Electronic Supplementary Material (ESI) for Energy & Environmental Science.
This journal is © The Royal Society of Chemistry 2020

Electronic Supplementary Material (ESI) for Energy & Environmental Science.

This journal is © The Royal Society of Chemistry 2020

Supplementary Information

Computation-guided design of high-performance flexible thermoelectric modules for sunlight-to-electricity conversion

Shengduo Xu[a], Min Hong[b,a], Xiaolei Shi[b], Meng Li[a], Qiang Sun[a], Qixiang Chen[d], Matthew Dargusch[a], Jin Zou*[,a,c], Zhigang Chen*[,b,a]

Shengduo Xu, Min Hong, Meng Li, Qiang Sun, Matthew Dargusch, Jin Zou, Zhigang Chen

Materials Engineering, University of Queensland, Brisbane, Queensland 4072, Australia.

E-mail: Zhigang.Chen@uq.edu.au; j.zou@uq.edu.au

Min Hong, Xiaolei Shi, Zhigang Chen

Centre for Future Materials, University of Southern Queensland, Springfield central, Queensland 4300, Australia.

E-mail: Zhigang.Chen@usq.edu.au

Jin Zou

Centre for Microscopy and Microanalysis, University of Queensland, Brisbane, Queensland 4072, Australia.

Qixiang Chen

School of Energy Science and Engineering, Harbin Institute of Technology, 92 West Dazhi Street, Harbin 15001, China.

The *σ* evolution of the EG-H_2SO_4-treated PEDOT:PSS films

In the main context, we directly applied an ultrahigh *σ* of 4000 Scm^{-1} for the EG-H_2SO_4-treated PEDOT:PSS sample. Yet, the discussion about the *σ* evolution as functions of treatment duration and treating temperature is rare. Here, **Fig. S1a** shows the *σ* evolution of the EG-H_2SO_4-treated PEDOT:PSS films versus H_2SO_4 post-treatment duration and treating temperature. Notably, Notably, elevating the treating temperature yields higher saturated *σ*. As a result, an ultrahigh *σ* of about 4000 $S{\cdot}cm^{-1}$ was obtained. Besides, heating up the samples during the H_2SO_4 post-treatment would promote the evolution of the *σ*, and therefore the *σ* of the treated samples reached saturated faster under higher treating temperature. As can be seen, it took only 6 hours for the PEDOT:PSS films treated under 140 ℃ while the *σ* saturations of the other samples were delayed.

Fig. S1b shows the GI-XRD patterns of the EG-H_2SO_4-treated PEDOT:PSS treated at various temperature after 10 hours' H_2SO_4 treatment. Clearly, the higher treating temperature, the sharper the (100) characteristic peak becomes, indicating a more pronounced lamellar structure in the treated films. **Fig. S1c** shows the XPS patterns of the EG-H_2SO_4-treated PEDOT:PSS treated at 140 °C for different durations. As can be seen, the PSS-PEDOT ratio decreases as the films were treated for longer duration. After 6 hours' H_2SO_4 post-treatment, the PSS-PEDOT ratio reaches a constant value, indicating the limited removal effect of PSS, which is in line with the evolution of *σ* in **Fig. S1a**.

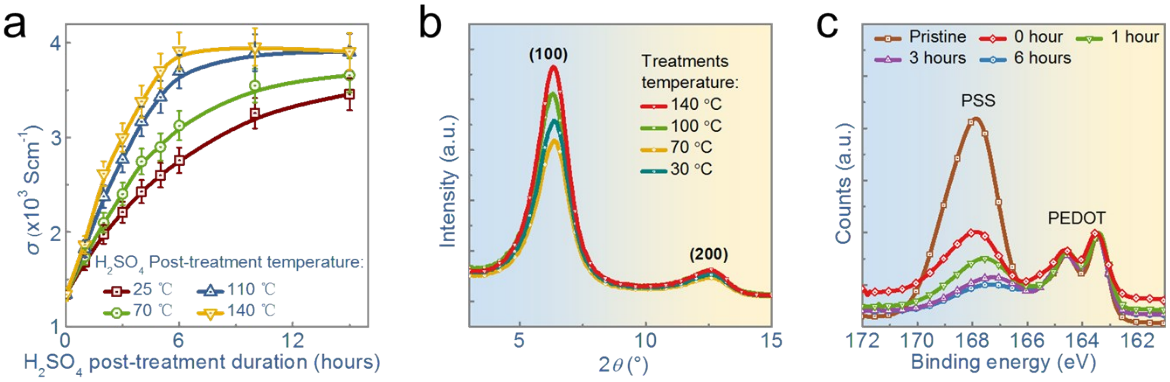

Figure S1 a) The σ evolution of the EG-H_2SO_4-treated PEDOT:PSS films versus H_2SO_4 post-treatment duration and treating temperature; b) GI-XRD patterns of the EG-H_2SO_4-treated PEDOT:PSS treated at various temperature after 10 hours' H_2SO_4 treatment; c) the XPS patterns of the EG-H_2SO_4-treated PEDOT:PSS treated at 140 °C for different durations.

Thermoelectric module assembling process

Fig. S2 shows the schematic diagrams of the assembling of a thermoelectric element consists of five pieces of as-treated PEDOT:PSS films and the thermoelectric module composed of five thermoelectric elements. Here we applied a silica aerogel substrate to contain as much heat as possible within the PEDOT:PSS films. Given the thermal conductivity of the silica aerogel is around 0.011 ~ 0.013 $Wm^{-1}K^{-1}$,[1] heat loss can only occur on one surface, as shown in **Fig. S3**.

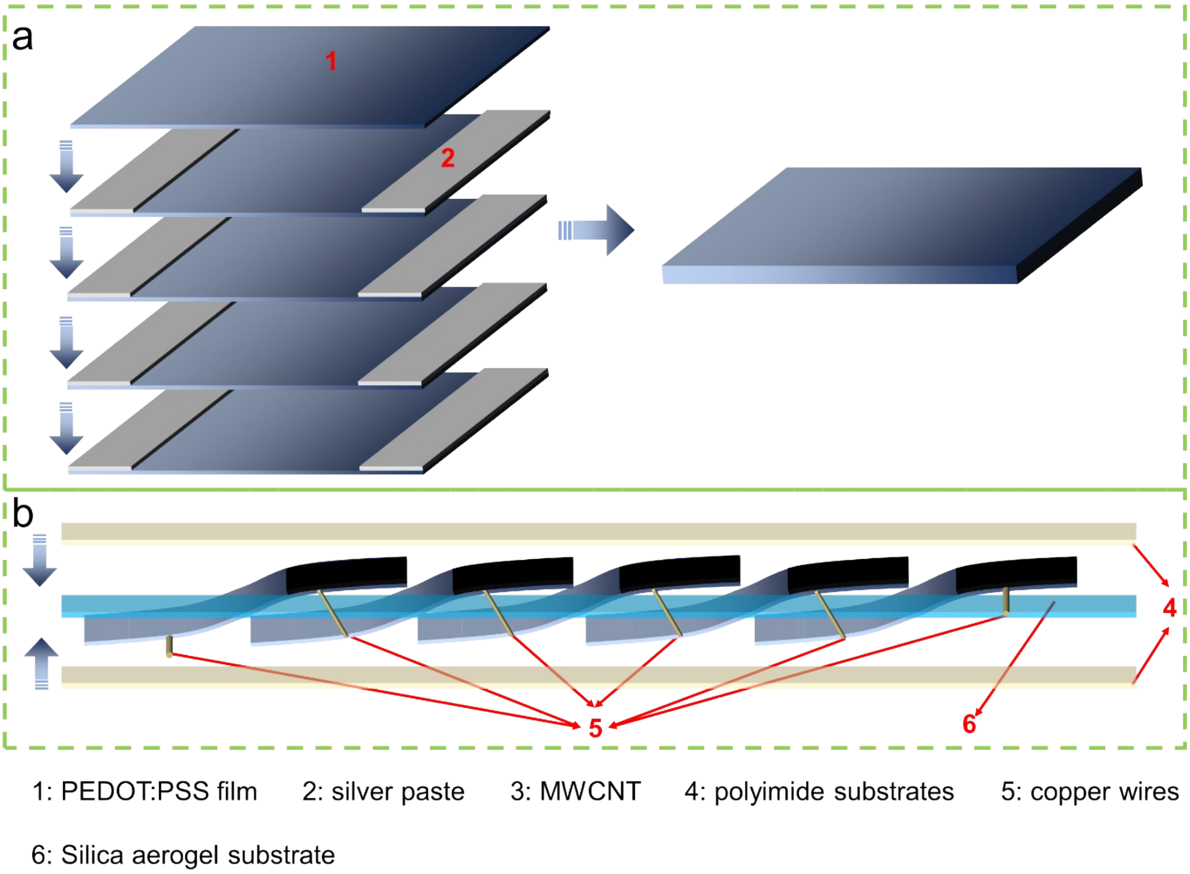

Figure S2 Schematic diagrams of a) assembling of a thermoelectric element consists of five pieces of as-treated PEDOT:PSS films; b) the thermoelectric module composed of five thermoelectric elements.

Thermal analysis for the PEDOT:PSS films

To theoretically obtain the temperature difference on the PEDOT:PSS films caused by the solar energy, a simplified model was built as shown in **Fig. S3**.

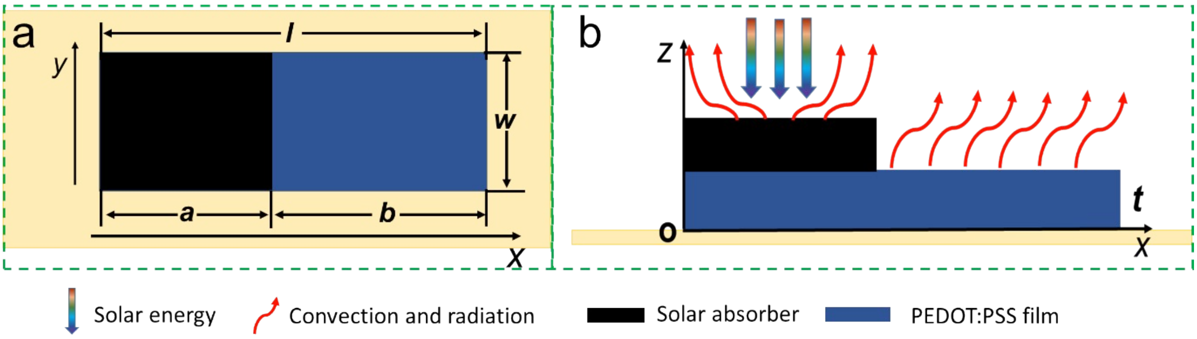

Figure S3 Schematic diagrams of a) vertical view and b) front view of a thermoelectric element.

Generally, the incident solar energy absorbed by the solar energy absorber elevates the film temperature until the balance between the absorbed energy and the energy loss by means of natural convection and thermal radiation is established. Such energy balance creates a thermal steady state for the films, yielding an energy conservation equation as following:

$$A_{abs}\int_{0.3\mu m}^{4\mu m}\alpha_{abs}(\lambda)E_{in}(\lambda)d\lambda$$
$$=\int_{0}^{a}wdx\int_{1\mu m}^{20\mu m}\varepsilon_{abs}(\lambda)\bigl[E_b(\lambda,T(x)) - \quad E_b(\lambda,T_{amb})\bigr]d\lambda + \int_{a}^{b}wdx\int_{1\mu m}^{20\mu m}\varepsilon_{film}(\lambda)\bigl[E_b($$

(S1)

where A_{abs} is the area of the solar energy absorber, λ is wavelength, $\alpha_{abs}(\lambda)$ is the spectra absorptivity of the absorber, $E_{in}(\lambda)$ is the incident solar radiative heat flux at air mass 1.5 (AM 1.5) on sea level, w and l are the width and length of the film, $\varepsilon_{abs}(\lambda)$ is the spectra emissivity of the absorber, $E_b(\lambda, T(x))$ and $E_b(\lambda, T_{amb})$ are the blackbody radiative heat flux at $T(x)$ and at ambient temperature, $\varepsilon_{film}(\lambda)$ is the spectra emissivity of the film and h is the natural convection coefficient. Notably, the left side term represents the incident solar energy absorbed by the absorber while three terms on the right side represent the energy loss. Specifically, the first and second term on the right side represent the thermal radiation heat exchange with the environment of the absorber and the uncovered segment of the PEDOT:PSS film, and the third term represents the heat transfer by natural convection. It is noteworthy that the output electricity should have been taken into consideration if there are external loads connecting with the device. However, given the device efficiency would be rather small, the output electricity is neglected when we analyze the heat transfer problem for the film. The following part will verify this assumption.

The analytical solution of the temperature distribution $T(x)$ in the energy equation can be obtained by solving the Fourier's heat transfer equation. In our case, several reasonable assumptions can be made to simplify the problem:

1. Adiabatic boundary condition for the lateral surfaces. This assumption is valid due to the negligible heat loss from the lateral surfaces;
2. Identical temperature for any position in the z direction. This assumption is valid as the dimensionless Biot number tends to 0:[2]

   $$Bi = \frac{th}{\kappa} = \frac{5 \times 10^{-6} \times 12}{0.5} = 1.2 \times 10^{-4}$$

   where t denotes the thickness of the film, h is the natural convection coefficient, here equals 10 $Wm^{-2}K^{-1}$, κ represents thermal conductivity in z direction of the film, here equals 0.5 $Wm^{-1}K^{-1}$.
3. In thermal steady state, the absorber temperature is identical with the temperature of the covered section of the film

With above assumptions, the problem can be described by a 1-D heat transfer equation:[3]

$$\frac{\partial^2 T}{\partial x^2} + \frac{s}{\kappa} = 0 \tag{S2}$$

where s represents the net energy produced within the film in unit time and unit volume. For section a:

$$s = \frac{(E_{in} - h_a(T - T_{amb})) \cdot y \cdot dx}{y \cdot z \cdot dx} = \frac{E_{in} - h_a(T - T_{amb})}{z} \tag{S3}$$

Set $\vartheta = (T - T_{amb})$, equation S2 can be re-wrote as:

$$\frac{\partial^2\theta}{\partial x^2}-\frac{h\theta}{\kappa z}=-\frac{E_{in}}{\kappa z} \tag{S4}$$

With boundary conditions:

$$\begin{cases} x=0, \dfrac{d\theta}{dx}=0 \\ x=a, \theta=\theta_a \end{cases} \tag{S5}$$

The general solution of equation S4 is given as:

$$\theta=C_1e^{m_ax}+C_2e^{-m_ax}+\frac{E_{in}}{h_a} \tag{S6}$$

where $m_a^2 = h_a/\kappa z$. By substituting boundary conditions into the general solution, the constants C_1 and C_2 can be obtained as:

$$C_1=C_2=\frac{\theta_a-E_{in}/h_a}{e^{m_a\cdot a}+e^{-m_a\cdot a}} \tag{S7}$$

Therefore, the temperature distribution in section a can be given as:

$$\theta_a(x)=\frac{\theta_a-E_{in}/h_a}{e^{m_a\cdot a}+e^{-m_a\cdot a}}\left(e^{m_ax}+e^{-m_ax}\right)+\frac{E_{in}}{h_a} \tag{S8}$$

For section b, the net energy produced within the film is given as:

$$s=\frac{(-h_b(T-T_{amb}))\cdot y\cdot dx}{y\cdot z\cdot dx}=\frac{-h_b(T-T_{amb})}{z} \tag{S9}$$

Equation S2 can be re-wrote as:

$$\frac{\partial^2\theta}{\partial x^2}-\frac{h_b\theta}{\kappa z}=0 \tag{S10}$$

With boundary conditions:

$$\begin{cases} x = a, \theta = \theta_a \\ x = L, \dfrac{d\theta}{dx} = 0 \end{cases} \qquad \text{S11}$$

Similarly, the general solution of equation S10 is:

$$\theta = C_1 e^{m_b x} + C_2 e^{-m_b x} \qquad \text{S12}$$

Where $m_b^2 = h_b / \kappa z$. By substituting the boundary conditions, the constant C_1 and C_2 can be obtained as:

$$\begin{cases} C_1 = \dfrac{\theta_a}{e^{m_b \cdot a} + e^{2m_b l} \cdot e^{-m_b \cdot a}} \\ C_2 = \dfrac{\theta_a e^{2m_b l}}{e^{m_b a} + e^{2m_b l} \cdot e^{-m_b a}} \end{cases} \qquad \text{S13}$$

Therefore, the temperature distribution in section b can be given as:

$$\theta_b(x) = \theta_a \frac{e^{m_b x} + e^{2m_b l} \cdot e^{-m_b x}}{e^{m_b a} + e^{2m_b l} \cdot e^{-m_b a}} \qquad \text{S14}$$

Notably, there is a common unknown variable in both equation S8 and S14, i.e. ϑ_a. To obtain this variable, the heat flow boundary condition is applied at the interface of section a and section b:

$$\frac{d\theta_a(x)}{dx}\Big|_{x=a} = \frac{d\theta_b(x)}{dx}\Big|_{x=a} \qquad \text{S15}$$

By substituting equation S8 and S11 into equation S15, ϑ_a is given as:

$$\theta_a = \frac{m_a E_{in} / h_a \cdot \left(e^{m_a a} - e^{-m_a a}\right) / \left(e^{m_a a} + e^{-m_a a}\right)}{m_a\left(e^{m_a a} - e^{-m_a a}\right) / \left(e^{m_a a} + e^{-m_a a}\right) - m_b\left(1 - e^{2m_b b}\right) / \left(1 + e^{2m_b b}\right)} \qquad \text{S16}$$

Where $h_a = h_{con} + h_{rad}^{a}$, here h_{con} represents the natural convection coefficient and h_{rad}^{a} is the effective convection coefficient resulted from the thermal radiation heat transfer given by the following equation:

$$\varepsilon_{abs}\sigma\left(T_{abs}^{4} - T_{amb}^{4}\right) = h_{rad}^{a}(T_{abs} - T_{amb}) \qquad \text{S17}$$

Where ε_{abs} is the spectra emissivity of the absorber and equals 1, σ is the Stefan constant, equals 5.67×10^{-8} $W\cdot m^{-2}\cdot K^{-4}$, T_{abs} is the absorber temperature. We assume that T_{abs} is around 360 K, 60 K higher than the ambient temperature, then the effective convection coefficient equals 8.21 $W\cdot m^{-2}\cdot K^{-1}$. Similarly, $h_b = h_{con} + h_{rad}^{b}$, however, due to the ultra-high thermal resistance in x direction within the film, the h_{rad}^{b} is assumed to be identical as the ambient temperature. Therefore, $h_b = h_{con}$. Besides, to obtain m_a and m_b, the determination of κ is necessary. According to previous report, the in-plane κ of the film is around 0.3~0.5 $Wm^{-1}K^{-1}$, hence we set κ to be 0.5 $Wm^{-1}K^{-1}$. Interestingly, altering the value of κ doesn't impact the temperature difference of the film, as shown in **Fig. S4**, which can be explained by the energy equation S1 (there is no term containing κ, meaning that the steady state is unrelated with κ).

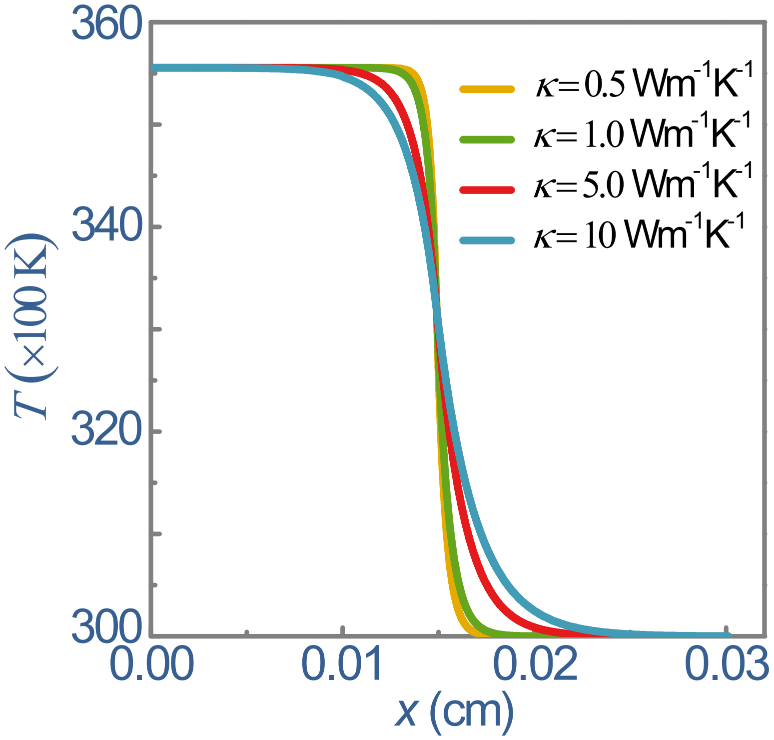

Figure S4 The temperature distributions on PEDOT:PSS films with various assumed *κ*

Performance discussion of two connection models

In this section, the performances of two connection models composed of the EG-H_2SO_4-TDAE-treated PEDOT:PSS films are investigated, as shown in **Fig. S5**. Here the width and the length of the substrate are *W* and *L* respectively. In an ideal situation, the films sit one by one firmly. Therefore, in x direction, there are *W*/*w* pieces of films and *L*/*l* pieces of films.

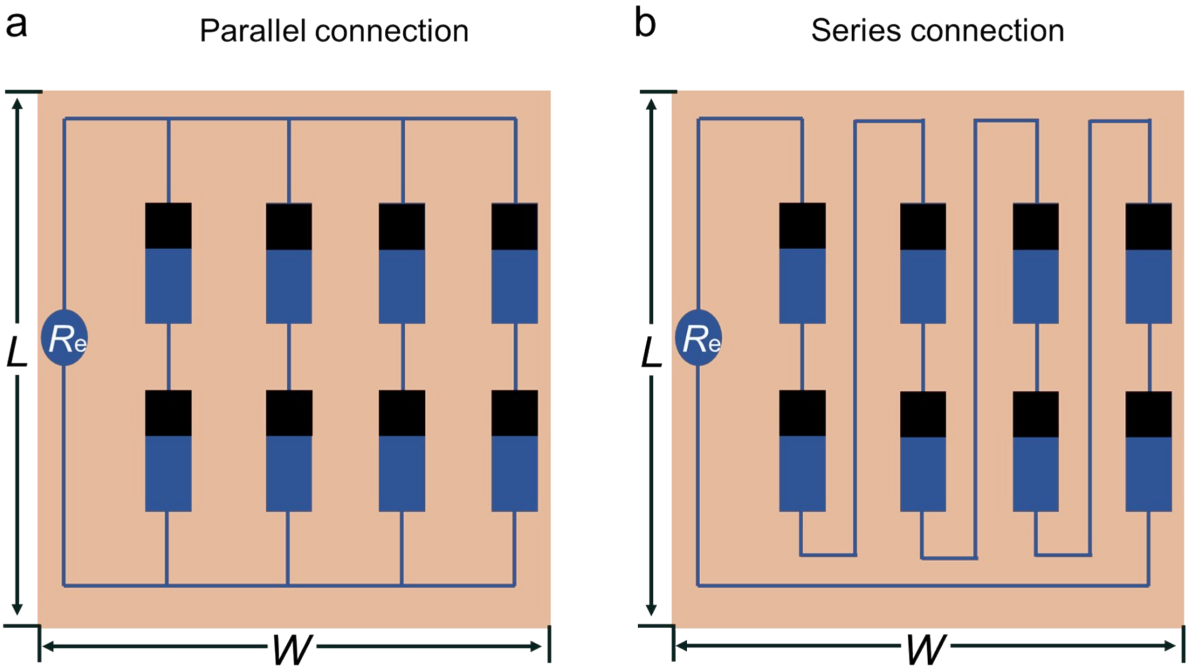

Figure S5 Schematic diagrams of a) parallel connection model and b) series connection model.

For parallel connection model, the open circuit voltage induced under certain temperature difference ΔT is given as:

$$V = S\Delta T\frac{L}{\beta l} \tag{S18}$$

where β is the area ratio between the absorber and the entire film. The overall internal resistance is:

$$R_P = \frac{(L/\beta l)\ R_f}{W/w} = \frac{(L/l)\quad l}{W/w\sigma wt} = \frac{L}{\beta W\sigma t} \tag{S19}$$

where R_f represents the resistance of each film

The output power is maximized when the external resistance equals the overall internal resistance, i.e.:

$$P_m = \frac{V^2}{4R_P} = \frac{S^2 \Delta T^2 \frac{L^2}{\beta^2 l^2}}{\frac{4L}{\beta W \sigma t}} = \frac{S^2 \sigma W L t \Delta T^2}{4\beta l^2} = \frac{PFWLt\Delta T^2}{4\beta l^2} \tag{S20}$$

Similarly, for the series connection model, the open circuit voltage induced under certain temperature difference ΔT is given as:

$$V = S\Delta T \frac{L}{\beta l} \cdot \frac{W}{w} \tag{S21}$$

The overall internal resistance of the model is:

$$R_S = R_f \frac{L}{\beta l} \cdot \frac{W}{w} = \frac{l}{\beta \sigma w t} \frac{L}{l} \cdot \frac{W}{w} = \frac{LW}{\beta w^2 \sigma t} \tag{S22}$$

The output power is maximized when the external resistance equals the overall internal resistance, i.e.:

$$P_m = \frac{V^2}{4R_S} = \frac{S^2 \Delta T^2 \frac{L^2 W^2}{\beta^2 w^2 l^2}}{\frac{4LW}{\beta w^2 \sigma t}} = \frac{S^2 \sigma W L t \Delta T^2}{4\beta l^2} = \frac{PFWLt\Delta T^2}{4\beta l^2} \tag{S23}$$

Interestingly, the maximum output powers of both models are identical. Besides, the maximum output power of the model is related to the power factor and the volume of the PEDOT:PSS films used, the temperature difference and the length of each film. Decreasing the length of each film can significantly improving the maximum output power. As discussed in the main text, the smallest length of each film is the transition length Δx. Therefore, the largest maximum output power density can be given as:

$$p_m = \frac{P_m}{WL} = \frac{PFt\Delta T^2}{4\beta\Delta x^2} \tag{S24}$$

In this study, the absorber area equals the area of the uncovered PEDOT:PSS segment, i.e. β equals 0.5. As a result, equation S24 can be simplified as:

$$p_m = \frac{P_m}{WL} = \frac{PFt\Delta T^2}{2\Delta x^2} \tag{S25}$$

References

1. G. Wei, Y. Liu, X. Zhang, F. Yu and X. Du, *Int. J. Heat Mass Transf.*, 2011, **54**, 2355-2366.
2. A. S. M. Omini, and A. Strigazzi, *Appl. Phys. A*, 1990, **50**, 35-37.
3. J. A. López Molina, M. J. Rivera and E. Berjano, *P Roy. Soc. A-Math Phy.*, 2014, **470**, 20140547.