Feature article

Electrical transport and magnetoresistance in advanced polyaniline nanostructures and nanocomposites

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1. Introduction

Magnetoresistance (MR, a resistance change upon applying a magnetic field) is often defined as MR = (R(H) - R(0))/R(0), where R(0) is the resistance without a magnetic field and R(H) is the resistance under the magnetic field of H. The Nobel Prize in Physics of 2007 was awarded to Drs. Fert and Grünberg for their discovery of giant magnetoresistance (GMR) phenomenon [1,2]. Since its first discovery in a multilayered thin-film structural metallic nano-composite consisting of a couple of ferromagnetic Fe layers separated by a nonmagnetic Cr layer in 1988 [3,4], much more scientific and technological efforts have been dedicated to this topic. On one hand, scientists are working to disclose the knowledge of GMR effects and to understand its behind physics, aiming to guide the design and creation of new structural GMR devices [5–12]. On the other hand, engineers are optimizing the design of GMR based devices for wide practical applications including rotation/speed sensing, angular position sensing, biosensors and biochips, magnetic field sensors, hard disc drivers and magnetic random access memory (MRAM) in computers [13–18]. Recently, a new technology “spintronics” has emerged in the condensed-matter physics area. Spintronics utilizes the electron spins rather than the charges to store the information and operates the logic in the solid-state systems, which can decrease the power consumption and increase the data processing speed compared to the conventional semiconductor devices [19]. More recently, organic spintronics as a class of promising electronics have gained more attentions [20] owing to their light-weight, easy processing, low-cost, chemical stability and biocompatible capability compared to the traditional metal matrix materials [21–24].

Especially, the GMR effect in the conducting polymer systems has attracted intensive attentions due to their easy synthesis, low cost, high conductivity and relatively high GMR signals compared with other organic spintronic materials [25,26]. Conducting polymers, such as polycrylonitrile (PA), polyaniline (PANI), polypyrrole (PPy), polythiophenes (PTs), poly(DNTD) and poly(p-phenylenebenzobisthiazole) (PBZT), have been widely used as electronics, electrodes for electodeposition [27] and supercapacitors [28–30], substrate to form composite nano-catalysts for hydrocarbon fuel oxidation [31], membrane for chemical separation [32],...
electrochromic (a reversible color change upon applying an electrical field) devices [33–36], coupling agents for epoxy nano-composites [37,38] and fire retardants for polymer nanocomposites [39–41]. The conductivity of conducting polymers can be increased by several orders of magnitude through doping processes [42]. Among these conducting polymers, PANI is one of the most studied conducting polymers over the last few decades due to its easy synthesis, low cost, environmental stability, simple doping/dedoping process, high conductivity and high pseudocapacitance [43–45]. It has been widely applied in many fields including supercapacitors [46–48], electrochromic materials [28], hydrogen photoproduction [49], gas sensors [50], and environmental remediation [51,52]. PANI is distinct from other conducting polymers, in which the nitrogen atom is contributed to the π-band formation and conduction mechanism [53]. PANI consists of alternating reduced (amine groups) and oxidized (imine groups) repeating units and has three different oxidation states. Normally, the first state gives a completely reduced state; the second state stands for the “half-oxidized” polymer state; and the third state represents the fully oxidized state [54]. These states are termed as “leucoemeraldine base” (LEB), “emeraldine base” (EB) and “pernigraniline base” (PB) forms, respectively [55]. Generally, LEB and PB forms are insulating in nature, even after doping; only EB form can become conductive after doping/protonation process and be converted to emeraldine salt (ES) form. Interestingly, different states of PANI have different colors. The LEB form is colorless or sometimes light yellow, the EB base form is blue, the ES form is green (which is conductive), and the PB form is violet or black [56]. The exhibition of different colors at different states makes PANI serve as the electrochromic materials possible for the smart windows and displays [28,56].

There are some reviews focusing on the preparation, processing and applications of PANI [57], negative permittivity of PANI nanocomposites [53], PANI based biosensors [58], and PANI membranes for separation and purification of gases, liquids, and electrolyte solutions [59]. However, the review on the GMR effects in the PANI and its nanocomposites does not exist in the literature yet. In this article, the electrical transport in the disordered PANI nanostructures and nanocomposite systems is critically presented, and the recent researches on the observed GMR effects in the PANI nanostructures and nanocomposites are critically reported. Meanwhile, the theoretical analysis of the GMR effects by numerical models including the wave-function shrinkage model and forward interference model is presented together with some prospective on this topic.

2. Fundamentals of GMR in disordered polyaniline nanostructures and nanocomposites

2.1. Electrical transport mechanism

PANI is a heterogeneous system composed of partially ordered crystalline regions and disordered amorphous regions upon doping [60]. The crystalline domain is metallic in nature (called metallic islands), Fig. 1(a) [61]. The conduction in this region occurs through electron delocalization or hopping of the charge carriers after the formation of polarons [57]. The polarons are formed after the proton doping of the emeraldine base form [62]. The metallic domain is surrounded by the amorphous region that has disordered or folded chains and the existence of these disordered chains can reduce the conductivity of PANI, Fig. 1(b–f). Tunneling or hopping of the charge carriers can occur between two metallic islands through amorphous regions [57] and the charge transport is governed by the disorder presented in the system [60]. The disorder in the conducting polymer systems can arise from the variations in the conjugation length, rotations and kinking of the polymer chains, van der Waals interactions with neighboring conjugated molecules, impurities [63], dipole moments of the neighboring dopant molecules and dipole moments of the molecules of the polymer matrix [64]. Soukoulis et al. [65] mentioned that the
disorder would cause tails to appear at the band edges in the density of states (DOS), which is firstly documented by Urbach and called Urbach tail, Fig. 2(a). When the disorder became stronger, the amplitude fluctuations of the wave-functions $|\psi(x)|$ at scales started to become larger than the atomic size. Eventually, the eigenstates (the measured state having quantifiable characteristics, such as position, momentum et al. [66]), in which the amplitudes decayed away from a center (called localized states), were appeared, Fig. 2(b). The appeared decay was exponential and became zero over a very large distance. Since the mean free path (the distance, where the phase of the wave-function deviates evidently from that of the plane wave) is comparable to the wavelength, the eigenstates became localized. This phenomenon, first proposed by Philip Anderson at Bell labs in 1958, was called Anderson localization [67]. Physically, the mechanism of localization is the suppression of electron tunneling over a very large distance due to the de-coherent effect induced by the random potential. The parameter of localization length ($a_0$, nm) is used to characterize this distance and defined as the logarithmic average of the absolute value of the wave-functions $|\psi(x)|$ [65].

Generally, the disorder is at microscopic scale and induces the localization of electronic wave-functions [68]. As the density of localized states near the Fermi level for the charge carriers is finite, the stronger temperature dependent conduction via “hopping” of the charge carriers with variable activation energy ($\epsilon$, related to the temperature) and hoping length ($R_{hop}$) is called variable range hopping (VRH) [69]. The best experimental support of the localization is the observation of VRH. The concept of VRH was originally given by Nevil F. Mott (a Nobel Prize Laureate in Physics in 1977) [70]. In the disordered systems, the charge carriers can hop from one site to other sites separated spatially by a certain distance (hopping length), which increases with decreasing temperature. This is the origin of the “VRH” [71].

Meanwhile, the charge transport in the VRH system is a combination of tunneling and thermal activation provided by the phonons [72]. Thermal activated hopping conduction by electrons in states near the Fermi energy is shown in Fig. 3, which illustrates two possible hops: one is from A (an occupied state, below the Fermi energy) to B state (above the Fermi energy) and another one is from B state to C state (both B and C are above the Fermi energy). The hopping process from A state to B state is the rate-determining process for these two types of hops [73]. The hopping probability ($p_{ph}$) per unit time of this process is expressed as $p_{ph} \exp(-2aR_{hop} - W/k_B T)$, where $p_{ph}$ is the optical phonon frequency and depends on the phonon spectrum (phonon is the quantized normal modes of atomic vibrations in the solids [74]), $k_B$ is Boltzmann constant, $a$ is inverse of $a_0$ of the wave-function, $R_{hop}$ is the hopping length, and $W$ is the hopping energy between two sites and can be expressed as Equation (1):

$$W = \frac{3}{4\pi R_{hop}^3 N(E_F)}$$

where $N(E_F)$ is the density of states at the Fermi level [73]. Thus, the electrical transport process requires the charge carriers to hop between the localized states with the hopping energy $W$ as low as possible. This means that the charge carriers will hop to the site, which is above the Fermi level and has the minimum energy difference with respect to its original site irrespective of the spatial distance [72,75].

In the VRH regime, at moderate temperatures, the Mott’s law describes the conduction caused by the phonon-assisted tunneling (hopping thermal energy dependent $k_B T$) between the electronic localized states centered at different positions and the electrical conductivity ($\sigma$) can be presented as Equation (2):

$$\sigma = \sigma_0 \exp\left(-\frac{T}{T_0}\right)^{\frac{1}{2n}}$$

where the pre-exponential factor $\sigma_0$ is a constant and represents the conductivity at infinite low temperature limit, $T$ is the Kelvin temperature, $T_0$ (the Mott characteristic temperature) is related to the energy needed for the hopping conduction of the charge carriers and can be expressed as Equation (3) [76]:

$$T_0 = \frac{24}{\pi k_B N(E_F) a_0^3}$$

where $a_0$ (nm) is the localization length of the wave function for the localized charge carrier. Normally, the defects (e.g., dopants or impurities) can perturb the electronic structure of the semiconductors and act as scattering centers to affect the charge carrier transport in the semiconductors [77]. A higher $T_0$ indicates a stronger charge carrier scattering. The $n$ value of 3, 2 and 1 in Equation (2) represents three-, two- and one-dimensional system, respectively. The $\sigma_0$ and $T_0$ can be obtained from the intercept and
slope of the linear fitting \( \ln(\sigma) \sim T^{-1/(n+1)} \). The \( a_0 \) is expected to be diverged to infinity as the metal-insulator transition (MIT) is approached \((T_0 \rightarrow 0 \, K)\). The \( R_{\text{hop}} \) must be greater than the \( a_0 \) in order to make the Mott’s law valid, since the \( R_{\text{hop}} \) is described as Equation (4) [78].

\[
R_{\text{hop}} = \left( \frac{3}{8} \right) (T_0/T)^{1/4} a_0
\]  

(4)

In the Mott’s VRH mechanism, \( T_0, a_0, R_{\text{hop}} \) and \( W \) are important parameters to characterize VRH transport. The \( T_0 \) is reported to be strongly dependent on the disorder presented in the samples [79]. Generally, the disorder in the PANI systems can be evaluated by the resistivity ratio \( \rho_{\text{high}}/\rho_{\text{low}} \), where \( \rho_{\text{low}} \) is the resistivity measured at the lowest temperature; and \( \rho_{\text{high}} \) is the resistivity measured at the highest temperature, normally, around 290 K. Normally, the higher the \( \rho \), the stronger disorder in the samples will be [80]. Sarkar et al. [81] studied the influence of the \( \rho \) on the \( T_0 \) and \( a_0 \) in the oxalic acid (OX) doped PANI samples and revealed the relations as: \( T_0 \propto \rho \) and \( a_0 \propto \rho^{-1} \). Meanwhile, the magnetococonductivity (MC) was found to be related to \( \rho_r \), the interface and grain boundary effects.

Meanwhile, after considering the Coulomb interaction between the localized electrons, which creates a “soft” gap in the \( N(E_F) \). Efros and Shklovskii showed that the \( N(E_F) \) should quadratically vanish at the Fermi level and the conductivity (Equation (2)) was modified to Equation (5) in all dimensions (called ES’s law) [82]:

\[
\sigma(T) \propto \exp \left[ \left(-\frac{T_{ES}}{T}\right)^{1/2} \right]
\]  

(5)

where \( T_{ES} \) is the characteristic temperature for the ES’s law. It’s observed that the Coulomb interaction can be neglected at temperatures above certain critical temperature \( T_C \) (shown in Equation (6)) and the conductivity will follow the Mott’s law.

\[
T_C = \frac{e^4 a_0 N(E_F)}{k_B (4\pi e^2 r_0)}
\]  

(6)

where \( e \) is the electron charge, \( \varepsilon \) is the dielectric constant, \( r_0 \) is the dielectric constant of vacuum.

At temperatures below the \( T_C \), the conductivity will obey ES’s law [83].

2.2. Theoretical analysis of GMR effect

The mechanisms of the GMR effect in the organic systems including conducting polymers are still open for discussion. The common models to explain the GMR effects in the organic systems are excitonic pair mechanism model [84], electron–hole \((e-h)\) recombination model [85], bipolaron model [86], forward interference model (also called orbital magnetoconductivity theory) and wave-function shrinkage model [78]. The basic idea of the excitonic pair mechanism model is from the spin-dependent effect relating to a negative polaron and a positive polaron. The injected electrons and holes from the cathode and anode into the material form the negative and positive polarons, respectively. They will form bound polaron pairs and the pair may further become exciton. The formed different kinds of excitons change with time due to the spin dynamics induced by the hyperfine interaction (which comes from the atomic physics for the interaction of the electron magnetic moment with the nuclear magnetic moment [87]). The transition rate constant between different kinds of excitons changes under the applied magnetic field, causing the current change. This current change is related to the square of the transition rate constant ratio, which finally leads to a positive MR in the materials [84]. Normally, the \( e-h \) recombination model is used to explain the large anomalous MR under a small magnetic field [85]. In this model, the electrons \((e)\) and holes \((h)\) can form the \( e-h \) pairs. The \( e-h \) recombination process includes the formation of \( e-h \) pairs and the annihilation of \( e-h \) pairs with different spin interconversion of \( e-h \) pairs. The formed \( e-h \) pairs include one singlet and three triplets and these singlet and triplet \( e-h \) pairs may either dissociate or recombine. In the \( e-h \) recombination model, the MR is related to the square of the dissipation rates of both the singlet and triplets. However, after assuming that the dissipation rate constant does not show a strong spin dependence and the fastest process is the singlet recombination, the MR is only described by the recombination rate and dissipation rate of triplets. Then the MR will be simplified to a negative value as \(-1/2[\langle q_1(k_1+q_k)\rangle]\), where \( q_1 \) and \( k_1 \) is the dissociation and recombination rate of the triplets, respectively [85]. Bipolaron means two positive or two negative charges combined together. In the bipolaron model, the positive MR is associated with the blocking of electron transport through the bipolaron states; the negative MR is caused by the increase in polaron population at the expense of bipolarons with increasing magnetic field [88]. These three models discussed the GMR mechanism from the viewpoint of exciton pairs, polaron of electron–hole, and bipolaron.

However, the wave-function shrinkage model and forward interference model are two numerical electrical transport models, which have been successfully adopted to describe the MR behavior of the highly disorderedly localized systems in the VRH regime [89]. The forward interference model, originally proposed by Nguyen, Spivak, and Shklovskii (NSS) [90], is often used to predict the negative MR. NSS considered the effect of interference among all possible hopping paths, which might substantially change the hopping probability between two sites [89]. The conductivity is proportional to the sum of all the possible paths between two sites. As a result of forward interference under a magnetic field, an increased conductivity (or decreased resistivity) is envisioned, i.e. negative MR [91]. Strong positive MR with a magnetic field was firstly predicted by Tokumoto et al. [92] and Shklovskii [72,93], and it was developed further by Shklovskii and Efros using the wave-function shrinkage model [78,94]. Normally, the wave-function of the impurity electrons is squeezed in the transverse direction under the strong magnetic field. This means that the spherical symmetric wave-functions without a magnetic field will become cigar-shaped (spindle-shaped and tapering at each end) with the magnetic field [94]. In the wave-function shrinkage model, the cigar-shaped wave functions in the magnetic field leads to a sharp decrease in the overlap of the wave function “tails” for an average pair of neighboring impurities and a reduction in the hopping probability between two sites, causing an increased resistivity with increasing magnetic field and a positive MR [94]. Fig. 4 shows the related information for the wave-function shrinkage model.

Fig. 4. The wave-function of the impurity electrons in the condition (a) without magnetic field and (b) with magnetic field.
2.2.1. Forward interference model

In the forward interference model, the hopping paths include the scattering sequence of tunneling electrons by the impurities located within the cigar-shaped domain of length $R_{\text{hop}}$ and width $(R_0 \delta_0)^{1/2}$ between the hopping sites. NSS [91] proposed the forward interference model for a hop as shown in Fig. 5. The electron hopping from site $i$ to site $f$ experiences various possible hopping paths and the conductivity is proportional to the sum of all the possible paths from site $i$ to site $f$. After the numerically logarithm averaging the conductivity over many different possible paths in the presence of a magnetic field, a linear negative MR was obtained in the low magnetic field limit. Later on, a quadratic negative MR at small magnetic fields, which was saturated at high magnetic fields, was observed [91]. Actually, the linear MR (LMR) was often observed in the low magnetic field and the quadratic MR was only occasionally observed in some samples at very weak magnetic field. Thus, the resistance ratio caused by forward interference effects, $r_{\text{forward}} = R(H)/R(0)$, is expressed approximately by empirical Equation (7) (which neglects the quadratic term in $H$) [95]:

$$r_{\text{forward}} = 1/(1 + C_{\text{sat}}[H/H_{\text{sat}}]/[1 + H/H_{\text{sat}}])$$

(7)

where the fitting parameter $C_{\text{sat}}$ is the saturation constant and temperature independent. The fitting $H_{\text{sat}}$ is the effective saturation magnetic field. Equation (7) is observed to be saturated at high magnetic fields to a value of $1 + C_{\text{sat}}$ and yields a linear dependence on $H$ at intermediate fields.

For the Mott VRH system, $H_{\text{sat}}$ is given by Equation (8) [89]:

$$H_{\text{sat}} \approx 0.7 \left( \frac{8}{3} \right)^{3/2} \left( \frac{1}{\alpha_0^2} \right) \left( \frac{h}{c} \right) \left( \frac{T}{T_0} \right)^{3/8}$$

(8)

where $h$ is the Planck’s constant. When the $H/H_{\text{sat}}$ and $C_{\text{sat}}$ are small, Equation (7) becomes Equation (9):

$$r_{\text{forward}} = 1 - C_{\text{sat}}[H/H_{\text{sat}}]$$

(9)

i.e., Equation (10).

$$\text{MR} = \frac{\Delta R(H, T)}{R(0, T)} = \frac{R(H, T) - R(0, T)}{R(0, T)} \approx - C_{\text{sat}}[H/H_{\text{sat}}]$$

(10)

The MR value in Equation (10) is always negative and associated with the $H/H_{\text{sat}}$ and $C_{\text{sat}}$.

2.2.2. Wave-function shrinkage model

In the wave-function shrinkage model, by means of the percolation theory (which is a quantitative model to describe the clustering, diffusion, phase transition, and electrical property in disordered systems for studying the more complicated critical phenomenon [the critical point in physics] [96]), the magnetic field dependent MR in the VRH regime can be easily calculated. The resistance ratio $r_{\text{wave}} = R(H)/R(0)$ in terms of the critical percolation parameter $\xi_c(H)$ (also known as the optimum hopping probability parameter) is described as Equation (11) [89]:

$$r_{\text{wave}} = \exp\{\xi_c(0)|\xi_c(H)/\xi_c(0) - 1\}$$

(11)

where $\xi_c(0) = (T_0/T)^{1/4}$ for the 3-D Mott VRH system [97], $\xi_c(H)/\xi_c(0)$ is the normalized hopping probability parameter and is a function of $H/P_c$ for the Mott system. $P_c$ is fitting parameter for the Mott VRH system:

Setting $AE_1$: to be an energy interval around Fermi energy whose extension depends on the percolation parameter $\xi$, a function of vector $r$ which connects two different sites, $\xi$ can reach percolation threshold to determine the electrical conductivity in a random disordered system, and setting $V_f$ to be the corresponding volume around one site [97], with $E_0$ being the binding energy of the localized state, $m$ is the effective mass of the electron and the cyclotron frequency ($\omega_c$) is defined as $\omega_c = eH/m$, the $V_f$ can be described as Equation (12):

$$V_f = \frac{8\pi}{3} \left( \frac{2|E_0|}{m\omega_c^2} \right)^{3/2} F \left( \frac{\xi_0\omega_c}{4|E_0|} \right)$$

(12)

where $h = \hbar/2\pi$, $F$ is the wave-function that is the distribution function of $\xi$ [94]:

$$F(s) = \frac{s}{\tau(s)} \left[ \frac{1}{2} (shx + x - 2s) + (s - x)x \right]$$

$$\times \left( \frac{(shx + x - 2s)^{1/2} \cdot x \cdot shx}{(shx - x)^{1/2}} \right) dx$$

(13)

with $\tau(s)$ being the solution of $s\tau + \tau - 2s = 0$, where $x$ is the position, $s = \xi_0\omega_c(4|E_0|)$, $shx$ and $thx$ are the hyperbolic sine ($shx = (e^x - e^{(-x)})/2$) and hyperbolic tangent ($thx = (e^x - e^{(-x)})/(e^x + e^{(-x)})$) functions, respectively. The Equation (12) describes the gradual change of $V_f$ from the sphere to the double paraboloid as the magnetic field increases.

Thus, in point view of percolation theory, a lower bound $\xi_c(H)$ was defined as the critical percolation parameter for percolation to occur for the appropriate $V_f$, and this $\xi_c(H)$ can be determined by introducing the reduced variables, Equation (14):

$$\xi_c = \xi_c(H)/\xi_c(0)$$

(14)

and the normalized magnetic field ratio $H''$ can be expressed as Equation (15):

$$H'' = H/P_c$$

(15)

where $P_c$ is defined as Equation (16):
This positive MR for the VRH conduction system was believed to be GMR in the PANI systems. In 1998, Ghosh et al. [99] tested the GMR of the metal-insulator transition. This is the earliest report on the system of the inorganic semiconductors that were doped to be near wavefunctions, which was similar to the negative MR in the VRH associated with a quite large localization length of the electronic field range (0 ~ 0.2 T) at 1.2 K in 1993. This negative GMR was reported a very large negative GMR around 44% in the weak magnetic field of 8 T using Equation (21) via wave-function shrinkage model. However, the MR at higher temperature was not reported.

In 2004, Long et al. [100] observed a negative MR around –12% in a β-naphthalene sulfonic acid (NSA) doped PANI hollow microsphere synthesized by a self-assembly method at 90 K and around –0.6% was obtained in the same PANI microsphere at 260 K.

The forward interfere model and wave-function shrinkage model are often used together to explain the MR transition from negative to positive or from positive to negative, in which the MR is contributed from both forward interference effect and wave-function shrinkage effect. Then the total MR ratio should be written as Equation (22):

\[
\Delta R(H, T) = \Delta R(0, T) = \frac{\rho(H) - \rho(0)}{\rho(0)} = \frac{e^2 a_0^2}{36 \hbar^2} \left( \frac{T_0}{T} \right)^{3/4} H^2
\]

where the numerical constant \( t_2 = 5/2016 \) [94]. Thus, the wave-function shrinkage model can have another formula under weak magnetic fields [94,98]:

\[
\rho(H) = \rho(0) \left( \frac{L}{L_0} \right)^4 \left( \frac{T_0}{T} \right)^{3/4}
\]

where \( L = (\hbar/eH)^{1/2} \) is the magnetic length (also called Landau magnetic length, which is related to the Larmor radius, meaning that the radius of the classical cyclotron orbit with the zero-point energy).

The forward interfere model and wave-function shrinkage model are often used together to explain the MR transition from negative to positive or from positive to negative, in which the MR is contributed from both forward interference effect and wave-function shrinkage effect. Then the total MR ratio should be written as Equation (22):

\[
r_{\text{total}} = \exp \left[ \xi_c(0) / \xi_c(H) - 1 \right] + 1 / \left[ 1 + C_{\text{sat}} |H/|H_{\text{sat}}|/|1 + H/|H_{\text{sat}}| \right] - 1
\]

The last term, –1, is to assure that the \( r_{\text{total}} \) is equal to 1 when \( H = 0 \).

3. Giant magnetoresistance in advanced polyaniline nanostructures

In the last decades, there are some researches focusing on the GMR effect in the PANI systems. For example, Reghu et al. [68] reported a very large negative GMR around –100% in the PANI film protonated by camphor sulfonic acid (CSA) in the weak magnetic field range (0 ~ 0.2 T) at 1.2 K in 1993. This negative GMR was associated with a quite large localization length of the electronic wavefunctions, which was similar to the negative MR in the VRH system of the inorganic semiconductors that were doped to be near the metal-insulator transition. This is the earliest report on the GMR in the PANI systems. In 1998, Ghosh et al. [99] tested the GMR property of the HCl doped PANI synthesized in an aqueous ethanol medium (30% by volume) in the 3-D VRH conduction system. A GMR around 30% was reported in this PANI system at 1.9 K, Fig. 6. This positive MR for the VRH conduction system was believed to be due to the shrinkage in the overlap of the electronic wave functions of the localized states after applying a magnetic field. The calculated localization length \( a_0 \) was about 5.6 nm for the PANI with \( \rho_0 \) of 460 at a constant magnetic field of 8 T using Equation (21) via wave-function shrinkage model. However, the MR at higher temperature was not reported.

In 2006, this group also reported an MR value up to 91% in the PANI nanotube pellet doped with NSA at 3 K [101]. Fig. 8 shows the MR property of the PANI nanotube pellet between 3 and 250 K. The MR value increased with either increasing the magnetic field or decreasing the temperature.
decreased with increasing the temperature significantly and an MR transition from positive to negative between 50 and 100 K was observed. Meanwhile, the obtained negative MR was very small, less than $-0.2\%$. The wave-function shrinkage effect and quantum interference effect on the hopping conduction were used to illustrate the positive and negative MR, respectively. The change of the MR sign indicated that both effects coexist and compete. The wave-function shrinkage effect made the main contribution at low temperatures. However, as the temperature increased, the localized states became less localized and the wave-function shrinkage effect became weaker. In this situation, the negative MR contribution from quantum interference effect was dominated. Thus, an MR value was changed from positive to negative. Interestingly, in order to confirm the origin of the MR effect in these pellet samples, the MR in a single nanotube attached on platinum (Pt) microleads was measured. The results indicated that the MR in a single PANI nanotube was quite smaller than that of the pellet at a magnetic field of 10 T: for the single PANI nanotube, MR $-2.5\%$ (2 K); for the pellet samples, MR $-91\%$ (3 K). This difference suggested that the MR in the bulk pellet sample of PANI nanotubes mainly originated from a random network of inter-fibril contacts.

In 2010, Bozdag et al.\cite{102} reported a large positive MR ($-55\%$ in 8 T at 2.5 K) in the PANI nanofibers doped with camphor sulfonic acid (CSA), which were fabricated by dilute chemical oxidative polymerization method. This MR property was observed to be temperature and magnetic field dependent, Fig. 9. The MR was observed to decrease with increasing temperature and decreasing magnetic field. A crossover of MR value from positive to negative was observed with increasing temperature at around 87.5 K. Interestingly, the MR property of the PANI nanofibers was observed to change with applying an electrical field, Fig. 10. A higher electrical field enhanced the conductance by reducing the activation energy and hopping length. Thus, the effect of wave-function shrinkage arising from the magnetic field decreased with increasing the electrical field. The electrical field is a new parameter on the effect of MR property in the PANI systems so far. However, the electrical field dependent MR property at different magnetic fields and temperatures was not reported.

Generally, the electrical conductivity of PANI depends on the molecular weight, oxidation level\cite{30,103}, molecular arrangement, crystallinity, inter-chain separation, degree of doping \cite{57} and dopant \cite{104}. Depending on the dopant, the electrical conductivity of the doped PANI can be 8–11 orders of magnitude ($10^{-1} - 10^{2}\, \text{S cm}^{-1}$) higher than that of the PANI base ($10^{-9}\, \text{S cm}^{-1}$)\cite{105}. Recently, Gu et al.\cite{26,44,79} studied the effects of dopant, oxidant and dose of oxidants on the GMR property of pure PANI. Specifically, 53% of GMR value at room temperature was obtained in the p-tolene sulfonic acid (PTSA) doped pure PANI synthesized by ammonium persulfate (APS), Fig. 11(a)\cite{26}. A room temperature GMR value of 65.5% was observed in the phosphoric acid (H$_3$PO$_4$) doped pure PANI oxidized by APS, Fig. 11(b)\cite{79}.

Gu et al.\cite{44} also used the hexavalent chromium (Cr(VI)) as oxidant to prepare the PANI samples and the MR property of the synthetic PANI was reported. Only around 5% room temperature MR value was reported in these prepared PANI samples, Fig. 11(c). Meanwhile, the dose level of oxidants is found to affect the MR property of PANI, Fig. 11(c). These phenomena were due to the fact that the molecular arrangement and crystallinity of PANI could be affected by the dopants and oxidants. For example, the crystallinity of PANI-0.75 (K$_2$Cr$_2$O$_7$:0.75 mmol vs PTSA 15 mmol, aniline: 18 mmol) and PANI-3 (K$_2$Cr$_2$O$_7$:3 mmol vs PTSA 15 mmol, aniline: 18 mmol) was 48.6 and 57.6%, respectively. This resulted in different disordered structures in the synthesized PANI as aforementioned, which led to a different distribution of the metallic islands and amorphous regions in the PANI system. Thus, different charge carrier hopping
probability and hopping length were obtained to yield different MR behaviors in the PANI systems under different polymerization conditions.

4. Giant magnetoresistance in polyaniline nanocomposites

Recently, a great progress on the MR effect was observed in the PANI nanocomposites. For example, Long et al. [106] obtained a series of MR $\approx 4.15\% (2\ K, 6\ T)$, $1.9\% (4\ K, 5.4\ T)$ and $1.6\% (6\ K, 6\ T)$ in the Au/PANI microfibers with a core–shell structure synthesized by reacting aniline monomers with HAuCl$_4$ via a self-assembly process with CSA as dopant. In the PANI nanocomposite systems, besides temperature and magnetic field strength, GMR can also be affected by the loading level of nanofillers. For example, negative GMR of the carbon nanotubes (CNTs)/PANI nanocomposites was observed at 10 K and decreased with increasing the CNT loading, the reduced GMR effect was thought to be associated with the long 1-D localization length of CNTs [107]. Gupta et al. [108] fabricated the PANI nanotubes/La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO) composites using a two-step method including pyrophoric reaction process (an aqueous solution of stoichiometric amount of high-purity lanthanum oxide (La$_2$O$_3$), manganese acetate (Mn(CH$_3$COO)$_2$), and strontium nitrate Sr(NO$_3$)$_2$) was stirred with triethanolamine in a hot plate to form the black, fluffy powders, then was calcined at 650 °C to prepare LSMO and in-situ chemical oxidative polymerization to synthesize PANI. The low field regime MR about 57, 67 and 73% was reported in these PANI nanocomposites with an LSMO loading of 10, 20 and 30 mg at a magnetic field of 3 kG ($=0.3$ T) and 77 K, respectively [108].

Rakhimov et al. [109] reported a new GMR system consisting of PANI, polystyrene (PS), manganese (II) acetylacetonate (Mn(Acac)$_2$), lanthanum (III) chloride hexahydrate (LaCl$_3$·6H$_2$O), praseodymium (III) chloride hexahydrate (PrCl$_3$·6H$_2$O) and element sulfur (S) polymeric composites with a component ratio of (LaCl$_3$·6H$_2$O):[Mn(Acac)$_2$]:[PANI]:[PS]:[S] = 0.1:0.1:0.15:0.35:0.1:0.2. The applied current is a transient current, which is changed with time. The obtained GMR value of this system was changed from 300 to 1800% within various time (0–250 s) under a magnetic field of 6000 Oe at room temperature, Fig. 12. The GMR effect in this composite system strongly depended on the element S and was not observed in the composite without element S. The element S might have the ability to cross-link with the aromatic chains of PS and PANI during the mechanochemical treatment. The obtained composites in the presence of manganese ions could provide a physical basis for the

![Fig. 10. I–V behavior of the PANI nanofiber network. Inset shows the current dependent MR property. Reprinted with permission from Ref. [102].](image1)

![Fig. 11. GMR of the PANI doped with (a) PTSA and (b) H$_3$PO$_4$; and (c) PANI-0.75 and PANI-3 samples at room temperature. PANI-0.75 represents that the used K$_2$Cr$_2$O$_7$ was 0.75 mol and PANI-3:K$_2$Cr$_2$O$_7$ was ~3 mol. Reprinted with permission from Refs. [26,44,79].](image2)
GMR effect, which is like lanthanum manganites. In fact, lanthanum manganites are a typical example for the inorganic MR materials. Manganites, such as LaSrMnO$_3$ and LaCaMnO$_3$, are the materials with the colossal magnetoresistance (CMR) which arises from the interplay of electron-phonon coupling [110] and ferromagnetic (FM)-to-paramagnetic phase transition [111].

Prasanna et al. [67] reported the temperature dependent MR observed in the PANI/ZnFe$_2$O$_4$ nanocomposites with different loadings of ZnFe$_2$O$_4$ nanoparticles at a magnetic field of 2 T, Fig. 13. The MR value of pure PANI was very small. The MR in these PANI nanocomposites increased with increasing the ZnFe$_2$O$_4$ nanoparticle loading. This phenomenon was believed to arise from the increased charge carrier scattering with increasing the ZnFe$_2$O$_4$ nanoparticle loading due to the presence of magnetic ferrite impurities. Recently, Guo’s group has made a significant progress on the room temperature GMR effect in the PANI nanocomposites [26,112]. Different nanofillers including magnetic, insulating and semi-conducting types have been used for the synthesis of the nanocomposites using the surface initiated polymerization (SIP) method. The GMR effects in both the magnetic and the nonmagnetic PANI nanocomposites were reported. Meanwhile, a very large GMR value at room temperature in the nonmagnetic silica/PANI nanocomposites was reported and could be comparable with that in the magnetic Fe$_3$O$_4$/PANI nanocomposites. For example, around 95% GMR was reported in the magnetic PANI nanocomposites with a Fe$_3$O$_4$ nanoparticle loading of 30 wt%, Fig. 14(a) [26]. A GMR value up to 95.5% was reported in the nonmagnetic PANI nanocomposites with 20 wt% silica nanoparticle loading, Fig. 14(b) [79]. In addition, a GMR of 20% in the nonmagnetic PANI nanocomposites with a BaTiO$_3$ (500 nm) loading of 20 wt% synthesized by SIP method and around 35% GMR in the 20 wt% BaTiO$_3$ (500 nm)/PANI nanocomposites prepared by simple physical mixture of PANI and BaTiO$_3$ powders were observed [113]. In the PANI nanocomposites with different carbon nanostructures fabricated with APS as oxidant, a small negative MR (<1%) was observed at 130 K, Fig. 15(a and c). The significantly larger positive MR (15 ~ 30%) was observed at 290 K, Fig. 15(b and d). The quantum interference effect among many possible paths in the magnetic field was used to explain the negative MR at 130 K [91]. The room temperature GMR obtained in the PANI nanocomposites with 5 wt% graphene higher than that of the PANI nanocomposites with the same loading of 1-D filler (CNTs and carbon nanofibers (CNFs)) was due to the π–π stacking-induced efficient electrical transport at the PANI and graphene interface, Fig. 15(d) [112].

In contrast, multi-walled carbon nanotubes (MWNTs)/PANI nanocomposites were prepared with Cr(VI) as oxidant and the GMR...
behaviors of these MWNTs/PANI nanocomposites were investigated [114]. Fig. 16(A) shows the MR of the synthesized MWNTs/PANI nanocomposites. The MWNTs/PANI nanocomposites with an MWNT loading of 5.0, 10.0 and 20.0 wt% synthesized with Cr(VI) as oxidant were named as T5, T10, T20, respectively. The aniline was further polymerized on T20 sample with APS as oxidant, which was named as T205. The aniline was further polymerized on T20 by Cr(VI), named as TCr205. Meanwhile, the nanocomposites containing 5.0 wt% MWNTs were also prepared by oxidizing aniline with APS, named as TA05. Fig. 16(B) depicts the MR property of these nanocomposites. A negative GMR around –2% was observed in the T5 and T20 nanocomposites synthesized by Cr(VI) and positive GMR around 7.9 and 11% in the TA05 and T205 nanocomposites synthesized by APS.

A room temperature GMR effect of around 22% in the nonmagnetic PANI nanocomposites with a silicon loading of 20.0 wt% under magnetic field of 9 T was reported [115]. Generally, the magnetic field detectors are based on the MR effect and the linear MR with respect to the magnetic field at the low magnetic field regime can be used to describe the sensitivity of the materials to the magnetic field [116]. A very high magnetic field sensitivity at low magnetic field was observed in these nonmagnetic silicon/PANI nanocomposites. A room temperature MR transition from positive to negative was found in the silicon/PANI nanocomposites with a silicon loading of 10.0 wt% in the VRH regime, Fig. 17 [117].

Meanwhile, the obtained GMR property in the nonmagnetic PANI nanocomposites has been theoretically analyzed by using wave-function shrinkage model and forward interference model for positive and negative MR, respectively. The obtained positive MR in the PANI nanocomposites was investigated by wave-function shrinkage model through Equation (20). In this model, in the low
magnetic field, the applied \( H \) decreased the overlap probability between two sites, resulting in an increased resistance with increasing the \( H \) [78]. In the higher magnetic field, the VRH between the localized states having a Coulomb gap in the \( N(E_F) \) caused the quadratic \( H \) dependent behavior [97]. According to Equation (20), the \( a_0 \) can be calculated from \( T_{0b} \) a positive MR value and \( H \) by Equation (23):

\[
a_0^2 = \frac{36\hbar^2MR}{\tau_2^2e^2} \left( \frac{T_{0b}}{T} \right)^{-3/2} H^{-2}
\] (23)

From the obtained \( a_0 \), the \( N(E_F) \) and the \( R_{hop} \) could be calculated from Equations (3) and (4), respectively. The calculated parameters of the PANI nanocomposites by wave-function shrinkage model are listed in Table 1. It is observed that the \( a_0 \), \( N(E_F) \) and \( R_{hop} \) are magnetic field dependent. The \( a_0 \) and \( R_{hop} \) decreased with increasing the magnetic field, the \( N(E_F) \) increased with increasing the magnetic field and the average hopping energy had no magnetic field dependent property [118]. Different parameters were obtained in the PANI nanocomposites filled with different nanofillers due to the synergistic interaction between the nanofillers and the PANI matrix as confirmed in the FT-IR test, etc. [79,115], leading to different GMR values in these PANI nanocomposites. For the silica/PANI nanocomposites, different GMR values were obtained in the nanocomposites with different silica loadings. The GMR value increased as the silica loading was increased to 20.0 wt% and then decreased as the silica loading was increased further. Different GMR values were observed to be reflected by the \( \Delta R_{hop} \). The more reduced \( R_{hop} \), the higher value of the MR was obtained. They proposed GMR mechanism in the silica/PANI nanocomposites is shown in Fig. 18. In the silica/PANI nanocomposites, the \( R_{hop} \) decreased with increasing the magnetic field. Meanwhile, it was found that the higher \( \Delta R_{hop} \), the higher GMR was obtained in the silica/PANI nanocomposites.

In the MWNTs/PANI nanocomposites synthesized by Cr(VI) [114], the negative MR was studied by the forward interference model. In the forward interference model, by non-linear fitting \( R/H/R(0) \) - \( H \) via Equation (7) using Polymath software, the obtained \( C_{sat} \) value for T5 and T20 samples (Fig. 10(B)-e and f) was 0.0251127 and 0.0317174, respectively. The calculated \( a_0 \) values for the T20 via Equations (8) and (10) as shown in Table 1 are 696.5, 487.0 and 428.4 nm at \( H \) of 0.5, 4 and 9 T, respectively. The obtained \( a_0 \) for the negative MR value in the MWNTs/PANI nanocomposites oxidized by Cr(VI) was larger than that of the positive MR value in the nanocomposites TA05 (Fig. 16(B)-b) formed by APS as oxidant at the same magnetic field. This was due to the fact that in the negative MR VRH system, the localization was relatively weak, thus the quantum interference effect was dominated.

In the PANI nanocomposites with 10.0 wt% silicon loading, the MR transition from positive to negative at a magnetic field of 5.5 T demonstrated that there were two kinds of contributions including positive and negative contributions to the GMR value, coexistent and competing [67]. This MR sign was separated by both the forward interference model and the wave-function shrinkage model using Equation (22) in order to further understand the origin of the GMR in the PANI nanocomposite system [5]. After calculation, both the forward interference effect and the wave-function shrinkage effect were observed to contribute to the positive MR part, but only the forward interference effect contributed to the negative MR part. The separated positive MR sign and negative MR sign are shown in Fig. 19(a and b), respectively.

Generally, most of the researches focused on the conducting form of PANI in the nanocomposites to investigate the GMR property. However, Lin et al. [119] obtained room temperature GMR of 85.7% at a magnetic field of 0.6 T by using the non-conducting EB form of PANI nanocomposites embedded with iron oxide nanoparticles, Fig. 20(a and b). Interestingly, they observed that as the magnetic field gradually decreased from 0.6 to 0 T, the electrical resistance remained approximately constant with small fluctuations, Fig. 20(c), which was called “memory effect”. This memory effect originated from the used insulating nature of PANI, which prevented the trapped charges from leaking out of the system after the magnetic field was switched off. They also analyzed the obtained positive GMR with the wave-function shrinkage model and further confirmed that the positive GMR was attributed from the

<table>
<thead>
<tr>
<th>Model</th>
<th>Sample</th>
<th>Parameters</th>
<th>Magnetic field ( H ) (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wave-function shrinkage model (APS as oxidant)</td>
<td>20 wt% loading of silica/PANI [79]</td>
<td>( a_0 ) (nm)</td>
<td>32.2 14.7 10.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( N(E_F) ) (eV cm(^{-2}))</td>
<td>( 8.2 \times 10^{15} 8.6 \times 10^{14} 2.4 \times 10^{15} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( R_{hop} ) (nm)</td>
<td>220.4 100.8 71.9</td>
</tr>
<tr>
<td></td>
<td>20 wt% loading of silicon/PANI [115]</td>
<td>( a_0 ) (nm)</td>
<td>39.2 13.6 7.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( N(E_F) ) (eV cm(^{-2}))</td>
<td>( 6.5 \times 10^{15} 1.6 \times 10^{15} 8.3 \times 10^{15} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( R_{hop} ) (nm)</td>
<td>245.8 84.9 48.8</td>
</tr>
<tr>
<td></td>
<td>MWNTs/PANI:TA05 [114]</td>
<td>( a_0 ) (nm)</td>
<td>31.2 12.5 8.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( N(E_F) ) (eV cm(^{-2}))</td>
<td>( 9.3 \times 10^{14} 1.4 \times 10^{16} 4.3 \times 10^{16} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( R_{hop} ) (nm)</td>
<td>119.3 47.9 33.3</td>
</tr>
<tr>
<td>Forward interference model (Cr(VI) as oxidant)</td>
<td>5 wt% loading of MWNTs [114]</td>
<td>( a_0 ) (nm)</td>
<td>97.0 56.0 43.9</td>
</tr>
</tbody>
</table>

Fig. 17. MR transition from positive to negative in the 10.0 wt% silicon PANI nanocomposites. Reprinted with permission from Ref. [117].
Fig. 18. Proposed GMR mechanism in the silica/PANI nanocomposites. Reprinted with permission from Ref. [79].

Fig. 19. (a) MR+ obtained from wave-function shrinkage model; and (b) MR− obtained from forward interference model. Reprinted with permission from Ref. [117].

Fig. 20. (a) Schematic of PANI-iron oxide organic hybrid nanocomposite device; (b) magnetic field dependence GMR (obtained from $I-V$ curve) in PANI-iron oxide nanocomposites with 10% iron nanoparticles by volume; (c) resistance in 10% loading of PANI-iron oxide nanocomposites remained approximately constant after switching off the magnetic field, exhibiting a memory effect. Reprinted with permission from Ref. [119].
decreased $a_0$ of the charge carriers. This organic hybrid device was easily synthesized with a lower power consumption and cost, which has the possibility for practical applications in the magnetic field sensor devices at room temperature.

5. Conclusions and perspectives

In this paper, the up-to-date knowledge of the GMR phenomenon in the PANI and its nanocomposite systems has been reviewed. The electrical transport in the PANI systems without magnetic field and the MR mechanism including forward interference model and wave-function shrinkage model for the PANI systems are discussed as well. The MR effect is a common phenomenon in the PANI nanostructures and nanocomposites. Only the MR values or property (negative or positive) are different. Different PANI nanocomposites have different MR values arising from the synergistic interaction between PANI and nanofilbers. However, the GMR effect in the PANI system is still a crucial and puzzling problem due to the temperature dependent GMR property [120], which is normally decreased with increasing the temperature [115,119]. The synergistic interactions between nanofilbers and PANI matrix on the electrical transport within the hybrid systems are still open for discussing. Meanwhile, the crystallinity arising from the dopant type and doping degree should play a role in the GMR as well. How to prepare the PANI system with high room temperature MR values in the large-scale for practical applications still remains a challenge.

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