Reviews in Physics 3 (2018) 15–25

Contents lists available at ScienceDirect

Reviews in Physics

journal homepage: www.elsevier.com/locate/revip

A critical review of experimental results on low temperature charge transport in carbon nanotubes based composites

Ravi Bhatia[a,*], Kiran Kumari[b], Reena Rani[a], Anil Suri[c], Ushma Pahuja[d], Devinder Singh[d]

[a] Department of Physics, Guru Jambeshwar University of Science and Technology, Hisar 125001, India.
[b] Department of Chemistry, Birla Institute of Technology and Science (BITS), Pilani – K.K. Birla Goa Campus, 403726, India
[c] School of Materials Science and Engineering, Nanyang Technological University, Block N4.1 Nanyang Avenue, Singapore 639798, Singapore
[d] Department of Physics, Panjab University, Chandigarh 160014, India

ARTICLE INFO

Keywords:
Carbon nanotubes
Percolation threshold
Variable range hopping and fluctuation induced tunneling conduction

ABSTRACT

Owing to their low density, high aspect ratio and excellent charge transport properties, Carbon nanotubes (CNTs) are proven to be one of the best reinforcing materials in the fabrication of composite materials. CNTs dispersed in a non-conducting matrix is an interesting system for condensed matter physicists and materials scientists; CNT based composites offer an opportunity to physicists to design different experiments for fundamental studies while these composites are suitable for several technological applications that are of interest to materials scientists. In this review article, we summarize interesting experimental results on low temperature charge transport properties of composites based on multi-wall carbon nanotubes (MWCNTs) that have been reported in the past decade. In particular, we critically review different conduction mechanisms that have been identified through detailed investigations of charge transport characteristics as functions of MWCNT loading in the composites, temperature, and magnetic field.

Introduction

Carbon nanotubes (CNTs) exhibit a combination of exceptional mechanical and electrical properties that make them an important material for next generation technological applications to such areas as specific molecule detection of minute amounts, integrating basic components in the digital electronic systems, field emission displays, etc. [1–6]. Other than its technological significance, CNTs are quite fantastic one-dimensional molecular nanostructures for fundamental research, especially for the electronic transport studies owing to sp^2 hybridization of carbon atoms in a cylindrical honeycomb lattice. Electrical properties of CNTs have been widely studied in the last two decades [7–12]. It has been noticed that the charge transport in CNTs depends on a number of parameters including defects, doping of tubes, number of tube junctions, scattering centers, tube-tube interactions, number of walls, semiconducting/metallic nature, etc. These parameters play a major role in determining transport behavior that can vary from ballistic to diffusive. For an instance, room temperature (RT) resistivity for CNTs with a diameter of ~10 and 18 nm were estimated to be ~10 and 50 mΩ m, respectively [13,14]. Interestingly, at low temperatures an isolated CNT (with no defects) behaves like a one-dimensional quantum wire in which the electrons follow ballistic transport along the length of the wire (i.e. electrons travel without being scattered) [15]. This happens if the length of CNT (L) is small enough in comparison to the mean free path (L_m) and phase relaxation length (L_φ) of charge carrier. The mean free path is the distance which a carrier traverses between two consecutive scattering events.

* Corresponding author.
E-mail addresses: ravibhatia@gjust.org, bhatia.phy@gmail.com (R. Bhatia).

https://doi.org/10.1016/j.revip.2017.12.001

Available online 08 December 2017

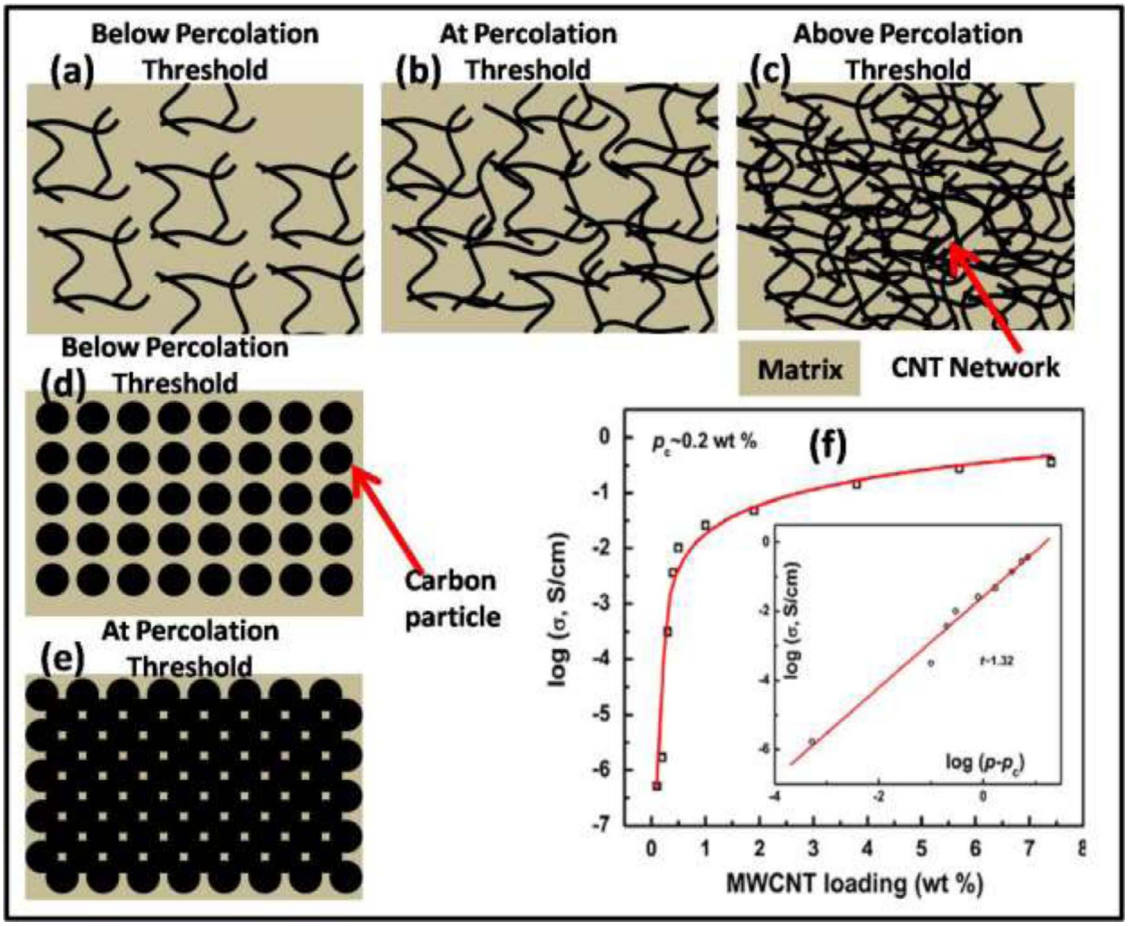

Fig. 1. Schematic illustration of electrical percolation in the case of (a-c) CNTs i.e. one dimensional material and (d-e) spherical carbon particles. Electrical percolation can be achieved at low wt fraction in CNT than in carbon particles. (f) Variation of dc electrical conductivity of MWCNT-PVC composites as a function of MWCNT loading (p). The dots represent the experimental points and the solid line is fit to$\sigma = \sigma_o(p - p_c)^t$. Electrical percolation at 0.2 wt.% of MWCNT is achieved. Inset. log σ vs. (p-p_c). The solid line is a linear fit to $\log\sigma = \log\sigma_o + t\log(p - p_c)$; the estimated value of the critical exponent t is 1.32. From ref. [21].

The distance over which the phase coherence is retained is called a phase relaxation length (or inelastic scattering length). This length scale is unaffected by elastic scatterings (scatterings where the scattering potential does not change the carrier energy but a phase shift occurs in the wavelength that is coherent). Further, when the length of CNT is larger than both phase coherence length and mean free path i.e. $L > > L_\phi > > L_m$, localization phenomenon is expected. In this case characteristic length scale is the localization length, L_c. Depending upon whether L_c is larger (smaller) than L_φ, the conductivity of the sample lies in weak (strong) localization regime. Another possibility can exist in which $L > > L_m > > L_\phi$, in this case classic transport is followed i.e. $R \propto L$ (Ohm's law). Other transport phenomena relevant to CNTs include universal conductance fluctuations, positive magneto conductance and wave function shrinkage in the presence of magnetic field. These can occur for samples in the localization regime. Bachtold et al. have also observed Aharnov-Bohm oscillations in the magneto conductivity of an isolated SWCNT under parallel field whereas hopping transport involving localization of carriers has been extensively reported in CNTs [8,16–19]. Positive magneto-conductance and wave function shrinkage have been reported for bulk forms of SWCNTs [17].

Further, CNTs are proved to be one of the most promising reinforcing materials owing to their low density and high aspect ratio. The inclusion of CNTs in polymer matrix in small quantities improves the mechanical, electrical and thermal properties [5,6]. We shall be considering only the improvement in the electrical properties of composites after the inclusion of CNTs. The room temperature electrical properties of CNT reinforced-polymer composites is governed by classical percolation theory [20], according to which the electrical conductivity of polymer composite depends on the content of the conducting filler material. The conductivity of the composite sample increases abruptly as the filler content just crosses a particular value p_c, called *percolation threshold* when the conductive path is established within the polymer matrix. The onset for establishing the conductive path is called *electrical percolation*. Apparently, the conductivity increases with further addition of filler material and saturates at high loading. The phenomenon of electrical percolation is explained using a schematic presentation in Fig. 1(a)–(e), which attempts to illustrate the importance of one dimensional nature of CNTs over spherical carbon particles in achieving low percolation threshold. A typical plot demonstrating the phenomenon of electrical percolation published by Vasanthkumar et al. [21] as presented in Fig. 1(f) that shows variation of room

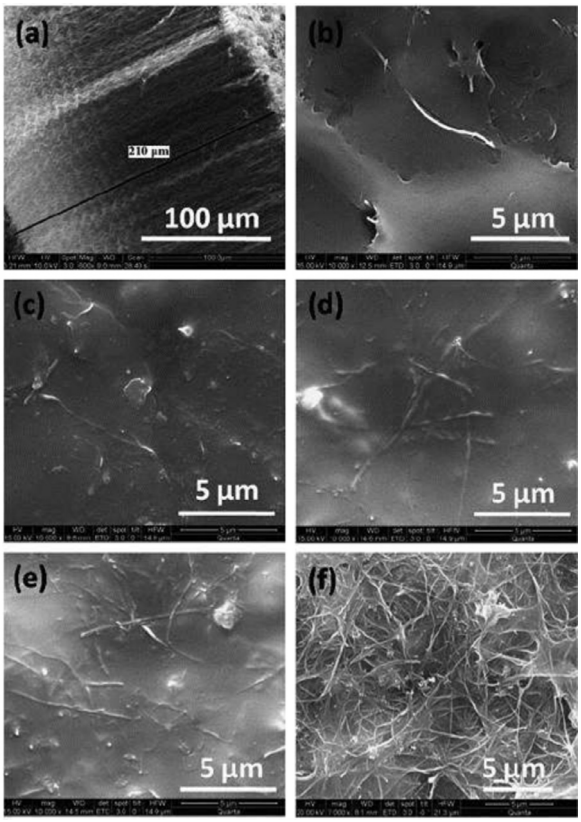

Fig. 2. SEM micrographs of (a) CVD-grown MWCNTs, and MWCNT–PVC composites of (b) 0.2 wt%, (c) 1.9 wt%, (d) 7.4 wt%, (e)16.7 wt% and (f) 44.4 wt%. From ref. [21].

temperature electrical conductivity (σ_{dc}) of MWCNT–polyvinyl chloride (PVC) nanocomposites as a function of MWCNT loading. It can be easily noticed that the σ_{dc} gets enhanced by a million times as MWCNT loading (p) increases from 0.1 to 7.4 wt.%. Further increase of MWCNT content to 44.4 wt.% gives rise to a saturated conductivity of 9 S/cm. The estimated value of p_c is 0.2 wt.%, which is obtained by fitting the electrical percolation equation i.e. $\sigma = \sigma_o(p - p_c)^t$, where t is a positive constant. It is worth pointing out that the reported value of p_c is generally less than 0.5 wt.% in the CNT-based composites, whereas for other fillers such as carbon particles it is as high as 16 wt.%. The electrical percolation in the CNT-polymer composite depends on factors like the degree of dispersion, aspect ratio, waviness of CNTs and on thickness of composite film, as well [22–24]. The physical dimensions and surface morphology of MWCNTs and MWCNT-PVC composite samples can be observed in Fig. 2 [21]. It can be seen that nanotubes possess high aspect ratios and the network of MWCNTs dispersed in the polymer composites improves with the loading of MWCNTs; the better connectivity of MWCNTs within the polymer with increase of MWCNT loading causes an improvement of conductivity from 1 µS/cm (0.1 wt.%) to 9 S/cm (44.4 wt.%).

Further, as the polymer composites are cooled to low temperatures (near the liquid helium temperature); various interesting charge transport phenomena have been observed and reported in composite materials. For example, a composite sample near the percolation threshold has finite conductivity at room temperature due to propagation of carriers through the barely connected network of conducting filler dispersed in polymer matrix. But as the temperature is decreased down to 1 K the conductivity decreases by several orders of magnitude, indicating towards activated-type transport [25]. The charge transport in the conducting filler-polymer composite films at temperatures ranging from 300 to 1 K has been described in terms of different known theoretical models such as variable range hopping, fluctuation induced tunneling, etc. [25–27]. In this review we shall restrict our consideration to experimental results of charge transport studies on carbon nanotubes-based polymer composites in the temperature ranging from 300 K to below liquid helium temperature, and discuss how the application of magnetic field affect their charge transport properties [28–30]. We shall review the interesting and unexpected experimental results in the context of low temperature charge transport in the MWCNT-based composite materials.

Theoretical background

Before we review the experimental results on the charge transport in CNT-based composite systems, it is worth providing an overview of the relevant physical phenomena and related parameters. The relevant charge transport mechanisms to this review are briefly described in the following sections, with special emphasis on the understanding of various charge transport regimes for

disordered materials. The role of magnetic field in modifying charge transport in the metallic regime is also discussed.

Transport regimes in CNT-based composite materials

Insulating regime

Variable range hopping

Variable range hopping is a theoretical model for low temperature conduction in strongly disordered systems with localized states. In the strongly disordered systems the electrical conductivity approaches zero at sufficiently low temperatures. The low temperature charge transport follows variable range hopping conduction in these materials, which is expressed by the following expression,

$$\sigma = \sigma_{\circ} \exp\left[\frac{-T_c}{T}\right]^n \tag{1}$$

The pre-factor $\sigma_{\bigcirc}$ has feeble temperature dependence. The value of exponent n depends on the extent of disorder, the dimensionality of the system, morphology, granularity and interaction between the charge carriers. The exponent n is positive and is dependent also strongly dependent on the shape of density of states (DOS) near the Fermi level. If the DOS takes the form of$N(E) = N_{\circ}|(E - E_F)|^{\nu}$, then $n = (\nu + 1)/(\nu + 4)$ in three dimensions and $n = (\nu + 1)/(\nu + 3)$ in two dimensions [31]. In three dimensions the DOS is constant (i.e. $\nu = 0$), Eq. (1) takes the form of the Mott variable range hopping for which $n = 1/4$. Hence the Mott VRH is expressed by following formula [32],

$$\sigma = \sigma_{Mott} \exp\left[\frac{-T_{Mott}}{T}\right]^{1/4}; \quad T_{Mott} = \frac{18.1}{k_B L_c^3 N(E_F)} \tag{2}$$

where T_{Mott} is a characteristic temperature referred as the Mott temperature, k_B is Boltzmann constant, L_c is localization length and $N(E_F)$ is the DOS (which is constant) at the Fermi level. In the case $N(E)$ varies quadratically near to the Fermi level (*i.e.*$\nu = 2$) the exponent n becomes 1/2 and Eq. (2) transforms into the Efros-Shklovskii variable range hopping (ES-VRH) and is given by the following expression [33],

$$\sigma = \sigma_{ES} \exp\left[\frac{-T_{ES}}{T}\right]^{1/2}; \quad T_{ES} = \frac{\beta e^2}{k_B L_c \kappa} \tag{3}$$

where T_{ES} is the characteristic temperature known as Efros–Shklovskii temperature, β is a numerical constant equal to 2.8 in 3D (6.2 in 2D), e is the electronic charge and κ is the dielectric constant of the medium. The ES-VRH is the extended form of the hopping conduction developed to include the effects of the long range Coulomb interaction between localized states [34].

More specifically, the ES-VRH takes care of the Coulomb interaction not accounted for in the Mott-VRH derivation: The Coulomb interaction between localized electrons creates a 'soft' gap in the DOS near the Fermi level known as the Coulomb gap [35]. Efros and Shklovskii have shown that in the case of Coulomb interaction the DOS varies quadratically near to Fermi energy $[N(E) = N_{\circ}|(E - E_F)|^2]$ and approaches to zero at E_F [33,34]. In many systems a transition from the Mott VRH to the ES-VRH has been observed at sufficiently low temperatures. At higher temperatures the hopping energy is generally larger than the Coulomb gap and so its effect is suppressed [34].

Fluctuation induced tunneling

It was shown by Sheng et al. [26,27] that the electrical conduction for disordered materials characterized by large conducting pathways separated by small insulating barriers can be well described by a novel mechanism, called fluctuation induced tunneling (FIT). In this case the electrical conductivity follows the following relation:

$$\sigma(T) = \sigma_{\circ} \exp\left[\frac{-T_1}{T_{\circ} + T}\right] \tag{4}$$

Here, T_1 and $T_{\bigcirc}$ are characteristic temperatures defined as

$$T_1 = \frac{8\varepsilon_{\circ}}{e^2 k_B}\left(\frac{AV_{\circ}^2}{w}\right); \quad T_{\circ} = \frac{16\varepsilon_{\circ}\hbar}{\pi(2m)^{1/2}e^2 k_B}\left(\frac{AV_{\circ}^{3/2}}{w^2}\right) \tag{5}$$

where $\varepsilon_{\bigcirc}$ the permittivity of vacuum is, e is the electronic charge, $2\pi\hbar$ is Planck's constant, and m is the electronic mass. T_1 is the temperature below which the conduction is dominated by the tunneling of carriers through the barrier, and $T_{\bigcirc}$ is the temperature above which the thermally activated conduction over the barrier begins to occur. In the derivation of Eq. (4), the conduction mechanism was first modeled [26,27] as the tunneling of electrons through a single potential barrier of width w, height $V_{\bigcirc}$, and junction area A, which is the size at the point of the closest approach of two large conducting regions.

Critical regime

Disordered materials, for which the localization length shows a power-law dependence on the available DOS at critical point of

disorder-induced metal-insulator (M-I) transition, lie in the critical regime. In this regime the electrical conductivity is not activated-type. Rather, it follows a power law dependence on the temperature which is given by the following relation [36],

$$\sigma(T) \sim \frac{e^2 p_F}{\hbar^2}\left(\frac{k_B T}{E_F}\right)^{1/\eta} \propto T^{\beta} \tag{6}$$

Here p_F is the Fermi momentum. The theoretically predicted range of validity for η is between 1 and 3, i.e. $0.33 < \beta < 1$. The power law dependence is universal and requires only that the disordered system be in the critical regime. There is a class of materials such as conducting polymers and critically doped semiconductors which lie in the M-I boundary [37,38] and their conductivity behavior neither follow metallic nor insulating. These materials are placed in the critical regime, i.e. near the M-I boundary.

Identification of different charge transport regimes

Metals possess high electrical conductivity (10^4–10^6 S/cm) and a positive temperature coefficient of resistivity (TCR). A metal has essentially a finite DOS at the Fermi energy, E_F even at low temperatures, and hence has finite conductivity at low temperatures. On the other hand, not all materials that have finite conductivity at low temperatures show a positive TCR. For instance, in disordered metals, negative TCR is quite often observed together with finite conductivity at low temperatures. In contrast, for an insulator, conductivity tends to zero as temperature approaches absolute zero and has a negative TCR. The characteristic behavior of conductivity can be explicitly described by plotting the reduced activation energy (W) vs. temperature on the log-log scale. The reduced activation energy is defined as [39]

$$W = \frac{d[\ln \sigma(T)]}{d[\ln(T)]} \tag{7}$$

The temperature dependences of W in various regimes are schematically presented in Fig. 3.

AC conductivity of CNT-based composite materials

In the case of CNT-based polymer composites, the total electrical conductivity at a particular frequency and temperature can be written as: $\sigma_T = \sigma(\omega) + \sigma_{dc}$; where $\sigma(\omega)$ and σ_{dc} are frequency dependent (i.e. AC) and independent (i.e. DC) conductivities, respectively. AC conductivity of such disordered systems does not vary much or remains constant at low frequencies whereas at high frequencies, the AC conductivity displays pronounced frequency dependence which follows a power law i.e. $\sigma(\omega) \propto \omega^s$ [29]; where the exponent s is generally less than or equal to unity. At low frequencies, the AC conductance is nearly constant and it increases as $\sim \omega^s$ ($s < 1$) above a certain threshold frequency, denoted as the onset frequency. This frequency response is characteristic of many other disordered systems, including CNT-based polymer composites.

Effect of the magnetic field

The information obtained from the temperature dependence of electrical conductivity should be validated by the behavior of magneto-conductance (MC). The magneto-conductance is a sensitive probe for investigating the scattering process in the disordered systems and is defined as: $MC = \Delta\sigma = \sigma(H) - \sigma(0)$; where $\sigma(H)$ and $\sigma(0)$ are the conductivity in the presence and absence of magnetic field, respectively. The temperature and field dependence of MC depends on the transport regime. MC is sensitive to

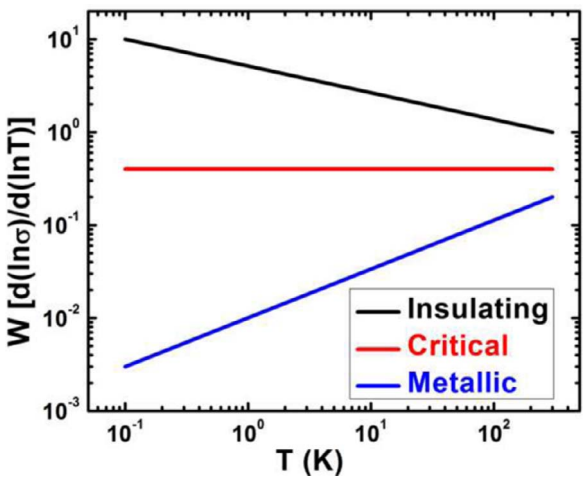

Fig. 3. Reduced activation energy (W) vs. temperature (T) plot (Schematic). The negative and positive slopes of W-T plot correspond to insulating and metallic regimes. In the critical regime, W is independent of T.

disorder and electron interactions, and it can provide not only relevant temperature dependent scattering mechanisms but also the corresponding length scales. The influence of magnetic field on charge transport in metallic regime is outlined below. For example, the contributions of weak localization and e-e interactions to conductivity near the critical regime become modified under the presence of magnetic field. As mentioned earlier, the conductivity is decreased at low temperatures due to the weak localization process. By application of a magnetic field, weak localization effects can be destroyed as magnetic field randomizes the phase of the electron waves, which completely aborts the constructive interference. Thus, weak localization theory predicts an increase in the conductivity (i.e. positive MC) when a magnetic field is turned on, and at low temperatures the effect is predicted to occur in fields as small as few tens of gauss. On the other hand, the e-e interactions cause a decrease in conductivity as a result of Zeeman splitting of the spin-up and spin-down bands [40]. When the electron and hole carry opposite spins, magnetic field H changes their relative energy by the Zeeman splitting energy $g\mu_B H$. This has a dephasing effect on the pair of wavefunctions representing the electron and the hole, leading to negative MC, which is opposite in sign to that due to weak localization. The total low-field MC is given by the following expression [27]:

$$\sigma(H, T) = [(1/12\pi^2)(e/\hbar)^2 G_0 (l_{in})^3 H^2] + [-0.041 (g\mu_B/k_B)^2 \alpha\gamma F_\sigma T^{-3/2} H^2] \quad (8)$$

where the first and second terms on the right-hand side are due to weak localization and e-e interaction contributions, respectively; $G_\circ = e^2/\hbar$ and l_{in} is the inelastic scattering length, the parameter α depends on the diffusion coefficient D as, $\alpha = (e^2/\hbar)(1.3/4\pi^2)\,(kB/2\hbar D)^{1/2}$ and γF_σ is the interaction parameter.

Review of experimental observation

Almost a decade after the discovery of CNT (in 2002), Benoit et al. [28] reported the experimental results of the low temperature charge transport properties of SWCNT-PMMA composites (0.1–8.0 wt.%) with percolation threshold $p_c \sim 0.33$ wt %. For SWCNT sample in the form of pallet, the low temperature resistivity (or conductivity) was found to follow typical Mott's VRH model i.e. $n = 1/4$. However, the exponent n takes a value of 1/2 for SWCNT-PMMA composite samples above p_c at temperatures below 50 K, indicating the contributions from Coulomb interactions. The observation of hopping transport in the SWCNT sample is understandable due to the fact that, statistically, it contains two-third of semiconducting and only one-third of metallic tubes. The conduction mechanism in the bulk MWCNTs at low temperatures is reported to follow a power-law model. In 2011, Bhatia et al. [12] studied the temperature dependence of conductivity and magneto-conductance (MC) of aligned and random multiwall carbon nanotube samples in order to probe inter-tube transport. The normalized resistance vs. temperature data are presented in Fig. 4 [12], where the metallic regime of conductivity of MWCNT samples was confirmed through the manifestation of a positive slope in the W–T plot which is shown as the inset of Fig. 4 [12]. The low temperature conductivity of both samples was observed to follow the weak localization ($T^{3/4}$ dependence) and e-e interaction model ($T^{1/2}$ dependence), obeying a relationship $\sigma(T) = \sigma_\circ + mT^{1/2} + BT^{3/4}$, where σ_0, m and B are temperature independent coefficients. MC data in both samples consisted of both positive and negative contributions, arising from weak localization (at lower fields and higher temperatures) and e-e interaction (at higher fields and lower temperatures). These findings are in contrast to one of the first studies on the low temperature charge transport in MWCNT bulk samples published by Yoshida et al. (in 1999) [7], where the authors reported VRH conduction below 50 K.

In 2006, Kim et al. [30] published the first comprehensive work on the temperature dependent electrical conductivity of MWCNT-based films with a wide range of samples by varying the MWCNT loading (0.4–30 wt.%) in PMMA, which is reproduced in Fig. 5 [30]. The transport measurements were done from RT down to 0.5 K. The authors achieved the percolation in the dc electrical conductivity at 0.4 wt.% of MWCNT loading, as evidenced by the pronounced temperature dependence of conductivity (with conductivity ratio of

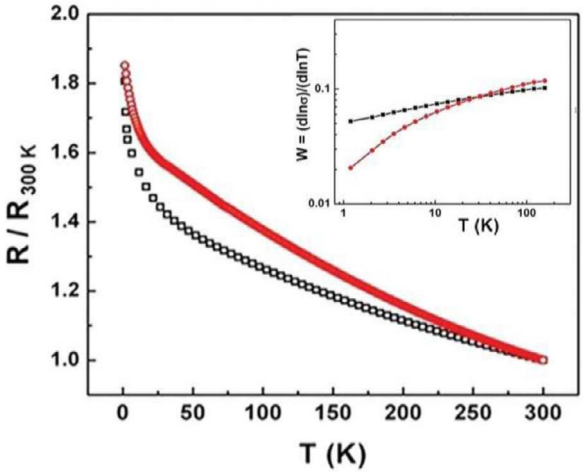

Fig. 4. Temperature dependence of normalized resistance of aligned and random MWCNT samples. Inset. Reduced activation energy (W) vs. temperature (T), indicating towards the metallic regime of electrical conductivity. From ref. [12].

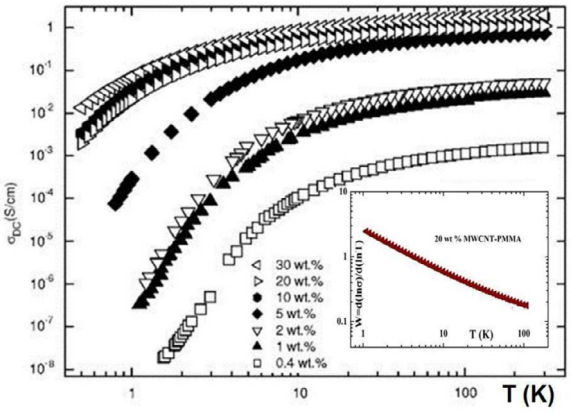

Fig. 5. Temperature dependence of dc conductivity of MWCNT-PMMA composites of MWCNT loading from 0.4 to 30 wt%. Inset. Reduced activation energy (W) vs. temperature (T) plot for 20 wt.% composite indicating towards the insulating regime of electrical conductivity. From ref. [30]. Inset is taken from ref. [42].

$\sim 10^4$ from RT to 0.5 K) for the sample with 0.4 wt.% loading, which is generally expected near the percolation threshold. Around the percolation threshold, charge transport is facilitated through the barely connected network of conducting fillers dispersed in non-conducting matrix that is sufficient to give rise to a finite conductivity at RT but the conductivity decreases by many orders of magnitude near the liquid helium temperature. This prominent suppression in the magnitude of conductivity indicates towards the fact that activated transport is prominent in percolating materials. The observation of such attributes in the charge transport near the percolation threshold in the MWCNT-based percolating systems poses an interesting question which is as follows. MWCNTs have excellent charge transport capabilities, and they possess high aspect ratios due to their intrinsic one-dimensional characteristics. Therefore, the inclusion of MWCNTs to insulating polymer matrix in a homogeneous manner should improve the charge transport so that the resulting conductivity should not exhibit such pronounced temperature dependence even near the percolation threshold. However, it is worth emphasizing here that the conductivity of composite films based on zero-dimensional conducting nanoparticles (such as carbon or Au nanoparticles) indeed exhibits a strong temperature dependence [26,41], and such systems have been reported to follow the VRH and FIT models. In the context, Kim and coworkers [30] have attempted to explain the low temperature charge transport of MWCNT-PMMA samples by using a linear combination of these theoretical models. It is rather surprising to notice the temperature dependence of conductivity for composite of 30 wt.% because conductivity becomes suppressed by $\sim$100 times as temperature decreases from 300 to 0.5 K. Further, very interesting features are seen in the magneto resistance data; Kim et al. [30] observed a negative MR in the samples of 20 and 30 wt.%. With the decrease of temperature from 10 to 0.7 K, the negative MR of the MWCNT-PMMA composite of 20 wt.% abruptly shoots from 2.8 to 32%. In general, the negative MR can be caused by the VRH process, FIT, or weak localization effect. The justification of employing both the VRH and FIT models could be acceptable owing to the complexity in the understanding of low temperature charge transport. In addition, it is rather surprising that the conductivity of MWCNT-PMMA samples well above the percolation threshold also exhibited the pronounced temperature dependence, for example, the analysis of the conductivity of 20 wt.% sample in terms of reduced activation energy indicates it to be lying in the insulating regime, with the corresponding W-T plot shown in the inset of Fig. 5 [42].

In 2010, Suchand et al. [43] utilized polyaniline (PANI; conducting polymer) for the fabrication of composite films to investigate the effect of conductive matrix on the charge transport mechanism. The conductivity vs. temperature data for MWCNT, PANI and MWCNTPANI composites are presented in Fig. 6 [43]. It is interesting to note that the conductivity of MWCNT sample hardly shows any temperature dependence, which is similar to the results reported by Bhatia et al. In contrast, the composite samples of MWCNT loading as high as 20 wt.% exhibit appreciable temperature dependence comparably. Quantitatively, the authors have shown that the conductivity of MWCNT sample lies on metallic side while that of composites and PANI films falls in the insulating regime, as indicated by the W-T plot shown in the inset of Fig. 6 [43]. On the other hand, low temperature transport studies reveal negative MR and so are consistent with the VRH mechanism. Overall, the aforementioned question of not observing the anticipated effect on charge transport due to the one-dimensional nature of nanotubes in a matrix remains unanswered, even in the case of using a conducting matrix.

In 2010, Bhatia et al. [29] studied the low temperature conductivity of MWCNT-polystyrene (PS) composites and reported rather weak temperature dependence of conductivity in comparison to other systems (for sample of 0.4 wt.%) near the percolation threshold, as shown in Fig. 7(a) [29]. The SEM image in the inset of Fig. 7(a) reveals the homogeneous distribution of MWCNTs in PS matrix. This observation was supported by the very minute increment of reduced activation energy with temperature below 50 K, as illustrated by the W–T data in Fig. 7(b). The left inset of Fig. 7(b) shows the variation of conductivity as a function of MWCNT loading from 0.1 to 7.0 wt.%. The conductivity was shown to follow power law behavior indicating metallic-like transport, unlike the usual activated transport for systems near the percolation threshold. The right inset of Fig. 7(b) indicates that low temperature conductivity of 0.4 wt.% sample follows $T^{0.3}$ dependence. The negligible frequency dependence of conductivity, in the temperature range of 300 to 5 K was presented as final confirmation on the correctness of the observed metallic transport near the percolation threshold. As presented in Fig. 7(c), the frequency dependence of conductivity data show that the onset frequency exhibits very weak temperature

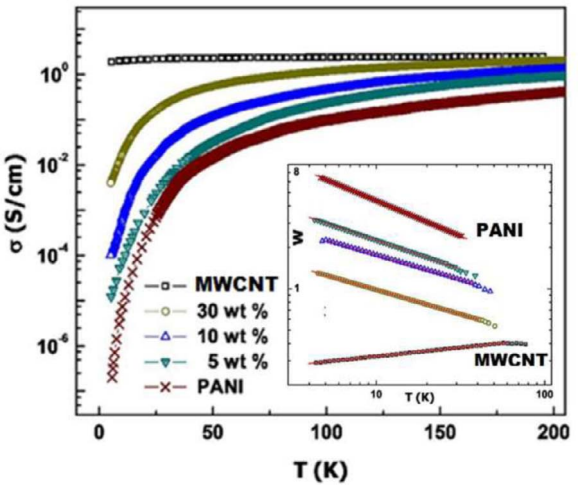

Fig. 6. Temperature dependence of conductivity of MWCNT and MWCNT–PANI composites. Inset. Reduced activation energy (W) vs. temperature (T) plots for MWCNT and composite samples. From ref. [43].

dependence (See inset of Fig. 7(c)), which further corroborates with the weak temperature dependence of dc conductivity. The achievement of quite homogeneous distribution of high quality MWCNTs (with high aspect ratio ~4500) within the non-conducting polymer matrix could be the reason for such a remarkable result. Further, these results suggest that the processing of composites without employing any surfactants was so well optimized that intrinsic charge transport capabilities of MWCNTs remained intact. This work therefore verifies the importance of one-dimensional nature of conducting filler materials (i.e. MWCNTs) to the improvement of charge transport in the resulting composite material.

In general, it is not straightforward to achieve a uniform dispersion of MWCNTs in processing the composites, and the use of surfactants or chemical functionalization of outer surface of nanotubes can facilitate better dispersion of MWCNTs in composites. However, this process inevitably induces defects and degrades the charge transport properties of CNTs [44]. Prolonged ultrasonic treatment can cause extensive damages to their structures, including shortening the lengths of CNTs, formation of defects on their walls, breaking away of graphene layers from the CNT walls and generation of amorphous carbon debris [45]. In particular, ultrasonication decreases the aspect ratios of the CNTs significantly, which badly affects electrical properties of the composite film as a whole, as it directly affects on their nanoscale connectivity. There are reports of groups having used as-prepared / as-received CNTs without purifying them prior to dispersing them in the polymer matrix [46]. However, CNTs, especially those synthesized by chemical vapor deposition, generally have a significant proportion of amorphous carbon impurity, the only reliable indicator of which is the thermo gravimetric analysis of the CNT material. This amorphous carbon may be present as a thin layer on the CNTs, and may significantly hinder contact of the CNTs with the polymer matrix. On the other hand, if a purification process is employed prior to composite formation, its effect on the CNTs needs to be carefully evaluated as the purification process too may lead to formation of amorphous carbon debris as well as defects on the CNT walls, which can also affect electrical properties [47]. Further, the rigorous ultrasonication of mixture of MWCNTs and polymer for longer intervals decreases the aspect ratios significantly which badly affects electrical properties. Lastly, it is very important to find suitable solvent which enhances the interfacial interactions between the polymer and MWCNTs. Other parameters such as evaporation rate of solvent, ambient physical conditions and self-organization of nanotubes before the composite material gets casted, also affects its charge transport characteristics at low temperatures.

Recently, Vasanthkumar et al. (in 2014) [21] studied the electrical conductivity as a function of temperature above the percolation threshold for MWCNT composites of 1.9 wt.% and above. As shown in Fig. 8 for the normalized resistivity vs. temperature data and in the inset for the corresponding W-T plots [21], the authors found that the regime of conductivity crossed over from insulating to metallic as MWCNT loading increases from 1.9 to 7.4 wt.%. The conductivity of 1.9 wt.% sample followed the 3D VRH behavior while samples of 7.4 wt.% and above followed a power law model. Interestingly, comparison of the temperature dependence of 7.4 wt.% (Vasanthkumar et al. [21]) with that of the 10 wt.% samples (Kim et al. [30]) revealed the conductivity ratios to be ~ 4 and ~ 100, respectively. This comparison further shows that the situation in the low temperature charge transport characteristics in the CNT- based composites is rather complex, and it requires more efforts to unravel the reasons for observing distinct results though essential ingredients of the system are similar.

Summary

In this review, we attempted to establish a consistent understanding on the low temperature charge transport properties of multiwall carbon nanotube (MWCNTs)-based composites by analysis of published experimental results. Notably, a pronounced temperature dependence of conductivity has been reported mostly at the percolation threshold and well above the percolation threshold. A strong dependence of electrical conductivity as a function of temperature is somehow understandable near the percolation threshold, although it is not trivial to account for the temperature dependent conductivity of samples above the percolation

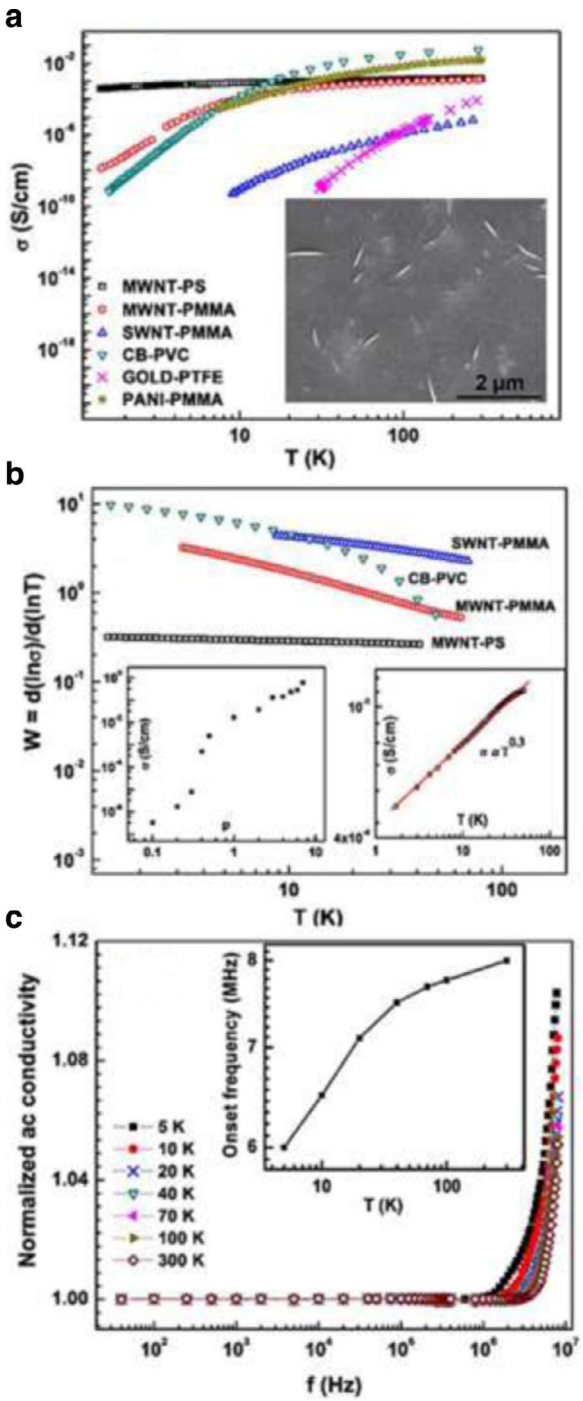

Fig. 7. (a) Temperature dependence of conductivity for various systems near the percolation threshold. Inset: SEM image of the MWCNT-PS composite of 0.4 wt.%. (b) Reduced activation energy (W) vs. temperature (T). Left inset: conductivity of MWCNT-PS samples vs MWNT weight percentage. Right inset: power law fit of the conductivity of MWCNT-PS composite of 0.4 wt.%. (c) Frequency dependence of normalized ac conductivity of MWCNT-PS composite of 0.4 wt.%. Inset: onset frequency vs. temperature. From ref. [29].

threshold. On the other hand, while the charge transport in the MWCNTs-based composites is expected to improve due to the one dimensional nature of MWCNTs even at the percolation threshold, most experimental results reported to date deviate significantly from this expectation. A recent investigation by Bhatia et al. [29] on a MWCNT-PS sample near the percolation threshold seems to shed light on this puzzling phenomenon: By achieving homogeneous distribution of MWCNTs in PS matrix, Bhatia et al. [29] observed much weaker temperature dependence of the conductivity for a MWCNT-PS sample near the percolation threshold, with

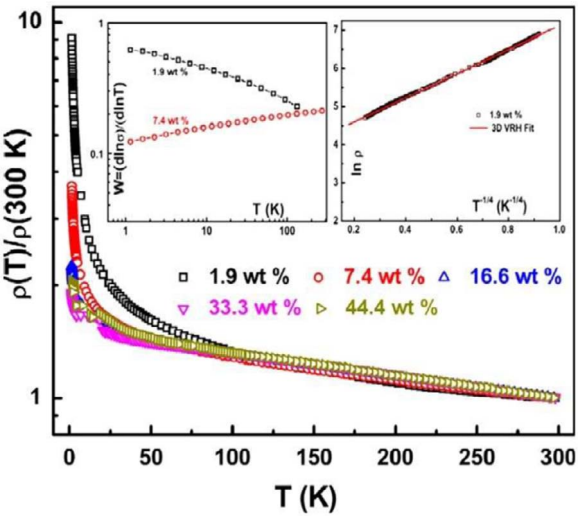

Fig. 8. Temperature dependence of normalized resistivity MWCNT–PVC composites MWCNT loading from 1.9 to 44.4 wt.%. Left inset. Reduced activation energy (W) vs. temperature (T) plot for 1.9 and 7.4 wt.% composites. Right inset. ln(ρ) vs. $T^{1/4}$ plot for the 1.9 wt% composite indicating the Mott-VRH mechanism of conduction. From ref. [21].

conductivity ratio (σ300 K/1.4 K) ~3 in comparison to reports by others, such as a conductivity ratio ~500 observed by Kim et al. [30] for a MWCNT-PMMA samples even well above the percolation threshold (~20 wt.%). This finding suggests that uniform dispersion of MWCNTs in the composite without excess ultrasonication may be critically important to improving the charge transport in the MWCNT-based matrix. More efforts are still needed to fully quantify how various parameters may affect the conduction mechanisms of the MWCNT-based composite films.

Acknowledgments

Two of the authors (Ravi Bhatia and Devinder Singh) gratefully acknowledge the financial support from Department of Science and Technology, New Delhi in the form of INSPIRE Faculty Award [DST/INSPIRE/04/2015/000902] and [IFA12-PH-39], respectively.

References

[1] P. Qi, O. Vermesh, M. Grecu, A. Javey, Q. Wang, H. Da, S. Peng, K.J. Cho, Toward large arrays of multiplex functionalized carbon nanotube sensors for highly sensitive and selective molecular detection, Nano Lett. 3 (2003) 347–351.
[2] V. Derycke, R. Martel, J. Appenzeller, P. Avouris, Carbon nanotube inter- and intramolecular logic gates, Nano Lett. 1 (2001) 453–456.
[3] Y. Zhou, A. Gaur, S.-H. Hur, C. Kocabas, M.A. Meitl, M. Shim, J.A. Rogers, p-Channel, n-channel thin film transistors and p−n diodes based on single wall carbon nanotube networks, Nano Lett. 4 (2004) 2031–2035.
[4] T. Dürkop, S.A. Getty, E. Cobas, M.S. Fuhrer, Extraordinary mobility in semiconducting carbon nanotubes, Nano Lett. 4 (2004) 35–39.
[5] E.T. Thostenson, Z. Ren, T.W. Chou, Advances in the science and technology of carbon nanotubes and their composites: a review, Compos. Sci. Technol. 61 (2001) 1899–1912.
[6] M. Moniruzzaman, K.I. Winey, Polymer nanocomposites containing carbon nanotubes, Macromolecules 39 (2006) 5194–5205.
[7] Y. Yosida, I. Oguro, Variable range hopping conduction in multiwalled carbon nanotubes, J. Appl. Phys. 83 (1998) 4985.
[8] Y. Yosida, I. Oguro, Variable range hopping conduction in bulk samples composed of single-walled carbon nanotubes, J. Appl. Phys. 86 (1999) 999.
[9] M. Baxendale, G.A.J. Amaratunga, Metallic conductivity in bundles of intercalated multiwall carbon nanotubes, Synth. Met. 103 (1999) 2496.
[10] M. Baxendale, V.Z. Mordkovich, S. Yoshimura, R.P.H. Chang, Magnetotransport in bundles of intercalated carbon nanotubes, Phys. Rev. B 56 (1997) 2161.
[11] J.M. Benoit, B. Corraze, O. Chauvet, Localization, Coulomb interactions, and electrical heating in single-wall carbon nanotubes/polymer composites, Phys. Rev. B 65 (2002) 241405(R).
[12] R. Bhatia, V. Prasad, R. Menon, Probing the inter-tube transport in aligned and random multiwall carbon nanotubes, J. Appl. Phys. 109 (2011) 053713.
[13] C. Schönenberger, A. Bachtold, C. Strunk, J.P. Salvetat, L. Forró, Interference and Interaction in multi-wall carbon nanotubes, Appl. Phys. A 69 (1999) 283.
[14] M. Ahlskog, O. Herranen, A. Johansson, J. Leppäniemi, D. Mtsuko, Electronic transport in intermediate sized carbon nanotubes, Phys. Rev. B 79 (2009) 155408.
[15] R. Saito, G. Dresselhaus, M.S. Dresselhaus, Physical Properties of Carbon Nanotubes, Imperial College Press, London, 1999.
[16] M.S. Fuhrer, W. Holmes, P.L. Richards, P. Delaney, S.G. Louie, A. Zettl, Nonlinear transport and localization in single wall-carbon nanotubes, Synth. Met. 103 (1999) 2529.
[17] M. Jaiswal, W. Wang, K.A.S. Fernando, Y.P. Sun, R. Menon, Magnetotransport in transparent single-wall carbon nanotube networks, Phys. Rev. B 76 (2007) 113401.
[18] V. Skákalová, A.B. Kaiser, Y.S. Woo, S. Roth, Electronic transport in carbon nanotubes: From individual nanotubes to thin and thick networks, Phys. Rev. B 74 (2006) 085403.
[19] J. Vavro, J.M. Kikkawa, J.E. Fischer, Metal-insulator transition in doped single-wall carbon nanotubes, Phys. Rev. B 71 (2005) 155410.
[20] A. Aharony, D. Stauffer, Introduction to Percolation Theory, second ed., Taylor and Francis, London, 1993.
[21] M.S. Vasanthkumar, R. Bhatia, V.P. Arya, I. Sameera, V. Prasad, H.S. Jayanna, Characterization, charge transport and magnetic properties of multi-walled carbon nanotube–polyvinyl chloride nanocomposites, Phys. E 56 (2014) 10.
[22] F. Du, J.E. Fischer, K.I. Winey, Effect of nanotube alignment on percolation conductivity in carbon nanotube/polymer composites, Phys. Rev. B 72 (2005) R121404.

[23] Q. Wang, J. Dai, W. Li, Z. Wei, J. Jiang, The effects of CNT alignment on electrical conductivity and mechanical properties of SWNT/epoxy nanocomposites, Compos. Sci. Technol 68 (2008) 1644.
[24] C. Li, E.T. Thostenson, T.W. Chou, Effect of nanotube waviness on the electrical conductivity of carbon nanotube-based composites, Compos. Sci. Technol. 68 (2008) 1445.
[25] M. Reghu, C.O. Yoon, C.Y. Yang, D. Moses, P. Smith, A.J. Heeger, Transport in polyaniline networks near the percolation threshold, Phys. Rev. B 50 (1994) 13931.
[26] P. Sheng, E.K. Sichel, J.I. Gittleman, Fluctuation-induced tunneling conduction in carbon-polyvinylchloride composites, Phys. Rev. Lett. 40 (1978) 1197.
[27] P. Sheng, Fluctuation-induced tunneling conduction in disordered materials, Phys. Rev. B 21 (1980) 2180.
[28] J.M. Benoit, B. Corraze, O. Chauvet, Localization, Coulomb interactions, and electrical heating in single-wall carbon nanotubes/polymer composites, Phys. Rev. B 65 (2002) 241405(R).
[29] R. Bhatia, C.S.S. Sangeeth, V. Prasad, R. Menon, Unusual metallic-like transport near the percolation threshold, Appl. Phys. Lett. 96 (2010) 242113.
[30] H.M. Kim, M.S. Choi, J. Joo, Complexity in charge transport for multiwalled carbon nanotube and poly(methyl methacrylate) composites, Phys. Rev. B 74 (2006) 054202.
[31] E.M. Hamilton, Variable range hopping in a non-uniform density of states, Philosph. Mag. 26 (1972) 1043–1045.
[32] N.F. Mott, Conduction in non-crystalline materials, Philosph. Mag. 19 (1969) 835.
[33] A.L. Efros, B.I. Shklovskii, Coulomb gap and low temperature conductivity of disordered systems, J. Phys. C 8 (1975) L49.
[34] M. Pollak, M.L. Knotek, Electronic properties and structure of amorphous solids, J. Non Cryst. Solids. 32 (1979) 141.
[35] B.I. Shklovskii, A.L. Efros, Electronic Properties of Doped Semiconductor, Springer-Verlag, Berlin, 1984.
[36] A.I. Larkin, D.E. Khmelnitskii, Activation conductivity in disordered systems with large localization length, Sov. Phys. JETP 56 (1982) 647.
[37] M. Reghu, CO. Yoon, D. Moses, AJ. Heegar, in Handbook of Conducting Polymers, vol. 2, edited by Skotheim TA, Elsenbaumer RL, Reynolds JR (Marcel & Dekker, New York 1996).
[38] R.F. Milligan, T.F. Rosenbaum, R.N. Bhatt, G.A. Thomas, in Electron-Electron in Disordered Systems, vol. 10 , edited by Efros AL, Pollak M (North-Holland, Amsterdam,1985).
[39] A.G. Zabrodskii, K.N. Zinov'eva, Low-temperature conductivity and metal-insulator transition in compensate n-Ge, Sov. Phys. JETP 59 (1984) 425–433.
[40] P.A. Lee, T.V. Ramakrishnan, Magnetoresistance of weakly disordered electrons, Phys. Rev. B 26 (1982) 4009.
[41] V. Augelli, T. Lignozo, M.C. Masellis, M.F. Mascarella, L. Schiavulli, A. Valentini, Electrical properties of gold–polymer composite films, J. Appl. Phys. 90 (2001) 1362.
[42] R. Bhatia, J. Galibert, R. Menon, Magnetic field induced delocalization in multi-wall carbon nanotube-polystyrene composite at high fields, Carbon 69 (2014) 372.
[43] C.S.S. Sangeeth, P. Jiménez, A.M. Benito, W.K. Maser, R. Menon, Charge transport properties of water dispersible multiwall carbon nanotube-polyaniline composites, J. Appl. Phys. 107 (2010) 103719.
[44] H. Hu, B. Zhao, M.A. Hamon, K. Kamaras, M.E. Itkis, R.C. Haddon, Sidewall functionalization of single-walled carbon nanotubes by addition of dichlorocarbene, J. Am. Chem. Soc. 125 (48) (2003) 14893.
[45] K.L. Lu, R.M. Lago, Y.K. Chen, M.L.H. Green, P.J.F. Harris, S.C. Tsang, Mechanical damage of carbon nanotubes by ultrasound, Carbon 34 (6) (1996) 814.
[46] S. Barrau, P. Demont, A. Peigney, C. Laurent, C. Lacabanne, Dc and ac conductivity of carbon nanotubes-polyepoxy composites, Macromolecules 36 (2003) 5187.
[47] A. Suri, K.S. Coleman, The superiority of air oxidation over liquid-phase oxidative treatment in the purification of carbon nanotubes, Carbon 49 (9) (2011) 3031.