Thermoelectric thin hybrid films based on PEDOT:PSS and inorganic nanoparticles

Thermoelectric (TE) materials, which can directly convert heat into electricity and vice versa, facilitate electric power generation as well as refrigeration without any liquid coolants, corresponding to Seebeck effect and Peltier effect, respectively. A dimensionless figure of merit *ZT* is commonly used to evaluate the energy conversion efficiency of a TE material and defined as $ZT=S^2\sigma T/\kappa$. Here, σ represents the electrical conductivity, *S* the so-called Seebeck coefficient, κ the thermal conductivity, and *T* the absolute temperature and $S^2\sigma$ is defined as the power factor. Recently, organic semiconductors have gained intense attention because of their potential application in mechanically flexible, lightweight, and inexpensive electronic devices. In particular, poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (see Figure 1) is the widest-studied conducting polymer system due to their intrinsically high electrical conductivity, extremely low thermal conductivity, and potentially high mechanical flexibility in thermoelectric devices.[1] These factors render PEDOT:PSS a promising candidate for TE generators based on organic materials operating at moderate temperatures. However, pristine PEDOT:PSS thin films show low electrical conductivity of around 1 S cm^{-1} and Seebeck coefficient of about 15 μV K^{-1}. Therefore they are not viable for many applications.[2] Furthermore, it is generally considered that it is difficult to obtain a high *ZT* value of TE materials, due to the fact that the parameters *S, σ,* and *k* are interdependent as a function of carrier concentration and hard to be optimized simultaneously. In generally, several strategies such as additive technique, post-treatment and forming inorganic-organic nanocomposites, and *etc* are applied to accurately optimize and even overcome the conflicting relationship between *S* and σ for optimum TE performance.

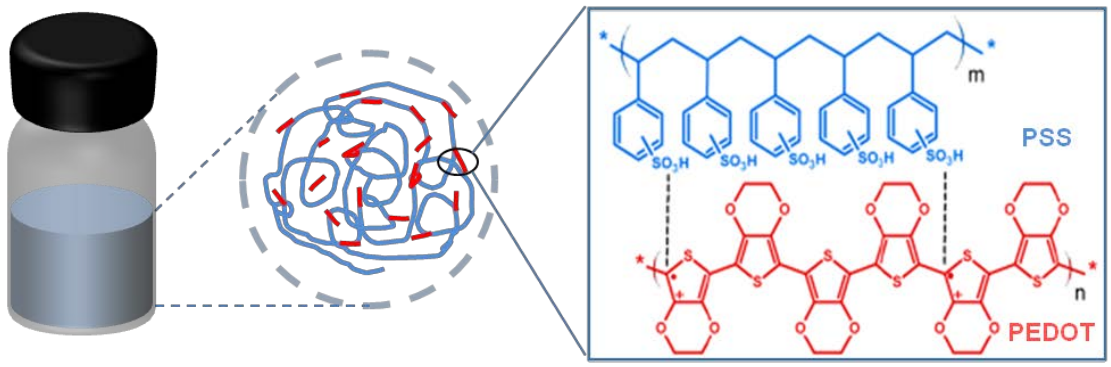

Figure 1 Hypothesis for the morphology and chemical structure of a typical PEDOT:PSS.

Especially, synthesizing inorganic-organic nanocomposites is regarded as a promising and simple technique in which *S* and σ are decoupled through energy filtering effect at interfaces of components in a composite. The nanocomposites may take the

advantages of both the low thermal conductivity of the polymer and high power factor of inorganic TE fillers. Herein, PEDOT:PSS thin films nanostructured with inorganic nanoparticles (NPs) as a function of NPs content is deeply investigated. Due to different work functions of PEDOT:PSS and NPs, an interfacial potential barrier exists (see Figure 2). When the carriers transport through the interface, this energy barrier can selectively scatter low-energy carriers and allow high-energy carriers to cross over the barrier. The average energy of the carriers in the material can be enhanced and the effective density of states of composites can be sharpened; therefore, the *S* is enhanced. Introduction of NPs could lead to a disruption of the intermolecular order of PEDOT chains or the polymer matrix in general and thus impede charge transport between chains. This may result in increased *S*.

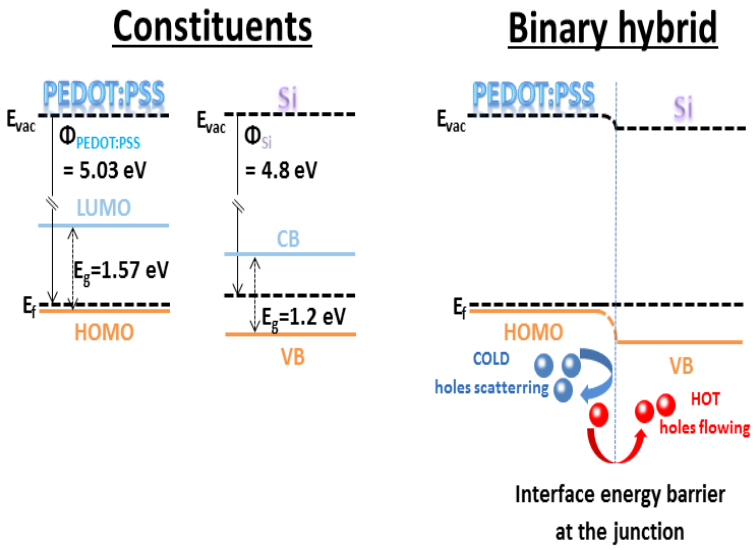

Figure 2 Schematic illustration of the energy-filtering effect: Energy diagram of the typical PEDOT:PSS/Si heterojunction showing energy filtering at the junction.

With characterization methods such as atomic force microscopy, grazing-incidence wide/small-angle X-ray scattering,[3] UV-Vis spectroscopy, Raman spectroscopy and X-ray photoelectron spectroscopy and *etc*, the mechanism behind of TE performance improvement are deeply investigated in our group.

[1] N. Saxena, M. Čorić, A. Greppmair, J. Wernecke, M. Pflüger, M. Krumrey, M.S. Brandt, E.M. Herzig, P. Müller-Buschbaum: Morphology-function relationship of thermoelectric nanocomposite films from PEDOT:PSS with silicon nanoparticles; *Adv. Electronic Mater.* **3**, 1700181 (2017)

[2] N. Saxena, J. Keilhofer, A.K. Maurya, G. Fortunato, J. Overbeck, P. Müller-Buschbaum: Facile optimization of thermoelectric properties in PEDOT:PSS thin

films through acido-base and redox dedoping using readily available salts; *ACS Appl. Energy Mater*. **1**, 336-342 (2018)

[3] P. Müller-Buschbaum: The active layer morphology of organic solar cells probed with grazing incidence scattering techniques (invited progress report); *Adv. Mater*. **26**, 7692-7709 (2014)