Supporting Information

High-Performance Tailored Ag_2Se Thermoelectric Networks via Electrodeposition for Body Heat Recovery

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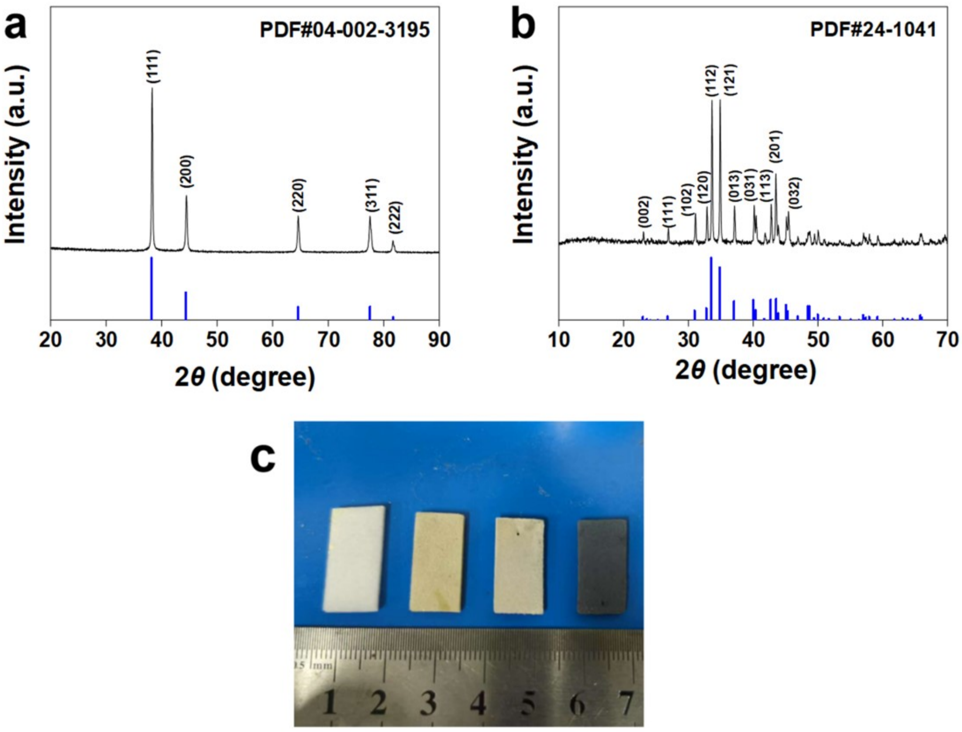

Figure S1. X-ray diffraction (XRD) patterns of **a** the E-Ag network, **b** the E-Ag_2Se network and **c** photographs of E-Ag_2Se networks at various stages.

Microstructures of E-Ag_2Se

Here, "A cm^{-3}" represents the apparent volumetric current density, defined as the ratio of the total applied current (I) to the volume (V) of the porous template：

$$J_V = \frac{I}{V}$$

Since the electrodeposition occurs within a three-dimensional macroporous template, a volumetric current density more accurately represents the metal ions reduction rate per unit volume of the active region, rather than the conventional areal current density (A cm^{-2}) used for planar substrates.

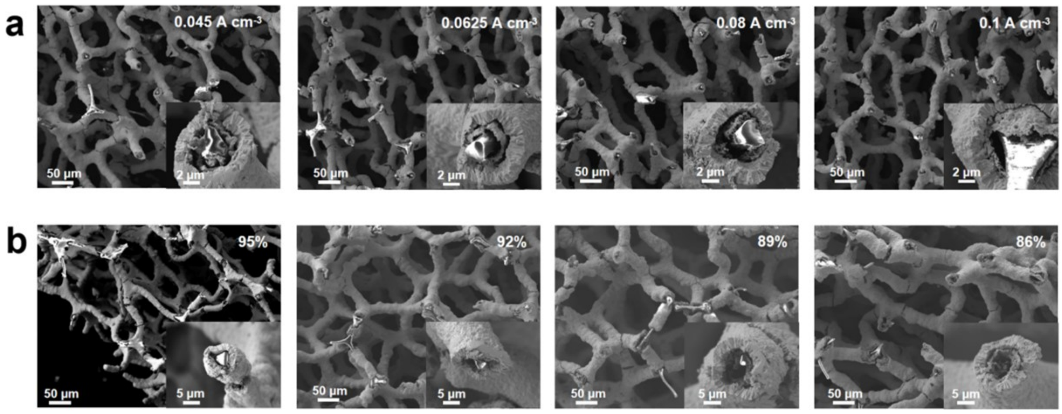

Figure S2. Microstructures of E-Ag_2Se under **a** different apparent current densities and **b** different porosities. The insets show the cross-sectional view of the network wires.

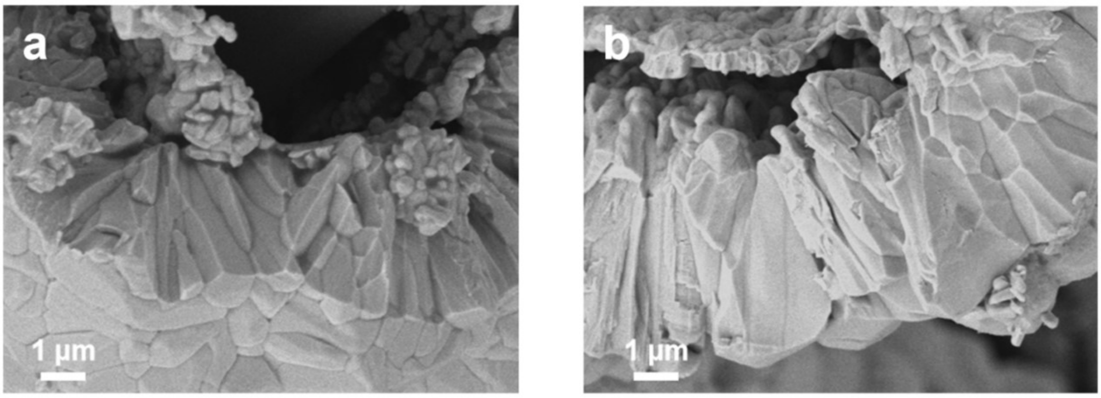

Figure S3. Cross-sectional microstructures of **a** internal and **b** surface wires in the E-Ag_2Se networks, highlighting the uniformity of electrodeposition.

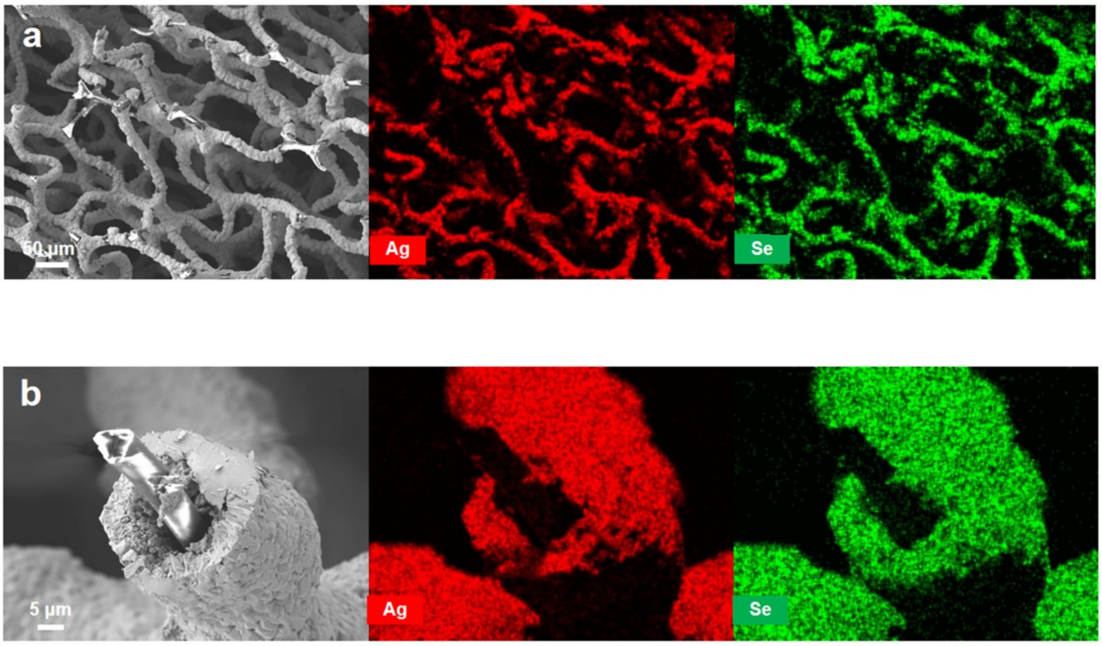

Figure S4. EDS elemental mapping of the **a** overall E-Ag_2Se thermoelectric network and **b** the cross-section of individual fiber.

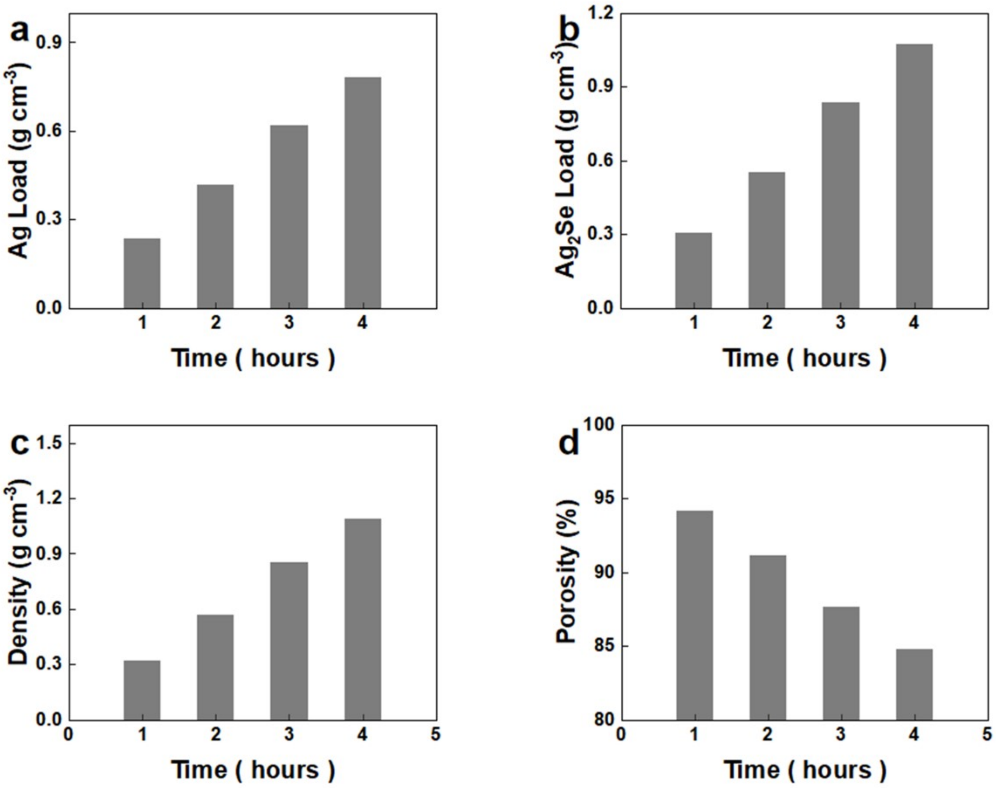

Figure S5. Variation of **a** Ag loading per unit volume, **b** Ag_2Se loading per unit volume, **c** density and **d** porosity of E-Ag_2Se networks under different electrodeposition times.

Thermal Network Thermal Conductivity Calculation

Based on the Bruggeman model[1], the Ag_2Se solid skeleton is treated as the continuous phase, while air is considered as the dispersed phase, with the formula given as follows.

$$(1-P)=\frac{\left(\kappa-\kappa_{\mathrm{air}}\right)}{\left(\kappa_{\mathrm{Ag_2Se}}-\kappa_{\mathrm{air}}\right)}\left(\frac{\kappa_{\mathrm{Ag_2Se}}}{\kappa}\right)^{\frac{1}{3}}$$

Where $\kappa_{\mathrm{Ag_2Se}}$ represents the thermal conductivity of pure-phase Ag_2Se—a value highly dependent on the preparation process, which we set at 0.6 W m^{-1} K^{-1} based on the chemically synthesized Ag_2Se reported in the literature[2]. *P* is the porosity of Ag_2Se networks, approximately 95% and κ_{air} is the thermal conductivity of air, taken as 0.026 W m^{-1} K^{-1}. The calculated theoretical thermal conductivity of the Ag_2Se thermoelectric network with 95% porosity is 0.038 W m^{-1} K^{-1}. This value closely aligns with the experimentally measured data (0.038 W m^{-1} K^{-1}). The strong agreement between theory and experiment confirms the reasonableness of the measured thermal conductivity.

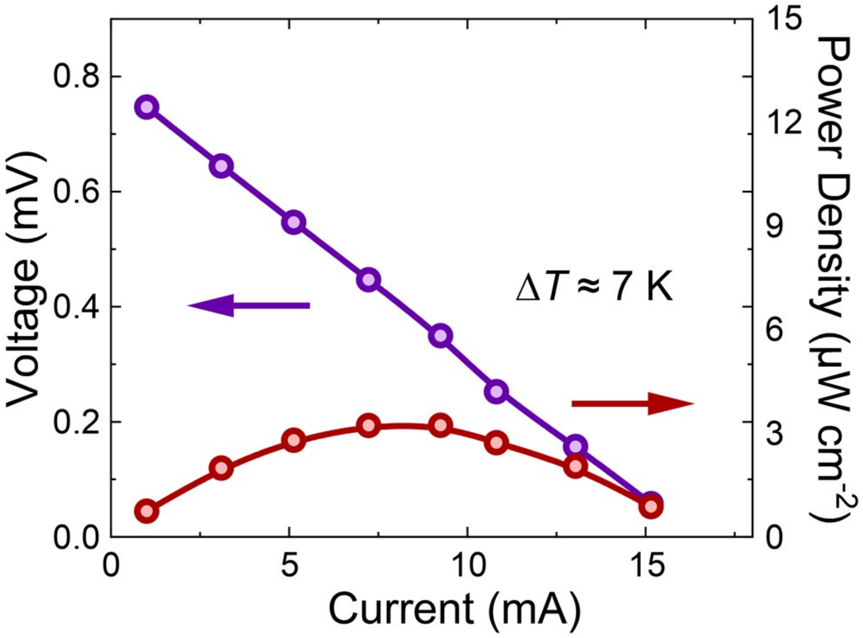

Figure S6. *I-V* (left penal) and power density (right penal) curves upon finger contact with the hot end of the 92% porosity device.

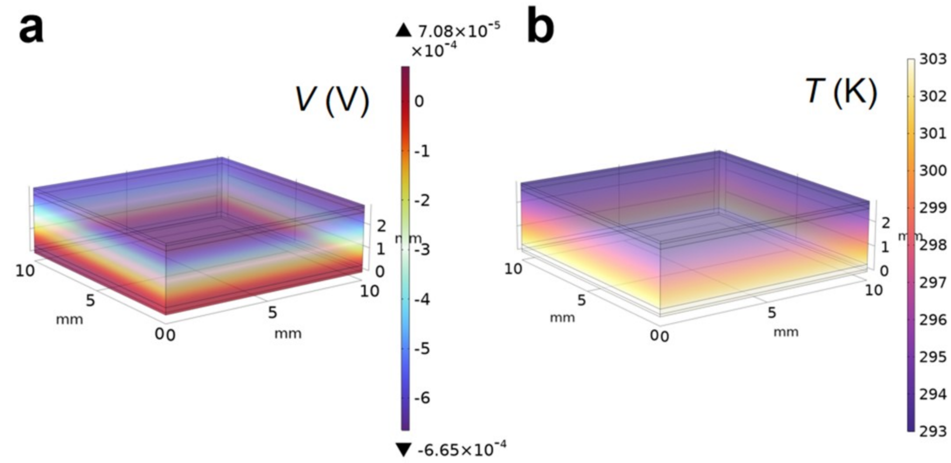

Figure S7. COMSOL simulation illustrating the **a** potential and **b** temperature distribution within the E-Ag_2Se network device.

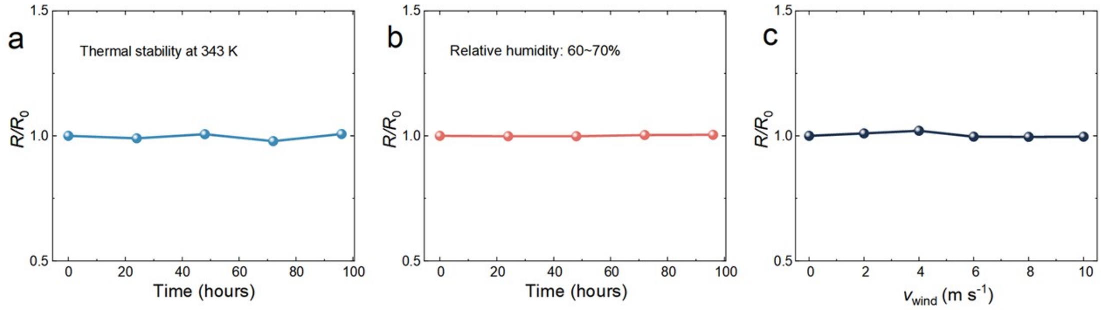

Fig. S8 The resistance stability of the 92% porosity thermoelectric network under **a** 343 K, **b** 60~70% relative humidity, and **c** different airflow velocities.

Custom-built testing platform:

The schematic diagram of the custom-built testing platform is shown in Fig. S6. The uncertainty of the output power can be calculated using the following formula.

$$\delta(P) = \sqrt{\delta(I)^2 + \delta(U)^2}$$

The uncertainty of *I*, *U*, and *T* are 1%, 1%, and ±0.01 K, respectively. Therefore, the uncertainty of the output power is calculated to be 1.44%.

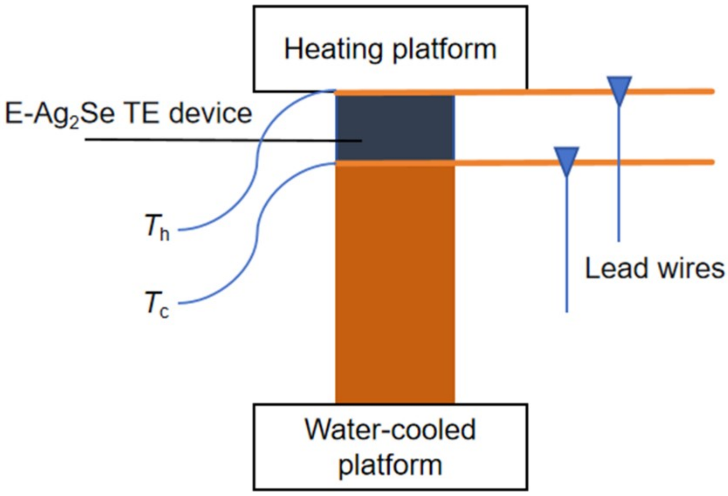

Fig. S9 The homemade power generation efficiency testing platform.

Table S1. Cyanide-free thiosulfate-based silver plating bath formulation[3]

Component	Concentration (g L^{-1})	Role
$AgNO_3$	45	Main salt
$Na_2S_2O_3$	225	Complexing agent
$K_2S_2O_5$	40	Stabilizer
CH_3COONH_4	25	pH regulator
CH_5N_3S	0.6	Brightening agent

Table S2. The simulation conditions and parameters.

parameters	Values	Source
Thermal conductivity of 92% porosity E-Ag_2Se networks	0.053 W m^{-1} K^{-1}	This work
Thermal conductivity of 86% porosity E-Ag_2Se networks	0.059 W m^{-1} K^{-1}	This work
Thermal conductivity of copper	387.1 W m^{-1} K^{-1}	COMSOL material database
Thermal conductivity of silver paint	4 W m^{-1} K^{-1}	Product datasheet from SPI supplies
Resistivity of 92% porosity E-Ag_2Se networks	0.034 Ω cm	This work
Resistivity of 86% porosity E-Ag_2Se networks	0.011 Ω cm	This work
Resistivity of coppers	1.7×10^{-6} Ω cm	COMSOL material database
Resistivity of silver paint	3×10^{-5} Ω cm	Product datasheet from SPI supplies
Seebeck coefficient of 92% porosity E-Ag_2Se networks	-140.2 μV K^{-1}	This work
Seebeck coefficient of 86% porosity E-Ag_2Se networks	-142.9 μV K^{-1}	This work
Seebeck coefficient of silver paint	6.7 μV K^{-1}	This work
Module height	2.2 mm	This work
Module side length	10 mm	This work
Silver paint height	0.1 mm	This work

Table S3. Simulated and measured resistance of devices with different porosities

Porosity of TE legs (%)	The measured resistance (mΩ)	The simulated resistance (mΩ)
92	28.28	28.04
86	19.25	16.91

Porosity calculation method：

In this study, the porosity of the thermoelectric network can be calculated using the following formula:

$$V = abl$$

$$V_{\mathrm{MA}} = V(1 - P_{\mathrm{MA}})$$

$$P = \left(\frac{V - \frac{m_{\mathrm{Ag_2Se}}}{\rho_{\mathrm{Ag_2Se}}} - V_{\mathrm{MA}}}{V}\right) \times 100\%$$

where P is the porosity of the thermoelectric network, m_{Ag2Se} is the mass loading of Ag_2Se in the network, V is the apparent volume of the sample, where a, b, and l are the length, width, and height of the sample, respectively, measured with a vernier caliper, $\rho_{\mathrm{Ag_2Se}}$ is the density of Ag_2Se (8.22 g mL^{-1} at room temperature), and V_{MA} is the volume of the melamine skeleton, which is determined by both the porosity (99%) of the commercial sponge and the apparent volume of the sample.

References

1. Mallick MM, Rösch AG, Franke L, Gall A, Ahmad S, Geßwein H, et al. New frontier in printed thermoelectrics: Formation of β-Ag_2Se through thermally stimulated dissociative adsorption leads to high ZT. Journal of Materials Chemistry A. 2020;8(32):16366-75.
2. Wu H, Shi X-l, Duan J, Liu Q, Chen Z-G. Advances in Ag_2Se-based thermoelectrics from materials to applications. Energy & Environmental Science. 2023;16(5):1870-906.
3. Ren F-z, Yin L-T, Wang S-S, Volinsky A, Tian B-h. Cyanide-free silver electroplating process in thiosulfate bath and microstructure analysis of Ag coatings. Trans Nonferrous Met Soc China. 2013;23(12):3822-8.