



Simultaneously enhanced electrical conductivity and Seebeck coefficient in Poly (3,4-ethylenedioxythiophene) films treated with hydroiodic acid



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ABSTRACT

Poly(3,4-ethylenedioxythiophene)-tosylate-polyethylene glycol- polypropylene glycol-polyethylene glycol (PEDOT-Tos-PPP) films were prepared via a vapor phase polymerization (VPP) method. The thermoelectric (TE) properties of the films before and after treated with various concentrations of HI acid have been studied. The electrical conductivity and Seebeck coefficient of the films simultaneously increased after treated with dilute HI acid solutions (<5 wt%). The electrical conductivity of the film treated with 5 wt% HI acid increased from 1532 to 1690 S cm⁻¹ and the Seebeck coefficient increased slightly from 14.9 to 20.3 μV K⁻¹. The maximum power factor value of the treated film is 69.6 μW m⁻¹ K⁻² at 304 K, which is about twice as high as that of the pristine film (33.8 μW m⁻¹ K⁻²). Field emission scanning electron microscopy (FESEM), Raman spectroscopy analyses and the thickness measurement of the films indicate that the tri-block copolymer PPP have been removed by the HI acid treatment. The UV–vis–NIR absorption spectroscopy and X-ray photoelectron spectroscopy (XPS) analyses reveal that iodine anions (I⁻, I₃⁻ and I₅⁻) exist as dopants in the film after the treatment. The TE properties enhancement are, therefore, attributed to the combined effects of the removal of the insulating PPP and Tos⁻ and iodine ions doping by the HI acid treatment.

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1. Introduction

One possible solution for powering the explosive growth of wearable electric devices is to harvest energy from the human body to generate electricity using a thermoelectric (TE) generator [1,2]. Obviously, conventional inorganic TE materials are not suitable for such application due to their nonflexibility, expensive and non-scalable manufacturing processes. Conducting polymers, such as polyaniline, polythiophene, and poly(3,4-ethylenedioxythiophene) (PEDOT), are flexible and easy to process, low cost, abundance and with extrinsic low thermal conductivity. Hence, TE properties of conducting polymers and conducting polymer based nanocomposites have attracted increasing attention recently [3–12]. Conducting polymers and conducting polymer based nanocomposites can be more economical alternatives to conventional inorganic TE materials, and have been considered as

potential candidates for TE materials around room temperature. Much progress has been made in organic thermoelectrics [13–16]. For example, Bubnova et al. [13] reported tosylate (Tos) optimum doped PEDOT film with $ZT = \alpha^2 \sigma T / \kappa$, where α is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature and κ is the thermal conductivity) value of 0.25; Kim et al. [14] reported PEDOT: polystyrenesulfonate (PSS) film with $ZT = 0.42$ by reducing the content of PSS in the film treated with ethylene glycol (EG) and dimethyl sulfoxide. Note that Weathers et al. [15] reveal that the ZT value is somewhat overstated due to the samples measured for electrical properties being different from that for thermal conductivity measurement; Lee et al. [15] reported increased electrical conductivity and optimized redox level of PEDOT:PSS films via sequential doping and dedoping, resulting in an improved ZT value being 0.31. Most recently, Wang et al. [16] reported a record ZT value of 0.5 for carbon nanotube/PEDOT composite films treated by tetrakis(dimethylamino)ethylene.

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PEDOT is one of the most extensively explored conducting polymers for thermoelectrics. Usually PEDOT films are synthesized by either a chemical oxidative polymerization or an electrochemical polymerization of its monomer in a liquid phase. [17,18]. Recently, Fabretto et al. [19] prepared a PEDOT-Tos film with an electrical conductivity of $\sim 3400 \text{ S cm}^{-1}$, using a tri-block copolymer polyethylene glycol-polypropylene glycol-polyethylene glycol (PPP) as an inhibitor via a vacuum vapor-phase polymerization (VPP) method. Compared with other methods, VPP is simpler, more rapid and convenient to manufacture highly conductive PEDOT films. Recently, we [20] have successfully prepared PEDOT-Tos-PPP films by a VPP method in air and then treated the films with H_2SO_4 . After treatment, the electrical conductivity of the films was significantly increased from 944 to 1750 S cm^{-1} , the Seebeck coefficient of the film reduced slightly from 16.5 to $14.6 \mu\text{V K}^{-1}$, and the maximum power factor was about $37.3 \mu\text{W/mK}$ at room temperature. Later, we [21] also prepared PEDOT-Tos-PPP films by the VPP method in air and then treated with a mixture of NaBH_4 and DMSO. The electrical conductivity of the films continuously decreased from 1550 to 5.7 S cm^{-1} , whereas the Seebeck coefficient steeply increased from 14.9 to $143.5 \mu\text{V K}^{-1}$. A peak power factor of $98.1 \mu\text{W/mK}$ at room temperature was achieved. Bubnova et al. [13] reported the PEDOT-Tos-PPP films prepared by the VPP method have electrical conductivity in the range of $800\text{--}1500 \text{ S cm}^{-1}$ and Seebeck coefficient in the range of $35\text{--}50 \mu\text{V/K}$ depending on the molecular weight and with or without adding dimethylformamide (DMF) as a solvent. Compared with the result reported in Ref. [13], our pristine films showed lower Seebeck coefficient values. However, most recently, Xu et al. [22] also prepared PEDOT-Tos-PPP films by the VPP method in vacuum and reported the Seebeck coefficient value is $\sim 15 \mu\text{V/K}$, which is in good agreement with our result.

Although, high power factor of the vapor-phase polymerized PEDOT-Tos-PPP film can be achieved by post-treated with NaBH_4 /DMSO, as the reducibility of NaBH_4 is too strong, the power factor is very sensitive to the concentration of NaBH_4 in the mixture and hence it is a challenge to conduct the treatment. Therefore, it is very desirable to find a suitable reductant. Pei et al. [23–25] used hydroiodic (HI) acid to efficiently reduce graphene oxide (GO) films. The reduced GO (rGO) film shows a high electrical conductivity, which is attributed to simultaneous reduction and iodine doping during the HI acid treatment. Our previous work [26] also indicates HI is a good reductant. We prepared rGO/PEDOT:PSS films by immersing GO/PEDOT:PSS films in a HI acid, and the power factor of the rGO/PEDOT:PSS film is about 1.5 times as high as that of a neat PEDOT:PSS film resulting from simultaneous enhanced electrical conductivity and Seebeck coefficient. Therefore, in this work, HI acid was chosen to be the reductant for the vapor phase polymerized PEDOT-Tos-PPP films. TE properties of the films before and after the HI acid treatment have been investigated and the TE properties have greatly been enhanced after the HI treatment. To understand the enhancement mechanism, the films have also been characterized by X-ray photoelectron spectroscopy (XPS), UV–vis–NIR absorption spectra and Raman spectroscopy, respectively.

2. Experimental

Iron(III) *p*-toluene sulfonate hexahydrate ($\text{Fe}(\text{Tos})_3 \cdot 6\text{H}_2\text{O}$, 99%) and PPP (Mw = 5800 Da) were obtained from Sigma-Aldrich. 3,4-ethylenedioxythiophene (EDOT, 99.9%) monomer was purchased from Bohong Electronic Chemicals Co., Ltd., China. Pyridine (Py) was purchased from Sinopharm Chemical Reagent Co., Ltd. HI was purchased from Alfa Aesar Co., Ltd. All chemicals were used as received without further purification.

PEDOT-Tos-PPP films were prepared by a VPP technique described by Fabretto et al. [19], but our VPP process was carried out in air rather than under vacuum. Films were synthesized on $2.5 \times 3.5 \text{ cm}^2$ quartz glass substrates, which were pre-cleaned by using detergent, ethanol and deionized water sequentially in an ultrasonic bath for 30 min. After the polymerization process, the excess Fe(III) tosylate, unreacted monomers and byproducts were removed by washing with ethanol. In order to further enhance the TE properties, the PEDOT-Tos-PPP films were dipped in a HI acid aqueous solution (0–55%) in a dark container that was placed on a hot plate at 60°C for about 5 min and then washed repeatedly with ethanol to remove the residual HI. Finally, the treated film was dried using a hot-air gun for 1 min in an ambient atmosphere to remove the residual ethanol.

3. Characterization

The thicknesses of the polymer films were determined with a Dektak 150 profilometer. Seebeck coefficient was obtained from the slope of the linear relationship between thermal electromotive force and temperature difference ($\sim 10 \text{ K}$) of two points on each film. Electrical conductivity was measured using a steady-state four-probe technique with a square wave current ($\sim 10 \text{ mA}$ in amplitude). Out-of-plane thermal conductivity (κ) was measured by TC3010 using the transient hot wire method (Xia Xi Electronic Technology Co., Ltd, Xi'an, China). Samples for thermal conductivity measurements were prepared by multi-layer structures (each layer formed by repeating the above-mentioned polymerization process) to achieve a sample thickness large enough ($\sim 300 \text{ nm}$) for accurate measurement.

Field emission scanning electron microscopy (FESEM, XL30FEG) was used to examine the surface images of the polymer films. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) was used to investigate incorporation of different counterions into PEDOT films with Al $K\alpha$ radiation (1486.6 eV). The UV–vis–NIR absorption spectra of the polymer films were taken with a Shimadzu UV-2501PC UV–vis–NIR spectrometer. The Raman spectroscopy of the polymer film was examined by a Jobin Yvon HR800 Raman spectrometer using a laser diode at an excitation wavelength of 514.5 nm.

4. Results and discussion

Fig. 1 shows the electrical conductivity, Seebeck coefficient, and power factor for the PEDOT-Tos-PPP films before (corresponding to the concentration of HI acid being 0) and after treated with various concentrations of HI acid at room-temperature (RT, 295 K). The Seebeck coefficient quickly increases after treated with low concentrations of HI acid (from $14.9 \mu\text{V/K}$ to $20.3 \mu\text{V/K}$), and then

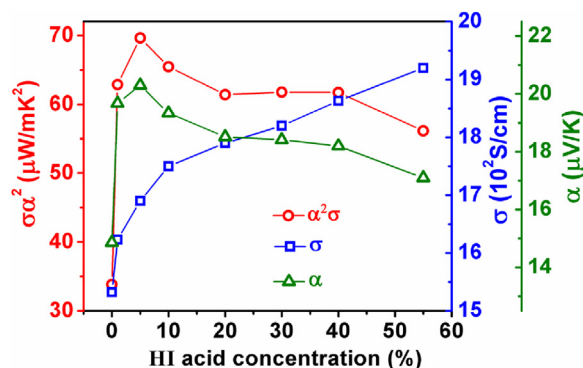


Fig. 1. TE properties of the PEDOT-Tos-PPP films at room-temperature (295 K) before and after treated with different concentration of HI acid.

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