

Synthesis of New Polyaniline/Nanotube Composites Using Ultrasonically Initiated Emulsion Polymerization

Milena Ginic-Markovic,^{*,†} Janis G. Matisons,[†] Raoul Cervini,[‡] George P. Simon,[‡] and Peter M. Fredericks[§]

School of Chemistry Physics and Earth Science, The Flinders University of South Australia, GPO Box 2100, SA 5001, Australia, Department of Materials Engineering, Monash University, Clayton VIC 3800, Australia, and School of Physical & Chemical Sciences, Queensland University of Technology, GPO Box 2434 Brisbane, QLD 4001, Australia

Received June 8, 2006. Revised Manuscript Received October 4, 2006

Ultrasonically initiated, in situ emulsion polymerization was used to prepare multiwalled carbon nanotube/polyaniline composites (MWNTs/PANI). Transmission electron microscopy (TEM) showed that the nanotubes were coated with a PANI layer, with the thickness of this coating varying with the content of carbon nanotubes and polymerization conditions. Whereas polyaniline/carbon nanotube composite particles prepared by the conventional stirring method have a highly structured, nodular morphology, ultrasonic initiation leads to long, thin, polymer-wrapped tubes. In the case of ultrasonically initiated in situ emulsion polymerization, Fourier transform infrared (FTIR) spectra suggested that site-selective interactions between the quinoid ring of the PANI and the MWNTs facilitate charge-transfer between the two components. In such composites, CNT improved the polymer properties, such as thermal stability, as determined by thermogravimetric analysis and conductivity measured using the four-probe method.

Introduction

Carbon nanotubes (CNTs) have been a focus of considerable research since their first observation by Iijima.¹ Their remarkable properties include their interesting mechanical, electrical, and thermal conductivity behavior, and they offer tremendous opportunities for the development of fundamentally new material systems for application in nanoscale devices and in materials in particular.² Similarly, composites based on polymers and nanotubes have the potential to make an impact on a variety of applications ranging from general low-cost circuits and displays to power devices, microelectromechanical systems, super capacitors, solar cell sensors, and displays.^{3,4}

Despite their appealing properties, the low solubility of CNTs in most organic solvents and their poor compatibility within a polymer matrix makes the uniform dispersion of carbon nanotubes in the polymer matrix very difficult, limiting their applications. Nanotube dispersion into polymers can be improved by either mixing in a conical twin-screw extruder,⁵ using surfactants as processing aids,⁶ functionalization,⁷ or in situ polymerization.⁸

The ability to combine CNT with conducting matrices such as polythiophene, polyaniline (PANI), and poly(phenylenevinylene) to produce nanocomposite materials has stimulated much research interest, particularly in organic electronics.^{9,10} PANI is one of the more important conducting polymers because of its relatively facile processability, electrical conductivity, and environmental stability. More recently, synthesis and properties of polyaniline/carbon nanotube composites have been reported by a number of authors.^{11–15} An effective utilization of the CNTs, as filler materials for either conductive or mechanical properties, can be achieved only with homogeneous dispersion within the matrices, without damaging their integrity. Such dispersibility can be optimized by coating the individual carbon nanotubes with a polymer layer, creating the core–shell nanowires by inverse microemulsion,¹⁴ or in situ polymerization, where the matrix polymer is formed in the presence of CNTs.^{16–18}

* Corresponding author. E-mail: milena.ginic-markovic@flinders.edu.au. Fax: 61 8 8201 5571. Phone 61 8 8201 5541.

[†] The Flinders University of South Australia.

[‡] Monash University.

[§] Queensland University of Technology.

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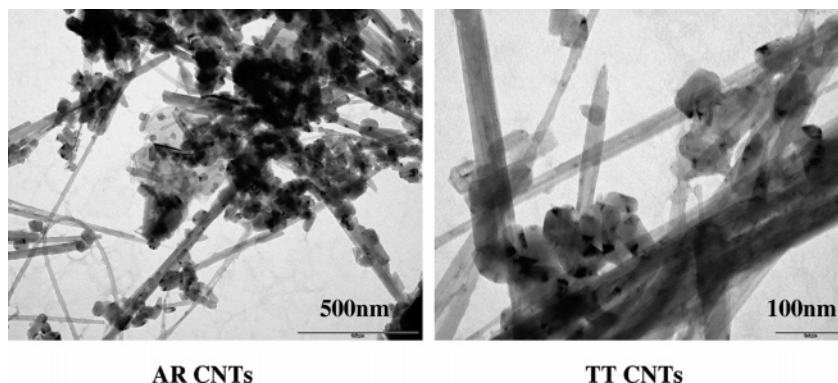


Figure 1. TEM images of AR CNTs and TT CNTs.

In this work, we report a new approach for the preparation of a homogeneous nanocomposite of PANI and MWNTs by ultrasonically initiated in situ emulsion polymerization. Although the ultrasonic irradiation approach has previously been successfully used for the preparation of polyaniline/nanocrystalline TiO₂ composite particles¹⁹ and poly(butyl acrylate) (PBA) or poly(methyl methacrylate) (PMMA/MWNT) composites,²⁰ to the best of our knowledge, no work has been published on polyaniline/MWNT composites. The effect of ultrasound is to aid reduction in the agglomeration and entanglement of carbon nanotubes in the aqueous solution, so that in situ polymerization of aniline on the surface of CNTs can proceed with a significantly reduced concentration of initiator. For comparison, we have also prepared a composite without such ultrasonic irradiation.

Experimental Methods

Materials. MWNT were obtained from Materials and Electrochemical Research Corporation (MER). They are synthesized by the arc discharge process, are between 8 and 20 nm in diameter and 2 and 20 μm in length, and have approximately 10–40% purity. They are assigned as AR CNTs. Purification was performed by treating CNTs at 590 °C in the furnace for 3 h in air, which removed the amorphous carbon, and they are denoted as TT CNTs. This treatment still produces some other graphitic carbon and multi-shelled fullerene particles with a structure very similar to that of nanotubes.²¹ TEM images of both AR CNTs and TT CNTs are presented in Figure 1. The aniline monomer used was obtained from Fluka and is of greater than 99.5% purity. The initiator used was ammonium persulfate (NH₄)₂S₂O₈, 98%, from Sigma-Aldrich. The surfactant, sodium dodecyl sulfate (SDS), was obtained from BDH Chemicals Ltd.

Ultrasonically Initiated in Situ Emulsion Polymerization. The ultrasonic irradiation device (VCX 750, Sonic & Mater Co) was equipped with a standard titanium horn with replaceable tip diameter of 13 mm and temperature controller, and the energy output of the

probe was set to 300 W. PANI/CNT composites were prepared according to the following procedure. First, approximately 500 mg of CNT, thermally treated at 590 °C in the furnace for 3 h in air, was sonicated in 100 mL of 0.7% SDS solution for 1 h. The solution was deoxygenated with oxygen-free nitrogen for 2 min, and water circulated around the vessel to maintain a low temperature of around 30 °C. The process removes aggregation in the CNT and allows the surfactant to wet the surface of the CNT, creating a micellar structure, admicelles, around the CNT molecule, which becomes soluble in water for a period of time.²⁰ Hydrophobic chains of surfactant attach to the surface of individual carbon nanotubes because of the hydrophobic–hydrophobic interactions. At this point, usually only 5 or 2 mL of aniline, for the preparation of SNSP25 in particular, was added to the mixture and sonicated for another 2 min so that the monomer was able to site-selectively coat the surface of the CNT.²⁰ The aniline, because of its hydrophobicity, is able to strongly interact with the surfactant along the CNT, forming a thin film. Next, only 0.65 or 0.2 g of ammonium persulfate (NH₄)₂S₂O₈ (AP), for the preparation of SNSP25 in particular, dissolved in 50 mL of 1 M hydrochloric acid was added to initiate the polymerization, followed by a further 60 min of sonication. Acid doping (1 M HCl) is required for forming the conductive states of PANI. In addition, positively charged particles such as CNTs adsorb anionic surfactants more easily in an acidic media. Because high-powered ultrasonic radiation alone cannot create sufficient free radicals for reaction, a reduced amount of ammonium persulfate (AP) is added. Many authors reported^{11–15} a monomer:initiator ratio of 1:1.25 used in the polymerization. In this study, a significantly reduced monomer:initiator ratio of 1:0.12 was used (even less with SNSP25, 1:0.1), leading to the polymerization reaction being an excess of monomer or oligomers. The amount of AP used is thus the minimum amount needed to initiate the polymerization process and create the conductive state of polyaniline. During the ultrasonically initiated reaction (without any chemical initiator added), a brown solution formed, which is indicative of the presence of such an oligomer. With the addition of the minimum amount of AP (0.65 g), the dark suspension becomes green, indicating polymerization of aniline and the formation of a conductive emeraldine salt (ES) layer around CNTs, this being samples SNSP10 and SNSP25, respectively, as presented in Table 1. The composite was obtained by filtering and washing the obtained product with distilled water to remove the surfactant, and then with ethanol, methanol and diethyl ether to remove oligomers;¹⁹ the product was subsequently vacuum-dried. As a comparison, to prepare the neat polymer, the same procedure was undertaken in the absence of CNTs.

For comparison, composites of MWNT/PANI were prepared by conventional stirring, using the same formulation as sample SNSP10 that was made with ultrasonic irradiation, resulting in sample MNCP10, shown in Table 1. As a final variation to elucidate the

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Table 1. Sample Identification and Description of PANI-Encapsulated CNT Samples

sample ID	description
SNSP10	sonicated nanotubes, sonication polymerized, 0.65 g of AP, CNT/PANI ratio:0.5 g/5 mL:0.10
SNSP25	sonicated nanotubes, sonication polymerized, 0.2 g of AP, CNT/PANI ratio:0.5 g/ 2 mL:0.25
SNCP10	sonicated nanotubes, chemically polymerized, 0.65 g of AP, CNT/PANI ratio: 0.5 g/5 mL:0.10
MNCP10	mixed nanotubes, chemically polymerized, 0.65 g of AP, CNT/PANI ratio: 0.5 g/5 mL:0.10

ultrasonic effect, we prepared another set of samples with sonication at only the first stage for better dispersion of CNTs in SDS solution, before transferring them to a beaker for polymerization using conventional stirring (sample SNCP10).

Composite Solubility. Aniline was the only solvent able to suspend the previously mentioned nanocomposites, in concert with the sonicator, in minimal aniline, at a 50:50 ratio of each. The dissolved/suspended nanocomposite aniline solution was applied with a pipet onto a glass cover slide, or spin-coated followed by heating in a vacuum oven at 50 °C, to allow the aniline to evaporate for an hour, and then left overnight to harden. Thicker layers were achieved by repeating the previous procedure.

Characterization. Elemental mapping was performed using X-ray photoelectron spectroscopy (XPS) on a Kratos Axis Ultra device, with an Al monochromatic X-ray source (1486.6 eV). Survey spectra were acquired at 160 eV and region spectra at 20 eV pass energies, respectively. The morphology of MWNTs and the formation of the PANI thin layer were investigated by transmission electron microscopy (TEM) using a Philips TEM CM100 instrument operating at 100kV.

Fourier transform infrared (FTIR) spectra were recorded on a Thermo Nicolet Nexus 870 FTIR spectrometer. The spectra were collected in absorbance mode using a transmission cell, DTGS detector, with a resolution of 4 cm⁻¹ over 128 scans on KBr disks.

Raman spectroscopy was carried out using a Renishaw Model 1000 microprobe spectrometer equipped with a single grating and an electrically cooled CCD detector. Excitation was at 632.8 nm from a He-Ne laser, which was focused to a spot size of about 1 μm with a 50× objective. The laser power was about 5 mW at the sample for most samples, and the measurement time was 16 min.

The thermal stability of the composites was determined using a thermogravimetric analyzer (TGA 2950, TA Instruments). Nitrogen gas was used with a flow rate of 50 mL/min and a heating rate of 10 °C/min. Temperature calibration was performed with Ni as a standard.

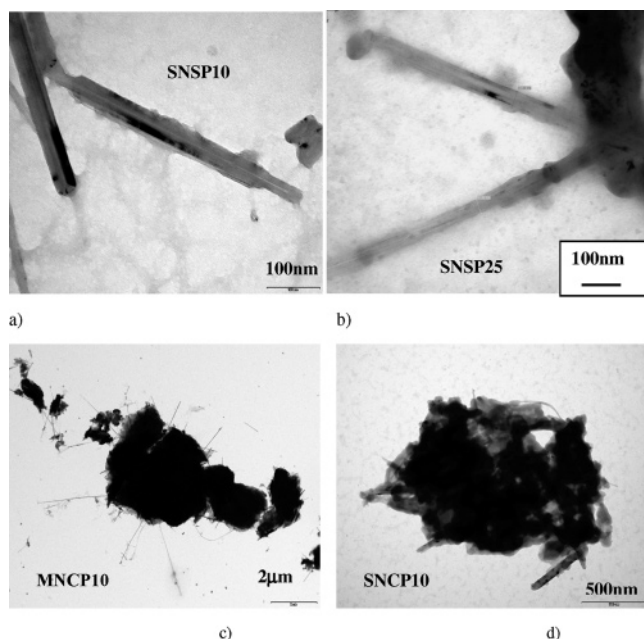


Figure 2. TEM images of different CNT/PANI composites.

The electrical conductivity of PANI and MWCNT/PANI composites was measured by the four-probe method at room temperature. In each case, compressed pellets were formed using a Graseby Specac Press at 10 t of pressure for 5 min. The film thickness was deduced using vernier callipers (Boyer Tool Company). The four-point probe linear conductivity measurement was used to determine DC electrical resistivity. The two faces of the compressed disc were measured, and an average determined. An in-house linear four-point probe device with a pin spacing of 1.0 mm was used to determine the electrical characteristics. A Keithley multimeter (Model 2400) was used to evaluate the voltage, and a constant current source was used to fix the current.

Results and Discussion

Effect of PANI Coating on the Surface Chemistry of CNTs. Morphology of PANI Coating around CNTs. The thickness and uniformity of the PANI coating produced by the different polymerization methods can be compared from the TEM images shown in Figure 2. From this figure, it is evident that the diameter of sample SNSP10 composites prepared by ultrasonication is between 38–50 nm. An increase in diameter from that of the TT CNTs (10–20 nm), shown in Figure 1, is indicative of the formation of a very thin, uniform layer of 10–15 nm around the CNTs. PANI consists mainly of aromatic rings on the polymer backbone, and these structures intrinsically have strong interactions with CNT surfaces due to π - π interactions.^{22,23}

With such a degree of potential interaction, PANI can clearly be encouraged to form intimate coatings around the CNTs. The use of ultrasonics ensures both dispersion of the CNTs in aqueous solution without agglomeration and prevention of coagulation of CNTs during emulsion polymerization. With an increase in concentration of CNTs in the composite SNSP25 sample, the coating becomes less uniform and partially covers the CNTs with a diameter between 31 and 40 nm.

To compare the effects of ultrasonication on the morphology of the PANI coating formed around CNTs, we obtained images for MNCP10 and SNCP10. Figure 2 shows agglomerates of CNTs formed in MNCP10; it is clear that polymerization took place in bulk rather than on the surface of the nanotubes, because formation of very large particles of polymers around the CNTs occurs that is due to an uneven dispersion of the CNTs. The average size of these polymer particles is around 1–4 μm, and closer examination of images of individual tubes (not presented here) shows no evidence of a polymer coating on the surface, with the PANI layer simply cloaking bundles of CNTs.

For the coating prepared with initial sonication of CNTs only (SNCP10), the images show smaller aggregated particle

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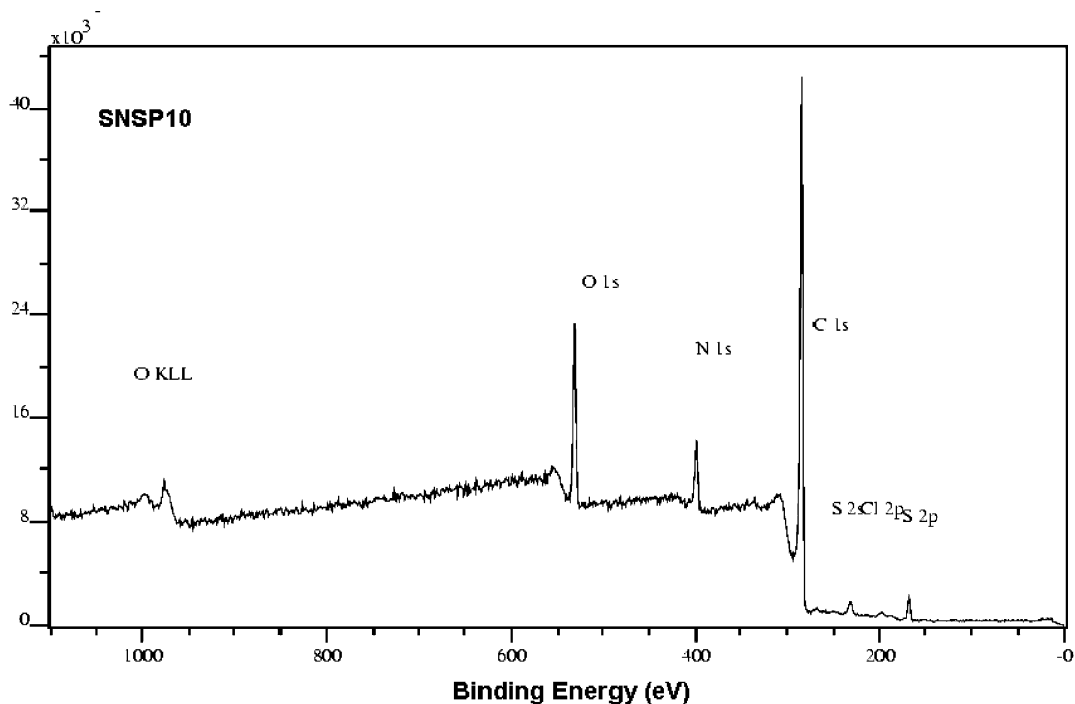


Figure 3. Survey XPS spectrum of SNSP10.

sizes of around 0.5–2 μm, with the particles being more dispersed than in the previous case, where there has been no sonication at all. However, there is still no dispersion between individual nanotubes due to the coagulation developed during emulsion polymerization. From the magnified image of the nanotubes (not shown here), the presence of some polymer coating on the surface was evident, but it is important to note that in both cases, the dispersion of encapsulated CNT was still not achieved. The polymerization procedure without the use of sonication allows the size of polymer particles to simply grow as they form, creating larger structures. Despite the similar chemical nature of the coating and potentially favorable interactions with the CNT, the surface morphology of encapsulated CNTs is quite dependent on the method of polymerization, with the preparation of well-dispersed CNTs having uniform coatings clearly requiring the ultrasonication process at both the dispersion and polymerization stages.

X-ray Photoelectron Spectroscopy (XPS) Studies. For quantitative estimation of chemical elements on the surface, XPS studies were undertaken. The survey spectrum of SNSP10 (Figure 3) exhibits three major peaks at 532, 400, and 285 eV, corresponding to O 1s, N 1s, and C 1s photoemission. Two minor peaks at 169 and 199 eV corresponding to S 2p and Cl 2p photoemission are also detected.²⁴ The survey spectra (not shown) of the as-received (AR) and thermally treated (TT) CNTs samples revealed only two major peaks, at about 534 and 284 eV, corresponding to O1s and C1s photoemission. Furthermore, atomic concentration of oxygen in TT CNTs is slightly higher at 0.98%, compared to the AR CNTs at only 0.59%.

Figure 4 reveals the representative plots of C1s and N1s peaks of sample SNSP25 in the range of 282–292 and 396–

404 eV, respectively. It is clear from the C1s peak that it exhibits a broad tail, and the common charge-corrected binding energies and corresponding bonds are summarized in Table 2. The nitrogen (N1s) envelope for sample SNSP25 also depicts a broad tail, and the bonds are assigned in Table 2 for all composite samples.²⁵

Atomic concentrations obtained from multiplexed spectra were used for the calculation of the ratios of carbon:nitrogen and chloride:nitrogen on the surface of PANI/CNTs composites, which are presented in Figure 5. As discussed, the thickness of the coating is also polymerization-process dependent. Therefore, the qualitative information of the coating thickness present in composite samples can be obtained by the evaluation of nitrogen from the PANI to carbon from the CNTs ratio.

From Figure 5, it is clear that SNSP25 has the highest C:N ratio and, ultimately, the thinner layer of PANI on the CNT surface, because of the greater concentration of CNTs and a concomitant reduction in amount of monomer. The changing C:N ratio is an indication that the thickness of the PANI coating is different on the surface of each sample and that the amount of the PANI and the coverage morphology is also dependent on the method of polymerization. The thin layer of coating that results from the sonication process enables carbon atoms to be detected by X-rays, whereas conventionally stirred samples lead to bulk PANI formation over a bundle of CNTs, which prevents the ready passage of X-rays. Samples prepared using ultrasonic polymerization are able to form better polymer-encapsulated CNT structures; this encapsulation can be thin and uniform, in agreement with TEM studies. Xia et al. also reported similar findings²⁰ in terms of the formation of PBA-encapsulated CNTs. In

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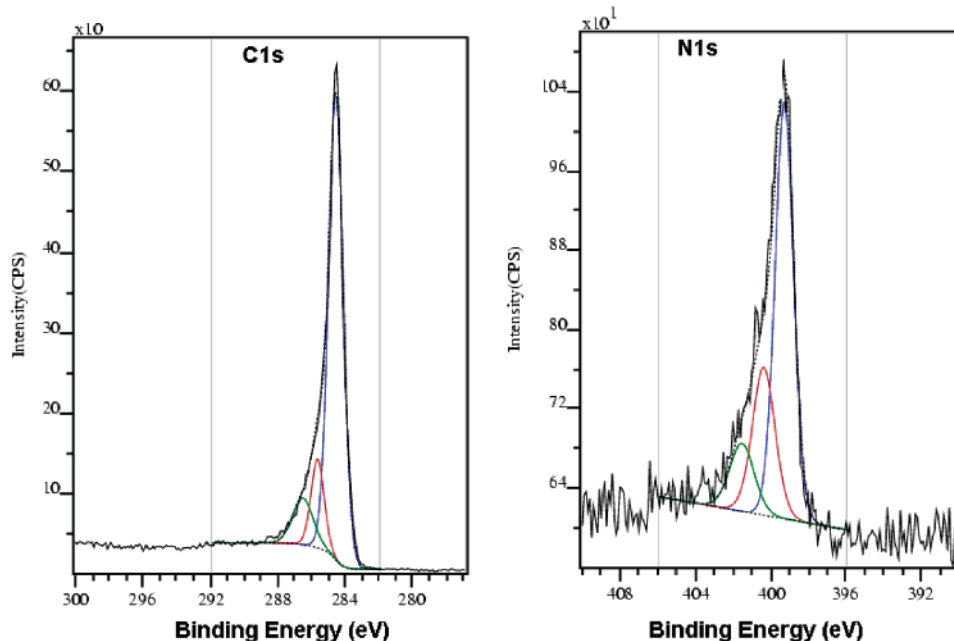


Figure 4. Carbon (C1s) and Nitrogen (N1s) XPS envelopes for SNSP25 sample.

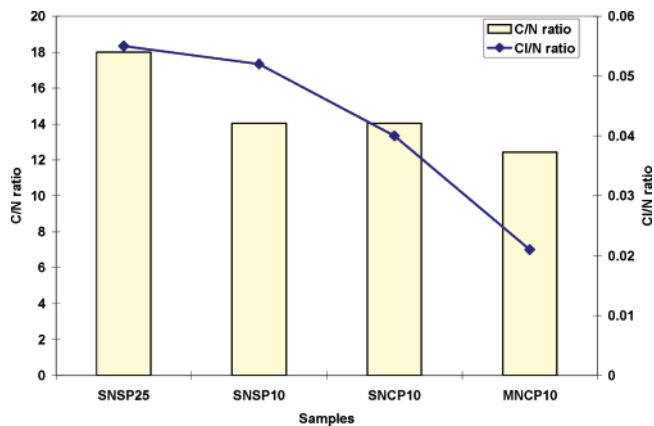


Figure 5. C/N and Cl/N ratio of composites prepared both using ultrasonication and by conventional stirring methods.

Table 2. XPS Binding Energies and Relevant Bond Assignment

peak	bond assignment	binding energy (eV)
N 1s 1	N-H	399.35
N 1s 2	NH ₂	400.45
N 1s 3	NH ₃ ⁺	401.77
C 1s 1	sp ² C=C	284.60
C 1s 2	sp ³ C-C	285.79
C 1s 3	C-O/C-NH ₂	286.85

contrast, polymerization with no sonication forms more bulklike polymers and coats a bundle of CNTs, forming round particles rather than long, thin tubes. It is important to note that under conventional stirring, the aggregates of CNT are difficult to break apart, resulting in the reduction of surface area of the nanoparticles¹⁹ and preventing their encapsulation. Along with the C:N ratio, the chloride:nitrogen ratio was determined here in order to evaluate the effect of the method of polymerization on the proposed interaction between composite components. Smith et al.¹⁷ proposed that the chloride:nitrogen ratio should not change when CNTs are added to the emeraldine salt (ES) form of PANI if nitrogen content is used as a reference. They found, however, that this ratio decreases because of the competitive reaction

of CNTs with chloride ion in the presence of CNTs. Given that in the present study all the samples are prepared and washed the same way, possible contamination with HCl is the same for all samples, and the effect of the polymerization method on the competitive reaction of the CNTs and chloride can thus be evaluated by the magnitude of the chloride:nitrogen ratio. From Figure 5, it is clear that during conventional, stirring polymerization, the Cl:N ratio decreases because of the exchange of chloride ions with carbon nanotubes, compared to that obtained during ultrasonically initiated polymerization, leading to less-conductive materials.

Analysis of Chemical Structure by Infrared Spectroscopy. FTIR spectra of polymer-encapsulated CNT are shown in Figure 6. FTIR studies were also carried out on the neat PANI, obtained by sonication, and assignments of various peaks are listed in Table 3.²⁶ Compared with thermally treated CNTs, each composite has new peaks corresponding to the polymer coating around CNTs. From the spectrum of thermally treated CNTs, two major peaks at ~ 1631 and ~ 1100 cm⁻¹ are observed and can be assigned to the stretching mode of quinone groups and C-O bonds, respectively. However, the composites exhibit additional features attributable to the characteristics of the polymer.

Comparing spectra of PANI and PANI/CNTs, we can observe a significant decrease in the intensity of the peaks in the composites prepared by the sonication process due to the adhesion of the polymer to the MWNTs and the restricted motion of the chains in polyaniline that results.

Second, the intensity of the peak at 1631 cm⁻¹ for thermally treated CNTs compared to the composite is more pronounced. The corresponding absorbance is according to the trend

$$\text{SNSP25} > \text{SNSP10} > \text{SNCP10} \approx \text{MNCP10}$$

indicating that the carbon:polymer ratio is much higher in composites prepared by the sonication process and that SNSP25 has a thinner coating on the surface than SNSP10.

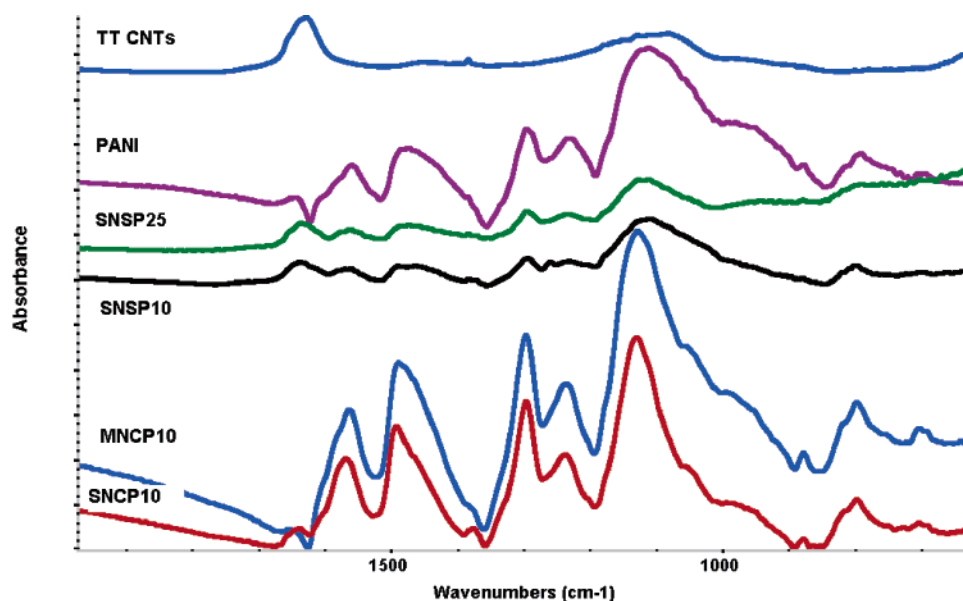


Figure 6. FTIR spectra of PANI/CNT composites with (a) PANI, (b) TT CNT, (c) SNSP25, (d) SNSP10, (e) MNCP10, and (f) SNCP10.

Table 3. Vibrational Frequencies of PANI

interatomic bond	vibrational frequency (cm ⁻¹)
N-H	1647
C-C of quinoid ring	1561
C-C of benzene ring	1480
C-N	1294
C-H of benzene ring	1232
C-H of quinoid ring	1112
benzene and quinoid ring C-H	793

The same effect is evident in SNCP10 and MNCP10, where the nanotubes are covered by a large amount of polymer, with a resulting decrease in absorbance at 1631 cm^{-1} , all of which correlate well with the results from XPS and TEM.

All PANI-encapsulated CNTs exhibit the clear presence of both the quinoid ring and benzenoid ring, which show bands at ~ 1580 and $\sim 1480\text{ cm}^{-1}$, respectively. In this process, the PANI exists in its primary doped form, called the emeraldine salt, in which two structures coexist: the polaronic form and bipolaronic structure. The polaronic form has mainly benzene ring structure, with HCl doped along the polymer chain.²⁷ The bipolaronic structure is similar; however, the benzene can be replaced with a quinoid ring, which gives the polymer more conductivity.²⁸ The benzenoid band is always more intense than that of the quinoid band in the emeraldine salt. The PANI-encapsulated CNT spectra arising from the quinoid units of samples SNSP25 and SNSP10 are more intense than in the pure PANI.^{11,14} It is important to note that the calculated value of I_{1580}/I_{1480} increases with the increasing CNT content in the PANI-encapsulated CNT and thus with decreasing thickness of the PANI layer. The surface of the CNTs may interact strongly with PANI, especially through the quinoid ring, indicative of the presence of the more conductive bipolaronic structure. This may also be related to the charge-transfer process between the components of the system, which can cause an

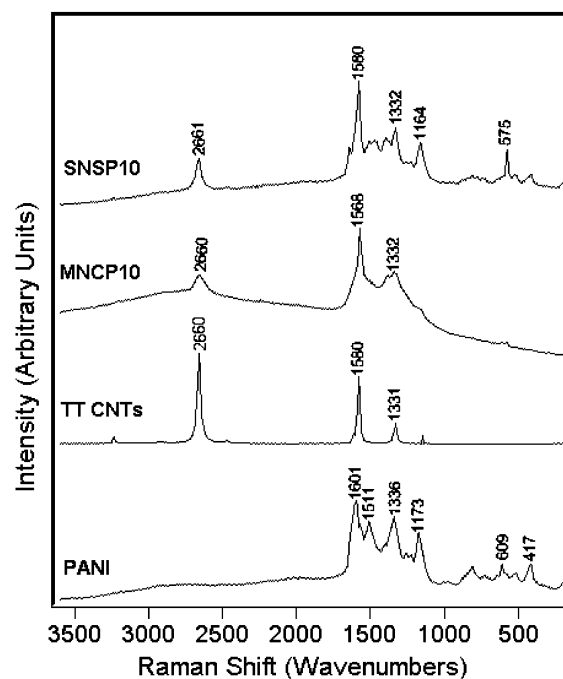


Figure 7. Raman spectra of thermally treated CNTs, neat PANI, and composites, prepared by different polymerization methods.

increase in the conductivity of the resulting composite.¹⁴ Application of the in situ polymerization process by ultrasonication in both dispersion and polymerization steps allows the aniline to have a more site-selective interaction with CNTs, increasing the effective degree of electron delocalization and enhancing the conductivity of the polymer chains.

Investigations Using Raman Spectroscopy. Raman spectroscopy can be used to measure the vibrational spectra of nonpolar bonds such as crystal-lattice vibrations and carbon-carbon bonds. This technique, in combination with FTIR spectroscopy, can give a more complete picture of the sample bonding structure. The spectra for the encapsulated CNTs, the thermally treated CNTs, and the neat polymer are shown in Figure 7. The spectrum of TT CNTs exhibits a strong band at $\sim 1580\text{ cm}^{-1}$ (G-band), indicative of the amount of

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perfectly crystalline CNTs. The other band at $\sim 1330\text{ cm}^{-1}$ (D-band) can be related to the presence of disorder in the graphite lattice. The same effect of defects can be seen in the second-order spectra at $\sim 2659\text{ cm}^{-1}$, an overtone of the first-order mode at 1330 cm^{-1} .^{29,30} The spectrum of neat PANI shows bands at 1597, 1507, 1337, and 1172 cm^{-1} corresponding to C–C stretching of the benzenoid ring, N–H bending of the bipolaronic structure, C–N⁺ stretching of the bipolaron structure, and C–H bending of the benzenoid ring, respectively.^{31–33}

In the case of PANI-encapsulated CNTs (sample SNSP10), more peaks characteristic of both the PANI and CNTs are evident. The PANI-encapsulated CNTs have almost the same spectra as the neat polymer, albeit with these peaks originating from the carbon structure of CNTs. A new peak is observed at 1466 cm^{-1} for the encapsulated CNTs sample (SNSP10), corresponding to the C=N stretching of the quinoid ring. This peak is not present in the neat polymer or in the composite prepared by conventionally stirring MNCP10. In addition, the C–H bending of the benzenoid ring at 1173 cm^{-1} has shifted to 1166 cm^{-1} . Both of these changes are evidence that the composites prepared by ultrasonication are rich in quinoid rings, rather than benzenoid rings, as a result of specific polymer–CNT interaction. The aromatic structures are known to interact strongly with the plane of graphitic surfaces via π -stacking, but the observed increase in quinoid rings in the PANI-CNT structure indicates that the CNTs interact more strongly with the quinoid than with the benzene ring, in good agreement with the infrared results above. Interaction occurs because of the specific packing of the rigid PANI backbone into the platelike layers, whereas alkyl side chains fill the space between the layers.³⁴ CNTs clearly form intermolecular interactions with six-membered ring molecules such as benzene, and very effective π -stacking interactions of aromatic molecules may result in strong interactions with the graphitic sidewalls of CNTs.

Thermal Stability of CNT/PANI Composites. PANI is a hydrophilic molecule, because it consists of many amine groups, but it also has aromatic moieties in its backbone, and so most interactions arise between the π -bonds of the aromatic ring of PANI and graphitic structures of the CNTs.

Figure 8 shows the TGA traces of PANI prepared by ultrasonication and conventional stirring, together with related composites of PANI and CNT prepared by ultrasonication. From this figure, it is clear that decomposition of the neat PANI prepared by ultrasonication occurs in two steps. The first step takes place at approximately $270\text{ }^\circ\text{C}$, the decomposition of the acid dopant,¹⁴ and the second step at $464\text{ }^\circ\text{C}$, due to decomposition of the polymer chain. It is

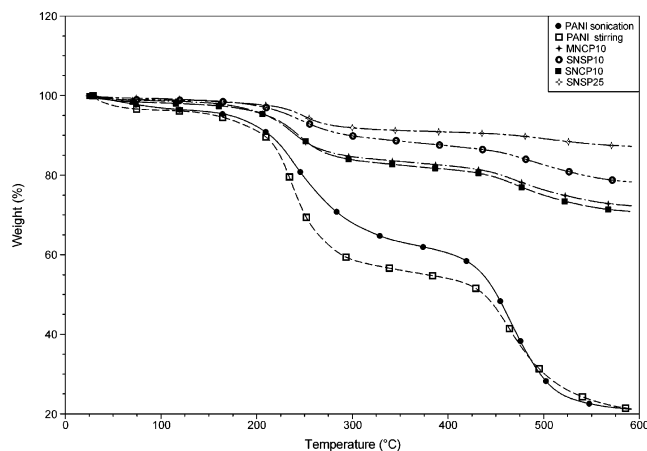


Figure 8. TGA traces of neat PANI and CNT/PANI composites.

Table 4. Conductivity of PANI, CNT, and PANI/CNT Composites

sample	conductivity (S/cm)
PANI 0.65 g of AP	0.1
AR CNTs	20.6
TT CNTs	27.3
SNSP10	6.3
SNSP25	27.0
MNCP10	4.6
SNCP10	2.5

also important to note that the neat PANI prepared by ultrasonication is more thermally stable than PANI prepared by conventional stirring, as the decomposition temperature of PANI in the composites is greater. Thermal stability is dependent on the method of polymerization and the concentration of CNTs. As discussed previously, the shift in decomposition temperature is related to the interaction between the polymer and CNT surface; composite MNCP10 in particular shows a temperature shift of $\sim 10\text{ }^\circ\text{C}$ relative to the neat PANI produced by ultrasonication. Although the CNTs are not well-coated in the case of composites produced by conventional stirring (as can be seen in the TEM images), some interactions in the resulting composites appear to still exist, and there is an increase in thermal stability.

Composites prepared by sonication polymerization show better thermal stability than those prepared by conventional stirring, the most significant shift in the temperature of decomposition is detected in SNSP25, the composite with the highest concentration of CNTs. The thermal stability increased by $\sim 35\text{ }^\circ\text{C}$; additional evidence of these strong interactions of the polymers with the surface of CNTs.

Conductivity of CNT/PANI Composites. The electrical conductivity measurements of PANI, CNTs, and MWNT/PANI composites were carried out using a four-point probe apparatus, and the room-temperature conductivities of the above-mentioned materials are presented in Table 4. The conductivity of the pure PANI is 0.15 S cm^{-1} , and the table shows that the TT CNTs are more conductive than the AR CNTs. In CNTs, electrons are free to flow along the tube from the sp^2 hybridized structure, whereas a sample without thermal treatment exhibits reduced conductivity due to the range of impurities present. Composite samples prepared using CNTs and PANI with full sonication show a higher conductivity than samples with partial or no sonication at all. However, the coating layer in SNSP25 is thin and only

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partially covers the CNT, so the CNT surface itself is thus pretty exposed and involved in the conductive process. Findings from FTIR that the quinoid:benzenoid ratio is significantly higher in SNSP25 than SNSP10 is also in the good agreement with the difference in their conductivity. The conductivity of MWNT/PANI composites prepared by in situ inverse microemulsion¹⁴ have been reported to have values approaching that of pure MWNTs, 0.20 S cm^{-1} . This is in good agreement with our findings, but the level of conductivity is much higher; for example, with sample SNSP25 sharing a conductivity of some 27.02 S cm^{-1} . Room-temperature conductivity thus increased by an order of magnitude compared to that of PANI. Sonication of CNT prevents their agglomeration and produces more uniform polymer coatings without the coagulation of CNTs within the polymer. Electrons flow through the composite because the CNT is a good electron acceptor and aniline a good electron donor,^{35,36} and an increase in conductivity can thus be attributed to increased interactions between quinoid units of PANI and CNTs, promoted by ultrasonicated polymerization.

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Conclusions

In summary, in situ polymerization allows the monomer to site-selectively interact with the CNT surface, producing an enclosed nanotube wrapped and stabilized by polymer. By comparison with pure PANI, the MWNT/PANI nanocomposites show enhanced electric conductivity and thermal stability. Such characteristics, which appear inherent to MWNT/PANI core-shell nanowires, provide new potential applications in a number of scientific and technological fields, such as photovoltaic and other devices. In contrast, polymerization with no sonication forms agglomerated polymers and it is now coated CNT bundles forming bulk, multicomponent structures rather than long thin polymer-wrapped tubes. Thus it appears that ultrasonic processing is necessary at a number of stages to stimulate and achieve appropriate nanoscale coverage.

Acknowledgment. This work is supported by the Australian Research Council, Discovery Scheme (DP0449692), and the International Science Linkages program established under the Australian Government's innovation statement Backing Australia's Ability (CG060005). We thank Mr. Yui Yue for carrying out ultrasonication, TGA and FTIR and Ms. Tara Schiller for Raman spectroscopy tests.

CM061344C