

# Magnetoresistance of carbon nanotube-polypyrrole composite yarns

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## ABSTRACT

Three types of samples, carbon nanotube yarn and carbon nanotube-polypyrrole composite yarns had been investigated by measurement of the electrical conductivity as a function of temperature and magnetic field. The conductivity was well explained by 3D Mott variable range hopping (VRH) law at  $T < 100$  K. Both positive and negative magnetoresistance (MR) were observed by increasing magnetic field. The MR data were analyzed based a theoretical model. A quadratic positive and negative MR was observed for three samples. It was found that the localization length decreases with applied magnetic field while the density of states increases. The increasing of the density of states induces increasing the number of available energy states for hopping. Thus the electron hopping probability increases in between sites with the shorter distance that results to small the average hopping length.

## 1. Introduction

In recent years, carbon nanotubes (CNTs) have been of great interest due to very good electrical, chemical and mechanical properties and much research have been done on their synthesis method and properties [1,2]. These properties make them promising for a broad range of applications such as electronic nano-devices, biosensors, chemical micro-sensors and energy storage [3]. Recently, yarn microstructures were made to make better use of the CNT features [4–6]. The composite of CNT and the conducting polymers such as polyacetylene (PA), polyaniline (PANI), polypyrrole (PPy) and polythiophenes (PTs) were highly regarded. Therefore, their transport properties have been studied by using chemical doping in order to improving their physical, chemical and mechanical properties [7,8]. The heterogeneous systems such as CNT, conducting polymer are neither fully amorphous nor completely crystalline [9]. The electrical transport in disorder systems are described by the phenomena such as quasi-one dimensional transport, localization effects, hopping and tunnelling transport [10], and percolation [11]. Results show that the conductivity varies by temperature and applying magnetic [12–15].

In this paper, three types of pristine CNT and carbon nanotube-polypyrrole (CNT/PPy) composite yarns were studied by measurement of the electrical conductivity as a function of temperature and magnetic field. Samples were prepared by the electrochemical (CNT/PPy Elec. Chem.) and chemical (CNT/PPy Chem.) polymerization of pyrrole on the surface and within the Multi-Wall CNT. Results show that the

temperature dependence of conductivity is well explained by 3D Mott-VRH model at the temperature of the smaller than 100 K. The magnetic field dependence of MR is investigated by calculated physical parameters such as the localization length, density of states, and the average hopping length.

## 2. Results and discussion

The temperature dependence of the resistivity,  $\rho$  (T), has been shown in the inset of Fig. 1 for the CNT yarn, the electrochemically, and the chemically prepared CNT/PPy yarns in the absence of a magnetic field. It can be seen that the resistivity of the CNT/PPy yarns were smaller than the resistivity of pristine CNT yarn. For these systems, the temperature dependence of the conductivity of yarns is explained at  $T < 100$  K by Mott's law, which is the exponential temperature dependence characteristic of variable range hopping (VRH) model [11]. Based on this model, the number of available energy states for hopping decrease with decreasing thermal energy  $k_B T$  and this leads to the following expression for the conductivity [11]

$$\sigma(T) = \sigma_0 \exp \left[ - \left( \frac{T_{Mott}}{T} \right)^\gamma \right] \quad (1)$$

where  $\gamma = 1/(1 + d)$  and  $d = 1, 2$  and  $3$  is hopping dimension. The pre-exponential  $\sigma_0$  represents the conductivity at low temperatures and it is temperature independent [11].  $T$  is the temperature.  $T_{Mott}$  called the Mott characteristic temperature, which is related to the effective energy

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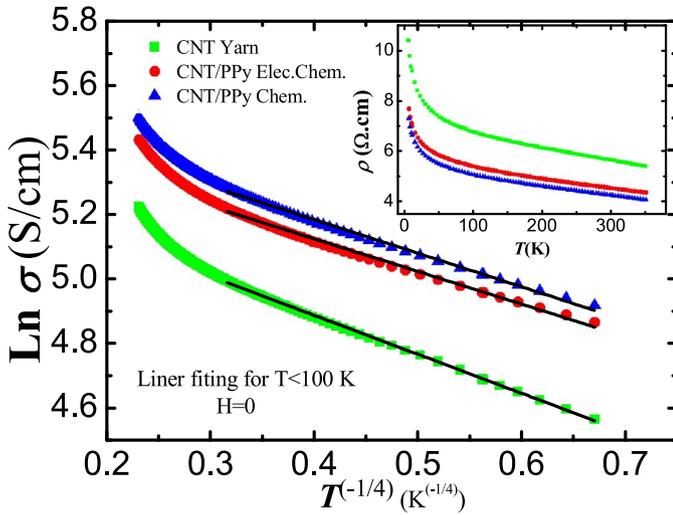


Fig. 1.  $\text{Ln } \sigma$  vs.  $T^{-1/4}$  for three samples in the absence of a magnetic field, the solid line shows the linear fitting for  $T < 100$  K. Inset: Temperature dependence of resistivity.

separations between localized states and it can be expressed as [11,12]:

$$T_{\text{Mott}} = \frac{24}{\pi k_B N(E_F) \xi^3} \quad (2)$$

Where  $N(E_F)$  is the density of states at the Fermi level,  $\xi$  is the localization length of the wave function for the localized charge carrier. Figs. 1 and 4 show  $\text{Ln } \sigma(T)$  vs.  $T^{-1/(1+d)}$  with  $d = 3$  for the pristine CNT yarn and the electrochemically and chemically prepared CNT-PPy yarns. For  $T < 100$  K, results of the conductivity are supported by the conduction mechanisms correspond to a 3D Mott-VRH model in all three samples.

The Mott's characterization temperature  $T_{\text{Mott}}$  and  $\sigma_0$  obtained from best fitted values and are shown in Table 1 for three samples. These results show that the effective energy needed for the hopping conduction for both the electrochemically and chemically prepared CNT/PPy yarns were smaller than that for the pristine CNT yarn by a factor 2. These values will be used to infer different parameters such as the localization length, the average hopping length and density of states at Fermi level later.

The magnetoresistance defined as  $\text{MR}\% = [\rho(B, T) - \rho(0, T)] / \rho(0, T) * 100\%$ , where  $\rho(0, T)$  and  $\rho(B, T)$  are the resistivities in the absence and presence of magnetic field  $B$ , respectively. Fig. 2 shows MR% versus magnetic field for CNT/PPy electrochemically prepared yarn at different temperatures. Results show both the positive and negative MR in various range of magnetic fields. There is a small positive MR at the low magnetic field and it reached to large negative values by increasing the magnetic field.

The mechanisms of the MR phenomena in the organic systems including CNTs and conducting polymers are explained by different models [13,14]. High increasing of the positive resistance (or the positive MR) with a magnetic field had been predicted by Shklovskii and Efros using the wave function shrinkage model (WFSM) [15]. According to this model, overlap probability between two sites are decreased by applied a magnetic field, so the resistivity increases in a magnetic field. At the weak magnetic field, based on the WFSM in the Mott-VRH regime, the MR is given by following expression [16]:

Table 1  
Conductivity parameters ( $T_{\text{Mott}}$  and  $\sigma_0$ ) of samples.

Sample	$T_{\text{Mott}}$ (K)	$\sigma_0$ (s/cm)
CNT Yarn	2.14	215.10
CNT/PPy Elec.Chem. Yarn	1.05	252.03
CNT/PPy Chem. Yarn	1.18	270.79

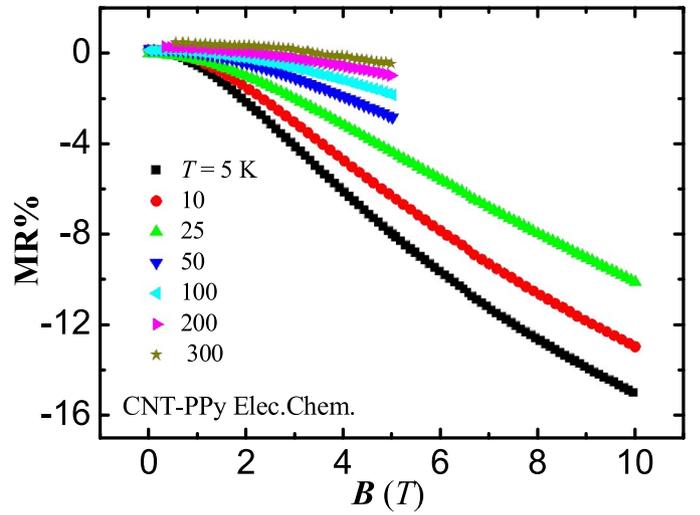


Fig. 2. Magnetic field dependence of MR for CNT/PPy electrochemically prepared yarn at different temperatures.

$$\text{MR} = \frac{\Delta\rho(B, T)}{\rho(0, T)} \approx t \frac{e^2 \xi^4}{36 \hbar^2} B^2 \left[ \frac{T_{\text{Mott}}}{T} \right]^{\frac{3}{4}} \quad (3)$$

Where  $t = 5/2016$  is a numerical constant. Also,  $\rho(0, T)$  is the resistivity at the zero magnetic fields and the temperature of  $T$ .  $e$  and  $\hbar$  are the electron charge and the reduced Planck's constant, respectively.

Fig. 3 show the MR% versus  $B^2$  at the temperature of 5 K. As can be seen in Fig. 3, the MR decreases linearly with increasing of magnetic field in positive MR region for all three samples and it is well described by Eq. (3) up to the  $B_D$  where a deviation occurs. The MR transition occurs from the positive to the negative with increasing magnetic field. The transition field is about 0.5, 0.3 and 0.7 T for the pristine CNT, the electrochemically, and the chemically prepared CNT/PPy yarns.

The localization length,  $\xi$ , can be obtained from the expression of

$$\xi^4 = \frac{36 \hbar^2}{te^2} \text{MR} \left[ \frac{T}{T_{\text{Mott}}} \right]^{\frac{3}{4}} B^{-2} \quad (4)$$

By using of Mott temperature values in Table 1 and the positive MR, localization length  $\xi$  for positive MR region was obtained. The  $\xi$  results as a function of magnetic field have been plotted in Fig. 4(a) for three samples at temperature of 5 K. The localization length decreases with increasing magnetic field. This behavior can be due to squeezed of the

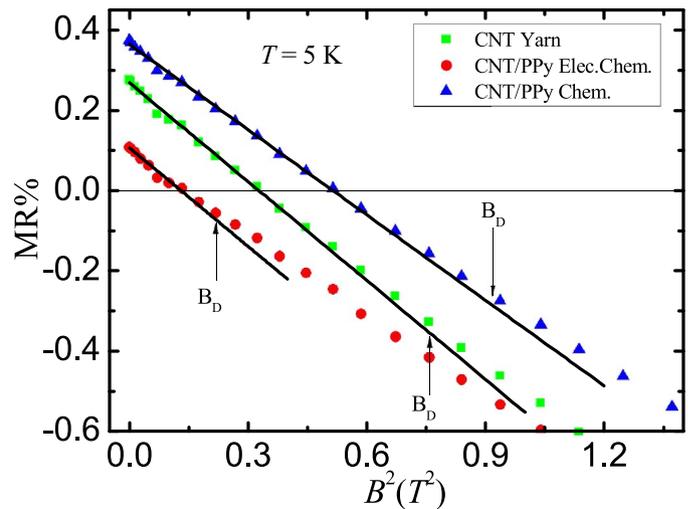


Fig. 3. MR% vs.  $B^2$  at the low magnetic field for three samples at temperature of 5 K.  $B_D$  is deviation magnetic field.

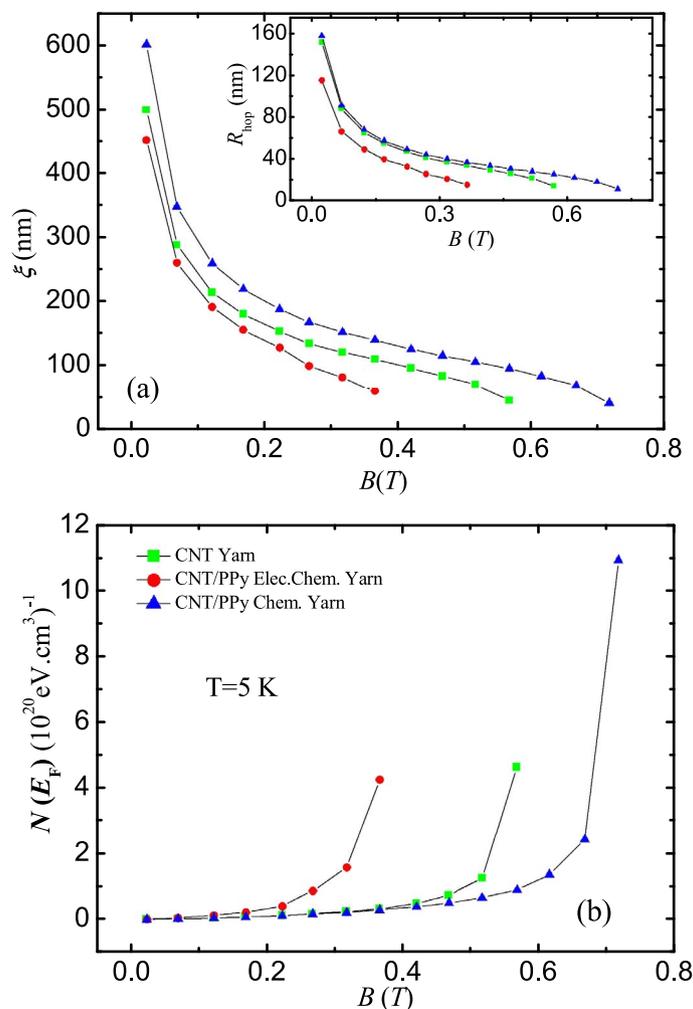


Fig. 4. (a) The localization length and (b) density of states at the Fermi level vs.  $B$  for three samples at temperature of 5 K for positive MR region. Average hopping length has been shown in the inset of Fig. 4(a).

wave function of the impurity electrons under the applied magnetic field. The average hopping length,  $R_{hop}$ , in Mott's VRH regime is also given by [17]:

$$R_{hop} = \left(\frac{3}{8}\right) \left(\frac{T_{Mott}}{T}\right)^y \xi \quad (5)$$

From the obtained results for the localization length, the average hopping length and the density of states at the Fermi level,  $N(E_F)$ , are obtained by using Eqs. (2) and (5). Fig. 4(b) shows  $N(E_F)$  (for positive MR) vs. magnetic field for three samples at temperature of 5 K. It can be seen from Fig. 4(b), the density of states at the Fermi level has increased with increasing magnetic field. As expected, the wave function of charge carriers was squeezed and leads to decreasing of the localization length with applied magnetic field result created new states around the Fermi level and caused to increases of the density of states. The average hopping length,  $R_{hop}$  (for the positive MR) has been shown in the inset of Fig. 4(a) as a function of magnetic field for all three samples. Results show that the average hopping length decreases with increasing magnetic field. The increasing of the density of states results to increasing the number of available energy states for hopping. Therefore, the electron hopping probability increases in between sites with the shorter distance and thus the average hopping length decreases. These results supported increasing the electrical resistivity and induced the positive MR.

In conclusion, results show that the resistivity of CNT/PPy yarns smaller than that of the pristine CNT yarn. The temperature dependence

of the conductivity is well explained by 3D Mott-VRH model at the temperature of the smaller than 100 K. All three samples of the CNT/PPy and the pristine CNT yarns show a small positive MR at low magnetic field and it reached to large negative values by increasing the magnetic field. The quadratic MR behavior observed at small magnetic fields. The wave function of charge carriers was squeezed by applied magnetic field and it results in decreasing of the localization length and increasing density of states. The increasing of the density of states enhanced the number of available energy states for hopping and thus the average hopping length decreases. Therefore, the resistivities of all samples are increased by applied magnetic field and results to induce the positive MR.

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