Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Experimental details

***Synthesis*:**

Solvothermal

Commercial $SnCl_2 \cdot 2H_2O$ (99%, Aladdin, China) and $Na_2S \cdot 9H_2O$ (99%, Aladdin, China) were used as raw materials and polyethylene glycol (PEG, molecular weight 400, 99%, China) were used as dispersant. Dispersant was added to the ethanediol with the 10 g/L concentration. 0.1M $SnCl_2 \cdot 2H_2O$ and 0.3M $Na_2S \cdot 9H_2O$, ethanediol solution were made and stirred for 20 minutes. 16 mL $SnCl_2 \cdot 2H_2O$ ethanediol solution and 16 mL $Na_2S \cdot 9H_2O$ ethanediol solution were mixed and stirred for 2 minutes. Then the mixture was transferred to a 40 ml solvothermal synthesis reactor made of Teflon at 200 °C for 12 h. After the completion of the reaction, the product was washed with deionized water and ethanol alternately several times and then dried in vacuum at 40 °C overnight.

Mechanical alloying

Commercial powders of 99.99% Sn and 99.99% S (Aladdin, Shanghai) were used as raw materials. The SnS were synthesized by the nominal composition powders using mechanical alloying (QM-1SP2, Nanjing University, China) at 450 rpm for 24 h in the purified argon (>99.5%) atmosphere. Stainless steel vessel (250 mL) and balls were used, and the weight ratio of ball to powder was 20:1.

Rapid annealing

The powder was pressed into small cylinder of 10mm in diameter and 7mm in height, followed by cold isostatic pressing under 200 MPa. The sample was finally annealed by a rapid thermal processing at 650 °C for 5 minutes with a heating rate of 5°C/s

Spark plasma sintering

The powder was loaded into a graphite die in diemeter of 15 mm and then sintered by SPS (SPS-211Lx, Fuji Electronic Industrial, Japan) at 933 K for 5 min under a uniaxial pressure of 50 Mpa.

***Phase structures and microstructures*:** The phase structures were examined by X-ray diffraction (XRD) using Cu Kα radiation (D/max-2500, RIGAKU Japan). The morphologies of the bulk samples were observed by field-emission scanning electron microscopy (FESEM, LEO1530, Germany and JOEL JSM-7001F, Japan) and

transmission electron microscopy (field emission TEM, JEM-2010F). High-resolution transmission electron microscopy (HRTEM) images of the pieces were recorded at 200 kV. The composition analysis was measured by electronic probe microscopic analysis (EPMA, JXA-8230, JEOL, Japan).

***Thermoelectric properties*:** The Seebeck coefficient and electrical resistivity were measured using a Seebeck coefficient/electrical resistivity measuring systems (ZEM-2, Ulvac-Riko, Japan). The thermal conductivity was calculated by the relationship $\kappa = DC_p\rho$, where D, C_p and ρ are the thermal diffusivity, heat capacity and the sample density, respectively. Thermal diffusivity D was measured by the laser flash method (TC9000, Ulvac-Riko, Japan). The thermal diffusivity D was measured along the same direction with that of electrical transport property using the same samples. The carrier concentration and mobility were measured using the Hall measurement system (ResiTest 8400, Tokyo, Japan). The cutting and testing direction of the bulk samples were shown in Figure S1.

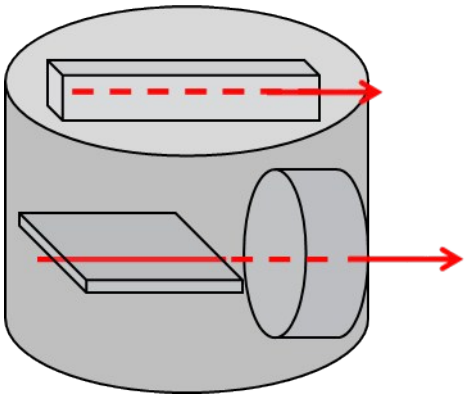

Figure S1 The schematic of cutting and testing direction

Morphology:

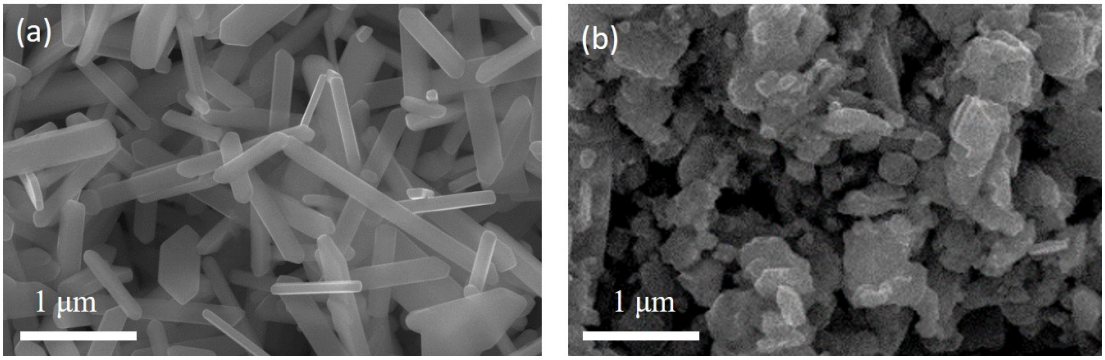

Figure S2 SEM images of the powders synthesized by ST (a) without any dispersant and the (b) powders synthesized by MA