

Research Article

Elucidating How Surface Functionalization of Multiwalled Carbon Nanotube Affects Nanostructured MWCNT/Titania Hybrid Materials

Cheng-Fu Yang,¹ Wei-Chieh Hsu,¹ Song-Mao Wu,² and Chean-Cheng Su¹

¹Department of Chemical and Materials Engineering, National University of Kaohsiung, No. 700, Kaohsiung University Road, Nan-Tzu District, Kaohsiung 811, Taiwan

²Department of Electrical Engineering, National University of Kaohsiung, No. 700, Kaohsiung University Road, Nan-Tzu District, Kaohsiung 811, Taiwan

Correspondence should be addressed to Chean-Cheng Su; ccsu@nuk.edu.tw

Received 30 September 2014; Accepted 18 November 2014

Academic Editor: Andrew R. Barron

Copyright © 2015 Cheng-Fu Yang et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The new class of multiwalled carbon nanotube (MWCNT)/titania nanocomposites was prepared using a sol-gel technique. The addition of titania to MWCNTs has the potential to provide new capability for the development of electrical devices by taking advantage of the favorable electric characteristics of MWCNTs. MWCNTs were first functionalized with carboxyl, acyl chloride, amine, and hydroxyl groups and were then dispersed in a tetraisopropyl titanate (TIPT) solution via ultrasonic processing. After gelation, well-dispersed titania in the MWCNT/titania nanocomposites was obtained. Functionalized MWCNTs with varied functional groups were proved by Fourier transform infrared spectroscopy (FT-IR). For the nanocomposites, the degree of the sol-gel process were proved by Raman spectroscopy and wide-angle X-ray diffraction (WAXD). Furthermore, the morphology of the MWCNT/titania nanocomposites was observed using transmission electron microscopy (TEM). In the sol-gel process, the functionalized MWCNTs with carboxyl, acyl chloride, amine, and hydroxyl groups have resulted in the carbon nanotube-graft-titania nanocomposites with a network structure of titania between the carbon nanotubes.

1. Introduction

Carbon nanotubes (CNTs) have attracted considerable attention because of their unique structure [1, 2]. CNTs, as a novel crystalline carbon form, are unique nanostructured materials with remarkable physical and mechanical properties, such as high tensile strength and Young's modulus, high thermal conductivity, and high current density [3–7]. These excellent properties draw interest in using CNTs as fillers in polymer composites in order to enhance the electrical conduction, thermal transport, and mechanical properties of the polymer matrixes [8, 9]. In particular, few researches on microwave properties of polymer/CNTs nanocomposites, such as the shielding effectiveness (SE) of the novel CNTs plastic nanocomposites, were studied for the purpose of the electromagnetic interference (EMI) protection and the electromagnetic susceptibility (EMS) improvement in the

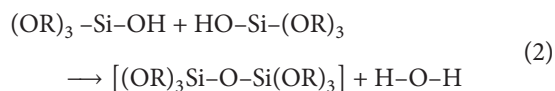
application of the optical transmitter and receiver modules [10, 11]. The CNTs with a good microwave-proof property at room temperature were proved by Highstrete et al. [12].

There are many applications for sol-gel-derived products, such as the thin films, protective and decorative coatings, and electrooptic components and composites. The sol-gel methods are used for the fabrication of metal oxide starting from a chemical solution that acts as the precursor for an integrated network of either discrete particles or network polymers. Typical precursors are metal alkoxides and metal chlorides, which undergo various forms of hydrolysis and polycondensation reactions [13, 14]. A well-studied alkoxide is a tetraethyl orthosilicate (TEOS). Alkoxides are ideal chemical precursors for sol-gel synthesis because they react efficiently with water. The mechanism for the sol-gel process is as follows.

(1) Hydrolysis process:



(2) Condensation process:



Polymerization is associated with the formation of a 1-dimensional, 2-dimensional, or 3-dimensional network of siloxane [Si-O-Si] bonds accompanied by the production of H-O-H and R-O-H species [15–22].

In preparation of the MWCNT/titania nanocomposites, it is difficult to make the uniform dispersion of nanotubes in the polymer matrixes because of the inherently poor compatibility and little interactions between the matrixes and the MWCNTs. Therefore, it is important to enhance the physical or the chemical interaction between the organic and the inorganic materials, which can make the MWCNTs homogeneously distributed throughout the matrixes. In the study, the modification of MWCNTs surface with carboxylic acid (–COOH), acyl chloride (–COCl), amine (–NH₂), and hydroxyl (–OH) groups would increase the interactions between the MWCNTs and matrix, which would be beneficial for the homogenous dispersion of CNTs and titania in the nanocomposites.

2. Materials and Methods

2.1. Materials and Surface Modification of MWCNTs. MWCNTs (95% pure by TGA analysis) were purchased from BASF. Thionyl chloride, ethylene chloride, sodium hydroxide, hydrochloric acid, sulfuric acid, nitric acid, allyl alcohol, hexamethylenediamine (HMDA), tetrahydrofuran (THF), chloroform, ethylene glycol, ethanol, and tetraisopropyl titanate (TIPT) were purchased from Merck Chemical Co. and were used without any further purification. The method of surface modification of MWCNT was covalent attachment onto the π -conjugated skeleton of MWNT through carboxylic acids treatment. MWCNTs (2 g), sulfuric acid (8 mL), and nitric acid (24 mL) were charged in a 125 mL round bottom flask equipped with a condenser and a stirrer. The flask was sonicated for 30 min with an ultrasonic apparatus. The chemical oxidation reaction was carried out at 60°C for 48 hrs. After acid treatment, MWCNTs were functionalized with the carboxylic acid groups (COOH) on the surface. After cooling down to room temperature, the mixture was vacuum filtered through a 0.1 mm Teflon filter. The surface modification of MWCNTs was then washed with deionized water until the pH of the filtrate reached near 7.0 [23]. 1 gm of MWCNTs after carboxylation was placed in a 250 mL flat bottom flask with 100 mL of ethylene chloride and sonicated for 1 hr to disperse the MWCNT in the solvent. 15 mL of thionyl chloride was added to the flat bottom flask and the mixture was stirred with a magnetic stirrer and refluxed for 24 hrs. After the chlorination of the MWCNTs, the unreacted thionyl chloride and solvent were distilled off and 50 mL

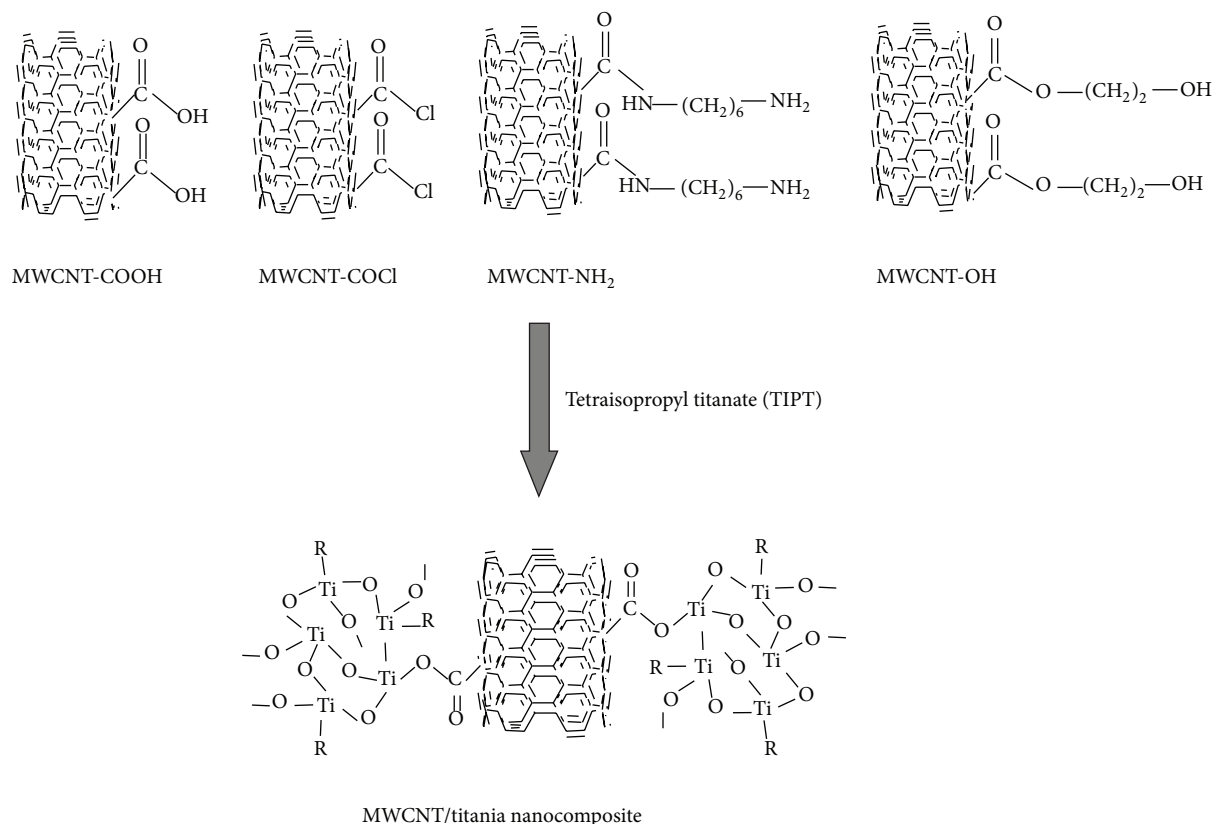
allyl alcohol was added to the acid chloride MWCNTs and stirred at 50°C for 24 hrs. Following the esterification of the MWCNTs with allyl chloride, excess allyl chloride was distilled off. The synthesized acyl chloride functionalized MWCNTs were washed with acetone to remove unreacted chemicals. The generated acyl chloride functionalized MWCNTs were reacted with HMDA in the THF solution at 50°C for 12 hrs. The amine functionalized MWCNTs were synthesized, and then the products were washed with THF to remove unreacted chemicals. Furthermore, the acyl chloride functionalized MWCNTs were reacted with ethylene glycol at 80°C for 12 hrs. The hydroxyl functionalized MWCNTs were synthesized, and then the products were washed with ethanol to remove unreacted chemicals. Finally, the functionalized MWCNTs were dried in a vacuum oven at 40°C for 12 hrs [24, 25].

2.2. Preparation of MWCNT/Titania Nanocomposites. MWCNTs were first functionalized with carboxyl, acyl chloride, amine, and hydroxyl groups and were then dispersed in a tetraisopropyl titanate (TIPT) solution via ultrasonic processing. After gelation, well-dispersed titania in the MWCNT-graft-titania nanocomposites was obtained. Scheme 1 represents the schematic procedure for the synthesis of functionalized MWCNTs and MWCNT/titania nanocomposite.

2.3. Characterization of MWCNT/Titania Nanocomposites. Morphology of MWCNT/titania nanocomposites was examined using transmission electronic micrographs (TEM, model JEOL JEM 1200 EX). The characterization of MWCNT/titania nanocomposites was identified by Raman spectroscopy using the 532 nm line of a YAG laser, which was operated at a laser power of 500 mW. The laser beam with a beam size of approximately 2 μm in the diameter was focused by a 1000x objective onto the MWCNTs surface. Fourier transform infrared spectroscopy instrument (FT-IR) was used to measure the functional group of the chemical modification of MWCNT. For wide-angle X-ray diffraction (WAXD) experiments, a Shimadzu/XRD-6000 with a copper K_α radiation ($\lambda = 0.1542 \text{ nm}$) was used for the WAXD measurements. The scanning 2θ angle covered a range between 5 and 55° with a step scanning of 0.2°.

3. Results and Discussion

3.1. FT-IR Spectra Analysis. In order to overcome self-aggregation, chemical modification of the MWCNTs' surface is regarded as an effective way to improve the adhesion to MWCNTs. Figure 1 shows the Fourier transform infrared (FT-IR) spectrum in the range 500–4000 cm^{-1} of the surface of the chemically modified MWCNTs. In the IR spectra analysis, characteristic main absorption peak due to the hydroxyl group is observed in the 3200–3700 cm^{-1} range. The infrared absorption of amine group is observed at 3000 cm^{-1} . The infrared absorption of carboxylic acid is observed at 3300 cm^{-1} . The infrared absorption of acyl chloride group is observed at 3400 cm^{-1} . Figure 1 shows that, for the original



SCHEME 1: Schematic procedure for the synthesis of functionalized MWCNTs and MWCNT/titania nanocomposite.

MWCNT, there is an apparent greater hydroxyl absorption peak at 3570 cm^{-1} in the MWCNT. On the contrary, the IR absorption intensity for carboxyl, acyl chloride, amine, and hydroxyl groups increased apparently. However, the increase in IR absorption intensity in the MWCNTs with chemical modification suggests that, after chemical modification on the surface of MWCNTs, the hydroxyl group, amine group, carboxyl group, and acyl chloride group were grafted onto the surface of MWCNTs. As a result, the hydroxyl group, amine group, carboxyl group, and acyl chloride group occurring were covalent attachment onto the π -conjugated skeleton of MWCNTs through carboxylic acids treatment in the study. The surface of MWCNTs with chemical modification has attached more polar functional groups such as $-\text{COOH}$, $-\text{COCl}$, $-\text{NH}_2$, and $-\text{OH}$ groups, which could lead to an improvement of the interface chemical interaction between MWCNTs and TIPT.

Characteristic main absorption peaks due to the titania-oxide group are observed in the $700\text{--}1700\text{ cm}^{-1}$ range. Figure 2 shows that, in the MWCNT-graft-titania nanocomposites, there is an apparent greater Ti-O absorption at 1680 and 850 cm^{-1} . In the figures, IR absorption intensity for the four functional groups on the surface of MWCNTs decreased apparently after sol-gel process. The titania-oxide group was observed in the MWCNT-graft-titania nanocomposites simultaneously. As a result, the surface of MWCNTs with

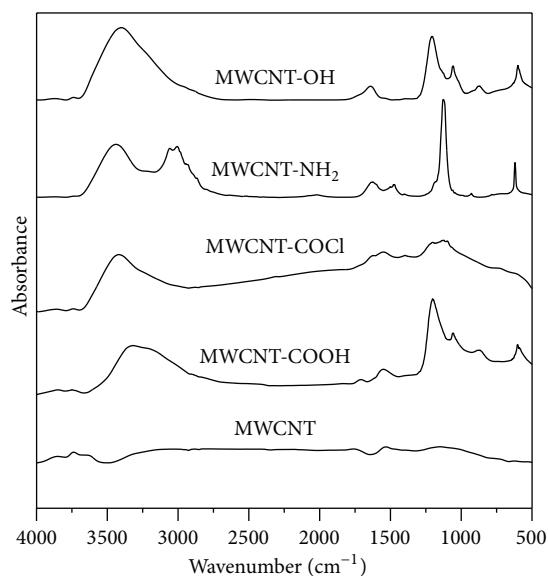


FIGURE 1: FT-IR spectra of chemical modification on the MWCNT.

chemical modification has attached more polar functional groups such as carboxyl, acyl chloride, amine, and hydroxyl groups that could lead to an improvement of the formation of MWCNT-graft-titania nanocomposites.

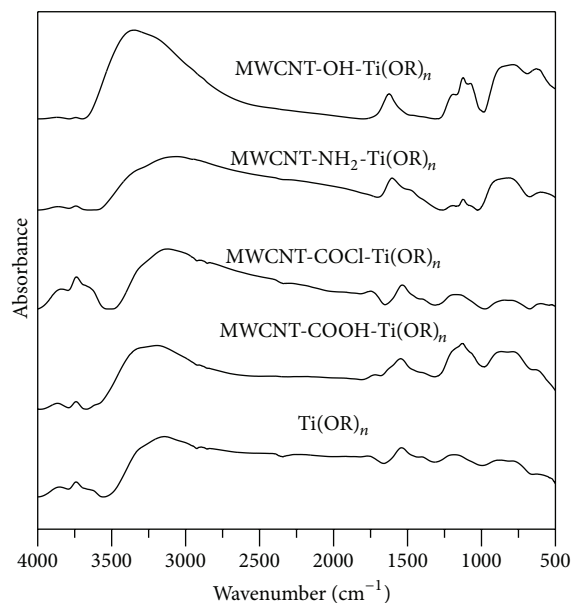


FIGURE 2: FT-IR spectra of MWCNT/titania nanocomposites.

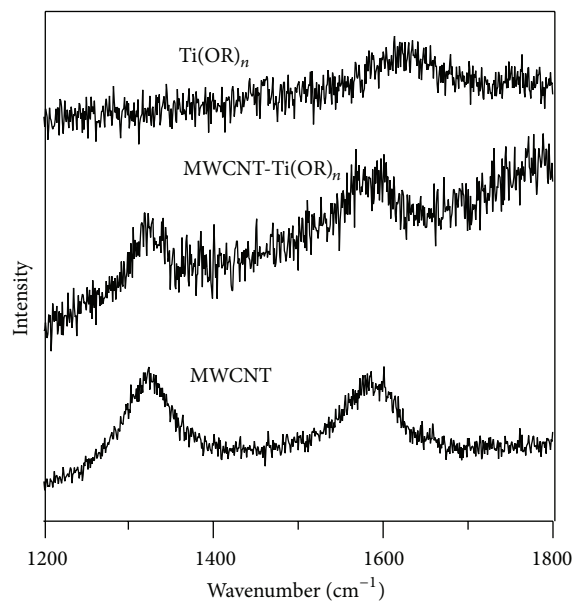


FIGURE 4: Raman analysis of MWCNT/TiO₂ nanocomposites.

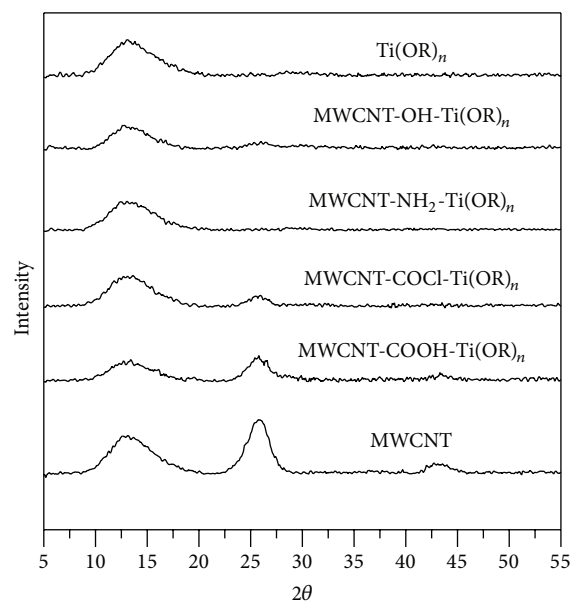


FIGURE 3: XRD patterns of MWCNT/TiO₂ nanocomposites.

3.2. Characterization of MWCNT/Titania Nanocomposites.

Figure 3 shows the wide-angle X-ray diffraction (WAXD) of MWCNT/titania nanocomposites. The examination of XRD patterns of different MWCNT/titania nanocomposites revealed that only TiO₂ in amorphous phase could be identified as TiO₂ and MWCNT/TiO₂ hybrid materials. The anatase, rutile, and brookite phases of TiO₂ were not observed in the MWCNT/titania nanocomposites. It is noteworthy that the characteristic peaks of MWCNT can hardly be identified from the patterns of hybrid materials with different initial MWCNT weight ratio varied from 1 to 30%. It is observed

that the peaks width broadened slightly and gradually with the increase in MWCNT amount for the composite materials.

The resonance Raman spectrum of the MWCNTs was shown in Figure 4. In the figures, characteristic peaks of MWCNTs register at 1321 and 1582 cm⁻¹. The G-band which originates from the graphitic sheet is at 1582 cm⁻¹. The broad peak near 1321 cm⁻¹ shows the D-band, which indicates the existence of defective, graphitic layer, and/or some carbon particles, which remain even after the purification procedure [23]. The relative intensity ratio of the D-band to G-band peak (i.e., I_D/I_G) was 1.21 for crude MWCNTs. In the MWCNT/titania nanocomposite, it was found that the I_D/I_G of MWCNTs increased to 1.66. It indicates that more defective graphitic layers were formed by the acid-treated process. From the FT-IR and Raman analysis, it demonstrated that the MWCNT/titania nanocomposites were synthesized during the sol-gel process.

Figure 5 shows the thermal stability of MWCNT/titania nanocomposites. It is apparent that an obvious mass loss occurred for MWCNT/titania nanocomposites, while the oligomer in neat TiO₂ and MWCNT/TiO₂ nanocomposites may be gasified in an air flow within this range [23]. The MWCNT/TiO₂ hybrid materials, containing 5–10% weight ratio of the unity weight basis of neat TiO₂, exhibit a mass loss of 15% due to the oligomer gasification, which agrees very well with the calculated value from initial ratio. This result indicates that there is no appreciable loss of MWCNT during the preparation procedure, where a calcination temperature of 550°C in a N₂ flow was used for 2 hrs.

3.3. Morphology Analysis. The effect of the chemical modification on the morphology in the MWCNT was examined using transmission electron microscopy (TEM). Figures 6(a)–6(d) show the TEM results of the surface of MWCNTs with chemical modification have attached

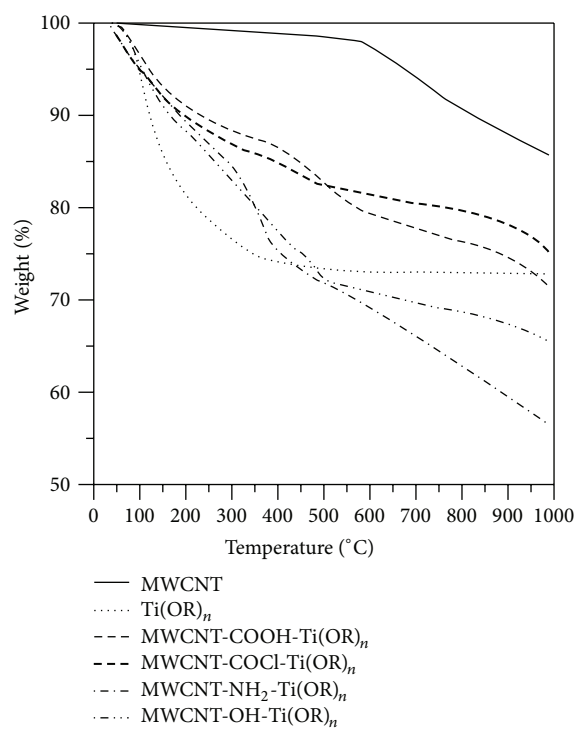


FIGURE 5: Thermal stability of MWCNT/TiO₂ nanocomposites.

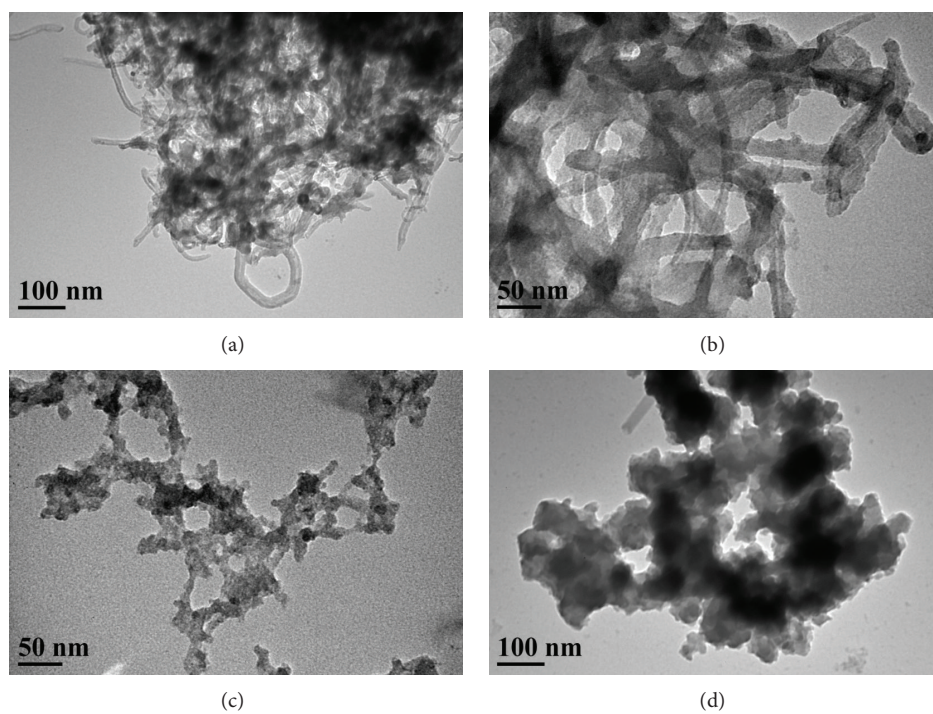


FIGURE 6: TEM images of MWCNT/TiO₂ nanocomposites: (a) MWCNT-NH₂-Ti(OR)_n, (b) MWCNT-COOH-Ti(OR)_n, (c) MWCNT-COCl-Ti(OR)_n, and (d) MWCNT-OH-Ti(OR)_n.

more polar functional groups such as carboxyl, acyl chloride, amine, and hydroxyl groups that could lead to an improvement of the formation of MWCNT-graft-titania nanocomposites. The TiO_2 size distribution centered at 25 nm, 35 nm, 20 nm, and 50 nm for the functionalized MWCNTs with hydroxyl, amine, carboxyl, and acyl chloride group in the nanostructured MWCNT/titania hybrid materials, respectively. In the previous study [23], the aggregation of chemical modified MWCNT was less than that of the crude MWCNT due to the increased polarity from functional groups such as carboxyl and hydroxyl groups on the surface of the MWCNT and the short length and low aspect ratio for the MWCNT. The length of the MWCNT is about several ten microns and the diameter of MWCNT is about 10–30 nm. In the sol-gel process, the functionalized MWCNTs with hydroxyl, amine, carboxyl, and acyl chloride groups have resulted in the carbon nanotube-graft-titania nanocomposites with a network structure of titania between the carbon nanotubes. MWCNT was introduced into TiO_2 particles from agglomerating, consequently increasing its surface area of the composite materials. Meanwhile, the absence of MWCNT aggregated pores in the composite catalysts suggests a homogeneous coverage of TiO_2 over MWCNT [26]. This effect was also supported by SEM observation. The morphology of MWCNT/ TiO_2 composite materials features relatively homogeneous TiO_2 supported on MWCNT without apparent agglomeration of TiO_2 particles. Additionally, EDX spectra analysis of MWCNT- TiO_2 nanocomposites confirmed only the presence of C, O, and Ti elements.

4. Conclusions

New class of multiwall carbon nanotube (MWCNT)/titania nanocomposites was prepared using a sol-gel technique. In the study, functionalized MWCNTs with varied functional groups (carboxyl, acyl chloride, amine, and hydroxyl groups) were proved by Fourier transform infrared spectroscopy (FT-IR). Furthermore, the morphology of the new class of MWCNT/titania nanocomposites was observed using transmission electron microscopy (TEM). In the sol-gel process, the functionalized MWCNTs with hydroxyl, amine, carboxyl, and acyl chloride groups have resulted in the carbon nanotube-graft-titania nanocomposites with a network structure of titania between the carbon nanotubes. In the MWCNT/titania nanocomposites, the functionalized MWCNTs with hydroxyl and acyl chloride group could enhance the nanostructured titania mesh-reinforced carbon nanotube composites.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

This study is sponsored by the National Science Council of Taiwan which financially supported this research under Contract no. NSC 101-2221-E-390-006-MY2.

References

- [1] S. Iijima, "Helical microtubules of graphitic carbon," *Nature*, vol. 354, no. 6348, pp. 56–58, 1991.
- [2] S. Iijima and T. Ichihashi, "Single-shell carbon nanotubes of 1-nm diameter," *Nature*, vol. 363, no. 6430, pp. 603–605, 1993.
- [3] J. W. Mintmire and C. T. White, "Electronic and structural properties of carbon nanotubes," *Carbon*, vol. 33, no. 7, pp. 893–902, 1995.
- [4] J. N. Coleman, U. Khan, W. J. Blau, and Y. K. Gun'ko, "Small but strong: a review of the mechanical properties of carbon nanotube-polymer composites," *Carbon*, vol. 44, no. 9, pp. 1624–1652, 2006.
- [5] M. M. J. Treacy, T. W. Ebbesen, and J. M. Gibson, "Exceptionally high Young's modulus observed for individual carbon nanotubes," *Nature*, vol. 381, no. 6584, pp. 678–680, 1996.
- [6] M.-F. Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly, and R. S. Ruoff, "Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load," *Science*, vol. 287, no. 5453, pp. 637–640, 2000.
- [7] M. J. Biercuk, M. C. Llaguno, M. Radosavljevic, J. K. Hyun, A. T. Johnson, and J. E. Fischer, "Carbon nanotube composites for thermal management," *Applied Physics Letters*, vol. 80, no. 15, pp. 2767–2769, 2002.
- [8] S. Frank, P. Poncharal, Z. L. Wang, and W. A. de Heer, "Carbon nanotube quantum resistors," *Science*, vol. 280, no. 5370, pp. 1744–1746, 1998.
- [9] K. Tsukagoshi, B. W. Alphenaar, and H. Ago, "Coherent transport of electron spin in a ferromagnetically contacted carbon nanotube," *Nature*, vol. 401, no. 6753, pp. 572–574, 1999.
- [10] C.-M. Chang, J.-C. Chiu, W.-S. Jou, T.-L. Wu, and W.-H. Cheng, "New package scheme of a 2.5-Gb/s plastic transceiver module employing multiwall nanotubes for low electromagnetic interference," *IEEE Journal on Selected Topics in Quantum Electronics*, vol. 12, no. 5, pp. 1025–1030, 2006.
- [11] C.-M. Chang, J.-C. Chiu, Y.-F. Lan et al., "High electromagnetic shielding of a 2.5-Gbps plastic transceiver module using dispersive multiwall carbon nanotubes," *Journal of Lightwave Technology*, vol. 26, no. 10, pp. 1256–1262, 2008.
- [12] C. Highstrete, E. A. Shaner, M. Lee, F. E. Jones, P. M. Dentinger, and A. Alec Talin, "Microwave dissipation in arrays of single-wall carbon nanotubes," *Applied Physics Letters*, vol. 89, no. 17, Article ID 173105, 2006.
- [13] L. C. Klein and G. J. Garvey, "Kinetics of the sol/gel transition," *Journal of Non-Crystalline Solids*, vol. 38–39, no. 1, pp. 45–50, 1980.
- [14] C. J. Brinker, K. D. Keefer, D. W. Schaefer, and C. S. Ashley, "Sol-gel transition in simple silicates," *Journal of Non-Crystalline Solids*, vol. 48, no. 1, pp. 47–64, 1982.
- [15] E. Matijević, "Monodispersed colloids: art and science," *Langmuir*, vol. 2, no. 1, pp. 12–20, 1986.
- [16] C. J. Brinker and S. P. Mukherjee, "Conversion of monolithic gels to glasses in a multicomponent silicate glass system," *Journal of Materials Science*, vol. 16, no. 7, pp. 1980–1988, 1981.
- [17] S. Sakka and K. Kamiya, "Glasses from metal alcoholates," *Journal of Non-Crystalline Solids*, vol. 42, no. 1–3, pp. 403–421, 1980.
- [18] B. E. Yoldas, "Monolithic glass formation by chemical polymerization," *Journal of Materials Science*, vol. 14, no. 8, pp. 1843–1849, 1979.

- [19] S. Prochazka and F. J. Klug, "Infrared-transparent mullite ceramic," *Journal of the American Ceramic Society*, vol. 66, no. 12, pp. 874–880, 1983.
- [20] A. Ikesue, T. Kinoshita, K. Kamata, and K. Yoshida, "Fabrication and optical properties of high-performance polycrystalline Nd:YAG ceramics for solid-state lasers," *Journal of the American Ceramic Society*, vol. 78, no. 4, pp. 1033–1040, 1995.
- [21] A. Ikesue, "Polycrystalline Nd:YAG ceramics lasers," *Optical Materials*, vol. 19, no. 1, pp. 183–187, 2002.
- [22] K. D. Ausman, R. Piner, O. Lourie, R. S. Ruoff, and M. Korobov, "Organic solvent dispersions of single-walled carbon nanotubes: toward solutions of pristine nanotubes," *Journal of Physical Chemistry B*, vol. 104, no. 38, pp. 8911–8915, 2000.
- [23] C.-C. Su, C.-C. Wu, and C.-F. Yang, "Developing the dielectric mechanisms of polyetherimide/multiwalled carbon nanotube/(Ba_{0.8}Sr_{0.2})(Ti_{0.9}Zr_{0.1})O₃ composites," *Nanoscale Research Letters*, vol. 7, article 132, 2012.
- [24] S. Swain, R. A. Sharma, S. Patil, S. Bhattacharya, S. P. Gadiyaram, and L. Chaudhari, "Effect of allyl modified/silane modified multiwalled carbon nano tubes on the electrical properties of unsaturated polyester resin composites," *Transactions on Electrical and Electronic Materials*, vol. 13, no. 6, pp. 267–272, 2012.
- [25] K. Zhang, J. Y. Lim, and H. J. Choi, "Amino functionalization and characteristics of multi-walled carbon nanotube/poly(methyl methacrylate) nanocomposite," *Diamond and Related Materials*, vol. 18, no. 2-3, pp. 316–318, 2009.
- [26] W. Wang, P. Serp, P. Kalck, C. G. Silva, and J. L. Faria, "Preparation and characterization of nanostructured MWCNT-TiO₂ composite materials for photocatalytic water treatment applications," *Materials Research Bulletin*, vol. 43, no. 4, pp. 958–967, 2008.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

