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# Flexible films of poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate)/SnS nanobelt thermoelectric composites

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ABSTRACT

Organic polymer/inorganic thermoelectric (TE) composites are emerging green energy materials for diverse applications including harvesting waste or low-quality heat, local cooling, sensing and wearable electronics. Here, we report flexible films of new TE composites by employment of SnS nanobelt into polymer matrix. First, the SnS nanobelts with high purity were prepared by a convenient hydrothermal process. Then, the poly (3,4-ethylenediox-ythiophene): poly (styrenesulfonate) (PEDOT:PSS)/SnS nanobelt composites were obtained by a solution mixing procedure aided by ultrasonication. The structure and morphology of the SnS nanobelts as well as the PEDOT:PSS/SnS composites were characterized by X-ray diffraction (XRD) and field-emission scanning electroscopic (FESEM) techniques. The effects of the SnS content and the dispersing agent (organic solvent) on the dispersion state and the TE performance for the composites were investigated. The highest power factor at room temperature reached $27.8 \pm 0.5\ \mu W\ m^{-1}\ K^{-2}$ for the PEDOT:PSS/SnS nanobelt composite prepared in *N*,*N*-Dimethylformamide. The present study opens a novel avenue to exploit of excellent polymer TE composites by introduction of inorganic nanoparticles with large Seebeck coefficients.

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## 1. Introduction

Due to their capability to realize direct energy conversion between heat and electricity, thermoeletric (TE) materials provide an alternative green way to replace the conventional fossil fuels [1]. Previous research focuses on inorganic TE materials, such as bismuth telluride ($Bi_2Te_3$) and tin selenide (SnSe) [2,3]. In recent years, organic TE materials, especially conducting polymers and their composites with carbon nanoparticles, have received significant attention [4–10]. The main conducting polymers include poly (3,4-ethylenediox-ythiophene):poly (styrenesulfonate) (PEDOT:PSS), polyaniline (PANI) and polypyrrole (PPy), *etc*. Because organic and their composite materials always display low thermal conductivities ($\kappa$) between 0.1 and $0.5\ W\ m^{-1}\ K^{-1}$, their TE performance is often evaluated by power factor ($PF = S^2\sigma$) rather than figure of merit ($ZT = S^2\sigma T/\kappa$), where $S$, $\sigma$ and $T$ stand for the Seebeck coefficient or thermopower, the electrical conductivity, and the absolute temperature, respectively [1,4–10].

Because of the interdependency between $S$ and $\sigma$, it is always difficult to greatly enhance the power factor of conducting polymer composites. So far, several main strategies have been conducted. The first is the surface coating of carbon nanoparticles with conducting polymers *via* $\pi$-$\pi$ interactions, where the carbon nanoparticles act as templates for *in situ* polymerization [11–15]. For example, PEDOT/graphene composite prepared by *in situ* polymerization reveals simultaneous enhancements of the electrical conductivity and the Seebeck coefficient compared with the neat PEDOT [11,12]. The second strategy is the construction of polymer nanostructures/carbon nanoparticle composites by either *in situ* polymerization or physical mixing [16–18]. For instance, a three-dimensional (3D) interconnected architecture consisting of graphene nanosheets sandwiched by PPy nanowires was fabricated by interfacial adsorption-soft template polymerization method [16].

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And the third strategy is the addition of inorganic TE particles such as $Bi_2Te_3$ nanoparticles in organic conducting polymers [19,20].

PEDOT:PSS is perhaps the most promising polymer material in TE applications, due to its versatile advantages such as high electrical conductivity, water processable, thermal stability and easiness to dope. Nevertheless, its Seebeck coefficient is usually not large [21]. In order to enhance the TE performance, theoretically, inorganic TE materials having large Seebeck coefficients are strongly desired to be added in PEDOT:PSS. Tin sulfide (SnS) nanostructure has been extensively investigated in energy materials, because of its optical, electrical and physical properties. Compared with $Bi_2Te_3$ and PbTe, SnS is non-toxic, earth abundant and low cost. Recently, SnS has been found to display a large Seebeck coefficient ($350\,\mu V\,K^{-1}$), low thermal conductivity ($0.5–1\,W\,m^{-1}\,K^{-1}$) and high carrier mobility ($>30\,cm^2\,V^{-1}\,s^{-1}$) at room temperature [22,23]. Unfortunately, no report about PEDOT:PSS/SnS TE composites has been found in a literature survey.

Here, we report new TE composites of PEDOT:PSS/SnS nanobelt by introducing SnS nanobelt as the inorganic constituent. First, SnS nanobelts with high purity were prepared by a facile hydrothermal method without any surfactant. Then, flexible films of the PEDOT:PSS/SnS composites were obtained by physical mixing with the help of ultrasonication. After that, the effects of SnS content and organic solvents on the dispersion state and the TE performance of the PEDOT:PSS/SnS nanobelt composite were investigated. Finally, the optimum power factor was deduced. The present study benefits the exploitation of novel polymer TE composites by introduction of inorganic nanoparticles with large Seebeck coefficients.

## 2. Materials and methods

### 2.1. Reagents and raw materials

Stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$) and PEDOT:PSS (Clevios PH 1000) were purchased from Aladdin and Heraeus, respectively. Urea ($CO(NH_2)_2$), *N*,*N*-Dimethylformamide (DMF, $C_3H_7NO$), and anhydrous ethanol (EtOH, $C_2H_5OH$) were purchased from Beijing Chemical Corporation. Thioacetamide (TAA, $CH_3CSNH_2$) was provided by Sinopharm Chemical Reagent Co., Ltd. All of the raw materials were used without any further purification. Deionized water was used in all of the experiments.

### 2.2. Preparation of SnS nanobelts

As shown in the first step of Fig. 1, p-type SnS nanobelts were prepared using a convenient hydrothermal method without any surfactant, which was essentially based on the literature [24]. In brief, urea (10 mmol) and TTA (10 mmol) were firstly dissolved in 40 mL of deionized water with stirring. Then, $SnCl_2 \cdot 2H_2O$ (0.6 mmol) was added into the above mixture, and was stired for 5 min. After that, the resulting mixture was transferred into a Teflon-lined autoclave (50 mL), and reacted for 10 h at 170 °C.

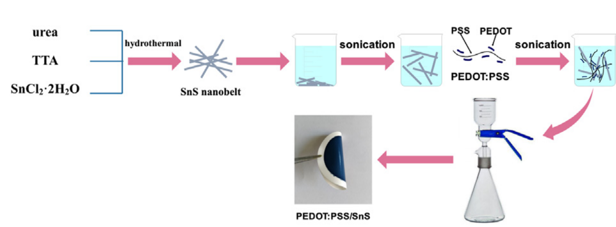


**Fig. 1.** Schematic illustration showing the preparation process of the flexible films of PEDOT:PSS/SnS nanobelt composites.

Finally, a silver gray product was obtained, after filtering, washing with deionized water for five times to remove the impurity, and subsequently dried at 70 °C for 10 h.

### 2.3. Preparation of composite film of PEDOT:PSS/SnS nanobelt

Fig. 1 shows the schematic illustration of the preparation process for the flexible films of the PEDOT:PSS/SnS nanobelt composites. Firstly, SnS nanobelt (20 mg) was dispersed in 200 mL DMF or EtOH solvent under continuous ultrasonication for 2 h to afford the SnS nanobelt dispersion ($0.1\,mg\,mL^{-1}$). Then, the SnS nanobelt dispersion was mixed with 200 μL aqueous dispersion of PEDOT:PSS. Subsequently, the mixture was diluted to 10 mL with DMF or EtOH, and ultrasonicated for 1 h at room temperature. After that, the resultant mixture was vacuum filtrateded using a plastic membrane (PVDF, pore size: 0.22 mm). Finally, the composite (containing 0–12 wt% SnS nanobelt) films were achieved after drying at 60 °C in vacuum for 10 h.

### 2.4. Characterization

Powder X-ray diffraction (XRD) measurements were carried out using a Rigaku D/max 2400 diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm) at a scanning rate of $3°\,min^{-1}$ in the range of $2\theta = 10–80°$. The field-emission scanning electron microscopic (FESEM) images and the energy-dispersive X-ray spectroscopy (EDS) for the neat SnS nanobelts and the PEDOT:PSS/SnS composite films were directly observed using a HITACHI S-4800 scanning electron microscope.

### 2.5. Measurement of film flexibility

The quantitative measurements of the film flexibility were conducted by rolling the films on cylindrical objects. After the films were successfully mounted on the objects, their radii were used as the bending radii. The minimum radii were used to quantitatively characterize the film flexibilities.

### 2.6. Measurement of TE performance

During the electrical conductivity and Seebeck coefficient measurements, film samples with a rectangular shape were used. The thicknesses of the films were measured using an optical microscope (PDV JX-40). The electrical conductivity and the Seebeck coefficient at room temperature were measured by a commercial instrument, Thin-Film Thermoelectric Parameter Test System (MRS-3RT, Wuhan Joule Yacht Science & Technology Co., Ltd). During the measurements, a quasi-steady-state mode was adopted. At least five samples were measured, and the average values were used.

## 3. Results and discussion

Fig. 2 shows the morphological observations by low- and high-magnification FESEM images. Distinctly, a large amount of SnS nanobelts with rectangular morphology are prevalent. The length and the width are in the ranges of 2–11 μm and 100–600 nm, respectively. From Fig. 2(c), it can be seen that the thickness of the nanobelt is around 100 nm. Thus, the aspect ratios (length/thickness) are high, about 20–110. As a result, the synthesized SnS nanobelts are flexible and easily bent, as shown in Fig. 2(c). In addition, an EDS analysis of the SnS nanobelt was conducted. Sn and S are the main elements in the EDS spectrum (Fig. 2(d) and (e)). The presence of C and O elements in the SnS nanobelt originates from the absorption of $CH_3COO^-$ ions remained in the reaction

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