Supplementary Information

The potential of perovskite solar cell-thermoelectric tandem devices

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Method:

The simulation process involved in model is presented in Fig. S1, through which we can obtain steady-state temperature T_D and PCE.The device structure is needed for optical model. Besides, the temperature of environment and cold source, solar spectrum must be given for simulation.

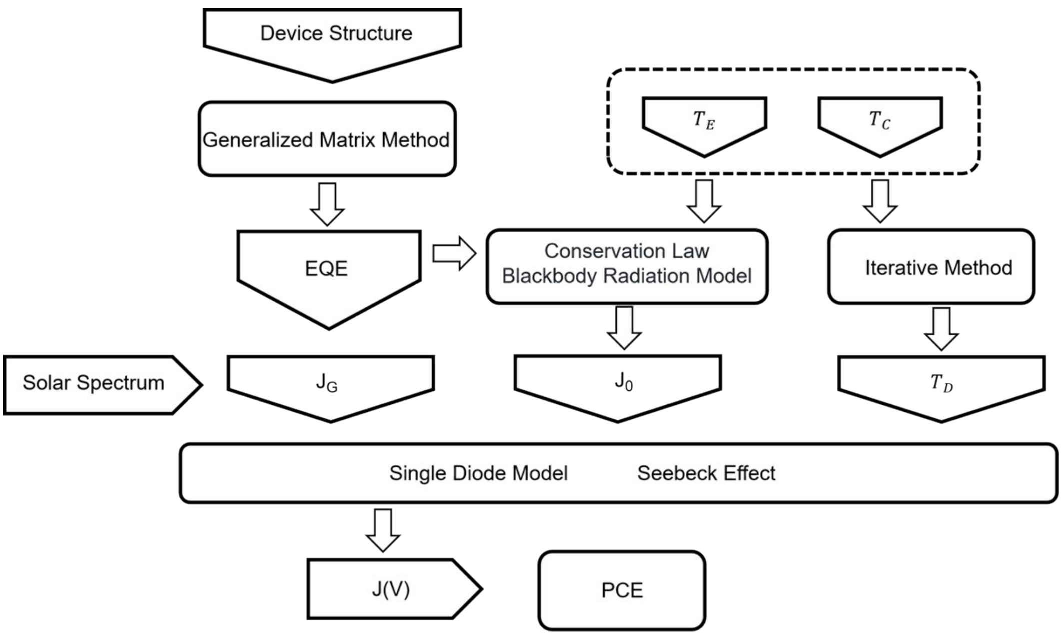

Fig. S1. Illustration of simulation process.

The non-ideal diode model that the current density (J) can be described as:

$$J = J_G - \frac{V + J \times R_s}{R_{sh}} - J_0 \times \left(exp\left(\frac{q \times (V + J \times R_s)}{nKT} \right) - 1 \right) \quad (1)$$

Where R_s is series resistance, R_{sh} is parallel resistance corresponding to p-n junction leakage current, *K* is the Boltzmann constant, *T* is device temperature, *V* is biased voltage of device, J_0 is the saturation current related to recombination, and n=1 as ideality factor [1]. And we can calculate J_G from:

$$J_G = \int_0^{+\infty} EQE(\lambda, d_i)\phi_{sun}(\lambda)d\lambda \quad (2)$$

In the equation, EQE is a function of light wavelength λ and film thickness d_i, ϕ_{sun} is photon flux spectrum of the sun on earth. It's a function of λ. For the sake of judgement, and to be more representative, we use AM1.5G(1000W/m^2) spectrum in the model. While J_0 can be given by a more complex equation:

$$J_0 = \frac{J_{0,rad}}{PLQY} + \left(\frac{eD_pP_{n0}}{L_p} + \frac{eD_nP_{pn}}{L_n} \right) \quad (3)$$

$J_{0,rad}$ is radiative part, PLQY can be defined by: $PLQY = \frac{J_{0,rad}}{J_{0,rad} + J_{non,rad}}$, $J_{non,rad}$ is nonradiative part, the second term on the right is about carrier diffusion in the device. Compared to the first term, the second term is too small to be ignored. And PLQY measured from experiment is almost equal one. Radiative recombination will release photons to the outside, the amount of that will equal to that of blackbody radiation to device. So,

$$J_0 = \int_0^{+\infty} EQE(\lambda, d_i)\phi_{BB}(T, \lambda)d\lambda \quad (4)$$

ϕ_{BB} is photon flux spectrum of blackbody radiation, it totally depends on the temperature. The voltage of PSC: V, is limited by the open-circuit voltage (V_{oc}).

$$V_{oc} = \frac{KT}{q} ln\left(\frac{J_G}{J_0} \right) \quad (5)$$

Up to now, we can calculate the PCE of PSC according to:

$$PCE = \frac{(V \times J)_{max}}{P_s} = \frac{\left[V \times \left(J_G - J_0\left[exp\left(\frac{qV}{kT} - 1\right)\right]\right)\right]_{max}}{P_s} \tag{6}$$

P_s is power of sun radiation. Couple with efficiency of TE device, we can get total PCE of tandem system. And efficiency of TE device can be calculated from equation according to Seebeck effect. A sketch map of Seebeck effect can be seen in Fig. 1(b).

$$Efficiency = \frac{\left[V \times \left(J_{sc} - J_0\left[exp\left(\frac{qV}{KT}\right) - 1\right]\right)\right]_{max} + P_{H-C} \times \frac{T_H - T_C}{T_H} \frac{\sqrt{1+ZT}}{\sqrt{1+ZT} + \frac{T_C}{T_H}}}{P_s} \tag{7}$$

Here P_{H-C} is the heat transport from hot side to cold side, T_H is the temperature of hot side, T_C is the temperature of cold side, T is the average temperature, and Z is a constant about device given by $Z = \frac{\sigma S^2}{\kappa}$, σ is electrical conductivity, κ is thermal conductivity and S is Seebeck constant. Next, we will calculate P_{H-C} and T_H in another part of model while other parameters are given. Coupled the equations with given environment temperature and iterative method, the steady-state temperature can be got.

Next part of model is what we called heat dissipation model, which is based on two hypothesizes. In the absence of thermoelectric devices, solar cells mainly dissipate heat through thermal radiation [2]. In the presence of a TE device and a cold source, the system dissipates heat both through thermal radiation and heat conduction, as schematically illustrated in Fig. 1(c, d and e).

First, we consider a much simpler situation, for example, just a PSC (as show in Fig. 1(d)). According to blackbody radiation equation $q = \sigma T^4$, we can get heat balance equation in such condition:

$$E_{heatPSC}(T_{PSC}) = 2 \times \left(\sigma {T_{PSC}}^4 - \sigma {T_0}^4\right) \tag{8}$$

Where $E_{heatPSC}$ is the low-grade heat generate by PSC, T_{PSC} and T_0 are temperature of PSC and surrounding environment sequentially.

Next, we move on to the condition of tandem system, as show in Fig. 1(e). Different from the perovskite single junction system, there exist heat conduction in a

PSC-TE tandem system, the equation can be given as $q = -\kappa\frac{\Delta T}{\Delta X}$ .Combine it with blackbody radiation equation and conservation of energy equation, we can get an equation set:

$$T_1 - T_2 = Q_1\sum_i\frac{\Delta X_i}{\kappa_i} = Q_1\beta_1 \tag{9}$$

$$T_2 - T_{cooling} = Q_2\sum_i\frac{\Delta X_i}{\kappa_i} = Q_2\beta_2 \tag{10}$$

$$E_{heatPSC} = Q_1 + \sigma T_{PSC}{}^4 - \sigma T_0{}^4 \tag{11}$$

$$E_{heatSSA} = Q_2 - Q_1 \tag{12}$$

Where T_1 is the temperature of PSC, T_2 is the temperature of photothermal film, Q_1 is the heat transport from perovskite materials to photothermal film, β_1 is $\sum_i\frac{\Delta X_i}{\kappa_i}$ representing any relevant parameters of the buffer layers between two the perovskite and SSA films, i.e. C60/ITO in our case, Q_2 is the heat transport from photothermal film to cold source, β_2 represent buffer layer between the two parts, i.e. the TE device. Besides, $E_{heatPSC}$ and $E_{heatSSA}$ can also calculate from the method of GMM and single diode model. Thus, we can get Q_1, Q_2, T_1, T_2 from equation set.

Actually, the buffer layer between perovskite active layer and photothermal film always only include C60 and ITO, with thickness of nanoscale. But between photothermal film and cold source was TE materials, which always involve P/N particles, the thickness of that always at millimeter scale. So, we always have inequation $\beta_2 \gg \beta_1$. As a result, the whole system can be simplified as:

$$E_{heatPSC} + E_{heatSSA} = \frac{T - T_{cooling}}{\beta_2} + \left(\sigma T^4 - \sigma T_0{}^4\right) \tag{13}$$

, where T1 and T2 is identical and we use a unified T to represent the temperature of the PSC/SSA. Obviously, since both the PCE and $E_{heatPSC}$ are a function of T, it is a complex equation, we cannot get the result directly. We therefore chose iterative method instead to solve the equation.

First, we apply the temperature of environment as the temperature of device to calculate $E_{heatPSC}$, and applied $E_{heatPSC}$ in equation above to calculate device temperature T. After that, we use the T we get as a new device temperature to repeat the calculation. Continue the circle until we get a device temperature with constant two decimal places. A presentation of the method can be seen in Fig. 1(f).

To assess the reliability of the model, we introduce the application in ideal situation (EQE is step function) to support the model and discuss about the performance of device under ideal situation. First, we introduce the model to calculate the energy yield by PSCs with specific band gap, as show in Fig. S4(a). Obviously, it fits the famous S-Q limit very well. We can also show the PCE of the tandem device having different band gaps of the perovskite photoactive layer with different device temperatures (T_D) and with a room temperature (300 K) environmental temperature (T_E), as show in Fig. S4(b) and Fig. S4(c). All the data above are in good agreement with the reported results in literatures. Calculated efficiency curve has the maximal PCE of 33.7% at the energy gap of about 1.34 eV when the T_D is 300 K, and the efficiency curve changes as the temperature of device various. Lower temperature means lower recombination current, thus induce an overall increase in efficiency, achieving 40.3% at 250 K.

Actually, with the exist of radiative recombination, the T_D will be somewhat higher than T_E. And the temperature can be determined by the equation: $E_{heatPSC} = 2 \times \sigma(T_{PSC}^4 - T_0^4)$, where the value on the left side of equation represent heat released from the device, σ is the Stepan-Boltzmann constant ($5.67 \times 10^{-8} W/m^2K^4$), T_{PSC} is the temperature of device and T_0 is the temperature of surroundings. According to Fig. S4(c), the solar cells with energy gap from 1 eV to 1.8 eV have a temperature range from 60 °C to 40 °C, this in line with the reality, or might be higher, for the solar cell always be put in the cold table with a certain thermal conductivity. We can also conclude from Fig. S4(c) that decreasing band gap leads to increasing temperature which can be detrimental to device performance. This phenomenon attribute to the heat released from the absorption of high frequency photon, so the energy gap of the top cell can't be too narrow. This can be instructive result for the energy gap combination of the tandem solar cells. Besides, we can see that even the temperature of solar cell with the energy gap of 1.4 eV would maintain above 50 °C, that's a pretty high temperature, which is harmful to the device. And the use of thermoelectric device can make use of low-grade heat, low down the temperature and thus strengthen the stability of the device.

We can see the influence that thermoelectric device brings to the energy generate system in Fig. S4(c and d). In this case, we add photothermal film and thermoelectric device to form a system, as show in Fig. 1(a). The value of β_2 here is used in the parameters of the *SEGRET TEG-12708*, which uses BiTe as the P/N particle material, and the thermal conductivity: $k = 0.5Wm^{-1}K^{-1}$, thickness: $\Delta x = 4mm$, then β_2 is $0.008m^2KW^{-1}$. We put device in a 300K environment, and temperature of cold source is 273.15K. We can infer from Fig. S4(c) that the steady state temperature of device goes through a sharp decrease to below 10 ℃, which is much more friendly to long-time stability of PSC. According to Fig. S4(d), the tandem of TE device help device to break through Shockley–Queisser limit, with efficiency up to 38.4%. And the data implies that the promotion of PCE are the contribution of both PCE of TE device itself and the promotion of PSC's PCE introduced by TE device. Just in the ideal situation, we can have a rudimentary look of PSC-TE tandem system's great potential in efficiency and stability. These advantages could decrease the non-module costs, which take up a great percentage in the costs of perovskite PV.

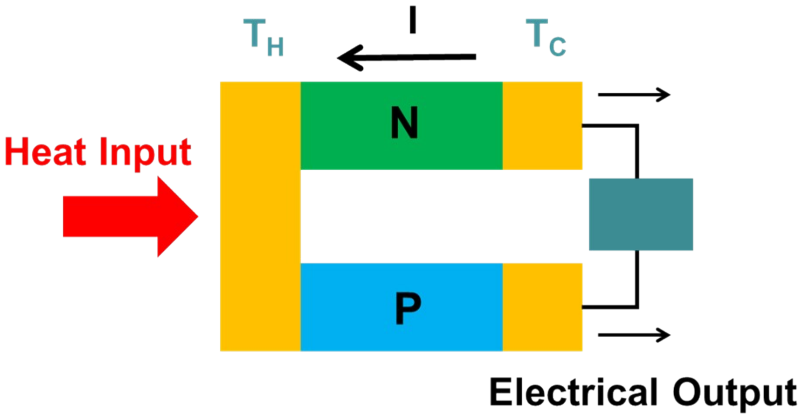

Fig. S2. Illustration of Seebeck effect.

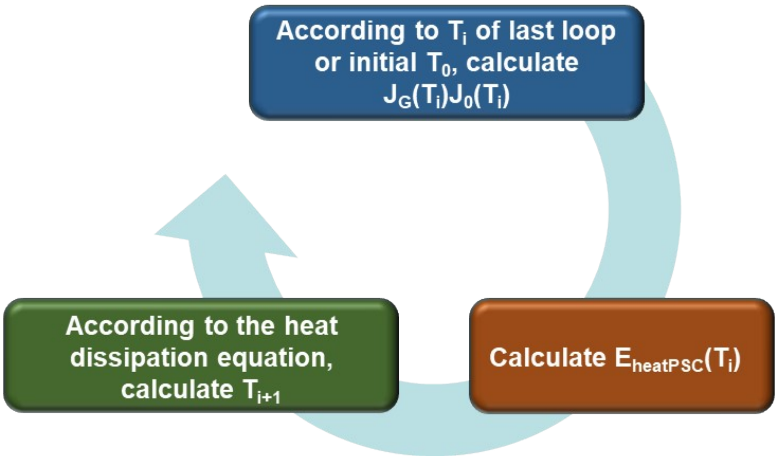

Fig. S3. Illustration of iterative method applied in simulation to calculate device temperature.

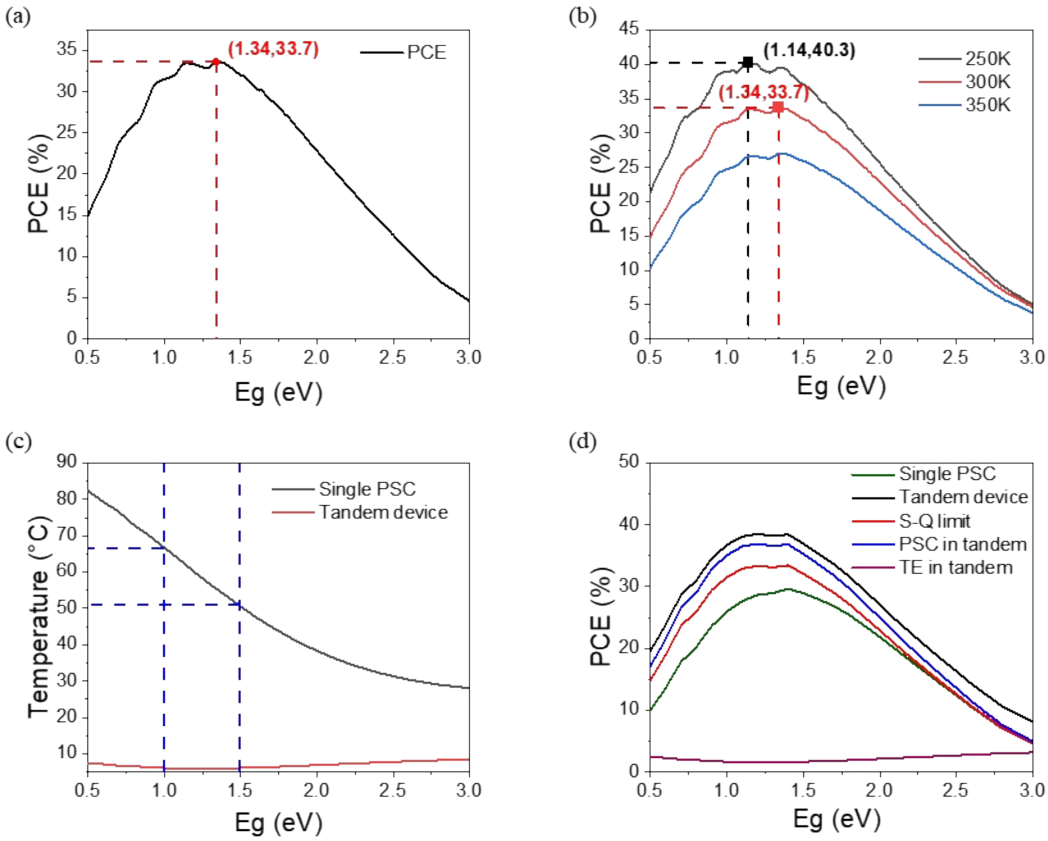

Fig. S4. (a) PCE-Eg curve while device temperature is 300K. (b) PCE-Eg curve while device temperature is 250K, 300K, 350K, as the temperature increase, uplift of J_0 caused the decrease of PCE. (c) Steady-state temperature of single PSC and PSC-TE tandem device in room temperature (300K), temperature of cold source is 273.15K. (d) PCE-Eg curve of different device or part of device, while T_E=300k, T_C=273.15K.

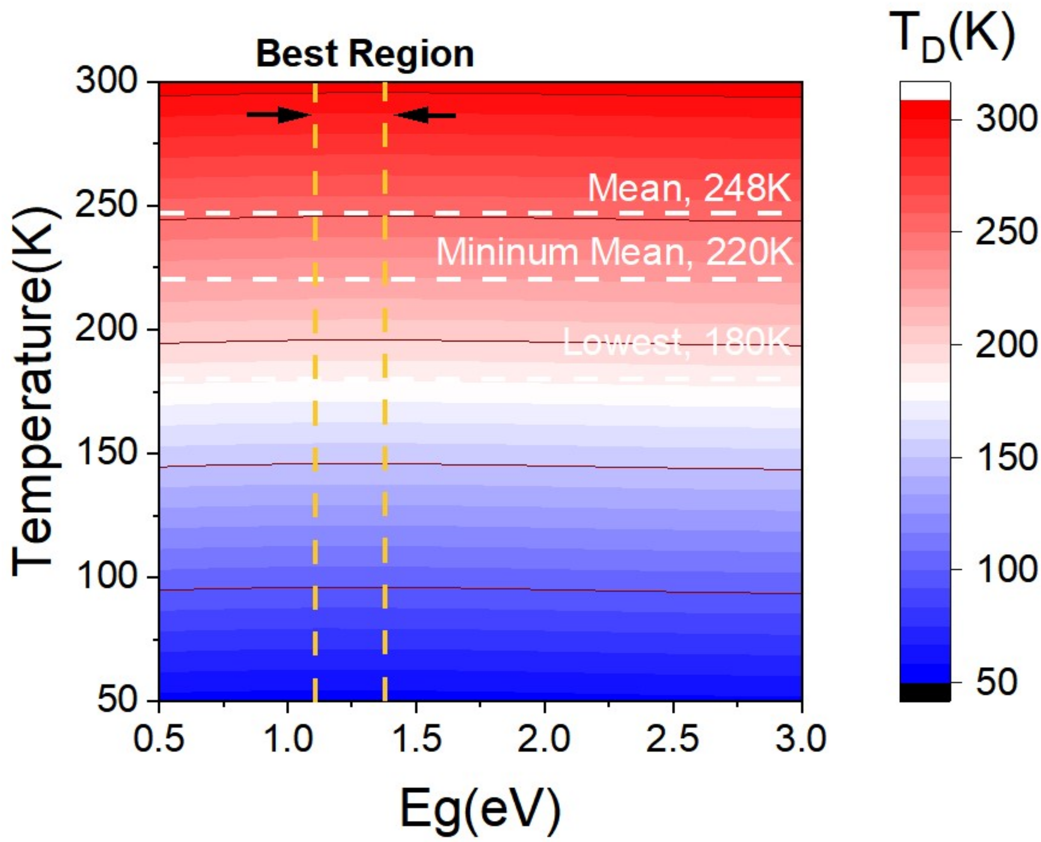

Fig. S5. The steady-state T_D of PSC-TE tandem system with different Eg and T_E, T_C in Antarctic region. T_E=T_C and varying according to y-axis.

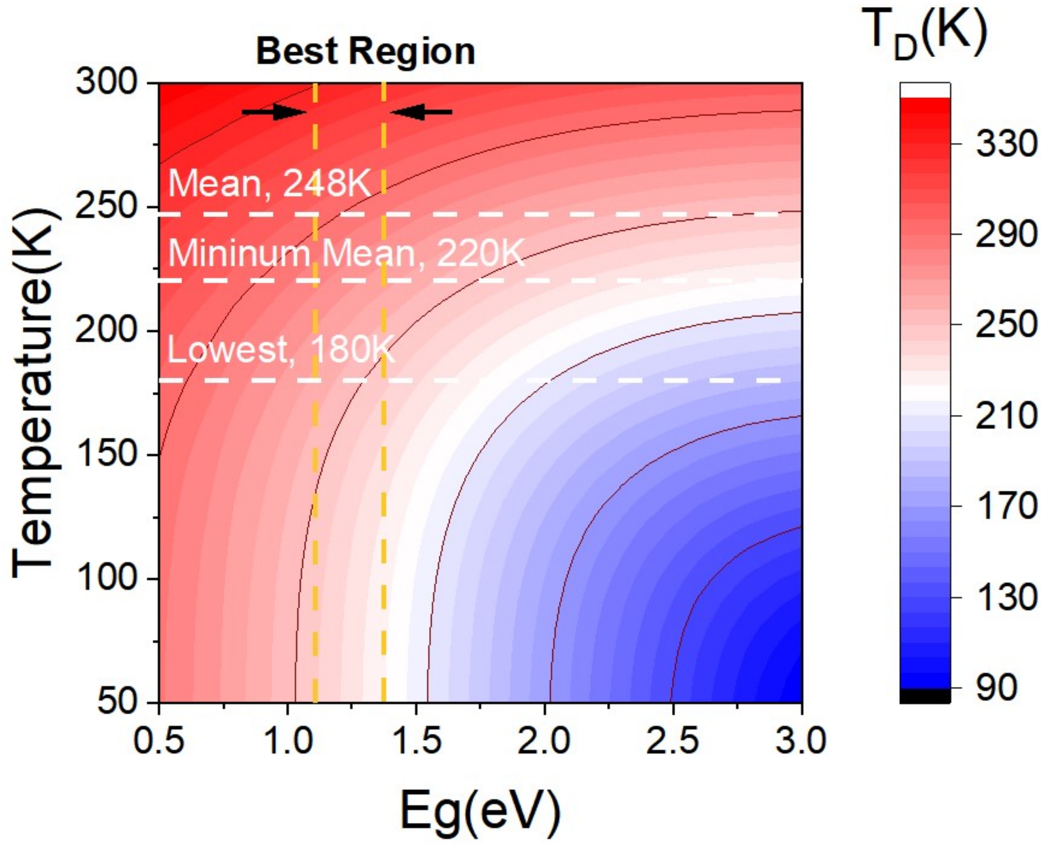

Fig. S6. The steady-state T_D of single-junction PSC with different Eg and T_E, T_C in Antarctic region. T_E=T_C and varying according to y-axis.

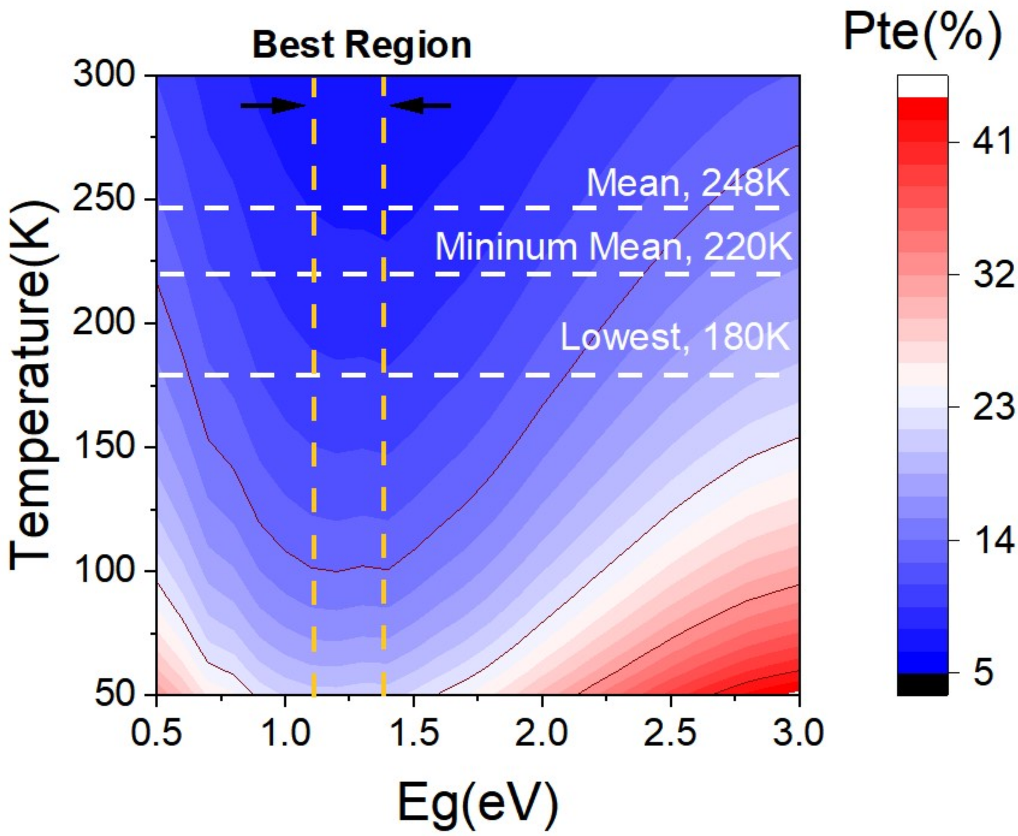

Fig. S7. The PCE of TE device in concentrated PSC-TE tandem system in Antarctic region. Pte denotes the PCE of TE device. T_E=T_C and varying according to y-axis.

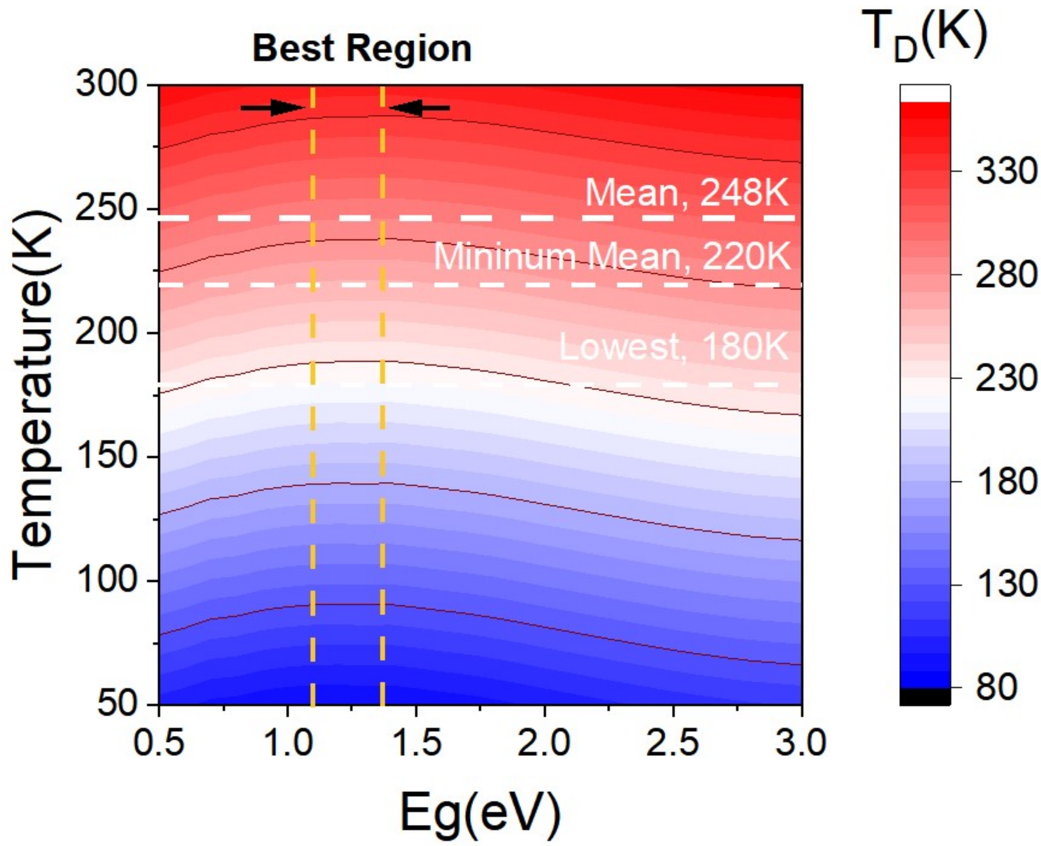

Fig. S8. The steady-state T_D of concentrated PSC-TE tandem system. T_E=T_C and varying according to y-axis, concentrating factor = 10.

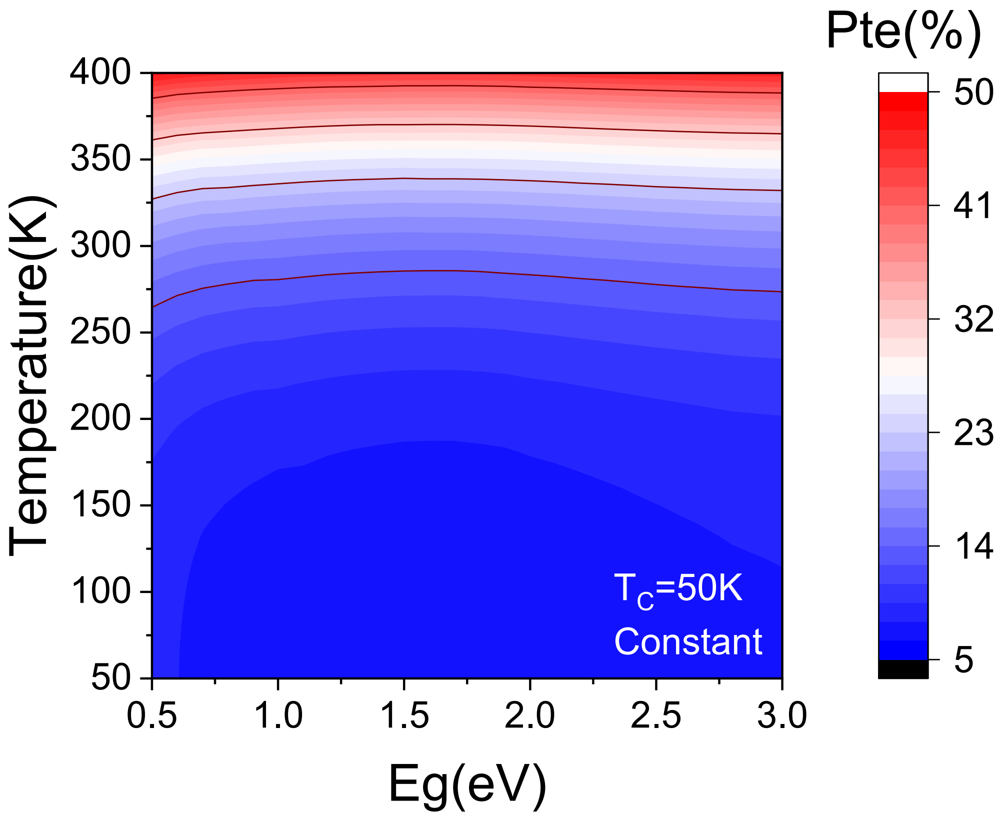

Fig. S9. PCE of TE device in space. T_C=50K as a constant, while T_E varying according to y-axis. And Pte denotes the PCE of TE device.

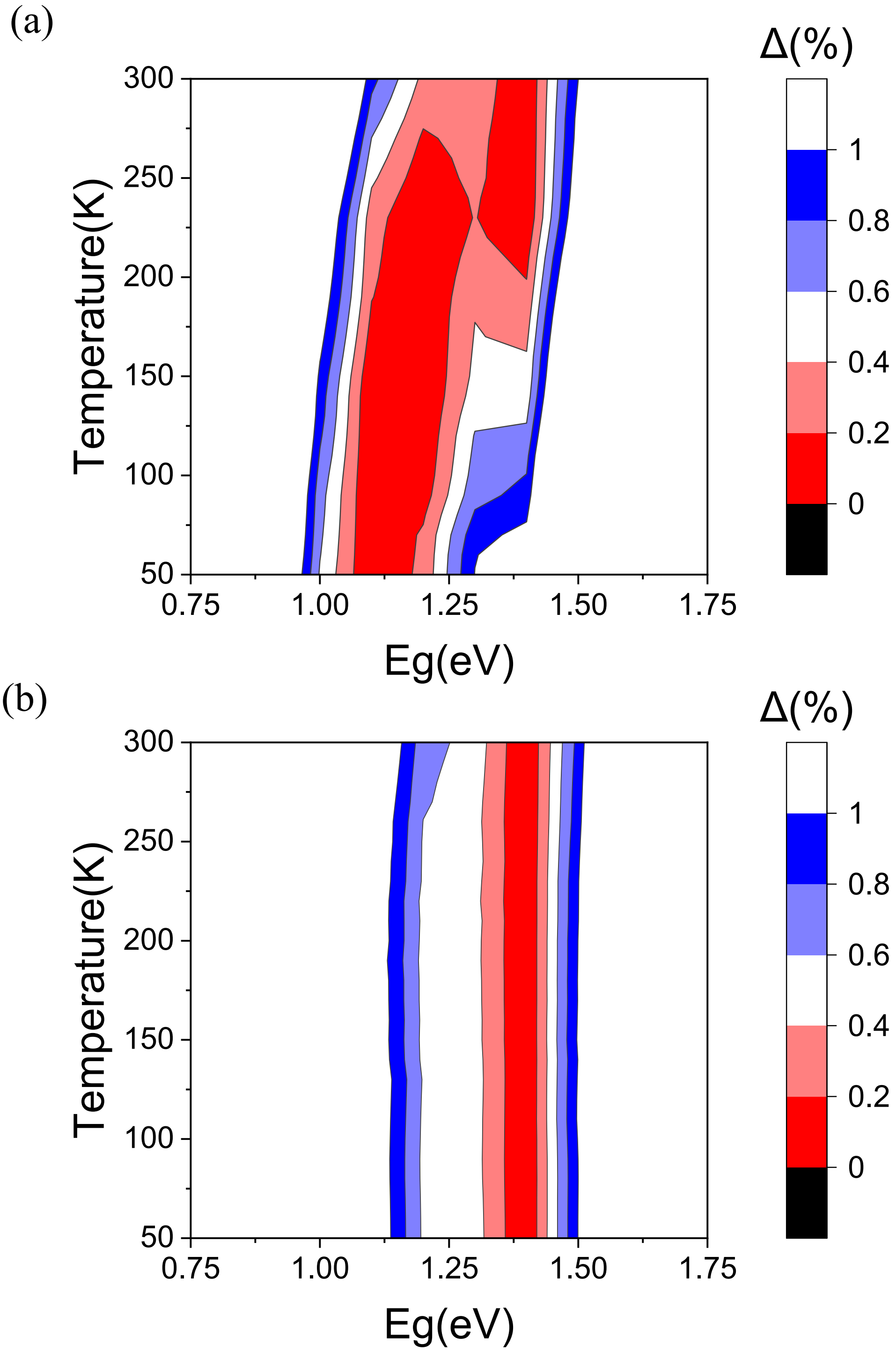

Fig. S10. The PCE distribution of (a) PSC-TE tandem and (b) PSC single device around optimum bandgap. T_E=T_C, varying according to y-axis. A larger area in (a) demonstrate a wider bandgap region around optimum bandgap, especially a much larger red area in (a). While y axis denotes identical T_E and T_C, different color represents difference value between PCE and highest PCE under identical temperature.

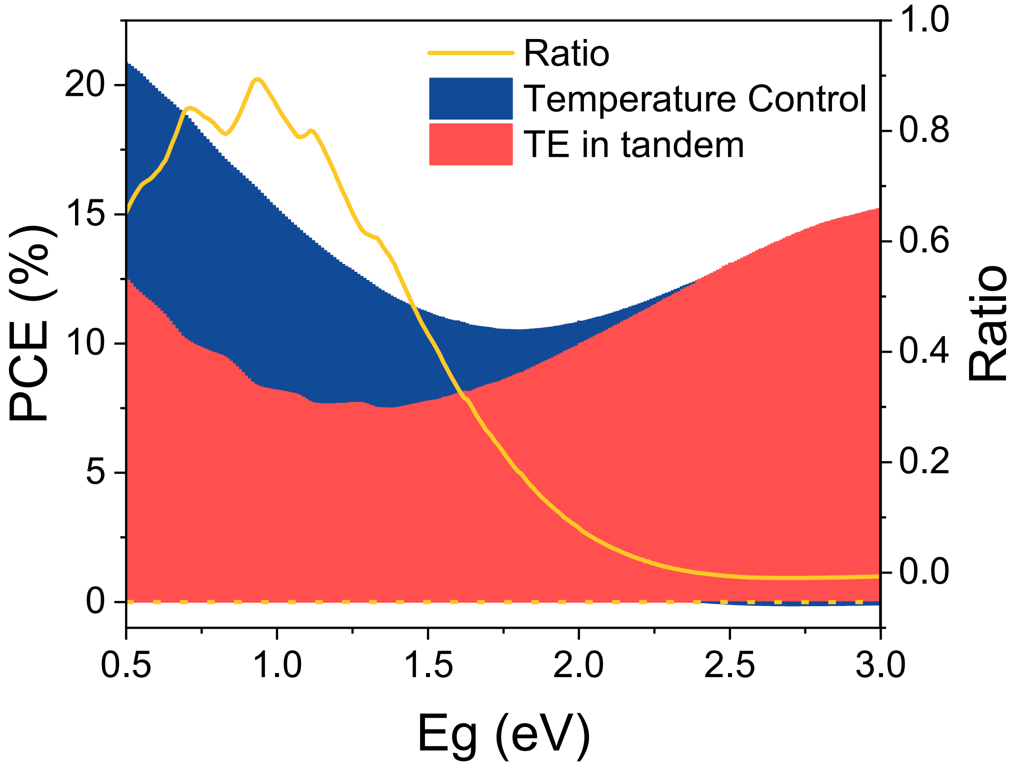

Fig. S11. The enhancement of PCE from temperature control (blue) and TE part directly (red). Here $T_E=T_C=250k$, and concentrating factor is 10. The yellow solid line is the ratio between the values of contribution from temperature control and directly from TE part. While we notice there is minus contribution from temperature control at large bandgap (Eg > 2.5 eV), which comes from poor absorption of photoelectric device.

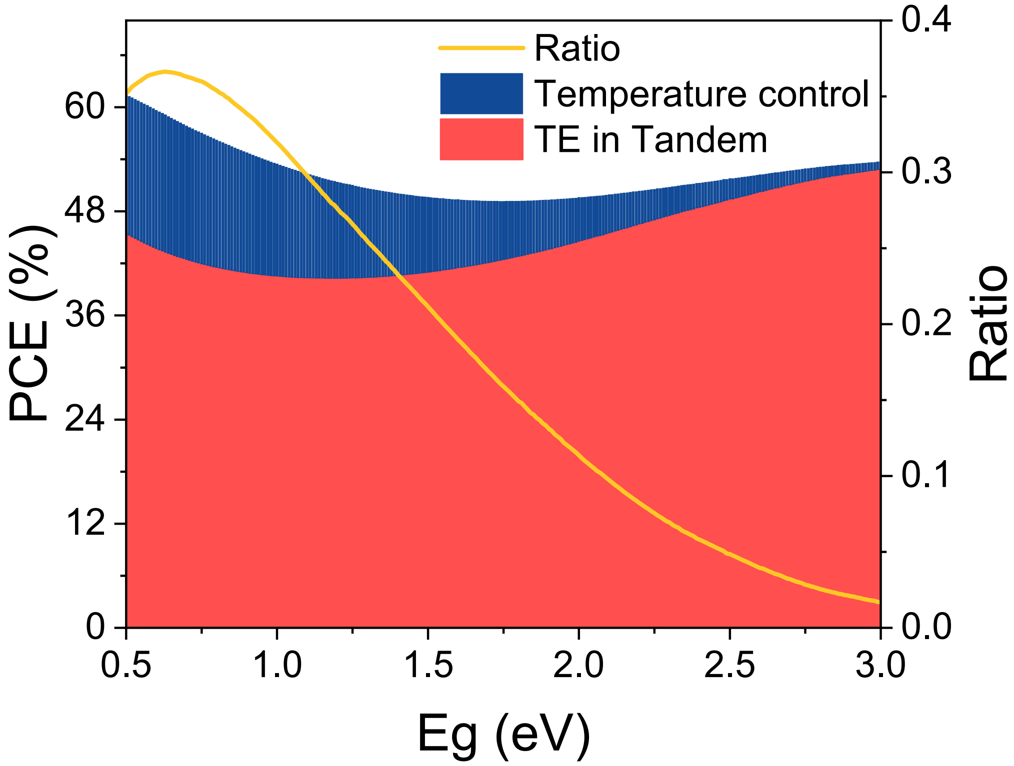

Fig. S12. The promotion of PCE from temperature control (blue) and TE part directly (red) in space. Here T_E=400K, T_C=50k. The yellow solid line is the ratio between the values of contribution from temperature control and directly from TE part.

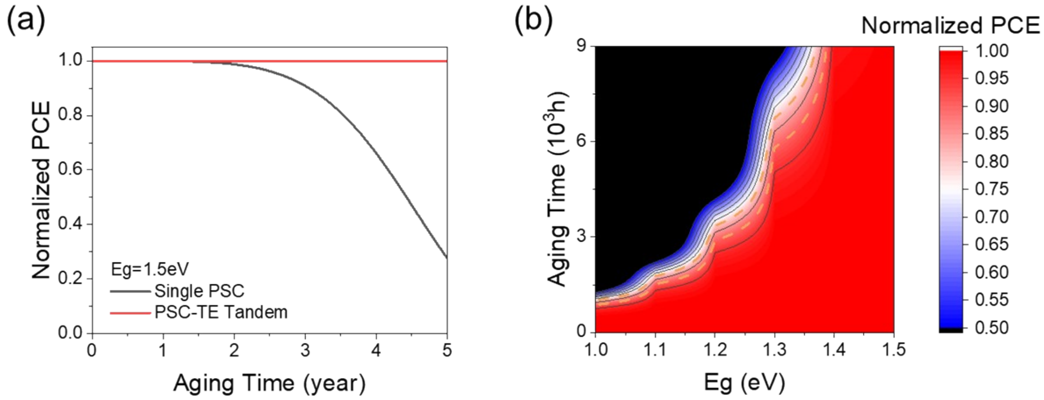

Fig. S13. The thermal aging simulation of device, the device temperature maintaine as steady state T_D showed in Fig. 2a, and relative humidity is 85%. The thermal aging model is based on pervious work in silicon photovoltaic[3,4], and we modify the parameter describes material stability in model to make it more close to PSC. And note that here only thermal aging is taking into consideration. (a) Thermal aging simulation for single PSC and PSC-TE tandem device with Eg (1.5 eV) in Antarctic region (T_E=T_C=250K) within 3000 h. (b) Thermal aging simulation of single PSC of various Eg in Antarctic region (T_E=T_C=250k) within 9000 hours (1 year). Two origin dashed lines represent 0.9 and 0.8 normalized PCE separately. And under this situation PSC-TE tandem device shows almost no thermal degradation within 9000 hours, so we don't show it here.

Supplementary references

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