Effect of host-mobility dependent carrier scattering on thermoelectric power factors of polymer composites

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Abstract

The interfacial carrier scattering was thought to be ineffective in enhancing thermoelectric (TE) properties of polymer hybrids and there was also a lack of fundamental understanding of carrier scattering at polymer/polymer interfaces. Here we unravel the mechanism behind the role of polymer/polymer interfacial scattering on the TE properties through integration of computation and experiments. We discover that the effect of interfacial scattering at polymer/polymer interfaces on TE properties of polymer hybrids is strongly dependent on the carrier mobility of host polymers besides interfacial barriers. Only when the host carrier mobility is above a threshold, the effect of interfacial scattering on TE enhancement can be significant. Simulation suggests that the host mobility threshold is $\sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for PEDOT-based polymers. The polymer hybrid system of poly(3,4-ethylenedioxythiophene) (PEDOT) nanowires/PEDOT was successfully employed to verify the theoretical results. These

findings offer groundbreaking knowledge on polymer/polymer interfacial carrier-transport and will advance the design and fabrication of high-efficiency organic thermoelectric materials.

Keywords: Thermoelectric, polymer hybrid, carrier scattering, host mobility

Introduction

Thermoelectric (TE) materials convert thermal energy to electricity and *vice versa*. The conversion efficiency is governed by the TE figure of merit (ZT), $ZT = S^2\sigma T / \kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature at operation [1]. Organic TE materials are very attractive since they are composed of earth-abundant elements (and thus low cost), lightweight, and easy to process [2]. Because organic materials (e.g. conjugated polymers) usually present intrinsically low thermal conductivity [3-6], enhancing the power factor $S^2\sigma$ is crucial to achieve high ZT for efficient energy conversion. Several state-of-art methods have been employed for enhancing the power factors of conjugated polymers, including doping control [7-14], the addition of carbon nanofillers (e.g. carbon nanotubes (CNTs) [15-22], graphene [23-27]) and high-TE-performance inorganic semiconductors [28-30], metal coordination polymers [31], metal-organic frameworks (MOFs) [32] and polymer blends [33,34]. Recently, the conducting polymer, highly doped poly(3,4-ethylenedioxythiophene) (PEDOT), has been intensively studied as a promising organic TE material [7-13]. The thermoelectric power factor is significantly improved by engineering the doping levels and morphology of PEDOT [7-14].

It is paramount to significantly increase S so as to maximize $S^2\sigma$. It has been well reported that the carrier scattering can significantly improve the Seebeck coefficient of inorganic TE materials for enhanced power factor and ZT [35]. However, there is a lack of fundamental understanding and consensus on the significance potential of interfacial carrier scattering for

enhancing the Seebeck coefficient and thus power factor of fully organic TE materials. Previous attempts using polymer blends have not yet uncovered a significant improvement to the Seebeck coefficient *via* such a mechanism [33,34]. Therefore, it is worth to explore the potential of carrier scattering for enhancing TE properties in fully organic materials.

In this work, we for the first time explore the mechanism behind the role of interfacial carrier scattering on the TE transport (Seebeck coefficient) of polymer/polymer hybrids through theoretical calculations and experimental verification. We theoretically simulated the host mobility-dependent carrier scattering effect by calculating Seebeck coefficient enhancement as function of host carrier mobility. Experimental results were employed to confirm these theoretical findings.

Experimental

Transport property calculation: The carrier scattering induced Seebeck coefficient enhancement as a function of host carrier mobility is presented by the Seebeck coefficient ratio of S_I/S_0 , where S_I is the Seebeck coefficient of the host polymer after interfacial carrier scattering (with polymer nanowire), and S_0 is the Seebeck coefficient of the host without fillers. It was calculated by taking the relaxation time approximation [36]. Detailed simulation process can be found in Supporting Information.

Linear carrier mobility measurements: A electrolyte-gated organic electrochemical transistor (OECT) method was used to measure the linear carrier mobility of highly doped PEDOT:PSS as reported in the literature [37,38]. Ion gel was used to introduce a higher density of charge carriers. As shown in Figure S2, transistors with a channel length (L) of 50 μm and width (W) of 6 mm were fabricated in a side-gate configuration on the glass substrate. Au was used for source, drain, and gate electrodes. Ion gels based on poly(vinylidene fluoride-co-hexafluoropropylene)

(P(VDFHFP)) and the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMI⁺][TFSA⁻]) were used as the dielectric layer [37,38]. The thickness of PEDOT:PSS layer is 20–50 nm, and the thickness of ion gel dielectric layer is ~6 μm . The validity of measurement, operation procedures, calculation process and other experimental details of the linear mobility measurement by the electrolyte-gated OECT method can be found in Supporting Information.

Work function measurements: Kelvin probe work function measurements were performed on an SKP SPV LE 450 Scanning Kelvin Probe Surface Photovoltage instrument from KP Technology. KP measurements were performed in air with a probe oscillation frequency of 78 kHz.

Thermoelectric characterization: The Seebeck coefficient S was measured following the method previously reported [39]. The electrical conductivity measurement was conducted using the van der Pauw method. I-V sweeps were performed using a Keithley 6221 current source and a Keithley 2182A nanovoltmeter.

Detailed information regarding theoretical calculations, carrier mobility measurements, work function measurements, and thermoelectric property measurements can be found in Supporting Information.

Results and discussions

Organic materials are usually disordered and show much lower carrier mobility (typically, $\mu < 0.1 \text{ cm}^2/\text{V.s}$) and mean free path (MFP) than inorganic materials. However, recent research presents that the carrier transport in conjugated polymers can be significantly facilitated by engineering polymer morphology (e.g. conformation of conducting chains) or synthesizing novel conducting polymers *etc* [15,37-38,40]. As the carrier mobility increases, the carrier MFP is believed to increase significantly. For instance, it has been intensively reported that highly doped

PEDOT polymers perform their metallic or semi-metallic transport properties [10, 41, 42]. To some extent, their carrier transports may be different from typical organic semiconductors (hopping transport), while they are more likely to be similar to that in some inorganic semiconductors (e.g. band-like transport [43,44]). So we first modeled the effects of host carrier mobility μ and interfacial barrier E_b on the Seebeck coefficient in the polymer/polymer hybrids.

In theory, when carriers are scattered in single-phase organic materials, the inverse of total relaxation time is defined as $\tau_0(E)^{-1} = \sum_i \tau_i(E)^{-1}$, where $\tau_i(E)$ refers to the relaxation times of scattering by acoustic phonons, optical phonons, and ionized impurities [35,45]. When a second phase is integrated into the organic host, the resultant interfacial barrier E_b introduces an additional relaxation time associated with the interface scattering [35,45]. The modified total relaxation time can be described as $\tau_1(E)^{-1} = \tau_0(E)^{-1} + \tau_b(E)^{-1}$, where τ_b is the relaxation time due to the interfacial scattering, which is typically on the order of 10^{-13} s [45]. The Seebeck coefficient is defined as $S = (E_{tr} - E_F)/eT$, where e is the elementary charge, T is the absolute temperature, E_F is the Fermi level, and E_{tr} is the mean transport energy [46]. E_{tr} is defined as $E_{tr} = \int_0^\infty E \sigma(E) dE / \sigma$, where $\sigma(E)$ is the differential conductivity [47], and can be described as $\sigma(E) = q^2 \tau(E) \nu(E)^2 g(E) (-\partial f(E) / \partial E)$, where $\tau(E)$ is the total relaxation time; $\nu(E)$ denotes the average velocity of carriers; $-\partial f(E) / \partial E$ is the Fermi window factor [47]; and $g(E)$ is the Gaussian density of states (DOS) for carriers in organic materials. In the lack of better knowledge about the DOS shape in highly doped organic materials, the Gaussian distribution is commonly used to describe DOS. A plenty of references indicate that Gaussian DOS could rationally represent the energy disorder in conducting polymer, including doped or neutral polymers [8,46,48-50], though the DOS of conducting polymer is very complex.

The ratio of S_I/S_0 is calculated by taking the relaxation time approximation [36], where S_I is the Seebeck coefficient of the host polymer after interfacial carrier scattering (with polymer nanowire), and S_0 is the Seebeck coefficient of the host without fillers. The computational results are shown in Fig. 1. At a low carrier mobility $\mu \ll 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $S_I/S_0 < 1.1$ (Fig. 1), it indicates that only very limited enhancement of the Seebeck coefficient regardless of the E_b value. At a low carrier mobility, the calculation indicated $\tau_0 \ll \tau_b$, and thus $\tau_0^{-1} \gg \tau_b^{-1}$, so the contribution of interfacial carrier scattering to the total relaxation time is negligible. This result indicates only a very limited enhancement of S (and thus $S^2\sigma$) for any value of E_b for typical low-mobility (typically, $\mu < 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) organic materials. However, significant enhancement of S_I/S_0 is observed when μ is above a critical value (μ_c). This μ_c is reduced for larger values of E_b , but it is always above $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, indicating that the carrier mobility is crucial to improve S . **In addition, S_I/S_0 is not affected by E_b when $E_b > 0.15 \text{ eV}$, an observation related to the asymmetry of $\sigma(E)$ and/or the position of E_{tr} . The calculated energy E of carriers under the Fermi window is up to $\sim 0.3 \text{ eV}$ for PEDOT:PSS. Larger E_b results in more carriers with $E < E_b$ filtered, leading to the increase of E_{tr} towards its maximum value and simultaneous enhancement of the asymmetry of $\sigma(E)$ for higher Seebeck coefficient [51]. In terms of relaxation time, according to the defined equation of τ_b as described in Supporting Information, it can be expected that higher barrier E_b leads to the scattering of carriers with higher energy E , leading to the increase of the inverse relaxation time τ_b^{-1} [36]. Thereby, at sufficiently large E_b , the total inverse relaxation time $\tau_1(E)^{-1} = \tau_0(E)^{-1} + \tau_b(E)^{-1}$ is dominated by the contribution of interfacial scattering (the inverse relaxation time τ_b^{-1} due to energy scattering) [45]. Meanwhile, as E_b is sufficiently enough (for example, $E_b = 0.15 \text{ eV}$ in this case), τ_b is almost non relevant to the barrier height ($\tau_b(E) \sim L \sqrt{\frac{m^*}{2E}}$)**

[36]. Hence, S_I/S_0 at a given high mobility will be insensitive to large E_b because E_{tr} is saturated at $E_b > 0.15$ eV.

Fig. 1 The simulated mobility-dependent Seebeck coefficient enhancement S_I/S_0 with respect to the carrier mobility μ of PEDOT:PSS matrix. S_0 is the Seebeck coefficient of PEDOT:PSS matrix without PEDOT nanowires. S_I is the Seebeck coefficient of PEDOT:PSS composites with 0.2 wt% PEDOT nanowires. The calculations are run for eight different barriers E_b , from 0.04 to 0.40 eV. The inset shows a typical calculated differential conductivity $\sigma(E)$ with respect to the carrier energy E to explain the energy filtering, where E_{tr} is the mean transport energy level, E_b is the energy barrier level, E_F is the Fermi level.

Experimental verification of interfacial carrier scattering simulations was employed by incorporating PEDOT nanowires (NWs) into host PEDOT-based polymers. PEDOT NWs were synthesized as reported elsewhere. As displayed in Fig. S1a, the length of PEDOT NWs is $\sim 1.2 \mu\text{m}$ in the length with an average diameter of ~ 12.2 nm, thick nanowires with large diameter are

bundles of single nanowires. Resultant PEDOT NWs show high aspect ratio (>100). The X-ray diffraction (XRD) patterns of PEDOT NWs (Fig. S1b) indicate highly ordered structures in nanowires owing to the sharp peak at $2\theta=6.4^\circ$, which represents layer structures of PEDOT chains [52]. The diffraction peak at $2\theta=26.2^\circ$ corresponds to the inter-chain planar ring-stacking distance [53].

Most importantly, the calculations suggested that the carrier mobility of host polymers should be above a critical value to demonstrate the effective interfacial carrier scattering in organic TE materials. The PEDOT:PSS film, deposited from the as-received dispersion (PH1000, H. C. Starck) with 5 vol% dimethyl sulfoxide (DMSO) added, was treated with the high-boiling-point solvent ethylene glycol (EG) to enhance the carrier mobility and designed electronic structure. PEDOT NWs were dispersed into aqueous 5 vol% DMSO/ PEDOT:PSS suspension at various weight fractions with the aid of methanol and DMSO. Nanocomposites comprised of a mixture of 0.2 wt% PEDOT NWs/PEDOT:PSS were treated in the same way as the PEDOT:PSS host. The nanowire weight fraction is well below the geometric percolation threshold, which was calculated to ~ 0.269 wt% according to the percolation model [54]. The second host, PEDOT:tosylate (PEDOT:Tos), was synthesized *via* a vapor phase polymerization (VPP) method [55].

The carrier mobility for all samples was measured with electrolyte-gated organic electrochemical transistor (OECT) methods as reported in the literature [37,38,56-58]. All the mobility data in this work were measured as the linear carrier mobility, since there is only linear regime (NO saturation regime) in the output characteristics of these high-carrier-concentrations PEDOT based OECTs. The validity of the measurement was briefly discussed. (Details are given in Supporting Information) Fig. 2 shows typical output characteristics (a-f) and transfer curves

(g-l) for each type of samples. As displayed in Fig. 2 (a-f), clear field effect can be observed for all devices; however, there is no saturation regime in output characteristics, which may be due to the high carrier concentration of PEDOT-based polymer channels. Hence, only the evaluation of linear carrier mobility in the linear regime is plausible. Additionally, as shown in Figure 2 (a-f), the non-linearity of the output characteristics as the source drain voltage is -0.6-1.0 V might be related to the fact that the OECT transistors don't have purely electrostatic effect but also the migration of ions at high gate voltage. Ions from the channel polymer (PEDOT:PSS) and dielectric materials may all contribute to the rapid increase of source-drain current as the gate voltage and source-drain voltage is high.

As shown in Fig. 2 (g-l), as the gate voltage is small enough, the conductance decreases linearly as the gate voltage increase, which is essentially attributed to the linear decrease of carrier concentration in the linear regime, in principle. However, as the gate voltage is large, the conductance dramatically decrease with a large slope, which has been verified by Wei *et al* that the electrochemical doping would lead to the penetration of ions from gels into the bulk of PEDOT channels [37]. It is worth noting that the diffusion rate of ions depends not only on the gate voltage but also on the scan rate. In order to furthest eliminate the effect of scan rate and obtain a good linear relationship for the conductance versus gate voltage, a proper scan rate (0.1-0.15 V) was used. Hence, the carrier transport in this regime would be a three-dimensional transport. As both the applied gate voltage and drain voltage are small, the carrier transport should mainly occur at the interface between electrolyte and PEDOT channels, thus would be a two-dimensional transport in this regime [57,58], the formula for the linear mobility calculation in organic field-effect transistors is valid and applicable in this work. It must be noted that this type of measurement gives us a reasonable linear mobility level based on our multiple

measurements (at least three samples for each type), even though there might be certain errors, such as the different structure on the surface and in the bulk of PEDOT films. It is rational to use as they were measured under the same device configuration and the same measurement conditions.

Fig. 2 (a-f), output curves of OECT with different channel materials: (a), PEDOT:PSS; (b), PEDOT:PSS/5 vol% DMSO; (c), PEDOT:PSS/5 vol% DMSO with 50 min EG treatment; (d), PEDOT:PSS/5 vol% DMSO with 120 min EG treatment; (e), PEDOT:PSS/5 vol% DMSO with 220 min EG treatment; (f), PEDOT:Tos. (g-i), conductance curves as a function of gate voltage for OECT with different channel materials: (g), PEDOT:PSS; (h), PEDOT:PSS/5 vol% DMSO;

(i), PEDOT:PSS/5 vol% DMSO with 50 min EG treatment; (j), PEDOT:PSS/5 vol% DMSO with 120 min EG treatment; (k), PEDOT:PSS/5 vol% DMSO with 220 min EG treatment; (l), PEDOT:Tos.

The carrier concentrations were calculated based on the equation $\sigma = qn\mu$, where σ is electrical conductivity of PEDOT:PSS, q is the unit charge, $\sim 1.60217657 \times 10^{-19}$ A.s, n is carrier concentration, and μ is the measured carrier mobility with the organic electrochemical transistor method reported elsewhere. The carrier concentration in PEDOT:PSS host matrices under different EG treatments is almost constant within the time frame of 0-120 min (Table 1). In Table 1, the carrier concentration of as-prepared 5 vol% DMSO/PEDOT:PSS matrix is $\sim 2.04 \times 10^{21} \text{ cm}^{-3}$. As the EG treatment time increased, the carrier concentration is almost constant within the time frame of 0-120 min, as the EG treatment time extends to 220 min, the carrier concentration is $1.12 \times 10^{21} \text{ cm}^{-3}$, which is almost half of that of 5 vol% DMSO/PEDOT:PSS matrix before EG treatment. Based on the relationship between Seebeck coefficient S and carrier concentration n for degenerated semiconductors, $S \sim n^{-2/3}$, lower carrier concentration will result in larger Seebeck coefficient [59]. This slight reduction of carrier concentration in neat PEDOT:PSS matrices may have certain contribution to the increase of S_0 of neat PEDOT:PSS **matrices** from $13.6 \mu\text{V K}^{-1}$ to $\sim 22\text{-}25 \mu\text{V K}^{-1}$ after EG treatments.

However, the change of carrier concentration in polymer matrices should have nothing to do with the increase of S_I of PEDOT NWs/PEDOT:PSS nanocomposites. The increase of S_I is actually on the basis of S_0 , the only difference between PEDOT NWs/PEDOT:PSS nanocomposites (S_I) and neat PEDOT:PSS samples (S_0) is that there are PEDOT NWs in PEDOT matrix for PEDOT NWs/PEDOT:PSS nanocomposites (S_I). In other words, due to the exactly same EG treatment time, the PEDOT:PSS matrix component in PEDOT

NWs/PEDOT:PSS nanocomposites should have the similar carrier concentration to the PEDOT:PSS host matrix without PEDOT NWs. Furthermore, the carrier concentration of PEDOT NWs/PEDOT:PSS nanocomposites might be slightly higher in comparison to that of PEDOT:PSS host matrix because of the extra addition of carriers from PEDOT NWs. However, since the weight fraction of PEDOT NWs is very small (0.2 wt%), the carrier concentration of PEDOT:PSS/PEDOT NWs composites may not change too much. So the increase of S_I in PEDOT NWs/PEDOT:PSS nanocomposites does not stem from the change of carrier concentration. To further confirm our discussion here, we measured the Seebeck coefficient of PEDOT NWs films, it was found that an as-prepared film of PEDOT NWs shows a Seebeck coefficient of $\sim 15 \mu\text{V K}^{-1}$ and possesses an almost constant Seebeck coefficient ($\sim 15\text{-}17 \mu\text{V K}^{-1}$) in the EG treatment time frame. It may imply that the PEDOT NWs have similar or higher carrier concentration and the addition of PEDOT nanowires should not reduce the carrier concentration of PEDOT:PSS matrix.

Table 1 Measured electrical conductivity, carrier mobility and calculated carrier concentration of EG treated 5 vol% DMSO/PEDOT:PSS matrices.

EG treatment time (min)	Electrical conductivity (S/cm)	Carrier mobility ($\text{cm}^2/\text{V.s}$)	Carrier concentration (estimated, cm^{-3})
0 min	645.7 ± 14.9	1.98 ± 0.12	2.04×10^{21}
50 min	762.6 ± 34.1	2.41 ± 0.26	1.98×10^{21}
120 min	934.4 ± 47.8	2.93 ± 0.35	1.99×10^{21}
220 min	629.8 ± 22.1	3.51 ± 0.18	1.12×10^{21}

Seebeck coefficients were measured with the previously reported method [39] at low humidity ($\sim 17\%$). The enhancement of Seebeck coefficient S_I/S_0 with respect to the host carrier

mobility μ for all polymer nanocomposites is displayed in Fig. 3. As aforementioned, the Seebeck coefficient enhancement S_I/S_0 is defined as the ratio of Seebeck coefficient of the PEDOT:PSS matrix with (S_I) and without (S_0) the addition of PEDOT NWs under the same conditions (e.g. EG treatments). The carrier mobility of as-received PEDOT:PSS is $\sim 0.06 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Table 1), and the enhancement of Seebeck coefficient is negligible ($S_I/S_0 \sim 1.06$, Fig. 3) when 0.2 wt% PEDOT NWs were integrated to the host. Intriguingly, significant enhancement of Seebeck coefficient ($S_I/S_0 \sim 1.68$, Fig. 3) is observed as the linear carrier mobility of the host PEDOT:PSS is raised to $\sim 1.98 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Table 1) through the addition of polar solvent DMSO (5 vol%) to the as-received PEDOT:PSS dispersion. The mobility observed here is on the same order as values reported in recent studies [37,60], where the addition of DMSO into PEDOT:PSS was believed to be the intrinsic reason for the mobility improvement [8], because of the transition of polymer molecules from benzoid to quinoid structure and conformational changes of polymer chains [37,61]. Further EG post-treatment (of the DMSO-added PEDOT:PSS) increases the carrier mobility to $\sim 2\text{-}4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ because EG treatment can further improve the molecular conformation and electrostatic interactions [8]. The corresponding S_I/S_0 of PEDOT NWs/PEDOT:PSS composites (0.2 wt% PEDOT NWs) is observed to be larger than 1.45. In another case, incorporation of nominal 0.2 wt% PEDOT NWs into PEDOT:Tos host ($\mu = 1.68 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for as-synthesized PEDOT:Tos host, Table S3) results in a Seebeck coefficient enhancement of $S_I/S_0 \sim 1.19$. These experimental results further confirm our theoretical predictions that the carrier mobility of host polymer should be large enough for effective carrier scattering in polymer/polymer hybrids.

Fig. 3 Experimental results of the enhancement of Seebeck coefficient S_1/S_0 as a function of linear carrier mobility μ for PEDOT-based host polymers integrated with 0.2 wt% PEDOT NWs. The open squares are the experimentally measured Seebeck coefficient ratios S_1/S_0 . The error bars represent the variations of measured carrier mobility. The samples with their linear mobility data shown in this figure have their energy barrier E_b from 0.07 eV-0.15 eV. (Details of mobility and Seebeck coefficient ratio data are given in Table S2-S3 and Table S5-S6, respectively.)

Additionally, as discussed in the simulation results, the barrier height E_b is another important factor that can significantly influence the Seebeck coefficient. Highly doped PEDOT polymers have infinitesimal band gaps [10], and the PEDOT:PSS and PEDOT NWs equilibrate their Fermi levels within the polymer hybrid, the offset of work functions between PEDOT:PSS and PEDOT NWs is regarded as E_b . The measured work functions (WF) and corresponding WF

offsets were summarized in Table 2. As presented in Fig. 1, larger E_b leads to larger Seebeck coefficient ratio (S_I/S_0) because more carriers with energy $E < E_b$ are filtered, leading to the increase of mean transport energy E_{tr} . In Fig. 4, in comparison to 5 vol% DMSO/PEDOT:PSS host matrix under the same EG treatment time, Seebeck coefficient, electrical conductivity and power factor ratios ($S_I^2\sigma_I/S_0^2\sigma_0$) of PEDOT NWs/PEDOT:PSS nanocomposites as a function of barrier E_b were plotted to characterize the effect of barrier E_b on TE performance. The Seebeck coefficient ratio S_I/S_0 is defined as the ratio of Seebeck coefficient of the PEDOT:PSS matrix with (S_I) and without (S_0) the addition of PEDOT NWs under the same EG treatment time. It can be seen that enhanced S_I is observed with increasing E_b since larger barrier E_b leads to higher energy offset $E_{tr}-E_F$. Larger E_b values initially increase both S_I/S_0 and $S_I^2\sigma_I/S_0^2\sigma_0$ and then diminish their levels, while their electrical conductivity ratio ranges around 0.7-0.8 and seems to be not that sensitive to the barrier height. As the nanowire fraction is 0.1 wt% (Fig. 4a), S_I slightly increases with S_I/S_0 of ~1.3-1.5. σ_I/σ_0 fluctuates between ~0.7-0.8 as the barrier height changes. It seems that σ_I/σ_0 is not very sensitive to the barrier height, but the introduction of PEDOT NWs definitely decreases the electrical conductivity. It might be due to the ultralow weight fraction (0.1 wt%) of PEDOT NWs in the polymer nanocomposites. Smaller weight fraction of PEDOT NWs indicates lower density of scattering interfaces, thus it might be possible that the reflected energy scattering at different barrier heights might be very similar. $S_I^2\sigma_I/S_0^2\sigma_0$ first increases and then slightly decreases leading to the maximum $S_I^2\sigma_I/S_0^2\sigma_0 = \sim 1.66$. As the nanowire fraction is 0.2 wt% (Fig. 4b), the maximum S_I/S_0 ratio of ~1.75 shows at $E_b = 0.09$ eV (120 min EG treatment) where $S_I = \sim 38.9 \mu\text{VK}^{-1}$, and $S_0 = 22.2 \mu\text{VK}^{-1}$ (5 vol% DMSO/PEDOT:PSS with 120 min EG treatment), and σ_I/σ_0 monotonously decreases from ~0.8 to ~0.7, which indicates that the higher the barrier height the smaller σ_I/σ_0 . This is very different from σ_I/σ_0 of 0.1 wt% samples

where it shows no trends but random fluctuation. Finally, the maximum $S_I^2\sigma_I/S_0^2\sigma_0$ ratio is ~2.22. Hence, the maximum power factor was calculated to $\sim 102.7 \mu\text{Wm}^{-1}\text{K}^{-2}$ at $E_b = 0.09 \text{ eV}$ for 0.2 wt% PEDOT NW/PEDOT:PSS nanocomposite, which is almost 9-fold of that of 5 vol% DMSO/PEDOT:PSS ($\sim 11.9 \mu\text{Wm}^{-1}\text{K}^{-2}$). The optimized barrier height is $E_b = 0.09 \text{ eV}$, which is close to the optimized barrier height ($< 0.1 \text{ eV}$) for efficient energy filtering in inorganic materials [47].

Table 2 Work functions of EG treated PEDOT NWs, and EG treated 5 vol%

DMSO/PEDOT:PSS measured by the Kelvin probe method.

EG treatment time (min)	WF of 5 vol% DMSO/PEDOT:PSS (eV)	WF of PEDOT NWs (eV)	Interfacial barrier E_b (eV)
0	4.88	4.78	0.10
50	4.92	4.78	0.14
120	4.87	4.78	0.09
220	4.85	4.78	0.07
300	4.82	4.78	0.04

Fig. 4 The measured Seebeck coefficient (black), electrical conductivity (red) and power factor (blue) ratios as a function of interfacial energy barrier E_b for (a) 0.1 wt% and (b) 0.2 wt% PEDOT NWs/PEDOT:PSS nanocomposites. The Seebeck coefficient ratio S_I/S_0 , electrical conductivity ratio σ_I/σ_0 , and power factor ratio $S_I^2 \sigma_I / S_0^2 \sigma_0$ were calculated with the average values of S_0 , S_I , σ_0 , σ_I , $S_0^2 \sigma_0$, and $S_I^2 \sigma_I$.

As discussed in Fig. 4, higher nanowire fraction leads to higher Seebeck coefficient and thus higher power factor. It should stem from the higher interface volume between nanowires and PEDOT matrix. Below the nanowire geometric percolation threshold, higher filler fraction results in the shorter distance between nanowires, which can be approximately treated as the barrier distance L .³⁶ Smaller L results in more frequent carrier scattering from the barriers [36], and thus higher Seebeck coefficient S_I and reduced electrical conductivity σ_I . We theoretically evaluated the average distance L between nanowires with the interparticle distance (IPD) model [62].

$$p = \frac{\pi d^2 l}{4 \left[\langle \cos^2 \theta \rangle \cdot (l + IPD) \right]^3}$$

where, p is the volume fraction of one-dimensional (1D) filler in host matrix, d is the diameter of 1D filler, l is the length of 1D filler, θ represents the angle between the 1D filler and the direction of preferred orientation, and the angular brackets $\langle \rangle$ denote the orientation average. For a three-dimensional (3D) random distribution [62,63],

$$\langle \cos^2 \theta \rangle = \frac{1}{3}$$

IPD (or L) is the interparticle distance, or the interdistance between 1D fillers. Since the density of solid PEDOT:PSS was measured to $\sim 1 \text{ g/cm}^3$ [64], the weight fraction 0.2 wt% can be converted to the corresponding volume fraction, 0.2 vol%. To calculate the interdistance between PEDOT NWs, $d=12.2 \text{ nm}$ and $l=1.2 \mu\text{m}$ (Figure S1) is applied to the above equation. As the nanowire volume fraction is 0.1 vol%, the estimated distance L between PEDOT NWs is only $\sim 358.8 \text{ nm}$. As the nanowire volume fraction is 0.2 vol%, the estimated distance L between PEDOT NWs is only $\sim 37.2 \text{ nm}$.

The effect of the barrier distance L ($L>0$) between nanowires in host matrix on the Seebeck coefficient enhancement (the Seebeck coefficient ratio) S_1/S_0 was simulated as shown in Fig. 5. For a given host carrier mobility, smaller L leads to higher Seebeck coefficient ratio, which has been verified in Fig. 4. Meanwhile, when the carrier mobility of host polymer is very small ($\mu=0.06 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$), even the barrier distance L is small enough; the Seebeck coefficient ratio is still close to 1, indicating the contribution of interfacial scattering is negligible. As the carrier mobility increases to $1 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$, the Seebeck coefficient enhancement becomes distinct. As the host carrier mobility further increases to $3 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$, the Seebeck coefficient ratio is significant as the barrier distance L is relatively small. For instance, as the barrier distance $L=37.2 \text{ nm}$, $S_1/S_0=1.58$, which is comparable with the data shown in Fig. 3.

Fig. 5 The Seebeck coefficient ratio S_1/S_0 with respect to the barrier distance L in host matrix. The distance L is defined as the mean distance between nanowires in host polymer matrix. μ represents the carrier mobility of host polymer.

Conclusions

In summary, we demonstrate for the first time that the carrier scattering can be applied to enhancing TE performance of polymer/polymer hybrid TE materials. Through theoretical calculations and experimental verification, it is suggested that the efficiency of interfacial carrier scattering in organic nanocomposites strongly depends on the host carrier mobility. It is found that only when the host carrier mobility is above a critical value, which is $\sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for PEDOT-based polymers, interfacial carrier scattering can result in a significant enhancement of the Seebeck coefficient and power factor. Additionally, high power factor can be achieved with further optimization of energy barrier and filler fraction. These results open up a new route for the design and fabrication of high-efficiency organic thermoelectric materials and will significantly advance the corresponding technology of solid-state energy conversion.

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