Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2013, Article ID 937697, 9 pages
http://dx.doi.org/10.1155/2013/937697

Research Article

Purification and Functionalization of Single-Walled Carbon Nanotubes through Different Treatment Procedures

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Received 29 November 2012; Accepted 28 January 2013

Academic Editor: Anukorn Phuruangrat

Single-walled carbon nanotubes (SWCNTs) were purified by the combined use of ultrasonic- and microwave-assisted acid digestion. The results show that the method efficiently eliminates impurities, reduces solvent consumption, and prevents damage to the structure of the SWCNTs. The purified SWCNTs were given functionalization treatments with a nitric acid/sulfuric acid mixture. These acid-treated SWCNTs (A-SWCNTs) were then grafted with 3-isocyanatopropyl triethoxysilane (A-SWCNTs-Si). The A-SWCNTs and A-SWCNTs-Si were used to improve interfacial interactions with polymers and to produce a well-dispersed SWCNT composite.

1. Introduction

Carbon nanotubes (CNTs) are the focus of continued study, because of their structural, mechanical, and electronic properties [1, 2]. Common methods of manufacturing CNTs include chemical vapor deposition [3, 4], arc-discharge [5–7], pyrolysis [8, 9], combustion [10, 11], glow discharge [12], and laser ablation [13]. However, the use of these methods to prepare CNTs always produces impurities, such as disordered carbon, graphite, fullerenes, and catalysts. The CNTs must be thoroughly purified, if they are to be used in a variety of projected applications and basic studies.

Many purification methods for the removal of impurities in CNTs have been investigated, such as physical separation [14], chemical oxidation [15, 16], and combinations of chemical and physical techniques [17, 18]. However, almost all of these methods are time consuming and require high temperature and large amounts of chemical reagents. They also damage the structure of the CNTs. Moreover, CNTs have inert surfaces and tend to agglomerate in organic solvents, making further processing difficult, or even impossible [19]. Therefore, CNTs are often functionalized using physical or chemical reactions.

This study proposes an efficient procedure for the purification of SWCNTs using a combination of ultrasonic-c and microwave-assisted acid digestion. After purification, thermo-gravimetric analysis (TGA), Raman spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to evaluate the efficiency of the purification, bonding structure, and morphology of SWCNTs. The purified SWCNTs were further functionalized using chemical reactions and examined by Fourier transform infrared (FTIR).

2. Experimental

2.1. Material. SWCNTs (diameter < 2 nm, length: 5 to 15 μm, purity 95%) were supplied by Scientech Co. Ltd, Taiwan. 3-isocyanatopropyltriethoxysilane (IPTES, purity > 95%) was produced by TCI, Japan. Tetrahydrofuran (THF), acetone (CH_3COCH_3), and potassium bromide (KBr) were purchased from ECHO chemical Co. Ltd, Taiwan. Nitric acid (HNO_3, purity > 98%) and sulfuric acid (H_2SO_4, purity > 98%) were purchased from Rich biotech Co. Ltd, Taiwan.

2.2. The Purification of SWCNTs Using Ultrasonic-Assisted Acid Digestion. 0.5 g SWCNTs was bath sonicated in 100 mL of 0.5 M HNO_3, for 0.5 hr, and subsequently refluxed at 120°C, for 24 hr. The solution was then filtered and rinsed with distilled water, until the pH of the filtrate was neutral. The

Table 1: The TGA analysis of SWCNTs using a combination of ultrasonic and microwave for various treatment times (5, 10, 20, and 30 min) with various HNO_3 concentrations (0.5, 1, and 3 M).

Microwave treatment time (min)	HNO_3 concentration (M)					
	3 M		1 M		0.5 M	
	T_{d5}[a] (°C)	Char yield (%)	T_{d5} (°C)	Char yield (%)	T_{d5} (°C)	Char yield (%)
0	678.7	90.2	678.7	90.2	678.7	90.2
5	619.6	86.6	655.9	89.0	692.2	91.1
10	553.7	82.5	571.2	86.4	717.7	92.9
20	522.8	81.3	534.8	84.2	815.9	95.7
30	490.5	80.4	522.8	80.7	752.7	93.8

[a]Decomposition temperature at 5% weight loss.

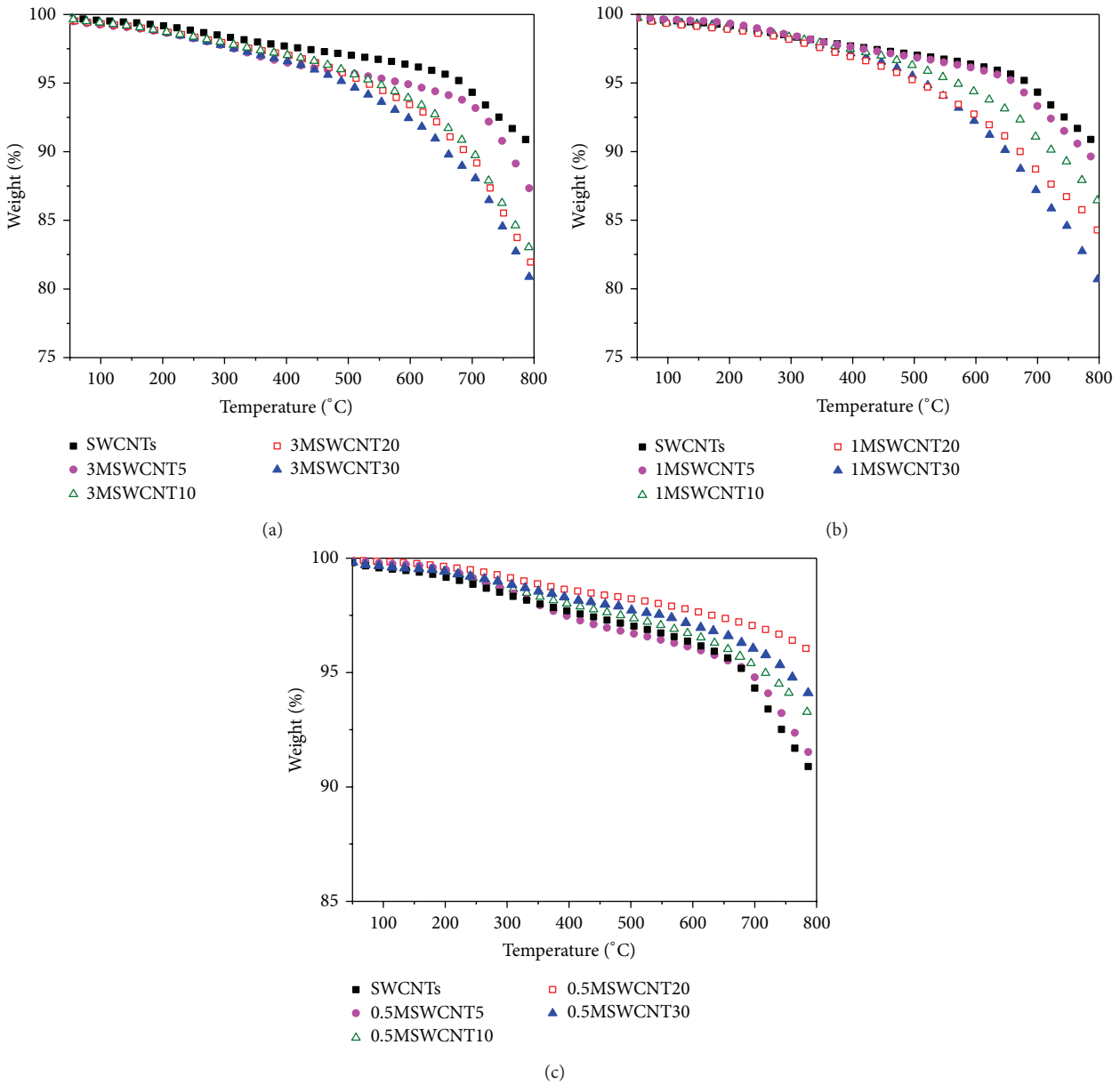


Figure 1: The TGA traces of SWCNTs using a combination of ultrasonic and microwave for various treatment times (5, 10, 20 and 30 min) with various HNO_3 concentrations: (a) 3, (b) 1, and (c) 0.5 M.

sample was bath sonicated in water, for 0.5 hr, and finally dried at 100°C, for 12 hr. After drying, a thin, black mat comprised of cleaned SWCMTs (CSWCNTs) was obtained.

2.3. The Purification of SWCNTs by a Combination of Ultrasonic- and Microwave-Assisted Acid Digestion. 0.5 g of SWCNTs was bath sonicated in 100 mL HNO_3 (0.5, 1, and 3 M) for 0.5 hr. After sonication, the solution was purified by microwave-assisted purification, for 5, 10, 20, and 30 min at 120°C, with the microwave power set to 300 W. Then, the solution was filtered and rinsed with distilled water, until the pH of the filtrate was neutral. The sample was bath sonicated in water for 0.5 hr and finally dried at 100°C for 12 hr. The resulting material was designated MSWCNTs and was used as the initial material for the following functionalization procedures.

2.4. Functionalization Treatment. The MSWCNTs were placed in an ultrasonic bath at 50°C, for 2, 5, and 8 hr, with a 3 : 1 (v/v) mixture of H_2SO_4 and HNO_3. It was then filtered and rinsed with distilled water, until the pH of the filtrate was neutral. Finally, the sample was dried at 120°C in a vacuum, overnight. After drying, a thin, black mat designated for A-SWCNTs was obtained.

The A-SWCNT was subjected to an ultrasonic bath environment for 2 hr with THF. It was then mixed with IPTES (A-SWCNTs/IPTES = 1 : 2; v/v), and the solution was subsequently refluxed at 65°C, for 24 hr. This solution was then filtered, using a 200 nm pore size hydrolyzed polytetrafluoroethene (PTFE) membrane, and rinsed with THF. The functionalized A-SWCNTs (A-SWCNTs-Si) were then placed in an oven to remove the solvent and finally dried at 120°C, for 12 hr.

2.5. Characterization. TGA was performed on a TA instrument (model number Q500), and the samples were heated from 50 to 800°C at a heating rate of 30°C min^{-1}. Raman spectra were obtained using a Renishaw 1000 Raman spectrophotometer. The wavelength region of 1000 to 2000 cm^{-1} was investigated using a laser with a power of 0.3 Mw and a wavelength of 633 nm. Morphology was evaluated using a SEM (TOPCON ABT-150S) and TEM (JEOL JEM-2010). FTIR spectra were recorded on a Nicolet320 FTIR spectrometer, using the KBr pellet technique.

3. Results and Discussion

3.1. TGA Analysis. Figures 1(a)–1(c) plot the TGA traces of SWCNTs using a combination of ultrasonic and microwave for various treatment times (5, 10, 20, and 30 min) with various HNO_3 concentrations (0.5, 1, and 3 M). The variations in degradation temperature at 5% weight loss (T_{d5}) and char yield are summarized in Table 1. Figure 1(a) shows that the T_{d5} of SWCNTs at 678.7°C was due to the burning of amorphous carbon. An increase in temperature causes a sharp decrease in the weight of the SWCNTs during the oxidation of the SWCNTs. The T_{d5} of SWCNTs decreases as the purification time is increased. This result clearly shows that excessive concentrations of HNO_3 solution (3 M) cause the surface structure of the SWCNTs to be destroyed and lead to functionalization at around 300°C. After further dilution in HNO_3 solution, Figure 1(b) shows that the purification of the SWCNTs by 1 M HNO_3 solution has a less destructive effect than the 3 M HNO_3 solution. Figure 1(c) shows the obvious increase in T_{d5} for the SWCNTs purified by ultrasound and microwaves in 0.5 M HNO_3 solution, which indicates that the MSWCNTs effectively remove amorphous carbon. Also, the increase was most pronounced when the purification treatment time was 20 min (0.5MSWCNT20), because the 0.5MSWCNT20 surface is composed of a stable carbon-carbon structure, in which the sp^2 bond forms a perfect hexagonal crystal structure.

Table 2: Comparative TGA analysis of SWCNTs, 0.5MSWCNT20, and CSWCNTs.

Item	SWCNTs	0.5MSWCNT20	CSWCNTs
T_{d5} (°C)	678.7	815.9	686.6
Char yield (%)	90.2	95.7	88.0

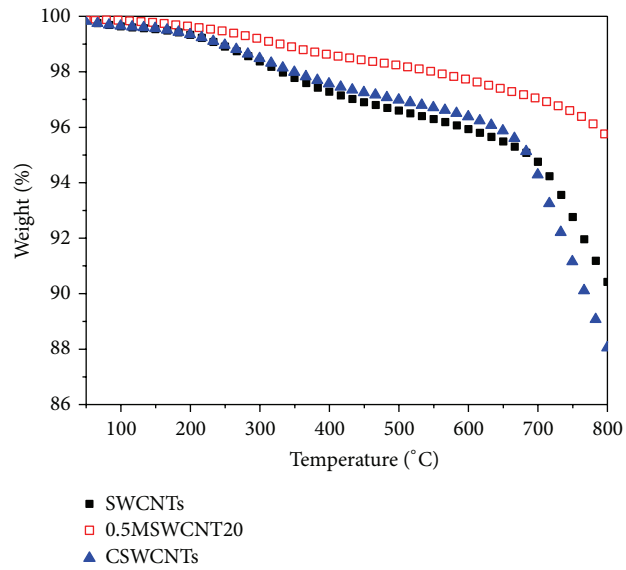


Figure 2: TGA traces of SWCNTs, 0.5MSWCNT20, and CSWCNTs.

Figure 2 plots the TGA traces of SWCNTs, 0.5MSWCNT20, and CSWCNTs. The variations in degradation temperature in 5% and char yield are summarized in Table 2. The curve shows that a combination of ultrasound and microwave purification of SWCNTs is much more effective than ultrasonic purification alone. Therefore, this study takes no further interest in ultrasound purification.

3.2. Raman Analysis. Figures 3(a)–3(c) plot the Raman analysis of SWCNTs using a combination of ultrasonic and microwave treatment for various treatment times (5, 10, 20, and 30 min) with various HNO_3 concentrations (0.5, 1, and 3 M). In Figure 3(a), the graphitic band (G) peak decreases proportionally and the disorder band (D) increases

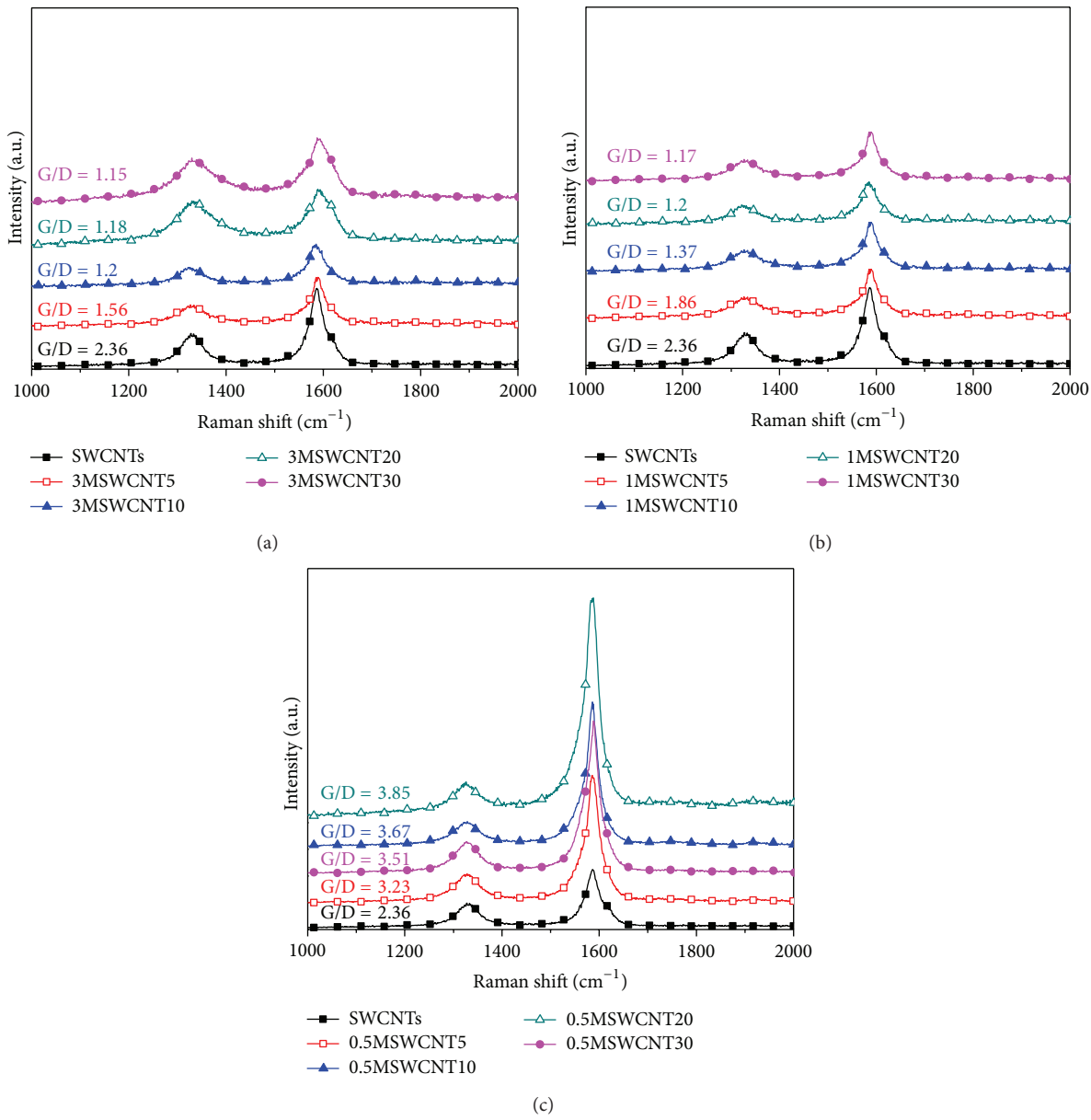


Figure 3: The Raman analysis of SWCNTs using a combination of ultrasonic and microwave treatment for various treatment times (5, 10, 20, and 30 min) with various HNO_3 concentrations: (a) 3, (b) 1, and (c) 0.5 M.

proportionally as the purification treatment time is increased. The G/D ratio decreases from 2.36 to 1.15. Figure 3(b) shows that the G/D ratio of SWCNTs is a little higher than that for a 3 M HNO_3 concentration, which indicates that purification has not yet been achieved. In addition, the G/D ratio from 3 M and 1 M HNO_3 was lower than SWCNTs, which indicates that high acid treatment concentration and long acid treatment time would result in the break of tubes. Figure 3(c) shows an obvious increase in the G/D ratio from 2.36 to 3.85, when the SWCNTs are purified by ultrasound and microwave treatment with a 0.5 M HNO_3 concentration. The G/D ratio from 0.5 M HNO_3 was higher than SWCNTs, which indicates efficient elimination of amorphous carbon without damage to the structure of the tubes and strengthens the three-dimensional structure of SWCNTs. These results are consistent with those of the TGA analysis.

In order to enhance the MSWCNTs dispersion in solution and to improve their interfacial interactions with polymers, the MSWCNTs were functionalized using an oxidative process with a mixture of H_2SO_4 and HNO_3 (A-SWCNTs). Figure 4 shows the Raman analysis results, which show a higher D peak for the SWCNTs than the A-SWCNTs at 1582 cm^{-1}. This is due to the mixture of H_2SO_4 and HNO_3, which breaks the carbon-carbon double bonds and causes the G/D ratio to be decreased from 2.36 to 1.09.

3.3. FTIR Spectral Analysis. The functionalization of the SWCNTs' outer surface was examined by FTIR spectroscopy.

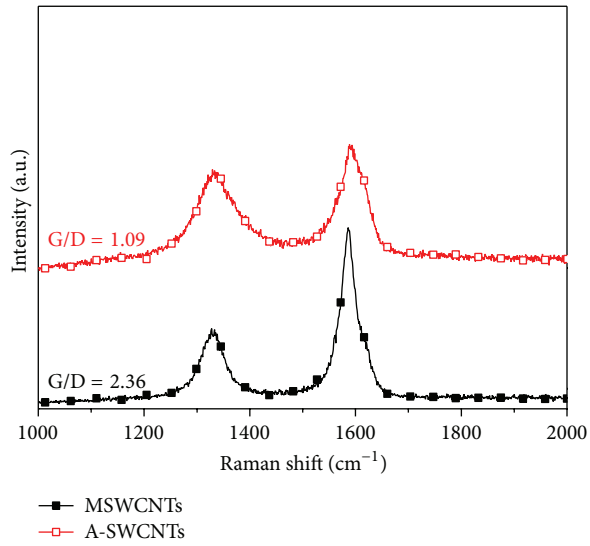


Figure 4: The Raman curves of MSWCNTs and A-SWCNTs.

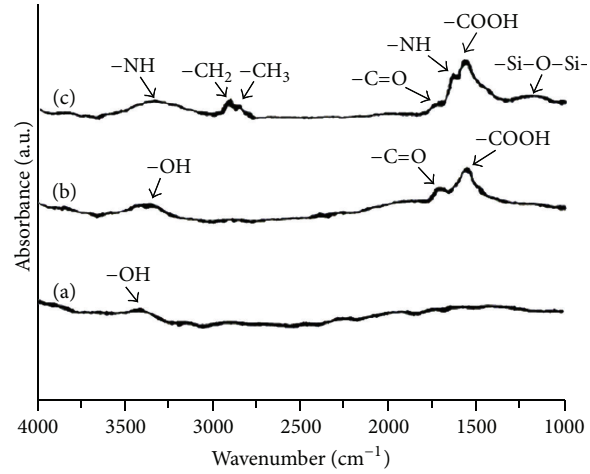
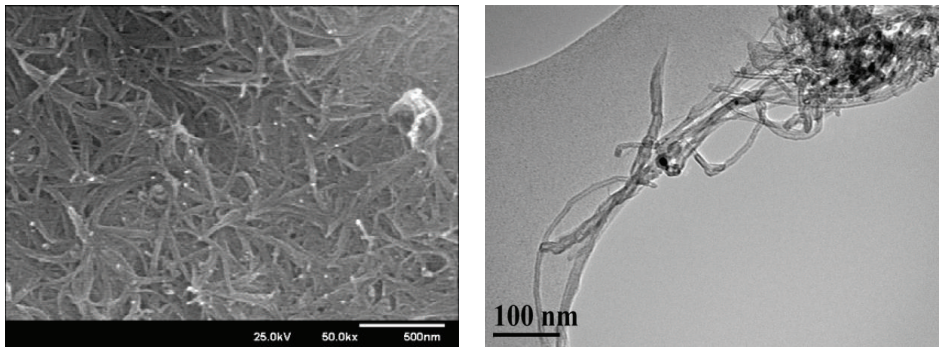


Figure 5: The FTIR curves of (a) MSWCNTs, (b) A-SWCNTs, and (c) A-SWCNTs-Si.

The FTIR spectra of (a) MSWCNTs, (b) A-SWCNTs, and (c) A-SWCNTs-Si are presented in Figure 5. Figure 5(a) shows the characteristic peaks of SWCNTs that appear at 3400 to 3500 cm^{-1}, due to hydroxyl group stretching [20]. Figure 5(b) shows the main characteristic peaks of A-SWCNTs, which occur at 1550, 1740, and 3400 cm^{-1}, which can be assigned to carboxylic acid (–COOH), carbonyl groups (C=O) and hydroxyl groups (–OH), respectively. The C=O and –OH on the A-SWCNTs' surface show enhanced dispersion in solution and increases in the intermolecular hydrogen bonds, when blended in polymers. This also helps the A-SWCNTs to graft to other functional groups.

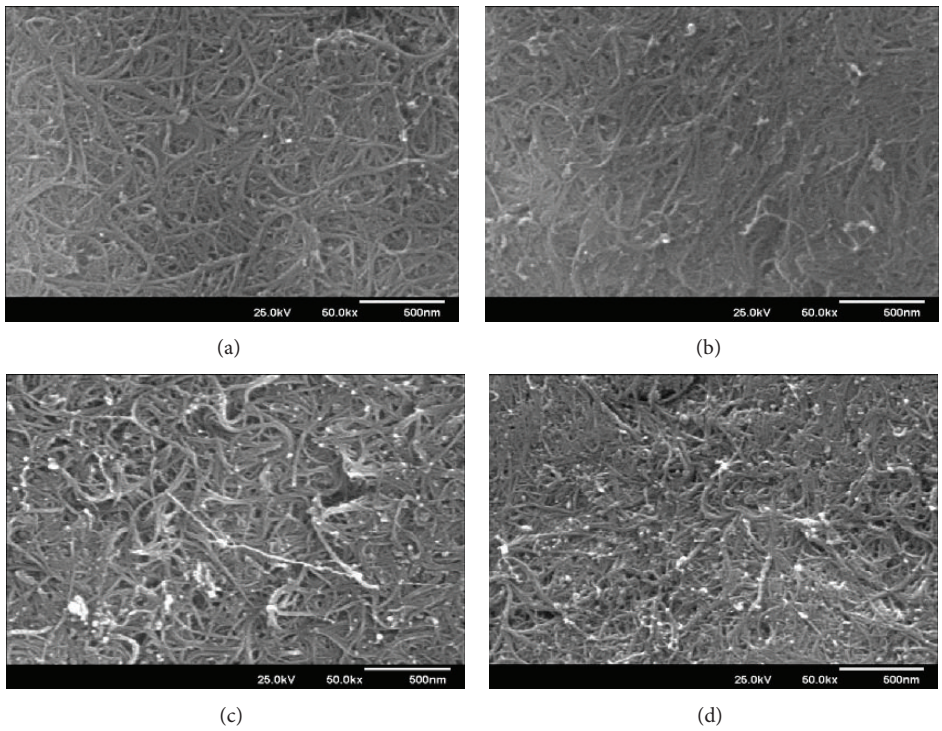
Figure 5(c) shows that the main characteristic peaks of A-SWCNTs-Si, which occur at 2850 and 2930 cm^{-1}, are methyl group (–CH3) stretching. The characteristic peaks at 3350 and 1600 cm^{-1} are amino group (–NH) stretching, which indicates that the –COOH groups of A-SWCNTs were efficient reacted with isocynate (–NCO) ends of IPTES. The characteristic peak at 1550 cm^{-1} is C=O. This can be attributed to the residual –COOH groups on the A-SWCNTs-Si surface that have not reacted completely with IPTES. The characteristic peak at 1180 cm^{-1} is Si–O–Si [21].

3.4. Morphology. Figure 6 shows the (a) SEM and (b) TEM images for SWCNTs. It is clearly seen that the SWCNTs are arranged in a disorderly manner (entanglement) and that impurities are present (amorphous carbon and metal particles). Figures 7–9 present the SEM images for SWCNTs using a combination of ultrasonic and microwave treatment for various treatment times: (a) 5, (b) 10, (c) 20, and (d) 30 min, with various HNO_3 concentrations (0.5, 1, and 3 M). In Figure 7, it is seen that the SWCNTs' surface structures are damaged by purification treatment. The damage is caused by excessive HNO_3 concentrations. When there is dilution of the HNO_3 solution, Figure 8 illustrates that the SWCNTs' surface structures exhibit less damage than with the



(a) (b)

Figure 6: The (a) SEM and (b) TEM images for SWCNTs.



(a) (b)

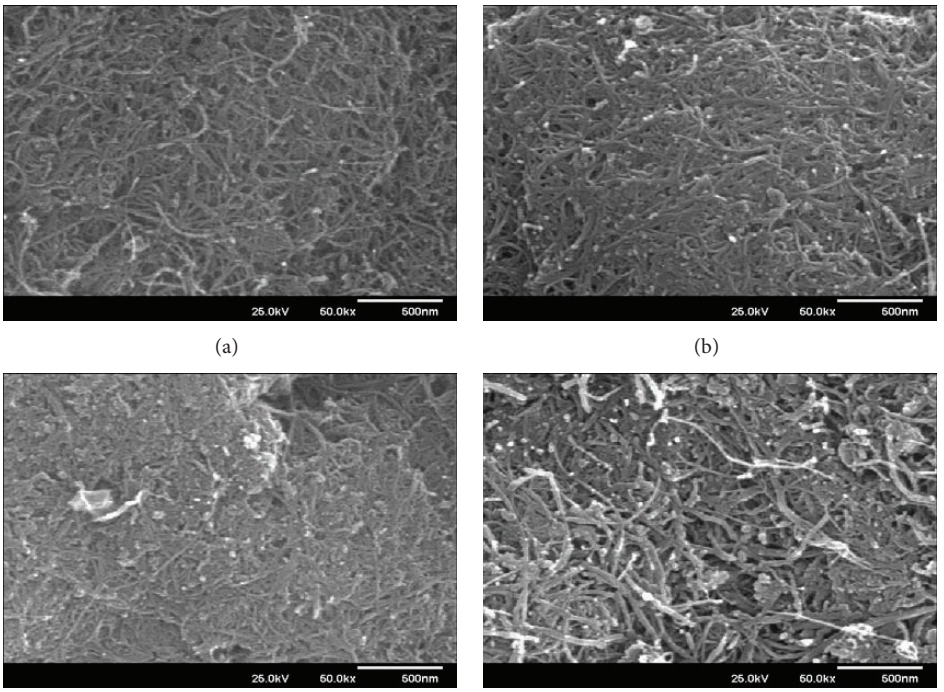
(c) (d)

Figure 7: The SEM images of SWCNTs using a combination of ultrasonic and microwave for various treatment times: (a) 5 min, (b) 10 min, (c) 20 min, and (d) 30 min with 3 M HNO_3 concentration.

3 M HNO_3 purification solution. Figure 9 indicates obvious improvements in the entanglement and no damage to the SWCNTs purified by ultrasound and microwaves in 0.5 M HNO_3 solution for 20 min.

Figures 10(a)–10(d) show the SEM and TEM images of 0.5MSWCNT20 for various treatment times with a 3 : 1 (v/v) mixture of H_2SO_4 and HNO_3 (A-SWCNTs). Figure 10(a) shows that the surface and length of the A-SWCNTs' are damaged and unevenly truncated, due to acid digestion for 2 hr. Figure 10(b) shows that the length of the tubes is more evenly truncated, but the original A-SWCNTs shapes are not lost by acid digestion for 5 hr. Figure 10(c) shows that the A-SWCNTs are destroyed by acid digestion for 8 hr. This indicates that the acid digestion time is too long and that the A-SWCNTs are too truncated. To determine, in more detail, the morphologies of the A-SWCNTs that are subject to acid digestion for 5 hr, the TEM image in Figure 10(d) shows that most of the impurities have been removed and that the clustering of A-SWCNTs is significantly improved, but that the surfaces of the A-SWCNTs are not smooth (laminated structures appear). These results are consistent with those for the Raman analysis.

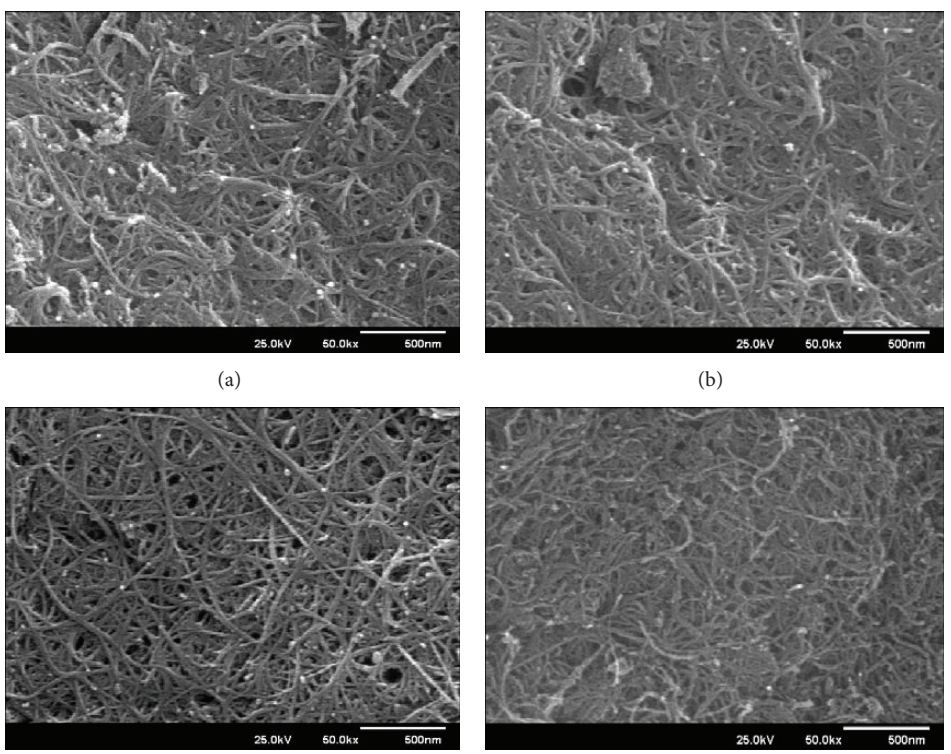
Figure 11 presents the (a) SEM and (b) TEM images for A-SWCNTs-Si. It can be seen that A-SWCNTs-Si are entangled, compared to the A-SWCNTs (Figure 10(d)). The results indicate the attachment of silane molecules to the surface of the functionalized A-SWCNTs. These results are confirmed by FTIR analysis.



(a) (b)

(c) (d)

Figure 8: The SEM images of SWCNTs using a combination of ultrasonic and microwave for various treatment times: (a) 5 min, (b) 10 min, (c) 20 min, and (d) 30 min with 1 M HNO_3 concentration.



(a) (b)

(c) (d)

Figure 9: The SEM images of SWCNTs using a combination of ultrasonic and microwave for various treatment times: (a) 5 min, (b) 10 min, (c) 20 min, and (d) 30 min with 0.5 M HNO_3 concentration.

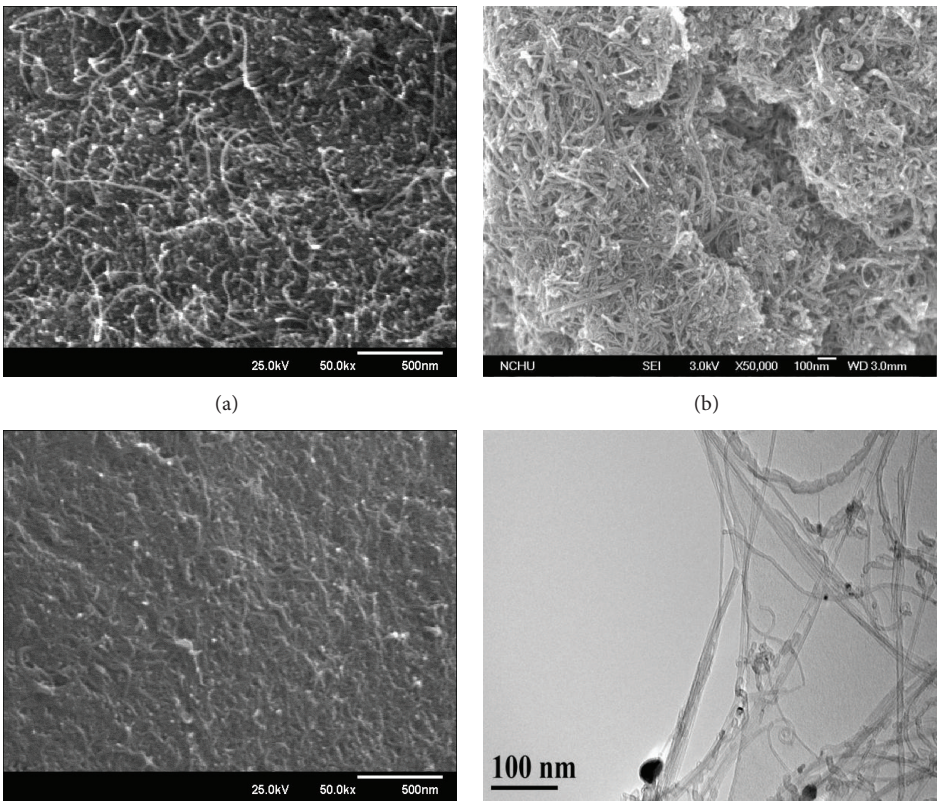


Figure 10: The SEM images of 0.5MSWCNT20 for various treatment times: (a) 2, (b) 5, and (c) 8 h and TEM image of 0.5MSWCNT20 for (d) 5 h treatment times, with a 3 : 1 (v/v) mixture of H_2SO_4 and HNO_3.

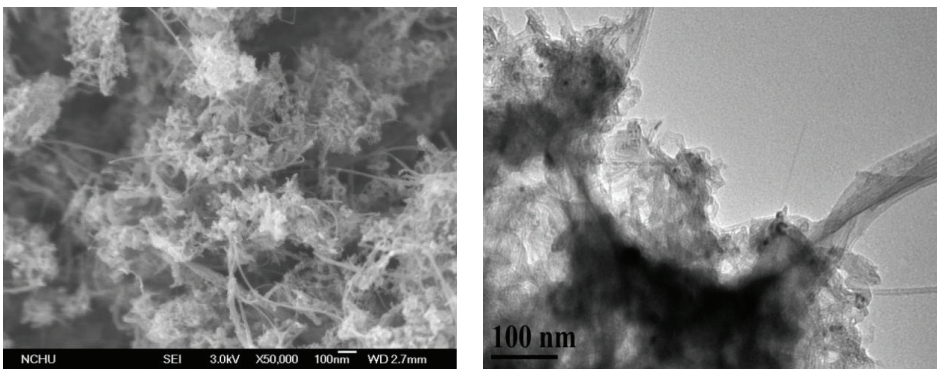


Figure 11: The (a) SEM and (b) TEM images for A-SWCNTs-Si.

4. Conclusion

The purification and functionalization of SWCNTs using different treatment procedures were investigated. The optimization of the purified SWCNTs was combined using ultrasonic- and microwave-assisted acid digestion in 0.5 M of HNO_3 for 20 min, which ensured the efficient elimination of impurities and prevention of damage to the structure of the SWCNTs. The purified SWCNTs were heated in an ultrasonic bath at 50°C for 5 hr with a 3 : 1 (v/v) mixture of H_2SO_4 and HNO_3 to produce A-SWCNTs. Then, the A-SWCNTs were also grafted with IPTES to produce SWCNTs-Si. The A-SWCNTs and A-SWCNTs-Si were used to improve interfacial interactions with polymers, and to produce a well-dispersed SWCNT composite, which will be the focus of future work.

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