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Enhanced thermoelectric properties of poly(3,4-ethylenedioxythiophene) thin films treated with H₂SO₄

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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 H₂SO₄ at different concentrations were measured at 295 K. The TE properties of the films have been significantly improved by the H₂SO₄ treatment. For example, after treated with H₂SO₄ at 1 M, the electrical conductivity of the film has increased remarkably from 944 to 1750 S cm⁻¹, the Seebeck coefficient of the film reduced slightly from 16.5 to 14.6 μV K⁻¹, and the thermal conductivity decreased from 0.495 to 0.474 W/mK. Hence, the *ZT* value at 295 K has increased from 0.016 to 0.024. The electrical conductivity (Seebeck coefficient) of the untreated and 1 M H₂SO₄ treated PEDOT-Tos-PPP films decreases (increases) with increasing temperature from 295 to 375 K. And the power factor of the films monotonically increases with temperature. The power factor at 375 K of the 1 M H₂SO₄ treated film is almost twice as high as that at 295 K. Atomic force microscope (AFM) and X-ray photoelectron spectroscopy (XPS) analyses, and the thickness measurement of the films indicate that the tri-block copolymer PPP have been removed from the PEDOT-Tos-PPP films after the H₂SO₄ treatment, and the UV-Vis-NIR absorption spectroscopy and Raman spectroscopy analyses reveal an increasing in the doping level in the PEDOT chains after the H₂SO₄ treatment. Therefore, the TE properties enhancement may be attributed to the combined effects of the removal of the insulating PPP from the PEDOT-Tos-PPP film, increase the doping level and conformational change of the PEDOT chains resulted from the H₂SO₄ treatment.

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1. Introduction

Thermoelectric (TE) materials have recently attracted worldwide attentions because of their great potential applications in fields such as solid-state refrigeration and

power generation without any moving parts. The TE performance of a material can be evaluated by its dimensionless figure of merit $ZT = \alpha^2 \sigma T / \kappa$, where α , σ , T , and κ are the Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively. TE material with high *ZT* requires a high α , a high σ but a low κ ; however, it is very difficult to modulate the three parameters synchronously to get a high *ZT* value because they are dependent on each other.

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Until now, most of the previous efforts in TE community have been mainly focused on traditional inorganic TE materials, including Bi–Te based alloys [1] and PbTe based alloys [2,3]. These inorganic TE materials show high ZT values, but they consist of heavy or rare metals, which are hazardous, expensive and difficult to recycle, and they usually need a complicated preparation processing. Although conducting polymers usually have power factors (PF , $S^2\sigma$ ranging from 10^{-6} to 10^{-10} $W m^{-1} K^{-2}$), which are about 3 orders of magnitude lower than those of the state-of-the-art inorganic TE materials [4–7], they possess unique features such as low thermal conductivity, low density, low cost, easy synthesis, and relatively facile to be processed into versatile forms, and they are very promising for mass-production and large-area applications. Hence, more and more attentions have recently been paid to the TE properties of conducting polymers and polymer based nanocomposites [7–16] and much progress has been made [17–19]. For example, a tosylate (Tos) optimum doped poly(3,4-ethylenedioxythiophene) (PEDOT, see Fig. 1a) film with $ZT = 0.25$ at room temperature (RT) [20] and a poly(styrenesulfonate) (PSS) optimum doped PEDOT film with $ZT = 0.42$ at RT [21] were successively reported. The TE properties of PEDOT:PSS can be optimized through chemically or electrochemically control of their oxidation level [22–24], as well as treatment with high-boiling-point solvents [21,25]. PEDOT-Tos [26] can be considered as the polyanion PSS in PEDOT:PSS being replaced by a small anion Tos, preventing the excess of insulating phase generated with polyanions, and as a result the electrical conductivity of PEDOT-Tos films is higher than that of PEDOT:PSS films.

Usually, conducting polymers are synthesized by either a chemical oxidative polymerization or an electrochemical polymerization of its monomer in a liquid phase [27,28]. Recently, a new and more effective method has been developed for formation of conducting polymers, which is called vapor-phase polymerization (VPP) method. Pioneering work on VPP done by Winther-Jensen and West, achieved an electrical conductivity of ~ 1000 $S cm^{-1}$ of a PEDOT-Tos film, using an oxidant iron *p*-toluenesulfonate ($Fe(Tos)_3$, see Fig. 1b) coupled with a volatile base pyridine

[29]. Fabretto et al. [30] prepared a PEDOT-Tos film with a conductivity of ca. 3400 $S cm^{-1}$, using a tri-block copolymer polyethylene glycol–polypropylene glycol–polyethylene glycol (PPP, see Fig. 1c) as an inhibitor via a vacuum VPP method. Compared with other methods, VPP is simpler, and more rapid and convenient to manufacture highly conductive polymer films. To the best of our knowledge, almost all the studies on high conducting PEDOT film via the VPP method are for transparent conducting electrodes. The TE properties of high conducting PEDOT film prepared via VPP method have rarely been reported.

In this paper, successful fabrication of PEDOT-Tos films via a VPP method is reported. The TE properties of the films before and after the H_2SO_4 treatment have been investigated. The TE properties were significantly improved by the 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 *p*-toluenesulfonate heptanedionate ($Fe(Tos)_3 \cdot 6H_2O$) and tri-block copolymer polyethylene glycol–polypropylene glycol–polyethylene glycol (PPP) $M_w = 5800$ Da. were obtained from Aldrich. 3,4-Ethylenedioxythiophene (EDOT) monomer was purchased from Bohong Electronic Chemicals Co., Ltd, Yancheng, China. All chemicals were used as received without further purification.

PEDOT-Tos-PPP films were prepared by a VPP technique described by Fabretto et al. [30]; however, our VPP process was carried out at atmosphere rather than under vacuum. PEDOT films were synthesized on 2.5×3.5 cm^2 glass substrates, which were cleaned by using detergent, ethanol and deionized water sequentially in an ultrasonic bath for 30 min.

Synthesis was carried out using an oxidant solution containing 20% $Fe(Tos)_3 \cdot 6H_2O$ and 20% PPP in an ethanol and butanol (1:1) solution. The tri-block copolymer PPP was added as an inhibitor to the oxidant solution to control the kinetics of the polymerization as well as a template for growing the PEDOT-Tos-PPP films by the VPP technique

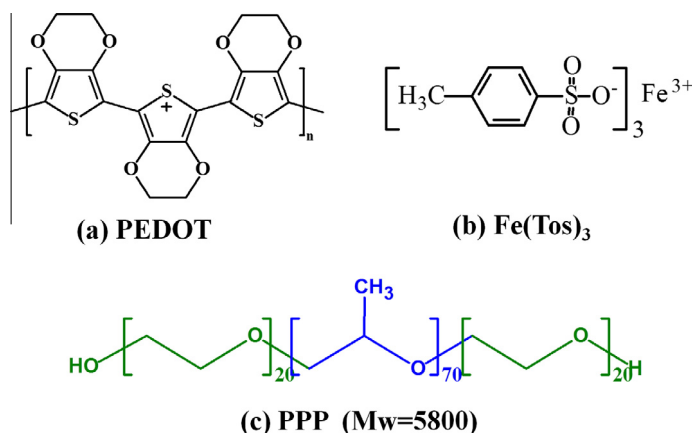


Fig. 1. Molecular structures of (a) PEDOT (b) $Fe(Tos)_3$ and (c) tri-block copolymer PPP.

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