

## 論文の要旨

# Development of conducting polymer based organic thermoelectric materials and their applications

(導電性高分子系有機熱電材料の開発と応用)

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As one kind of “green” energy conversion materials, organic TE materials have caused more and more concerns. In order to practical application, researchers are strived to improve the thermoelectric properties. Experimentally, it is important to control the structure and surface morphology of organic materials, and optimize the doping level, thereby enhancing the TE properties. Here, we studied on the typical organic TE materials such as polyaniline and PEDOT, and then developed their thermoelectric performance for a promising TE material. The details for this thesis are as follow:

Chapter 1 is “General introduction”. In this part, we introduce the development process and working mechanism of thermoelectric materials. Influencing factors for the thermoelectric properties are also discussed. Finally, several effective methods to improve the thermoelectric performance for organic semiconductors have been summarized detailedly.

Chapter 2 is “Thermoelectric properties of PEDOT films prepared by electrochemical polymerization”. Thermoelectric (TE) properties of flexible and free-standing poly(3,4-ethylenedioxythiophene) (PEDOT) films synthesized via galvanostatic polymerization of 3,4-ethylenedioxythiophene in propylene carbonate containing sulfated poly( $\beta$ -hydroxyethers) (S-PHE) as polymer electrolyte were elaborately studied. Both electrical conductivities ( $\sigma$ ) and Seebeck coefficients ( $S$ ) of the PEDOT:S-PHE films were increased by decreasing the temperature ( $T$ ) or by increasing the current density ( $J$ ) during electrosynthesis. Possible reasons for the lack of a trade-off relation commonly observed between  $\sigma$  and  $S$  are discussed on the basis of SEM and oxidation-level measurements.

Preparation of the PEDOT:S-PHE films was optimized with respect to  $T$  and  $J$ . In addition, the oxidation level of the PEDOT:S-PHE films was controlled by potential and the change of their TE performances was discussed in conjunction with the change of chemical species involved. The power factor ( $PF = \sigma S^2$ ) of the PEDOT:S-PHE films reached  $7.9 \mu\text{W m}^{-1} \text{K}^{-2}$ , leading to a dimensionless TE figure-of-merit ( $ZT$ ) of 0.013.

Chapter 3 is “Thermoelectric performances of graphene/polyaniline composites prepared by one-step electrosynthesis”. Composite films comprising graphene and polyaniline were prepared in one step by a facile electrochemical technique with graphene oxide (GO) and aniline monomer as raw materials, and their thermoelectric properties were investigated. Electrical conductivities of the composite films generated on the fluorine-doped tin oxide (FTO) electrode were dependent on the weight ratio of GO and aniline, and they exhibited a peak value of  $30 \text{ S cm}^{-1}$  at the GO/aniline ratio between 5:1 and 10:1, while Seebeck coefficients were less dependent on the weight ratio. The maximum power factor ( $PF$ ) for the composite films was *ca.*  $1 \mu\text{W m}^{-1} \text{K}^{-2}$ . When the FTO electrode was replaced by the stainless steel electrode, conductivities of the composite films with the GO/aniline ratio of 8:1 were increased up to *ca.*  $130 \text{ S cm}^{-1}$ . As a result, the  $PF$  and the dimensionless thermoelectric figure-of-merit ( $ZT$ ) at room temperature reached  $3.6 \mu\text{W m}^{-1} \text{K}^{-2}$  and 0.008, respectively. The  $ZT$  value is the highest among those reported so far for graphene/PANI composites. Possible reasons for the conductivity enhancement on the stainless steel electrode are also discussed on the basis of electrochemical measurements and X-ray photoelectron spectroscopy.

Chapter 4 is “Electrosynthesis of multilayer film stacked alternately by poly(3,4-ethylenedioxythiophene) and reduced graphene oxide from aqueous solution”. Multilayer films stacked alternately by poly(3,4-ethylenedioxythiophene) and reduced graphene oxide layers were electrochemically synthesized from a single aqueous solution containing 3,4-ethylenedioxythiophene (EDOT) and graphene oxide (GO) by oxidizing EDOT and reducing GO repeatedly on the conductive substrate. In the proposed

technique, film thicknesses of the respective layers were easily tuned by the electrolysis time, and the number of layers was increased just by repeating the potential-step sequence.

Chapter 5 is “Highly improved thermoelectric performances of PEDOT:PSS/SWCNT composites by solvent treatment”. Composites of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and single-wall carbon nanotube (SWCNT) were prepared by mixing aqueous dispersions of PEDOT:PSS and SWCNT at different weight ratios. By being soaked with DMSO for two minutes at room temperature, the PEDOT:PSS/SWCNT composite with an optimized SWCNT weight ratio of 74 wt% exhibited a high electric conductivity of  $3,800 \text{ S cm}^{-1}$  and a reasonable Seebeck coefficient of  $28 \mu\text{V K}^{-1}$ , leading to a promising power factor of  $300 \mu\text{W m}^{-1} \text{ K}^{-2}$ . Such *PF* is the highest among the PEDOT:PSS/CNTs composites.

Chapter 6 is “Conclusions”. Several important conclusions of this study are given in detail and suggestions are provided for further study.