Electronic Supplementary Material (ESI) for Nanoscale.

Electronic supplementary information

Solution synthesis of telluride-based nano-barbell structures coated with PEDOT:PSS for spray-printed thermoelectric generators

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Experimental section

Preparation of Te–Bi_2Te_3/PEDOT:PSS hybrid solutions

Sodium telluride (Na_2TeO_3, Aldrich) and bismuth chloride ($BiCl_3$, Aldrich) were used as the bismuth telluride (Bi_2Te_3) source. First, 0.99 g ascorbic acid (Aldrich) was dissolved in 40 mL of deionized water; 1 mL of PEDOT:PSS (Clevios PH 1000) solution filtered through a PVDF syringe filter (0.45 μm) was added to this solution. Subsequently, 0.07 g Na_2TeO_3 and 0.06 g $BiCl_3$ were added to the mixture under stirring. The temperature of the mixture was then increased to 60 °C and maintained for 20 h. Pure Te–Bi_2Te_3/PEDOT:PSS nano-barbell structures were collected by centrifugation of the reaction mixture at 9000 rpm for 30 min at least two times. The final product was resuspended in 30 mL of pure deionized water.

Preparation of Te–Bi_2Te_3/PEDOT:PSS hybrid films

For spray-printing, a commercially available spray gun (HP-SB Plus, Iwata, Japan) with a nozzle diameter of 0.2 mm was used. The Te–Bi_2Te_3/PEDOT:PSS hybrid solutions were spray-printed onto a glass or polyimide substrate in air. We used air at a pressure of 30 psi as a carrier gas, and solutions were successfully sprayed without clogging the nozzle. During the spray deposition, the temperature of hot plate was maintained at 150 °C to remove residual solvent and finally yield films with a high-quality surface. The thickness of the Te–Bi_2Te_3/PEDOT:PSS hybrid films was approximately 1.5 μm.

Acid treatment of Te–Bi_2Te_3/PEDOT:PSS hybrid films

For the acid treatment, Te–Bi_2Te_3/PEDOT:PSS hybrid films were immersed in H_2SO_4 (Samchun Pure Chemicals, Korea) solutions with various volume ratios (20–100%) for 10 min under ambient conditions. The films were then washed in methanol and annealed at 160 °C for 10 min.

Fabrication of thermoelectric generators

Thermoelectric generators using Te–Bi_2Te_3/PEDOT:PSS hybrids were fabricated on a glass or flexible polyimide substrate. For the formation of fifteen thermoelectric legs, Te–Bi_2Te_3/PEDOT:PSS hybrid solutions were sprayed onto substrates by using a shadow mask (size of 1 leg: 2 mm × 15 mm, gap between legs: 1 mm). The sprayed thermoelectric arrays were then treated with H_2SO_4 at a concentration of 80 vol%. To connect the spray-printed thermoelectric legs, metal electrodes were dispensed through a 200 μm nozzle (SHOMASTER 200 DS-S, Musashi Engineering Inc., Japan) by using conductive silver paste (NB05, Soulbrain, Korea). The printed thermoelectric generator was then annealed at 150 °C on a hotplate for 30 min to improve the electrical conductivity of the Ag electrodes and reduce the contact resistance between the Ag electrodes and thermoelectric elements.

Instrumentation

The nanostructure of Te–Bi_2Te_3/PEDOT:PSS hybrids was evaluated via TEM (Tecnai G2, FEI, USA) analysis. The composition of the Te–Bi_2Te_3/PEDOT:PSS hybrids was evaluated via TEM-EDAX analysis. The TEM samples were prepared by dropping the Te–Bi_2Te_3/PEDOT:PSS hybrid solutions onto a copper grid. The surface morphology of the Te–Bi_2Te_3/PEDOT:PSS hybrid films was investigated by SEM (XL30S FEG, Philips, Netherlands), and the atomic percent of the films was investigated by SEM-EDAX. Before analysis of the films, platinum layers with a thickness of approximately 100 nm were deposited onto the prepared films with a coating machine (E-1030, Hitachi Ltd., Japan). The thickness of the films was determined by using an alpha-step surface profiler (α-step IQ, KLA Tencor, USA). The chemical compositions in the Te–Bi_2Te_3/PEDOT:PSS hybrid films were characterized by using XPS (AXIS NOVA, Kratos Analytical Ltd., UK). To compensate for the effects of surface charges, all binding energies were referenced to the C1s neutral carbon peak at 284.5 eV. The electrical conductivity was measured via the four-point probe method by combining a Keithley 220 current source and Keithley 195A digital multimeter. The Seebeck coefficient was measured by using the sample with silver electrodes and a home-built setup. Two silver electrodes that were 3 mm in width were separated by a distance of 30 mm. The temperature gradient between the two electrodes was varied from 1 to 10 °C. The setup consisted of two Peltier devices to maintain controlled stages that could independently function as the hot or cold part. For the measurement, a combination of a Keithley 2460 source meter, Keithley 2700 multimeter/data acquisition system, Keithley 2182A nanovoltameter, and Keithley 2200-30-5 power supply was used.

Additional figures

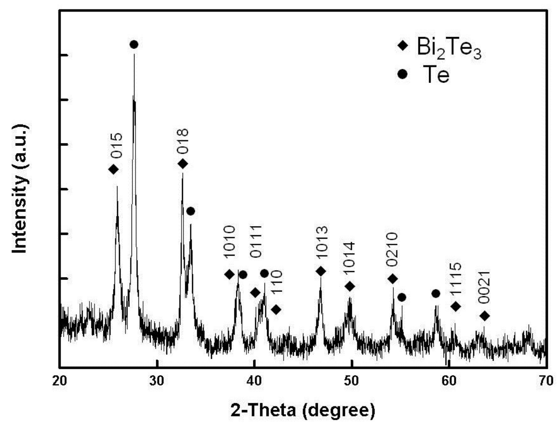


Fig. S1 XRD patterns of Te–Bi_2Te_3/PEDOT:PSS hybrids (circles: peaks from Te, diamonds: peaks from Bi_2Te_3).

(a) (b)

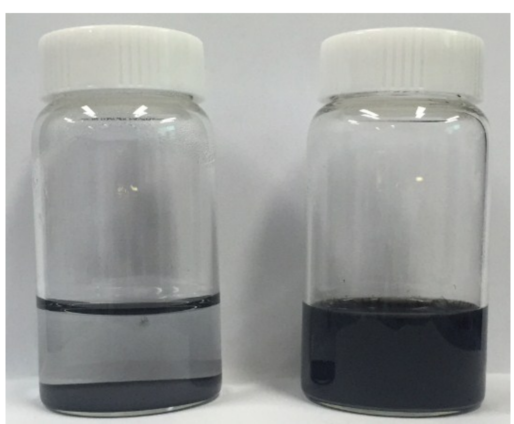
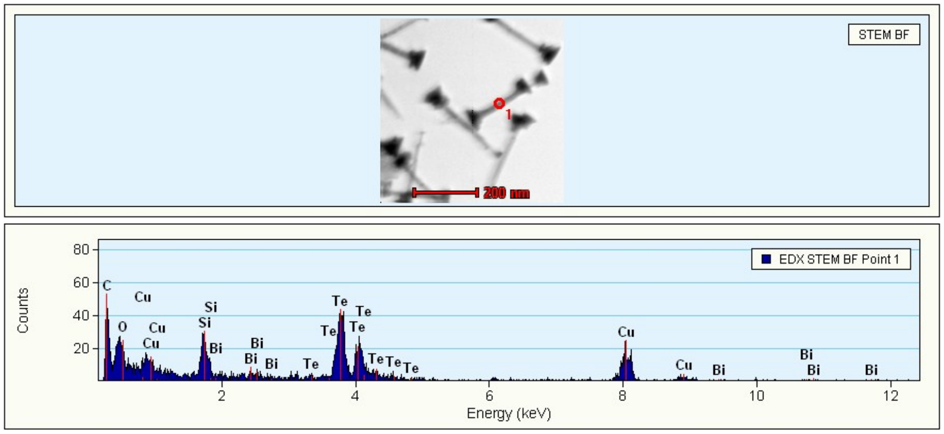


Fig. S2 Solution images of Te–Bi_2Te_3 nanowire heterostructures: (a) without PEDOT:PSS and (b) coated with PEDOT:PSS in water to compare the water dispersity.

(a)



(b)

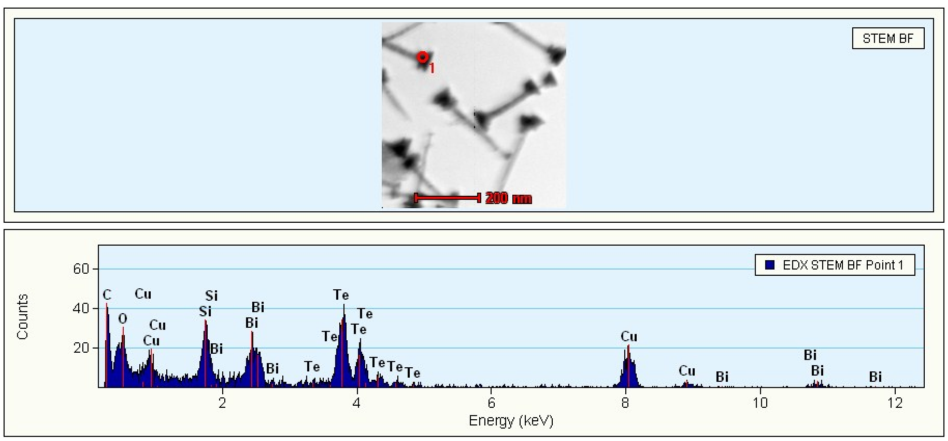


Fig. S3 TEM-EDAX images of Te–Bi_2Te_3/PEDOT:PSS hybrids: (a) nanobar and (b) plate part.

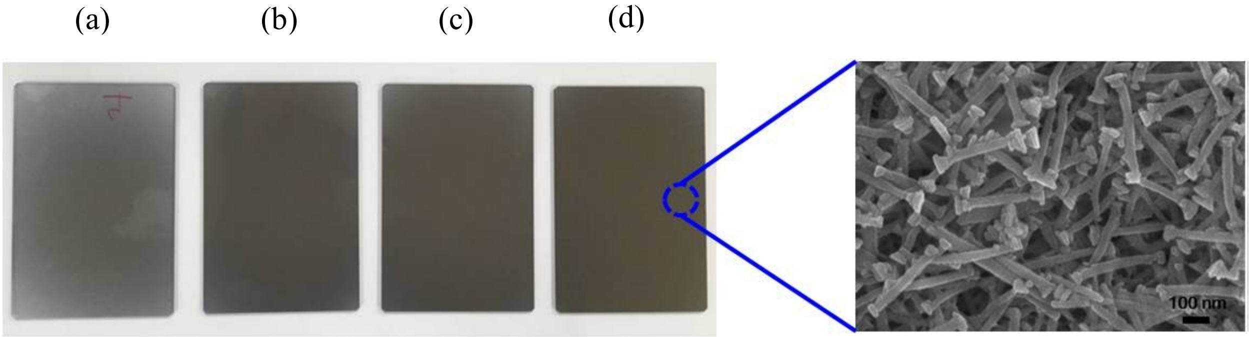


Fig. S4 Images of thin thermoelectric films of Te–Bi_2Te_3/PEDOT:PSS hybrids deposited by spray-coating depending on sprayed solution volume: (a) 5, (b) 10, (c) 15, and (d) 20 mL, respectively.

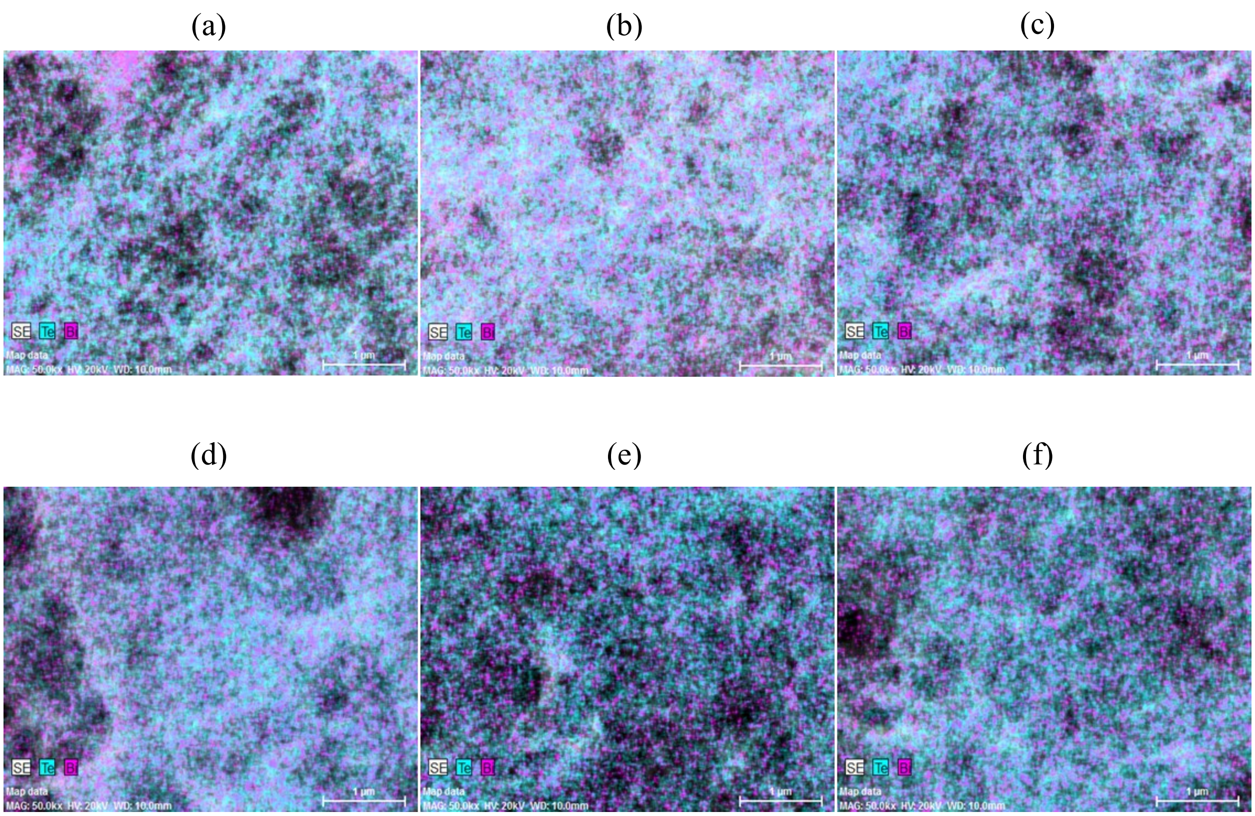


Fig. S5 SEM-EDAX mapping images of Te–Bi_2Te_3/PEDOT:PSS hybrid films treated with various concentrations of H_2SO_4: (a) 0, (b) 20, (c) 40, (d) 60, (e) 80, and (f) 100 vol%, respectively.

Table S1 Atomic percentages from SEM-EDAX mapping of Te–Bi_2Te_3/PEDOT:PSS hybrid films treated with various concentrations of H_2SO_4

H_2SO_4 concentration (%)	Atomic percent (at. %)		Total (at. %)
	Bi	Te	
0	20.17	79.83	100
20	12.25	87.75	
40	11.34	88.66	
60	9.73	90.27	
80	5.80	94.20	
100	2.95	97.05	