

Research Article

A Nanocellulose Polypyrrole Composite Based on Tunicate Cellulose

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The water-dispersed conductive polypyrrole (PPy) was prepared via the *in situ* oxidative chemical polymerization by using ammonium persulfate (APS) as oxidant and tunicate cellulose nanocrystals (T-CNs) as a dopant and template for tuning the morphologies of PPy nanoparticles. Highly flexible paper-like materials of PPy/T-CNs nanocomposites with high electrical conductivity values and good mechanical properties were prepared. The structure of nanocomposites of PPy/T-CNs was investigated by using Fourier transform infrared spectroscopy. Scanning electron microscopy and transmission electron microscopy analyses of the composites revealed that PPy consisted of nanoparticles about 2.5 nm in mean size to form a continuous coating covered on the T-CNs. The diameters of the PPy nanoparticles increased from 10 to 100 nm with the increasing pyrrole amount. Moreover, electrical properties of the obtained PPy/T-CNs films were studied using standard four-probe technique and the electrical conductivity could be as high as 10^{-3} S/cm.

1. Introduction

The demand for new technologies that require high performance materials has driven materials research towards the development of novel functional nanoscaled materials with superior properties. Conducting polymers are a promising class of materials that possess unique properties that allow them to be used in a wide variety of applications [1]. The conductive properties of polyacetylene resulted in the 2000 Nobel Prize in chemistry and various analogues of it have been investigated throughout the years including polyphenylene, polyaniline, polythiophene, and polypyrrole [2]. PPy, one of the most prominent types of conjugated polymers, is a promising conducting polymer in electronics and biological and medical areas due to its straightforward polymerization, environmental stability, and high electrical conductivity that can be controlled by changing the doping degree [3]. But the poor processability and inadequate mechanical properties limit its commercial applications. In order to overcome these problems, several processing methods have been studied.

The first approach toward PPy nanoparticles was reported by Bjorklund and Liedberg, who polymerized pyrrole in

water in the presence of methyl cellulose. Particles of 100 nm to 200 nm size were observed in films spread from the reaction mixture [4]. Arms and Vincent prepared colloiddally stable dispersions of PPy nanoparticles by aqueous dispersion polymerization in the presence of polyvinylpyrrolidone (PVP) or polyvinyl alcohol (PVA) as a stabilizer [5]. PPy spherical nanoparticle dispersions have been prepared by a dispersion or microemulsion polymerization [6, 7]. One of the motivations of these studies was the desire to overcome the difficult processing of conjugated polymers, most of which are insoluble unless substituted with appropriate side chains.

However, all these approaches need external stabilizers, and pure PPy nanoparticles with a clean surface cannot simply be obtained unless the heavy contamination of the stabilizer is carefully removed. Unfortunately, the PPy nanoparticles without the protection of stabilizers are likely to aggregate to some extent in a few minutes, leading to instability [8]. Deposition of conducting polymers on fiber surface of fabrics, such as xylan [9], cotton [10], bacteria cellulose (BC) [1], cellulose microcrystal (CMC) [11], and cellulose derivatives

[12–14], has been widely investigated in the last few years due to its importance in emerging technologies. These materials were generally obtained through *in situ* oxidative polymerization of pyrrole by introducing an oxidant agent such as ferric chloride (FeCl_3) or ammonium persulfate (APS) [9, 12, 15, 16]. For providing finely structured heterogenic mixtures of cellulose and conducting polymers that are able to form films, it is necessary to provide both polymers in sufficiently dispersed or disintegrated form. The conducting organic polymers are not able to form films when cast and dried from dispersion as their H-bond forming ability is low or even absent. In this case, cellulose provides the stabilizing and film-forming matrix and is also able to stick to a supporting substrate, such as glass plates [17]. Paper-like *Cladophora* cellulose/PPy composites with highly porous surface have been proposed for ion-exchange applications [18–21].

Another material having high specific area is T-CNs, mainly composed of nanocrystals. Tunicate cellulose (TC) exhibits an ultrafine fibrous network, highly crystalline structure and aspect ratio, purity monoclinic cellulose I_β allomorph, low density, and remarkable mechanical strength [22–27]. Although TC is not a starting material for the textile industry, it is a versatile biopolymer with a wide range of properties that can be used for several innovative applications, including biomedical devices and scaffolds for tissue engineering [28]. Due to the presence of some amorphous regions, T-CNs may have better film-forming properties when compared to *Cladophora* [29].

This work reports the production of a new functional material that exploits the inherent properties of TC with electrical conductivity of PPy. For this purpose, the T-CNs doped PPy had been prepared via the chemical oxidative polymerization of Py with T-CNs as both polymeric template and dopant, and using APS as oxidant agent in aqueous solution. The electrically conducting membranes composed of T-CNs were coated with PPy as new promising polymer composite that presents a successful combination of the inherent properties of each single component. These properties include high tensile strength, toughness, biocompatibility, high surface areas of the TC, and electronic and chemical properties of PPy. However, the conductivity of the composites is still not comparable to that associated to solvent-cast PPy films. However, tunicate cellulose, already used as reinforcing agents in polymeric nanocomposites, appears as outstanding candidate for the production of highly flexible full paper-like materials. The structure of nanocomposites of PPy/T-CNs was investigated at a microscopic level using Fourier transform infrared spectroscopy. The morphology of the nanocomposites was also investigated at macroscopic level by scanning electron and transmission electron microscopies. Moreover, electrical properties of the obtained PPy/T-CNs films were studied using standard four-probe technique.

2. Experimental

2.1. Materials. Tunicate Cellulose was extracted from *Styela clava*, collected from the Yellow Sea near Yantai, China. The pyrrole (Py) monomer used was a product of TCI Development Co. Ltd. (Shanghai, China) and was used without

further purification. The sulfuric acid (H_2SO_4) was obtained from Yantai Sanhe Co. Ltd. (Yantai, China). The ammonium persulfate (APS) as oxidant was purchased from Tianjin Bodi Co. Ltd. (Tianjin, China). Water was distilled before use.

2.2. Preparation of T-CNs Suspension. Suspensions were prepared from tunicate cellulose (*Styela clava*, collected from the Yellow Sea). The cellulose mantles were separated from the rest of the organs and were cut into small pieces. 200 g of *Styela clava* was soaked in a 10 wt% KOH solution for 24 h followed by washing and then bleached at 60°C with 30 mL of NaClO in 1 L of acetic buffer for 24 h, and the resultant white mantles were washed till neutrality. The previous procedure was repeated 3 times. Then, the pieces were homogenized into millimeter-size fragments using a multiblender mill (IKA-A11, Germany) and mixed with 64 wt% H_2SO_4 and stirred at 50°C for 5 h to obtain T-CNs. Then, the acid was removed through centrifugation and prolonged dialysis with distilled water until the pH outside dialysis bag was neutral. The sample thus obtained was concentrated by osmotic compression using molecular weight cutoffs of 14000 and the nanocrystal aggregates were disrupted by sonication for about 10 minutes under ice-water bath. The sample was poured into the dialysis bag and concentrated by a 15 wt% poly(ethylene glycol) ($M_w = 20000$) solution. Then, the T-CNs were dispersed by sonication and the concentration of the suspension was measured gravimetrically before and after evaporation of the water. The concentration of the sample suspension was 1.5 wt%.

2.3. Preparation of PPy/T-CNs Nanocomposites. PPy was synthesized via an oxidative synthetic approach in this study. Py monomer of different amounts was dissolved in 50 mL T-CNs dispersion (1.5 wt%) at room temperature for 1 h. The solutions were then cooled down, which was followed by the addition of APS solution (dissolved in 50 mL distilled water) with $\text{APS/Py} = 1.25 \text{ mol/mol}$, in drops. The polymerization was carried out by using magnetic stirring in ice-water bath. After 6 h, the black suspensions of PPy/T-CNs could be observed and the reaction mixtures remained suspended. Aqueous suspensions of PPy/T-CNs were then prepared by washing the reaction mixtures with distilled water and dispersed by sonication. Films were deposited onto polystyrene petri dishes by casting directly from the solution of PPy/T-CNs and drying at room temperature for 3 days.

2.4. FT-IR Measurement. Fourier transform infrared (FT-IR) spectra of the PPy/T-CNs nanocomposites, PPy, and T-CNs were recorded with a FT-IR spectrometer (VERTEX70, Bruker Corporation, Germany) in the range of 200–4000 cm^{-1} . The dried samples were ground into powder and then blended with KBr before pressing the mixture into ultra-thin pellets.

2.5. Scanning Electron Microscopy (SEM). Morphology of the samples was studied by a scanning electron microscope (JSM-7500FA, JEOL, Japan). The electron energy (3–8 keV) was used to facilitate the imaging of the composite samples and



FIGURE 1: Photograph of a flexible film of the PPy/T-CNs nanocomposite.

neat T-CNs. All the samples were coated with a thin layer of gold to prevent charging and all the samples were not stained.

2.6. Transmission Electron Microscopy (TEM). The PPy/T-CNs nanocomposites suspensions were diluted by ethanol and then the as-prepared samples were deposited into glow-discharged carbon-coated TEM grids. They were observed after the specimen has been completely dried. Images were recorded using a TEM (JEOL, JEM-2100, Japan), operating at 200 kV with a CCD camera at different magnifications. All the samples were not stained.

2.7. Conductivity Measurements. The conductivities of the PPy/T-CNs nanocomposites films were measured by the four-probe technique at room temperature using a semiconductor device analyzer (RST-8, Guangzhou Four-Probe Technology Co., Ltd., China). The voltage U , which was scanned between -1 and $+1$ V, was applied with titanium needle probes and the resulting dc current I was measured. The conductivity σ was then calculated. Each sample was measured five times and the average value was taken.

3. Results and Discussion

3.1. Mechanical Properties. We prepared highly flexible paper-like materials from the PPy/T-CNs suspensions by casting it onto the polystyrene petri dishes (Figure 1). Previous work on PPy coated on other cellulose materials employed the addition of a steric stabilizer in order to maintain a stable suspension and an insulating matrix to produce the films. In the present work, no stabilizer was used to maintain the solution nor was another polymer matrix required to cast the film.

The new nanocomposites might find interesting uses in chemical sensors or paint formulations for antistatic applications, as well as in the development of electrically conductive nanocomposites with better mechanical properties due to the high mechanical strength of the CNs.

3.2. FT-IR Analysis. Fourier transform infrared spectroscopy in combination with attenuated total reflectance has been

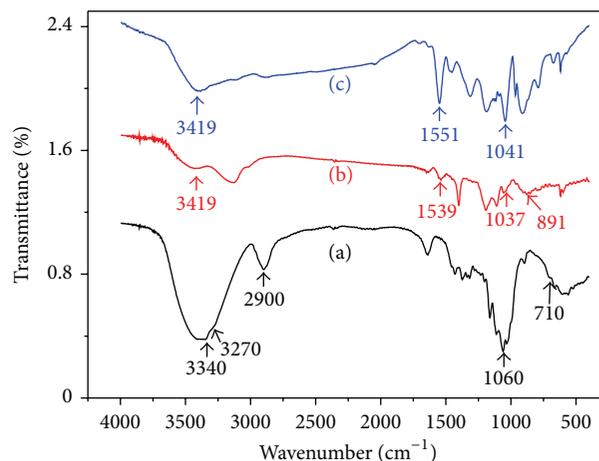


FIGURE 2: FT-IR spectra of TC (a), PPy (b) and the film of PPy/T-CNs nanocomposite (c).

shown to be an extremely powerful tool for surface characterization of materials, particularly when the composite material is constituted by fibers coated with an external conducting polymer layer. This technique can also be applied to evaluate specific surface interactions between composite components.

The FT-IR spectra of T-CNs, PPy, and the film of PPy/T-CNs nanocomposite are shown in Figure 2. The peaks near 3340 , 3270 , 2900 , 1060 , and 710 cm^{-1} in Figure 2(a) were associated with cellulose. The characteristic broad band of cellulose O-H group appears at 3340 cm^{-1} . The band at 2900 cm^{-1} is attributed to the asymmetrically stretching vibration of C-H. The broad absorption band in the range of 1060 to 1030 cm^{-1} is attributed to the contribution of various functional groups, such as C-O and C-O-C. The peaks at 3270 and 710 cm^{-1} were attributed to the I_{β} phase of cellulose. Figure 2(b) was the FT-IR spectrum of PPy. The peaks at 3419 cm^{-1} could be attributed to N-H stretching vibrations. The peaks at 1539 and 1450 cm^{-1} could be attributed to C-N and C-C asymmetric and symmetric ring stretching, respectively. Additionally, the strong peaks near 1170 and 891 cm^{-1} present the doping state of PPy; the peak at 1037 cm^{-1} is attributed to C-H deformation and N-H deformation vibrations, and the broadband at 1300 cm^{-1} demonstrates the C-H and C-N in-plane deformation vibration, respectively. Moreover, these characteristic peaks of T-CNs and PPy were also found in that of the PPy/T-CNs nanocomposites. However the band at 1539 cm^{-1} for pure PPy is blue-shifted to 1551 cm^{-1} for composites and the bending modes for OH groups of T-CNs were weakened, which indicates the existence of PPy coating layer. The observed shift of the band may be caused by chemical bonding between -N-H in the Py ring and the -OH functional group of cellulose, although the -OH absorption band of the composites is too weak to confirm that OH groups of the cellulose are intermolecularly bonded to -N-H in the Py ring [2]. The results indicated that the *in situ* polymerization of Py onto the T-CNs still retains its chemical structures well.

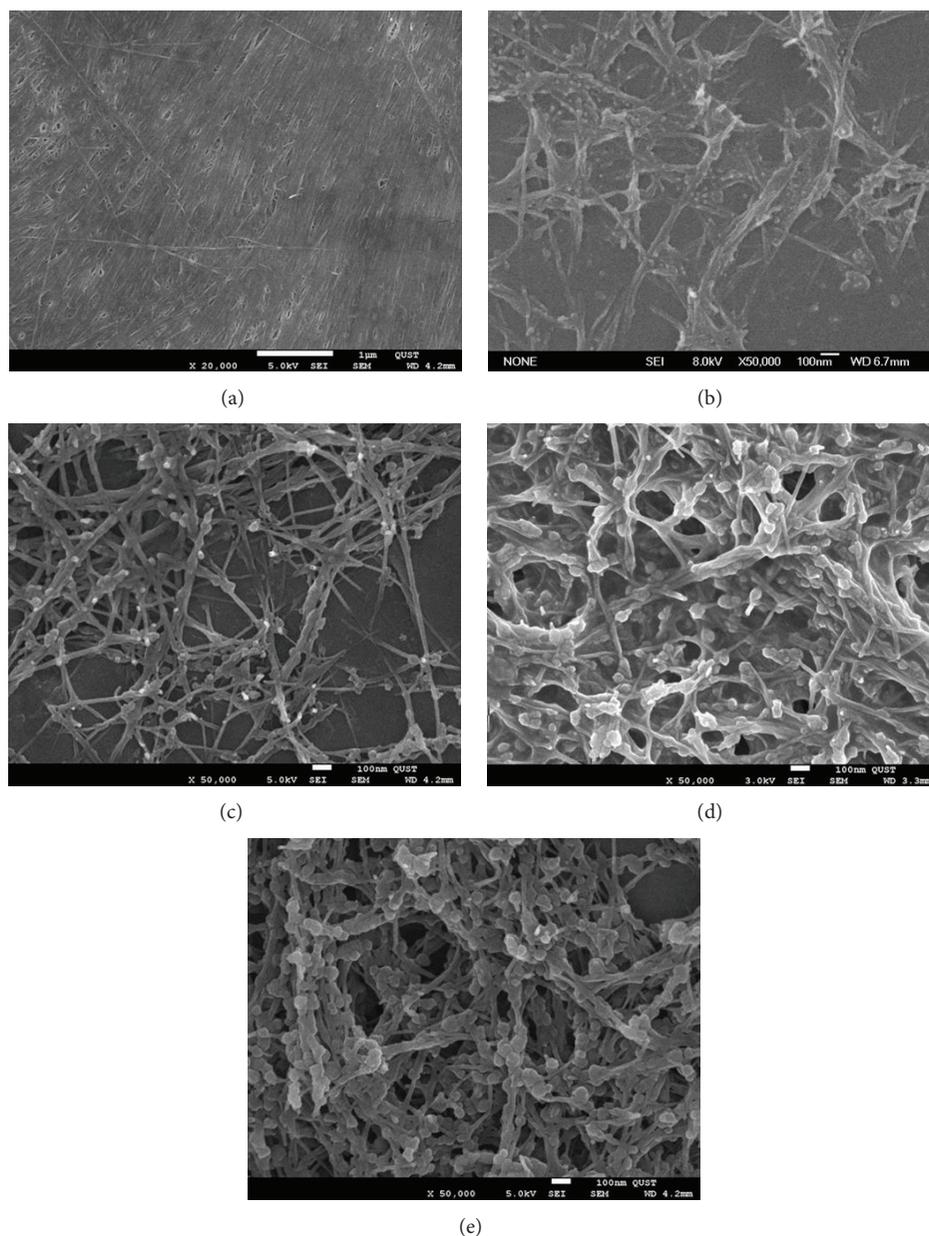


FIGURE 3: SEM images of T-CNs (a) and the PPy/T-CNs nanocomposites (b)–(e). The amount of Py in the nanocomposites was 0.5 (b), 1.0 (c), 2.0 (d), and 5.0 mmol (e), respectively.

3.3. SEM Analysis. Morphological analysis showed that the string-like T-CNs (Figure 3(a)) length ranges from $1\ \mu\text{m}$ to $2\ \mu\text{m}$ and width averages 25 nm, and the aspect ratio is about 40 to 80. Moreover, such high aspect ratio nanocrystals should create a huge entanglements network, and thus, it is responsible for such highly mechanical stiffness and highly flexible paper-like materials. The influence of the amount of Py on the structure and morphologies of the PPy/T-CNs nanocomposites was investigated by SEM (as shown in Figures 3(b)–3(e)). The size of PPy particles increased from 10 nm to 100 nm with the increasing Py. The adhesion of PPy particles to the cellulose surface could attribute to the formation of hydrogen bonds between cellulose hydroxyl

groups and Py NH moieties. The formed PPy particles on cellulose surface had spherical shape and controlled size, which was probably due to the charge density on T-CNs that impeded, further, disordered growth [11]. And the increase of the T-CNs may have prevented the aggregation of PPy particles and acted as the separant and dispersant during the *in situ* polymerization of Py which eventually decreased the particles size.

3.4. TEM Analysis. In order to further prove the previous speculation, the TEM images of the PPy/T-CNs nanocomposites dispersed in ethanol were given in Figure 4. The

TABLE 1: Electrical conductivities of the PPy/T-CNs films.

Sample	Py, mmol	Resistivity, $K\Omega \cdot cm$	Conductivity, S/cm
1	0.5	4.9	2.1×10^{-4}
2	1.0	3.4	2.9×10^{-4}
3	2.0	1.5	6.7×10^{-4}
4	5.0	0.7	1.4×10^{-3}

morphologies of the composites became smaller with the increasing T-CNs. The width of the T-CNs was about 20 nm while the composites were 30 nm to 50 nm. A thickness layer of PPy about 30 nm was deposited on the T-CNs. It is found that on the surface of the nanocomposites absorbed a lot of uniform spherical nanoparticles and their diameters are about 2.5 nm. According to the previous work, they might be PPy nanoparticles [7, 30]. And we could also find on the surface of the covered layer adhered lots of spherical nanoparticles ranging from about 20 nm to 100 nm, which is consistent with the SEM results. This indicated that the T-CNs molecules acted as the templates as well as the dopant, as reported previously [31]. The micrographs revealed that PPy was constituted of particles that uniformly coated on the surface of T-CNs. The polymer coating adhered to the nanofiber and a continuous conducting pathway was formed which was responsible for the high electrical conductivity values.

3.5. Conductivity Measurements. Electrical conductivities of the samples were determined and the results were shown in Table 1. It was observed that the conductivity could be up to 1.4×10^{-3} S/cm without the addition of any external dopants. Additionally, T-CNs are not an electric conductor and the conductivity decreased with decreasing the amount of Py. This behavior is attributed to the formation of a continuous conducting PPy layer that homogeneously coated the surface of T-CNs. As expected, the amount of PPy incorporated on T-CNs increased with increasing monomer concentration and the conductivity also increased with the increase of the ratio of Py. Thus, we could conclude that T-CNs play a good role of dopant as well as template.

4. Conclusions

In conclusion, we have developed a renewable resource T-CNs and utilized it as a dopant for water-dispersed and electrically conductive nanocomposites by the *in situ* oxidative chemical polymerization of Py onto T-CNs. Highly flexible paper-like materials of PPy/T-CNs nanocomposites with electrical conductivities as high as 10^{-3} S/cm were also obtained. These films have interesting properties that may find important technological applications such as sensors, electronic devices, antistatic and anticorrosive nanocoatings, intelligent clothes, flexible electrodes, and tissue engineering scaffolds.

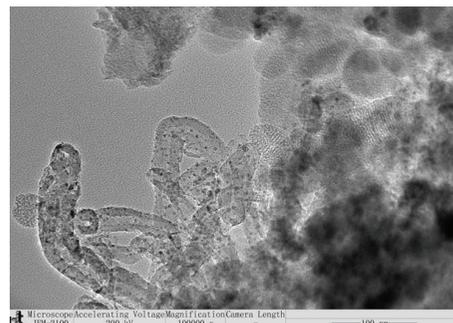


FIGURE 4: TEM image of the PPy/T-CNs nanocomposite. The amount of Py in the nanocomposite was 2.0 mmol.

Conflict of Interests

The authors declare that they have no conflict of interests.

Acknowledgments

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