Conductive Polypyrrole/Tungsten Oxide Metacomposites with Negative Permittivity

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Polypyrrole (PPy) nanocomposites reinforced with tungsten oxide (WO3) nanoparticles (NPs) and nanorods (NRs) are fabricated by a surface-initiated polymerization method. The electrical conductivity is observed to depend strongly on the particle loadings, molar ratio of oxidant to pyrrole monomer, and the filler morphology. The electron transportation in the nanocomposites follows a quasi-three-dimensional variable range hopping (VRH) conduction mechanism as evidenced by the temperature-dependent conductivity function. Unique negative permittivity is observed in both pure PPy and its nanocomposites, and the switching frequency (frequency where the real permittivity switches from negative to positive) can be tuned by changing the particle loading, ratio of oxidant to pyrrole monomer, and the filler morphology. The extent of charge carrier localization calculated from the VRH mechanism is well-correlated to the dielectric properties of the nanocomposites. WO3 NRs are observed to be more efficient in improving the electrical conductivity, dielectric permittivity, and thermal stability of the resulting nanocomposites as compared to those with WO3 NPs. The microstructures of pure PPy and its nanocomposites are observed by scanning electron microscopy and transmission electron microscopy. Powder X-ray diffraction analysis demonstrates the crystalline structure of WO3 nanostructures, as well as their corresponding nanocomposites. Thermogravimetric analysis reveals a significantly enhanced thermal stability with the addition of nanofillers.

1. Introduction

Polymer nanocomposites (PNCs) have attracted great interest recently owing to their novel properties derived from the successful combination of the characteristics of parent constituents into a single material. The unparallel advantages such as cost-effective processability, light weight, and tunable mechanical, magnetic, and electric properties1−9 make it possible for the diverse applications such as proton conducting membranes for fuel cells,9 microwave absorption layers,10,11 fire retardant composites,12,13 chromatic sensors,14 electrochromic devices,15 electronics,16 sensors.27 Fe2O3/PPy,21 and SiC/PPy22 PNCs with an appropriate particle loading, while following the same reaction mechanism but different experimental procedures. The increase of the electrical conductivity is thought to be a direct consequence of the improved compactness of the polymer. Moreover, electrochemical technique, another major route, provides a convenient way to fabricate conductive PNC thin films.23,24 A template-guided method has been proved to be an efficient way for fabricating PNCs with special morphologies, such as nanotubes and fibrils.25

Tungsten oxide (WO3), an n-type semiconductor with a band gap of 2.6 eV and its unique electronic properties including the small difference in electrode potential difference between W(V) and W(IV),26,27 has found wide applications, such as electrochromic “smart” windows, optical modulation devices, and gas sensors.27–29 WO3 nanostructures, including nanoparticles,30 nanodisks,31 nanorods,32 nanowires,33 and nanofibers34 have been widely synthesized. WO3/PANI composite films, prepared by
a double-pulse electrodoposition technique, have an electrochromic window between the anodic coloration of PANI and the cathodic coloration of WO₃.35 Rangari et al.,36 incorporated porous WO₃ nanoparticles into epoxy resin matrix to enhance the thermal stability and mechanical properties of the resulting PNCs. Most of the current reported research work concentrates on the synthesis of WO₃ with different nanostructures and exploration of their extensive applications in electrochromic devices, gas sensors, and catalysts with photoelectronic activities. Metamaterials are of great interest due to their unique negative permittivity, which can be applied in cloaking, superlens, wave filters, and superconductors.37–39 It is well-recognized that the unusual dielectric property is arising from the special structure rather than the composition of the materials. Materials with special structures, such as metallic mesostructures38 and nanostructures,40 and nanopores41 are widely studied. However, the electrical and dielectric properties of the PNCs filled with WO₃ are rarely reported and even fewer for their conjugated counterparts.

In this work, polymer metacomposites through controlling the composition as well as nanostructures are fabricated by the surface-initiated polymerization (SIP) method. Both WO₃ nanoparticles and nanorods are coated with PPy, and their dielectric properties, electrical conductivity, and thermal stability are comparatively investigated. Unique negative permittivity at low frequencies is observed, which provides some insight on their potential applications in the high-temperature superconductors for providing an attraction between similar charges.42 The large dielectric constant observed in the developed PNCs is significantly important for designing supercapacitors. The difference in the final performance of the PNCs arising from the filler morphological difference gives us a simple approach to design materials with the desired properties.

2. Experimental Section

2.1. Materials. Pyrrole (C₄H₅N), ammonium persulfate (APS, [NH₄]₃S₂O₈), and p-toluene sulfonic acid (PTSA, C₇H₈O₃S) are all purchased from Sigma Aldrich. All the chemicals are used as-received without any further treatment. Tungsten oxide nanoparticles (WO₃ NPs) with an average diameter of 30 nm are obtained from Nanostructured & Amorphous Materials, Inc. Tungsten oxide nanorods (WO₃ NRs) used in this study are synthesized as previously reported.43 Typically, 3 M HCl is slowly dropped into a 19 mL aqueous solution of 0.825 g Na₂WO₄·2H₂O and 0.290 g NaCl with stirring until its pH value reaches 2.0. Subsequently, the solution is transferred into a Teflon-lined autoclave of 45 mL capacity and hydrothermally processed at 180 °C for 24 h in an oven. After that, the white precipitate is repeatedly washed with deionized water to obtain the WO₃ NRs.

2.2. Polypyrrole and Its Nanocomposite Preparation. The WO₃ NPs are initially mixed with the solution of PTSA and APS with a fixed ratio of 60 mmol:36 mmol in 400 mL deionized water, following by 1 h sonication in an ice-water bath. The pyrrole solution (74 mmol in 100 mL deionized water, molar ratio of APS:PTSA:pyrrole = 0.81:0.49:1) is mixed with the above WO₃ NPs suspended solution at 0 °C and then sonicated for additional 1 h in an ice-water bath for further polymerization. The resultant solution turns to greenish immediately and then black, indicating the polymerization of pyrrole. The product is precipitated naturally and washed with deionized water until the supernatant is transparent. 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. Pure PPy, 10 wt % WO₃ NRs/PPy PNCs, and WO₃ NPs/PPy PNCs with a particle loading of 2, 5, 10, 20, and 30 wt % are fabricated, respectively. In addition, 10 wt % WO₃ NPs/PPy with different molar ratios of APS:pyrrole (0.28:1, 1.10:1) are fabricated following the same procedures.

2.3. Characterizations. Fourier transform infrared spectroscopy (FT-IR, Bruker Inc. Vector 22, coupled with an ATR accessory) is used to characterize the WO₃ NPs, pure PPy, and WO₃/PPy PNCs in the range of 500–4000 cm⁻¹ at a resolution of 4 cm⁻¹.

X-ray diffraction (XRD) analysis is performed on a Bruker D8 Focus diffractometer equipped with a Sol-X detector using a copper radiation source. Data are collected over a 2θ range of 15°–70° at a resolution of 0.05°/step with a 6 s integration time per step.

The morphology of the PNCs is characterized with scanning electron microscope (SEM, JEOL field emission scanning electron microscope, JSM-6700F). The nanofiller distribution and interaction with PPy are determined by TEM using a Philips CM-200 transmission electron microscope with a LaB₆ filament. The measurement is operated at an accelerating voltage of 120 kV. Samples for TEM analysis are made from drying a drop of PPy/WO₃ nanocomposite powder dispersion in ethanol after a brief sonication for about 30 s on carbon-coated copper TEM grids.

The thermal degradation of the PNCs with different particle loadings is studied with thermogravimetric analysis (TGA, TA Instruments TGA Q-500). TGA is conducted on pure PPy and WO₃/PPy PNCs from 25 to 800 °C with an air flow rate of 60 mL/min and a heating rate of 10 °C/min.

The dielectric properties are measured by a LCR meter (Agilent, E4980A) equipped with a dielectric test fixture (Agilent, 16451B) at frequencies of 20–2 MHz.

Pure PPy and its nanocomposite powders are pressed in the form of disk pellets with a diameter of 25 mm by applying pressure of 95 MPa in a hydraulic presser, and the average thickness is about 0.5 mm. The same sample is used to measure the electrical conductivity by a standard four-probe method. The temperature-dependent resistivity is used to investigate the electron transport mechanism in the WO₃/PPy PNCs.

3. Results and Discussion

3.1. FT-IR Analysis. Figure 1 shows the FT-IR spectra of the WO₃ NPs, pure PPy, and WO₃/PPy PNCs. Pure PPy and the nanocomposites show the same peak locations at 1523 and
1428 cm\(^{-1}\), which are due to C═C and C—N stretching, respectively. The peak near 1129 cm\(^{-1}\) corresponds to the breathing vibration of the pyrrole ring, and the peaks at ca. 1271, 1003, and 702 cm\(^{-1}\) can be assigned to the C—H in-plane and out-of-plane deformation vibration, respectively. The small band at 958 cm\(^{-1}\) is assigned to the C—O out-of-phase deformation vibration.\(^{22,44-46}\) It can be observed that the spectra of the PNCs have no obvious difference compared with that of pure PPy except for the one filled with WO\(_3\) nanorods, which shows peak shifts from 1003 to 1025 cm\(^{-1}\) and 1129 to 1148 cm\(^{-1}\) in Figure 1h. The peak shifts of the PNCs are attributed to the interaction between the NPs and the polymer matrix.\(^{22,47}\) In this case, the peak shift in the PNCs with WO\(_3\) NRs as compared to PNCs with WO\(_3\) NPs indicates the different interfacial interactions between the nanofillers and the PPy matrix.

3.2. XRD Analysis. Figure 2 illustrates the XRD patterns of the WO\(_3\) NPs and WO\(_3\) NRs and their corresponding PNCs, respectively. The XRD patterns of WO\(_3\) NPs (Figure 2a) match well to the previous reported monoclinic structure,\(^{34,48-51}\) and the strong intensity of the diffraction peaks indicates a highly crystalline structure. The diffraction peaks (2\(\theta\)) at 23.1, 23.6, 24.4, 26.6, 28.9, 33.3, 34.2, and 36.2\(^\circ\) are assigned as the (002), (020), (200), (120), (112), (022), (202), and (212) planes of the monoclinic WO\(_3\), respectively. Figure 2b─f show the XRD patterns of the PNCs with different particle loadings. No additional peaks are observed for the PNCs as compared to that of the pure particles. However, a broad peak of the semicrystalline PPy around 20 = 21─25\(^\circ\) is observed in the previous reports.\(^{22,52}\) In this work, it is reasonable to consider that the broad peak of PPy is overlapped by the large diffraction intensities of the (002), (020), and (200) crystal faces of WO\(_3\) NPs. Compared to the pure particles, the decrease in the intensities of the WO\(_3\) peaks in the PNCs (Figure 2b─f) suggests that the WO\(_3\) NPs are highly dispersed in the PPy matrix,\(^{50}\) and the broadness of the peaks remains the same, which further suggests a uniform dispersion of the nanoparticles without serious agglomeration, as revealed by the SEM observation in Figure 4. The XRD patterns of the WO\(_3\) NRs are quite consistent with the other work.\(^{43}\) However, it is worth noting that the XRD pattern of the WO\(_3\) NRs (Figure 2g) is quite different in comparison to the WO\(_3\) NPs. Preferentially oriented nanorods with limited crystal faces satisfying the Bragg requirements might be the major contribution to this unorthodox distribution of the diffraction peaks. The major peaks of the WO\(_3\) NPs/PPy PNCs (Figure 2h) are well consistent with the pure WO\(_3\) NRs while the intensity of the peaks decreases due to the coating of PPy on the surface and the low amount of WO\(_3\) NRs available for diffraction.

3.3. SEM and TEM Observations. The morphologies of the WO\(_3\) NPs and NRs are shown in Figure 3. Figure 4 shows the SEM microstructures of pure PPy (Figure 4a) and PPy PNCs filled with WO\(_3\) NPs (Figure 4b─f) and WO\(_3\) NRs (Figure 4g,h), respectively. Both pure PPy and its PNCs are observed to exhibit particulate structures with a fairly uniform size distribution. The pure PPy particles are observed to be relatively loosely packed as compared to the PNCs. For the PNCs filled with different loadings of WO\(_3\) NPs, the particles are closely packed and no bare nanoparticles are observed even at the highest loading of 30 wt %, which suggests the feasibility of this SIP method to fabricate well-dispersed nanoparticles with a uniform coating layer. It is not easy to observe the bare WO\(_3\) NRs in Figure 4g owing to the heavy wrinkling of PPy on the surface. The enlarged image (Figure 4h) clearly shows the fully covered nanorods with a thick layer of PPy particles. The TEM images shown in Figure 5 for both WO\(_3\) NPs and NRs reinforced PNCs are quite consistent with the SEM observations. The WO\(_3\) NPs are coated with PPy and embedded in the bulk PPy matrix with a small fraction of the coated particles adhered to the matrix surface, Figure 5a. The well-dispersed WO\(_3\) NRs with a diameter of ∼40 nm are fully wrapped with a thick layer of PPy, Figure 5b.

3.4. Electrical Conductivity and Electron Transport Mechanisms. Figure 6a shows the variation of resistivity as a function of temperature for pure PPy and its PNCs with particle loadings of 2, 5, 10, and 20 wt %, respectively. Generally, the resistivity decreases with the increase of temperature, indicating the semiconducting behavior in the whole range of temperature.\(^{53}\) The conductivity of the PNCs is significantly higher as compared to that of pure PPy within the whole temperature range, which is similar to our previous observations.\(^{22,54}\) However, it is interesting to find that the conductivity decreases gradually with the particle loading increasing from 2 to 10 wt % and surprisingly increases sharply at the loading of 20 wt %. Pure PPy and nanocomposites with a loading of 2, 5, 10, and 20 wt % exhibit a room temperature conductivity of 4.9×10\(^{-4}\), 0.12, 0.11, 0.04, and 0.23 S/cm, respectively. The sharp increase of the conductivity in PNCs with a loading of 20 wt % indicates particle network/packing dependent electron transport behaviors.

Figure 6b shows the effect of molar ratio of oxidant (APS): pyrrole and filler morphology on the electrical conductivity. For convenient comparison, set monomer as 1 mol, and the corresponding amount of APS is calculated. The lowest molar ratio (0.28) of APS gives the highest conductivity (1 S/cm at RT). Similar reduced conductivity is observed when the APS ratio (0.28) of APS gives the highest conductivity (1 S/cm at RT). Owing to the larger aspect ratio of NRs than that of NPs, an interconnected network structure is formed at relatively lower filler loadings, and thus higher conductivity is obtained when the PNCs are filled with NRs as compared to the PNCs filled with the same loading of NPs.

To better understand the electron transportation, the relation between ln(\(\sigma\)) and \(T^{-1/n}\) is investigated for each sample, where \(n = 2, 3,\) and 4. The best fits (standard deviation 0.01) for each sample are obtained with \(n = 4\) in the temperature range of 15─290 K. The linear relation between ln(\(\sigma\)) and \(T^{-1/4}\) obtained from the experimental results, Figure 7, indicates a quasi-three-
dimensional variable range hopping (VRH, the low temperature behavior of the resistivity in strongly disordered systems where states are localized). The temperature-dependent VRH conductivity is given by eq 1

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

where $T_0$ is the characteristic Mott temperature related to the electronic wave function localization degree and $\sigma_0$ is the conductivity at high temperature limit. The value of $n$ assumes 4, 3, and 2 for three-, two-, and one-dimensional systems, respectively.

Figure 8 depicts the $T_0$ and room temperature conductivity ($\sigma$) as a function of particle loadings. Generally, 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. The experimental results are in good agreement with the theoretical expectations. $T_0$ increases with an increase of particle loading from 2 to 10 wt %, indicating the enhanced localization of the charge carriers and thus a decreased conductivity. However, the $T_0$ decreases significantly as the loading reaches percolation (20 wt %), which is accompanied by a sharp increase of conductivity. The inset of Figure 8 demonstrates the feasibility of this model to predict the results while changing the molar ratio of oxidant and filler morphology. The $T_0$ is much lower for the PNCs filled with NRs as compared to that of the PNCs filled with NPs, indicating a weak charge carrier localization, which corresponds to the higher conductivity and leads to larger resonance owing to the attraction between similar charges.

3.5. Dielectric Properties. 3.5.1. Effect of WO$_3$ Particle Loadings. Figure 9 shows the real permittivity as a function of the frequency for pure PPy and its PNCs with different particle loading at room temperature. The $\varepsilon''$ for the PNCs with loadings not higher than 10 wt % shows excellent stability within the whole frequency range. However, it is worth noting that a large enhancement in $\varepsilon''$ is observed for PNCs when the particle loading is above 10 wt %, Figure 9a. The interfacial polarization is determinant to the electric properties for PNCs, which are strongly related to the motion of electrons in the interface. The significant increase in the permittivity originated from the Maxwell–Wagner–Sillars effect, in which the charge carriers are accumulated at the internal interfaces. The increased charge carrier localization is verified previously by the enhanced $T_0$ in Figure 8. The attained value of the $\varepsilon''$ for the 30 wt % WO$_3$ NPs/PPy PNCs at 10$^4$ Hz and room temperature is 7 $\times$ 10$^4$, which is about 2000 times larger than that of the pure WO$_3$ particles and about 350 times larger than that of 2–10 wt % WO$_3$/PPy PNCs, respectively. In addition, the largest $\varepsilon''$ is found to be 2.9 $\times$ 10$^5$ at 10$^2$ Hz, which is approximately 360 times larger than that reported in MWNT-PVDF PNCs with a giant-dielectric permittivity (~8000). The steplike decrease of the $\varepsilon''$ (30 wt % WO$_3$ NPs/PPy) at high frequency is induced by the dielectric relaxation, which suggests that the established percolation network structure is not stable and easily affected by the external frequency disturbances, similar to the multi-walled carbon nanotubes/poly(vinylidene fluoride) nanocomposites.

It is interesting to find that the nanocomposites filled with 2–10 wt % WO$_3$ NPs show negative permittivity at low frequency, while this negative value vanishes as the particle
loading further increases to 20 and 30 wt %. Similar negative permittivity is also reported in pure PPy, which is attributed to the large resonance at low frequencies. It is believed that the negative permittivity of PPy is also dependent on the fabrication method. Unsworth et al. detected only positive permittivity with the electrochemically synthesized PPy, while Miyauchi et al. demonstrated the negative permittivity of BaTiO$_3$/PPy derived from the chemical polymerization method. In this work, the SIP method is used to fabricate the PPy PNCs, and unique dielectric properties are observed. The negative permittivity is maintained for WO$_3$/PPy PNCs before reaching the percolation (20 wt %) and disappears after forming the percolation network accompanied with a significant enhancement of positive permittivity. Pure PPy shows a switching frequency from negative to positive at around 5300 Hz, Figure 9b, which is significantly larger than that of the PNCs. The switching frequency of the PNCs increases from 10$^4$ to 240 Hz as particle loading increases from 2 to 10 wt %.

Figure 9c shows the dependence of the dielectric loss ($\tan \delta$, where $\tan \delta = \varepsilon''/\varepsilon'$) on the frequency. At high frequency (>5 $\times$ 10$^4$ Hz), $\tan \delta$ decreases with the increase of the particle loading. Interestingly, a peak is observed in the dielectric loss curve for pure PPy and its PNCs filled with 5 and 10 wt % NPs, which is well corresponding to the switching permittivity from negative to positive due to the induction of polarization at high frequencies. In the composites with higher particle loadings, the dielectric loss decreases monotonically with the increase of the frequency, and the dielectric loss peak disappears together with the vanishing of the negative permittivity. After comparing the above observations, it is reasonable to conclude that the negative permittivity causes lower dielectric loss, which is necessary for designing supercapacitors to achieve high energy density.

3.5.2. Effect of APS:Pyrrole Molar Ratio and Filler Morphology. Figure 10 shows the effects of APS:pyrrole molar ratio (0.28:1, 0.49:1, and 1.11:1) and filler morphology on the dielectric properties of 10 wt % WO$_3$/PPy PNCs. The permittivity is found to increase with the increase of the APS:pyrrole molar ratio at high frequency, inset of Figure 10a, which is about 75, 175, and 300 in the composites fabricated with a ratio of
0.28:1, 0.49:1, and 1.10:1, respectively. In addition, negative permittivity is observed for all the samples at low frequencies. The magnitude of negative permittivity for the PNCs obtained with higher molar ratio (1.1:1) is several orders of magnitude lower than that of the one fabricated with a lower molar ratio (0.28:1 or 0.49:1). It is well-known that the conductivity of PPy increases with an appropriate increase of the APS/pyrrole ratio. However, it decreases again as the ratio goes extremely high due to the formation of low conductive aggregates from a faster polymerization. Similar dielectric change is observed when varying the APS/pyrrole ratio. The lowest switching frequency (240 Hz) is observed with a molar ratio of 0.49:1, Figure 10b, and both increase and decrease of the molar ratio simultaneously shifts the switching frequency to a higher value, which is approaching 7000 Hz for the sample with ratio of 1.1:1. Previous reports attributed the low frequency resonance phenomenon (negative permittivity) to the nonsymmetrical crystalline regions in the doped PPy. It is reasonable to consider that the crystalline structure of PPy is affected by the different polymerization rate induced by the varied APS/pyrrole ratios, thus exhibiting different dielectric properties. The dielectric loss peaks are also observed in Figure 10c, which well correlates to the switching frequencies, Figure 10b.
The dielectric property of the WO3/PPy PNCs is also greatly influenced by the filler morphology, Figure 10. The PNCs filled with WO3 NRs exhibit 10 times larger negative permittivity at 10^5 Hz than that of the PNCs filled with WO3 NPs, Figure 10a. However, the permittivity does not differ a lot at high frequencies, inset of Figure 10a, and it is worth noting that the permittivity is relatively stable for the WO3 NR filled PNCs, which is a key requirement for the high-performance capacitors. Dielectric relaxation, the decrease of permittivity with the increase of the frequency, is still observed for the WO3 NPs/PPy PNCs, inset of Figure 10a. The plasmon resonance frequency, studied in the metal nanostructures, has revealed that a larger aspect ratio of a metal nanorod has more field lines spread out in the dielectric medium for field polarization parallel to the rod and, hence, a lower plasmon resonance frequency in a nanostructure.40 This theoretical prediction well explains the significantly lower negative permittivity of the NRs filled nanocomposites as compared to that of the NPs filled PNCs, Figure 10b. Correspondingly, the dielectric loss is relatively lower for the WO3 NPs/PPy at low frequency, while it shows unexpected higher dielectric loss as the frequency is above 10^5 Hz, Figure 10c.

3.6. Thermal Stability. Figure 11 shows the thermal stability of pure PPy and its WO3/PPy PNCs with a particle loading of 2, 5, 10, 20, and 30 wt %, respectively. All the samples show two distinct weight loss stages. The first stage, which corresponds to 5–10% weight loss from 25 to 260 °C, is due to the evaporation of moisture and solvent residue in the samples. The major weight loss above 260 °C is attributed to the degradation of PPy. With the addition of the WO3 NPs, the degradation temperature (10% weight loss) of PPy (231 °C) increases to 269.4, 275.0, 277.0, 282.9, and 297.0 °C for the PNCs filled with a particle loading of 2, 5, 10, 20, and 30 wt %, respectively. The enhanced thermal stability of the nanocomposites is attributed to the more compact structure of PPy induced by the addition of the WO3 nanofillers, as observed in SiC22 and Fe2O354 NPs reinforced PPy PNCs. The continuous increase of the thermal stability with the increase of the particle loading indicates the uniform coating of PPy on the WO3 particle surface, even at high loadings such as 20 and 30 wt %, which can also be observed in the SEM and TEM investigation, Figures 4 and 5. From traditional blending approach, particle agglomeration (>1 wt %) induced lower thermal stability was reported in WO3 NPs/epoxy PNCs.36 It is worth to notice that the degradation temperature is even higher for the PNCs filled with WO3 NRs, which show an enhancement of 5.5 °C as compared to that of the PNCs filled with NPs with the same loading of 10 wt %, inset of Figure 11. The larger aspect ratio of the WO3 NRs as compared to that of the WO3 NPs is the major contribution to the superior thermal stability of the corresponding PNCs. This result is well consistent with the reported work by Milena et al.65 that the larger aspect ratio of β-FeOOH nanorods introduces higher thermal stability of the β-FeOOH/poly(methyl methacrylate) (PMMA) PNCs.

4. Conclusions

Polyppyrole nanocomposites filled with both WO3 nanoparticles and nanorods have been successfully prepared by a surface-initiated polymerization method and show a significantly enhanced thermal stability. A SEM investigation shows the homogeneous dispersion of the nanofillers with a uniform PPy coating layer. Systematic studies on the electrical conductivity of the resulting PNCs reveal that nanofiller loading, ratio of oxidant to pyrrole monomer, and the filler morphology simultaneously affect the conductivity in different ways. Generally, the introduction of nanofillers, lower oxidant to pyrrole ratio, and filler with larger aspect ratio bring higher electrical conductivity. Negative dielectric permittivity is observed in both pure PPy and PNCs, which is due to the resonance at low frequencies.59 The extent of charge carrier localization calculated from the VRH mechanism is well correlated to the change of dielectric properties of the PNCs. The negative permittivity can be easily tuned by changing the filler loading, oxidant to monomer ratio, and filler morphology. This unique property of PPy PNCs provides a platform to systematically study the novel conducting polymer nanostructures. It should also stimulate the exploration of applications of these materials in fields such as superlens,64 wave filters,63 and superconductors66,67 at high temperatures.

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References and Notes


![Figure 11. Thermogravimetric curves of the pure PPy and WO3 NPs/PPy PNCs. The inset shows the thermal degradation curves of the 10 wt % WO3/PPy PNCs.](image-url)