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Supplementary Information

Synergistically enhanced thermoelectric performance by optimizing the composite ratio between hydrothermal Sb_2Se_3 and self-assembled β-Cu_2Se nanowires

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Supplementary Information:

1. Experimental

1.1 Materials

Sodium selenite (99.9%, Na_2SeO_3) and Selenium powder (99.5%, 100 mesh, Se) were acquired from Sigma-Aldrich. Antimonyl potassium tartrate (99.5%, $C_8H_4K_2O_{12}Sb_2 \cdot 3H_2O$) was purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). Sodium hydroxide (97%, pellet, NaOH), Copper(II) nitrate trihydrate (99%, $Cu(NO_3)_2 \cdot 3H_2O$), Hydrazine monohydrate (80%), and Tetrahydrofuran (99%) were acquired from Daejung Chemical and Metals Co., Ltd. (Seoul, Korea). All reagents were used as received without further purification.

1.2 Sample preparation

1.2.1 Synthesis of Sb_2Se_3 nanowires

100 ml of distilled water dissolved 0.665 g of antimonyl potassium tartrate and 0.51 g of sodium selenite with vigorous magnetic stirring. The color of the solution became whiter with stirring. Then, 20 ml of hydrazine monohydrate was added to the solution and the color became peach-like. The peachy-colored solution was shifted into the Teflon-lined autoclave with 40 ml of tetrahydrofuran. The sealed autoclave was heated at 135 ℃ for 9 h. The product was centrifugated at 10,000 rpm for 1 h, washed with ethanol and hot distilled water several times, and then dried in a vacuum oven at 80 ℃ overnight.

1.2.2 Synthesis of Cu_2Se nanowires

0.45 g of selenium powder, 15 g of NaOH, and 60 ml distilled water were dissolved in a 100 ml round-bottom flask which was heated at 90 ℃ using an oil bath with magnetic stirring to dissolve selenium powder. After the color of the solution became deep red, 0.5M of 5ml $Cu(NO_3)_2$ solution was combined with the solution in the flask. Then, the solution was transferred into a 250 ml beaker and maintained at 140 ℃ in an oven for 12 h to evaporate the

water. After the water was evaporated, the precipitated product was precipitated on the bottom of the beaker. Hot distilled water was used to collect the product and product was washed with hot distilled water and ethanol several times, and then dried in a vacuum oven at 60 ℃ overnight.

1.2.3 Preparation of disk pellets

The Sb_2Se_3 and Cu_2Se nanowires were mixed at different ratios (10:90, 30:70, 50:50, 70:30 and 90:10, respectively). Each mixed powder was transferred into a Fe mold and then hot pressed under 70 MPA for 5 min at 600 K to make 12.7 mm diameter disk pellets.

1.3 Characterization

X-ray diffraction, XRD (D8 Advance, AXS Bruker), was conducted to describe the crystalline structure of the prepared nanowire powders and disk pellets. The Cu K_α radiation ($\lambda = 0.154056$ nm) was used as diffractometer which was scanned with a 2θ scan rate of $1° s^{-1}$ at 40 kV and 40 mA over a 2θ range from 10° to 80°. X-ray photoelectron spectroscopy, XPS (K-Alpha, Thermo U.K.) was used to interrogate the binding energies of the synthesized nanowire using a 1486.6 eV Al K_α X-ray source. The Raman spectra was recorded by Raman spectrometer II (DXR2xi, Thermo) using a near infrared laser operating at 532 nm with a CCD detector. Field-emission scanning electron microscopy, FE-SEM (SIGMA), and field-emission transmission electron microscopy, FE-TEM (JEM-F200), were used to visualize the shape and microstructures of the Sb_2Se_3 and Cu_2Se nanowires samples. Energy-dispersive X-ray spectroscopy, EDS (JEM-F200, JEOL) was conducted to obtain elemental mapping of the nanowire powders and EDX (Thermo NORAN System 7) was conducted to obtain elemental mapping of the disk pellet samples. Diameter of prepared disk pellets was 12.7 mm and thickness of disk pellets was measured with a digital micrometer. Thermoelectric properties, Seebeck coefficients, electrical conductivities and thermal conductivities, were measured in

the direction parallel to the pressing direction. From room temperature to 473 K, four-probe method was used to quantify the electrical conductivity and the Seebeck coefficient was calculated with the relationship $S = \Delta V/\Delta T$, by the change in ΔV (thermal electromotive force), and ΔT (temperature difference), between the top and bottom planes of the pellets using homemade device including a pair of thermocouples and a pair of voltmeters. The thermal conductivity (κ) was calculated by relationship, $\kappa = \alpha \cdot \rho \cdot C_p$, where ρ, α, C_p is pellet density, thermal diffusivity and specific heat capacity, respectively. LFA 447 Nanoflash (NETZSCH) equipment was used to measure the thermal diffusivity and Differential scanning calorimetry, DSC (DSC 131 Evo, Setaram Instrumentation), was used to quantify the specific heat capacity of disk pellets. The density of the disk pellets was calculated by using Archimedes method.

Figure

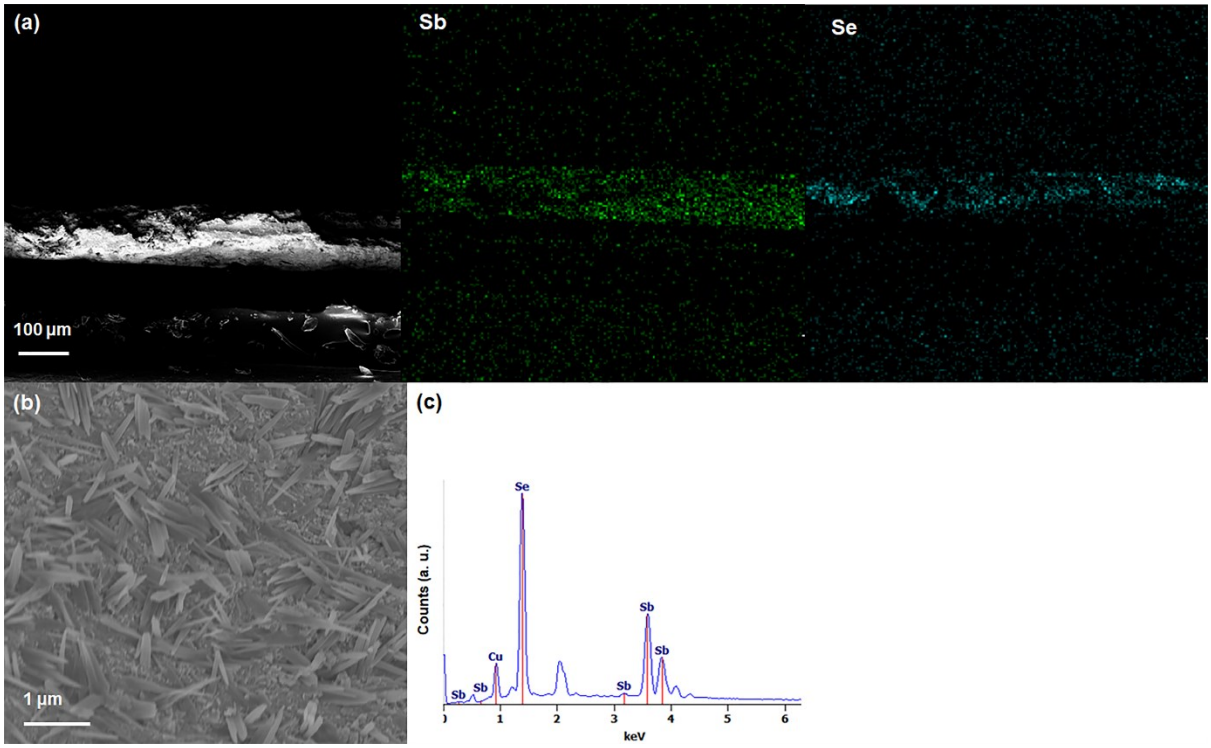

Figure S1. (a,b) The cross-sectional FE-SEM image and EDS mapping of the disk pellet with 30% β-Cu_2Se and 70% Sb_2Se_3, (c) the EDX image of disk pellet with 30% β-Cu2Se and 70% Sb2Se3.

Table

Table S1. Comparison of thermoelectric properties

	Seebeck coefficient (μV/K)	**Electrical conductivity (S/m)**	**Power factor (μW/m•K²)**	**Thermal conductivity (W/m•K)**	**Figure of merit**	**Reference**
Sb_2Se_3	661	4.37×10^{-4}	1.9×10^{-5}	0.037	1.55×10^{-6}	[1] At 300 K
Cu_2Se	95	5×10^{4}	460	1.3	1.82	[2] At 664 K
70%-Sb_2Se_3 30%-β-Cu_2Se	441	2000	389.19	0.64	0.288	This work At 473 K

1. Ko, T. Y.; Shellaiah, M.; Sun, K. W., Thermal and Thermoelectric Transport in Highly Resistive Single Sb2Se3 Nanowires and Nanowire Bundles. Sci. Rep., 2016, 6, 35086.

2. Lin, Z.; Hollar, C.; Kang, J. S.; Yin, A.; Wang, Y.; Shiu, H. Y.; Huang, Y.; Hu, Y.; Zhang, Y.; Duan, X., A Solution Processable High-Performance Thermoelectric Copper Selenide Thin Film. Adv. Mater., 2017, 29 (21).