Giant magnetoresistance in non-magnetic phosphoric acid doped polyaniline silicon nanocomposites with higher magnetic field sensing sensitivity†

Hongbo Gu,ab Jiang Guo,ac Huige Wei,a Yudong Huang,b Cunyu Zhao,d Ying Li,d Qingliu Wu,e Neel Haldolaarachchige,† David P. Young, Suying Weiac and Zhanhu Guoa

Phosphoric acid doped conductive polyaniline (PANI) polymer nanocomposites (PNCs) reinforced with silicon nanopowders have been successfully synthesized using a facile surface initiated polymerization (SIP) method. The chemical structures of the nanocomposites are characterized using Fourier transform infrared (FT-IR) spectroscopy. The enhanced thermal stability of the silicon–PANI PNCs compared with pure PANI is obtained using thermogravimetric analysis (TGA). The obtained optical band gap of the nanocomposites is calculated using Ultraviolet–visible diffuse reflectance spectroscopy (UV-vis DRS) decreases with increasing silicon loading. The dielectric properties of the PNCs are strongly related to the silicon loading level. Temperature dependent resistivity analysis reveals a quasi 3-D variable range hopping (VRH) electrical conduction mechanism for the synthesized PNCs. Room temperature giant magnetoresistance (GMR) is observed in the synthesized non-magnetic nanocomposites and analyzed using the wave-function shrinkage model.

Introduction
Conductive polymer nanocomposites (PNCs) have gained tremendous attention owing to their unique electrical conductivity combined with other unique properties, such as light weight, easy processability, flexibility,1,2 good environmental stability3 and optical properties,4 which render them wide potential applications including electronic devices,5 sensors,6 electrocatalysts,7,8 electrochromic devices,9–11 and performances of the PNCs could be achieved by adjusting filler type, size, shape and loading level in the polymer matrix.3

Recently, many different fillers have been introduced in the conductive polymer matrix to provide the polymer with unique properties. For example, the dielectric properties of conductive polymers and their PNCs are observed to be dependent on the dopant,13,14 the fabrication method,14 the fillers and the morphologies of polyaniline (PANI).15 Gu et al.13 and Zhang et al.14 have reported negative permittivity in the magnetite–PANI and barium titanate–PANI PNCs doped with p-toluene-sulfonic acid (PTSA) within the frequency range from 20 to 10⁶ Hz at room temperature, respectively. Zhang et al.14 have also reported positive permittivity in the physical mixture of barium titanate and PANI doped with PTSA. Zhang et al.15 have reported negative permittivity in the PANI fibers prepared using the interfacial polymerization method. Zhu et al.16,17 have noticed positive permittivity in the Al₂O₃–PANI PNCs, in which the permittivity is related to the morphology and dispersion quality of the nanofillers. Zhu et al.18 have reported negative permittivity in the tungsten oxide–polypyrrole (PPy) PNCs, which could be easily tuned by varying the nanofiller loading, the chemical ratio, and filler morphology. Meanwhile, Gu et al.13 reported a room temperature giant magnetoresistance (GMR), which is defined as a significant change normally larger than 1% in resistance in response to an external magnetic field,16,19 of 95% in the magnetite–PANI PNCs compared with pure PANI (53%).
PANI is one of the most studied conducting polymers over the last 50 years because of its easy doping–dedoping process, low cost, good stability, high conductivity and pseudocapacitance and wide potential applications including supercapacitors, environmental remediation and coupling agents between epoxy resin and nanofillers. Generally, the electrical conductivity of the acid doped PANI is strongly dependent on the electron donor ability of the dopant and is about 8–11 orders of magnitude higher than that of the PANI base. Most of the research studies focus on the properties of PANI doped with hydrochloric acid (HCl), sulfuric acid (H$_2$SO$_4$) and camphorsulfonic acid (CSA), but there are only a few reports on the electrical conductivity of PANI doped with phosphoric acid.

Silicon, as an intrinsic semiconductor, has been intensively investigated for use as visible light-emitting devices, electronic memory devices, anode materials for lithium-ion batteries, spintronics and as photosensitzers for singlet oxygen and phototoxicity against cancer cells. Silicon can also be introduced into the polymer matrix to provide unique properties. For example, Liu et al. have fabricated the supercapacitors electrodes based on the silicon–PANI PNCs, which demonstrated significantly improved capacitance compared with that of PANI. Ng et al. have reported on the carbon coated silicon nanocomposites as anodes for lithium-ion batteries synthesized using a spray-pyrolysis technique, which can reversibly store lithium with both a high capacity of 1489 mAh g$^{-1}$ and a high coulombic efficiency of above 99.5% even after 20 cycles. However, the dielectric properties, optical properties and GMR behaviour of the PANI doped with phosphoric acid and its silicon PNCs have been rarely reported so far.

In this work, phosphoric acid doped PANI PNCs reinforced with different silicon nanopowder loading levels have been successfully synthesized using a facile surface initiated polymerization (SIP) method. The chemical structures of the PANI PNCs are characterized using Fourier transform infrared (FT-IR) spectroscopy. The thermal stability of the nanocomposites is determined using thermogravimetric analysis (TGA). Both scanning electron microscope (SEM) and transmission electron microscope (TEM) are used to characterize the morphologies of the PNCs. The electrical conduction mechanism is studied using the temperature dependent resistivity analysis. The frequency dependent dielectric property and GMR behavior are systematically investigated as well. The GMR was also analyzed using the wave-function shrinkage model for these non-magnetic silicon–PANI PNCs.

**Preparation of silicon–PANI PNCs**

The silicon–PANI PNCs were prepared using a SIP method. First, the silicon nanopowders (0.186–2.511 g), H$_3$PO$_4$ (15 mmol) and APS (9 mmol) were added into 100 mL deionized water in an ice-water bath for one-hour 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 deionized water) was mixed with the above solution and mechanically stirred and sonicated continuously for additional one hour 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 silicon–PANI PNC powders were dried at 60 °C in an oven overnight. The silicon–PANI PNCs with a particle loading of 10.0, 20.0, 40.0 and 60.0 wt% were synthesized. Pure PANI doped with H$_3$PO$_4$ was also fabricated following the above procedures without adding any nanopowders for comparison.

**Characterization**

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 of 500 to 4000 cm$^{-1}$ at a resolution of 4 cm$^{-1}$. The morphologies of the synthesized PNCs were observed in a JEOL JSM-6510LV SEM after being coated with carbon. The high resolution transmission electron microscopy (HRTEM) was performed on the Hitachi H9000NAR. Thermogravimetric analysis (TGA) was conducted using TA instruments TGA Q-500 at a heating rate of 10 °C min$^{-1}$ and at an air flow rate of 60 mL min$^{-1}$ from 30 to 800 °C.

Ultraviolet-visible (UV-vis) diffuse reflectance spectroscopy (DRS) of PANI and its silicon PNCs was recorded on a UV/VIS/NIR spectrophotometer (PC, JASCO Model V-670) equipped with a Jasco ISN-723 diffuse reflectance accessory. The samples were prepared by pressing pure PANI and its PNC powders into 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 samples were also used to measure the dielectric properties, resistivity and magnetoresistance (MR). The dielectric properties were investigated using an LCR meter (Agilent, E4980A) equipped with a dielectric test fixture (Agilent, 16451B) at the frequency from 20 to 2 x 10$^6$ Hz at room temperature. The resistivity ($\rho$) was measured using a standard four-probe method from 100 to 290 K. The temperature dependent resistivity was used to determine the electrical conduction mechanism in pure PANI and its PNCs. MR was carried out using a standard four-probe technique by a 9-Tesla Physical Properties Measurement System (PPMS) by Quantum Design at room temperature. The four probes were 0.002 inch diameter platinum wires, which were attached by silver paste to the sample. And the magnetic field was applied perpendicular to the sample.

**Results and discussion**

**FT-IR analysis**

Fig. 1 shows the FT-IR spectra of the as-received silicon, pure PANI doped with H$_3$PO$_4$ and its PNCs filled with different
Silicon nanopowder loadings. The strong absorption peaks at 1557 and 1472 cm\(^{-1}\) for pure PANI doped with H\(_3\)PO\(_4\), Fig. 1(b), correspond to the C=C stretching vibration of the quinoid and benzenoid rings, respectively.\(^{17}\) The band at 1288 cm\(^{-1}\) is related to the C–N stretching vibration of the benzenoid unit.\(^{16}\) The peak at 1239 cm\(^{-1}\) is assigned to the C–H in-plane vibration of the quinoid rings.\(^{13}\) The out-of-plane bending of C–H in the substituted benzenoid ring of PANI is reflected in the peak at around 785 cm\(^{-1}\).\(^{41}\) The one located at 3220 cm\(^{-1}\) is due to the N–H stretching vibration.\(^{42}\) These observations are consistent with the previous FT-IR spectroscopic analysis of PANI.\(^{21,22}\) These characteristic peaks of PANI (1557, 1472, 1288, 1239, 785 cm\(^{-1}\)) are also observed in the FT-IR spectra of the silicon–PANI PNCs, Fig. 1(c–f), and have a little bit shift (about 2–13 cm\(^{-1}\)). These shifts indicate the presence of a strong interaction between silicon and PANI, which is related to the charge delocalization on the polymer backbone.\(^{13}\) The absorption peaks at around 1036 cm\(^{-1}\) are attributed to the stretching vibrations of Si–O bonding,\(^{43,44}\) which indicates the presence of oxygen on the surface of silicon nanopowders, Fig. 1(a). These FT-IR spectra analyses have demonstrated the coexistence of PANI and silicon in the PNCs.

Thermogravimetric analysis

Fig. 2 shows the TGA curves of the as-received silicon nanopowders, pure PANI doped with H\(_3\)PO\(_4\) and its PNCs with different silicon nanopowder loadings in the air. For the as-received silicon nanopowders, the weight percentage increases after temperature reaches 500 °C and the weight residue at 800 °C is 102.4%. This is due to the oxidation of silicon nanopowders in the presence of oxygen at high temperature. Pure PANI doped with H\(_3\)PO\(_4\) is almost completely decomposed in the air at high temperature (>650 °C) with a little bit weight residue of about 2.26% left, which is due to the carbonized PANI.\(^{41}\) Two-stage weight losses are observed in the pure H\(_3\)PO\(_4\) doped PANI and its silicon PNCs. The first stage in the temperature range from room temperature to 300 °C is due to the elimination of moisture and the dopant H\(_3\)PO\(_4\) in PANI.\(^{13}\) The major weight loss of all the samples from 300 to 600 °C is due to the large scale thermal degradation of the PANI chains.\(^{45,46}\) Table 1 shows the summarized thermal properties of pure PANI doped with H\(_3\)PO\(_4\) and its PNCs. The thermal stability of the silicon–PANI PNCs is observed to increase with increasing silicon nanopowder loading. The 15 wt% loss decomposition temperature for pure PANI doped with H\(_3\)PO\(_4\) and its PNCs with a silicon loading of 10.0, 20.0, 40.0 and 60.0 wt% is 288, 326, 379, 430 and 503 °C, respectively. The 15 wt% loss only refers to the PANI fraction of the PNCs since the silicon does not decompose. The weight residues of the silicon–PANI PNCs with an initial silicon nanopowder loading of 10.0, 20.0, 40.0 and 60.0 wt% at 800 °C are 20.73, 35.33, 58.75 and 76.82%, respectively. This weight residue difference from the initially calculated particle loading is due to the incomplete polymerization of the aniline monomers.\(^{13}\)

Microstructures of the nanocomposites

Fig. S1(a and b) (ESI†) depict the SEM microstructures of the as-received silicon nanopowders and the silicon–PANI PNCs with a silicon loading of 60.0 wt%. The as-received silicon nanopowders show very smooth surfaces and have different shapes, Fig. S1(a) (ESI†), whereas the surface of the silicon nanopowders in the PNCs becomes rougher and the nanopowders were mixed well with PANI, Fig. S1(b) (ESI†), indicating that the polymerization
has occurred on the surface of the silicon nanopowders. The HRTEM microstructures, Fig. 3(a), illustrate a very thin amorphous silica layer outside the silicon nanopowders, which is consistent with the FT-IR results with a peak at 1036 cm\(^{-1}\) for Si–O bonding vibration. The clear lattice fringes observed in Fig. 3(a) indicate the high crystallization of the as-received silicon nanopowders and the calculated \(d\)-spacing value of 3.1 Å corresponds to the (1 1 1) crystallographic plane of the as-received silicon. The selected area electron diffraction (SAED) is introduced to identify the crystal structure of the as-received silicon, the inset of Fig. 3(a), which shows that the as-received silicon nanopowders are single crystals. The calculated \(d\)-spacing values of 1.9 and 3.1 Å correspond to the (2 2 0) and (1 1 1) crystallographic planes of silicon, which are consistent with the HRTEM observations. Fig. 3(b) clearly shows the core–shell structure of 60.0 wt% silicon–PANI PNCs, consisting of a crystalline silicon inner shell, a very thin amorphous silica layer (not obvious) and a thick layer of the PANI polymer outer shell.

**Optical properties and electronic band gap**

The optical property is one of the most important properties of the conjugated polymers in the applications such as polymer light emitting diodes (LEDs), thin film transistors and solar cells. Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) has been used for the measurement of the UV-vis spectra of powders, which can directly measure the UV-vis absorption edge (\(\lambda_{\text{edge}}\), which is defined as the transition between the strong short-wavelength and the weak long-wavelength absorption in the spectrum of a solid sample and the spectral position of this edge is determined by the energy separation between the valence and conduction bands of the materials). The band gap can be obtained from eqn (1) based on the onset of UV-vis diffuse reflectance spectra of the powdered materials:

\[
E_{\text{opt}}^g (eV) = \frac{1240}{\lambda_{\text{edge}} (\text{nm})} \tag{1}
\]

where \(E_{\text{opt}}^g\) is the optical band gap (or difference between the valence band and the conduction band, which is usually used to analyze the optical absorption at the fundamental edge in terms of band-to-band transitions) and the number 1240 is obtained from the relationship between frequency and wavelength as described following eqn (2):

\[
E(eV) = h \frac{c}{e \lambda} \tag{2}
\]

where \(h\) is Planck’s constant, \(c\) is the speed of light in a vacuum and \(e\) is the electron charge, the unit of \(\lambda\) is meter, then 1240 can be obtained from \(hc/e\).

The band gap of PANI is reported to be associated with many factors, such as the forms of PANI (including “leucoemeraldine” (LEB), “emeraldine” (EB) and “pernigraniline” (PB)), doping levels of the PANI, type of doped acid, and nanoparticles. Fig. 4 depicts the UV-vis diffuse reflectance spectra of pure PANI doped with H\(_3\)PO\(_4\), silicon–PANI PNCs with a silicon loading of 10.0 wt% and as-received silicon. The \(\lambda_{\text{edge}}\) for the pure PANI and silicon–PANI PNCs related to the \(\pi-\pi^*\) interband transition in the benzoid/quinoid ring structure and determined by the onset of the diffuse reflectance spectra in Fig. 4 is 434.7 and 434.4 nm for the pure PANI doped with H\(_3\)PO\(_4\) and 10.0 wt% silicon–PANI PNCs, respectively. The corresponding \(E_{\text{opt}}^g\) calculated according to eqn (1) based on these \(\lambda_{\text{edge}}\) values is 2.85 and 2.78 eV for the pure PANI doped with H\(_3\)PO\(_4\) and 10.0 wt% silicon–PANI PNCs, respectively, which are in agreement with the results.
reported previously in sulfonated PANI (2.47 eV) 60 and nitric acid (HNO₃) doped PANI (2.75 eV). 61 The absorption edge (\(\lambda_{\text{edge}}\)) and the corresponding calculated \(E_{\text{opt}}\) for the silicon–PANI PNCs with a silicon loading of 20.0, 40.0 and 60.0 wt% obtained from UV-vis DRS are listed in Table 2. The results show that the band gap of PANI decreases with increasing silicon loading, which may be due to the interaction between the PANI polymer backbone and the semiconductive silicon. This phenomenon is also observed in the silver–PANI nanocomposites 61 and graphene oxide–PPy systems. 53 The \(\lambda_{\text{edge}}\) and \(E_{\text{opt}}\) of silicon are shown in Table 3. The addition of silicon into the PANI matrix is observed to have no obvious effect on the \(E_{\text{opt}}\) of silicon. The Kubelka–Munk equation is often used to analyze the diffuse reflectance spectra with weakly absorbing materials. 62 After transforming the diffuse reflectance obtained from UV-vis DRS into the Kubelka–Munk equation, the information on the scattering and the absorption process can be separated. The Kubelka–Munk equation is expressed as eqn (3):

\[
F(R\%) = \left(1 - R\%ight)^{2/2} \times R\%
\]  

The obtained Kubelka–Munk transformation curves of the silicon, pure PANI and 10.0 wt% silicon–PANI PNCs are shown in the inset of Fig. 4. The \(E_{\text{opt}}\) obtained from the first peak in the curves for the silicon, pure PANI and 10.0 wt% silicon–PANI PNCs is 3.38, 2.77, and 2.72 eV. These results are consistent with the results obtained from UV-vis DRS.

### Dielectric properties

Fig. 5 shows the real permittivity (\(\varepsilon'\), Fig. 5(a)), imaginary permittivity (\(\varepsilon''\), Fig. 5(b)) and dielectric loss (\(\tan\delta\), where \(\tan\delta = \varepsilon''/\varepsilon'\), Fig. 5(c)) as a function of frequency for pure PANI doped with H₃PO₄ and its PNCs with different silicon loadings within the frequency range of 20 to 2 \(\times\) 10⁶ Hz at room temperature. In Fig. 5(a), the \(\varepsilon'\) for all the samples is positive within the measured frequency range and decreases sharply with increasing frequency at frequency lower than 110 Hz, after that \(\varepsilon'\) slightly decreases with further increase in the frequency. In the low frequency range (<110 Hz), the \(\varepsilon'\) of pure PANI doped with H₃PO₄ and its silicon PNCs shows very large values (10⁴–10⁵), which represents that the charge delocalization in PANI occurs in the mesoscopic range. 63 Generally, the dielectric properties of the PNCs are strongly related to the interfacial polarization between the hosting polymer matrix and the nanofillers 64 arising from Maxwell–Wagner–Sillars (MWS) polarization, which often occurs at the inner dielectric boundary layers on a mesoscopic scale and the charge carriers have been trapped at the interface within the bulk of the samples. 65

### Table 2
Absorption edges and optical band gaps of pure H₃PO₄ doped PANI and its silicon–PANI PNCs at different silicon loadings

<table>
<thead>
<tr>
<th>Samples</th>
<th>Absorption edge of PANI ((\lambda_{\text{edge}}, \text{nm}))</th>
<th>Optical band gap of PANI ((E_{\text{opt}}), eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₃PO₄ doped PANI</td>
<td>434.7</td>
<td>2.85</td>
</tr>
<tr>
<td>Silicon–PANI PNCs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicon loading of 10.0 wt%</td>
<td>433.4</td>
<td>2.78</td>
</tr>
<tr>
<td>Silicon loading of 20.0 wt%</td>
<td>459.2</td>
<td>2.70</td>
</tr>
<tr>
<td>Silicon loading of 40.0 wt%</td>
<td>487.5</td>
<td>2.54</td>
</tr>
<tr>
<td>Silicon loading of 60.0 wt%</td>
<td>580.5</td>
<td>2.14</td>
</tr>
</tbody>
</table>

### Table 3
Absorption edges and optical band gaps of pure H₃PO₄ doped PANI and its silicon–PANI PNCs

<table>
<thead>
<tr>
<th>Samples</th>
<th>Absorption edge of silicon ((\lambda_{\text{edge}}, \text{nm}))</th>
<th>Optical band gap of silicon ((E_{\text{opt}}), eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>223.8</td>
<td>5.54</td>
</tr>
<tr>
<td>Silicon–PANI PNCs</td>
<td></td>
<td>4.53</td>
</tr>
<tr>
<td>Silicon loading of 10.0 wt%</td>
<td>224</td>
<td>5.54</td>
</tr>
<tr>
<td>Silicon loading of 20.0 wt%</td>
<td>223</td>
<td>4.51</td>
</tr>
<tr>
<td>Silicon loading of 40.0 wt%</td>
<td>224</td>
<td>4.53</td>
</tr>
<tr>
<td>Silicon loading of 60.0 wt%</td>
<td>225</td>
<td>4.51</td>
</tr>
</tbody>
</table>

Fig. 5 (a) Real permittivity, (b) imaginary permittivity and (c) dielectric loss of pure PANI doped with H₃PO₄ and the silicon–PANI PNCs with a silicon loading of 10.0, 20.0, 40.0 and 60.0 wt%, respectively.
The $\varepsilon'$ of the silicon–PANI PNCs is found to decrease with increasing silicon loading (for the 60.0 wt% silicon–PANI PNCs, the $\varepsilon'$ is a little bit higher than that of 20.0 and 40.0 wt% silicon–PANI PNCs at 20 Hz, but after that the $\varepsilon'$ becomes lower). The $\varepsilon''$ of PANI doped with H$_3$PO$_4$ and its silicon PNCs is also observed to decrease with increasing frequency, Fig. 5(b). However, the $\varepsilon''$ decreases as the silicon loading increases to 20.0 wt% and after that $\varepsilon''$ slightly increases as the silicon loading increases to 40.0 and 60.0 wt%. Fig. 5(c) shows the frequency dependent $\tan\delta$ properties. The $\tan\delta$ has very high values ($10^2$–$10^3$) in the low frequency range ($10^3$–$10^4$ Hz) and low values in the high frequency range ($< 10$). This huge change indicates that these PNCs can be used in microelectronics depending on the frequency range.\(^{23}\) It is also found that $\tan\delta$ has no obvious silicon loading dependent properties.

**Temperature dependent resistivity – the electrical conduction mechanism**

Fig. 6(a) shows the temperature dependent resistivity of the H$_3$PO$_4$ doped PANI and its nanocomposites with different silicon loadings within the measured temperature scale from 100 to 290 K, respectively. The resistivity of all the prepared samples is observed to decrease with increasing temperature, which exhibits typical semiconductor behaviour within the measured temperature range.\(^{66}\) The resistivity of the silicon–PANI PNCs is higher than that of pure PANI doped with H$_3$PO$_4$, which is almost one order of magnitude higher within the temperature range from 100 to 290 K. The resistivity of the silicon–PANI PNCs with a silicon loading of 20.0 and 60.0 wt% only has a slight difference between 120 and 290 K and decreases with increasing silicon loading as temperature is below 120 K. However, the silicon–PANI PNCs with a silicon loading of 40.0 wt% show the lowest resistivity compared with the silicon–PANI PNCs with other loadings within the whole measured temperature scale. These results indicate that the silicon loading has a different effect on the resistivity of the silicon–PANI PNCs. The value of the resistivity ratio ($\rho_i/\rho_f$) is used to evaluate the disorder (random potential fluctuation of quantum-well structures in the semiconductor\(^{68}\)) in the PANI doped with H$_3$PO$_4$ and silicon–PANI PNCs. The obtained results are shown in Table 4. From the calculated $\rho_i$ results, the $\rho_i$ increases with increasing silicon loading in the PANI polymer matrix, indicating that the disorder of silicon–PANI PNCs becomes larger after adding silicon into the PANI polymer matrix.\(^{69}\)

![](image1)

![Image](image2)

**Fig. 6** (a) Resistivity vs. temperature; and (b) the ln(\(\sigma\)) and $T^{-1/4}$ curve of pure PANI doped with H$_3$PO$_4$, and the silicon–PANI PNCs with a nanopowder loading of 20.0, 40.0 and 60.0 wt%, respectively.

To better investigate the charge transport behaviour of PANI doped with H$_3$PO$_4$ and silicon–PANI PNCs, the electrical conduction mechanism is elucidated via the obtained temperature dependent resistivity using the Mott variable range hopping (VRH) approach, which is represented as eqn (4)\(^{70}\) to describe the low temperature resistivity in the strongly disordered systems with the localized states:\(^{70}\)

$$\sigma = \sigma_0 \exp \left[ -\frac{T_0}{T} \right]^{\frac{1}{n+1}}$$  \hspace{1cm} (4)

where the constant $\sigma_0$ stands for the conductivity at infinite low temperature, $T$ (K) is the Kelvin temperature and constant $T_0$ (K) is the characteristic Mott temperature, which is related to the localization length of the localized wave-function of charge carriers and is given by eqn (5):\(^{71}\)

$$T_0 = 24/[(\pi k_B N(E_F) a_0^3)]$$  \hspace{1cm} (5)

where $a_0$ (nm) is the localization length of the localized wave function, $k_B$ is the Boltzmann constant and $N(E_F)$ (1 cm$^{-3}$) is the density of states at the Fermi level. The value $n$ in eqn (4) is the dimension of the system and $n = 3, 2,$ and 1 stands for a 3-, 2-, and 1-dimensional system, respectively.\(^{71}\) The $\sigma_0$ and $T_0$ can be obtained from the intercept and the slope of the linear fitting $\ln(\sigma) \sim T^{-\frac{1}{n+1}}$. The best linear fit of $\ln(\sigma) \sim T^{-\frac{1}{n+1}}$ for each sample obtained from Fig. 6(a) is shown in Fig. 6(b) with

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_0 \times 10^3$ (K)</th>
<th>$\sigma_0$ (S cm$^{-1}$)</th>
<th>$\rho_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_3$PO$_4$ doped PANI</td>
<td>0.96</td>
<td>5313</td>
<td>68.21</td>
</tr>
<tr>
<td>Silicon–PANI PNCs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicon loading of 20.0 wt%</td>
<td>2.25</td>
<td>10289</td>
<td>100.33</td>
</tr>
<tr>
<td>Silicon loading of 40.0 wt%</td>
<td>2.13</td>
<td>27784</td>
<td>115.50</td>
</tr>
<tr>
<td>Silicon loading of 60.0 wt%</td>
<td>2.38</td>
<td>14164</td>
<td>130.21</td>
</tr>
</tbody>
</table>

Table 4 $T_0$, $\sigma_0$ and $\rho_i$ for the H$_3$PO$_4$ doped PANI and silicon–PANI nanocomposites.
n = 3 in the temperature range of 100–290 K, indicating a quasi 3-D VRH electrical conduction mechanism. The obtained $\sigma_0$ and $T_0$ values from Fig. 6(a) are summarized in Table 4. The $T_0$ of the silicon–PANI PNCs is found to decrease with increasing silicon loading to 40.0 wt% ($2.25 \times 10^7$ and $2.13 \times 10^7$ K for the silicon–PANI PNCs with a loading of 20.0 and 40.0 wt%, respectively) and then increases as the silicon loading increases to 60.0 wt% ($2.38 \times 10^7$ K). Generally, a larger $T_0$ indicates a stronger localization of the charge carriers, which is usually accompanied by an increased resistivity.73 Interestingly, it is observed that the $T_0$ has the same trend with $E_g^{opt}$ obtained from UV-vis DRS as silicon loading increases to 40.0 wt%, which is consistent with the results that the band gap is related to the conductivity. However, as the silicon loading increases to 60.0 wt%, the $T_0$ is not consistent with $E_g^{opt}$ any more. This may be due to the continuous phase transition, which is also observed in the Fe$_2$O$_4$–PPy PNCs. The $\sigma_0$ shows the silicon loading independent property. This is different from the Fe$_3$O$_4$–PPy PNCs. 74 The materials with high MR sensitivity to the external magnetic field could be used as magnetic field sensors.76

Generally, the wave-function shrinkage model is often used to formulate the positive MR of highly disordered localized systems in the VRH regime.77 As aforementioned, pure PANI doped with H$_2$PO$_4$ and its silicon PNCs exhibit a quasi 3-D Mott VRH electrical conduction mechanism. In the wave-function shrinkage model, the ratio of $R(H,T)/R(0,T)$ can be described by eqn (7):78

$$R(H,T)/R(0,T) = \exp[\xi_c(T)/(\xi_c(0) - 1)]$$

where $\xi_c = (T/T_0)^{1/4}$ for the 3-D Mott VRH electrical conduction mechanism, $\xi_c(T)/\xi_c(0)$ is the normalized hopping probability parameter and is a function of $H/P_C$ for the Mott VRH electrical conduction mechanism. $H$ is the magnetic field (Tesla, unit of magnetic field, $1\, T = 10^4\, \text{Oe}$), $P_C$ is the fitting parameter given by eqn (8) for the Mott VRH electrical conduction mechanism:

$$P_C = 6h/[(e\alpha_0^0(T_0/T))^{1/4}]$$

where $e$ is the electron charge, $h$ is the reduced Planck’s constant and $\hbar = h/2\pi$, $h$ is Planck’s constant and $T_0$ is the Mott characteristic temperature (K). In the low magnetic field limit, eqn (7) is simplified to eqn (9):

$$R(H,T)/R(0,T) \approx 1 + H^2/(P_C^2 T_0/(T))^1/4$$

and the MR is defined in eqn (10):

$$MR = \Delta R(H,T) - R(0,T)/R(0,T) \approx t_2 H^2/(P_C^2 T_0/(T))^{1/4} = t_2 e^2\alpha_0^0(T_0/T)^{3/4} H^2$$

where the numerical constant $t_2 = 5/2016$.79

According to eqn (10), the localization length $\alpha_0$ could be obtained by $T_0$, the MR value and magnetic field $H$:

$$\alpha_0^0 = 36h^2MR/(t_2e^2T_0/(T))^{3/4} H^{-2}$$

For example, $T_0$ is $2.13 \times 10^7$ K for the 40 wt% silicon–PANI PNCs, and the calculated $\alpha_0$ from eqn (10) for temperature at $T = 290$ K is 96.0, 39.0 and 25.2 nm for $H$ of 0.5, 4 and 9 T. The calculated $\alpha_0$ for the silicon–PANI PNCs with different silicon loadings is shown in Table 5. From the listed results in Table 5, the $\alpha_0$ has different values under different $H$. After obtaining the $\alpha_0$, the $N(E_F)$ can be calculated from eqn (12):

$$N(E_F) = 24/[\pi k_B T_0 \alpha_0^0]$$

The calculated $N(E_F)$ values are also listed in Table 5. Generally, the hopping probability between the localized states increases.
Table 5  \( a_0, N(E_f) \) and \( R_{\text{hop}} \) for the H$_3$PO$_4$ doped PANI and its silicon PNCs at different magnetic fields (T)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Parameters</th>
<th>0.5</th>
<th>4</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_3$PO$_4$ doped PANI</td>
<td>( a_0 ) (nm)</td>
<td>94.3</td>
<td>52.5</td>
<td>38.9</td>
</tr>
<tr>
<td></td>
<td>( N(E_f) ) (1 cm$^{-1}$)</td>
<td>( 6.9 \times 10^{21} )</td>
<td>( 4.0 \times 10^{12} )</td>
<td>( 9.8 \times 10^{32} )</td>
</tr>
<tr>
<td></td>
<td>( R_{\text{hop}} ) (( \mu \text{m} ))</td>
<td>0.48</td>
<td>0.27</td>
<td>0.20</td>
</tr>
<tr>
<td>Silicon–PANI PNCs</td>
<td>20.0 wt% silicon ( a_0 ) (nm)</td>
<td>120.6</td>
<td>42.9</td>
<td>24.6</td>
</tr>
<tr>
<td></td>
<td>( N(E_f) ) (1 cm$^{-1}$)</td>
<td>( 1.4 \times 10^{31} )</td>
<td>( 3.1 \times 10^{12} )</td>
<td>( 1.7 \times 10^{33} )</td>
</tr>
<tr>
<td></td>
<td>( R_{\text{hop}} ) (( \mu \text{m} ))</td>
<td>0.75</td>
<td>0.26</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>40.0 wt% silicon ( a_0 ) (nm)</td>
<td>96.0</td>
<td>39.0</td>
<td>25.2</td>
</tr>
<tr>
<td></td>
<td>( N(E_f) ) (1 cm$^{-1}$)</td>
<td>( 2.6 \times 10^{31} )</td>
<td>( 3.9 \times 10^{12} )</td>
<td>( 1.5 \times 10^{33} )</td>
</tr>
<tr>
<td></td>
<td>( R_{\text{hop}} ) (( \mu \text{m} ))</td>
<td>0.59</td>
<td>0.24</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>60.0 wt% silicon ( a_0 ) (nm)</td>
<td>97.0</td>
<td>39.1</td>
<td>25.0</td>
</tr>
<tr>
<td></td>
<td>( N(E_f) ) (1 cm$^{-1}$)</td>
<td>( 2.5 \times 10^{31} )</td>
<td>( 3.9 \times 10^{12} )</td>
<td>( 1.5 \times 10^{33} )</td>
</tr>
<tr>
<td></td>
<td>( R_{\text{hop}} ) (( \mu \text{m} ))</td>
<td>0.62</td>
<td>0.25</td>
<td>0.16</td>
</tr>
</tbody>
</table>

with increasing \( N(E_f) \).\(^{80}\) From Table 5, the observed higher \( N(E_f) \) means a more hopping probability of charge carriers. The average hopping length \( R_{\text{hop}} \) could be obtained from eqn (13):\(^{81}\)

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

The calculated \( R_{\text{hop}} \) (\( \mu \text{m} \)) is shown in Table 5 and the results show the \( H \) dependent \( R_{\text{hop}} \) properties. The \( R_{\text{hop}} \) decreases with increasing \( H \) and the MR increases with increasing \( H \), which indicates that the MR value is associated with the \( R_{\text{hop}} \). Generally, 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.\(^{81}\) Our results have further confirmed this statement.

Conclusions

Phosphoric acid doped conductive PANI PNCs filled with different silicon loading levels have been successfully synthesized using a facile SIP method. The TGA results show that the silicon nanopowders can dramatically enhance the thermal stability of the PANI matrix and the thermal stability of the silicon–PANI PNCs increases with increasing silicon loading. The optical band gap of the silicon–PANI PNCs obtained from the UV-vis diffuse reflectance spectra decreases with increasing silicon loading. The positive permittivity and resistivity of these PNCs are strongly related to the silicon loadings. The electrical conduction mechanism of these nanocomposites obeys a quasi 3-D VRH conduction mechanism according to the Mott VRH model. A room temperature GMR is observed in the synthesized non-magnetic PANI and its silicon nanocomposites. This GMR phenomenon is well explained using the wave-function shrinkage model by the calculated average hopping length \( R_{\text{hop}} \).

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References


