

Boosting the Thermoelectric Properties of PEDOT:PSS via Low-Impact Deposition of Tin Oxide Nanoparticles

Jingjin Dong, Dominic Gerlach, Panagiotis Koutsogiannis, Petra Rudolf, and Giuseppe Portale*

Poly(3,4-ethylenedioxy thiophene):poly(styrenesulfonate) (PEDOT:PSS) exhibits valuable characteristics concerning stability, green-processing, flexibility, high electrical conductivity, and ease of property modulation, qualifying it as one of the most promising p-type organic conductors for thermoelectric (TE) applications. While blending with inorganic counterparts is considered a good strategy to further improve polymeric TE properties, only a few attempts succeed so far due to inhomogeneous embedding and the non-ideal organic-inorganic contact. Here a new strategy to include nanoparticles (NPs) without any ligand termination inside PEDOT:PSS thin films is proposed. Spark discharge-generated tin oxide NPs (SnO_x -NPs) are “gently” and homogeneously deposited through low-energy diffusion mode. Strong interaction between naked SnO_x -NPs and PSS chains occurs in the topmost layer, causing a structural reorganization towards an improved PEDOT chains crystalline packing at the bottom, providing a positive contribution to the electrical conductivity. Meanwhile, dedoping and energy filtering effect introduced by the SnO_x -NPs cause dramatic Seebeck coefficient enhancement. The optimized power factor of $116 \mu\text{W m}^{-1} \text{K}^{-2}$ achieved is more than six times higher than the value found for the film without NPs. This easy and efficient strategy promises well for future mass production of flexible TE devices and the mechanism revealed may inspire future research on TEs and flexible electronics.

materials' efficiency to convert heat into electricity remains still quite low in the low-temperature range. To quantify the TE performances, the figure of merit zT is introduced, which is described by the equation $zT = \frac{\sigma S^2 T}{\kappa}$,^[4,5] where σ is the electrical conductivity, S the Seebeck coefficient, κ the thermal conductivity, and T the absolute temperature. Due to the intrinsically low thermal conductivity of polymeric TE materials, the power factor, which is described as $PF = \sigma S^2$, is the main factor to be improved.^[6,7] However, σ and S influence each other and usually in an opposite way, meaning that when one of them increases, the other one will decrease. A large amount of research has been done to probe the relationship between these two variables and to try to improve them.^[8–10]

Poly(3,4-ethylenedioxy thiophene):poly(styrenesulfonate) (PEDOT:PSS, structure shown in Figure 1a) is one of the most studied among polymeric TE materials, being highly stable, easily processable, and showing the best TE properties for this family of materials so far.^[11,12] Although various strategies including polar solvents

treatment, acids/bases treatment, ionic liquids treatment, inorganic nanomaterials incorporation, etc. have been applied to improve the TE performance of PEDOT:PSS,^[7] and PF as high as $380 \mu\text{W m}^{-1} \text{K}^{-2}$ can be achieved with the incorporation of 2D SnSe nanosheets,^[13] effective and cost-effective methods simple enough that can be used for mass production are still lacking.

Here we propose a new method to add “naked” nanoparticles (NPs) to PEDOT:PSS in order to improve its TE properties. The improvement in TE properties is achieved by a reorganization of the film structure induced by the NP addition via a specific interaction with the PSS[−] chains. Key in this work is the use of “naked” NPs. Indeed, Zhang et al. proved the negative effect of the surface layer on inorganic Bi_2Te_3 when embedded in PEDOT:PSS.^[14] To incorporate “naked” inorganic NPs we selected a physical pathway for NP generation, namely spark discharge generation, which is one of the least expensive and most environmentally friendly methods to produce large amounts of NPs.^[15,16] A flow of gas (Ar) can be used to carry the generated NPs towards the polymer target (see Figure 1b). Instead of applying the so-called *impaction mode*, where the NPs impinge vertically on the substrate, an alternative low

1. Introduction

Polymeric thermoelectric (TE) materials have recently attracted increasing interest from the scientific community.^[1,2] Their flexibility and low weight make them highly suitable for a broad range of applications such as portable electronic devices powered by human body temperature.^[3] However, polymeric TE

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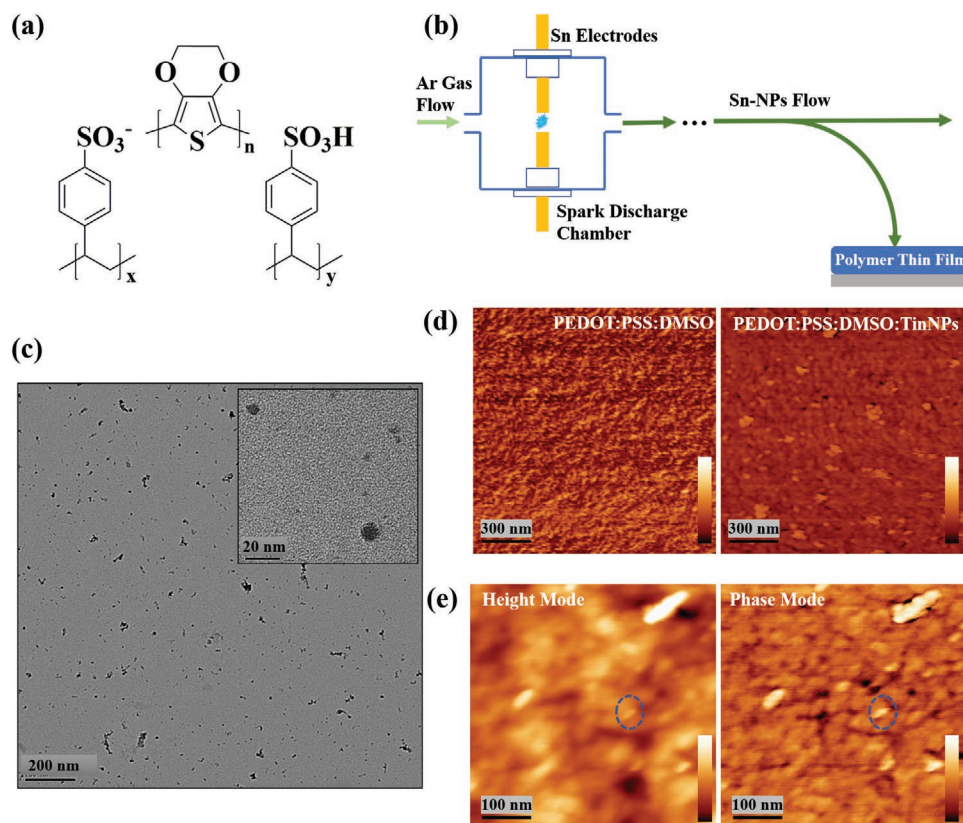


Figure 1. a) Structure of PEDOT:PSS. b) Experimental setup for preparing the hybrid system of polymer thin film and SnO_x NPs using the low energy diffusion mode. c) TEM of SnO_x -NPs. d) Phase mode AFM images of PEDOT:PSS:DMSO thin film (left) and PEDOT:PSS:DMSO: SnO_x -NPs thin film (right). e) Height mode (left) and phase mode (right) AFM images of PEDOT:PSS:DMSO: SnO_x -NPs thin film. Scale bars are 40° and 10 nm for the phase mode and height mode, respectively.

energy diffusion mode was employed here to avoid destructively altering the polymer structure. In this case, the NPs flow is set parallel to the substrate and NPs are allowed to gently land onto the polymeric film. In this way, the impact of the NP incorporation onto the polymer structure is minimal and the conductive network of the polymer is maintained. Tin (Sn) electrodes were selected to prepare Sn-based NPs because they are non-toxic, active in electrical performance and Sn and its oxides were recently reported to have interesting TE properties.^[17]

2. Results and Discussion

The morphology of the NPs produced by spark discharge was studied at first. To this aim, we deposited them on Cu grids and analyzed them by transmission electron microscopy (TEM), as shown in Figure 1c. As observed, the NPs were widely and homogeneously dispersed on the Cu grid, which is very important for the preparation of homogeneous hybrid films with PEDOT:PSS. Their shape is spherical with sizes ranging between 10 and 20 nm. This value is further confirmed by scanning electron microscopy (SEM) and grazing incidence small-angle X-ray scattering (GISAXS) as shown in Figure S1, Supporting Information. In particular, an average diameter of 10.3 nm was derived from fitting the GISAXS data (see Figure S1b, Supporting Information). Before analyzing the hybrid

film, a thicker layer of NPs was deposited to perform grazing incidence wide-angle X-ray scattering (GIWAXS) as shown in Figure S2, Supporting Information. The GIWAXS pattern exhibits a sharp peak located at $q = 1.85 \text{ \AA}^{-1}$ suggesting a d -spacing of 3.4 Å, which can be attributed to the (110) plane of SnO_2 .^[18] Oxidation of the NPs is indeed expected in our case due to the exposure to air. The exact composition of the NPs will be further discussed below based on X-ray photoelectron spectroscopy (XPS) results. We will thus call the NPs as SnO_x -NPs in the following.

Next, the SnO_x -NPs were deposited on PEDOT:PSS thin films and the surface morphology of the hybrid was investigated by atomic force microscopy (AFM). Figure 1d shows phase mode AFM images of the PEDOT:PSS:DMSO thin film before and after deposition of SnO_x -NPs. Comparing the two images, it is obvious that the SnO_x -NPs (the brighter objects in the phase images) were successfully deposited onto the PEDOT:PSS:DMSO thin films. In line with what was observed by TEM for the deposition on Cu grids, SnO_x -NPs appear well dispersed onto the polymer film, with minimal aggregation (Figure 1d). After NP deposition, the roughness as calculated from AFM increased only slightly, from 1.8 nm for the pristine PEDOT:PSS:DMSO film to 2.0 nm for the PEDOT:PSS:DMSO: SnO_x -NPs one. This observation indicates that during the deposition process the SnO_x -NPs penetrate into the polymer matrix, in line with a previous report identifying

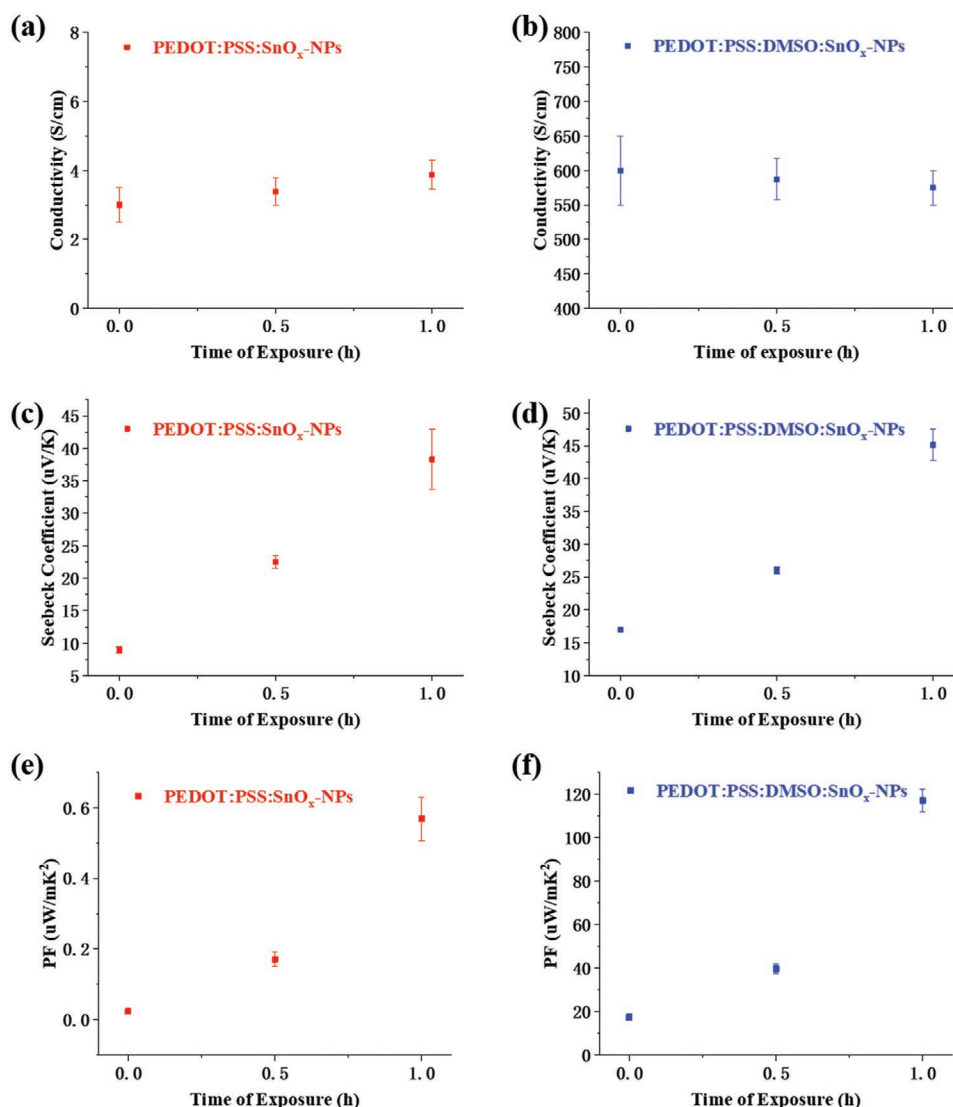


Figure 2. TE properties of the PEDOT:PSS:SnO_x-NPs (left) and PEDOT:PSS:DMSO:SnO_x-NPs (right). a,b) electrical conductivity, σ ; c,d) Seebeck coefficient, S ; e,f) Power Factor, PF.

the reduction of the Gibbs surface free energy as the driving force for embedding NPs inside polymer films.^[19] Moreover, a specific interaction between the charged PSS⁻ and the SnO_x-NPs can act as an additional driving force for the embedding in our case, as will be discussed below based on XPS data.

The TE properties (namely σ , S , and PF) against the NP deposition time are summarized in **Figure 2**. The effect of the SnO_x-NP incorporation was studied both on neat PEDOT:PSS and PEDOT:PSS:DMSO thin films. As shown in Figure 2a,b, the electrical conductivity varies little upon NP deposition. An opposite trend is observed here: while after continuous deposition of SnO_x-NPs for 1 h the conductivity of the neat PEDOT:PSS system increased from 3 ± 0.5 to 4 ± 0.5 S cm⁻¹, for PEDOT:PSS:DMSO thin films a decrease of the conductivity from 600 ± 50 to 575 ± 25 S cm⁻¹ was observed. An additional PEDOT:PSS:SnO_x-NPs sample was prepared using 2 h deposition time and it exhibited a slight decrease in conductivity to ≈ 3.3 S cm⁻¹, suggesting that prolonging the deposi-

tion time well behind 1 h is not necessary. In both cases, the observed conductivity changes are minor, implying that the *diffusion mode* deposition adopted here is a mild method to add NPs to the polymer thin film. Interestingly, a marked positive effect was observed for the Seebeck coefficient (Figure 2c,d). Both PEDOT:PSS:SnO_x-NPs and PEDOT:PSS:DMSO:SnO_x-NPs thin films exhibit a great increase in S , when compared to the respective pristine films. For PEDOT:PSS:SnO_x-NPs, the S value increased to 22.5 ± 1.0 and 38.3 ± 4.7 μV K⁻¹ for 0.5 h and 1 h deposition, while for PEDOT:PSS:DMSO:SnO_x-NPs, the S value increased to 26.0 ± 0.5 and 46.1 ± 2.4 μV K⁻¹, respectively. The PF results calculated from the σ and S values are shown in Figure 2e,f, where due to the dramatic increase in Seebeck coefficients, the PF is found to have increased by 28 times from 0.02 ± 0.004 to 0.57 ± 0.06 μW m⁻¹ K⁻² for PEDOT:PSS:SnO_x-NPs and by almost seven times from 173 ± 1.2 to 116 ± 5.1 μW m⁻¹ K⁻² for PEDOT:PSS:DMSO:SnO_x-NPs. These TE properties are among the highest reported for the PEDOT:PSS based

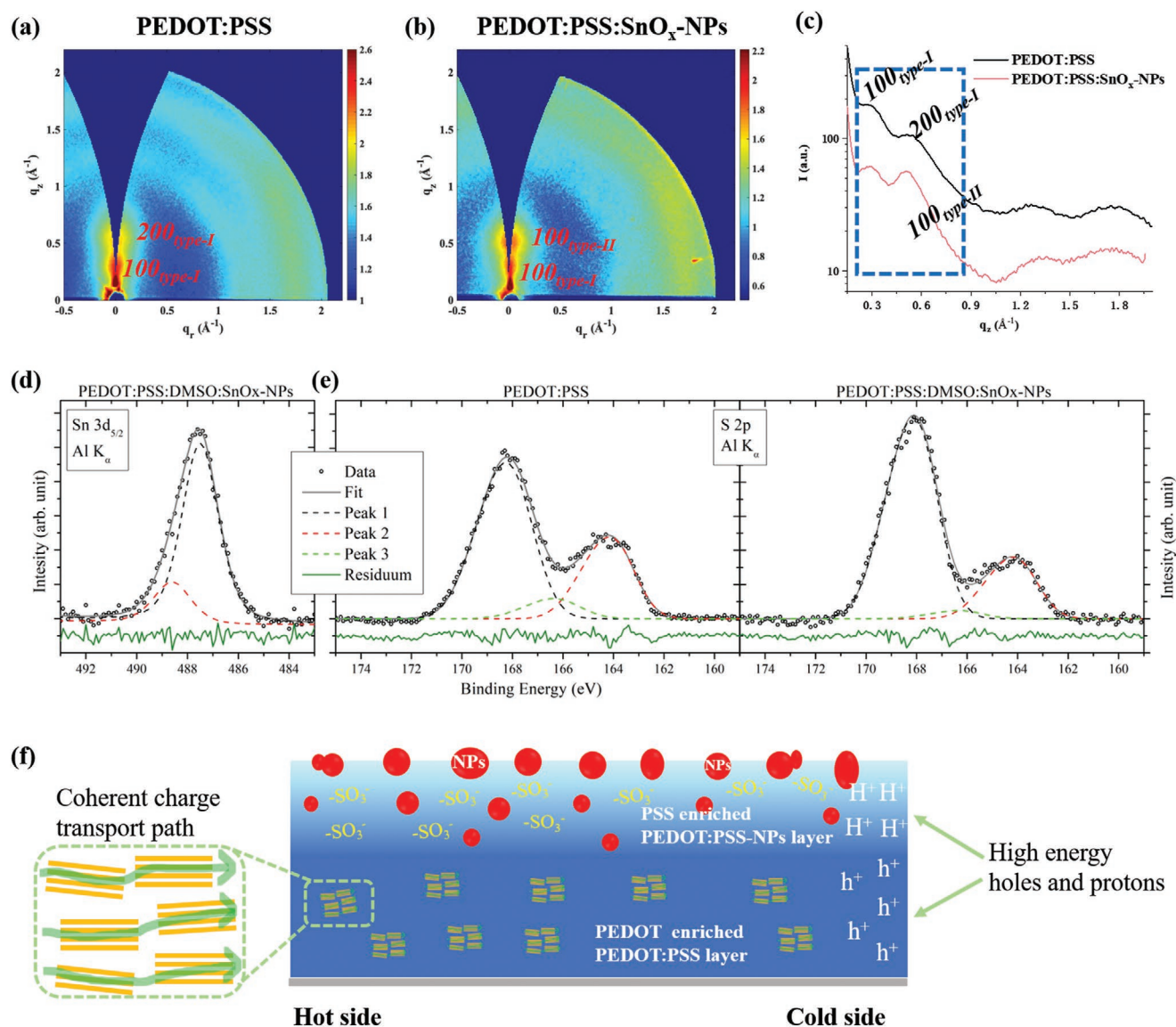


Figure 3. GIWAXS images of a) PEDOT:PSS thin film, b) PEDOT:PSS:Sn-NPs hybrid thin film, and c) the out-of-plane linecut profiles. d) XPS spectra of the Sn3d_{5/2} and S2p core-level regions of PEDOT:PSS:DMSO and PEDOT:PSS:DMSO:SnO_x-NPs thin films (dots) corresponding fits (grey continuous lines), fit components (dashed lines), and residua (green line). f) Scheme of the hybrid film structure and possible working principle.

organic-inorganic hybrid systems so far.^[20,21] Moreover, the preparation method reported here is extremely simple, without any complex chemical synthesis, post-treatment or washing steps, holding great potential in industrialized large-scale production.

To shed more light onto the possible mechanism for the observed TE property increase, we first verified the (surface) composition of the deposited SnO_x-NPs. As already mentioned, Sn is very sensitive to oxygen and can be easily oxidized in air, forming SnO and SnO₂ at the surface. Oxygen vacancies at the NP surface would render the SnO_x-NPs a p-type semiconductor.^[17] To quantify the composition of the SnO_x-NPs, XPS spectra of the Sn3d core level region were collected. The Sn3d_{5/2} component is shown in Figure 3d. The slightly asymmetric structure of the line suggests the presence of Sn with

different oxidation states or in different chemical environment. The fitting suggests that there is predominantly Sn⁴⁺ from SnO₂, giving rise to the component at a BE of 487.0 eV (black dashed line in Figure 3d). This is consistent with reports for SnO_x films of thickness below 60 nm, where the same high oxidation state was observed.^[17] The peak at higher binding energy (BE) (red dashed line in Figure 3d), is attributed to Sn⁴⁺ coordinated by oxygen from PSS.^[22,23] This is clear evidence for the interaction between SnO_x-NPs and PSS.

We then employed GIWAXS to learn more about the polymer blend structure. GIWAXS is particularly suited to probe the crystal structure of thin films on molecular length scales and has been proven highly successful in characterizing PEDOT:PSS.^[24] Figure 3a,b shows the GIWAXS patterns of the PEDOT:PSS thin film and of the PEDOT:PSS:SnO_x-NPs

hybrid film, respectively; the out-of-plane linecut profiles are presented in Figure 3c. The PEDOT:PSS thin film exhibits the typical structure with an intense low angle peak located at $q_z = 0.26 \text{ \AA}^{-1}$ together with a weaker peak located at $0.51 \text{ \AA}^{-1}$, both strongly focused along the out-of-plane q_z direction. It is generally accepted that in PEDOT:PSS the second peak at $q_z = 0.51 \text{ \AA}^{-1}$ is the second order 200 peak.^[25] At higher scattering angles, two more peaks are visible: the free PSS peak located at $q = 1.26 \text{ \AA}^{-1}$ and the π - π stacking PEDOT peak located at $q = 1.78 \text{ \AA}^{-1}$. Upon NPs deposition, a clear difference in the ratio of the intensities of the 100 and 200 diffraction peaks of PEDOT:PSS is observed; for PEDOT:PSS:SnO_x-NPs, the 200 peak shows a relative intensity increase of 80%. Similar effect is found for the PEDOT:PSS:DMSO:SnO_x-NPs films (see Figure S3, Supporting Information). This observation suggests a modification in the crystalline structure of the PEDOT crystals. As reported by Bießmann et al.^[26] and also as recently observed by us,^[24] the first order of diffraction of the so-called type-II packing mode of PEDOT ($100_{\text{type-II}}$) overlaps in position with the 200 peak for the type-I packing ($200_{\text{type-I}}$). Due to the relatively low doping efficiency of type-II, this process can be considered as a dedoping effect and can partially explain the increase in the Seebeck coefficient reported in Figure 2c,b.^[26] The driving force for the dedoping could be the strong interaction between SnO_x-NPs and the PSS⁻, which is normally combined with positively charged PEDOT⁺ by Coulombic interactions.^[27,28] The appearance of type-II PEDOT packing is paired by a shift in the peak position of the free PSS peak from 1.26 to $1.30 \text{ \AA}^{-1}$ after NPs incorporation, suggesting a concurrent change of PSS packing.

XPS spectra confirm the changes in the polymer blend observed by GIWAXS. In Figure 3e, the S2p core-level regions of the PEDOT:PSS:DMSO thin films without and with the SnO_x-NPs show clear differences. As commonly reported,^[29] the S2p signal of the PSS chains, is peaked at higher BE ($\approx 168.4 \text{ eV}$; Peak 1), than the one of PEDOT ($\approx 164.4 \text{ eV}$; Peak 2). Upon SnO_x-NPs incorporation, the ratio between the intensities of the PEDOT and the PSS S2p signals decreases from 1:2.1 to 1:3.2. This suggests that the amount of PSS in the topmost part of the thin film has increased upon NP deposition—taking into account the surface sensitivity of XPS (about 10 nm information depth for PEDOT:PSS for S2p and Al K α excitation as estimated from ref. [30,31]). This surface accumulation of PSS is the result of the interaction between PSS and the SnO_x-NPs, in line with the observation from GIWAXS. Fitting of the S2p core level spectra (shown in Figure 3d), discussed in Table S1, Supporting Information, reveals a third component ($\approx 166.1 \text{ eV}$; Peak 3) that can be attributed to S from highly doped PEDOT unit (labeled as PEDOT-S⁺).^[32,33] This indicates that the doping level of PEDOT in the hybrid system is slightly lower ($2 \pm 1\%$ PEDOT-S⁺) compared to the doping level in PEDOT:PSS ($8 \pm 1\%$ PEDOT-S⁺) and PEDOT:PSS:DMSO ($4 \pm 1\%$ PEDOT-S⁺). This is a confirmation of the dedoping process induced by the NPs and discussed above on the basis of the GIWAXS results.

To further verify the PSS migration towards the film/air interface in the thin films containing the NPs, GIWAXS patterns were acquired using two different incident angles (α_i), that is, two different penetration depths (see Figure S5, Supporting Information). The ratio between the free PSS and the

PEDOT π - π stacking peaks in the GISAXS linecuts along the q_z direction is higher when a $\alpha_i = 0.13^\circ$ is used (minimal penetration inside the film) with respect to $\alpha_i = 0.23^\circ$ (full film penetration), confirming the enrichment of PSS at the film/air interface as concluded from the XPS data. X-ray reflectivity (XRR) is then used to probe the vertical structure of the hybrid system as shown in Figure S6, Supporting Information. It can be clearly observed that there is a layer with higher electron density on the top region, the composition of which should be an enriched PSS phase (as verified by XPS) containing the SnO_x NPs. Compared with PEDOT:PSS:DMSO film, the hybrid system also shows a different electron density distribution at the film/air interface region, which indicates a restructuring of the film surface (even smoother) in line with our AFM observation.^[34] Besides, the lower electron density at the bottom part suggests that PSS migration on the top region of the film induces formation of a bottom region with more densely packed PEDOT crystallites, resulting in a more coherent carrier charge transport path. This positive effect on the electrical conductivity will compensate for the lowering in the doping level of the PEDOT chains,^[35] effectively limiting the drop in σ observed for PEDOT:PSS:DMSO:SnO_x-NPs (Figure 2b) and even enhancing slightly the conductivity in PEDOT:PSS:SnO_x-NPs (Figure 2a).

Another important aspect is that the incorporation of the SnO_x-NPs in the PSS enriched top layer implies the presence of phase boundaries acting as scattering centers, which allow only the high-energy charge carriers to go through.^[36] In addition, the PEDOT to PSS ratio decrease suggests a longer hopping length among the doped PEDOT crystallite, which can be considered as the increase of scattering center amount. According to the energy filtering theory, charge carriers with low energy contribute negatively to the Seebeck coefficient, and if the amount of low energy charge carriers is reduced, the Seebeck coefficient can be improved very effectively.^[36–38] This constitutes an additional important cause for performance improvements shown in Figure 2a,b. Our observations are in line with different works from the Ouyang group on energy filtering strategies applied to PEDOT:PSS based films, including blending with polyelectrolyte, ionic liquids, and even n-type MXene.^[39–41] Schemes of the morphology of the hybrid film and of the conduction contributing to the TE property enhancement are also included in Figure 3f.

3. Conclusion

In summary, we successfully created homogenous PEDOT:PSS/SnO_x-NPs hybrid thin films. SnO_x NPs generated using spark discharge, were deposited with low energy in *diffusion mode* onto the PEDOT:PSS surface. The NPs compose a p-type semiconductor and interact with PSS⁻, as shown by GIWAXS and XPS. The NP incorporation induces PSS migration toward the top surface of the films with subsequent structural modifications strongly impacting the TE properties of the thin films. The phase boundaries introduced by NPs and the prolonged hopping length act as scattering centers and thus cause the energy filtering of charge carriers. Together with the observed PEDOT dedoping, energy filtering effect well explains the

dramatically improved Seebeck coefficient (43 uV K^{-1}) for the PEDOT:PSS:DMSO:SnO_x-NPs thin film. Moreover, because of the induced phase separation, more coherent carrier charge transport paths are formed in the PEDOT-rich regions, which compensate for the dedoping effect and counteract the electrical conductivity drop. As a consequence of this structural reorganization mechanism, one of the highest PF ($116 \text{ uW m}^{-1} \text{ K}^{-2}$) for hybrid PEDOT:PSS-based thin films is achieved using this non-expensive and easy-to-implement method. Our results highlight the importance of the interactions between the polymeric components and the added NPs. The method proposed here avoids any extra steps such as chemical synthesis, post-treatment, or washing, which is very important for possible, future industrial large-scale production. In other words, the easy and not expensive deposition method presented here shows great potential in the production of high-performance flexible p-type TE materials. We are confident that this new strategy will inspire future research towards using simple physical NP production methods to improve properties of polymer for soft electronics and TE applications.

4. Experimental Section

Materials: PEDOT:PSS aqueous solution (Clevios PH1000) was purchased from Heraeus. DMSO (99.8%) was purchased from Sigma Aldrich.

Film preparation: The borosilicate glass substrates ($10.0 \text{ mm} \times 10.0 \text{ mm} \times 0.7 \text{ mm}$) were sequentially washed using detergent, acetone, and isopropanol with sonication. Then, the substrates were dried using a nitrogen gun and treated by UV-Ozone for 10 min. The thin films were prepared by spin-coating PH1000 or PH1000-5% DMSO solution on the borosilicate glass at 2000 rpm. These films were subsequently annealed on a hot plate for 10 min at 130°C and let cool down to room temperature. The film thickness (d) was $60 \pm 2 \text{ nm}$ as determined by AFM. For NPs fabrication, a spark discharging generator (VSP-G1) from VSPARTICLE B.V (Delft, Netherlands) was used. The generating current and voltage were kept as $I = 8.1 \text{ mA}$; $V = 1.3 \text{ kV}$, pure tin (provided by VSParticle, Delft) was used as the electrode and an inert atmosphere was achieved with a constant argon flow set at 10 L min^{-1} . As discussed in the main text, diffusion mode, where the substrates are placed parallel to the gas flow, was used to get homogeneously distributed NPs. Before starting the deposition, the system was allowed to run 30 min to let it stabilize and to remove the possible tin oxides on the surface of the electrodes. The deposition process over the substrate was homogeneous, as the whole deposition chamber is filled by a cloud of NP, as verified by COMSOL calculations performed by VSParticle. Thus any in-plane gradient of NPs on the surface of the sample can be excluded and was never noticed by SEM or AFM investigations.

Characterization of the Thin Films: Four-point-probe measurements were performed in an N₂-controlled environment. The electrical conductivity was calculated with the equation:

$$\sigma = \frac{1}{V} \times \frac{L}{w \cdot d} \quad (1)$$

where L is the channel length (1 mm), w is the channel width (4.5 mm), and d is the thickness of the active layer.^[42] The final electrical conductivity was obtained by averaging 4 devices. For the Seebeck coefficient measurements, the setup was kept the same as reported before.^[43] The surface morphology was investigated by tapping mode AFM performed on a Bruker AFM multimode MMAFM-2 equipped with an RTESPA-300 probe (resonant frequency 300 kHz , spring constant 40 N m^{-1} , Bruker). The height images and phase images were captured at a scan rate of 0.8 Hz and 640 points per line.

The data were analyzed with the Nanoscope Analysis 1.5 program (provided by Bruker). To determine the thickness, small scratches were made in the film using a very fine needle. The scan direction was set perpendicular to the scratch direction, to allow for the determination of the height of the scratch (and therefore the film thickness). SEM images were recorded in vacuum on an FEI NovaNano SEM 650 with an acceleration voltage of 5 kV . GIWAXS measurements were performed using a MINA X-ray scattering instrument built on a Cu rotating anode source ($\lambda = 1.5413 \text{ \AA}$).^[44] 2D patterns were collected using a Vantec500 detector (1024×1024 pixel array with pixel size 136×136 microns) located 102 mm away from the sample. The beam center was estimated using the known position of diffracted rings from standard Silver Behenate and $\alpha\text{-Al}_2\text{O}_3$ powders. The scattering vector q was defined with respect to the center of the incident beam and has a magnitude of $q = (4\pi/\lambda)\sin(\theta)$, where 2θ is the scattering angle and λ is the wavelength of the X-ray beam. Herein the authors opted to present the wedge-shaped corrected images, where q_{xy} and q_z are the in-plane and near out-of-plane scattering vectors, respectively. The scattering vectors are defined as follows:

$$q = \begin{cases} q_x = \frac{2\pi}{\lambda}(\cos(2\theta_f)\cos(\alpha_f) - \cos(\alpha_i)) \\ q_y = \frac{2\pi}{\lambda}(\sin(2\theta_f)\cos(\alpha_f)) \\ q_z = \frac{2\pi}{\lambda}(\sin(\alpha_i) + \sin(\alpha_f)) \end{cases} \quad (2)$$

where α_f is the exit angle in the vertical direction and $2\theta_f$ is the in-plane scattering angle, in agreement with standard GIWAXS notation. An incident angle $\alpha_i = 0.23^\circ$ was used for all the samples except for the probe of different penetration length discussed in Figure S6, Supporting Information, where a small incident angle $\alpha_i = 0.13^\circ$ was applied. GISAXS measurement was performed with a Vantec2000 detector (pixel size 68×68 microns) and sample-to-detector distance equaled to 3000 mm . Fit of the GISAXS horizontal intensity cut has been performed using the equation for a polydisperse ensemble of spherical objects. In order to successfully fit the curve and take into account for aggregation and size dispersion properly, two different spherical populations have been considered. A single population did not allow to fit the data properly. Log-norm distributions have been assumed.

The scattered intensity, in this case, is given by the sum of the intensities scattered by the two populations of NPs according to the equations

$$I(q_y) = A \left(\int_0^\infty N_1(R)P(q,R)dR + \int_0^\infty N_2(R)P(q,R)dR \right) \quad (3)$$

where $N_1(R)$ and $N_2(R)$ are the log-norm distribution functions for the first and second populations of particles, characterized by the location and width parameters μ and σ :

$$N(R) = \frac{1}{R\sigma\sqrt{2\pi}} \exp\left(-\frac{(\ln R - \mu)^2}{2\sigma^2}\right) \quad (4)$$

and $P(q, R)$ is the well-known form factor for a spherical object:

$$P(q,R) = \left(\frac{4}{3} \pi R^3 \Delta\rho^3 \frac{\sin(qR) - qR \cos(qR)}{(qR)^3} \right)^2 \quad (5)$$

$\Delta\rho$ is the contrast term, in this case, given by the difference of the electron density of the SnO_x NPs and the surrounding media (air). The constant A , contains several terms including instrumental factors as well

as the Fresnel transmission and reflection coefficients, that are constant at a fix q_z .^[45] The fit was achieved using MATLAB. In the data, evidence for significant spatial correlation between the NPs was not seen. This is plausible for the low concentration of the particles and the disordered aggregated that are formed (as visible in TEM). So, any structure factor here was not assumed.

XRR measurements were performed using a PANalytical X'Pert thin-film diffractometer (lab source with $\lambda = 1.541 \text{ \AA}$) in the 2θ range from 0.15° to 4.00° and a step size of 0.01° . Analysis of the XRR curves was achieved using the GenX software.^[46] A model composed of bulk Si, SiO₂ layer, PEDOT:PSS bottom interfacial layer, PEDOT:PSS mid bulk layer and PEDOT:PSS (or PEDOT:PSS:SnOx-NPs) top interface layer was successfully used to fit the experimental data. A model composed of only two polymeric layers was not able to describe the XRR curves.

For TEM measurements, the NPs were directly deposited onto the Cu grid. The morphologies were observed under a Philips CM120 Microscope coupled to a 4k CCD camera using an acceleration voltage of 120 kV.

XPS data were collected with a Surface Science SSX-100 ESCA instrument with a monochromatic Al K α X-ray source ($h\nu = 1486.6 \text{ eV}$). The measurement was done at a pressure below 5×10^{-9} mbar. The spot size was 1000 μm . For each sample, at least two different spots were measured; fitting results are averaged over these spots. The energy resolution was set to 1.26 eV and the electron take-off angle with respect to the surface normal was 37° . The spectra were analyzed using the least-squares curve-fitting program Winspec, developed at the LISE laboratory, University of Namur, Belgium. A Shirley background was used. BEs are reported with a precision of $\pm 0.1 \text{ eV}$ and referenced to the C1s peak at 284.6 eV.^[47,48] The S 2p core-level spectra shown in Figure S4, Supporting Information, were fitted with three Voigt doublets, each consisting of two Voigt lines with the same width, separated by 1.16 eV and with intensity ratio (0.511) due to spin-orbit splitting.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data available on request from the authors

Keywords

diffusion mode spark discharge generation, energy filtering effect, organic–inorganic hybrid system, PEDOT:PSS, thermoelectric material

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