

PREPARATION AND CHARACTERIZATION OF CONDUCTING POLYMER/MULTI-WALLED CARBON NANOTUBE COMPOSITES

Tzong-Ming Wu, Yen-Wen Lin and Shih-Hsiang Lin

Department of Materials Science and Engineering, National Chung Hsing University,
250 Kuo Kuang Road, Taichung, Taiwan.

Introduction

Since the discovery of carbon nanotube (CNTs) in 1991 by Iijima [1], CNTs have been extensively studied by researchers in various fields such as chemical, physical, and materials science. CNTs have unique nanostructure with remarkably mechanical, thermal and electrical properties [2], which made them highly attractive for the use as reinforcement in nanotube-based composite materials. Recently, extensive efforts have been made to prepare functional conducting polymer/CNT composites, which are expected to exhibit excellent electrical conductivity and optical properties compared to the original conducting polymer matrix [3, 4].

Among various conducting polymers, polyaniline (PANI) and polypyrrole (Ppy) have potential uses in synthesizing conducting polymer/CNT composites owing to its environmental stability and good processability. This presentation reports the synthesis of PANI and PPy with multi-walled carbon nanotubes (MWCNT) by in situ chemical oxidation polymerization. To improve the dispersion and homogeneity of the MWCNTs within the conducting polymer matrix, the as-prepared MWCNTs, which contained carboxylic acid groups (designated as c-MWCNTs) at the defect sites, were treated using a 3:1 mixture of concentrated $H_2SO_4:HNO_3$. The structure, morphology and conductivity of PANI/c-MWCNT and PPy/c-MWCNT composites were characterized.

Experimental

Synthesis of PANI/c-MWCNT composites

The MWCNTs used in this study were synthesized by ethylene CVD using Al_2O_3 supported Fe_2O_3 catalysts. The purity of MWCNTs was higher than 90% after purification. The as-prepared MWCNTs were ultrasonically treated using a 3:1 mixture of concentrated H_2SO_4 and HNO_3 at 50 °C for 24 h, producing carboxylic acid groups at the defect sites and thus improving the solubility of the c-MWCNTs in HCl solution.

The composite of PANI with c-MWCNT was synthesized via in situ chemical oxidation polymerization. In a typical synthesis experiment, the c-MWCNTs were dissolved in 1.0 M HCl solution and ultrasonicated over 3 h, then transferred into a 500 ml four-neck flask with an ice-bath. Aniline

monomer also dissolved in 1.0 M HCl solution was added to the above c-MWCNTs suspension. A 1.0 M HCl solution containing 0.125 M ammonium persulfate was slowly added dropwise into the suspension with constant mechanical stirring at a reaction temperature of 0-5 °C for 1 h. The reaction mixture was stirred for a further 2 h at 0-5 °C, and then the resulting green suspension, indicating the formation of insoluble PANI in its emeraldine salt form, was filtered and rinsed several times with distilled water and methanol. The powder of PANI/c-MWCNT composites thus obtained was vacuum dried at 60 °C for 24 h.

Results and Discussion

Fig. 1 illustrates the FTIR spectra of MWCNTs and c-MWCNTs. As compared with the spectrum of MWCNTs (Fig. 1a), the new peaks at around 1718 and 1186 cm^{-1} were from the stretching vibration of C=O and C-O groups in c-MWCNTs (Fig. 1b), respectively. This result indicated that the oxygen-containing functional groups, such as hydroxyl (-OH), carboxyl (-COOH), and carbonyl (-C=O) have been introduced on the surface defects and more hydrophilic surfaces have been formed after treatment of chemical oxidation [5].

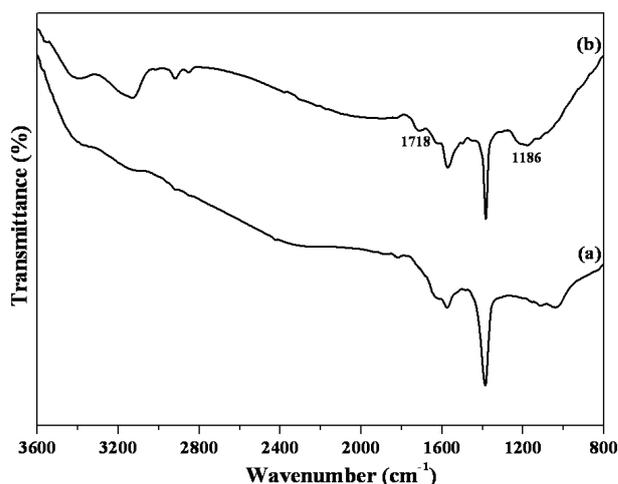


Figure 1 FTIR spectra of (a) MWCNTs and (b) c-MWCNTs.

To verify the structure of the synthesized composites, Fig. 2

presents typical field-emission scanning electron microscopy (FESEM) and high-resolution transmission electron microscopy (HRTEM) images of 3 wt% MWCNT-containing PANI/c-MWCNT composites. Clearly, a tubular layer of a highly uniformly coated PANI film is present on the c-MWCNT surface and the diameters of the PANI/c-MWCNT composites range from several tens to hundreds, depending on the PANI content. Therefore, this composite has a typical core-shell structure, and the c-MWCNT serves as the core and is dispersed individually into the PANI matrices. The aniline monomer is uniformly polymerized on the surface of the c-MWCNT and forms a tubular shell of the composites.

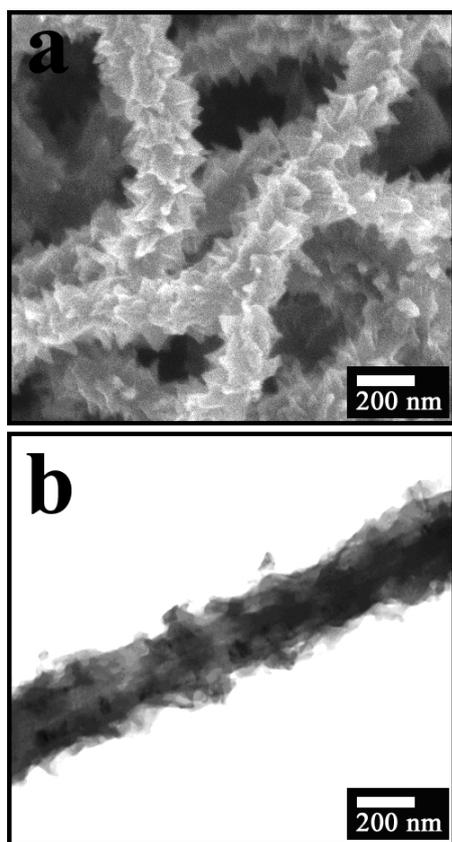


Figure 2 (a) FESEM and (b) HRTEM images of 3 wt% MWCNT-containing PANI/ c-MWCNT composites

Fourier transform infrared (FTIR) and Raman spectra were used to characterize the molecular structure of the resulting PANI/c-MWCNT composites. Obviously, these FTIR and Raman spectra of the composites are approximately the same to those of conducting polymer, supporting the idea that MWCNTs served as the core in the formation of a coaxial nanostructure for the composites. In addition, the electrical conductivities of conducting polymer and composites were measured with the standard Van Der Pauw

dc four-probe method [6]. The conductivities of c-MWCNT and protonic acid-doped PANI in its conductive emeraldine salt form at room temperature were 200 and 29.6 S/cm, respectively. Meanwhile, the conductivities of 0.5, 1 and 3 wt% MWCNT-containing PANI/c-MWCNT composites were 48.0, 51.8, and 58.4 S/cm, respectively. The electrical conductivities of all composites with low c-MWCNT content at room temperature are higher than those of PANI without MWCNTs, perhaps because MWCNTs have a large aspect ratio and surface area, and so could serve as a “conducting bridge” between the PANI conducting domains, increasing the effective percolation.

Conclusion

PANI/c-MWCNT composites were prepared via the in situ polymerization. MWCNTs that contained carboxylic acid groups were used as core in the formation of tubular shells of PANI/c-MWCNT composites. Moreover, the conductivities at room temperature of 0.5 wt% MWCNT-containing PANI/ c-MWCNT composites are about 50% higher than that of PANI without MWCNTs. That is because the addition of as little as 0.5 wt% MWCNT could be randomly dispersed in PANI matrix and serve as a “conducting bridge” between the PANI conducting domains, thus increasing the effective percolation.

References

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