Supporting Information

Thermopower Enhancement in Conducting Polymer Nanocomposites via Carrier Energy Scattering at Organic/Inorganic Semiconductor Interface

*Ming He, Jing Ge, Zhiqun Lin, Xuhui Feng, Xinwei Wang, Hongbin Lu, Yuliang Yang, Feng Qiu*
Figure S1. Representative $\Delta V \sim \Delta T$ curve for the measurement of Seebeck coefficient at room temperature. A series of temperature gradient, $\Delta T = T_{hot} - T_{cold}$ (i.e., $\Delta T$ of $0^\circ$C, $\pm 4^\circ$C and $\pm 6^\circ$C) were established between the two ends of the sample, the electrical potential differences, $\Delta V = V_{hot} - V_{cold}$ between the two ends were then measured. The Seebeck coefficient was calculated from the slope of curve. The inset shows holes transfer from the hot end to the cold end driven by the temperature gradient in a $p$-type semiconductor.
Thermal Characterization

The in-plane thermal conductivity is measured using the transient electrothermal (TET) technique. To apply this technique, a thin gold film (less than 20 nm thick) is coated to ensure the sample conductive. Then a step current is fed to induce step heating and obtain the voltage response for determination of thermal property. The impact of gold film is subtracted from the measured thermal properties based on the Wiedemann-Franz law for the gold coating. In our measurement, it is found that the gold coating has very little effect on thermal characterization, around 1~2%.

A superimposition relation between P3HT film on glass substrate is then applied, therefore the derived overall thermal property is determined as an average of thermal property of each part, based on thickness of each layer. It is expressed as

$$\alpha_{\text{overall}} = \frac{k_p \cdot d_p + k_g \cdot d_g}{(\rho c_{p})_p \cdot d_p + (\rho c_{g})_g \cdot d_g}$$

in which $\alpha$ is thermal diffusivity, $k$ is thermal conductivity, $d$ is thickness, $\rho$ is density and $c_p$ is specific heat. The subscripts $p$ and $g$ represent P3HT film and glass substrate, respectively. The thickness of the glass substrate is 0.15 mm while the thickness of the P3HT film is a few tens of micrometers. The thermophysical properties of glass substrate are known, so the thermal conductivity $k$ of P3HT film can be determined. The thermal-conductivity of glass substrate is 1.38 W/Km, which is the same order of that for P3HT. Therefore, the measurement has sufficient sensitivity to characterize the thermal conductivity of the P3HT film.
Figure S2. SEM images of P3HT and P3HT/Bi$_2$Te$_3$ films: (a) FeCl$_3$-doped P3HT solely; (b) FeCl$_3$-doped P3HT with 10 wt% Bi$_2$Te$_3$ nanowires; (c) FeCl$_3$-doped P3HT with 20 wt% Bi$_2$Te$_3$ nanowires.
Figure S3. Representative electrical conductivity and Seebeck coefficient of FeCl$_3$-doped P3HT as a function of the doping level.
Transport Properties

In semiconductors, the Seebeck coefficient depends on the energy derivative of the energy-dependent electrical conductivity taken at the energy level $E$.\textsuperscript{1, 2} The energy-dependent electrical conductivity $\sigma(E)$ can be given as the function of the carrier density $n(E)$, charge $q$ and carrier mobility $\mu(E)$:

$$\sigma(E) = n(E)q\mu(E) \quad \text{(S1)}$$

The carrier mobility $\mu(E)$ is defined as the drift speed of charge carrier divided by the applied electric field, which can be approximately related to the relaxation time $\tau$ by:

$$\mu(E) = |q| \frac{\tau(E)}{m^*} \quad \text{(S2)}$$

where $m^*$ is the carrier effective mass. In the case of solely considering the elastic collision, the frequency of the collision $\tau^1(E)$ relies on the density-of-state function $g(E)$ and the square of the matrix element of the scattering transition $w(E)$, which is related to the energy-dependent carrier scattering parameter $\lambda$ as $w(E) \propto E^{-\lambda}$. In general, the band structure of P3HT is regarded as nonparabolic, and the corresponding energy dispersion $\gamma(E)$ can be described by:\textsuperscript{3, 4}

$$\gamma(E) = E(1 + \frac{E}{E_g}) \quad \text{(S3)}$$

where $E_g$ is the band gap. The density of state function $g(E)$ can then be given by:

$$g(E) = \frac{\sqrt{2}(m^*)^{3/2}}{\pi^2 \hbar^3} \frac{d\gamma(E)}{dE} \gamma(E)^{1/2} \quad \text{(S4)}$$

where $\hbar$ is the Planck’s constant. The relation time $\tau(E)$ can thus be given by combining $w(E)$ and $g(E)$:\textsuperscript{3}

$$\tau(E) = \tau_0 \frac{\gamma(E)^{4-1/2}}{d\gamma(E)/dE} \quad \text{(S5)}$$
where \( \tau_0 \) is an energy-independent scaling factor. It is noted that, for the parabolic band structure, in which the energy dispersion \( \gamma(E) = E \), the relation time \( \tau(E) \) is simplified as:

\[
\tau(E) = \tau_0 E^{1.5 - \frac{1}{2}} \tag{S6}
\]

The value of \( \lambda \) for various scattering mechanism is given as follow:\(^5\)

- for scattering of electrons on acoustic phonons, \( \lambda = 0 \),
- for scattering of electrons on neutral impurities, \( \lambda = 0.5 \),
- and for scattering of electrons on ionized impurities, \( \lambda = 2 \).

The carrier concentration \( n(E) \) can then be given by:

\[
n(E) = \int_0^\infty g(E)(-\frac{\partial f_0}{\partial E})dE \tag{S7}
\]

where \( f_0 \) is the Fermi-Dirac distribution function:

\[
f_0(E) = \frac{1}{1 + \exp(-\frac{E_f - E}{kT})} \tag{S8}
\]

where \( E_f \) is the Fermi level, \( k \) is the Boltzmann’s constant and \( T \) is the absolute temperature.

Moreover, P3HT can be regarded as a non-degenerate semiconductor due to the unequal energy between the aromatic (i.e., in the pristine state) and the quinoid (i.e., in the doped state) structures.\(^6\) Hence, the electrical conductivity \( \sigma \), Seebeck coefficient \( \alpha \) and Hall efficient \( R_H \) can be given as follows:\(^3,7,8\)

\[
\sigma(E) = \frac{q\tau_0\gamma(E)^{1.5/2}}{m} \int_0^\infty g(E)(-\frac{\partial f_0}{\partial E})dE \tag{S9}
\]

\[
\alpha(E) = \frac{1}{qT} \left[ \int_0^\infty \frac{\gamma(E)^{3/2}}{d\gamma(E)} \tau(E) \left(-\frac{\partial f_0}{\partial E}\right) dE - \frac{E_f}{kT} \right] \tag{S10}
\]
The scattering parameter \( \lambda \) and the Fermi energy \( E_f \) were extracted from equations S10 and S11 by solving the nonlinear equations using Matlab \textit{fsolve} Toolbox (http://www.mathworks.cn/help/toolbox/optim/ug/fsolve.html), which has been widely used to solve nonlinear equations. We need to state several free parameters before solving the equations. For the heavily-doped P3HT matrix \( (i.e., 24 \text{ wt}\% \text{ FeC}l_3 \text{ doping}) \), the band gap \( E_g \) was estimated to be 0.2 eV,\(^9\)\(^-\)\(^11\) the effective mass \( m^* \) was assumed to be 1.7\( m_e \) \( (i.e., m_e \text{ is the free electron mass}) \),\(^12\)\(^,\)\(^13\) and the temperature was set at room temperature of 298.15 K. It should be noted that this method can now only be used in the heavily-doped P3HT matrix \( (i.e., 24 \text{ wt}\% \text{ FeC}l_3 \text{ doping}) \) unless we know the band gap of P3HT at the other doping levels. Moreover, in order to solve equations S10 and S11, we must set an initial value for \( \lambda \) and \( E_f \). According to literature, the \( \lambda \) for various scattering mechanism for the parabolic band ranges from 0 \~ \) 2,\(^5\) and the \( E_f \) for varied doping levels of polythiophene lies in the range of -0.6 eV \~\) -0.8 eV\(^9\)\(^,\)\(^14\), therefore the initial value of \([\lambda, E_f]\) was generally set as \([5, -0.8 \text{ eV}]\).

The precision of modeled values in Table 1 is related to the termination tolerance in Matlab \textit{fsolve} Toolbox used to solve the nonlinear equations S9, S10 and S11. In detail, two parameters in Matlab \textit{fsolve} Toolbox determine the solution precision: the termination tolerance on the function value \( f(x) \) (TolFun) and the termination tolerance on \( x \) (TolX). Both values of TolFun and TolX are set to 0.0001 in this work.
Table S1

Table S1. Summary of the transport parameters of P3HT and P3HT/Bi$_2$Te$_3$ nanocomposite. The doping level of P3HT matrix was about 24 wt%, and the Bi$_2$Te$_3$ nanowire content varied from 5 wt% to 20 wt%.

<table>
<thead>
<tr>
<th>Transport parameters</th>
<th>P3HT</th>
<th>P3HT/Bi$_2$Te$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5% Bi$_2$Te$_3$</td>
</tr>
<tr>
<td>Electrical conductivity $\sigma$ (S/m)</td>
<td>930</td>
<td>740</td>
</tr>
<tr>
<td>Seebeck coefficient $\alpha$ ($\mu$V/K)</td>
<td>24</td>
<td>47</td>
</tr>
<tr>
<td>Power factor $\sigma\alpha^2$ ($\mu$W/K$^2$m)</td>
<td>0.5</td>
<td>1.6</td>
</tr>
<tr>
<td>Hall coefficient $R_H$ (m$^3$/K)</td>
<td>1.4×10$^{-2}$</td>
<td>1.4×10$^{-2}$</td>
</tr>
<tr>
<td>Fermi level $E_f$ (eV)</td>
<td>-0.72</td>
<td>-0.72</td>
</tr>
<tr>
<td>scattering parameter $\lambda$</td>
<td>1.1</td>
<td>1.3</td>
</tr>
<tr>
<td>Carrier concentration $n$ (cm$^{-3}$)</td>
<td>1.29×10$^{20}$</td>
<td>1.24×10$^{20}$</td>
</tr>
<tr>
<td>Carrier mobility $\mu$ (cm$^2$/Vs)</td>
<td>0.45</td>
<td>0.37</td>
</tr>
</tbody>
</table>
Table S2

Table S2. Summary of the doping level and nanowire concentration of P3HT/Bi₂Te₃ nanowires in Figure 4b, which exhibits enhanced power factors as compared to their heavily-doped P3HT matrix.

<table>
<thead>
<tr>
<th>Doping Level / wt%</th>
<th>Power Factor / μWK²m⁻¹</th>
<th>0% Bi₂Te₃</th>
<th>5% Bi₂Te₃</th>
<th>10% Bi₂Te₃</th>
<th>15% Bi₂Te₃</th>
<th>20% Bi₂Te₃</th>
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<tr>
<td>32</td>
<td>1.9</td>
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<td>7.1</td>
<td>5.6</td>
<td>2.6</td>
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References