Polypyrrole/Silicon Carbide Nanocomposites with Tunable Electrical Conductivity

Pallavi Mavinakuli,† Suying Wei,† Qiang Wang,§ Amar B. Karki,∥ Sanjay Dhage,⊥ Zhe Wang,⊥ David P. Young,∥ and Zhanhu Guo*,†

Integrated Composites Laboratory (ICL), Dan F. Smith Department of Chemical Engineering, Lamar University, Beaumont, Texas 77710, Department of Chemistry and Physics, Lamar University, Beaumont, Texas 77710, Applied Catalysis, Institute of Chemical and Engineering Sciences (ICES), 1, Pesek Road, Jurong Island, Singapore 627833, Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803, and Department of Mechanical & Aerospace Engineering, University of California Los Angeles, Los Angeles, California 90095

Received: December 12, 2009; Revised Manuscript Received: February 2, 2010

Conductive polypyrrole/SiC nanocomposites are fabricated via a facile oxidative polymerization approach using p-toluene sulfonic acid as a dopant and ammonium persulfate as an oxidant. The effects of the nanoparticle loading, ratio of oxidant to monomers, and nanoparticle morphology (spheres and rods) on the physicochemical properties are investigated. Various characterization methods are carried out to determine the material properties. Thermal gravimetric analysis demonstrates an improved thermal stability of polypyrrole in the polymer nanocomposites (PNCs) with a higher decomposition temperature. The glass-transition temperature and melting temperature of the polymer and its nanocomposites are determined by differential scanning calorimetry with a decreased melting temperature of polypyrrole in the PNCs. The microstructures of pure polypyrrole and PNCs are observed by scanning electron microscopy. Powder X-ray diffraction analysis demonstrates the crystallinity of polypyrrole, and poor crystallinity is observed for the PNCs with higher nanoparticle loading. Fourier transform infrared spectrometry analysis shows a strong interaction between the SiC nanoparticles and the polypyrrole matrix with a shift of C=C stretching vibration of PPy to a lower band. The electron transport in PNCs follows a quasi 3-d variable range hopping conduction mechanism as evidenced by the temperature-dependent conductivity function. Experimental results demonstrate that PPy/SiC PNCs have higher conductivity than that of the pure PPy. The nanorods are also introduced into the polypyrrole matrix. Their effects on the physicochemical properties are investigated and compared.

1. Introduction

Polymer nanocomposites (PNCs) are formed by dispersing different functional nanoparticles with exceptionally higher specific surface area as compared with the micrometer particles into a polymer matrix and have attracted many researchers to explore their potential applications as high-performance materials.1–5 Compared to the metal-based nanocomposites and conventional polymer composites (with a filler size larger than 100 nm), PNCs have unique physical, chemical, and biological properties, such as lightweight, flexible, ductile, increased tensile strength, larger toughness, improved electrical/thermal conductivity, and enhanced clarity,6–9 which are essentially different from those of the components taken separately or physically combined properties of each component. In addition, the properties of the PNCs could be further tailored by the filler materials, filler loadings, surface functionalities of the fillers, and the nature of the polymer matrix.

Conducting polymers, such as polyaniline, polypyrrole, and polythiophene, have inspired a great deal of interest due to their high electrical conductivity,10 easy preparation, high yield, and environmental stability.11,12 Electrical conductivity of a conductive polymer mainly depends on the nature of the dopant.10,12 The material properties, such as environmental stability, processability, mechanical properties (strength and brittleness), solubility for processing, and thermal stability, can be improved by forming a polymer nanocomposite structure.13,14 Polypyrrole and its composite materials have been widely used as gas sensors,15,16 biosensors,17,18 electromagnetic irradiation shielding materials,19 actuators and artificial muscles,20,21 electrode materials,22–26 photovoltaic cells, coating materials, and corrosion inhibitors.27–31

The reported polypyrrole nanocomposite synthesis methods include an in situ chemical oxidative polymerization approach with either an ultrasonication method or a mechanical stirring method,32,33 in situ micron emulsion polymerization approach,34 and in situ oxidative polymerization of pyrrole with the aid of the supercritical carbon dioxide method.35 Various nanoparticles, such as iron oxide (Fe3O4),26,27 iron cobalt oxide (CoFe2O4),36 silver,37 gold,38 silicon oxide (SiO2),39 ZnO,40 and montmorillonite,41 have been reported for polypyrrole nanocomposite fabrication. Ceramic silicon carbide (SiC) is chosen in this study due to its wide and tunable band gap, favorable for high-temperature, high-frequency, chemical resistance, and high hardness required applications.42–46 Omastova et al.37 have prepared the micrometer SiC particles (0.8 μm) reinforced polypyrrole (PPy) composites by oxidative polymerization with ferric chloride as oxidant and reported the room-temperature electric conductivity of the composites. SiC nanoparticles have higher mechanical strength compared with those of the bulk
SiC, which made them a suitable material for strengthened structural polymer nanocomposite manufacturing. In this study, pure polypyrrole and polypyrrole/SiC nanocomposites with different SiC nanoparticle loadings are fabricated via oxidative polymerization using p-toluene sulfonic acid (P-TSA) as a dopant and ammonium persulfate (APS) as an oxidant. The addition of nanostructures (sphere or rod) and the particle loading levels on the physicochemical properties are investigated. The molar ratio of oxidant to monomers is also found to influence the physical properties of the polymer nanocomposites. The morphology, thermal stability, interaction between the PPy and SiC nanoparticles, and electrical conductivity of the resulting polypyrrole/SiC nanocomposites are characterized. The electric conductivity is investigated by a standard four-probe method, and the electron-transport mechanism is explored by the temperature-dependent electrical conductivity measurement.

2. Experimental Section

2.1. Materials. Pyrrole (C₄H₅N), ammonium persulfate (APS, [(NH₄)₂S₂O₈]), and p-toluene sulfonic acid (P-TSA, C₇H₈O₃S) are all purchased from Sigma Aldrich. Crystalline β-SiC nanoparticles are obtained from MIT Corporation with a reported average size of ∼30 nm and a specific surface area of 109 m²/g. All the chemicals were used as received without any further treatment.

2.2. SiC Nanorod Fabrication. The SiC nanorods are prepared by the published carbothermic reduction method. The reaction was carried out using the mixture of SiO₂ and activated carbon, grinding in a mortar, and transferring to a MgO crucible in a horizontal alumina tubular furnace. The mixture was heated in an Ar flow (50 cm³/min) to 1000 °C at a rate of 10 °C/min, then to 1450 °C at a rate of 2 °C/min, and maintained at this temperature for 1 h. After the furnace was cooled down to room temperature, the raw products containing SiC nanorods were collected. The raw products were heated in air at 800 °C for 2 h to remove the residual carbon in an air flowing (50 cm³/min) condition.

2.3. Polypyrrole and Nanocomposite Preparation. The β-SiC nanoparticle suspended solution is prepared by adding the required amount of β-SiC nanoparticles, P-TSA (6.0 mmol), and APS (3.6 mmol) in 40 mL of deionized water, followed by 1 h of sonication in an ice–water bath (Figure 1, step1). Aqueous pyrrole solution (7.4 mmol of pyrrole in 10 mL of deionized water) is rapidly mixed with the above nanoparticle suspended aqueous solution at room temperature. The solution turns to greenish immediately and then black, indicating the polymerization of pyrrole. The resulting solution is sonicated continuously for an additional 1 h in an ice–water sonication bath for further polymerization (Figure 1, step 2). The product is precipitated naturally and washed thoroughly with deionized water. The clear supernatant is decanted to remove any unreacted PTSA and APS. The precipitant is washed with methanol to remove any possible oligomers. The obtained powders are dried completely at 50 °C. PPy/SiC nanocomposites with a particle loading of 1.8, 5.0, 10.0, 25.0, and 40.0 wt % are fabricated. As a comparison, pure PPy is also synthesized following the same procedures as above without any filler.

SiC nanoparticles treated with P-TSA and APS are collected for the investigation of the nanocomposite fabrication mechanism. The samples are prepared by dispersing SiC nanoparticles in the acid and oxidative aqueous solution under 1 h of ultrasonication, washing with excessive deionized water, and drying naturally in air.

2.4. Characterizations. The crystal structure of the PPy/SiC nanocomposites is characterized by X-ray diffraction. The powder X-ray diffraction analysis of the samples is carried out with a Bruker AXS D8 Discover diffractometer with GADDS (general area detector diffraction system) operating with a Cu Kα radiation source filtered with a graphite monochromator (λ = 1.5406 Å). The detector used is a HI-STAR two-dimensional multiwire area detector. The samples are loaded onto double-sided scotch tape, placed on a glass slide, and mounted on a quarter-circle Eulerian cradle (Huber) on a XYZ stage. The X-ray beam is generated at 40 kV and 40 mA power and is collimated to about an 800 μm spot size on the sample. The incident ω angle was 5°. A laser/video system is used to ensure the alignment of the sample position on the instrument center. XRD scans are recorded from 7° to 77° for 2θ with a 0.050° step width and a 60 s counting time for each step.

Figure 1. Mechanism of nanocomposite fabrication.
The physicochemical interaction between polypyrrole and the SiC nanoparticles is investigated by using a Fourier transform infrared spectrometer (FTIR, Bruker Inc., Tensor 27) with a hyperion 1000 ATR microscopy accessory over the wavenumber range of 2500−400 cm−1 at a resolution of 4 cm−1.

The thermal stability of pure polypyrrole and PPy/SiC nanocomposites is examined by thermogravimetric analysis (TGA). The samples are heated from 26 to 800 °C under an air atmosphere flow condition with a flow rate of 40 cm3/min. The heating rate used is 20 °C/min.

The glass-transition temperature and melting temperature are investigated by differential scanning calorimetry (DSC) with a heating rate of 10 °C/min and a nitrogen flow rate of 20 mL/min. The samples are sealed in a standard aluminum pan, and the measurement is done in the temperature range of 10−400 °C. The weight of each sample is about 10 mg. The DSC heat flow and temperature values are calibrated with a standard indium.

The microstructures of polypyrrole and PPy/SiC nanocomposites are observed by a scanning electron microscope (SEM, JEOL field emission scanning electron microscope, JSM-6700F). The electrical resistivity of the PNCs is measured by a standard four-probe method. Pure PPy and the nanocomposite powders are pressed in the form of disk pellets with a diameter of 25 mm by applying a pressure of 95 MPa in a hydraulic presser, and the average thickness is about 1 mm. The electrical resistivity is used to investigate the electron-transport mechanism in the PPy/SiC nanocomposites.

3. Results and Discussion

3.1. Polypyrrole Nanocomposites with SiC Nanoparticles.

3.1.1. X-ray Diffraction Analysis. Figure 2 shows the XRD patterns of the as-received SiC nanoparticles, acid−oxidant−treated SiC nanoparticles, pure polypyrrole, and PPy/SiC nanocomposites with different nanoparticle loadings. The spectrum of pure polypyrrole shows an obvious broad peak at 2θ = 21.42° (Figure 2, pattern g), indicating a semicrystalline structure of the formed polypyrrole. The weak peaks at 2θ = 17.92°, 2θ = 26.4°, and 2θ = 30.36° in pure polypyrrole and polypyrrole/SiC nanocomposites with low particle loadings (Figure 2, patterns e−g) are associated with the formed low-molecule pyrrole oligomers and polypyrrole in the PNCs. The polypyrrole peak at 2θ = 21.42° in the nanocomposites is broader, indicating a poor crystallinity after introducing nanoparticles to the polymer matrix.

The d spacing between the crystal planes is calculated using the Bragg’s equation, eq 1

\[
d = \frac{n \times \lambda}{2 \sin \theta}
\]

where \( n \) is an integer determined by the order given, \( \lambda \) is the wavelength of the Cu Kα radiation source (\( \lambda = 1.5406 \) Å), and \( \theta \) is the angle between the incident ray and the scattering planes.

Four major peaks at 2θ = 35.72° (d = 2.52 Å), 2θ = 41.66° (d = 2.18 Å), 2θ = 60.18° (d = 1.54 Å), and 2θ = 72.06° (d = 1.31 Å) in all the samples containing SiC nanoparticles correspond to the (111), (200), (220), and (311) planes of SiC crystals, consistent with the peaks of standard SiC (standard XRD file PDF No. 29-1129).

The above major SiC peaks shift toward a lower diffraction angle in the corresponding nanocomposites, as compared with those of the pure SiC nanoparticles. This is different from the observed larger angles in polypyrrole/pillared clay nanocomposites.\(^52\) The peak at 2θ = 21.40° in the pure SiC sample (Figure 2, pattern a) is due to the silicon oxide (SiO\(_2\)), arising from the oxidation of the β-SiC during the SiC nanoparticle fabrication at high temperature, consistent with our former selected area electron diffraction (SAED) analysis.\(^50\) The silicon oxide peak disappeared when the SiC nanoparticles are treated with the acid−oxidative agent (Figure 2, pattern b).\(^33,54\) The silicon oxide is etched away by the acid. The average grain size is normally estimated by calculating from the full width at half-maximum (FWHM) at the major peak, using the Debye−Scherer equation, eq 2\(^55\)

\[
L = \frac{K \lambda}{\beta_{1/2} \cos \theta}
\]

where \( K \) is 0.9 (constant), \( \lambda \) is 1.5148 (radiation wavelength), \( \beta_{1/2} \) is the full width at half-maximum in radians, and \( \theta \) is the angle at maximum intensity. The grain size based on the major peak of the (111) plane is calculated to be 6.12 and 8.17 nm for the as-received SiC nanoparticles and SiC nanoparticles dispersed in the polypyrrole matrix, respectively. This differs from the reported size observed from TEM, which is consistent with the observed defects in the nanoparticles and indicates that the nanoparticles are composed of several grains.\(^50\)

3.1.2. FT-IR Analysis. Figure 3 shows the FT-IR spectra of pure PPy, as-received β-SiC nanoparticles, acid−oxidant−treated β-SiC nanoparticles, and PPy/SiC nanocomposites with different particle loadings. A sharp absorption band at 800 cm\(^{-1}\) with a shoulder at 912.5 cm\(^{-1}\) was observed in the as-received nanoparticles and the acid−oxidant-treated nanoparticles (Figure 3, spectrum a), which is related to the Si−C stretching vibration of the crystalline β-SiC.\(^56,57\) However, the spectrum of the SiC nanoparticles treated with acid and oxidant (Figure 3, spectrum b) is different from that of the as-received nanoparticles (Figure 3, spectrum a). The newly developed peaks indicate that the nanoparticles are coated with acid and oxidative agent, which is necessary for the subsequent polymerization surrounding the nanoparticles and similar to our recently reported surface-initiated-polymerization (SIP) approach for SiC\(^50\) and iron oxide\(^8\) nanoparticles reinforced polyurethane nanocomposite fabrication. The presence of polypyrrole in PPy/SiC nanocomposites is confirmed by the observation of PPy bands in the spectra.\(^12\)
The peaks at 1529 and 1419 cm\(^{-1}\) of pure PPy are due to C—C and C—N stretching vibrations, respectively. The band at 1529 cm\(^{-1}\), the C=C stretching vibration of PPy, shifts to 1517 cm\(^{-1}\) after the addition of nanoparticles in the polypyrrole matrix, indicating a strong interaction between polypyrrole and the SiC nanoparticles.\(^{13}\) The band of C—N stretching vibration at 1419 cm\(^{-1}\) in the spectrum of pure PPy\(^{12}\) is the same as that in the PPy/SiC nanocomposites. The band at 2354 cm\(^{-1}\) observed in all the samples is due to the adsorbed carbon dioxide.\(^{58}\)

3.1.3. Thermal Gravitational Analysis. Figure 4 shows the thermal stability of pure PPy and PPy/SiC nanocomposites with a nanoparticle loading of 5.0, 10.0, 25.0, and 40.0 wt %. All the samples are observed to exhibit two distinct weight loss stages. One is at 26—220 °C, and the other is at 220—650 °C. The steady weight loss at temperatures lower than 150 °C is due to the elimination of moisture and solvent in the sample. The major loss at temperatures higher than 220 °C in all the samples is due to the decomposition of PPy. With the addition of SiC nanoparticles, the decomposition temperature of PPy (234 °C) increases to 239, 258, 274, and 304 °C for the PPy/SiC nanocomposites with a nanoparticle loading of 5.0, 10.0, 25.0, and 40.0 wt %, respectively. The increased decomposition temperature is due to the relatively compact structure of PPy induced by the SiC nanoparticles, as observed in Fe\(_3\)O\(_4\)/PPy nanocomposites\(^{12}\) and polypyrrole doped with heptasulphonated β-cyclodextrin (β-CDSO\(_3\)).\(^{59,60}\) The retardation effect of the silicon carbide nanoparticles on the movement of the polypyrrole chains with respect to the inert nature of silicon carbide also contributes to the increased decomposition temperature, which has also been observed in polyurethane nanocomposites filled with SiC nanoparticles\(^{50}\) and in polybenzoxazine nanocomposites filled with the multiwalled carbon nanotubes.\(^{51}\)

After the TGA experiment, the weight percentage of the residue in the pure polypyrrole is about 1.3%, which is the carbonized polypyrrole and indicates that PPy cannot easily get decomposed in the air even at higher temperatures. From the TGA analysis, β-SiC in the nanocomposite samples is estimated to be 6.85% (5.0 wt %), 16.5% (10.0 wt %), 35.2% (25.0 wt %), and 53.6% (40.0 wt %). The nanocomposites have a weight loss much larger than that of the initial particle loading estimation, calculated from the initial weight of particles, monomers, and the catalysts. This is due to less conversion of monomers during the polymerization of polypyrrole.

3.1.4. DSC Analysis. Figure 5 shows the DSC of pure PPy and its nanocomposites with different particle loadings. Pure PPy shows a broad endothermic dip at 120.7 °C, which is the glass-transition temperature (\(T_g\)) of PPy. The addition of the SiC nanoparticles does not have an effect on the \(T_g\) of PPy in the nanocomposites. Pure PPy contains one more peak at 295.2 °C, which is the melting point of PPy. However, the nanoparticles do have a significant effect on the melting temperature of PPy in the polymer nanocomposites. The nanocomposites with an initial particle loading of 1.8, 25.0, and 40.0 wt % show a lower melting temperature at 294.4, 289.9, and 283.3 °C, respectively. The decreased melting temperature of PPy in the nanocomposites with a higher particle loading is due to the less crystalline structure of PPy induced by the addition of SiC, consistent with the XRD analysis.

3.1.5. Scanning Electron Microscopy. The morphologies of pure PPy and PPy/SiC nanocomposites are investigated by a scanning electron microscope operated at 5 kV. Figure 6a shows the pure PPy, a typical particulate structure with a uniform size distribution. The surface of the SiC covered with PPy is more spherical; see Figure 6b–d. The observed shining spots on the
nanoparticles are due to the image contrast, arising from the collected electrons. In other words, the collected electrons cannot be transferred due to the higher contact resistance among the nanoparticles with less conductive polymer surrounding the SiC nanoparticles, as compared with the polymer nanocomposites with a thicker polymer coating, smoother surface, and linked nanoparticles (Figure 6a–c), which is consistent with a higher final particle loading, as determined by the TGA results.

3.1.6. Electrical Conductivity and Electron-Transport Mechanism. The electrical conductivity ($\sigma$, S/cm) was measured by using a standard four-probe method to minimize the errors caused from the surface contact resistance. Figure 7b shows the temperature-dependent resistivity of pure PPy and PPy/SiC nanocomposites with different nanoparticle loadings. Resistivity decreases with an increase of the temperature in pure polypyrrole and PPy/SiC nanocomposite samples. The temperature-dependent resistivity of PPy/SiC nanocomposites decreases with an increase of the initial nanoparticle loading and then increases at higher particle loading. In other words, the optimum particle loading for the highest conductivity (0.41 S/cm) at room temperature is observed to be 10 wt %. The other values of resistivity at different temperatures are listed in Table 1. Pure PPy and the nanocomposites containing an initial particle loading of 1.8, 5.0, 10.0, 25.0, and 40.0 wt % of SiC show a room-temperature conductivity of about $4.9 \times 10^{-4}$, 0.048, 0.144, 0.41, 0.29, and 0.22 S/cm, respectively. The effect of particle loading on the electrical conductivity at different temperatures is shown in Figure 7a. The electrical conductivity of the nanocomposites with an initial particle loading of 1.8, 5.0, and 10.0 wt % increases, and the electrical conductivity decreases in the nanocomposites at higher particle loadings, such as 25.0 and 40.0 wt %. This is due to the dominating poor conductivity of the silicon carbide,36 similar to our prior observation in the Fe$_2$O$_3$/PPy nanocomposites.12 Electric conductivity increases with an increase of the temperature in each of the nanocomposite samples. The conductivity of all the nanocomposites is significantly higher than that of pure polypyrrole at room temperature.

To determine the electron-transport (conduction) mechanism in PPy and its nanocomposites, the temperature-dependent conductivity was measured by a standard four-probe technique in the range of 15–290 K. Electron transport in a material can be categorized into the following two modes. In the metallic conduction, the electrical conductivity ($\sigma$) will linearly increase with a decrease of the temperature. In other words, the temperature-dependent resistance shows a positive temperature coefficient of resistance.62 In the second semiconductor type, conductivity increases generally with an increase of the temperature. A linear relationship between the logarithmic resistance and square root of temperature $T^{-1/2}$ is observed, which is attributed to the interparticle tunneling/hopping conduction mechanism.63 The other relationship between the logarithmic resistance and $T^{-1/4}$ is also observed, indicating a quasi 3-d variable range hopping (VRH, the low-temperature behavior of the resistivity in strongly disordered systems where states are localized).12 Depending on the dimensionality ($d$) of the system, that is, $d = n - 1$, the general form of the temperature-dependent VRH conductivity is given by eq 3

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

where $T_0$ is the characteristic Mott temperature related to the electronic wave function localization degree and $\sigma_0$ is the high-
temperature limit of conductivity. The value of \( n \) assumes 4, 3, and 2 for three-, two-, and one-dimensional systems, respectively.\(^64,65\) A linear relation between \( \ln(\sigma(T)) \) and \( T^{-1/4} \) is obtained from the experimental results (Figure 7c), indicating a three-dimensional (3-d) variable range hopping (VRH) electron transport mechanism in the nanocomposites. A larger \( T_0 \) implies a stronger localization of the charge carriers, with the increase of the resistance at low temperatures. A small \( T_0 \) implies a weak localization.\(^66\) The values of \( \sigma_0 \) and \( T_0 \) of pure PPy and SiC/PPy nanocomposites at different particle loadings are evaluated and listed in Table 2.

### 3.2. Polymer Nanocomposites with SiC Nanorods.

The effect of the nanofiller morphologies on the polypyrrole nanocomposites is also investigated. Polypyrrole nanocomposites filled with nanorods are fabricated by using the same procedures.

#### 3.2.1. Thermal Gravitational Analysis.

Figure 8a shows the thermograms of pure polypyrrole and the PPy/SiC (nanorod) nanocomposites with different particle loadings taken from 23 to 800 °C. The major weight loss between 219 and 653 °C in pure polypyrrole is due to the decomposition of polypyrrole, and the decomposition temperature increases in the nanocomposites. Pure polypyrrole loses 98.7% of its total weight at 800 °C. The weight loss of the nanocomposites with different wt % loadings starts at 244 °C, which is higher than that (219 °C) of the pure polypyrrole. The nanocomposites with particle loadings of 1.8, 5.0, 10.0, 25.0, and 40.0 wt % lose 94.8, 93.1, 86.0, 64.5, and 35.9% of their total weight at 800 °C, respectively. These observations indicate that the thermal stability of polypyrrole/SiC nanocomposites is better than that of pure polypyrrole.

### 3.2.2. SEM Analysis.

Figure 8b shows the SEM microstructures of the as-prepared SiC nanorods (inset) and PPy/SiC nanocomposites with 40 wt % SiC nanorod loading. The as-

---

**TABLE 1: Resistivity for Pure PPy and Different SiC wt % Loadings**

<table>
<thead>
<tr>
<th>sample name</th>
<th>resistivity at 15 K (Ω·cm)</th>
<th>resistivity at 50 K (Ω·cm)</th>
<th>resistivity at 185 K (Ω·cm)</th>
<th>resistivity at 290 K (Ω·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>polypyrrole</td>
<td>454.914.34</td>
<td>69.402.66</td>
<td>4605.31</td>
<td>2008.38</td>
</tr>
<tr>
<td>1.8 wt %</td>
<td>640.40</td>
<td>132.62</td>
<td>33.40</td>
<td>20.63</td>
</tr>
<tr>
<td>5.0 wt %</td>
<td>223.21</td>
<td>43.62</td>
<td>11.12</td>
<td>6.91</td>
</tr>
<tr>
<td>10.0 wt %</td>
<td>42.16</td>
<td>10.99</td>
<td>3.51</td>
<td>2.44</td>
</tr>
<tr>
<td>25.0 wt %</td>
<td>127.78</td>
<td>22.60</td>
<td>5.4</td>
<td>3.45</td>
</tr>
<tr>
<td>40.0 wt %</td>
<td>280.83</td>
<td>33.9</td>
<td>7.16</td>
<td>4.50</td>
</tr>
</tbody>
</table>

**TABLE 2: Values of \( \sigma_0 \) and \( T_0 \) for Pure PPy and Different SiC wt % Loadings**

<table>
<thead>
<tr>
<th>sample name</th>
<th>conductivity(^a) ((\sigma_0), S/cm)</th>
<th>( T_0 ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>polypyrrole</td>
<td>0.312</td>
<td>314, 219.6</td>
</tr>
<tr>
<td>1.8 wt %</td>
<td>1.102</td>
<td>30, 608.7</td>
</tr>
<tr>
<td>5.0 wt %</td>
<td>1505.07</td>
<td>2016, 210.0</td>
</tr>
<tr>
<td>10.0 wt %</td>
<td>837.6</td>
<td>921, 734.8</td>
</tr>
<tr>
<td>25.0 wt %</td>
<td>6.9129</td>
<td>32, 097.6</td>
</tr>
<tr>
<td>40.0 wt %</td>
<td>3248.0</td>
<td>2 243, 770.9</td>
</tr>
</tbody>
</table>

\(^a\) Conductivity at infinite temperature.
prepared SiC nanorods show a smooth and beading surface morphology. The tip of the nanorod has a hexagonal shape, and the nanorod in the PPy/SiC nanocomposites shows a layer of covered PPy. The morphology of PPy/SiC nanocomposites filled with nanorods is different from that of the as-prepared SiC nanorod.

3.2.3. Electrical Conductivity. Figure 8c shows the temperature-dependent resistivity of pure polypyrrole and the PPy/nanocomposites with different SiC nanorod loadings. The temperature-dependent resistivity of PPy/SiC nanocomposites decreases with an increase of the initial nanorod loading and then increases at higher particle loading, similar to that observed in the PPy/SiC nanocomposites filled with nanoparticles. The optimum particle loading for the highest conductivity (0.078 S/cm) at room temperature is also observed to be the 10 wt % SiC nanorod loading, which is lower than the highest conductivity (0.41 S/cm) obtained for the PPy/SiC nanocomposites filled with the 10 wt % of SiC nanoparticles. This is due to the higher contact resistance between the nanoparticles and the polymer arising from the lower packing factor for fillers with a nonspherical shape. A linear relation between $\ln(\sigma(T))$ and $T^{-1/4}$ is obtained from the experimental results (Figure 8d), indicating a similar electron-transport mechanism to that of the nanocomposites filled with nanoparticles, that is, a three-dimensional (3-d) variable range hopping (VRH).

3.3. Ratio of Oxidant to Monomer. In this study, the effect of the oxidant-to-monomer molar ratio on the conductivity and morphology of the nanocomposites is investigated. PPy/SiC nanocomposites with a 10.0 wt % SiC nanoparticle loading are fabricated by using the same procedures as reported in the
Experimental Section, varying the oxidant to monomer molar ratio. Two different samples are prepared, one with 8.0 mmol and another with 2.0 mmol of APS (oxidant), while maintaining a constant amount of monomer (7.3 mmol) in both samples. The electrical conductivities of the resultant PPy/SiC nanocomposite pellets at room temperature are 0.2, 0.4, and 0.027 S/cm for the oxidant/monomer molar ratios of 0.27, 0.50, and 1.09, respectively (Figure 9). The electrical conductivity is observed to increase with the increase of the oxidant/monomer molar ratio. However, conductivity starts to decrease when the oxidant ratio is too high, which is due to the aggregates with a low electrical conductivity arising from the fast polymerization.

The oxidant/monomer molar ratio is one of the important factor influencing the conductivity and yield of the resultant PPY/SiC nanocomposites. When the APS/Py molar ratio increases gradually, the yield of PPY increases correspondingly. However, the oxidant-to-monomer ratio is not observed to affect the morphology of the resulting PPY/SiC nanocomposites (Figure 10a,b). The observed electrical conductivity change is due to the intrinsic structure change, as observed in the doped poly(p-phenylene-benzobisthiazole) thin film.

4. Conclusion

Polypyrrole/SiC nanocomposites with different nanoparticle loadings are successfully fabricated via an oxidation polymerization in the presence of β-SiC nanoparticles dispersed in deionized water. The obtained nanocomposites are analyzed by various techniques, including XRD, FT-IR, DSC, and SEM. A standard four-probe method is performed to characterize the electrical conductivity of the resulting polypyrrole/SiC nanocomposites. The SEM study shows a different morphology of PPY/SiC nanocomposites from the as-received β-SiC and pure PPY. XRD and FT-IR analyses demonstrate a strong interaction between SiC nanoparticles and PPY. A poorer crystalline structure of PPY in the nanocomposites than that of pure PPY is inferred from both XRD and DSC analyses. TGA observation shows that the PPY/SiC nanocomposites have higher thermal stability than that of pure PPY. The ability to tune the electrical conductivity of the polypyrrole nanocomposites is achieved by varying the particle loadings. The highest conductivity is observed in the nanocomposites with an initial particle loading of 10 wt %. A quasi 3-d variable range hopping (VHR) conduction mechanism is justified by the temperature-dependent conductivity investigation. The optimum particle loading (nanorod) for the highest conductivity (0.078 S/cm) at room temperature is 10 wt %. The electrical conductivity (0.078 S/cm) in the polymer nanocomposites filled with nanorods is lower than that (0.44 S/cm) of the polypyrrole nanocomposites filled with nanoparticles. In addition, the ratio of the oxidant to the monomer is found to have a significant effect on the electrical conductivity of the polymer nanocomposites.

Acknowledgment. This project is partially supported by a research startup grant and research enhancement grant (REG) from Lamar University. D.P.Y. acknowledges support from the NSF under Grant No. DMR 04-49022.

References and Notes

(2) Xie, X.; Gao, L. Carbon 2007, 45, 2365–2373.