials are metal catalysts, which are approximately 30% of the whole weight. The TGA graph indicates the existence of three phases in the sample. The differential TGA demonstrates a peak at 520 °C, which is suggested to be amorphous carbon and

other small peak at 630 °C indicates that high temperature oxidation damages the MWCNTs.

Fig. 4b is the TGA graph of the sample after microwave digestion and acid purification treatment. After acid treatment, some water remained in the sample. It shows the correspondence between the slow weight loss from 30 to 450 °C and the loss of water and minor loss of amorphous carbon. In the temperature range from 450 to 650 °C, the weight decreases sharply to 5.25 wt.%. The peak at 520 °C in the differential TGA is assumed to be major weight loss of amorphous carbon and another peak at 610 °C indicates the damage of MWCNTs due to high oxidation. Combustion temperature of MWCNTs begins at 600 °C. The curve slope is maintained almost the same in the temperature range between 490 and 650 °C. It shows a constant combustion speed. After 650 °C the weight of MWCNTs remains constant, and the remainders may be metals and metal oxides, which reside inside the tube before combustion. So, the optimum amorphous combustion temperature is approximately 520 °C. The burning temperature of CNTs is related to pre-treatment process and graphitization degree, so it has little in common. TGA is an effective method to detect the combustion temperature in air. Dillon et al. [25] reported that the combustion temperature of carbon nanotubes is 785 °C by TGA. In their procedure, carbon nanotubes were synthesized by using laser vaporization method. Colomer et al. [26] proposed that the optimum reaction temperature in air is 500 °C for CNTs synthesized by catalytic chemical vapor deposition method. Chen et al. [22] reported that the raw materials of CNTs produced by different catalyst and synthesis method are different in component and in graphitization degree. Therefore, the combustion temperature of raw carbon nanotubes synthesized by

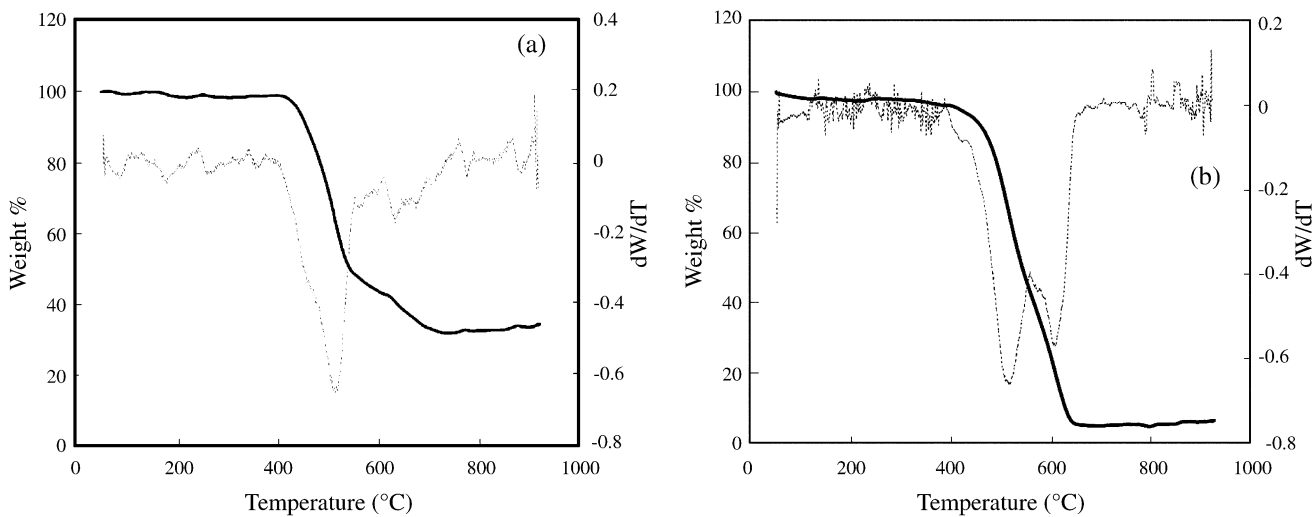


Fig. 4. (a) TGA graph of raw samples ranged from 30 to 900 °C at 20 °C/min under 10 sccm air flow rate. (b) TGA graph of the sample after microwave digestion acid-treatment ranged from 30 to 900 °C at 20 °C/min under 10 sccm air flow rate.

ECRCVD in our purification procedure begins at 520 °C. This conclusion is the same as that of Colomer et al. [26]. They reported the burning temperature in air is 500 °C for CNTs synthesized by catalytic chemical vapor deposition method.

While microwave digestion purification procedure for MWCNTs synthesized by catalyzed CVD method is an effective purification process, TGA is a good and accurate approach to evaluate the purity of MWCNTs on a weight percentage basis.

4. Conclusion

Presented in the research are MWCNTs of high yield and no damage by a two-step microwave digestion system with acidic treatment. In the microwave system, HNO₃ and HCl rapidly absorb microwave heat and energy and completely dissolve metals for purification with no damage and of high quality. The processing time of the two-step microwave-assisted and acid treated system to dissolve metals in the MWCNTs is below 1 h. After purification, the amounts of residual catalyst metals in the samples were reducing from 30 to 5.15 wt.%. The results show that no damage multi-walled carbon nanotubes with metals approximately 5% are obtained. Conclusion is attained that microwave digestion method is an effective purification procedure for MWCNTs

Acknowledgments

The authors thank the National Science Council of Republic of China, Taiwan for supporting this research under contract No. NSC91-2216-E-009-030. Technical support from the Semiconductor Research Center of National Chiao Tung University and National Nano Device Laboratory of NSC are also acknowledged.

References

- [1] S. Iijima, *Nature* 354 (1991) 56.
- [2] R. Stevens, C. Nguyen, A. Cassell, L. Delizeit, M. Meyyappan, J. Han, *Appl. Phys. Lett.* 77 (21) (2000) 3453.
- [3] X.K. Wang, X.W. Lin, V.P. Dravid, J.B. Ketterson, R.P.H. Chang, *Appl. Phys. Lett.* 66 (18) (1995) 2430.
- [4] L.C. Qin, D. Zhou, A.R. Krauss, D.M. Gruen, *Appl. Phys. Lett.* 72 (26) (1998) 3437.
- [5] Z. Shi, Y. Lian, X. Zhou, Z. Gu, Y. Zhang, S. Iijima, et al., *Carbon* 37 (1999) 1449.
- [6] Z.P. Hung, J.W. Xu, Z.F. Ren, J.H. Wang, M.P. Siega, P.N. Provencio, *Appl. Phys. Lett.* 73 (26) (1998) 3845.
- [7] C.F. Lee, J. Park, *Carbon* 39 (2001) 1891.
- [8] R. Andrews, D. Jacques, D. Qian, E.C. Dickey, *Carbon* 39 (2001) 1681.
- [9] P.X. Hou, S. Bai, Q.H. Yang, C. Lin, H.M. Cheng, *Carbon* 40 (2002) 81.
- [10] M. Yumura, S. Ohshima, K. Uchida, Y. Tasaka, Y. Kuriki, F. Ikazaki, et al., *Diamond Relat. Mater.* 8 (1999) 785.
- [11] Y. Saito, K. Hamaguchi, K. Hata, K. Tohji, A. Kasuya, Y. Nishina, et al., *Ultramicroscopy* 73 (1998) 1.
- [12] Y. Ando, X. Zhao, H. Kataura, Y. Achiba, K. Kaneto, M. Tsuruta, et al., *Diamond Relat. Mater.* 9 (2000) 847.
- [13] Y.S. Park, Y.C. Choi, K.S. Kim, D.C. Chung, D.J. Bae, K.H. An, et al., *Carbon* 39 (2001) 655.
- [14] S.C. Tsang, P.J.F. Harris, M.L.H. Green, *Nature* 362 (1993) 520.
- [15] T.Y. Ebbesen, P.M. Ajaya, F.H. Liou, H. Hiura, K. Tangaki, *Nature* 367 (1997) 519.
- [16] K. Tohji, H. Takahashi, Y. Shinoda, N. Shimizu, B. Jeyadevan, I. Matsuoka, et al., *J. Phys. Chem. B* 101 (1997) 1974.
- [17] B. Liu, T. Wagberg, E. Olssen, R. Yang, H. Li, S. Zhang, et al., *Chem. Phys. Lett.* 321 (2000) 365.
- [18] K.B. Shelimov, R.O. Esenaliev, A.G. Rinzler, C.B. Huffman, R.E. Smalley, *Chem. Phys. Lett.* 282 (1998) 429.
- [19] J.M. Moon, K.H. An, Y.H. Lee, Y.S. Park, D.J. Bae, G.S. Park, *J. Phys. Chem. B* 105 (2001) 5677.
- [20] M. Zhang, M. Yudasaka, A. Koshio, S. Iijima, *Chem. Phys. Lett.* 349 (2001) 25.
- [21] D. Chattopadhyay, I. Galeska, F. Papadimitrakopoulos, *Carbon* 40 (2002) 985.
- [22] X.H. Chen, C.S. Chen, Q. Chen, F.Q. Cheng, G. Zhang, Z.Z. Chen, *Mater. Lett.* 57 (2002) 734.
- [23] US EPA Method 3051, *Microwave-Assisted Acid Digestion of Sediments, Sludges, Soils and Oils*, Washington DC, 1994.
- [24] H. Kajiura, S. Tsutsui, H. Huang, Y. Murakami, *Chem. Phys. Lett.* 364 (2002) 586.
- [25] A.C. Dillon, G. Thomas, K.M. Jones, J.L. Alleman, P.A. Parilla, M.J. Heben, *Adv. Mater.* 11 (1999) 1354.
- [26] J.F. Colomer, P. Piedigrosso, A. Fornseca, *Synth. Met.* 103 (1999) 2482.