Electronic Supplementary Material (ESI) for Nanoscale.

Thermoelectric enhancement in multilayer thin-films of tin chalcogenide nanosheets/conductive polymer

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1. Experimental Methods

Fabrication of Te-s-SnSe NSs

A solid-state reaction and subsequent hydrothermal exfoliation were carried out to fabricate Te-s-SnSe NS, briefly as follows. Tin (99.999 %), selenium (99.999 %), and tellurium (99.999%) particles (Sn:Se:Te = 1:0.97:0.03) were placed and vacuum-sealed in a quartz ampoule that was successively loaded into a furnace for the solid-state reaction. The ampoule was heated to 1223 K over 10 h and this temperature was maintained for 6 h, after which it was cooled down to 298 K. The powder (0.5 g) grounded from the as-prepared Te-s-SnSe ingot was put into a Teflon-lined autoclave filled with ethylene glycol (100 ml) and lithium hydroxide (0.4 g) that was heated to 473 K for the Li^+ intercalation into the Te-s-SnSe layers. After 48 h of reaction, the resulting solution was naturally cooled down to 298 K, filtered, washed with acetone to remove residual ethylene glycol and LiOH, and then dried in a vacuum oven at 333 K for 24 h. The Li-intercalated Te-s-SnSe powder (0.1 g) and deionized water (40 mL) were placed in a beaker and sonicated for 1 h followed by centrifugation at 1000 rpm for 30 min; the supernatant was further centrifuged at 8000 rpm for 30 min and the product was washed several times with a 3 vol% HCl solution and ethanol and finally dried in a vacuum oven.

Fabrication of PEDOT-Te-s-SnSe NSs

As a surfactant, dodecylbenzenesulfonic acid (DBSA) (0.032 g) was put into a beaker containing the as-prepared Te-s-SnSe NS (0.5 g) and deionized water (100 mL). After stirring at 30 °C for 1 h, it changed into a black-colored colloidal solution. Various EDOT contents (0.023, 0.047, 0.094, and 0.189 g) were added to the beaker to prepare the different PEDOT-Te-s-SnSe samples (Table S1) and further stirred at 303 K for 1 h. As both an oxidant and a dopant, another solution containing ammonium persulfate (APS) (0.182 g) and deionized water

(10 mL) was added to the colloidal solution, which was stirred at 303 K for 24 h for the EDOT polymerization, centrifuged at 8000 rpm for 30 min, and re-dispersed in deionized water. The purified PEDOT-Te-s-SnSe NSs, obtained after several centrifugation and re-dispersion cycles, were finally dried at 333 K for 24 h in a vacuum oven.

Fabrication of multilayer films

The PEDOT(2)-Te-s-SnSe NSs (0.03 g) were dispersed in chloroform (30 mL) and successively sonicated for 30 min. A PEDOT:PSS solution (PH 1000, Heraeus Clevios GmbH) was mixed with DMSO (5 vol%), filtered through a 0.45 μm pore size syringe filter, further stirred and sonicated for 2 h, dropped onto a squared glass substrate (2 × 2 cm^2), and finally spin-coated at 1000 rpm for 120 s. The resulting film was heated at 413 K for 10 min to eliminate the residual solvent; then, the solution containing PEDOT(2)-Te-s-SnSe NSs was spin-coated onto this PEDOT:PSS-coated substrate under the same conditions, followed by another PEDOT:PSS spin-coating to obtain a PEDOT:PSS/PEDOT(2)-Te-s-SnSe NS/PEDOT:PSS layered structure, which was heated at 413 K for 10 min. The PEDOT:PSS and PEDOT(2)-Te-s-SnSe NSs solutions were alternately spin-coated onto a glass substrate and repeatedly stacked to fabricate multilayer films of (PEDOT:PSS/PEDOT(2)-Te-s-SnSe $NS)_n$/PEDOT:PSS ($(P/S)_n$/P) structures (where n indicates the 1–5 repetition cycles of the PEDOT:PSS/PEDOT(2)-Te-s-SnSe NS layers in the multilayer films, i.e., n = 1 indicates a P/S/P film and n = 2 a P/S/P/S/P one).

Characterizations

X-ray diffractometry (XRD) was performed with system (New D8-Advance, Bruker-AXS) using Cu Kα radiation (0.154056 nm) to identify the crystal structure of the products, while their binding energies were investigated via X-ray photoelectron spectroscopy (XPS) by using a system (Thermo UK K-alpha) with monochromated Al Kα radiation (1486.6 eV). Field

emission scanning electron microscopy (FE-SEM) and field emission transmission electron microscopy (FE-TEM) analyses were carried out with SIGMA and JEM-2100F microscopes, respectively, to investigate the microstructure of the samples and their atom-based maps were examined through an energy-dispersive X-ray spectroscopy (EDS) system (NORAN system 7, Thermo Scientific). The film thicknesses were measured by using an Alpha-Step 500 surface profiler (AS500, KLA-Tencor Co.). The σ values could be calculated from the electrical resistivity via using a four-point probe method, while S was determined with a pair of voltmeters and thermocouples. The charge-carrier concentration (n) and mobility (μ) of the samples were estimated by a Van der Pauw technique based Hall-effect measurements with a magnetic field of 0.55 T (HMS-3000, Ecopia). Five samples of each product were prepared and tested for the reproducibility of the experiments, all conducted at 300 K.

2. Figures

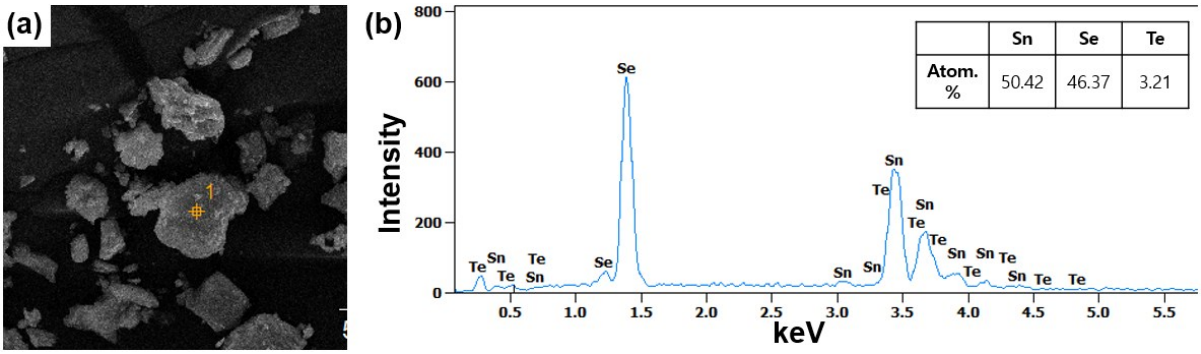

Fig. S1. FE-SEM image and the corresponding EDS result for the Te-s-SnSe powder.

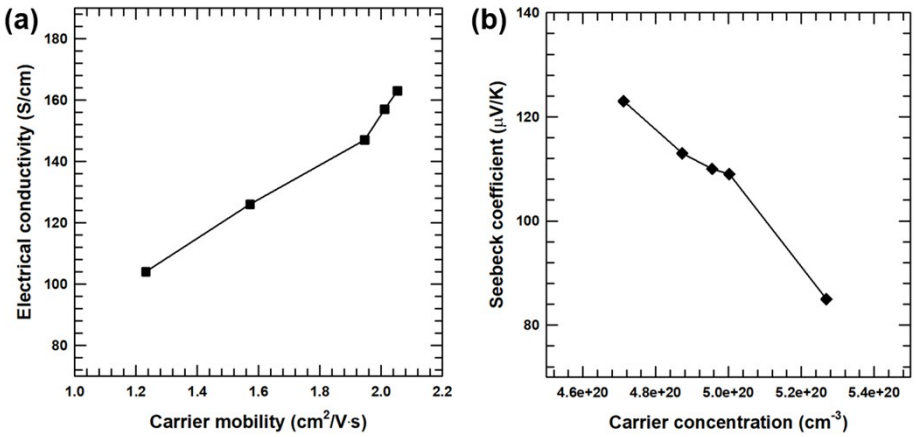

Fig. S2. (a) Electrical conductivity of the $(P/S)_n/P$ multilayer films as a function of a carrier mobility. (b) Seebeck coefficient of the $(P/S)_n/P$ multilayer films with different carrier concentration.

3. Tables

Samples	EDOT (g)	wt.% of PEDOT
PEDOT(1)-Te-s-SnSe	0.023	9.91
PEDOT(2)-Te-s-SnSe	0.047	13.64
PEDOT(3)-Te-s-SnSe	0.094	20.13
PEDOT(4)-Te-s-SnSe	0.189	30.65

Table S1. Nomenclature of PEDOT-Te-s-SnSe samples with different EDOT contents.

	n (cm^{-3})	μ ($cm^2/V \cdot s$)
PEDOT:PSS	7.869×10^{22}	0.051
$(P/S)_1/P$ multilayer	5.269×10^{20}	1.232
$(P/S)_2/P$ multilayer	5.003×10^{20}	1.572
$(P/S)_3/P$ multilayer	4.712×10^{20}	1.947
$(P/S)_4/P$ multilayer	4.873×10^{20}	2.011
$(P/S)_5/P$ multilayer	4.956×10^{20}	2.053

Table S2. Carrier concentration and mobility values of the various $(P/S)_n/P$ multilayer films.

4. Extended discussion

Extended Discussion S1. Detailed description for the parallel-connected model for the PEDOT(x)-Te-s-SnSe NS samples with different content of EDOT monomer. The parallel-connected model for the electrical conductivity and Seebeck coefficient of the PEDOT(x)-Te-s-SnSe NS can be written as:

$$\sigma_{C,P} = (1 - x_T)\sigma_P + x_T\sigma_T \quad (1)$$

$$S_{C,P} = \frac{(1 - x_T)\sigma_P S_P + x_T\sigma_T S_T}{(1 - x_T)\sigma_P + x_T\sigma_T} \quad (2)$$

where $\sigma_{C,P}$, $S_{C,P}$, x_T, σ_P, σ_T, S_P, and S_T are the parallel-connected electrical conductivity and Seebeck coefficient of the PEDOT(x)-Te-s-SnSe NS complex, volume fraction of the Te-s-SnSe NS, electrical conductivity of the PEDOT:PSS, electrical conductivity of the Te-s-SnSe NS, Seebeck coefficients of the PEDOT:PSS, and Seebeck coefficient of the Te-s-SnSe NS, respectively.