

A COMPARATIVE STUDY OF MULTI-WALLED CARBON NANOTUBES PURIFICATION TECHNIQUES

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Abstract

The purpose of the present work was to purify multi-walled carbon nanotubes (MWCNTs) produced by CVD using hydrochloric acid (HCl) and nitric acid (HNO_3), in order to remove the metal catalyst particles and amorphous carbon. The effect of acid treatment and sonication on the MWCNTs structure was obtained by X-ray diffraction (XRD), thermogravimetric analysis (TGA), environmental scanning electronic microscopy (ESEM), and Raman spectroscopy. Comparing the acid treatment in HCl solution with that in HNO_3 solution, the results showed better purification and exfoliation of the MWCNTs treated in HNO_3 at optimized sonication time. However, higher thermal stability of the HCl acid purified MWCNTs was obtained.

Keywords and phrases: carbon nanotubes, purification, acid treatment, morphology, vibrational spectroscopy, thermal analysis.

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1. Introduction

Multi-walled carbon nanotubes (MWCNTs) have attracted 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 vapour deposition [7]. Unfortunately, unwanted impurities may be included in the MWCNTs 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 MWCNTs, and therefore, it is inevitable to develop suitable purification methods. Various methods have been reported for purifying carbon nanotubes, such as chemical oxidation [8-11], thermal oxidation [12], filtration [13], and chromatography [14]. These methods can be divided into two groups: destructive and nondestructive.

The purpose of this work is to test the reaction of the MWCNTs material grown by the catalytic thermal CVD, to different purifications by acid treatments, in order to open the MWCNTs tips and remove the metal catalyst particles, and lead to the formation of functional groups. In this study, we report the effect of HCl treatment to the MWCNTs structure by X-ray diffraction (XRD), thermogravimetric analysis (TGA), environmental scanning electronic microscopy (ESEM), and Raman spectroscopy. Comparing the acid treatment in HCl solution with that in HNO₃ solution.

2. Experimental Section

In general, the pristine MWCNTs sample synthesized by the CVD method contains catalytic particles and the carbonaceous impurities, such as amorphous carbon and carbon nanoparticles, which need to be eliminated. The purification of CVD produced MWCNTs from Arkema was performed by three different steps in order to determine the optimum purification procedures. The systematic purification procedure is as follows: about 0.2g of raw CNTs was placed in the crucible and calcined in the oven at 400°C for 2h under air and then cooled down to room temperature. Further, the oxidized MWCNTs were sonicated in concentrated (HCl, HNO₃) acid (37%) for 15 min to dissolve the metal oxides formed and the catalyst particles exposed by the oxidation. The duration of sonication was optimized in order to prevent shortening of MWCNTs. These purified samples were filtered to remove the acid for several times, and dried at 100°C for 12h.

Environmental scanning electronic microscopy (ESEM) observation was carried out with a JSM-5900 LV scanning electron microscope operating to examine the morphology of the pristine and acid treated MWCNTs.

The XRD technique was carried out by using the X-ray diffraction instrument (PANalytical X'PRET) with CuK α radiation source ($\lambda = 1.54056\text{\AA}$). The scanning rate and sampling with 2θ from 20° to 80°, respectively.

Raman spectra, were obtained at room temperature, with a Nicolet Almega dispersive Raman spectrometer equipped with a visible Raman microscope and a charge-coupled detector with 785nm excitation wavelength. Spectra were recorded with a 10mW and a 4cm⁻¹ resolution.

Thermogravimetric analysis (TG-DTG) was performed with a Thermogravimetric Analyser SDT 2960 TA, under air. The samples were heated from room temperature to 800°C at a heating rate of 2°C/min Palatinum pans was used.

3. Results and Discussion

3.1. Morphology of MWCNTs

Environmental scanning electronic microscopy (ESEM) is used to observe the morphologies of the pristine and acid treated MWCNTs. The thermal oxidized nanotubes samples were purified by nitric acid (30ml) or hydrochloric acid (30ml).

Figure 1 illustrates ESEM images of the nanotubes before and after purification. In Figure 1(a), we observe that the raw sample contains not only bundles of carbon nanotubes but also significant amounts of amorphous carbon and metal particles entangled with them. Defect formation result possibly from variations in the deposition process arising from an inhomogeneous distribution of catalyst. From the ESEM images, we estimate that the percentage of nanotubes in the raw sample is 10%. Figures 1(b) and 1(c) show the morphology of acid treated MWCNTs. The impurities that were previously attached to the nanotubes gradually began to detach and dissolve into the HCl or HNO₃ solution. It is observed that the combination of thermal oxidation and ultrasonication in the presence of acid does remove most of the impurities (such as amorphous carbon, carbon nanoparticles, and metal catalysts). Ultrasonication can make the impurities detach from MWCNTs and disperse homogeneously. In addition, we observed exfoliation of the MWCNTs. These results show that the diameters of these nanotubes were reduced after purification by HCl and HNO₃ acids.

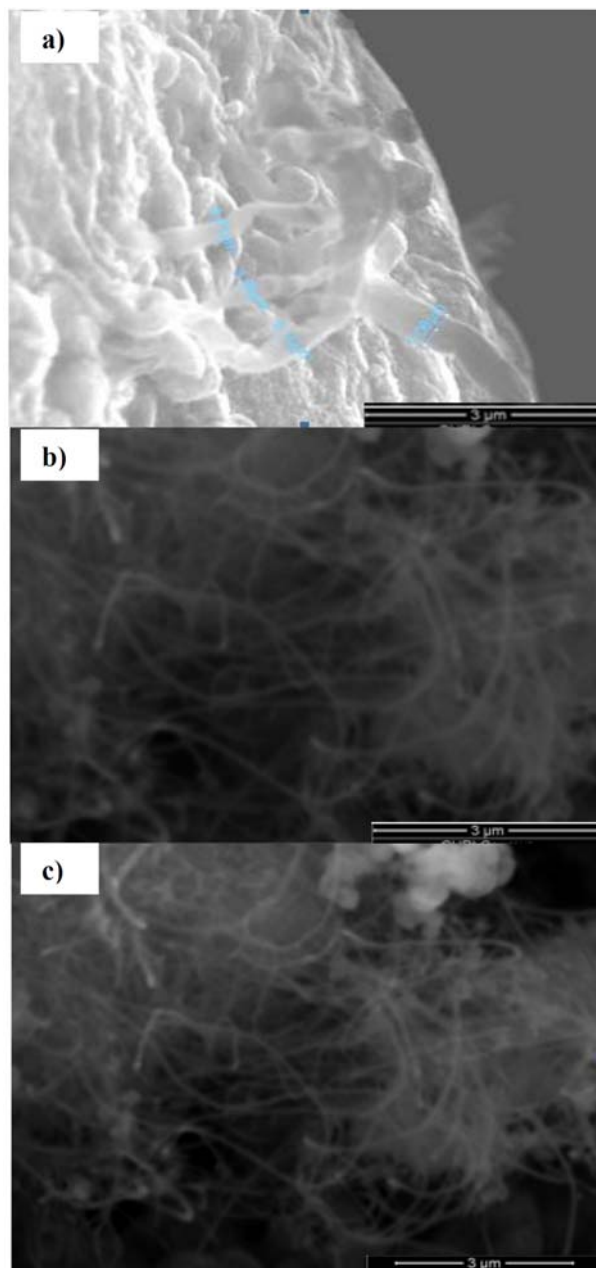


Figure 1. ESEM images of (a) pristine MWCNTs; (b) MWCNTs obtained after HCl treatment; and (c) MWCNTs obtained after HNO₃ treatment.

3.2. X-ray diffraction (XRD) of MWCNTs

The XRD profile of the pristine carbon nanotubes, Figure 2(a), shows that the sample contains carbon and nickel. There is one sharp reflection at about $2\theta = 26^\circ$ that can be attributed to the multi-wall carbon nanotubes. The other four diffraction peaks in the XRD profile (see Figure 2(a)) at about $2\theta = 43.60^\circ$, 49.05° , 50.72° , and 72.57° correspond to (101), (004), and (110) crystal planes of FCC nickel [15].

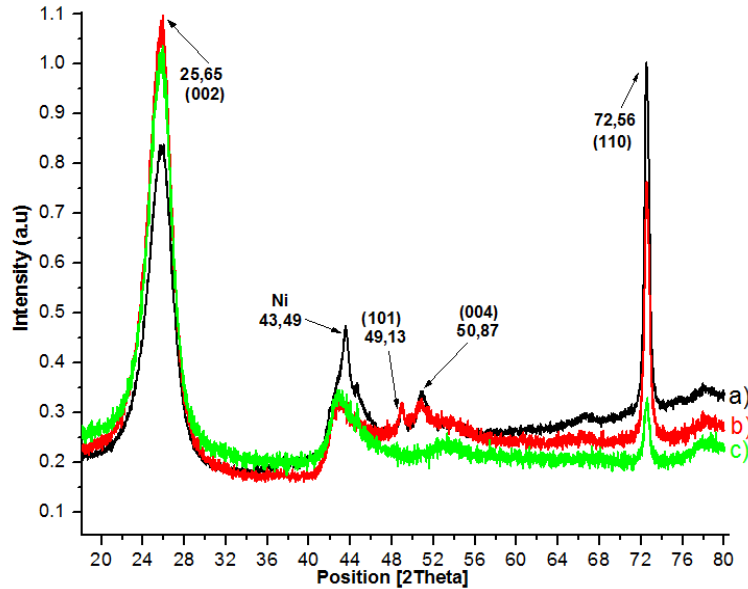


Figure 2. Powder XRD of (a) pristine MWCNTs; (b) purified MWCNTs in HCl; and (c) purified MWCNTs in HNO_3 .

Figures 2(b) and 2(c) show the XRD profile of the purified MWCNTs. It is observed that the intensity of the peak characteristic of MWCNTs at $2\theta = 25.65^\circ$ was increased, likewise, the intensity of all other peaks were decreased. In addition, it is observed in the acid-treated MWCNTs (see Figures 2(b) and 2(c)) sample, the width at half height of all peaks decreases. These results reflect an increase in the crystalline state in the MWCNTs. These results indicated that the purification in acids (HCl and HNO_3) lead to a reduction of the defects and other carbonaceous phases.

For the purified MWCNTs in HNO_3 (see Figure 2(c)), it is observed absence of peaks at about $2\theta = 49.05^\circ$, 50.72° corresponding to (101) and (004) crystal planes of FCC nickel and a decrease of the relative intensity of the peak at about $2\theta = 72.57^\circ$. These results indicated that the purification in HNO_3 was better than that in HCl (see Figures 2(b) and 2(c)).

3.3. Raman spectra of MWCNTs

Raman spectroscopy is a very valuable tool for the characterization of carbon-based nanostructures. The Raman spectra of pristine and purified MWCNTs by HCl and HNO_3 are shown in Figure 3. Each of the spectra consists of three characteristic bands, namely, the G-band appearing in the $1500\text{-}1605\text{ cm}^{-1}$ region, the D-band appearing in the $1250\text{-}1450\text{ cm}^{-1}$ region, and the G'-band appearing in the $2500\text{-}2600\text{ cm}^{-1}$ region. The G band is related to the C-C vibration of the carbon material with an sp_2 orbital structure [16] and the D band indicates disordered carbon atoms, defects such as pentagons and heptagons in graphite, edges of the graphite crystal, and amorphous carbon [17, 18].

The G' band, which is indicative of a clean sample, appears at the position of doubling frequency of the D-line band [19]. So, the ratio of intensities of the characteristic peaks (I_D/I_G) indicates the extent of defects and impurities in the nanotubes.

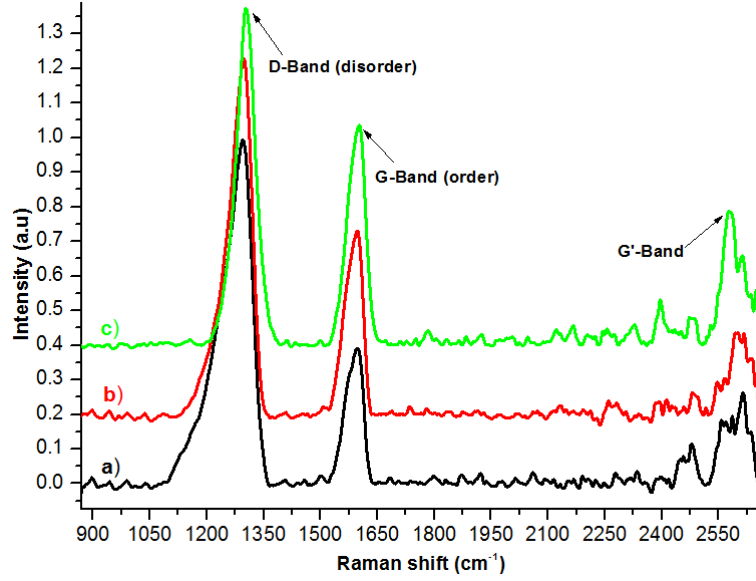


Figure 3. Raman spectra of (a) pristine MWCNTs; (b) purified MWCNTs in HCl; and (c) purified MWCNTs in HNO_3 .

The intensity of the D band decreases for purified samples indicating efficient removal of the amorphous carbon as seen in Figures 3(a) and 3(b). The peak still remains with low intensity implying that some degree of disorder is present along the tube. These can be pentagons, heptagonal defects, the pentagon-heptagon pairs, line defects [20]. In addition, it is observed that the I_D/I_G ratio for the pristine MWCNTs is 2.57, while markedly decreases to 1.69 after HCl treatment and 1.33 after HNO_3 treatment (see Table 1).

Table 1. Ratio of the integrated intensities of D and G band (I_D/I_G) of the pristine MWCNTs and purified MWCNTs

Sample	Intensity ratio, I_D/I_G
Pristine MWCNTs	2.57
Purified MWCNTs in HCl	1.69
Purified MWCNTs in HNO_3	1.33

These results mean that the amount of defects and other carbonaceous phases were reduced. So clearly, the combination of thermal oxidation and ultrasonication in the presence of acid appears to be the most effective method in eliminating catalyst and graphite. Also XRD analysis supported this conclusion.

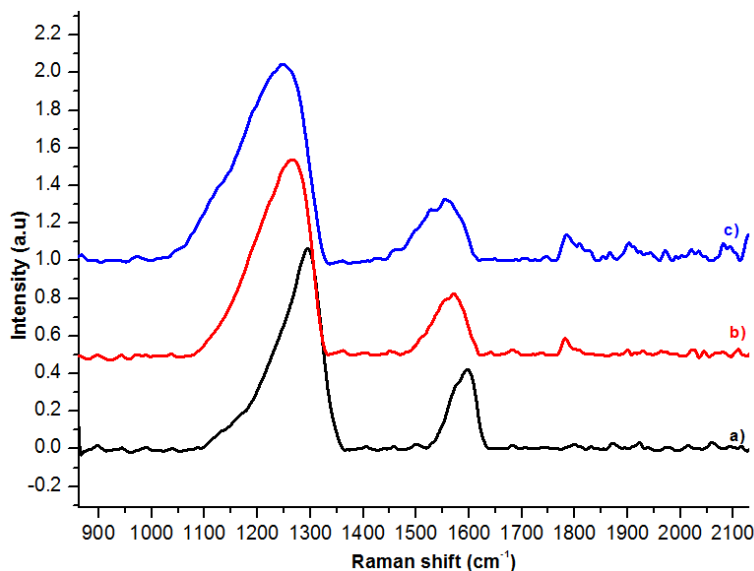


Figure 4. Raman spectra of (a) pristine MWCNTs; (b) purified MWCNTs in HNO_3 for 30 min of sonication; and (c) oxidized MWCNTs in HNO_3 at 500°C .

When the sonication of the MWCNTs in HNO_3 was followed by thermal oxidation (500°C), we noted that the intensity ratios of the D and G bands increase from 2.57 for the pristine MWCNTs to 3.22 for the treated-MWCNTs for 30 min of sonication in HNO_3 and 3.36 for oxidized-MWCNTs in HNO_3 at 500°C (see Figure 4 and Table 2). This increase suggests that the quantity of disordered carbon in the samples increases (i.e., the quality decreases). In addition, we observed that the D-band changed in position to lower frequencies after treatment of the MWCNTs in HNO_3 . These results indicated that carboxyl groups were introduced to the tip and sidewalls of the MWCNTs. These functional groups produced increase the surface polarity and further alter the surface charges.

Table 2. Ratio of the integrated intensities of D and G band (I_D/I_G) of the pristine MWCNTs and oxidized MWCNTs

Sample	Intensity ratio, I_D/I_G
Pristine MWCNTs	2.57
Treated MWCNTs in HNO_3 at 30 min of sonication	3.22
Oxidized MWCNTs in HNO_3 at 500°C	3.36

3.4. Thermal properties of MWCNTs

In thermogravimetric analysis (TGA), the sample was heated in air. Thermogravimetric curves shown in Figure 4 provide information regarding the thermal stability of acid treated MWCNTs.

TGA and derivative thermogravimetry curves determine the percentage of all carbon species (amorphous carbon and CNTs) and graphitization of CNTs. The percentages of the amorphous carbon and CNTs were obtained according to weight loss at 150-800°C.

Figure 5 shows TGA curves of pristine and purified MWCNTs. The initial weight loss for as-grown MWCNTs up to 460°C is due to the burning of amorphous carbon. Weight loss between 460°C and 700°C is attributed to the oxidation of MWCNTs. The MWCNTs are completely evaporated at 610°C. Final residual weights of 10%, 5%, and 2% were obtained for pristine and purified MWCNTs in HCl and purified MWCNTs in HNO_3 , respectively, revealing a purity of about 95% for the purified sample in HCl and about 98% for the purified sample in HNO_3 . The chemically treated sample in HNO_3 shows 2% residual weight indicating almost complete removal of the alloy catalyst particles. This result is in agreement with that of the XRD analysis and the Raman spectroscopy.

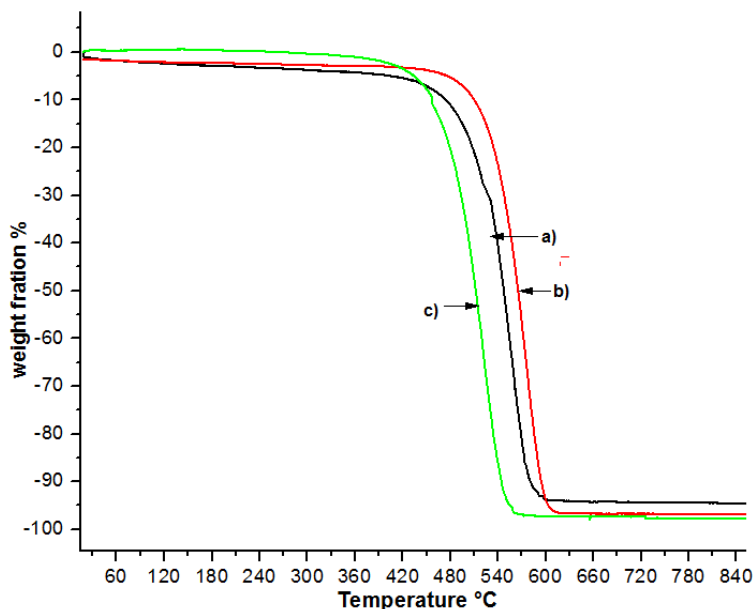


Figure 5. TGA of (a) pristine MWCNTs; (b) purified MWCNTs in HCl; and (c) purified MWCNTs in HNO₃.

The decrease in decomposition temperature to 470°C for treated sample in HNO₃ is due to the effect of the ultrasonication in presence of acid, which introduced more amorphous carbon. In addition, the thermal analysis in air led to thermal oxidation and probably shortening of carbon nanotubes.

The derivative thermogravimetric (DTG) curves for the pristine MWCNTs and purified MWCNT in HCl and HNO₃ at a constant heating rate of 2°C/min are shown in Figure 6. For each sample, the thermogram reveals that the TGA plot shows a maximum temperature of weight loss, so the peak temperatures of degradation can be determined. We observed that the temperature of degradation increased from 554°C for pristine MWCNTs to 573°C for the purified MWCNTs in HCl (see Figure 6). These results indicate that the purification in HCl increased the degradation temperature and improve the thermal stability of the MWCNTs. In

addition, it is observed also that the intensity of weight fraction decreased when the MWCNTs was purified. These results indicate that the purification of MWCNTs in acid reduced the amount of catalytic particles.

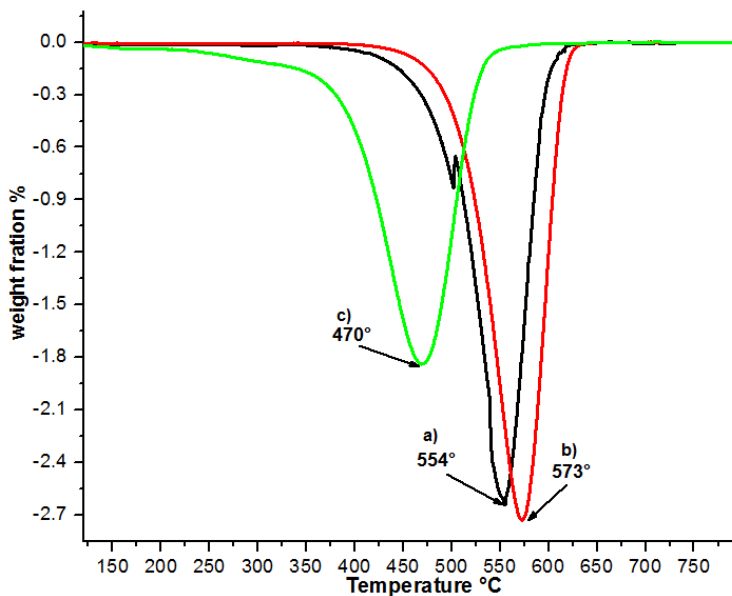


Figure 6. DTG of (a) pristine MWCNTs; (b) purified MWCNTs in HCl; and (c) purified MWCNTs in HNO_3 .

Figure 7 shows TGA curves of pristine, treated and oxidized MWCNTs. Furthermore, we observed that the weight decreases sharply from 92% for pristine MWCNTs to 85% and 88% for oxidized-MWCNTs in HNO_3 at 500°C and sonicated-MWCNTs for 30 min, respectively, which could be attributed to the functionalization of the MWCNTs after these treatments as shown in Raman results.

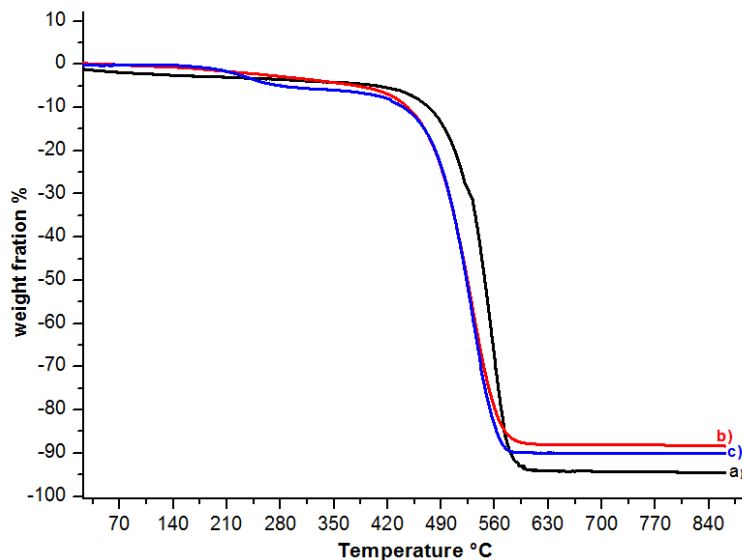


Figure 7. TGA of (a) pristine MWCNTs; (b) oxidized MWCNTs in HNO_3 at 500°C ; and (c) treated MWCNTs in HNO_3 for 30 min of sonication.

The TGA curve did not drop to zero weight percent, because the iron oxide was not degraded even at the highest temperature applied. It is well known that metal catalysts from the production of MWCNTs accelerate the oxidation rate of carbon at low temperatures.

4. Conclusion

We purified MWCNTs using combination of thermal oxidation and ultrasonication in the presence of acid HCl or HNO_3 . The degree of purification was determined. The morphology of the purified MWCNTs by HCl and by HNO_3 observed by ESEM indicated that the diameters of the bundles were reduced after purification. The XRD profile of the purified MWCNTs reflects an increase in the crystalline state in the MWCNTs. From Raman results, the decrease in ratio I_D/I_G of integrated intensities of D and G bands were attributed to a reduction of the amount of defects and other carbonaceous phases as compared with

pristine MWCNTs. However, the sonication and thermal treatment of MWCNTs in HNO_3 lead to an increase in the ratio I_D/I_G of intensities. In addition, TGA revealed that the purification by HCl improved the thermal stability in air of the MWCNTs compared with the purification by HNO_3 .

References

- [1] M. Majumdar, N. Chopra, R. Andrews and B. J. Hinds, Nanoscale hydrodynamics: Enhanced flow in carbon nanotubes, *Nature* 438 (2005), 44.
- [2] R. H. Baughman, A. A. Zakhidov and W. A. de Heer, Carbon nanotubes: The route toward applications, *Science* 297 (2002), 787-792.
- [3] H. Luo, Z. Shi, N. Li, Z. Gu and Q. Zhuang, Investigation of the electrochemical and electrocatalytic behaviour of single-wall carbon nanotube film on a glassy carbon electrode, *Anal. Chem.* 73 (2001), 915-920.
- [4] J. M. Nugent, K. S. V. Santhanam, A. Rubio and P. M. Ajayan, Fast electron transfer kinetics on multi-walled carbon nanotube microbundle electrodes, *Nano Lett.* 1 (2001), 87-91.
- [5] C. Journet, W. K. Maser, P. Bernier and A. Loiseau et al., Large-scale production of single-walled carbon nanotubes by the electric-arc technique, *Nature* 388 (1997), 756-758.
- [6] T. Guo, P. Nikolaev, A. Thess, D. T. Colbert and R. E. Smalley, Catalytic growth of single-walled nanotubes by laser vapourization, *Chem. Phys. Lett.* 243(1-2) (1995), 49-54.
- [7] A. M. Cassell, J. A. Raymakers, J. Kong and H. J. Dai, Large scale CVD synthesis of single-walled carbon nanotubes, *Phys. Chem. B* 103(31) (1999), 6484-6492.
- [8] S. C. Tsang, Y. K. Chen, P. J. F. Harris and M. L. H. Green, A simple chemical method of opening and filling carbon nanotubes, *Nature* 372 (1994), 159-162.
- [9] T. Saito, K. Matsushige and K. Tanaka, Chemical treatment and modification of multi-walled carbon nanotubes, *Physica B* 323 (2002), 280-283.
- [10] K. Esumi, M. Ishigami, A. Nakajima, K. Sawada and H. Honda, Chemical treatment of carbon nanotubes, *Carbon* 34 (1996), 279-281.
- [11] P. M. Ajayan, T. W. Ebbesen, T. Ichihashi, S. Iijima, K. Tanigaki and H. Hiura, Opening carbon nanotubes with oxygen and implications for filling, *Nature* 362 (1993), 522-526.
- [12] K. Tohji, H. Takahashi, Y. Shinoda, I. Mitsuoka and Y. Saito et al., Purification procedure of single-walled nanotubes, *Phys. Chem. B* 101 (1996), 1974-1978.
- [13] K. B. Shelimov, R. O. Esenaliev, A. G. Rinzler, C. B. Huffman and R. E. Smalley, Purification of single-wall carbon nanotubes by ultrasonically assisted filtration, *Chem. Phys. Lett.* 282 (1998), 429-434.

- [14] S. Niyogi, H. Hu, M. A. Hamon, P. Bhowmik, B. Zhao and S. M. Rozenzhak et al., Chromatographic purification of soluble single-walled carbon nanotubes (s-swnts), *Amer. Chem. Soc.* 123 (2001), 733-734.
- [15] M. A. Ermakova, D. Y. Ermakov, A. L. G. G. Chuvilin and Kuvshinov, *Catal.* 201 (2001), 183-197.
- [16] Chieng-Ming Chen, Mi Chen, Yong-Wang Peng, Cheng-Hsiung Lin, Li-Wei Chang and Chia-Fu Chen, Microwave digestion and acidic treatment procedures for the purification of multi-walled carbon nanotubes, *Diamond & Related Materials* 14 (2005), 798- 803.
- [17] M. S. Dresselhaus, G. Dresselhaus, A. Jorio and Souza Filho et al., Raman spectroscopy on isolated single-wall carbon nanotubes, *Carbon* 40(12) (2002), 2043-2061.
- [18] V. Datsyuk, M. Kalyva, K. Papagelis, J. Parthenios, D. Tasis, A. Siokou, I. Kallitsis and C. Galiotis, Chemical oxidation of multi-walled carbon nanotubes, *Carbon* 46 (2008), 833-840.
- [19] S. Osswald, E. Flahaut, H. Ye and Y. Gogotsi, Elimination of D-band in Raman spectra of double-wall carbon nanotubes by oxidation, *Chem. Phys. Lett.* 402 (2005), 422-427.
- [20] H. Zhang, C. H. Sun, F. Li, H. X. Li and H. M. Cheng, Purification of multi-walled carbon nanotubes by annealing and extraction based on the difference in van der Waals potential, *Phys. Chem. B* 110 (2006), 9477-9481.

