

## Supporting information

for

# Excellent Thermoelectric Performance Achieved in $\text{Bi}_2\text{Te}_3/\text{Bi}_2\text{S}_3@\text{Bi}$ Nanocomposites

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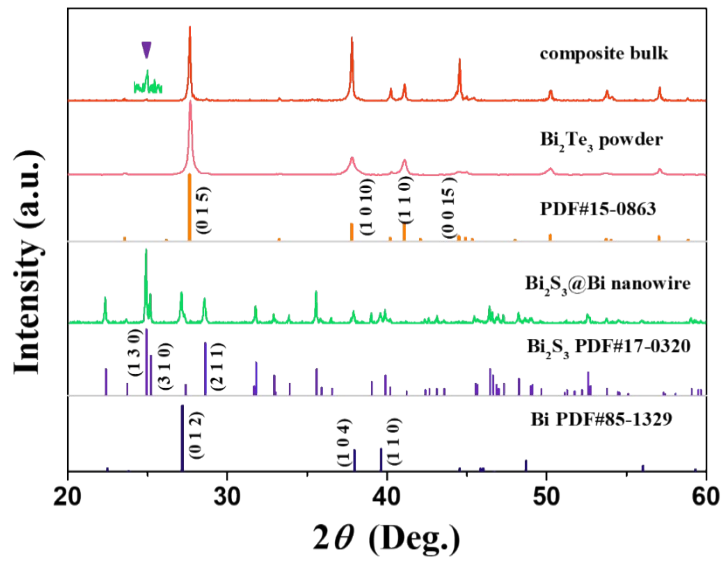
2. Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Forschungszentrum Jülich, 52425 Jülich, Germany.

## Experimental Details

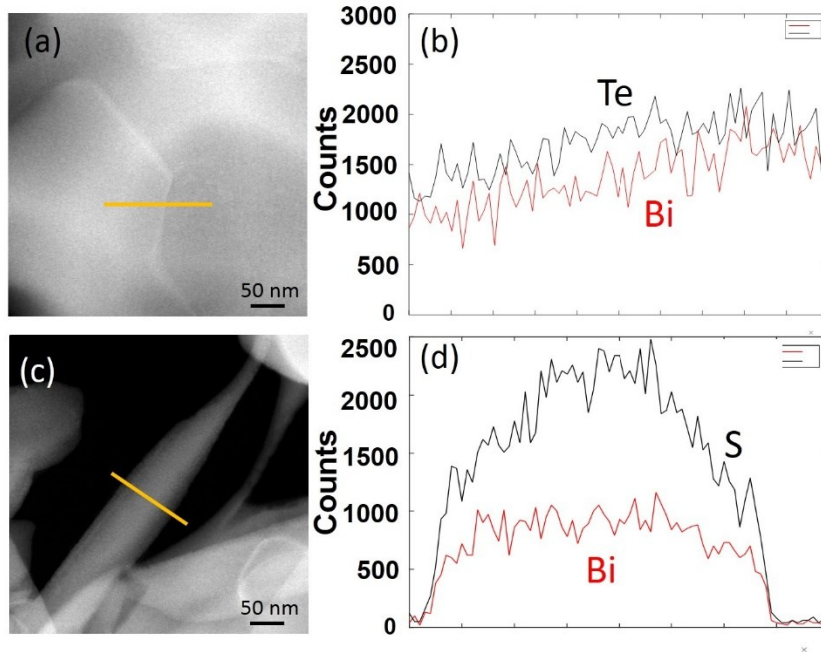
Chemicals used in this work were purchased from Alfa Aesar without any further purification. The nano powders were synthesized by a two-step hydrothermal method as described in our previous work [1]. The  $\text{Bi}_2\text{S}_3$  nanowire is used as a template. At first step, as template materials, [001] oriented single crystal  $\text{Bi}_2\text{S}_3$  nanowires with diameters of 50 to 200 nm and lengths of 500 nm to 10  $\mu\text{m}$ . The preparation of  $\text{Bi}_2\text{S}_3@\text{Bi}$  core-shell nanowires was based on a topical experiment. Initially, 1 g NaOH was added into 20 ml of deionized (DI) water, followed by stirring for 10 min. Then, 10 ml hydrazine was added to the solution, which was again stirred for 20 min. Finally, 0.5 mmol  $\text{Bi}_2\text{S}_3$  nanowire powder was added to the solution, and subjected to a further 30 min of stirring. These stirring steps throughout the process ensured thorough mixing of the solution. The resulting solution was then transferred into a Teflon-lined stainless-steel autoclave (100 ml capacity) together with an additional 30 ml of DI water. The autoclave was heated up to 180°C for 1 h to obtain  $\text{Bi}_2\text{S}_3@\text{Bi}$  core-shell nanowires. For the preparation of  $\text{Bi}_2\text{Te}_3$  nanowires the process is the same with the exception that Te

powder was added together with the resulting solution in the Teflon-lined stainless steel autoclave. The sealed autoclave was heated to 180°C for 1 h. The final black solid product was filtered and then washed with DI water and ethanol three times prior to drying under vacuum at room temperature.

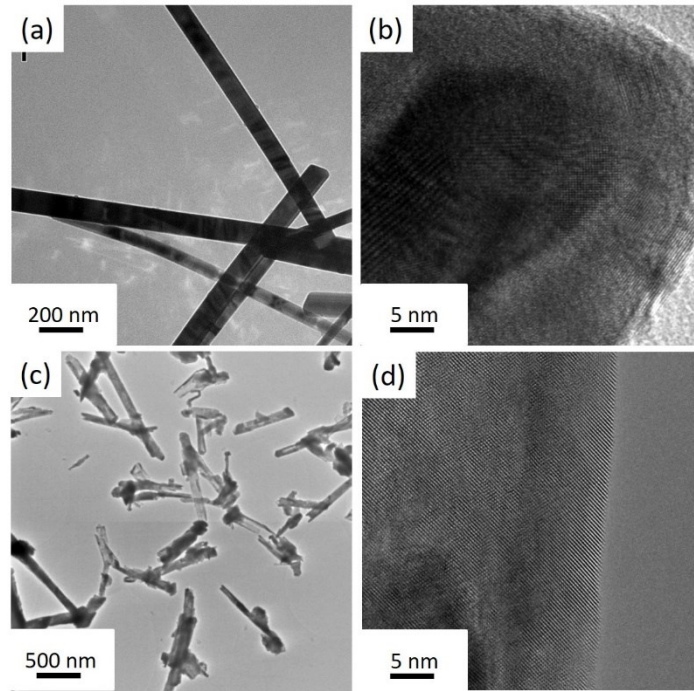
The powders were checked by X-ray diffraction (XRD; Bruker, Germany). Transmission electron microscopy (TEM) observations were performed by using a FEI Tecnai F20 microscope operated at 200 kV. The as-prepared Bi<sub>2</sub>Te<sub>3</sub> powders and Bi<sub>2</sub>S<sub>3</sub>@Bi nanowires with a weight ratio of 4:1 were mixed and densified by spark plasma sintering at 673 K for 5 min under the pressure of 50 MPa using an SPS system (Sumitomo SPS1050, Japan). The phase structure of the sintered samples was analyzed by XRD. The morphologies of fractography were observed by field emission scanning electron microscopy (FESEM; Zeiss Merlin, Germany). The TE properties were evaluated along the sample section perpendicular to the pressing direction of SPS. The Seebeck coefficient and electrical resistivity were measured from 323 to 523 K in a helium atmosphere by using the Seebeck coefficient/electric resistance measuring system (ZEM-3, Ulvac-Riko, Japan). The thermal conductivity  $\kappa$  was calculated via the relation  $\kappa = DC_p d$ . Among that the thermal diffusivity coefficient ( $D$ ) of the specimens was captured through laser flash method (NETZSCH, LFA457, Germany), the mass density ( $d$ ) was obtained via the Archimedes method, the  $C_p$  value was obtained by the Kopp's law. The Hall coefficients ( $R_H$ ) of the samples were measured at the range of 323-523 K using a physical properties measurement system (PPMS-9T, Quantum Design Inc., USA).



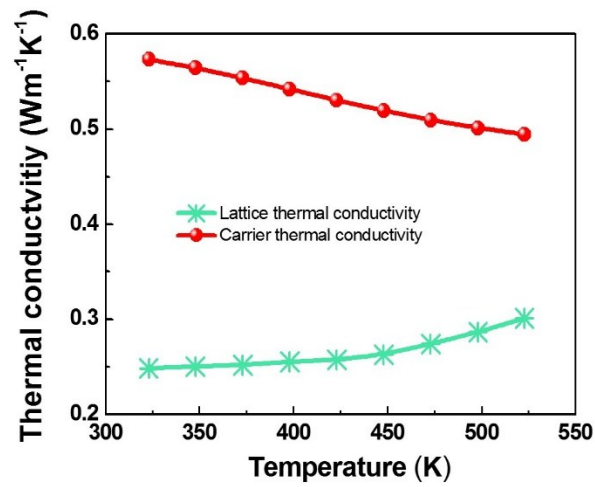
**Fig. S1** XRD patterns of  $\text{Bi}_2\text{S}_3@$ Bi powders,  $\text{Bi}_2\text{Te}_3$  powders, and composite bulk.



**Fig. S2** (a) The FESEM image of  $\text{Bi}_2\text{Te}_3$  bulk and (c)  $\text{Bi}_2\text{S}_3@$ Bi nanowires in the bulk sample and the EDS line scanning results along with the yellow line to the (b)  $\text{Bi}_2\text{Te}_3$  bulk and (d)  $\text{Bi}_2\text{S}_3@$ Bi nanowires in the bulk.



**Fig. S3** TEM images of the  $\text{Bi}_2\text{S}_3@\text{Bi}$  nanowires, which reveals the size uniformity of the  $\text{Bi}_2\text{S}_3@\text{Bi}$  nanowires and the thickness of Bi shell.



**Fig. S4** Lattice thermal conductivity and carrier thermal conductivity of the bulk composite

## References

- [1] Z.H. Ge, G.S. Nolas, Cryst. Growth Des. 14 (2014) 533-536.