Magnetic and Magnetoresistance Behaviors of Solvent Extracted Particulate Iron/Polyacrylonitrile Nanocomposites

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Iron nanoparticle reinforced polyacrylonitrile (PAN) nanocomposites are fabricated by a facile and environmentally benign solvent extraction method. Fourier transform infrared (FT-IR), thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC) results indicate a strong interaction between the iron nanoparticles and the polymer matrix for the as-prepared polymer nanocomposites. The heat treatment induces the carbonization of the polymer matrix. High-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD) analysis show a protecting carbon shell surrounding the iron nanoparticles within the carbon matrix against the particle oxidation. The magnetic properties, electrical conductivity, and magnetic field dependent resistivity of heat-treated nanocomposites with different particle loadings are carried out in a physical properties measurement system by Quantum Design and by a standard four probe method. The saturation magnetization increases and the coercivity decreases with an increase of the nanoparticle loading. The heat-treated nanocomposites possess a room temperature magnetoresistance (MR) of 5.1% at a field of 90 kOe. The nanoparticle loading has a significant effect on the resistivity of nanocomposites. The heat-treated nanocomposites show a particle loading dependent transport mechanism. A transition from semiconductive to metallic conduction was observed with an increase of the nanoparticle loading.

1. Introduction

Polymers have been considered as excellent host matrixes for composite materials. Polymer nanocomposites filled with nanoparticles have attracted much interest due to their lightweight,1 cost-effective processability1 and unique physicochemical properties, such as increased electric/heat conductivity,2,3 enhanced mechanical properties (stiffness and strength),4 magnetic properties,5 and even improved shape replicability.6 Therefore, polymer nanocomposites have been reported for wide applications such as UV shielding,7 electromagnetic interface shielding,8 and microwave adsorption.9 Up to now, various methods have been developed to fabricate polymer nanocomposites including ex situ methods (dispersion of the synthesized nanoparticles into a polymer solution),10–12 in situ monomer polymerization in the presence of the nanoparticles,13–16 in situ nanoparticle formation in the presence of polymer,17 drop casting,18 dip-coating,19 and spin-coating.20 Recent studies on magnetic polymer nanocomposites have shown great potential applications in high density magnetic recording, magnetic sensors, magnetic carriers, color imaging,21–24 biomedical, magnetic storage, and electronic devices25–27 by utilizing unique magnetic nanoparticles. Iron nanoparticles as one of the magnetic particles have received extensive attention due to their high saturation magnetization and large coercivity arising from the small size and high specific surface area, which differ from the corresponding bulk and atomic counterparts.25,27 However, the easy agglomeration, oxidation/corrosion, and flammable properties under ambient conditions and at room temperature are challenges for practical applications of iron nanoparticles.28,29

Different notable materials including metals,30,31 polymer,13,17,26 silica,28 and carbon23,26,27,32,33 have been reported to protect the nanoparticles from oxidation. Compared to polymer and silica shells, carbon shells exhibit much higher stability in harsh physical environments such as strong acid.26,27 Different polymers such as vinyl ester resin1 and polyurethane34 have been used as carbon precursors to protect the metal nanoparticles from oxidation. Polyacrylonitrile (PAN), chosen as the carbon precursor in the current study, is due to its high carbon content (has a continuous carbon backbone and the carbon content of acrylonitrile is 67.9%), easy processability with a fairly good solubility in dimethylformamide (DMF),35 dimethyl sulfoxide (DMSO),36 and dimethylacetate (DMAc),37 and easy carbonization to form carbon.38–40 The subsequent heat treatment of the magnetic nanocomposites can induce carbonization of the polymer matrix, which will protect the iron nanoparticles from oxidation.22 In addition, conductive carbon has been reported as a spacer for granular magnetic giant magnetoresistance (GMR) or tunneling magnetoresistance (TMR) nanocomposite applications.1,34

In this study, we report a solvent extraction method to produce iron nanoparticle reinforced PAN nanocomposites, which are converted to a PAN-based carbon composite by simple annealing. The solvent extraction nanocomposite fabrication method is based on the relative solubility of solutes in two different immiscible liquids. PAN can easily dissolve in DMF and has
little solubility in ethanol. DMF and ethanol have a structural similarity and can dissolve into each other.\textsuperscript{40} The thermal stability, crystal (phase) structure, and physicochemical interactions of the prepared PAN/Fe nanocomposites are characterized by various techniques including thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), X-ray diffraction (XRD), and Fourier transform infrared (FT-IR) spectroscopy. The microstructure of the heat-treated nanocomposites with different particle loadings is characterized by transmission electron microstructures (TEM). Magnetic properties are measured in a physical properties measurement system by Quantum Design. The electrical conductivity and the electron transport mechanism are investigated by a standard four-probe technique and analyzed by a temperature-dependent resistivity measurement.

2. Experimental Section

2.1. Materials. Polycrylonitrile (PAN, MW = 150 000, degree of polymerization 283) was purchased from Scientific Polymer Products Inc. Anhydrous N,N-dimethylformamide (DMF, 99.9\%) and ethanol (anhydrous) were purchased from Alfa Aesar. Iron nanoparticles with an average particle size of 20 nm were supplied by QuantumSphere, Inc. All of the materials were used as received without further treatment.

\textbf{Hazard Caution: Handling of the iron nanoparticles should be done in a fume hood, due to high risk of fire and respiratory health issues.}

2.2. PAN-Based and Carbon-Based Nanocomposite Fabrication. Under a nitrogen atmosphere, the nanoparticles were added into the PAN/DMF (10\%) solution with a particle loading of 10, 20, 30, 40, and 50 wt\%, respectively. The above particle-suspended solution was ultrasonically stirred in an ultrasonic bath for 1 h to disperse the nanoparticles in the polymer solution at room temperature. DMF was extracted by ethanol for the solid polymer nanocomposite formation. As a comparison, the conventional drop casting method was applied to prepare Fe/PAN nanocomposites by pouring the above solution into a Petri dish and dried naturally in the air. The iron/composites were put in a vacuum oven at 40 °C to remove the excessive DMF and dried completely. The polymer nanocomposites were annealed at 750 °C for 2 h and then allowed to cool down naturally to room temperature. All of the operations were carried out under a gas flowing condition containing 5 vol \% H\textsubscript{2}, balanced with argon in a tube furnace. The final product was treated with washing with excess pH 1 hydrochloric aqueous solution to remove the unprotected iron nanoparticles and dried naturally after washing with deionized water.

2.3. Characterization. A Fourier transform infrared (FT-IR) spectrometer (Jasco, FT-IR 420) in transmission mode under dry nitrogen flow (10 cm\textsuperscript{3}/min) was used to test the physicochemical interactions between the PAN and the nanoparticles. The morphology of the annealed samples was examined by transmission electron microscope (TEM, Joel 2100) with an accelerated voltage of 200 kV. The samples were prepared by grinding for a few minutes and dispersed in ethanol under sonication. A drop of solution was put onto a holey carbon coated copper grid and dried naturally in the air.

The powder X-ray diffraction analysis of the samples was carried out with a Bruker AXS D8 Discover diffractometer with a GADDS (General Area Detector Diffraction System) operating with a Cu K\textalpha\ radiation source filtered with a graphite monochromator (\(\lambda = 1.5406 \ \text{Å}\)). The detector used was a HI-STAR two-dimensional multwire area detector. The samples were loaded onto double sided scotch tape, placed on a glass slide, and mounted on a quarter-circle Eulerian cradle (Huber) on an XYZ stage. The X-ray beam was generated at 40 kV and 40 mA power and was collimated to about 800 \(\mu\)m spot size on the sample. The incident \(\omega\) angle was 5°. A laser/video system was used to ensure the alignment of the sample position on the instrument center. XRD scans were recorded from 7 to 77° for 20 with a 0.05° step-width and a 60 s counting time for each step. The XRD data were analyzed using the DIFFRAC-Plus EVA program (Bruker AXS, Karlsruhe, Germany), and the patterns were identified using the ICDD PDFmaint computer reference database.

The nanoparticle effects on the thermal properties of the polymer in the polymer nanocomposite samples were determined by differential scanning calorimetry (DSC), which was carried out on a DSC 2010 (TA Instruments, DuPont). The temperature and heat flow values were calibrated with an indium standard. Heating scans were performed at a rate of 10 °C/min from 25 to 400 °C in a continuous nitrogen flow with a flow rate of 20 cm\textsuperscript{3}/min (ccpm).

The thermal stability of the nanocomposites was determined by the thermogravimetric analysis (TGA, PerkinElmer). Samples were heated to 1000 °C at a heating rate of 10 °C/min in air, argon, and hydrogen environments, respectively.

The magnetic properties of the nanocomposites at room temperature were carried out in a 9-T physical properties measurement system (PPMS) by Quantum Design. Magnetic field dependent resistance and electrical conductivity were carried out using a standard four-probe technique. The samples were prepared by the standard cold-press method. The applied pressure was 10 000 psi, and the pressing duration time was 10 min. MR was calculated by the following equation:

\[
MR = \frac{\Delta R}{R(0)} = \frac{R(H) - R(0)}{R(0)} \times 100
\]

where \(R(0)\) and \(R(H)\) are the resistance at zero and any applied field of \(H\), respectively. The applied magnetic field is perpendicular to the film.

3. Results and Discussion

3.1. Microstructure of PAN. Figure 1a shows the microstructure of the as-received PAN powders, which show micrometer-sized particles with almost uniform size distribution. The microstructure variation after dissolution in DMF and solidification was observed by SEM. The sample was prepared by dissolving PAN powders in DMF at room temperature under 1 h of ultrasonication and 24 h of magnetic stirring to obtain a homogeneous PAN−DMF solution. A drop of PAN−DMF solution was casted on an aluminum tab. The solvent was extracted by ethanol and dried naturally in a vacuum oven. Figure 1b shows a smooth thin film without voids and microparticle structure. The dissolution and solidification process destroys the microstructure of the spherical shape, which is necessary for subsequent nanocomposite thin film formation.

3.2. Polymer-Based Nanocomposite Fabrication. The PAN/Fe nanocomposites are fabricated by the ethanol extraction method and drop casting method, respectively. In the solvent extraction process, iron nanoparticles suspended in PAN−DMF solution are mixed with ethanol, which extracts DMF from the nanocomposite solution and results in the formation of solid polymer nanocomposites. The experimental result shows that the nanocomposites produced via the solvent extraction method have better stability than the nanocomposites prepared by the conventional drop casting method (Supporting Information). In addition, solvent extraction has avoided the harms to human
beings arising from the natural drying process. As a result, only samples made from the solvent extraction method were used for further characterizations.

### 3.3. FT-IR

FT-IR spectra of the pure PAN and PAN/Fe nanocomposites with different nanoparticle loadings were recorded in the range 4000–500 cm\(^{-1}\). All of the FT-IR spectra, Figure 2, exhibit the PAN characteristic peaks such as the strong stretching vibration of nitrile groups (\(\equiv\text{CN}\)) at 2244 cm\(^{-1}\) and the stretching vibration and bending vibration of methylene (\(-\text{CH}_2\)) peaks at 2930 and 1453 cm\(^{-1}\), respectively.\(^{41,42}\) The peak at 1670 cm\(^{-1}\) is due to the oxidation of the as-received PAN in air, which results in the formation of carboxyl (C=O) groups.\(^{41}\) The peaks at 1251 and 1360 cm\(^{-1}\) are assigned to the aliphatic CH group vibrations of different modes in CH and CH\(_2\), respectively.\(^{41}\) When Fe nanoparticles are incorporated into the PAN matrix, the peaks at 1075, 1251, and 1360 cm\(^{-1}\) are observed to become stronger and sharper, which is due to the strong interaction between the PAN and the nanoparticles.\(^{44}\) PAN deposited from DMF solution shows a peak at about 1700 cm\(^{-1}\), which is assigned to the vibration of the C=O bonds in the DMF residue.\(^{42}\) This explains the phenomena that all of the PAN/Fe nanocomposites have stronger peaks at 1670 cm\(^{-1}\) as compared to that of the pure PAN powders. Meanwhile, the peak at 2930 cm\(^{-1}\) is observed broader for nanocomposites, Figure 2b–e. A strong stretching vibration of the hydroxyl group around 3500–3600 cm\(^{-1}\) is due to the physically absorbed moisture in the polymer nanocomposites, especially for nanocomposites with 40 wt % particle loading. The ratio of peaks at 1453 and 1360 cm\(^{-1}\) is observed to decrease and the peak at 2360 cm\(^{-1}\) becomes sharper when the particle loading reaches 40 wt %, indicating a stronger particle–polymer interaction.

### 3.4. Thermal Analysis of PAN/Fe Nanocomposites

#### 3.4.1. TGA

Figure 3 shows the TGA curves of the pure PAN and PAN/Fe nanocomposites. Pure PAN is observed to degrade through two steps in air environment. The first step around 272 °C is due to the cyclization of the nitrile groups into an extended conjugated ring system.\(^{41}\) This process is accompanied by degradative loss of H\(_2\), NH\(_3\), and HCN.\(^{37,45,46}\) In the second step, more than 70 wt % PAN decomposes completely between 500 and 654 °C. When the pure PAN is thermally treated in an argon atmosphere, the PAN/Fe nanocomposites show two stages of weight loss, which correspond to the degradation of PAN and Fe nanoparticles, respectively.\(^{44}\) The addition of Fe nanoparticles to PAN has a significant effect on the thermal stability of PAN. A significant decrease in the PAN weight loss temperature can be observed, which is due to the strong interaction between the PAN and the Fe nanoparticles.\(^{44}\) The TGA curves show that the PAN/Fe nanocomposites have a higher thermal stability compared to the pure PAN. This is because the Fe nanoparticles act as a heat sink and retard the thermal degradation of PAN.\(^{44}\)
environment, the weight loss at temperatures higher than 500 °C happens slowly as compared to that of the PAN treated in air environment and finally becomes constant at about 710 °C. More residues are observed in the nanocomposites treated with argon than in the nanocomposites treated with air, consistent with carbonization being more favorable under inert conditions. At higher temperatures, the graphite structure of carbon is more favorably formed in an inert atmosphere.47

As compared to the smaller loss of pure PAN at lower temperatures between 100 and 200 °C, about 5 wt % weight loss is observed for polymer nanocomposites, which is due to the evaporation of solvent and physicochemically absorbed moisture, Figure 3. When the samples are heated up to 300 °C, the weight loss of the polymer nanocomposites is also higher than that of the pure PAN. The thermal stability of the nanocomposites is greatly improved in the high temperature range due to the presence of transition metal iron oxide (shell) nanoparticles, which is consistent with the results as observed by Chae et al.48 This shows that the strong interactions between polymer and inorganic nanoparticles make a contribution to the enhancement of thermal stability at higher temperatures.48

The thermal stability of the PAN/Fe nanocomposites with heat treatment in different environments is observed to be in the increasing order of air, argon, and hydrogen at high temperatures, Figure 3. The total weight loss of the nanocomposites heated in argon is higher than that of the nanocomposites heated in hydrogen. When PAN is heated at high temperatures in an inert condition, the carbonization process happens, releasing the noncarbon elements present in the PAN in the form of different gases such as NH₃, HCN, CO₂, CO, and N₂.47 However, heated in a hydrogen atmosphere, hydrogen prohibits the volatile gas formation and the carbon element will not disappear in the form of oxycarbide.

Derivative thermal gravimetric (DTG) was further used to study the thermal stability of the nanocomposites as compared with that of the pure PAN. As compared to the two peaks observed in the DTG curve of pure PAN, three peaks are observed in the nanocomposites, Figure 3b. Among them, the peaks around 270 and 600 °C are more obvious. The first peak at 340 °C for pure PAN is due to the cyclization reaction of freely existing bulk PAN, and the second peak is arising from the oxidation and removal of the carbon phase of PAN.45 After introduction of Fe nanoparticles, the first decomposition peak shifts to a lower temperature at 270 °C. The second peak shifts from 550 to 595 °C after the nanoparticles are added into the polymer matrix, which is due to the higher crystalline structure of carbon induced by the introduced metal nanoparticles. A new peak around 390 °C is observed and is arising from the decomposition of the physicochemically attached PAN surrounding the nanoparticles.

3.4.2. DSC. The DSC heating-scan thermograms of PAN and PAN/Fe nanocomposites are shown in Figure 4 and the glass transition temperature (Tg), crystallization temperature (Tc), and exothermic heat (∆Hc) are summarized in Table 1. The as-received PAN powder displays a very sharp exothermic peak at 297.2 °C without a melting peak and also an unobvious glass transition temperature at about 106.0 °C, which is in agreement with the DSC pattern of pure PAN.49 It has been reported that the exothermic peaks of PAN arise from three principal exothermic reactions, i.e., dehydrogenation, instantaneous cyclization, and cross-linking reactions. Among these, the predominant one is instantaneous cyclization. The exothermic peak is regarded as the result of nucleophilic attack on a nitrile followed by instantaneous cyclization reaction to an extended conjugated structure, which corresponds to the exothermic oxidative stabilization process, Figure 4. In addition, the exothermic peaks of the as-prepared PAN/Fe nanocomposites become relatively broader compared to that of the pure PAN. The broadening peak in the presence of iron nanoparticles suggests that the Fe nanoparticles change the activity of the free radicals involved in the cyclization reaction.44,48

3.5. XRD of Polymer-Based and Carbon-Based Nanocomposites. Figure 5A shows the X-ray diffraction (XRD) patterns of the as-prepared PAN/Fe nanocomposites with different particle loadings. Two diffraction peaks at 2θ = 17 and 29° are observed, characteristic of the (1 0 0) and (1 1 0) planes of the PAN.41,50 In addition, the broad peak at 2θ = 24° agrees well with the research observation by Chae et al.48 The relative intensity of all three PAN diffraction peaks decreases with an increase of the particle loading. In addition, the peaks at 2θ = 45° are assigned to the planes of iron nanoparticles (1 1 0).10

After heat treatment, the sharp characteristic peak of PAN at 2θ = 17° disappears in all of the polymer nanocomposites, Figure 5B. Instead, all of the samples exhibit a peak at 2θ = 24°, which corresponds to the (0 0 2) crystal planes of carbon.51 With the increase of the iron nanoparticle loadings, these peaks become broader. In addition, the weaker peaks at around 2θ = 42–44° are due to the graphite peaks (1 0 0) and (1 0 1).51 The peak at 2θ = 45° is assigned to the plane of bcc iron.28,51–53

3.6. TEM. Figure 6 shows the HRTEM bright field microstructures of the PAN/Fe nanocomposites with a nanoparticle loading of 30 wt % after heat treatment at 750 °C for 2 h. The iron core and carbon shell structure can be easily distinguished from Figure 6. The clear lattice fringes in the HRTEM microstructure of the dark core indicate a highly crystalline structure. The measured d-spacing of 0.21 nm is assigned to the (1 0 0) plane of iron. The outer lattice fringe with a ring structure is clearly shown and the d-spacing is calculated to be

Table 1: Crystallization Behavior during Heating Scan for PAN and PAN/Fe Nanocomposites with Different Particle Loadings

<table>
<thead>
<tr>
<th>Particle Loading</th>
<th>Tg (°C)</th>
<th>Tc (°C)</th>
<th>∆Hc,PAN (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PAN Powder</td>
<td>106.0</td>
<td>297.2</td>
<td>419.5</td>
</tr>
<tr>
<td>20 wt % Fe/PAN</td>
<td>112.6</td>
<td>291.1</td>
<td>593.0</td>
</tr>
<tr>
<td>30 wt % Fe/PAN</td>
<td>104.1</td>
<td>287.7</td>
<td>667.0</td>
</tr>
<tr>
<td>40 wt % Fe/PAN</td>
<td>106.5</td>
<td>292.1</td>
<td>504.7</td>
</tr>
</tbody>
</table>

Figure 4. DSC heating scan thermograms of pure PAN (a) and PAN/Fe nanocomposites with a nanoparticle loading of (b) 20 wt %, (c) 30 wt %, and (d) 40 wt %, respectively.
0.42 nm, corresponding to the (1 1 1) plane of carbon. This indicates the formation of a carbon shell and that Fe nanoparticles are embedded in a carbon matrix, consistent with the XRD analysis. The formed carbon comes from the decomposition of carbon precursor PAN upon heat treatment in a reducing environment. No oxide contaminants are observed in the remaining heat-treated polymer nanocomposites, indicating that high-temperature heat treatment favors the reduction of iron oxides by hydrogen and the iron nanoparticles have been effectively protected by the carbon from oxidation.

3.7. Magnetic Properties. Figure 7 shows the room-temperature hysteresis loops of the PAN nanocomposites with a particle loading of 50 wt % before and after heat treatment. In Figure 7a, saturation magnetization \( M_s \) is determined by the extrapolated saturation magnetization obtained from the intercept of magnetization vs \( H^{-1} \) at high field.\(^{17}\) The saturation magnetization 91.8 emu/g of the nanocomposites corresponds to 183.6 emu/g of the pure iron nanoparticles. The lower \( M_s \) in the polymer nanocomposites than that of the bulk Fe (220 emu/g) is attributed to partial oxidation of the Fe NPs during the nanocomposite fabrication process and the particle-polymer surface interaction effect.\(^{34}\) However, after heat treatment, \( M_s \) increases to 132.9 emu/g and is still lower than that of the bulk Fe, which is due to the carbon residue arising from the PAN decomposition. Hydrogen bubbles are observed if the product is treated with pH 1 hydrochloride of aqueous solution, indicating the zero valence of iron nanoparticles. The observed ferromagnetic properties indicate that the formed carbon has protected the iron from oxidation and etching by the washed acid.

As compared to the reported coercive force (coercivity \( H_c \), the magnitude of the external applied magnetic field necessary to return the magnetic materials to a zero magnetization condition) of 5 Oe for the superparamagnetic iron nanoparticles,\(^{29}\) \( H_c \) is observed to increase to 172.0 Oe after the nanoparticles dispersed and solidified into the PAN matrix with a particle loading of 50 wt %. In other words, the iron nanoparticles became magnetically harder after they dispersed in the PAN matrix at room temperature.\(^{29}\) The big difference in the coercivity is due to the decreased interparticle dipolar interaction arising from the increased interparticle distance (left inset of Figure 7) within the single domain, consistent with particle-loading-dependent coercivity in nanoparticle assembly.\(^{54,55}\)

When the nanocomposites experience the heat treatment, mass loss and shrinkage in the matrix are observed, which dramatically increase the particle loading in the subsequent nanocomposites. All of these changes significantly increase \( M_s \) and reduce
The smaller coercivity observed in the heat-treated nanocomposites arises from the decreased interparticle distance concomitant with a stronger dipolar interaction, schematically shown in the inset of Figure 7. Moreover, the ratio of remnant magnetization ($M_r$) to saturation magnetization ($M_s$) of the polymer nanocomposites decreases to 0.03 from 1.0 after heat treatment. This indicates that the polymer nanocomposites after heat treatment behave more like a superparamagnetic material than that of the as-prepared polymer nanocomposites. The related magnetic properties are summarized in Table 2.

3.8. Magnetoresistance and Electron Transport. Figure 8 shows MR as a function of the applied magnetic field ($H$) of PAN/Fe nanocomposites after heat treatment. The particle loading is observed to have an effect on the MR performance of the annealed nanocomposites, arising from the different interparticle distances in the nanocomposites with different particle loadings (inset of Figure 8). A room temperature MR of 2.36% is observed in the heat-treated nanocomposites with an initial nanoparticle loading of 10 wt %, whereas the heat-treated nanocomposites with initial nanoparticle loadings of 20 and 30 wt % show a room temperature MR of 5.1 and 4.8%, respectively. All of these MR values are observed at a relatively high field of 90 kOe. Heat-treated nanocomposites with 20 wt % loading exhibit the highest MR value among these three samples. This deviates from our recent observation that MR increases with a decrease of the nanoparticle loading.\(^1\) Compared to the multilayered MR materials, a high magnetic field is required to saturate the MR, which is a characteristic of the tunneling conduction mechanism. We have recently discovered that the heat-treated polyurethane composites possess a room temperature MR of 7.3\(^{34}\) and 8.3\(^{3}\) for heat-treated vinyl ester resin nanocomposites.\(^1\) This suggests that the polymer matrix has a significant effect on the MR behaviors, arising from the nanoparticle loading difference in the carbon matrix and further research is needed to elucidate these phenomena.

The electrical resistivity is measured by a standard four-probe method. Figure 9 shows the temperature-dependent resistivity of PAN/Fe nanocomposites with different particle loadings after heat treatment. The resistivity is observed to decrease dramatically with an increase of the temperature and remains constant at about 100 K in Figure 9a. The nanocomposite with a particle loading of 20 wt % after heat treatment is observed to have a higher resistivity than that of the heat-treated nanocomposites with a particle loading of 30 wt %. This is due to the less conductive properties of the carbon matrix. Both samples after heat treatment exhibit semiconductive behavior. When the nanoparticle loading increases to 40 wt %, Figure 9b, the resistivity becomes lower in the magnitude of 5. This indicates that the conductivity of heat-treated nanocomposites increases significantly. As for the nanocomposites with an initial nanoparticle loading of 50 wt % in Figure 9b, the resistivity increases dramatically with an increase of temperature from 50 to 300 K, characteristic of a metallic behavior, indicating that the iron nanoparticles connect to each other and higher than the percolation threshold value.\(^3\) While the spacer effect of the carbon matrix becomes negligible. Figure 9b shows that the resistivity decreases with an increase of temperature within 0–50 K, increases from 50 to 150 K, and then decreases again for the nanocomposite with an initial particle loading of 40 wt % after the heat treatment. This is due to the transition from semiconductor to conductor, which is consistent with P. Love’s observation of metal–insulator transition.\(^5\) The linear relation between the logarithmic resistivity and the square root of temperature $T^{1/2}$ shown in Figure 10 indicates a tunneling/hopping conductive mechanism for the heat-treated nanocomposites with an initial particle loading of 20 wt %.\(^37\)

Conclusions

Polyacrylonitrile nanocomposites reinforced with iron nanoparticles are successfully fabricated by a facile environmental benign solvent extraction method. A simple heat treatment has effectively transferred the polymer into a carbon matrix, which
Fe nanocomposites with an initial particle loading of 20 wt %. The electron transport study suggests a semiconductive behavior for nanocomposites with a relatively low particle loading. The electron transport study shows a semiconductive behavior for nanocomposites with a relatively low particle loading after heat treatment. However, a metallic transportation behavior is observed when the initial particle loading reaches 50 wt %.

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Supporting Information Available: Figure showing 30 wt % Fe/PAN nanocomposites fabricated by the ethanol extraction method and the drop casting method. The difference between the nanocomposites manufactured from the two different methods can be clearly distinguished from the photos. This material is available free of charge via the Internet at http://pubs.acs.org.
Solvent Extracted Particulate Fe/PAN Nanocomposites


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