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Supplementary Material

High-performance and flexible thermoelectric generator based on solution-processed composites of reduced graphene oxide nanosheets and bismuth telluride nanoplates †

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INFORMATION ABOUT ELECTRONIC SUPPLEMENTARY MATERIAL. The experimental detail, some supporting characterizations about the rGO and devices, two tables about Hall testing results and state-of-art excellent examples of printed planar TEG devices, and a video that diplays the real time measurement of open circuit voltage (ΔT = 20K) of the thermoelectric generator device made from pure Bi_2Te_3 nanoplates

Thermoelectric properties measurement: After removal of PVP stabilizers, solution of Bi_2Te_3 nanoplates or rGO/Bi_2Te_3 composites was deposited on glass substrates to form thin films by spin coating. And then the films were sintered at 380°C for 1 h in glovebox. The temperature-dependent in-plane Seebeck coefficient and electrical conductivity of the films were measured following our previous report.[S1] Four Cr/Au (5 nm/200 nm) metal lines were defined on films by thermal evaporation through shadow mask. Six metal wires (50 μm in diameter) used in the measurement of Seebeck coefficient and electrical conductivity were pasted on the Au metal lines by silver paint. The localized temperature was determined from the calibration curve by measuring the four probe resistances of the metal lines. The voltage difference (ΔV) and temperature difference (ΔT) between the hot and the cold sides were tested between the two middle metal lines. The Seebeck coefficient was calculated by $S = \Delta V/\Delta T$. The electrical conductivity was measured through a standard four probe method simultaneously, where the four metal lines worked as four probes. The in-plane thermal conductivities of all films were measured by a steady-

state method in vacuum. The thermal conductivity of sample was determined by the total thermal conductivity including the test setup and the sample and the baseline thermal conductivity of the test setup, the difference of which yielded the sample thermal conductivity. The freestanding films (5 mm × 2 mm × 0.1 mm) were carefully removed from the substrates. The sample was carefully secured by a Kapton strip, which was used as the sample holder due to its low thermal conductivity. A heater was attached to the hot side of the sample holder to provide heat sources while a copper heat sink attached the cold side. The measurement was performed in a vacuum cryostat chamber at 10^{-5} Torr to minimize convection losses.

Hall measurement: The coating films were cut to a standard Van der Pauw (VdP) layout. Each measurement was preceded by a four points probe resistivity measurement using the VdP geometry followed by field and current reversal Hall measurements, which was characterized with Model 6000 physical property measurement system.

Characterization tools: Transmission electron microscope (TEM) imaging was performed on Tecnai G2 F20 S-TWIN TEM at 200kV. Scanning electron microscopy (SEM) images were obtained with a Hitachi S4800 scanning electron microscope at 30 kV. Powder X-ray diffraction (XRD) patterns were recorded with D/MAX-TTRIII (CBO) with Cu Kα radiation (λ = 1.542 Å) operating at 40 kV and 200 mA. The thickness of all films was measured by KLA-Tencor D-120 profilometry and proved by the cross section SEM images. The Raman spectrum was recorded by Renishaw inVia Raman Microscope. The electrical property of the thin film was characterized by Keithley 4200 Characterization System.

Thermal conductivity measurement: As shown in **Scheme S2**, the sample is secured by a sample holder. And a heater was attached to one side of the sample holder to provide heat source while a copper heat sink attached to the other side to cold it. In order to generate a steady-state temperature difference (ΔT) across the sample, DC currents (I) are introduced into the heater. The heating power (P), ΔT, and I follow the **Equation R1**:

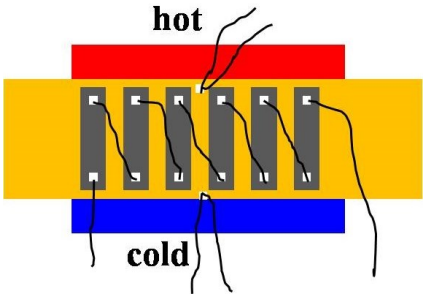
$$P = I^2 R = G\Delta T \quad \text{(R1)}$$

where R is the heater' resistance, and G is the corresponding thermal conductance we want to get. Accordingly, G is extracted from the $\Delta T \sim P$ plot based on the linearly relationship. We first measure the thermal conductance of the sample holder (we used the Kapton strip as holder in this work) (G_0), which is

the baseline thermal conductivity of the testing setup, and then measure the total thermal conductance of the sample and holder (G_1). The sample's thermal conductivity (κ) is determined by the **Equation R2**:

$$\kappa = (G_1 - G_0)L / A \quad \text{(R2)}$$

Where the L and A are the length and the cross-section area of the sample. The measurement was performed in a vacuum cryostat chamber at 10^{-5} Torr to minimize convection losses. The thermal conductivity of a glass coverslip was measured to calibrate the whole system.



Scheme S1. Printed six-element planar TEG on a flexible substrate.

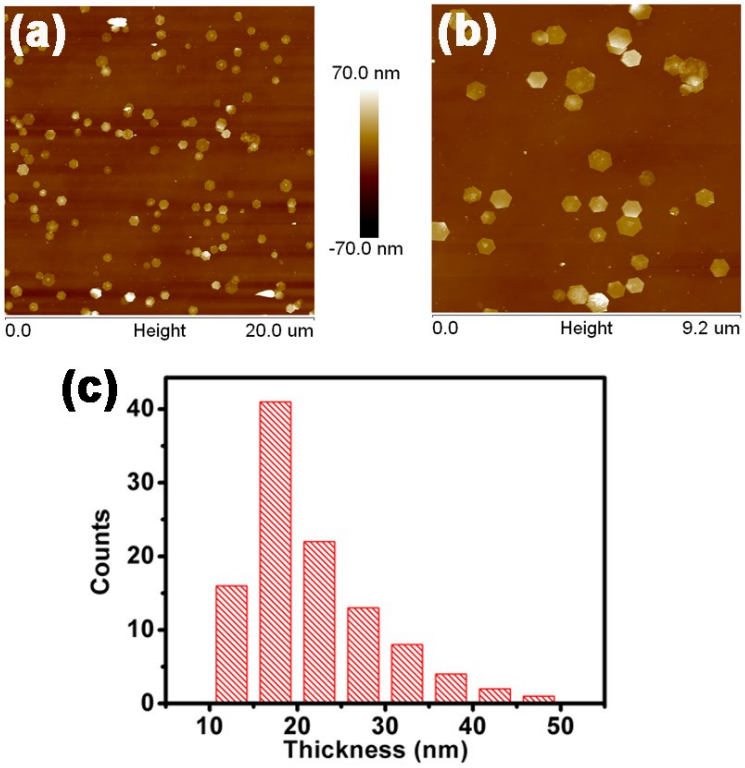


Figure S1. Atomic force microscope (AFM) images of Bi_2Te_3 nanoplates: (a) low-resolution image, (b) high-resolution image, and (c) thickness distribution histogram of Bi_2Te_3 nanoplates.

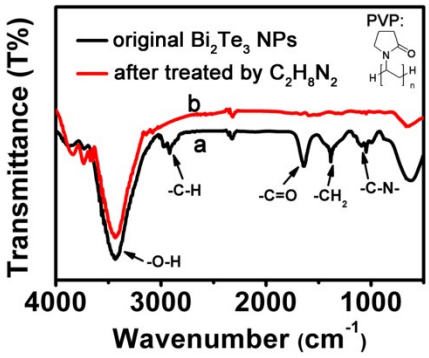


Figure S2. Fourier transform infrared (FTIR) spectra of (a) original Bi_2Te_3 nanoplates (NP) capped by PVP, (b) after treatment with ethylenediamine ($C_2H_8N_2$) solution.

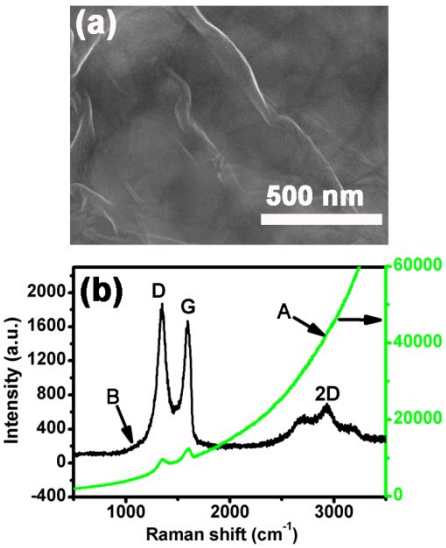
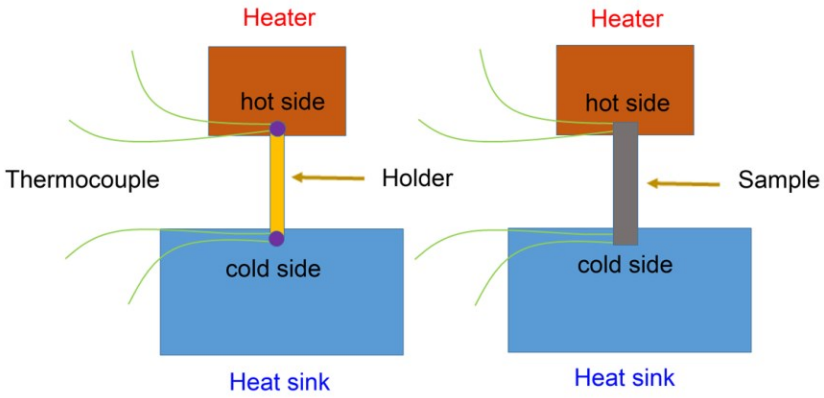


Figure S3. Morphology and Raman spectra of GO treated by hot ethylenediamine, (a) SEM image of rGO, (b) Raman spectra of GO before (A) and after (B) treated by ethylenediamine.



Scheme S2. The schematic diagram of the testing set-up.

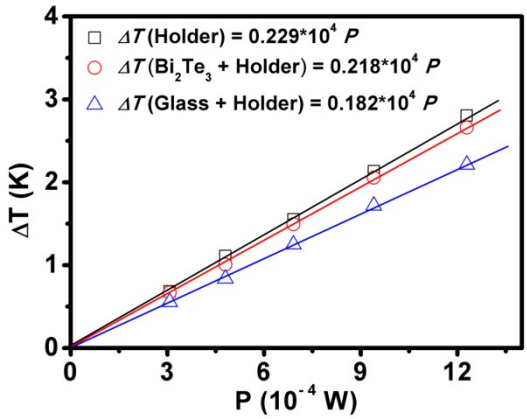


Figure S4. The measured $\Delta T \sim P$ plots that were used to extract the thermal conductance (G) by the linear fitting.

The figure shows the $\Delta T \sim P$ plots of holder, Bi_2Te_3 nanoplate film + holder, and glass + holder at 300K, which are used to extract the corresponding G values of them by linear fitting. As a result, the G_0 is 4.37×10^{-4} W K^{-1}, the G_1 of Bi_2Te_3 nanoplate film + holder and glass + holder are 4.58×10^{-4} W K^{-1} and 5.49×10^{-4} W K^{-1}.

Table S1. Parameters used to calculate the thermal conductivity (κ) of glass and pure Bi_2Te_3 nanoplate film at 300K.

	G_1 10^{-4} W K^{-1}	G_1-G_0 10^{-4} W K^{-1}	A mm^2	L mm	κ W m^{-1} K^{-1}
Baseline	4.37	0			
glass	5.49	1.12	3*0.15	4	0.996
Bi_2Te_3 nanoplate film	4.58	0.21	2*0.1	4	0.42

The table presents parameters used to calculate the thermal conductivity (κ) of glass and pure Bi_2Te_3 nanoplate film at 300K. At last, the κ of glass and pure Bi_2Te_3 nanoplate film at 300K are 0.996 W m^{-1} K^{-1} and 0.42 W m^{-1} K^{-1}.

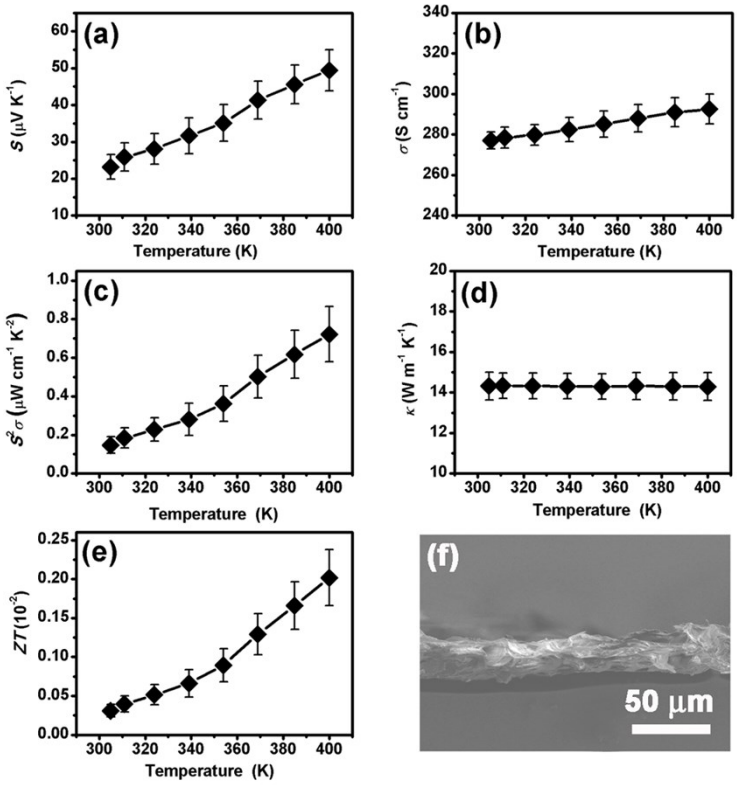


Figure S5. Temperature dependent (a) Seebeck coefficient (S), (b) electrical conductivity (σ), (c) power factor ($S^2\sigma$), (d) thermal conductivity (κ), figure-of-merit (ZT) and cross-section SEM image of pure rGO films after treatment with ethylenediamine solution and annealing at 380°C for 1 h. Error bars are estimated from repeatability of the experimental results: for each material-making condition, three samples are prepared and measured**.**

The electrical properties of pure rGO films fabricated by the same method were also measured. The σ of rGO films are from 277.3 S cm^{-1} to 292.5 S cm^{-1} in the temperature range from 300K to 400K.

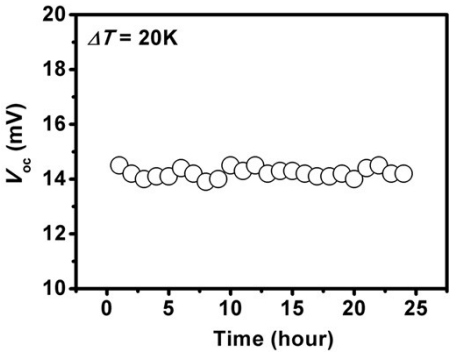


Figure S6. Open circuit voltage (ΔV_{oc}) plot of flexible TEG device made from pure Bi_2Te_3 nanoplates during 24 hours at temperature difference (ΔT) of 20 K.

References

S1 D. F. Ding, D. W. Wang, M. Zhao, J. W. Lv, H. Jiang, C. G. Lu, Z. Y. Tang, *Adv. Mater.*, 2017, ***29***, 1.