Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting information

A PCM-enhanced Thermoelectric Generator with Enhanced Power Density and Lifespan

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Section S1. Supplementary Discussion

1. Harman effect: [1]

The Harman effect provides a direct method for evaluating the thermoelectric figure of merit (ZT) of a material. ZT is a dimensionless parameter defined as a function of the Seebeck coefficient (α), electrical conductivity (σ), and thermal conductivity (κ). It serves as a key indicator of the efficiency with which a material can convert thermal energy into electrical energy, or vice versa.

Harman Effect and Customized ZT Characterization Platform

To determine ZT using the Harman effect, a controlled temperature gradient is applied across a thermoelectric device sample. The Seebeck coefficient is obtained from the voltage difference generated across the sample, while thermal conductivity is evaluated through the corresponding heat flux. Electrical conductivity is determined by measuring the current response under an applied voltage, as described in Equations (1) and (2).

$$T \cdot V_\alpha / \Delta T^2 = \kappa \cdot A / I \cdot L \qquad (1)$$

$$ZT = S^2 \cdot \frac{\sigma}{\kappa} \cdot T = \frac{V_\alpha^2}{\Delta T^2} \cdot \frac{I \cdot L}{V_R \cdot \kappa \cdot A} \cdot T = \frac{V_\alpha}{V_R} \qquad (2)$$

In Figure 1, the thermoelectric generator (TEG) is positioned between two metal electrodes. The left plate is maintained at a higher temperature than the right plate, thereby establishing a temperature gradient across the sample. The resulting voltage difference is measured using a voltmeter, while the current flow through the sample is monitored with an ammeter. The thermoelectric efficiency (η) of the material can then be calculated according to Equation (2).[2]

$$\eta = \frac{\Delta T}{Th} \cdot \frac{\sqrt{1 + ZT_m} - 1}{\sqrt{1 + ZT_m} + {}^{T_c}/{T_h}} \qquad (3)$$

where:

η is the thermoelectric efficiency,

ZT is the thermoelectric figure of merit,

T_h is the hot temperature (K),

T_c is the cold temperature (K).

Equation (3) is typically derived under the assumptions that the thermoelectric properties of the device remain constant with respect to temperature, that the n-type and p-type legs are perfectly matched, and that heat transfer occurs in a one-dimensional manner without additional losses.[3] In our customized ZT test experiments, the test chamber was maintained under sealed, standard atmospheric pressure and room temperature conditions. No current or heat loss occurred throughout the sample, except at the 1 mm external electrode connection interface. These controlled conditions ensured the accuracy and reliability of the experimental measurements. The thermoelectric efficiency represents the fraction of heat input to a thermoelectric device that is converted into electrical energy. A higher thermoelectric efficiency indicates a more effective conversion of heat into electricity, which is crucial for evaluating the performance of thermoelectric materials and devices.

The thermoelectric efficiency is a key parameter in the design of thermoelectric devices. A high efficiency is essential for practical applications such as power generation and refrigeration. Compared with traditional methods, our approach offers several advantages: (i) it enables much faster and simpler measurement of the ZT value of a TEG using the Harman effect, without the need to separately characterize individual material properties; (ii) it improves accuracy by accounting for interfacial effects between thermoelectric materials and substrates; and (iii) it enhances reliability by minimizing dependence on indirect estimates or assumptions.

In addition, the Thermoelectric Device Power Output Dynamic Test System provides further benefits for evaluating device performance. Specifically: (i) Real-time monitoring: continuous tracking of power output under varying temperatures, enabling direct insights into device operation under practical conditions. (ii) Controlled heat source: precise reproduction of real-world thermal instabilities for accurate assessment of device behavior. (iii) Data-driven insights: comprehensive analysis of TEG performance under dynamic thermal gradients, thereby supporting material optimization and device design improvements.

Moreover, our method enables direct measurement of the ZT value of TEGs at room temperature, which is particularly relevant for practical applications. This approach not only facilitates the development of more efficient TEGs but also accelerates the pathway toward commercialization of this technology. In our study, we employed a customized setup based on the Harman effect to evaluate the ZT values of thermoelectric devices under room-temperature conditions. Specifically, the device was placed in an oven at controlled temperatures, and the voltage difference across the sample was measured at room temperature to determine ZT using the Harman effect equation. Additionally, the thermoelectric conversion efficiency was calculated under a 30 °C temperature gradient, providing a realistic assessment of the device's capability to convert heat into electricity under operationally relevant conditions.

2. Different temperature expressions

$$\Delta T = \Delta T_{TEG} + \Delta T_{PCMh} + \Delta T_{PCMc} \tag{4}$$

Where

ΔT is the temperature difference between the hot side and cool side of the device,

ΔT_{TEG} is the temperature difference between TE units,

ΔT_{PCMh} is the temperature difference between two sides of PCM at hot,

ΔT_{PCMc} is the temperature difference between two sides of PCM at cool,

Only the temperature difference between the two ends of the thermoelectric assembly can produce an effective electrical output.

Section S2. Supplementary Figures

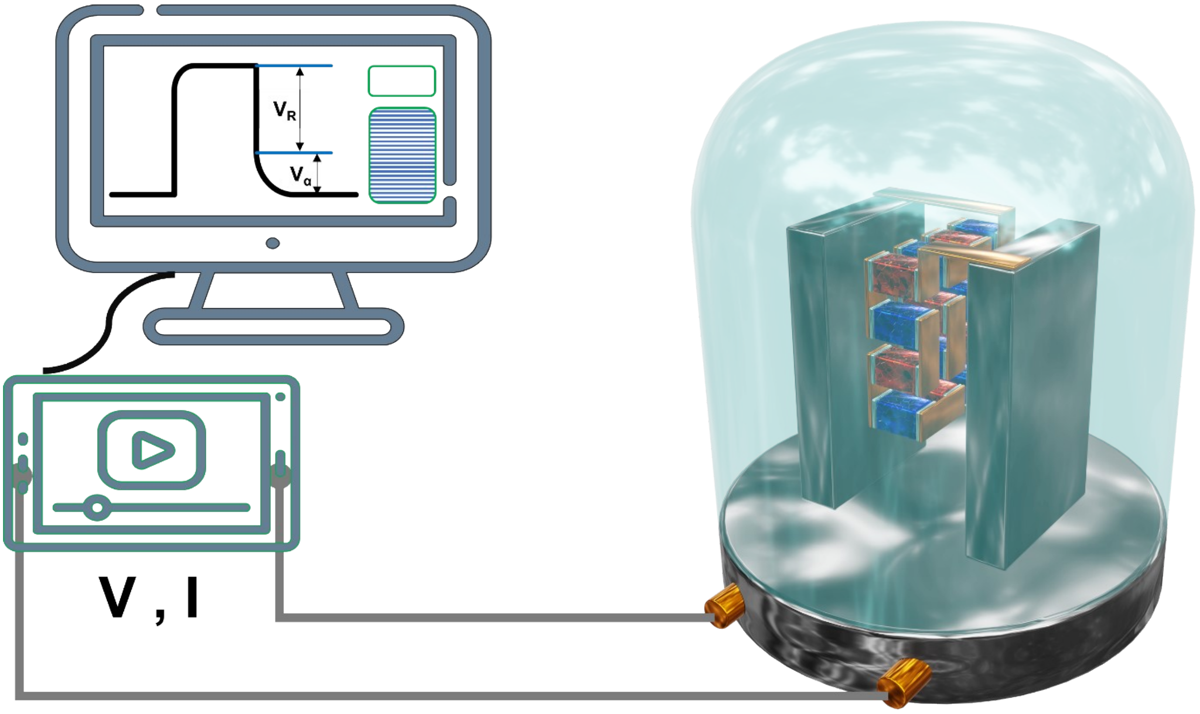

Fig. S1 Schematic illustration of the experimental setup used to evaluate ZT based on the Harman effect.

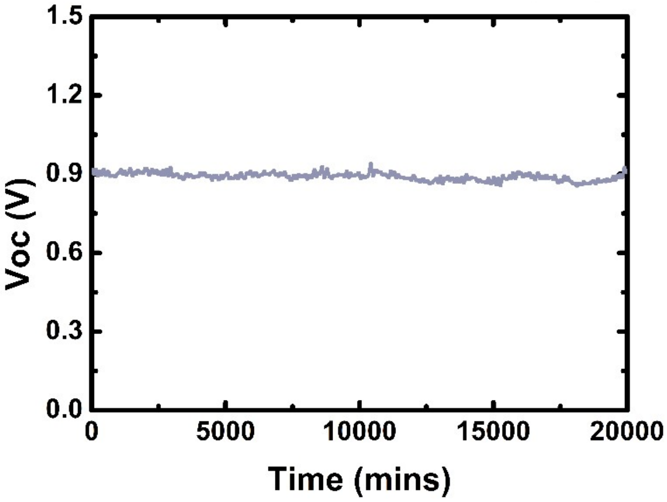

Fig. S2. The Voc characterization with continuous thermal exposure for 2 weeks at temperatures up to 130 °C, the Voc values show negligible changes (less than 5% fluctuation).

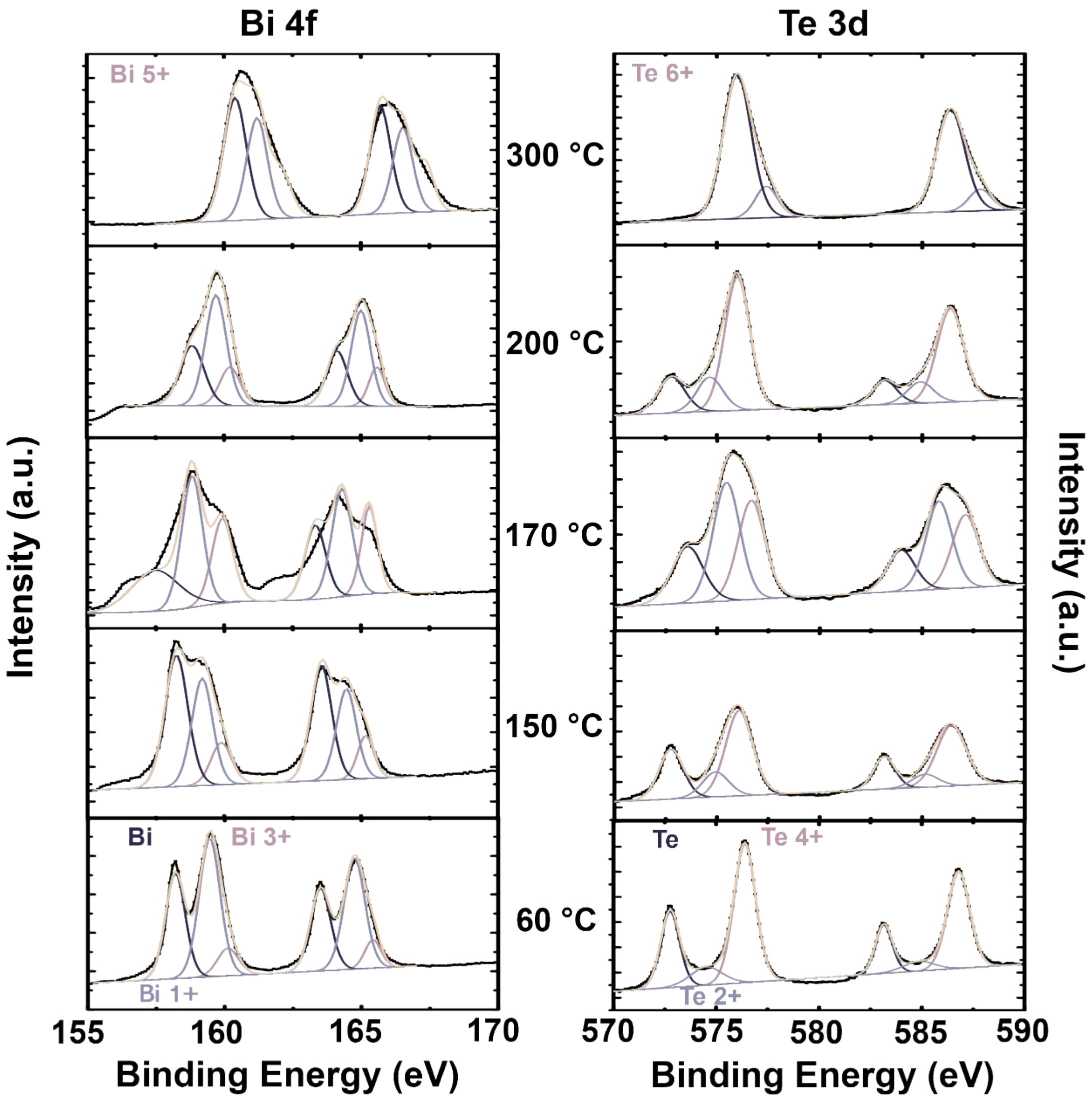

Fig. S3 XPS spectra of Bi 4f and Te 3d regions recorded before and after degradation experiments of the n-type Bi_2Te_3-based sample at 60 °C, 150 °C, 170 °C, 200 °C, and 300 °C.

The thermal degradation observed in both p-type and n-type Bi_2Te_3 materials has a profound influence on the practical performance and reliability of TEG devices. Such degradation imposes several constraints on thermoelectric applications: (i) Reduced waste heat recovery: Decreased TEG efficiency limits their capacity to harvest waste heat, diminishing effectiveness in scenarios such as industrial processes and exhaust gas power generation. (ii) Increased system costs: Shortened service lifetime and additional maintenance requirements due to degradation elevate overall system costs. (iii) Restricted technology adoption: The narrow operational temperature window caused by premature degradation hinders the broader deployment of Bi_2Te_3-based TEGs in high-temperature or demanding environments.

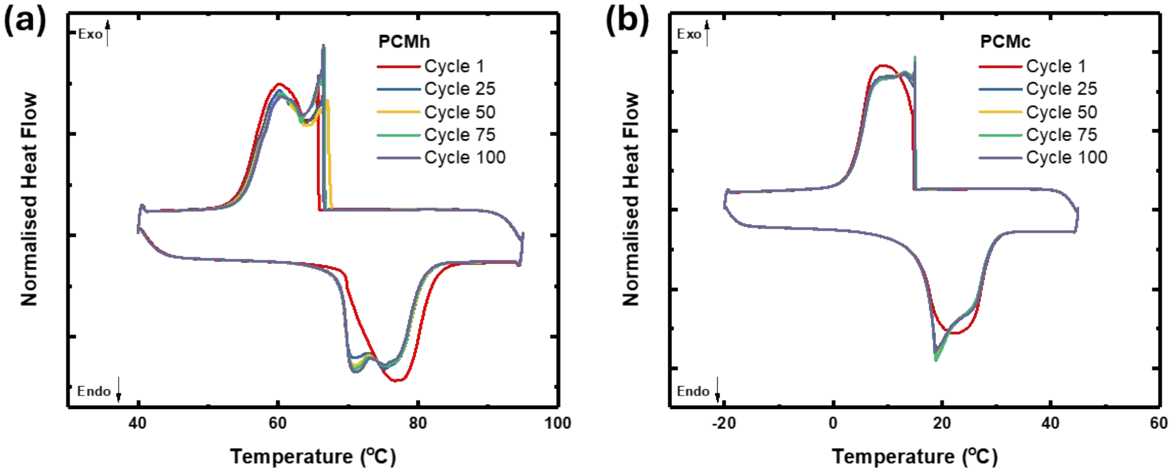

Fig. S4 DSC results of thermal cycling for (a) PCMh and (b) PCMc after 100 heat-cool cycles.

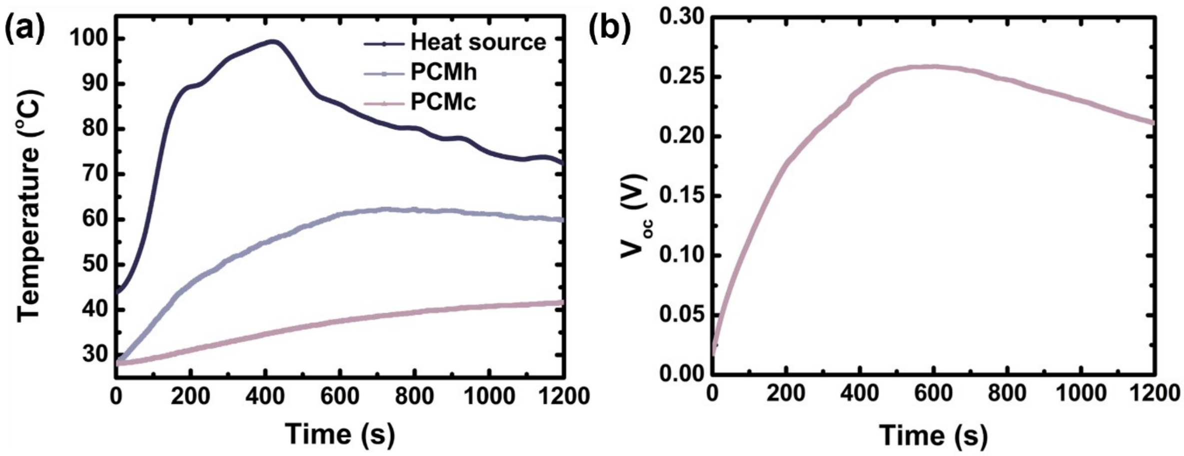

Fig. S5 Temperature variations in PCMs and the output performance of PCMs-TEGs. a) Temperature evolution at the hot and cold ends. b) The corresponding open-circuit voltage over time.

The system is modeled using an analogy to an RC electrical circuit, where:Thermal Resistance (Rth= L / kA): Represents the PCM thickness (L) and thermal conductivity (k).Thermal Capacitance (Cth = m ·Cp): Represents the sensible heat storage. Latent Heat Source (QL = m ·ΔH): Modeled as a constant temperature heat sink/source during the phase transition period.In our PCE-TE design, the copper conductive pins act as a parallel thermal resistance (Rpin) to the PCM resistance (Rpcm). This reduces the total internal thermal resistance of the composite layer, allowing for a higher heat flux (q) to reach the TEG legs while the PCM simultaneously absorbs excess thermal energy to maintain a stable ΔT.2. Impact of Design Parameters: PCM Thickness (L): Increasing L increases the thermal storage capacity (longer stable operation) but also increases the total thermal resistance, which can reduce the peak Δ T. Thermal Conductivity (k): By adding copper pins, we effectively increased the effective k, which minimizes the temperature drop across the PCM layer. Latent Heat (ΔH): A higher ΔH directly extends the duration of the "stable power" plateau by delaying thermal saturation. After continuous thermal exposure for several weeks at temperatures up to 130 °C, the ZT values showed negligible changes (less than **5% fluctuation**), and the performance was fully repeatable upon cooling and reheating. This confirms that the materials remain within their stable elastic and chemical regime.

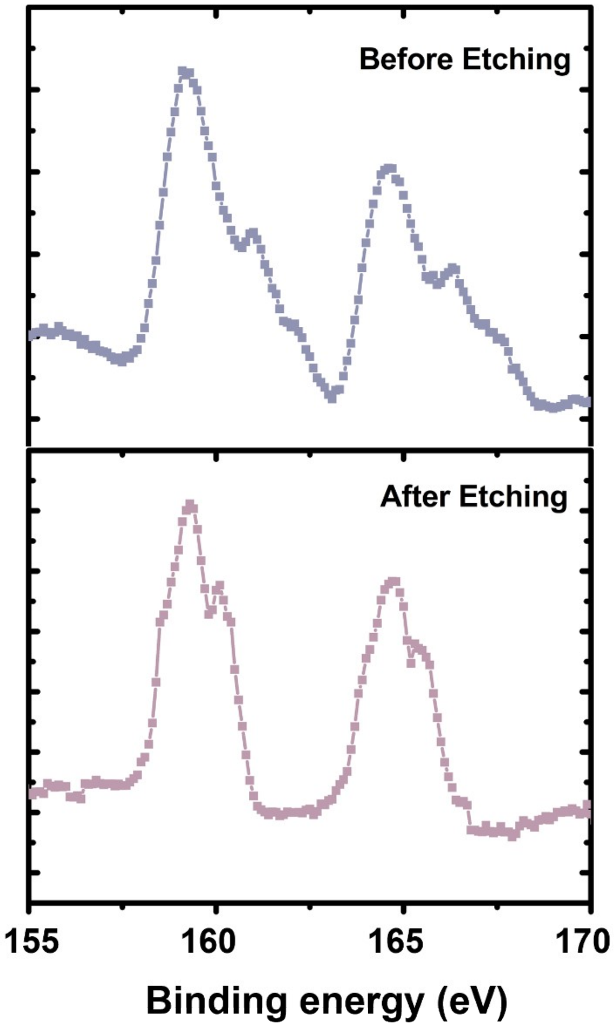

Fig. S6 XPS depth test on 300 °C degraded sample.

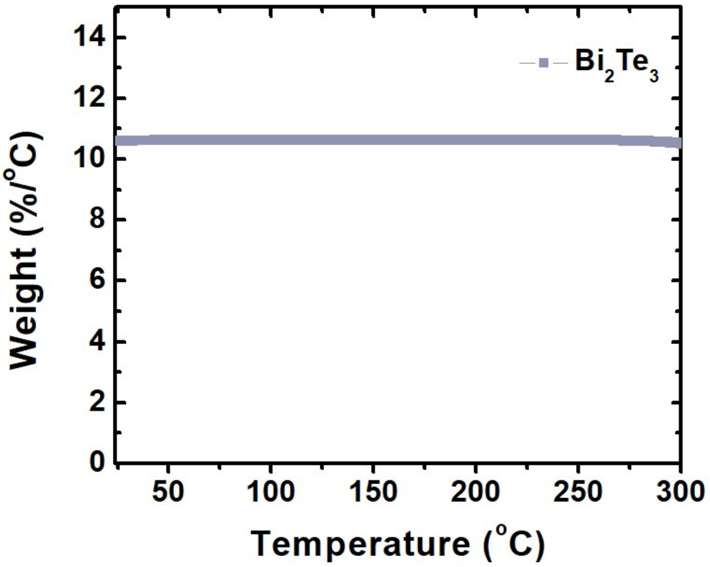

Fig. S7 TGA analysis of 300°C degraded Bi_2Te_3 sample.

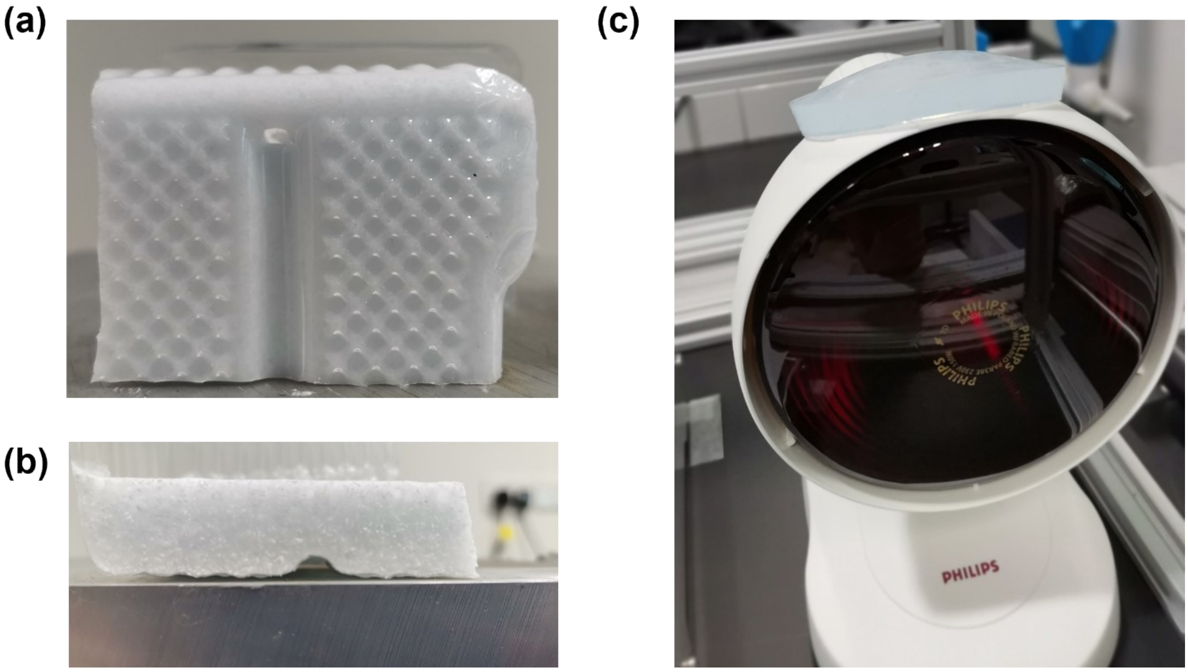

Fig. S8 Conformal integration of PCMs with thermoelectric devices. a) Interlocking structure formed by phase PCMs fitted to the heat source surface. b) Soft PCM conforming naturally to the curved surface of the heat source. c) Thermoelectric device with PCM conformal contact upon heating.

Table S1

The table of TEG, PCMs-TEGs and PCMs-TEGs pins performance comparation.

Method	Δ T	$\Delta W/W$	W_{output}	$W_{output}/\Delta T$	Power density*	Lifetime
TEGs	17.4-18.2K	>92%	0.018W	0.0010W/K	11.25 W/m^2	<1 week
PCMs-TEGs	14.4-16.2K	<4%	0.027W	0.0018W/K	16.75 W/m^2	>6 weeks
PCMs-TEGs pins	**20.2-22.7K**	**<15%**	**0.037W**	**0.0017W/K**	**23.13 W/m^2**	**>6 weeks**

Section S3. Supplementary References

1. T. C. Harman, *Journal of Applied Physics*, 2004, **29**, 1373-1374.
2. G. J. Snyder and A. H. Snyder, *Energy & Environmental Science*, 2017, **10**, 2280-2283.
3. R. R. Heikes and R. W. Ure, *Thermoelectricity: Science and Engineering*, Interscience Publishers, 1961.