Giant Magnetoresistive Phosphoric Acid Doped Polyaniline−Silica Nanocomposites

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ABSTRACT: The phosphoric acid doped conductive polyaniline (PANI) polymer nanocomposites (PNCs) filled with silica nanoparticles (NPs) have been successfully synthesized using a facile surface initiated polymerization method. The chemical structures of the nanocomposites are characterized by Fourier transform infrared (FT-IR) spectroscopy. The enhanced thermal stability of the PNCs compared with that of pure PANI is observed by thermogravimetric analysis (TGA). The dielectric properties of these nanocomposites are strongly related to the silica nanoparticle loading levels. Temperature dependent resistivity analysis reveals a quasi 3-dimensional variable range hopping (VRH) electrical conduction mechanism for the synthesized nanocomposite samples. A positive giant magnetoresistance (GMR) is observed with a maximum value of 95.5% in the PNCs with a silica loading of 20.0 wt % and 65.6% for the pure PANI doped with phosphoric acid. The observed MR is well explained by wave function shrinkage model by calculating the changed localization length ($\xi$), density of states at the Fermi level ($N(E_F)$), and reduced average hopping length ($R_{hop}$). The effects of particle size on the properties including thermal stability, dielectric properties, temperature dependent resistivity, electrical conduction mechanism, and GMR of the nanocomposites are also studied.

1. INTRODUCTION

Compared with traditional composites, conductive polymer nanocomposites (PNCs) have been deployed widely in areas including electronics,1 sensors,2 and electrocatalysts3 due to their easy processability, flexibility,4 and excellent electrical, optical, and magnetic properties.5,6 Therefore, a great variety of multifunctional conductive PNCs have been prepared using layer-by-layer,7 electrospinning,8 electropolymerization,9 and surface initiated polymerization techniques.10,11 Among the conductive PNCs, significant efforts have been devoted to the polyaniline (PANI)-based PNCs due to their unique easy synthesis, controllable doping/dedoping process, and electrical and electrochemical properties.12 As one of the most important conjugated polymers, PANI has many potential applications including sensors,13 electrochemical mechanical actuators,14 electrochromic supercapacitors,15 and flexible electrodes.16 Silica (silicon dioxide, SiO$_2$), formed by the strong directional covalent bonds (Si−O, four oxygen atom array at the corner of a tetrahedron around a central silicon atom17), is one of the most commonly used substrates in many areas such as electronics manufacturing,18 photodynamic therapy,19 drug delivery,20 bone regeneration,21 catalysis,22 and sensing23 due to its unique properties including water solubility, chemical inertness, biocompatibility, and optical transparency.24 Silica is often used to fabricate composites with high stability especially in harsh environments, including high temperatures and strong acids/bases.25 Recently, there has been some research reported on the silica/PANI PNCs regarding the inkjet-printing electrochromic devices (doped with p-toluene sulfonic acid (PTSA) and synthesized by in situ polymerization),26 conductive capsules and hollow spheres (doped with sulfonated polystyrene and synthesized by in situ polymerization),27 and electrorheological responses (doped with dodecylbenzene sulfonic acid and synthesized by interfacial interaction).28

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Since the first discovery of the giant magnetoresistance (GMR) effect in the thin-film structural metallic materials composed of a pair of ferromagnetic layers (Fe) separated by a nonmagnetic metal layer (Cr) in 1988,29 GMR-based sensors have been designed and widely used in the areas including magnetic data storage (hard disc driver) and biological detection.30 In the last few decades, carbon-based organic systems have been promising materials and have attracted more attention in the GMR effects, since the element carbon has weak spin–orbit coupling and hyperfine interaction.31 Though the GMR in the organic systems has been obtained at low temperatures, the room temperature GMR signal is still too weak32 and to obtain large GMR signal at room temperature is still a challenge. Recently, the GMR in the conductive polymers and their nanocomposites have been reported. For example, around 95 and 20% of GMR is observed in the 30 wt % Fe3O4/PANI nanocomposites33 and 20 wt % BaTiO3 (∼500 nm)/PANI PNCs synthesized by the surface initiated polymerization method, and around 35% GMR is observed in the 20 wt % BaTiO3 (∼500 nm)/PANI PNCs prepared by a simple physical mixture of PANI and BaTiO3 powders.34 However, the GMR behaviors of the phosphoric acid (H3PO4) doped PANI and its silica PNCs together with the electrical conduction mechanism and dielectric properties have not been reported yet.

In this work, phosphoric acid doped conductive polyaniline nanocomposites filled with different silica nanoparticle loading levels and two different silica sizes have been successfully synthesized using a facile surface initiated polymerization (SIP) method. The chemical structures of the silica/PANI PNCs are characterized by Fourier transform infrared (FT-IR) spectroscopy. The thermal stability of the silica/PANI nanocomposites is performed by thermogravimetric analysis (TGA). Both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are used to characterize the morphologies of the silica/PANI nanocomposites. The temperature dependent resistivity and frequency dependent dielectric property are systematically investigated. The electrical conduction mechanism is studied from the temperature dependent resistivity analysis. The GMR properties in these nonmagnetic polymer and polymer nanocomposites are explained by the wave function shrinkage model by calculating the changed localization length (ξ) at the Fermi level, and reduced average hopping length (Rhop). The particle size effects on the properties including thermal stability, dielectric properties, temperature dependent resistivity, electrical conduction mechanism, and GMR behavior of these silica/PANI PNCs are investigated as well.

2. EXPERIMENTAL SECTION

2.1. Materials. Aniline (C6H5N) and ammonium persulfate (APS, (NH4)2S2O8) were purchased from Sigma Aldrich. Phosphoric acid (H3PO4, 85 wt %) was obtained from Fisher Scientific. The silica nanoparticles (NPs) with a average diameter of 60–70 nm (98+%, amorphous, specific surface area: 160–600 m2/g) and 20–30 nm (99+%, amorphous, specific surface area: 180–600 m2/g) were obtained from US Research Nanomaterials Inc. All of the chemicals were used as received without any further treatment.

2.2. Fabrication of Silica/PANI Nanocomposites. The silica/PANI nanocomposites were prepared with a surface initiated polymerization method. Briefly, the silica NPs (0.186–2.511 g), H3PO4 (15 mmol), and APS (9 mmol) were first added into 100 mL of deionized water in an ice–water bath for 1 h of mechanical stirring (SCILOGEX OS20-Pro LCD Digital Overhead Stirrer, 300 rpm) combined with sonication (Branson 8510). Then, the aniline solution (18 mmol in 25 mL of deionized water) was mixed with the above solution and mechanically stirred and sonicated continuously for an additional 1 h in an ice–water bath for further polymerization. The product was vacuum filtered and washed with deionized water. The precipitant was further washed with methanol to remove any possible oligomers. The final dark green silica/PANI nanocomposite powders were dried at 60 °C in an oven overnight. The silica (60–70 nm)/PANI nanocomposites with a particle loading of 10.0, 20.0, 40.0, and 60.0 wt % were synthesized, and the silica (20–30 nm)/PANI nanocomposites with a particle loading of 10.0 and 20.0 wt % were also synthesized to investigate the particle size effect on the properties of nanocomposites. Pure PANI doped with H3PO4 was also synthesized following the above same procedures without adding any NPs for comparison.

2.3. Characterizations. The Fourier transform infrared (FT-IR) spectra of the products were obtained on a Bruker Inc. Vector 22 (coupled with an ATR accessory) in the range 500–4000 cm−1 at a resolution of 4 cm−1. The morphologies of the synthesized nanocomposites were observed on a field emission scanning electron microscope (SEM, JEOL, JSM-6700F system). The samples were prepared by adhering the powders onto an aluminum plate. Thermogravimetric analysis (TGA) was conducted by a TA Instruments TGA Q500 instrument with a heating rate of 10 °C min−1 under an air flow rate of 60 mL min−1 from 30 to 800 °C.

Dielectric properties were investigated by an LCR meter (Agilent, E4980A) equipped with a dielectric test fixture (Agilent, 16451B) at a frequency of 20 to 2 × 106 Hz at room temperature. Pure PANI and its nanocomposite powders were pressed in a disc pellet form with a diameter of 25 mm by applying a pressure of 50 MPa in a hydraulic presser, and the average thickness was about 1.0 mm. The same sample was used to measure the resistivity (ρ) by a standard four-probe method from 180 to 290 K. The temperature dependent resistivity was used to determine the electrical conduction mechanism in the pure PANI and its nanocomposites.

Magnetoresistance (MR) was carried out using a standard four-probe technique by a 9-T Physical Properties Measurement System (PPMS) by Quantum Design at room temperature.

3. RESULTS AND DISCUSSION

3.1. FT-IR Analysis. Figure 1 shows the FT-IR spectra of the as-received silica NPs (60–70 nm), pure PANI doped with H3PO4, and its nanocomposites reinforced with different nanoparticle loadings. The strong absorption peaks at 1559 cm−1 for the pure PANI doped with H3PO4 Figure 1f, correspond to the C=C stretching vibration of the quinoid and benzenoid rings, respectively.35 The peak at 1239 cm−1 is attributed to the C—N stretching vibration of the benzenoid unit.36 The peaks at 1239 and 1117 cm−1 are assigned to the C—H and C—N stretching vibrations of the quinoid rings, respectively.35 The peak at around 785 cm−1 is attributed to the out-of-plane bending of C—H in the substituted benzenoid ring.37 These peaks are in good agreement with previous FT-IR spectroscopic characterization of PANI38 and have a little bit of shift (about 3–25 cm−1) in the FT-IR spectra of the silica/PANI PNCs, Figure 1a–e, indicating a strong interaction between silica and PANI, which is related to the charge

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delocalization on the polymer backbone. The absorption peaks at around 1066 and 800 cm$^{-1}$ are attributed to the stretching and bending vibrations of Si–O bonding, respectively, Figure 1a, and the peak intensity at around 1066 cm$^{-1}$ increases with increasing silica nanoparticle loading in the silica/PANI PNCs, Figure 1b–d.

3.2. Thermogravimetric Analysis. Figure 2 shows the TGA curves of the as-received silica NPs (60–70 nm), pure PANI doped with H$_3$PO$_4$, and its nanocomposites with different silica nanoparticle loadings in the air. For the as-received silica nanoparticles, there is only a slight weight loss (6.1 wt %) around 150 °C during the measured temperature range from 30 to 800 °C due to the loss of moisture. Two-stage weight losses are observed in the pure PANI and its nanocomposites. The first stage in the temperature range from room temperature to 250 °C is due to the elimination of moisture and the doped H$_3$PO$_4$ in PANI. The major weight loss of all the samples from 250 to 600 °C is due to the large scale thermal degradation of the PANI chains. Table 1 shows the summarized thermal properties of pure PANI doped with H$_3$PO$_4$ and its nanocomposites. The thermal stability of the silica/PANI PNCs is observed to increase with increasing silica nanoparticle loading. The 15 wt % loss decomposition temperature for pure PANI doped with H$_3$PO$_4$ and its PNCs with a silica nanoparticle loading of 10.0, 20.0, 40.0, and 60.0 wt % is 288, 321, 384, 423, and 489 °C, respectively. This increased thermal stability is attributed to the strong interaction between PANI and silica NPs and the lower mobility of the polymer chains when the polymer is bounded on the surface of silica NPs. In addition, the thermal stability of the H$_3$PO$_4$ doped PANI is lower than that of the p-toluene sulfonic acid (PTSA) doped PANI due to the presence of the benzene ring in the PTSA chemical structure (the 15 wt % loss decomposition temperature for the former is 288 and 303 °C for the latter). The pure PANI is almost completely decomposed at 800 °C with only 2.11 wt % left, which is due to the carbonized PANI. The weight residues of the nanocomposites with an initial silica nanoparticle loading of 10.0, 20.0, 40.0, and 60.0 wt % at 800 °C are 18.48, 33.54, 56.34, and 73.06%, respectively. The difference in the weight residues from the initially calculated particle loading based on the monomers and particles is associated with the incomplete polymerization of the aniline monomers.

3.3. Microstructures of the Nanocomposites. Figure 3 shows the SEM microstructures of the as-received silica nanoparticles (60–70 nm), pure PANI doped with H$_3$PO$_4$, and its PNCs. The PANI doped with H$_3$PO$_4$ is observed to have a rough and flake-like surface, Figure 3A. However, the as-received silica nanoparticles have a fairly smooth and ball-like surface, Figure 3B. These obvious differences on the surface are used to distinguish PANI from silica nanoparticles. In the PNCs, the smooth and ball-like surface of the silica nanoparticles is observed to become rough and flake-like, Figure 3C, indicating the polymerization of PANI occurred on the silica nanoparticle surface.

3.4. Dielectric Properties. The dielectric properties of the PNCs are related to the charge carrier motion within the matrix and interfacial polarization between the hosting polymer matrix and the nano fillers. Figure 4 depicts the real permittivity ($\varepsilon'$, Figure 4A), imaginary permittivity ($\varepsilon''$, Figure 4B), and dielectric loss (tan δ, where tan δ = $\varepsilon''/\varepsilon'$, Figure 4C) as a function of frequency for the pure PANI doped with H$_3$PO$_4$, and its PNCs with different silica (60–70 nm) loadings within the frequency range from 20 to 2 × 10$^4$ Hz at room temperature. In Figure 4A, all the samples exhibit positive $\varepsilon'$ within the measured frequency range and have an extremely high value at low frequency (20 Hz), then the $\varepsilon'$ decreases sharply with increasing frequency at low frequency range (<110 Hz), and it finally slightly decreases with further increase of the frequency. Compared with the PTSA doped PANI (negative
permittivity from $-32$ to $-12$ within the whole measured frequency range from 20 to $2 \times 10^6$ Hz,$^{33}$ the H$_3$PO$_4$ doped PANI shows a huge positive $\varepsilon'$ with order of $10^5$ at a frequency of 20 Hz. The large positive permittivity of PANI represents charge delocalization that occurs in the mesoscopic range. However, for the nanocomposites with high silica nanoparticle loading, $\varepsilon'$ decreases dramatically owing to the low dielectric constant ($\approx 1.8-2.5$) of silica$^{45}$ compared with the H$_3$PO$_4$ doped PANI matrix. The $\varepsilon''$ is observed to have the same trend as $\varepsilon'$ and decreases as the frequency increases to $10^5$ Hz and then slightly decreases with increasing frequency to $10^6$ Hz. The tan $\delta$ is also observed to have the same trend as $\varepsilon'$ and $\varepsilon''$. In the high frequency range ($10^5-10^6$ Hz), tan $\delta$ has a very small value and almost reaches zero, indicating that these nanocomposites can be used as electronic devices with less energy waste.$^{35}$ The significantly higher tan $\delta$ of the silica/PANI PNCs with a silica
A nanoparticle loading of 60 wt % compared with other loadings within the whole frequency range is attributed to the completely constructed charge transport channel.\textsuperscript{11}

3.5. Temperature Dependent Resistivity - Electrical Conduction Mechanism. The temperature dependent resistivity of the H$_3$PO$_4$ doped PANI and its nanocomposites with different silica nanoparticle loadings is measured from 180 to 290 K, Figure 5A. Normally, the electrical conductivity of the acid doped PANI strongly depends on the doped acid with electron donor ability\textsuperscript{46} and is about 8–11 orders of magnitude (10$^{-1}$–10$^{0}$ S cm$^{-1}$)\textsuperscript{47} higher than that of the PANI base (10$^{-9}$ S cm$^{-1}$).\textsuperscript{148} In Figure 5A, all of the prepared samples exhibit a semiconductive behavior within the measured temperature range and the resistivity decreases with increasing temperature.\textsuperscript{49} The resistivity of the H$_3$PO$_4$ doped PANI (1.7 × 10$^3$ and 4.6 × 10$^2$ Ω cm for 180 K and room temperature, respectively) is higher than that of the PTSA doped PANI (6.0 × 10$^2$ and 2.0 × 10$^2$ Ω cm for 180 K and room temperature, respectively).\textsuperscript{33} The resistivity increases with increasing silica nanoparticle loading, since the silica nanoparticles affect the interaction between the PANI polymer matrix and the doped acid, which partially blocks the charge transport pathway.\textsuperscript{50}

The electrical conduction mechanism is explored by the Mott variable range hopping (VRH) approach,\textsuperscript{51} represented as eq 1:

$$\sigma = \sigma_0 \exp \left[-\left(\frac{T_0}{T}\right)^{1/(n+1)}\right]$$

where $\sigma_0$ is a constant, standing for the conductivity at infinitely low temperature, $T$ is the Kelvin temperature, and the constant $T_0$ (K) is the characteristic Mott temperature, which relates to the energy needed for the charge carrier’s hopping and given by eq 2:\textsuperscript{52}

$$T_0 = \frac{24}{\pi k_b N(E_F) \xi^3}$$

where $\xi$ (nm) is the localization length of the localized wave function of charge carriers, $k_b$ is Boltzmann’s constant, and $N(E_F)$ ((J cm$^{-3}$)$^{-1}$, ($J = kg m^2 s^{-2}$)) is the density of states at the Fermi level. Equation 2 indicates that $T_0$ is related to both the density of states at the Fermi level $N(E_F)$ and the localization length $\xi$. The $n$ value in eq 1 is related to the dimensionality of the conduction process and $n = 3, 2, 1$ for the 3-, 2-, and 1-dimensional systems, respectively.\textsuperscript{53} $\sigma_0$ and $T_0$ can be obtained from the intercept and the slope of the plot $\ln(\sigma) \sim T^{-1/(n+1)}$. The plot of $\ln(\sigma) \sim T^{-1/(n+1)}$ (obtained from Figure 5A) is shown in Figure 5B. The temperature dependent resistivity of pure PANI doped with H$_3$PO$_4$ and its nanocomposites with different silica nanoparticle loadings is observed to follow a $\ln(\sigma) \sim T^{-1/4}$ linear relationship, indicating a quasi 3-d VRH electrical conduction mechanism. The obtained $\sigma_0$ and $T_0$ values from Figure 5B are summarized in Table 2. Both $T_0$ and $\sigma_0$ of the H$_3$PO$_4$ doped PANI ((9.48 ± 0.23) × 10$^6$ K and 5319.289 ± 0.010 S cm$^{-1}$, respectively) are higher than those of the PTSA doped PANI (7.0 × 10$^6$ K and 1826 S cm$^{-1}$, respectively).\textsuperscript{33} $T_0$ is reported to be strongly dependent on the disorder (which represents random potential fluctuation in the semiconductor);\textsuperscript{54} in PANI, the disorder means the sequence of quinoid–benzenoid groups is random$^{55}$ presented in the samples and can be measured by the resistivity ratio $\rho_{200}/\rho_{180}$, $\rho_{200}/\rho_{180}$).\textsuperscript{56} Generally, both the disorder in the samples and $T_0$

![Figure 5. (A) Resistivity vs temperature and (B) ln(σ) and $\sigma_0$ of (a) pure PANI doped with H$_3$PO$_4$ and the silica (60–70 nm)/PANI PNCs with a nanoparticle loading of (b) 10.0, (c) 20.0, (d) 40.0, and (e) 60.0 wt %.

| Table 2. $T_0$, $\sigma_0$, and $\rho_2$ for the H$_3$PO$_4$ Doped PANI and Its Silica Nanocomposites |
|-----------------|-----------------|-----------------|
| samples         | $T_0 \times 10^2$ (K) | $\sigma_0$ (S cm$^{-1}$) | $\rho_2$ |
| H$_3$PO$_4$ doped PANI | 0.948 ± 0.023 | 5319.289 ± 0.010 | 3.641 |
| silica (60–70 nm)/PANI |
| 10.0 wt %       | 1.146 ± 0.017 | 4812.057 ± 0.007 | 4.358 |
| 20.0 wt %       | 3.217 ± 0.121 | 32039.987 ± 0.018 | 5.291 |
| 40.0 wt %       | 4.166 ± 0.033 | 32112.192 ± 0.004 | 7.087 |
| 60.0 wt %       | 5.784 ± 0.266 | 32130.789 ± 0.025 | 10.801 |
| silica (20–30 nm)/PANI |
| 10.0 wt %       | 1.157 ± 0.006 | 4998.984 ± 0.009 | 3.742 |
| 20.0 wt %       | 2.022 ± 0.072 | 8440.949 ± 0.017 | 5.031 |
increase with increasing $\rho_e$.\(^\text{57}\) In the silica/PANI nanocomposite system, the calculated $\rho_e$ is listed in Table 2. $\rho_e$ increases with increasing silica nanoparticle loading, indicating that the disorder in the silica/PANI nanocomposites increases with increasing silica nanoparticle loading. $T_0$ of the silica/PANI nanocomposites is also found to increase with increasing silica nanoparticle loading, indicating a larger number of defects and increased $\rho_e$.\(^\text{58}\) Normally, the defects (e.g., dopants or impurities) can perturb the electronic structure of the semiconductors and act as scattering centers for charge carriers and holes traveling through the semiconductors to affect the charge carrier transport in the semiconductors.\(^\text{59}\) Thus, the observed larger $T_0$ is attributed to the stronger charge carrier scattering. Table 2. The $\sigma_0$ slightly decreases as the silica nanoparticle loading increases to 10.0 wt % and then increases obviously with increasing silica nanoparticle loading to 20.0 wt %.

After that, the $\sigma_0$ slightly increases with increasing silica nanoparticle loading. A bigger $T_0$ corresponds to a higher $\sigma_0$ which is due to the modulated electromagnetic wave\(^\text{31}\) (the electromagnetic wave propagating in a semiconductor along the direction of an alternating magnetic field becomes modulated at the frequency of electrical field\(^\text{60}\)) in the nanostructures of the silica/PANI nanocomposites.

### 3.6. Magnetoresistance (MR)

The magnetoresistance (MR) is defined by eq 3:

$$MR\% = \frac{\Delta R}{R} = \frac{R(H) - R(0)}{R(0)} \times 100$$

where $R(0)$ and $R(H)$ are the resistance at zero magnetic field and at any applied magnetic field $H$, respectively. The MR results of the $H_3PO_4$ doped PANI and its nanocomposites with different silica nanoparticle loadings at 290 K are shown in Figure 6. The MR for all of the samples is observed to be positive within the whole measured magnetic field and increases with increasing applied magnetic field and then reaches the maximum value at high field. The MR of the $H_3PO_4$ doped PANI (65.6%) is found to be higher than that of the PTSA doped PANI (53%).\(^\text{33}\) The MR value of the silica/PANI nanocomposites increases as the silica nanoparticle loading increases to 20.0 wt % (95.5%) (MR is 11.5% for 10.0 wt % silica/PANI nanocomposites) and then decreases with increasing silica nanoparticle loading. The MR values of the silica/PANI nanocomposites with a silica nanoparticle loading of 10.0, 20.0, 40.0, and 60.0 wt % is 95.5% for 10.0 wt % silica/PANI PNCs with a nanoparticle loading of (b) 70 nm)/PANI PNCs with a nanoparticle loading of (b) $20.0$, (c) $40.0$, and (d) $60.0$ wt % at $290$ K.

**Figure 6.** Magnetoresistance of (a) pure PANI doped with $H_3PO_4$ and the silica (60–70 nm)/PANI PNCs with a nanoparticle loading of (b) 10.0, (c) 20.0, (d) 40.0, and (e) 60.0 wt % at 290 K.

The slope of MR curves for the $H_3PO_4$ doped PANI and its silica/PANI nanocomposites with a nanoparticle loading of 10.0, 20.0, 40.0, and 60.0 wt % is 0.0017, 0.0005, 0.0073, 0.0018, and 0.0015, respectively, indicating that the MR sensitivity obeys the following relationship: 10.0 wt % silica/PANI PNCs < 60.0 wt % silica/PANI PNCs < $H_3PO_4$ doped PANI < 40.0 wt % silica/PANI PNCs < 20.0 wt % silica/PANI PNCs. These materials with high MR sensitivity to the external magnetic field could be used as magnetic field sensors.\(^\text{62}\)

The wave function shrinkage model is often used to describe the MR of highly disorderedly localized systems in the variable-range hopping (VRH) regime.\(^\text{63}\) In this model, the contraction of the electronic wave function at impurity centers under a magnetic field leads to a reduction in the hopping probability between two sites, which causes a positive MR. In this model, the ratio of $R(H, T)$ and $R(0, T)$ is described as eq 4:\(^\text{63}\)

$$R(H, T)/R(0, T) = \exp\left[\frac{\xi_c(H)/\xi_c(0) - 1}{2}\right]$$

where $\xi_c(0) = (T_0/H)^{1/4}$ for the Mott VRH conduction mechanism and $\xi_c(H)/\xi_c(0)$ is the normalized hopping probability parameter and is a function of $H/P_\text{C}$ for the Mott VRH conduction mechanism. $H$ is the magnetic field (Tesla), unit of magnetic field, $1$ T = $10^4$ Oe, $T$ = $k_B$ C\(^{-1}\) s\(^{-1}\)), and $P_\text{C}$ is the fitting parameter given by eq 5 for the Mott VRH conduction mechanism:

$$P_\text{C} = 6h/([\epsilon^2(T_0/H)^{1/4}]$$

where $\epsilon$ is the electron charge (1.6021765 × $10^{-19}$ C), $h$ is the reduced Planck’s constant and $h = h/2\pi$, $h$ is Planck’s constant, and $T_0$ is the Mott characteristic temperature (K). In the low-field limit, eq 4 is simplified to eq 6:

$$R(H, T)/R(0, T) \approx 1 + t_2\frac{H^2}{P_\text{C}^2}\left(\frac{T_0}{T}\right)^{1/4}$$

And the MR is defined in eq 7:

$$MR = \frac{R(H, T) - R(0, T)}{R(0, T)}$$

$$\approx t_2\frac{H^2}{P_\text{C}^2}\left(\frac{T_0}{T}\right)^{1/4}$$

$$= t_2\frac{\epsilon^4}{36h^2}\left(\frac{T_0}{T}\right)^3H^2$$

where the numerical constant is $t_2 = 5/16$.\(^\text{64}\)

According to eq 7, the localization length $\xi$ could be obtained by eq 8 from $T_w$ MR value, and magnetic field $H$:

$$\xi^4 = \frac{36h^2MR}{t_2\epsilon^2}\left(\frac{T_0}{T}\right)^{-3/4}H^{-2}$$

For example, $T_w$ is $(9.48 \pm 0.23) \times 10^6$ K for the $H_3PO_4$ doped PANI, and the calculated $\xi$ from eq 8 for temperature at $T = 290$ K is $94.3 \pm 2.3, 52.5 \pm 1.3$, and $37.6 \pm 0.9$ nm for a magnetic field $H$ of 0.5, 4, and 9 T. The calculated localization length $\xi$ of the silica/PANI nanocomposites with different silica loadings is shown in Table 3. $\xi$ has different values under...
Table 3. $\xi$, $N(E_F)$, $R_{\text{hop}}$, and $\Delta R_{\text{hop}}$ for the H$_3$PO$_4$ Doped PANI and Its Silica Nanocomposites at Different Magnetic Fields $H$

<table>
<thead>
<tr>
<th>samples</th>
<th>parameters</th>
<th>0.5</th>
<th>4</th>
<th>9</th>
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<tbody>
<tr>
<td>H$_3$PO$_4$ doped PANI</td>
<td>$\xi$ (nm)</td>
<td>943 ± 2.3</td>
<td>52.5 ± 1.3</td>
<td>37.6 ± 0.9</td>
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<tr>
<td></td>
<td>$N(E_F)$ (J cm$^{-1}$)</td>
<td>(6.9 ± 0.5) × 10$^{11}$</td>
<td>(4.0 ± 0.3) × 10$^{11}$</td>
<td>(1.1 ± 0.1) × 10$^{11}$</td>
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<td></td>
<td>$R_{\text{hop}}$ (µm)</td>
<td>0.475 ± 0.012</td>
<td>0.264 ± 0.007</td>
<td>0.190 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>$\Delta R_{\text{hop}}$ (µm)</td>
<td>(0.5 → 4 T) = 0.211 ± 0.014, (0.5 → 9 T) = 0.285 ± 0.013, (4 → 9 T) = 0.074 ± 0.009</td>
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<tr>
<td>silica (60–70 nm)/PANI PNCs 10.0 wt %</td>
<td>$\xi$ (nm)</td>
<td>688 ± 1.0</td>
<td>32.6 ± 0.5</td>
<td>23.6 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>$N(E_F)$ (J cm$^{-1}$)</td>
<td>(1.5 ± 0.1) × 10$^{11}$</td>
<td>(1.4 ± 0.1) × 10$^{11}$</td>
<td>(3.7 ± 0.2) × 10$^{11}$</td>
</tr>
<tr>
<td></td>
<td>$R_{\text{hop}}$ (µm)</td>
<td>0.363 ± 0.005</td>
<td>0.172 ± 0.002</td>
<td>0.124 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>$\Delta R_{\text{hop}}$ (µm)</td>
<td>(0.5 → 4 T) = 0.191 ± 0.005, (0.5 → 9 T) = 0.239 ± 0.005, (4 → 9 T) = 0.048 ± 0.003</td>
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<tr>
<td>20.0 wt %</td>
<td>$\xi$ (nm)</td>
<td>1018 ± 3.8</td>
<td>46.6 ± 1.8</td>
<td>33.2 ± 1.2</td>
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<td></td>
<td>$N(E_F)$ (J cm$^{-1}$)</td>
<td>(1.6 ± 0.1) × 10$^{11}$</td>
<td>(1.7 ± 0.2) × 10$^{11}$</td>
<td>(47 ± 0.5) × 10$^{11}$</td>
</tr>
<tr>
<td></td>
<td>$R_{\text{hop}}$ (µm)</td>
<td>0.697 ± 0.027</td>
<td>0.319 ± 0.013</td>
<td>0.227 ± 0.009</td>
</tr>
<tr>
<td></td>
<td>$\Delta R_{\text{hop}}$ (µm)</td>
<td>(0.5 → 4 T) = 0.378 ± 0.030, (0.5 → 9 T) = 0.470 ± 0.016, (4 → 9 T) = 0.092 ± 0.016</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40.0 wt %</td>
<td>$\xi$ (nm)</td>
<td>686 ± 0.5</td>
<td>29.5 ± 0.2</td>
<td>20.9 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>$N(E_F)$ (J cm$^{-1}$)</td>
<td>(4.1 ± 0.1) × 10$^{11}$</td>
<td>(5.2 ± 0.1) × 10$^{11}$</td>
<td>(1.5 ± 0.1) × 10$^{11}$</td>
</tr>
<tr>
<td></td>
<td>$R_{\text{hop}}$ (µm)</td>
<td>0.501 ± 0.004</td>
<td>0.215 ± 0.008</td>
<td>0.153 ± 0.004</td>
</tr>
<tr>
<td></td>
<td>$\Delta R_{\text{hop}}$ (µm)</td>
<td>(0.5 → 4 T) = 0.286 ± 0.009, (0.5 → 9 T) = 0.348 ± 0.006, (4 → 9 T) = 0.062 ± 0.009</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60.0 wt %</td>
<td>$\xi$ (nm)</td>
<td>678 ± 3.1</td>
<td>29.7 ± 1.4</td>
<td>19.2 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>$N(E_F)$ (J cm$^{-1}$)</td>
<td>(3.1 ± 0.3) × 10$^{11}$</td>
<td>(3.7 ± 0.5) × 10$^{11}$</td>
<td>(1.4 ± 0.2) × 10$^{11}$</td>
</tr>
<tr>
<td></td>
<td>$R_{\text{hop}}$ (µm)</td>
<td>0.377 ± 0.025</td>
<td>0.233 ± 0.011</td>
<td>0.152 ± 0.007</td>
</tr>
<tr>
<td></td>
<td>$\Delta R_{\text{hop}}$ (µm)</td>
<td>(0.5 → 4 T) = 0.302 ± 0.027, (0.5 → 9 T) = 0.386 ± 0.026, (4 → 9 T) = 0.083 ± 0.013</td>
<td></td>
<td></td>
</tr>
<tr>
<td>silica (30–30 nm)/PANI PNCs 10.0 wt %</td>
<td>$\xi$ (nm)</td>
<td>686 ± 0.4</td>
<td>32.5 ± 0.2</td>
<td>23.5 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>$N(E_F)$ (J cm$^{-1}$)</td>
<td>(1.5 ± 0.1) × 10$^{11}$</td>
<td>(1.4 ± 0.1) × 10$^{11}$</td>
<td>(3.7 ± 0.1) × 10$^{11}$</td>
</tr>
<tr>
<td></td>
<td>$R_{\text{hop}}$ (µm)</td>
<td>0.363 ± 0.002</td>
<td>0.172 ± 0.001</td>
<td>0.125 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>$\Delta R_{\text{hop}}$ (µm)</td>
<td>(0.5 → 4 T) = 0.191 ± 0.002, (0.5 → 9 T) = 0.238 ± 0.002, (4 → 9 T) = 0.047 ± 0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.0 wt %</td>
<td>$\xi$ (nm)</td>
<td>1112 ± 4.0</td>
<td>50.6 ± 1.8</td>
<td>36.1 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>$N(E_F)$ (J cm$^{-1}$)</td>
<td>(1.9 ± 0.2) × 10$^{11}$</td>
<td>(2.1 ± 0.2) × 10$^{11}$</td>
<td>(57 ± 0.6) × 10$^{11}$</td>
</tr>
<tr>
<td></td>
<td>$R_{\text{hop}}$ (µm)</td>
<td>0.678 ± 0.025</td>
<td>0.308 ± 0.011</td>
<td>0.220 ± 0.008</td>
</tr>
<tr>
<td></td>
<td>$\Delta R_{\text{hop}}$ (µm)</td>
<td>(0.5 → 4 T) = 0.370 ± 0.027, (0.5 → 9 T) = 0.458 ± 0.026, (4 → 9 T) = 0.088 ± 0.014</td>
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</tbody>
</table>
different magnetic fields. After $\xi$ was obtained, the density of states at the Fermi level $N(E_F)$ could be calculated from eq 9:

$$N(E_F) = \frac{24}{\pi k_B T \xi^3}$$

and the calculated results are listed in Table 3. Generally, the increased $N(E_F)$ could increase the hopping probability between the localized states.

According to Entin-Wohlman et al.,66 the MR value in the small magnetic fields should be proportional to the square of the flux ($aH$, where $A$ is the area and $H$ is the magnetic field) inside a coherent threading loop and can be described by eq 10:

$$\text{MR} = \frac{\Delta R}{R} \sim A^2 H^2 = R_{\text{hop}}^3(T, c, H)a(c, H)H^2$$

where $R_{\text{hop}}$ is the average hopping length, $a$ is the microscopic length (i.e., the typical distance between impurities67), and $c$ is the carrier concentration. For a given sample under small magnetic fields, both $R_{\text{hop}}$ and $a$ are at the weakest functions of the field and thus MR is only related to $T$ and $H$ and can be simplified to eq 11.68

$$\text{MR} = \frac{\Delta R}{R} = f(T)H^2 \sim R_{\text{hop}}^3H^2$$

This equation confirms that the MR value is also related to the average hopping length $R_{\text{hop}}$. The average hopping length could be calculated by eq 12 from the localization length $\xi$:

$$R_{\text{hop}} = \frac{3}{8}(T_0/T)^{1/4} \xi$$

The calculated $R_{\text{hop}}$ (nm) values are shown in Table 3, and the results show that, in the silica/PANI PNCs, the more reduced $R_{\text{hop}}$ ($\Delta R_{\text{hop}}$), the higher value of MR obtained. Normally, the MR in the hopping system is due to the charge carrier hopping
conduction arising from the contraction of the charge carrier wave function and the subsequent reduced average hopping length.\textsuperscript{13} Our results in the silica/PANI nanocomposite systems further confirm this conclusion. The proposed GMR mechanism in the silica/PANI PNCs is shown in Scheme 1.

3.7. Effect of Particle Size on Properties of the Silica/PANI PNCs. In this work, the effect of particle size on the properties of the silica/PANI nanocomposites is studied. The small sized silica (20–30 nm)/PANI nanocomposites with a silica nanoparticle loading of 10.0 and 20.0 wt % were synthesized for comparison. The thermal stability of the small sized silica/PANI nanocomposites is summarized in Table 1. The TGA curves, dielectric properties, and temperature dependent resistivity are provided in the Supporting Information. The TEM images of the as-received silica nanoparticles and the synthesized small silica (20–30 nm)/PANI nanocomposites are shown in Figure 7A and B, respectively. The average size of the small silica nanoparticles is about 21.3 nm, which is consistent with the information provided by the company. A clear shell coating is observed outside the silica nanoparticles, Figure 7B, indicating the presence of the PANI layer. The electrical conduction mechanism is also evaluated by the Mott VRH approach as aforementioned eq 1, and the results are shown in Figure 7C. The obtained $T_0$, $\sigma_0$, and $\rho_0$ of the synthesized small sized silica (20–30 nm)/PANI nanocomposites are summarized in Table 2. For the PANI PNCs with 10.0 wt % loading of small silica NPs, the $T_0$ and $\sigma_0$ are very close to those of the PANI nanocomposites with the same loading of the big silica nanoparticles and have no obvious changes. However, as the loading increases to 20.0 wt %, the $T_0$ and $\sigma_0$ of the silica/PANI nanocomposites with small silica nanoparticles are much lower than those of the PANI nanocomposites with the same loading of big silica nanoparticles. The $\rho_0$ of the small silica/PANI nanocomposites is lower than that of big silica/PANI nanocomposites, indicating that less disorder is in the small silica/PANI PNC system.\textsuperscript{56}

The room temperature MR values of the small silica/PANI nanocomposites with a loading of 10.0 and 20.0 wt %, Figure 7D, are observed to be almost the same as those of the big silica/PANI nanocomposites, indicating that the nanoparticle size has no obvious effect on the MR value. Mahesh et al.\textsuperscript{69} have investigated the effect of particle size on the electron transport and magnetic properties of La$_{0.5}$Ca$_{0.5}$MnO$_3$ and found that the maximum MR of the samples at near $T_c$ (ferromagnetic Curie temperature, above which a ferromagnetic material becomes paramagnetic) is not sensitive to the particle size, but the MR at 4.2 K increases with decreasing particle size, which is attributed to a substantial contribution by the grain boundaries in the polycrystalline samples. The calculated localization length $\xi$, density of states at the Fermi level $N(E_F)$, and $R_{\text{hop}}$ according to eqs 8, 9 and 12 are also listed in Table 3. From Table 3, it can be concluded that even the $\xi$ and $N(E_F)$ are different for different sizes of the silica/PANI nanocomposites with the same particle loading due to the difference of $T_0$ the $\Delta R_{\text{hop}}$ is almost the same, which further confirms that the MR value in these silica/PANI PNCs is mainly related to the $\Delta R_{\text{hop}}$.

4. CONCLUSIONS

The polyaniline nanocomposites reinforced with different silica nanoparticle loading levels have been synthesized using a surface initiated polymerization method. The effects of particle size on the nanocomposite properties have been systematically investigated. The introduction of the silica nanoparticles dramatically enhances the thermal stability of PANI, and the thermal stability of the silica/PANI nanocomposites is increased with increasing silica nanoparticle loading. The SEM results indicate that the silica nanoparticles have been coated with PANI. The dielectric properties of these nanocomposites are strongly related to the silica nanoparticle loading, and the H$_3$PO$_4$ doped PANI and its nanocomposites show a positive permittivity, which is different from the PTSA doped PANI (negative permittivity). The resistivity of the silica/PANI nanocomposites is observed to increase with increasing silica nanoparticle loading. The Mott variable range hopping (VRH) model is used to evaluate the electrical conduction mechanism of these nanocomposites and reveals a quasi 3-d VRH electrical conduction mechanism. A large positive magnetoresistance (MR) is observed in the non-magnetic H$_3$PO$_4$ doped PANI (65.6%) and its nanocomposites with 20.0 wt % silica nanoparticle loading (95.6%). The observed GMR is well explained by the wave function shrinkage model by calculating the changed localization length $\xi$, density of states at the Fermi level $N(E_F)$, and reduced average hopping length $R_{\text{hop}}$. The particle sizes can affect the thermal stability, dielectric properties, and resistivity of the silica/PANI nanocomposites but have no obvious effect on the MR properties.


Effect of Particle Size on the Giant Magnetoresistance of La0.7Ca0.3MnO3. *Appl. Phys. Lett.* 2002, 80, 3417–3419.


Large Magnetoresistance of Al0.9Pd22,Re0.1 Quasicrystals in the Variable-Range Hopping Regime. *Phys. Rev. B* 2002, 66, 054438.