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Cite as: Appl. Phys. Lett. **85**, 1796 (2004); <https://doi.org/10.1063/1.1786370>

Submitted: 12 January 2004 . Accepted: 25 June 2004 . Published Online: 13 September 2004

Yunze Long, Zhaojia Chen, Xuetong Zhang, Jin Zhang, and Zhongfan Liu



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Synthesis and electrical properties of carbon nanotube polyaniline composites

Yunze Long^{a)} and Zhaojia Chen^{b)}

Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

Xuetong Zhang, Jin Zhang, and Zhongfan Liu

College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

(Received 12 January 2004; accepted 25 June 2004)

A multiwalled carbon nanotube/polyaniline composite with cablelike morphology has been synthesized by an *in situ* chemical oxidative polymerization directed with cationic surfactant cetyltrimethylammonium bromide. It is interestingly found that with increasing carbon nanotube loading from 0 to 24.8 wt%, the conductivity increases by two orders of magnitude and the Mott's characteristic temperature T_0 which depends on the hopping barrier decreases by three orders of magnitude. Furthermore, the low-temperature magnetoresistance has also changed the sign from positive to negative. The results reveal a strong coupling between the carbon nanotube and the tightly coated polymer chains, which enhances the average localization length and the electronic properties of the composites. © 2004 American Institute of Physics. [DOI: 10.1063/1.1786370]

Carbon nanotubes (CNTs) have excellent thermal stability, unique mechanical, and electronic properties and are of great interest in developing classes of multifunctional materials. In recent years, composites based on CNTs and conjugated polymers especially display the possibility of the resulting materials with some superior characteristics. For example, highly efficient organic photovoltaic cells based on composite materials of CNT with poly(3-octylthiophene) were reported.¹ It is found that aligned multiwalled CNT-polyppyrrrole composite films offer an exciting combination of exceptional charge storage capacities and improved device response times.² Significant enhancement of the mechanical properties for CNT-polytyrene composite was also observed.³

Polyaniline (PANI) is one of the most promising conducting polymers because of its relatively high conductivity, environmental stability, lower cost, and easy processibility. Recently, Wei *et al.*⁴ reported the use of sulfonated multiwalled CNTs as the self-assembled "template" for formation of PANI nanostructures. It is also reported that PANI-CNT composites show enhanced electronic properties (e.g., enhanced conductivity).⁵⁻⁷ However, previous studies focus mainly on the synthesis of CNT/conducting polymer composite films or nanostructures,³⁻⁷ further studies of the electrical properties such as magnetoresistance and temperature dependent conductivity have not been extensively explored.

In this letter, we have synthesized a nanotubular material of multiwalled CNT coated with PANI by using an *in situ* chemical oxidative polymerization method. The effects of a CNT on the conductivity and magnetoresistance of CNT/PANI composites are discussed in detail.

Multiwalled CNTs, used in this work were synthesized by ethylene chemical vapor deposition using Al_2O_3 -supported Fe catalysts.⁸ Aniline monomer and CNTs were purified before preparation. Ammonium persulfate was used without further purification. CNT/PANI composites

were synthesized by *in situ* chemical oxidative polymerization directed with cationic surfactant cetyltrimethylammonium bromide (CTAB). In a typical synthesis process, 0.125 g CTAB and 6.60 mg CNT were added into 30 ml 1.0 M HCl solutions and sonicated for 2 h to obtain well-dispersed suspensions, then cooled down to 1–5 °C. A precooled solution of 0.06 ml aniline monomer and 6.25 ml 1.0 M HCl containing 0.147 g ammonium persulfate were added sequentially to the above suspensions. The reaction mixture was sonicated for 2 min, and then left standing in the refrigerator at 1–5 °C for 24 h. After that, the resulting black precipitate was filtered and washed with distilled water and methanol several times, and finally dried at room temperature in a dynamic vacuum for 24 h.

The structure of the resulting CNT/PANI composites was identified by a Raman spectrum, scanning electron microscope (SEM), and transmission electron microscope (TEM). Figure 1 displays the typical SEM and TEM images of CNT/PANI composites with a coaxial structure. It is clear that PANI is tightly coated on the surface of CNTs. The diameter of CNT/PANI composites is much larger than that of CNT, i.e., about 10 nm in diameter for CNT and 30–50 nm for composites were observed. It is worth noting that the main advantage of this *in situ* chemical oxidative polymerization method directed with CTAB is to increase the solubility of CNT in water and achieve a more homogeneous dispersion of CNT in polymer matrix.

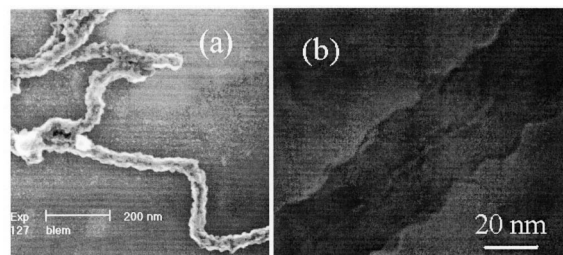


FIG. 1. (a) Typical SEM and (b) TEM images of CNT/PANI composites.

^{a)}Electronic mail: longyz@pc282.iphy.ac.cn

^{b)}Author to whom correspondence should be addressed; electronic mail: zjchen@aphy.iphy.ac.cn

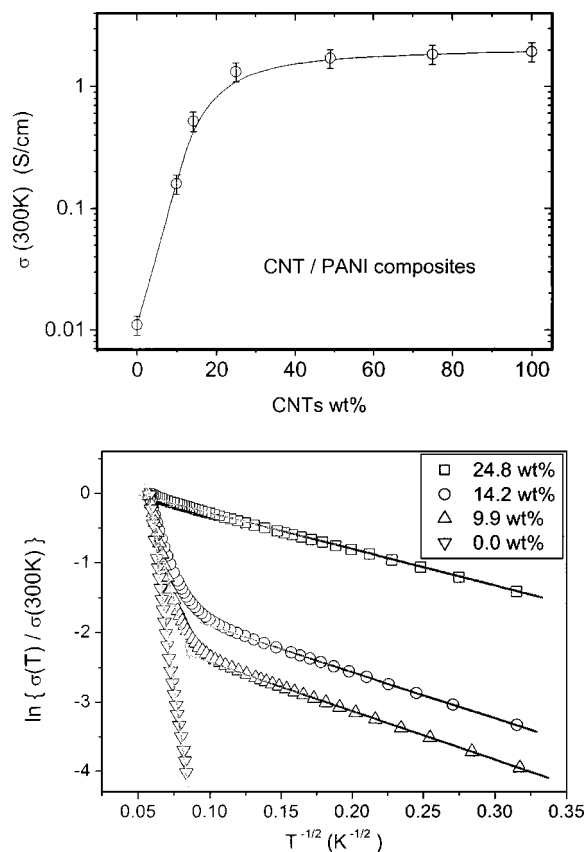


FIG. 2. (a) A semilogarithmic plot of the room-temperature conductivity of the composite vs the CNT loading. (b) Temperature dependence of conductivity of the composites.

Samples used in electrical conductivity and magnetoresistance measurements have a rectangular shape (approximately $8.0 \times 2.0 \times 0.12$ mm) obtained by applying a hydraulic pressure about 10 MPa. Electrical conductivity and magnetoresistance were measured by a standard four-probe method using a Physical Property Measurement System [PPMS) from Quantum Design, USA].

Figure 2(a) shows the room-temperature conductivity of CNT/PANI composites as a function of the CNT loading. The conductivity of the pure PANI and CNT is 1.1×10^{-2} and 2 S/cm, respectively. Up to 15 wt %, the conductivity of the composite increases rapidly with an increase of the CNT loading. For the 24.8 wt % composite, the conductivity is 1.27 S/cm, which increases by two orders of magnitude as compared with PANI. At higher concentrations, the increase of conductivity plateaus, namely, the curve asymptotically reaches toward pure nanotubes (2 S/cm). Here, we note that in many published articles,⁷ the loading of nanotubes is small (less than 5%) whereas the conductivity becomes saturated, which is possibly due to the highly conductive carbon nanotubes (5.1×10^4 S/cm).⁷

In order to explore how the CNTs affect the composite's conductivity, we measured the temperature dependence of conductivity, as shown in Fig. 2(b). The temperature dependence of conductivity becomes weaker and weaker with increasing CNT loading. Furthermore, the 9.9 and the 14.2 wt % composites show a different behavior compared with the pure PANI or the 24.8 wt % composite. As we know, the conductivity of PANI films or pellets^{9–11} usually follows the quasi one-dimensional variable-range hopping (1D–VRH) model:^{12,13} $\sigma(T) = \sigma_0 \exp[-(T_0/T)^{1/2}]$, where σ_0

TABLE I. Experimental values of the room-temperature conductivity and the characteristic Mott temperature T_0 for CNT/PANI composites.

Sample (wt %)	$\sigma(300\text{K})$ (S/cm)	$T_0(\text{K})$ (300–130 K)	$T_0(\text{K})$ (<130 K)
0.0 (pure PANI)	1.1×10^{-2}	2.8×10^4	2.8×10^4
9.9	0.10	8.7×10^3	51
14.2	0.58	3.6×10^3	44
24.8	1.27	32	32

is a constant, $T_0 = 24/[\pi k_B L_c^3 N(E_F)]$ is the characteristic Mott temperature which generally depends on the hopping barrier, k_B is the Boltzmann constant, L_c is the localization length, and $N(E_F)$ is the density of the states at the Fermi level. Figure 2(b) indicates that the pure PANI and the 24.8 wt % composite follow the $T^{-1/2}$ -hopping law very well in the measured temperature range. However, for both the 9.9 and the 14.2 wt % composites, there is an obvious kink at about 130 K. The T_0 values at higher temperatures (T_{0H}) and lower temperatures (T_{0L}) reveal this change evidently. As shown in Table I, the (T_{0H}) values (8.7×10^3 K and 3.6×10^3 K for the 9.9 wt % and the 14.2 wt % composites, respectively) decrease by two orders of magnitude as compared with the T_{0L} values (51 K and 44 K for the 9.9 wt % and the 14.2 wt % composites, respectively). The data demonstrate that the conductivity of the composites is dominated by CNT at lower temperatures.

A polymer composite with CNTs, can distinctly enhance the electronic properties of the polymer and even the CNT. For example, it is reported that the conductivity of PANI/CNT composites is higher than that of the pressed CNT (or PANI).⁵ The possible reason is attributed to the fact that there is some interaction between the CNT and the polymer chains. However, the nature of this interaction is not very clear yet. Maser *et al.*⁵ pointed out that out that the synthesis by an *in situ* process leads to effective site-selective interactions between the quinoid ring of the PANI and the CNT, which facilitate charge-transfer processes between the two components.

From the view point of the electrons, we argue that the “site-selective interactions” result from the fact that the localization length L_c of CNT is much larger than that of PANI. For highly conducting PANI, its localization length is about 4–7 nm;⁹ for poorly conducting or “amorphous” PANI, the localization length is no more than 2 nm.¹⁰ However, the localization length of CNT is usually larger than 10 nm due to a larger π -conjugated structure in carbon nanotubes. This length is also larger than the diameter of CNT (~ 10 nm), which suggests that the charge delocalization in transverse direction can overstep the bounds of CNTs. Therefore, CNT is tightly coated with polymer chains, the coupling (partial overlap of the wave functions of electrons) between the CNT and polymer chains is possibly becoming strong and enhances the average localization length of the composite. In fact, $T_0 = 24/[\pi k_B L_c^3 N(E_F)]$ tells us $L_c \propto 1/T_0^{1/3}$, while the T_0 value decreases with increasing CNT content (as shown in Table I), that means the average L_c of the composite increases with increasing CNT content. So there is no wonder that CNTs gradually control the electronic transport in the composites especially with increasing the CNT loading and at lower temperatures. This point of view is also supported by the magnetoresistance results (see the following text). Here, it is worth noting that the coupling between CNT and

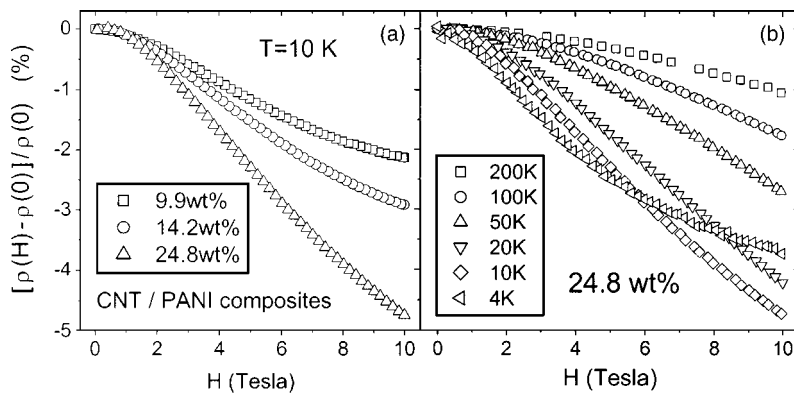


FIG. 3. (a) Magnetoresistance of the composites with different CNT loading at 10 K. (b) Negative magnetoresistance of CNT/PANI composite (24.8 wt %) at different temperatures.

polymer chains is deeply affected by the ways to incorporate a CNT with a polymer. For instance, the electrical properties of the *in situ* polymerized composites are better than that of the *ex situ* polymerized samples.⁵

The magnetoresistance of hopping systems arises from two effects. Applying a magnetic field results in a contraction of the wave functions of electrons and reduces the average hopping length.¹³ This corresponds to a positive magnetoresistance: $\ln[\rho(H)/\rho(0)] = t \cdot (L_c/L_H)^4 \cdot (T_0/T)^y \propto H^2 \cdot T^y$, where t is a constant, $L_H = (C\hbar/eH)^{1/2}$ is the magnetic length, the exponent $y=3/4$ for three-dimensional (3D)-VRH and $y=3/2$ for 1D-VRH. On the other hand, if a quantum interference effect on VRH is evaluated, Shklovskii *et al.*^{14,15} found that the modification of the quantum interference between many possible hopping paths in the magnetic field would lead to a negative magnetoresistance: $[\rho(H) - \rho(0)]/\rho(0) \propto -H^x \cdot T^{-y}$, where $x=1$ or 2 ,^{14,15} $y=3/4$ for 3D-VRH and $y=3/2$ for 1D-VRH.

Due to a small localization length of PANI, i.e., a small average hopping length $R_h = (3/8)(T_0/T)^{1/4}L_c$, the wave function shrinkage effect (a large positive MR) in PANI is evident and has been widely observed in PANI films and pellets.¹⁶ However, this effect is usually not evident in a CNT because of a much larger localization length. In recent years, a large negative magnetoresistance was widely reported for CNT films, mat and pellets at weak magnetic fields,¹⁷ and was interpreted in terms of the quantum interference effect. Figure 3(a) shows the magnetoresistance of CNT/PANI composites with different CNT content at 10 K. Figure 3(b) shows magnetoresistance of the 24.8 wt% sample at different temperatures. The negative magnetoresistance provides a strong evidence to support that the average localization length of the composites is obviously enhanced and the electronic transport is dominated by CNT, which is consistent with the above analysis. In addition, the magnetoresistance becomes more and more negative with increasing CNT content or decreasing temperature (except at very low temperatures). At higher magnetic fields ($H > 9$ T), the absolute value of magnetoresistance at 4 K is smaller than that at 10 K and 20 K, which is possibly due to the wave function shrinkage effect.¹⁷

In summary, CNT/PANI composites have been synthesized by an *in situ* chemical oxidative polymerization

method directed with cationic surfactant cetytrimethylammonium bromide. With increase of the CNT content from 0 to 24.8 wt % the conductivity increases by two orders of magnitude and becomes weakly temperature dependent, and the low-temperature magnetoresistance has also changed its sign from positive to negative. The reason is attributed to the strong coupling between CNT and the tightly coated PANI chains, which enhances the localization length and electronic properties of CNT/PANI composites.

This project was supported by National Natural Science Foundation of China (Grant No. 10374107).

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