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Electrical properties of multi-walled carbon nanotube/polypyrrole nanocables: percolation-dominated conductivity

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Abstract

A multi-walled carbon nanotube/polypyrrole (CNT/PPy) nanocomposite with cable-like morphology has been synthesized using an *in situ* chemical oxidative polymerization method. The temperature dependences of the conductivity and magnetoresistance (MR) have been studied. We found that the room temperature conductivity increases by two orders of magnitude with increasing carbon nanotube weight percentage. The temperature dependence of the conductivity follows a charge–energy-limited tunnelling model ($\ln \sigma(T) \propto T^{-1/2}$) and indicates clearly that the CNT weight percentages of 9.1 and 13.04 wt% are below the percolation threshold and 23.1 wt% is beyond the percolation threshold. At low temperatures the 23.1 wt% composite shows a negative MR whereas the pure PPy shows a positive one. The results reveal that at the percolation threshold the complete CNT conductive paths can change and enhance dramatically the electrical properties of the CNT/PPy composites.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In recent years, composites based on carbon nanotubes (CNTs) and conjugated polymers have been of great interest for developing new classes of multi-functional advanced materials [1–10]. Several good review articles have been written on doped CNTs and their composites (e.g. see [1]). For instance, highly efficient organic photovoltaic cells based on composite materials of CNTs with poly(3-octylthiophene) [2] or poly(*p*-phenylene vinylene) [3] have been reported. Composite structures of single-walled CNTs and poly(3-octylthiophene) have shown excellent field emission properties [4]. It has been found that aligned multi-walled CNT–polypyrrole (PPy) composite films

offer an exciting combination of exceptional charge storage capacities (several times larger than that of either CNT or PPy) and have potential applications in supercapacitors and secondary batteries [5]. In addition, significant enhancement of the mechanical properties of composites of fluorinated single-walled CNTs and poly(ethylene oxide) have also been observed [6, 7]. The enhancement of the properties of composites is usually attributed to the interfacial interactions between the CNT and the polymer matrix [4, 7–10].

By now, a large number of papers have been published on the synthesis and properties of composite films and nanostructures based on CNTs and conducting polymers [11–16]. For example, by studying the room temperature conductivity of composite films of CNTs and various polymers, Coleman *et al* [11], Blanchet *et al* [12] and Ramasubramaniam *et al* [13] have observed the percolative behaviour in these

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composites. The temperature dependence of the conductivity of composites [8, 12, 14, 16] the magnetoresistance (MR) of pure CNTs [17, 18] and conducting PPy [19] have also been reported; however, further discussions about the percolative behaviour in composites from the point of view of the temperature dependence of the conductivity and MR have not been presented.

In this work, we have synthesized a nanotubular material of multi-walled CNTs coated with PPy by using an *in situ* chemical oxidative polymerization directed with the cationic surfactant cetyltrimethylammonium bromide (CTAB). The temperature dependence of the conductivity and low-temperature MR are explored, which further verifies the percolative character in this composite system.

2. Experimental

The multi-walled CNTs used were synthesized through ethylene chemical vapour deposition (CVD) [20]. A total of 0.124 g CTAB and 6 mg CNTs were placed in 31 ml deionized water and sonicated for over 2 h to obtain well-dispersed suspensions. This enhanced the disaggregation of any nanotube bundles with dramatically reduced tube breakage. They were then cooled down to 0–5°. A solution of 0.06 ml pyrrole monomer was added to the above suspensions and sonicated for 5 min, and then 6.25 ml pre-cooled deionized water containing 0.204 g ammonium persulphate (APS) was added to the above mixture and sonicated for another 2 min. Then the reaction mixture was left standing in the refrigerator at 0–5° for 24 h. The resulting black precipitate was filtered and washed with distilled water and ethanol several times. The resulting precipitate was then dried under vacuum at room temperature for 24 h.

Four samples were prepared by means of this process. The weight percentage of CNTs in the CNT/PPy composites was 0, 9.1, 13.04 and 23.1 wt%. The weight percentage of CNTs in the composite was obtained as follows: in our experiments, we use the definition of CNT mass ratio to polymer monomer, e.g. a 9.1 wt% sample means that the CNT and pyrrole monomer mass ratio is 2 : 20 [$2/(2+20) \times 100\% = 9.1\%$, 3 : 20 for 13.04 wt% and 6 : 20 for 23.1 wt%], so that the actual weight percentage of CNTs in the composites is slightly different after polymerization. The samples had a rectangular shape (approximately $8.0 \times 2.0 \times 0.12$ mm), obtained by applying a hydraulic pressure of about 10 MPa. The electrical conductivity and MR were measured using a standard four-probe method using a Physical Property Measurement System from Quantum Design, USA.

3. Results and discussion

3.1. Morphology

The structure of the resulting CNT/PPy composites was identified through the infrared (IR) spectrum, as shown in figure 1. The CNT/PPy composites directed by CTAB showed nearly identical numbers and positions of the main IR bands. The broad band at 3000–3500 cm^{-1} could be attributed to N–H and C–H stretching vibrations [21, 22]. The strong peaks near 1195 and 920 cm^{-1} indicate the doping state of PPy [21, 22].

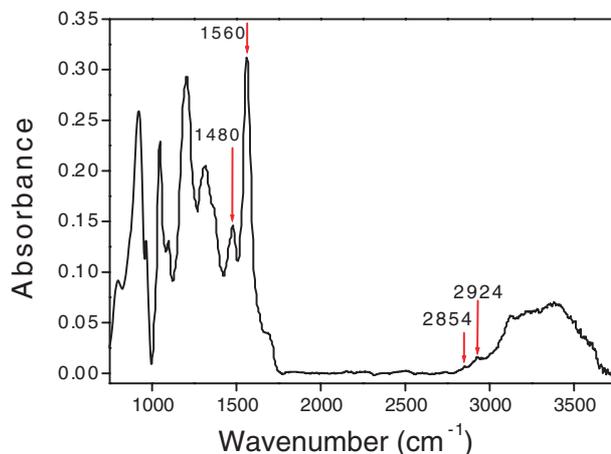


Figure 1. IR spectrum of CNT/PPy composites.

The peaks at 1050 cm^{-1} and 1315 cm^{-1} are attributable to C–H deformation vibrations and C–N stretching vibrations [21, 22], respectively. In addition, the peak around 1560 cm^{-1} and the peak around 1480 cm^{-1} correspond to the antisymmetric and symmetric ring-stretching modes, respectively, [23]. There are two very weak peaks around 2924 and 2854 cm^{-1} attributable to the stretching vibration mode of the methyl and methylene, indicating that the surfactants had been almost completely eliminated from the nanocables.

The nanotubular morphology was verified using a scanning electron microscope (SEM) and a transmission electron microscope (TEM). Figure 2 displays typical SEM and TEM images of CNT/PPy nanocables with a coaxial structure. The TEM image shows that PPy is tightly coated on the surface of the CNTs. The average outer diameter is about 16 nm for the pure multi-walled CNT and is about 29 nm, 38 nm and 50 nm for 23.1 wt%, 13.04 wt% and 9.1 wt% composites, respectively. It is worth noting that the main advantage of this *in situ* chemical oxidative polymerization method directed with CTAB is in increasing the solubility of CNTs in water and achieving a more homogeneous dispersion of CNTs in the PPy matrix. In addition, we note that we can get a composite with a higher percentage of CNT with our method, but the uniformity attained does not satisfy us.

3.2. Electrical conductivity

Figure 3 shows the room temperature conductivity, $\sigma(300\text{ K})$, of the CNT/PPy nanocables. It is obviously that the conductivity of the nanocables increases rapidly with increasing CNT weight percentage. The room temperature conductivity of the pure PPy is $7.3 \times 10^{-3} \text{ S cm}^{-1}$; however, for a 23.1 wt% composite, it is 0.23 S cm^{-1} , which represents an increase by two orders of magnitude as compared with pure PPy. For comparison, the $\sigma(300\text{ K})$ value of the pressed pellet of CNTs is about 2 S cm^{-1} . The increase in $\sigma(300\text{ K})$ as a function of the CNT mass fraction is usually due to the introduction of conducting CNT paths to the polymer, indicative of percolative behaviour [11–13]. Coleman *et al* [11] have reported that the percolation threshold is about 8.4 wt% for composite films of CNTs and poly(*p*-phenylenevinylene-*co*-2,5-dioctoxy-*m*-phenylenevinylene).

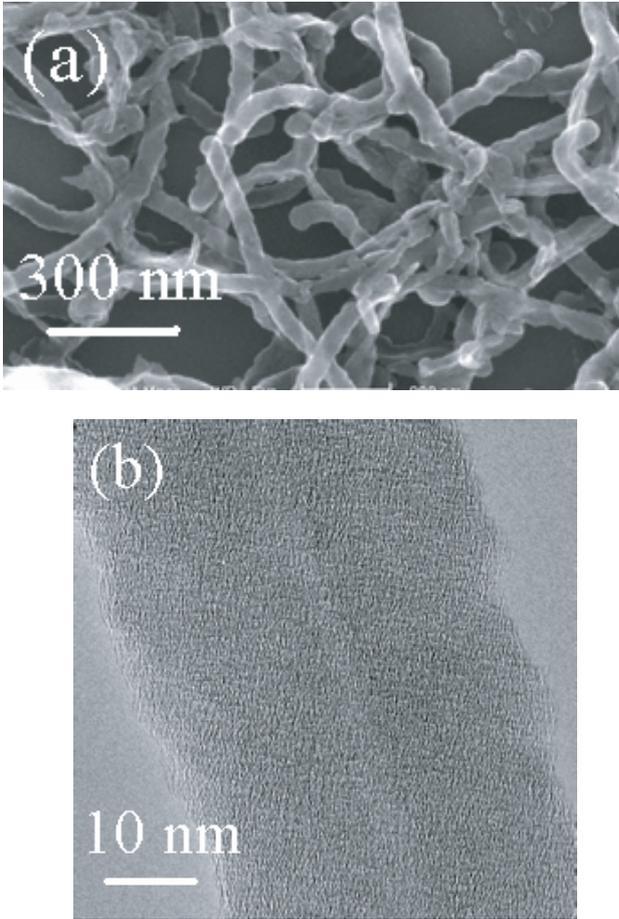


Figure 2. (a) Typical SEM and (b) TEM images of the 9.1 wt% CNT/PPy nanocables.

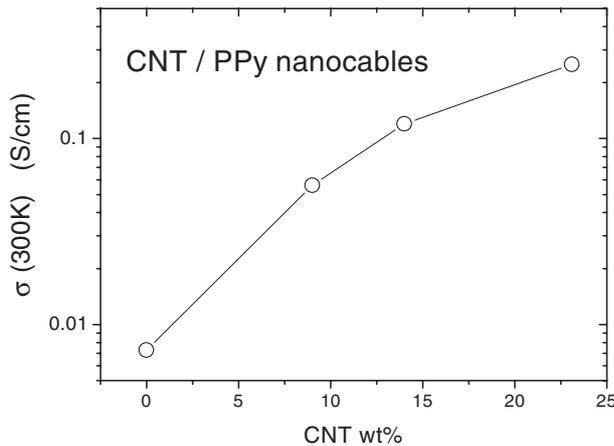


Figure 3. Room temperature conductivity of CNT/PPy nanocables versus the weight percentage of CNT.

In order to further verify the percolative behaviour and explore how the CNTs affect the composite's conductivity, we measured the temperature dependence of the conductivity of CNT/PPy nanocables, as shown in figure 4. The temperature dependence of the conductivity becomes weaker and weaker with increasing CNT content and shows $\ln \sigma(T) \propto T^{-1/2}$ behaviour, which can be interpreted in terms of charge-energy-limited tunnelling (CELT) model, which describes the charge

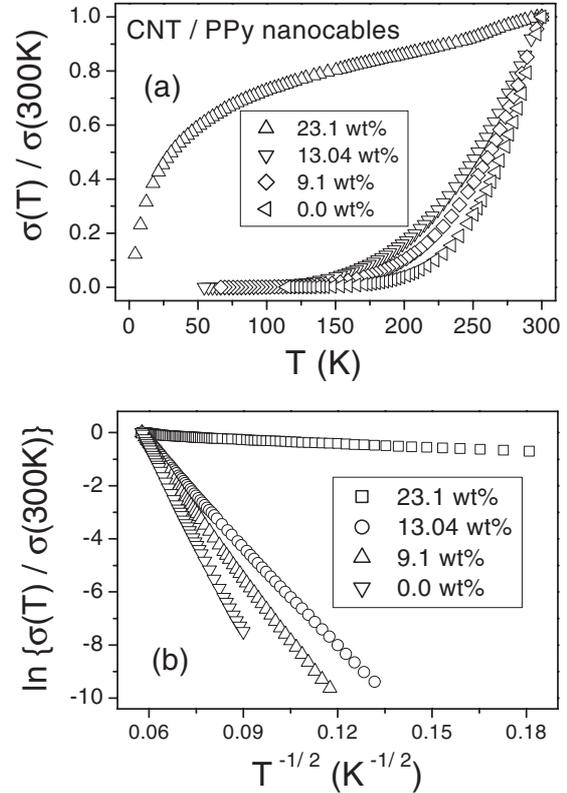


Figure 4. Temperature dependence of the conductivity for CNT/PPy nanocables with different T weight percentages of CNT.

Table 1. Experimental values of the room temperature conductivity, $\sigma(300\text{ K})$, and D for CNT/PPy nanocables.

Sample	0.0 wt% (pure PPy)	9.1 wt%	13.04 wt%	23.1 wt%
$\sigma(300\text{ K})$ (S cm^{-1})	7.3×10^{-3}	5.6×10^{-2}	9.6×10^{-2}	2.3×10^{-1}
D (K)	5.6×10^4	2.7×10^4	1.6×10^4	68 (>244 K) 23 (<244 K)

transport in a system of metallic particles embedded in a dielectric matrix [24]:

$$\sigma(T) = \sigma_0 \exp \left[- \left(\frac{D}{T} \right)^{1/2} \right]$$

where D is a constant and depends on the barrier height for the charge carriers and the charging energy. The values of D for the four samples are calculated from the slope of the $\ln \sigma(T)$ versus $T^{-1/2}$ plot, as shown in table 1. From table 1, we can see when the weight percentage of CNTs is 9.1 and 13.04 wt%, the D values are of the same order of magnitude as that of pure PPy ($D \sim 10^4$ K). However, for the 23.1 wt% composite, the D value is very small ($D < 10^2$ K), which indicates that the barrier height of the composite is significantly reduced when the CNT content is sufficiently high.

From the viewpoint of percolation theory, which deals with the effect of varying the number of interconnections present in a random system [25], the CNT weight percentages of 9.1 and 13.04 wt% are below the percolation threshold, no

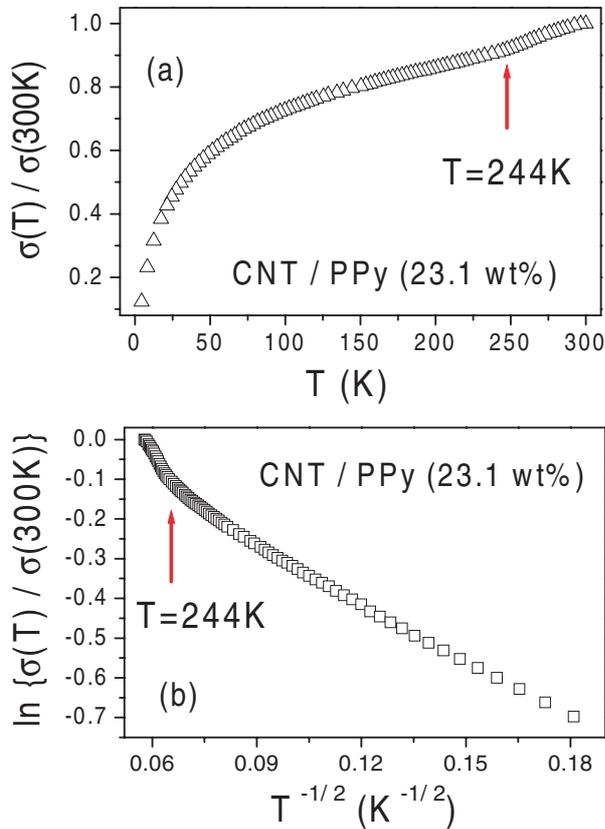


Figure 5. Temperature dependence of the conductivity for the 23.1 wt% CNT/PPy composite; it is noted that there is a kink at about 244 K.

complete CNT conductive paths occurring in such composites, and so the electronic transport is still dominated by the polymer. We note that partial conductive CNT paths in these composites play a key role in enhancing the room temperature conductivity as compared with pure PPy. However, for the 23.1 wt% composite, figure 4(a) strongly indicates that the weight percentage is above the percolation threshold (which is estimated between 15 and 20 wt%), and the complete CNT conductive paths dominate the electronic transport. Therefore, the temperature dependence of the conductivity of the 23.1 wt% composite shown in figure 4(a) is not like that of pure PPy but is similar to that of a CNT film [26]. The small D value shows similar behaviour. In addition, for the 23.1 wt% sample, a kink is observed at about 244 K in the temperature dependence of conductivity. This kink is shown clearly in figure 5. The D value above the kink temperature is 68 K, and at lower temperatures (<244 K) it is 23 K. The kink possibly comes from the competition between CNTs and PPy and demonstrates that the electronic transport of the composite is controlled more and more by the CNT conductive network with decreasing temperature because the CNTs have a much weaker temperature dependence of conductivity than that does the polymer [12] due to a larger π -conjugated structure (i.e. a larger localization length) in the CNTs.

Here, it is noted that the method of incorporation of CNTs in the polymer will deeply influence the electrical conductivity and other properties of the composite by changing the interfacial interactions between the two components [7–10].

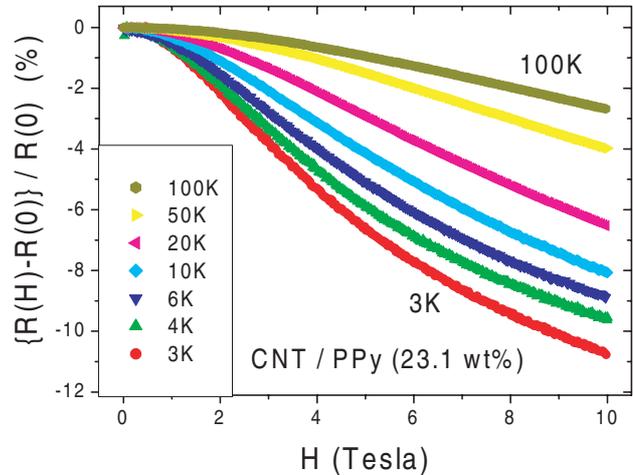


Figure 6. MR of the 23.1 wt% CNT/PPy composite at different temperatures.

For example, the conductivity of the *in situ* polymerized composites is higher than that of the *ex situ* polymerized samples [8]. The strength and modulus of a polystyrene coated carbon nanofibre composite are higher than those of uncoated composites [7].

3.3. Magnetoresistance

In order to verify the onset of the complete CNT conductive paths in the composite, we measured the low temperature MR. As we know, for a pure PPy sample, the low temperature MR (defined as $\{R(H) - R(0)\}/R(0)$) is positive [19, 27] because applying a magnetic field results in a shrinkage in the overlap of the wave function of the electrons and reduces the average hopping length [27, 28]. This positive MR with strong magnetic field and temperature dependences has been predicted in the theory of variable range hopping (VRH) [27–29]: $\ln(R(H)/R(0)) \propto H^2 T^{-y}$, where $y = \frac{3}{4}$ for three-dimensional VRH and $y = \frac{3}{2}$ for one-dimensional VRH.

However, for the CNT/PPy nanocomposites, the results are different. Figure 6 shows the MR for the 23.1 wt% composite at various temperatures between 3 and 100 K (the MR values of the 9.1 and 13.04 wt% composites are not measured because their low temperature resistances are too large). It has been observed that the MR is negative and the magnitude of the MR increases with decreasing temperature. Similar behaviours have also been observed for bulk samples composed of CNTs [17, 18]. Due to a larger localization length in CNTs, the above-mentioned wave function shrinkage effect in a weak magnetic field (positive MR) is not significant for CNTs. However, another effect, namely a quantum interference effect [30, 31], plays a key role. Nguyen *et al* [30] and Sivan *et al* [31] have evaluated a quantum interference effect on VRH, and found that the modification of the quantum interference between many possible hopping paths in the magnetic field would lead to a negative MR: $\text{MR} = \{R(H) - R(0)\}/R(0) \propto -H^x T^{-y}$, where $x = 1$ or 2 [30, 31], $y = 3/(1 + d)$ and d is the effective dimensionality of the hopping conduction.

Now, we can see the pure PPy shows a positive MR at low temperatures, whereas the pure CNT shows a negative one. If the electronic transport in the composite is still dominated

by the polymer, the MR will be positive; otherwise, it will be negative. So, the negative MR of the 23.1 wt% CNT/PPy composite provides strong evidence to support the claim that the electronic transport at low temperatures is dominated by the CNT conductive network, which is consistent with the temperature dependence of conductivity.

4. Conclusion

In summary, CNT/PPy nanocables have been synthesized through an *in situ* chemical oxidative polymerization method. With increasing nanotube weight percentage, an enhancement of conductivity by two orders of magnitude is observed and is indicative of percolative character. The percolative behaviour is further verified by the temperature dependence of the conductivity and the low temperature negative MR. The percolation threshold in these composites is estimated at between 15 and 20 wt%. In addition, a competition between CNTs and PPy is also observed in the 23.1 wt% composite.

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