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Supplementary Information

Enhanced thermoelectric performance of PEDOT:PSS/PANI-CSA polymer multilayer structures

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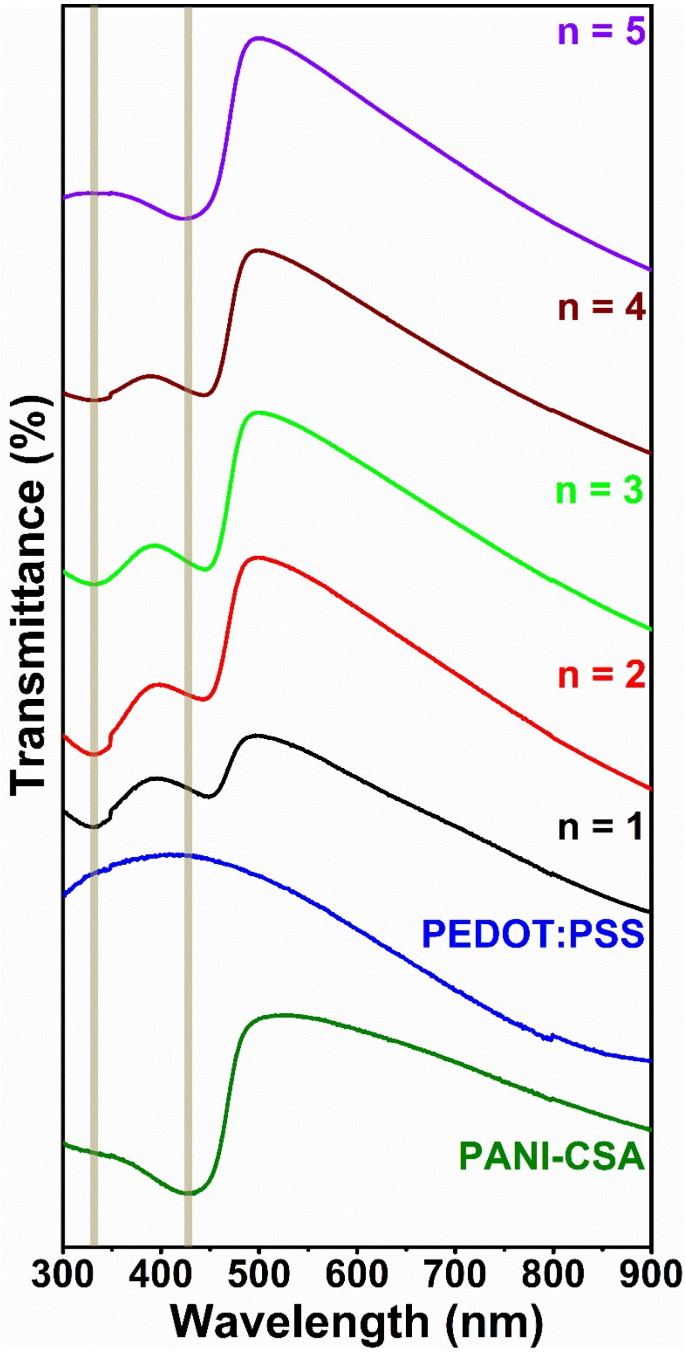

Figure S1. The transmission spectra of PANI-CSA, PEDOT:PSS films, and the corresponding multilayer films with repetition cycle of n in a range from 1 to 5.

The transmission spectra of PANI-CSA, PEDOT:PSS films and multilayer films are shown in the Fig. S1. The absorption edge of PANI-CSA is observed at 427 nm while PEDOT:PSS is entirely transparent in the wavelength ranged from 300 to 900 nm. As compared to the PANI-CSA film, the absorption edge in the spectra shift towards longer wavelengths in multilayer films indicating the stretching of the carbon chains in PANI [1].

In order to theoretically investigate the variation of thermoelectric (TE) properties of the PEDOT with stretching, we first carry out electronic structure calculations based density functional theory (DFT) using Vienna Ab-initio Simulation Package (VASP) [2]. The Kohn-Sham wave functions are expanded with 550 eV of plane wave cutoff, and local density approximation by Perdew and Zunger [3] is employed together with ultrasoft pseudopotential [4]. To obtain the transport coefficients such as σ and S, we consider the following function from Boltzmann transport equation (BTE) [5]:

$$L^{\alpha} = e^{2}\sum_{n}\int \frac{dK}{4\pi^{3}}\left(\frac{\partial f(\in_{n}(k))}{\partial \in_{n}(k)}\right)\tau(\in_{n}(k))V_{n}(k)V_{n}(k)[\in_{n}(k) - \mu]^{\alpha}. \tag{1}$$

Here, $\in_n(k)$ is the Kohn-Sham eigenvalue for the band index n at k, μ, the chemical potential, $f(\in_n(k))$ the Fermi-Dirac distribution function, and $V_n(k) = \left({}^{1}/_{\hbar}\right)\nabla_k \epsilon_n(k)$, the electron velocity, respectively, which are obtained from DFT calculations with 4354 irreducible k-points. To examine the effect of tensile strain on the TE properties of the PEDOT single crystal, the transport coefficients are computed with 1%, 2%, and 3% tensile strain along the polymer backbone as well as for strain-free case. The strain was applied on to the backbone of the crystalline PEDOT chains along the b-direction as shown in the Figure S2.

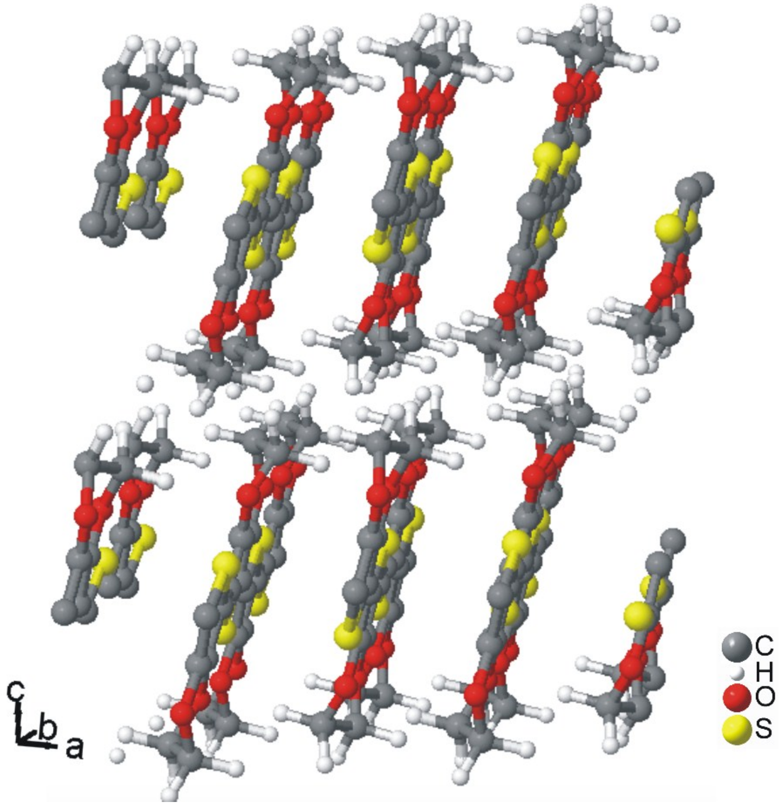

Figure S2. The structure of infinitely long PEDOT single crystal. In the polymer system, the strain is applied along *b*-direction and intra-chain electrical conductivity and Seebeck coefficient were calculated.

Lacking of the information of the relaxation time ($\tau(\in_n(k))$) of the polymer, only the relative values of σ and S with respect to those of the unstrained polymer are calculated within a constant relaxation time approximation. The theoretically obtained values are plotted in Fig. S3.

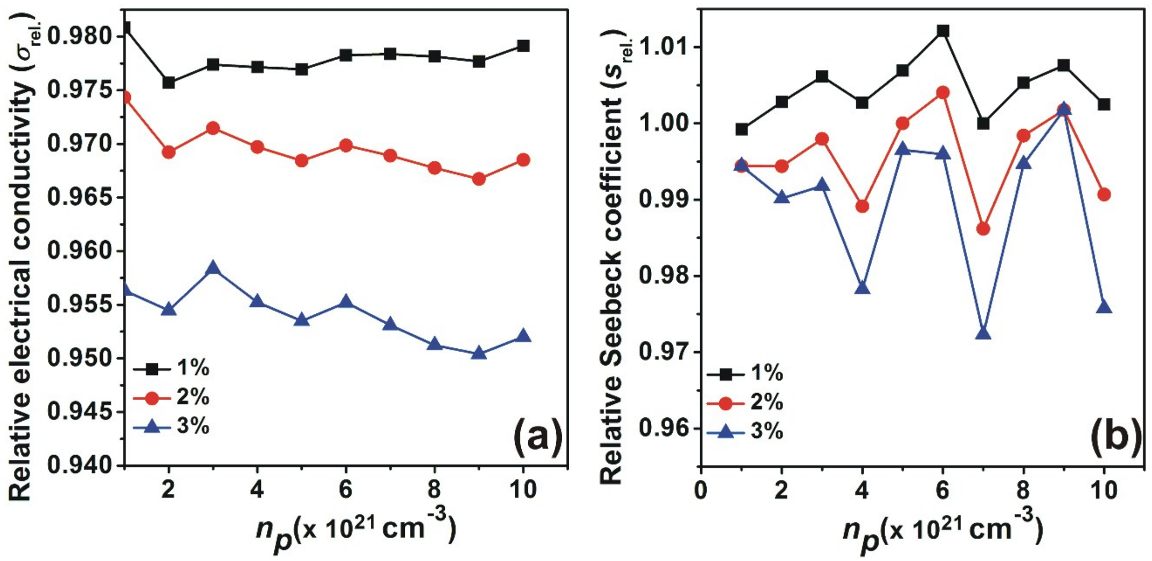

Figure S3. The variation of (a) relative electrical conductivity and (b) relative Seebeck coefficient as the function of hole concentration (n_p) of PEDOT chains under various strain applied along the polymer backbone.

It is apparent from the Fig. S3(a) that, with an increase in the strain, the relative conductivity (σ_{rel}) slightly decreases by less than 5%. This is contradictory to the trend of the σ which we obtained from the PEDOT:PSS/PANI-CSA multilayer systems. In our experiment, when the repetition cycle (n) was varied from 1 to 5, the PEDOT:PSS films show an increase in the σ (Fig.2 of the manuscript) along with the elongation of PEDOT backbone chain. The enhancement of σ in PEDOT:PSS films is attributed to various reasons such as increase in inter-chain interactions, conformational changes in PEDOT chains, and screening effects between polymer and dopant.[6] The enhancement in σ in our multilayer films is primarily due to the increase in inter-chain interactions and conformational variations from a coiled structure to linearly expanded structure along with the elongation of PEDOT backbone chain. As the chains stretch, an increased inter-chain interaction in the PEDOT:PSS occurs, which facilitates charge hoping among the PEDOT chains resulting in an enhanced σ. However, the theoretical values of σ were obtained for infinitely long, extended, and single crystal PEDOT chains which are already perfectly flat/stretched. An additional strain on the backbone of the crystalline polymer chain results in a decrease in σ due to the shrinkage of diameter and an increase in the scattering of the charge carriers.[7] Moreover, we have obtained the intra chain conductivity from the theoretical calculations. In our experiment, the as-deposited PEDOT:PSS thin films are amorphous (Fig. S4) and the chains are entangled. The electrical conduction in our films occurs through an inter-chain hopping of charge carriers between PEDOT chains and an increase in hopping of charge carriers occurs through flattening of the chains. Since, for the theoretical calculation, we considered single crystal PEDOT chains which are already flat/stretched, the inter-chain hoping conduction is not taken in to account.

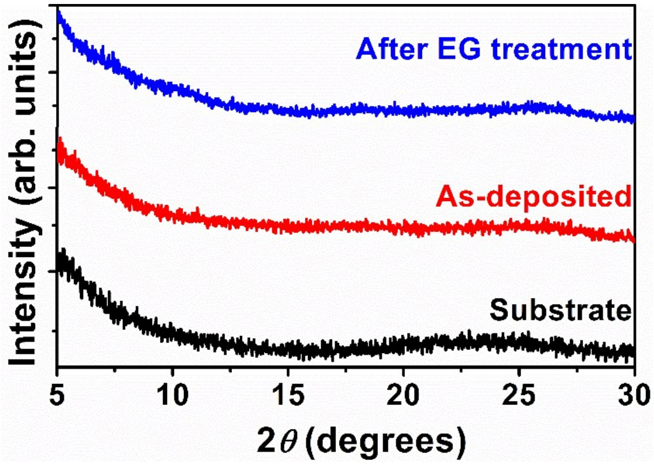

Figure S4. The XRD patterns of the glass substrate and PEDOT:PSS films before and after EG treatment. The XRD patterns show that the as-deposited and EG treated films are amorphous.

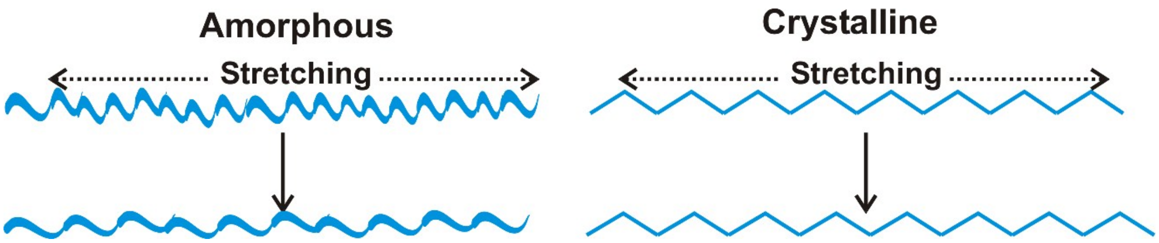

Figure S5. A schematic illustration of stretching in amorphous and crystalline PEDOT chains. As our deposited films are amorphous, stretching causes inter-chain hoping conduction which enhances the mobility and electrical conductivity of PEDOT:PSS films.

On the other hand, the experimental and the theoretical values of *S* remains almost constant in PEDOT:PSS films. The stretching/applied strain on the chains exhibits little impact on the Seebeck coefficient. We can express the σ as,

$$\sigma = pq\mu_p. \qquad (2)$$

Where p is the hole concentration, q is the electric charge and μ_p is the hole mobility

In terms of carrier concentration, the *S* can be represented as

$$S = \frac{\pi^2\kappa^2 m^* T}{(3\pi^2)^{2/3} hqn_p^{2/3}}. \qquad (3)$$

Where K is the thermal conductivity, m* is the effective mass, T the absolute temperature, h is the Planck's constant, p- hole concentration.

Doping in conjugated polymers results in increase in the carrier concentration, which consequently increases the σ, and decrease in the *S* value with respect to Eqs. (2) and (3). This is why the σ and *S* of polymers show opposite trend with doping. However, while the carrier concentration remains same and the σ is enhanced through an increase in the mobility (Eq.2), the

S value does not vary within 3% as the *S* has no direct relation with the mobility of the carriers (Eq.3). An enhancement in the mobility can be easily achieved through the stretching of polymer chains. This enhancement in the mobility results in the enhancement of σ while the *S* remains almost constant. Our experimental mobility values of single and multilayer PEDOT:PSS thin films are tabulated in Table 1. Due to the stretching of polymer chains, multilayer films have higher mobility than PEDOT:PSS single layer.

Table 1. Mobility of PEDOT:PSS and the corresponding multilayer films with n from 1 to 5.

Samples	**Mobility (10^{-2} cm^2/V·s)**
Multilayer (n=1)	4.66 ± 0.71
Multilayer (n=2)	5.89 ± 0.51
Multilayer (n=3)	5.40 ± 0.49
Multilayer (n=4)	6.13 ± 0.16
Multilayer (n=5)	6.51 ± 0.59
PEDOT:PSS single layer	2.76 ± 0.89

In PEDOT:PSS, due to high oxidation levels, mobility is considered as a quasi-constant with the carrier density (*N*), the *S* can be expressed as,

$$S \propto \left[\frac{d(\ln N(E))}{dE}\right]_{E = E_F}, \tag{4}$$

where *N*(*E*) is the number of particles with energy *E* and E_F is the Fermi energy. From Eq. 4, it is apparent that the *S* is primarily determined by the *E* dependence of the density of states.[8] As stretching or applied strain does not vary the density of states, the theoretical *S* value also remains almost constant. This suggests that by maintaining the value of *S*, the σ of the conducting polymers could be enhanced through a conformational variation from a coiled conformation to extended chain structure.

Reference

1. L. Wang, Q. Yao, H. Bi, F. Huang, Q. Wang and L. Chen, *J. Mater. Chem. A*, 2015, **3**, 7086-7092.
2. G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169-11186.
3. J. P. Perdew and A. Zunger, *Phys. Rev. B*, 1981, **23**, 5048-5079.
4. D. Vanderbilt, *Phys. Rev. B*, 1990, **41**, 7892-7895.
5. N. W. Ashcroft and N. D. Mermin, *Solid state physics*, Saunders College, 1976.
6. D. Alemu, H.-Y. Wei, K.-C. Ho and C.-W. Chu, *Energy Environ. Sci.*, 2012, **5**, 9662-9671.
7. H. X. He, C. Z. Li and N. J. Tao, *Appl. Phys. Lett.*, 2001, **78**, 811-813.
8. O. Bubnova, Z. U. Khan, H. Wang, S. Braun, D. R. Evans, M. Fabretto, P. Hojati-Talemi, D. Dagnelund, J.-B. Arlin, Y. H. Geerts, S. Desbief, D. W. Breiby, J. W. Andreasen, R. Lazzaroni, W. M. Chen, I. Zozoulenko, M. Fahlman, P. J. Murphy, M. Berggren and X. Crispin, *Nat. Mater.*, 2014, **13**, 190-194.