Single-walled Carbon Nanotube / Polypyrrole Thermoelectric Composite Materials

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Abstract. A single-walled carbon nanotube/polypyrrole (SWCNT/PPy) thermoelectric composites were prepared by an in situ oxidative polymerization method. The effect of SWCNT composition on the microstructure of the SWCNT/PPy nanocomposites was investigated. The thermoelectric properties of the composites were measured at different temperatures between 298 K and 398 K. Both of the electrical conductivity and the Seebeck coefficient of the SWCNT/PPy nanocomposites with 40% SWCNT loading increased simultaneously in the measured temperature. A maximum power factor of 5.46 μWm⁻¹K⁻² was obtained at 398 K for the SWCNT/PPy nanocomposite with 40 wt% SWCNT loading.

1. Introduction
Thermoelectric (TE) materials can directly convert heat energy into electrical energy. TE devices have many advantages, e.g. noise-free and no exhaust emission, etc. The conversion efficiency of a TE device is mainly determined by the material’s dimensionless figure of merit \( ZT = S^2 \sigma T/\kappa \), where \( \sigma \), \( S \), \( \kappa \), and \( T \) is the electrical conductivity, Seebeck coefficient, thermal conductivity, and absolute temperature, respectively [1].

Polypyrrole (PPy), as a major conducting polymer, has many virtues, such as, low cost, low density, easy of synthesis, and low thermal conductivity [2]. Recently, more and more researches have been devoted to the development of PPy and PPy based TE nanocomposites [3-7]. However, PPy still has a relatively low electrical conductivity, which severely constrains its applications as a TE material [8]. Carbon nanotubes (CNTs) also have great potential to be used for TE materials mainly due to their extraordinary electrical, mechanical and thermal properties, as well as high charge carrier mobility [9, 10]. Attention has been drawn on CNT/PPy nanocomposites. For example, multi-walled carbon nanotube (MWCNT)/PPy composite powders with different MWCNT/PPy ratios have been prepared by an in situ polymerization method [5]. A maximum power factor \((S^2\sigma)\) of 2.08 μWm⁻¹K⁻² was obtained at room temperature (RT) for the MWCNT/PPy nanocomposite containing 20 wt% MWCNTs; MWCNT/PPy composites with different MWCNT compositions (0 - 68 wt%), have been prepared by an in situ or an interfacial polymerization method [6]. A maximum power factor of 2.20 μWm⁻¹K⁻² was obtained at RT for the MWCNT/PPy nanocomposite with 68 wt% MWCNTs prepared by an in-situ polymerization method. This value is ~ 26.5 times higher than that of PPy [6].
It was known that single-walled carbon nanotubes (SWCNTs) have a much higher electrical conductivity than MWCNTs. The electrical conductivity and power factor of PPy could be further increased when it is composited with SWCNTs. Therefore, in this study, SWCNT/PPy nanocomposites were prepared by an in-situ polymerization method, and the effect of SWCNT composition on the microstructure and TE properties of the SWCNT/PPy nanocomposites with 40% SWCNT loading were examined.

2. Experimental

2.1. Raw materials

Pyrrole monomer, chloroform, iron (III) chloride anhydrous (oxidant) and other organic solvents were purchased from Sigma–Aldrich Chem. Co (reagent grade). SWCNTs were purchased from Shenzhen Nanotech Port Co., Ltd. All of these materials were used as received.

2.2. Preparation of SWCNT/PPY composite materials

Typically, the SWCNT/PPy composite materials was prepared by an in situ oxidative polymerization method described in ref. [11]: 1 mmol of pyrrole monomer was dissolved in a 50 mL 1 mol/L HCl solution (Solution I). 100 mL of a 1 mol/L HCl solution containing SWCNTs (varying amounts to obtain 10, 20, 30 and 40 wt % with respect to the pyrrole monomer weight) was added to a 500-mL beaker and sonicated for 1 hat RT (Solution II). Solution I was added to the Solution II and sonicated for 30 min (Solution III). 4 mmol of FeCl₃ was dissolved in 100 mL 1 mol/L HCl solution, and then added dropwise into the Solution III. After constantly stirred for 24 hat RT, the resultant was separated by centrifugation (5 min at 4000 rpm), repeatedly washed with 1 mol/L HCl and repeatedly centrifuged, and then dried in vacuum at 60 ºC for 24 h. Pure PPy was synthesized using the same procedure as described above but without SWCNT.

2.3. Characterization

The morphology and composition of the composite materials were examined by Field Emission Scanning Electron Microscopy (FESEM). To measure electrical conductivity and Seebeck coefficient, composite powders were cold pressed at 100 MPa into pellets. In-plane electrical conductivity and Seebeck coefficient were measured simultaneously in a helium atmosphere at temperatures ranging from 298 K to 398 K on a ULVAC-RIKO ZEM-3 instrument system (4-point steady-state direct current technique).

3. Results and Discussion

Figure 1 schematically depicts the procedure to prepare the SWCNT/PPy nanocomposites. When pyrrole was added into the SWCNT solution, the pyrrole was immediately absorbed onto SWCNTs surface due to the electrostatic attraction [11, 12], then SWCNT/PPy nanocomposites were formed by in situ oxidative polymerization of pyrrole after FeCl₃ was added.

![Figure 1. Illustration of the procedure for preparing SWCNT/PPy nanocomposites.](image)

Figure 2 shows typical FESEM images of the PPy particles and the SWCNT/PPy nanocomposites with different SWCNT compositions from 10 wt% to 40 wt%. The PPy particles were agglomerated
together to form an analogous spherical morphology with a size of 200 - 600 nm (Fig. 2a & b). The SWCNTs were well dispersed in PPy matrix for all the nanocomposites (Fig. 2c - f).

Figure 2. FESEM images of the PPy particles (a) & (b), SWCNT/PPy nanocomposites with different SWCNT compositions, 10 wt% (c), 20 wt% (d), 30 wt% (e), and 40 wt% (f). The insets in (c), (d), (e) and (f) are high-magnification SEM images of the blue-framed areas.

Figure 3 shows the temperature dependence of electrical conductivity, Seebeck coefficient, and power factor for the SWCNT/PPy nanocomposites with 40 wt% SWCNT loading. The electrical conductivity of the sample increased from 99.14 S/cm to 106.99 S/cm with increasing temperature from 298 K to 398 K, which was much higher than that of the PPy prepared by an in situ polymerization method (~ 21.5 S/cm at RT [5], 19.6 S/cm at RT [6]). This value is also much higher than the maximum electrical conductivity of MWCNT/PPy composites prepared by an in situ polymerization method (15 wt% MWCNTs, 72 S/cm at RT) [5], by an in situ polymerization method (MWCNTs ~ 50 wt%, 39.4 S/cm at RT) [6], and by an interfacial polymerization method (MWCNTs ~ 50 wt%, 25.9 S/cm at RT) [6]. This indicates that SWCNTs are effective fillers to enhance the electrical conductivity of PPy matrix.
Figure 3. Temperature dependency of (a) electrical conductivity, (b) Seebeck coefficient, and (c) power factor of SWCNT/PPy nanocomposites with 40 wt% SWCNT loading.

The Seebeck coefficient of the sample was positive throughout the temperature range investigated, indicating $p$-type conduction. The Seebeck coefficient for the SWCNT/PPy nanocomposites slightly increased from 19.43 μV/K to 22.59 μV/K in the measured temperature range increasing from 298 K to 398 K, which is much higher than that the highest value of pure PPy (5.18 μV/K at ~298 K). This may be attributed to the size-dependent energy-filtering effect caused by the nanostructured PPy coating layer on the SWCNTs [13]. This value is slightly lower than the maximum Seebeck coefficient of the MWCNT/PPy composites prepared by an in situ polymerization method (20 wt% MWCNTs, ~25 μV/K at RT) [5], by an in situ polymerization method (68 wt% MWCNTs, 24.4 μV/K at RT) [6], and by an interfacial polymerization method (64.5 wt% MWCNTs, 23.5 μV/K at RT) [6].

In the measured temperature range from 298 K to 398 K, the power factor of the SWCNT/PPy nanocomposites slightly increased, mainly because of the increased electrical conductivity and Seebeck coefficient. A highest power factor value 5.46 μWm$^{-1}$K$^{-2}$ was obtained at 398 K. This value is much higher than the maximum power factor of the MWCNT/PPy nanocomposites with 20 wt% MWCNT loading prepared by an in situ polymerization method (2.08 μWm$^{-1}$K$^{-2}$ at RT) [5], and a MWCNT/PPy composite with 68 wt% MWCNTs loading prepared by an in situ polymerization method (2.2 μWm$^{-1}$K$^{-2}$ at RT) [6], and a MWCNT/PPy composite with 64.5 wt% MWCNTs loading prepared by an interfacial polymerization method (~1.4 μWm$^{-1}$K$^{-2}$ at RT) [6]. This is a simple and effective method to enhance the TE properties of PPy.

4. Conclusion
Single-walled carbon nanotube/polypyrrole (SWCNT/PPy) composites were prepared by an in-situ polymerization method. Both of the electrical conductivity and the Seebeck coefficient of the SWCNT/PPy nanocomposites with 40% SWCNT loading increased simultaneously in the measured temperature range from 298 K to 398 K. As a result, a highest power factor value 5.46 μWm$^{-1}$K$^{-2}$ was obtained at 398 K. The results show that SWCNT composition may form an effective method to enhance the TE properties of PPy.

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