Supplementary Information (SI) for CrystEngComm.

Supporting Information

Multistage Pore Structure in Bi_2Te_3/SiC Composites: Achieving Lower Thermal Conductivity and Enhanced Thermoelectric Performance

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Supporting Information:

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Note 1. Experimental Methods

1.1. Materials.

The following chemicals were used for the synthesis of spherical Bi_2Te_3 and subsequent surface functionalization with hydroxyl and silane groups: bismuth(III) chloride ($BiCl_3$), nitric acid (HNO_3, 60%), thioglycolic acid ($HSCH_2COOH$), hydrazine monohydrate ($N_2H_2{\cdot}H_20$, 80%), hydrogen peroxide (H_2O_2, 35%), ethyl alcohol (C_2H_5OH, 94.5%), toluene ($C_6H_5CH_3$), deionized water (DI water), and octadecyltrichlorosilane ($CH_3(CH_2)_{17}SiCl_3$, 95%), which were purchased from Daejung Chemical & Metals Co. (Seoul, Republic of Korea). Additionally, telluric acid dihydrate (H_6TeO_6) was obtained from Alfa Aesar (Haverhill, MA, USA).

For the synthesis of spherical SiC and surface functionalization with hydroxyl and hydrophobic groups, Si nanoparticles (approximately 10 nm in size) and Brij56 [polyoxyethylene (10) cetyl ether] (C16H33(EO)10) were procured from Sigma-Aldrich (St. Louis, MO, USA). Furthermore, 1N-hydrogen chloride (HCl), hydrofluoric acid (HF), sulfuric acid (H_2SO_4, 95%), sodium hydroxide pellets (NaOH), ammonium hydroxide (NH_4OH, 30%), and CTAB ($C_{19}H_{42}BrN$) were obtained from Daejung Chemical & Metals Co. (Seoul, Republic of Korea).

1.2. Synthesis and Functional-Group Surface Treatment of Spherical Bi_2Te_3

In a typical synthesis, 0.37 g of H_6TeO_6 was dissolved in 20 mL of DI water. Separately, an aqueous solution was prepared by dissolving 0.335 g of $BiCl_3$ in a mixture of 6.67 mL of HNO_3 and 12.3 mL of H_2O. Subsequently, 1.4 mL of thioglycolic acid was added to this initially transparent solution, leading to a color change to yellow owing to the formation of a bismuth complex. The H_6TeO_6 solution was then combined with the yellow solution, followed by the addition of 285 mL of DI water, and the mixture was sonicated for 5 min. Subsequently, 75 mL of hydrazine was added dropwise to the sonicated solution, and the reaction mixture was aged at 300 K for 48 h. Upon completion of the reaction, the precipitate was collected via filtration and washed multiple times with DI water to remove unreacted materials. The final product was dried in a vacuum oven at 323 K for 24 h to remove residual moisture. Surface treatments were sequentially performed to introduce hydroxyl and silane functional groups to enhance the hydrophobicity of spherical Bi_2Te_3.

1.2.1. Hydroxylation of Bi_2Te_3 Surface

For surface hydroxylation, 0.1 g of the synthesized Bi_2Te_3 was dispersed in 100 mL of ethanol and ultrasonicated for 15 min to ensure a uniform suspension and generate reactive sites on the surface. Then, 10 mL of 35% H_2O_2 was added to the suspension to introduce hydroxyl groups. The reaction was carried out at 333 K for 12 h with continuous stirring. After completion, the hydroxylated Bi_2Te_3 was collected via centrifugation (8000 rpm for 15 min), washed with ethanol to remove residual impurities, and washed with DI water. The cleaned product was dried in a vacuum oven at 333 K for 24 h to remove the residual moisture.

1.2.2. Silane Functionalization of Bi_2Te_3 Surface

For silane functionalization, 10 mL of octadecyltrichlorosilane was dissolved in 100 mL of anhydrous toluene. Hydroxylated Bi_2Te_3 (0.1 g) was then dispersed in 100 mL of toluene via ultrasonication for 15 min to ensure proper dispersion. The silane solution was added dropwise to the dispersion under constant stirring, and the reaction was allowed to proceed at

333 K for 24 h under continuous stirring. After completion, a small amount of ethanol or DI water was added to quench any unreacted silane groups. The product was collected via centrifugation (10,000 rpm for 10 min), washed with ethanol to remove residual impurities, and then washed with DI water. The cleaned product was then dried in a vacuum oven at 333 K for 24 h to remove residual moisture.

1.3. Synthesis and Functional-Group Surface Treatment of Spherical SiC

In a typical synthesis, 0.917 g of Si nanoparticles were dispersed in 33 mL of DI water. Subsequently, 0.02 mL of HCl, 43.3 mL of ethanol, and 1.97 g of Brij56 were added, and the mixture was stirred for 1 h. The resulting mixture was ultrasonicated before being carried by Ar gas at a flow rate of 100 standard cubic centimeters per minute (sccm) into a tubular reactor. The tubular reactor consisted of two segments: a drying zone and heating zone. The drying and heating zones were heated to 423 K and 1523 K, respectively. At the entrance of the heating zone, ethanol was ultrasonically atomized and carried by Ar gas at a flow rate of 60 sccm. The synthesized particles were collected via filtration at the outlet of the heating zone. After the reaction was complete, the reactor was cooled to 300 K, and the obtained product was exposed to air and heated to 873 K for 4 h to remove excess carbon. The product was then treated with HF to eliminate the SiO_2 layer adsorbed on the surface of spherical SiC particles. Specifically, 10 g of SiC powder was placed in 300 mL of a 10% HF solution and stirred for 24 h. The sample was then washed with distilled water until the pH of the leaching water reached 7–8.

1.3.1. Hydroxylation of the SiC Surface

An acid oxidation treatment was performed to enhance the reactivity of the SiC surface. A mixture of concentrated H_2SO_4 and HNO_3 in a 3:1 ratio was prepared, and the synthesized SiC particles were added. The mixture was stirred at 300 K for 2 h using a magnetic stirrer to oxidize the SiC surface and introduce reactive sites for hydroxylation. For hydroxylation, the oxidized SiC particles were introduced into a 35% H_2O_2 solution and heated to 353 K, with continuous stirring for 6 h. Subsequently, the oxygen-containing functional groups on the SiC surface were converted into hydroxyl groups by immersing the oxidized SiC particles in a 2 M NaOH solution prepared in DI water and stirring at 300 K for 4 h.

1.3.2. CTAB Surface Modification of SiC

To modify the SiC surface, a CTAB solution was prepared by dissolving 2 g of CTAB in 200 mL of DI water. The solution was stirred on a hot plate at 323 K until CTAB was fully dissolved. Once prepared, 0.1 g of hydroxylated SiC was added to the solution, and the mixture was stirred at 323 K for 6 h, allowing the CTAB molecules to adsorb onto the SiC surface. After the reaction, the particles were centrifuged and washed thoroughly with DI water to remove the unadsorbed CTAB. Finally, the product was dried in an oven at 333 K for 6 h to complete the surface-modification process.

1.4. Fabrication of Multistage Pore-Structure Bi_2Te_3/SiC Composites

First, 28 mL of DI water (pH = 11.0) and 10.8 g of surface-treated Bi_2Te_3 were ball-milled at 300 rpm for 4 h to obtain a well-dispersed Bi_2Te_3 slurry (mass ratio of milling balls to slurry = 2:1). The pH of the Bi_2Te_3 slurry was adjusted to 11.0. Separately, surface-treated SiC (0.22, 0.45, 0.69, and 0.94g, corresponding to additions of 2 wt.%, 4 wt.%, 6 wt.%, and 8 wt.%, respectively) was sonicated in 10 mL of DI water (pH = 11.0) for 30 min. The dispersed SiC slurry was then added to the Bi_2Te_3 slurry and stirred at 600 rpm for 20 min to ensure uniform dispersion, forming a homogeneous ceramic slurry. CTAB foam was prepared by first dissolving 0.03 g of CTAB in 10 mL of DI water (pH = 11.0) under magnetic stirring at 300 rpm for 2 h. The solution was then mechanically stirred at 500 rpm for 5 min to generate foam. Subsequently, the prepared ceramic slurry was incorporated into the CTAB foam and mechanically stirred at 800 rpm for 5 min, and then at 2000 rpm for 10 min, to form a composite ceramic foam. The ceramic foam was then transferred into stainless-steel molds, which were placed on a gypsum board and allowed to rest for 20 min. Subsequently, the ceramic foam was demolded and dried in an oven at 313 K for 24 h. Finally, the dried green body was sintered at (450, 475, 500, 525, and 550 K, respectively) for 2 h at a heating rate of 10 K/min and naturally cooled to 300 K to produce the final composite.

1.5. Characterization

X-ray diffraction (XRD; New D8 Advance, Bruker AXS, TX, USA) was performed to confirm the crystalline structure of the Bi_2Te_3 and SiC microspheres. The analysis was performed at 40 kV and 40 mA, with a scan rate of 1°/s, covering a 2θ range from 10° to 80° under Cu Kα radiation ($\lambda = 0.154056$ nm). The morphology and microstructure were examined using field-emission scanning electron microscopy (FE-SEM; SIGMA 300, Carl Zeiss, Germany). Elemental mapping of the synthesized materials was performed by energy-dispersive X-ray spectroscopy (EDS; NORAN System 7, Thermo Scientific, Waltham, MA, USA). X-ray photoelectron spectroscopy (XPS; K-alpha plus, ThermoFisher Scientific, Waltham, MA, USA) with an Al Kα X-ray source (1486.6 eV) was employed to analyze the sample binding energies. Fourier transform infrared (FT-IR) spectroscopy (ATR mode, Spectrum One, Perkin-Elmer, Waltham, MA, USA) was performed to verify the chemical structures of the fillers. Using a custom-built device, the thermoelectric properties, including the Seebeck coefficient and electrical conductivity, were measured over ten repeated cycles at 300 K. The Seebeck coefficient (S) was calculated as $S = \Delta V/\Delta T$, where ΔT is the temperature difference, and ΔV denotes the change in the thermal electromotive force. Electrical conductivity was determined using the four-point probe method. By measuring the current (I) and voltage (V) to determine the resistance (R), the electrical conductivity (σ) was derived by sequentially calculating the sheet resistance (R_s) and resistivity (ρ), with a correction factor accounting for the thickness and size of the composite. Thermal conductivity (κ) was measured using laser flash analysis (NanoFlash LFA 467, Netzsch, Bayern, Germany) at 300 K.

2. Figures

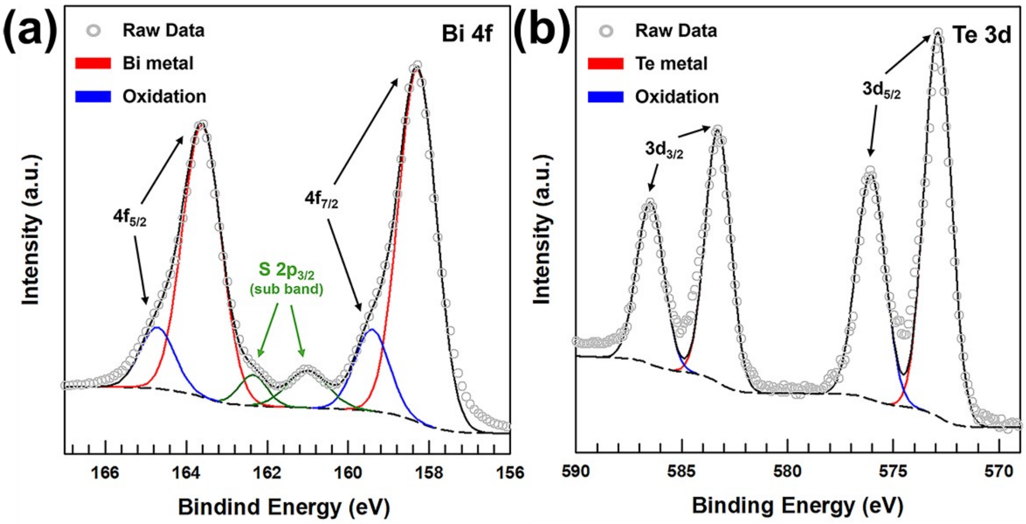

Fig. S1. High-resolution (a) Bi 4f and (b) Te 3d XPS spectra of pristine Bi_2Te_3.

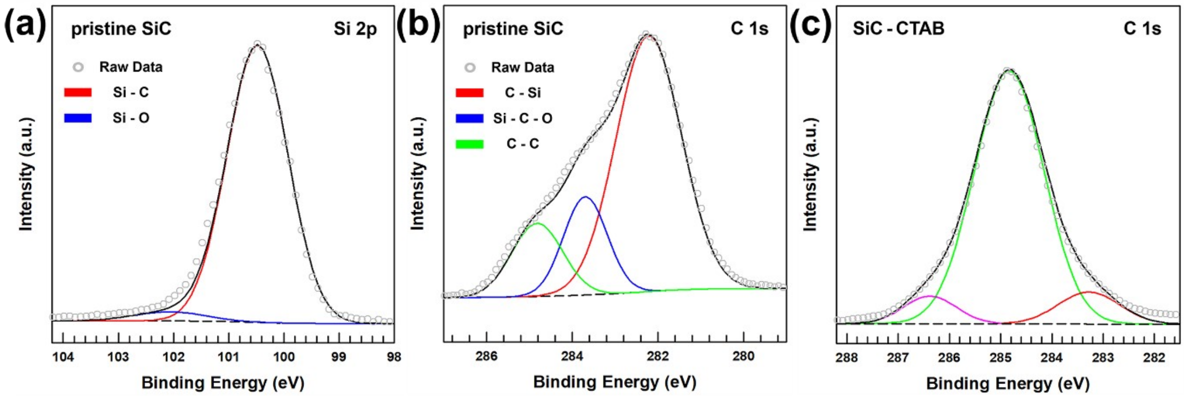

Fig. S2. High-resolution (a) Si 2p and (b) C 1s XPS spectra of pristine SiC. (c) High-resolution C 1s XPS spectra of SiC-CTAB.

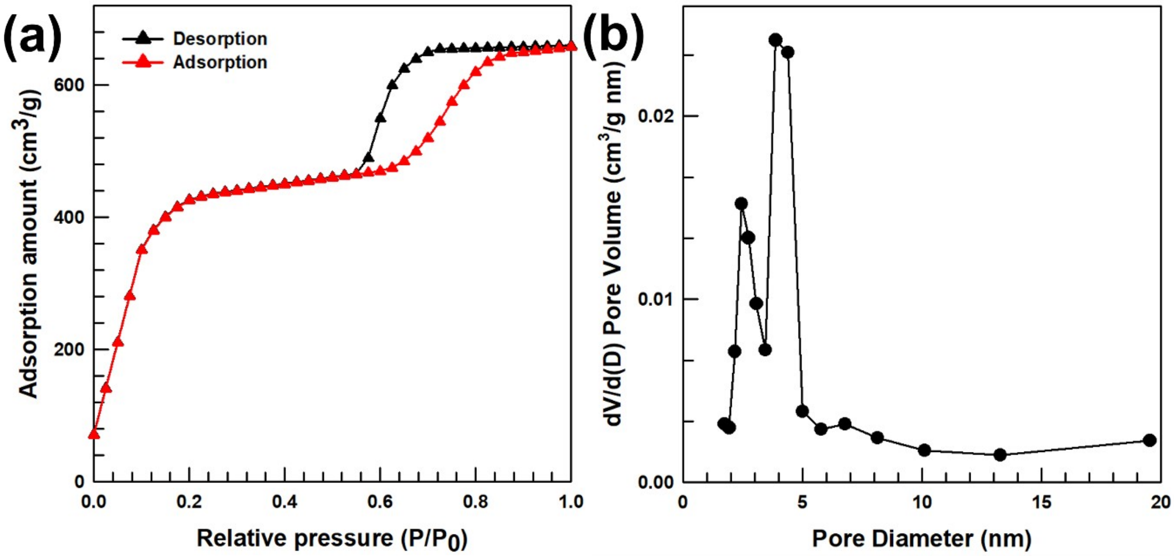

Fig. S3. (a) N_2 adsorption-desorption isotherm curves and (b) BJH pore size distribution curve.

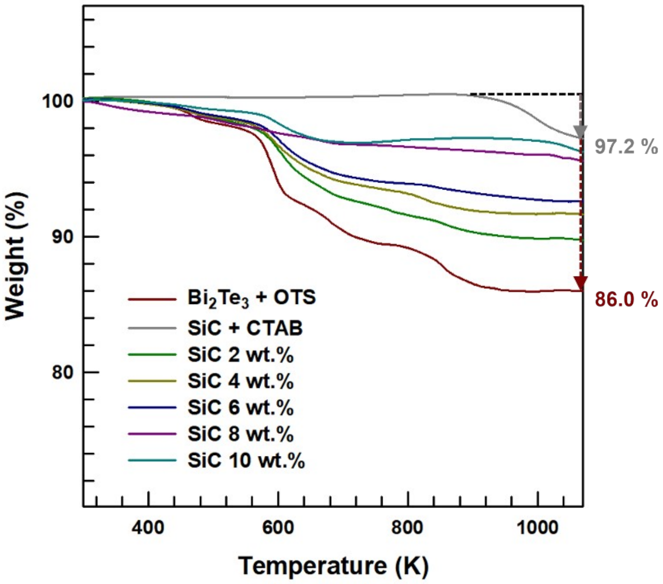

Fig. S4. TGA graphs of surface-treated Bi_2Te_3 and SiC, and each composite.

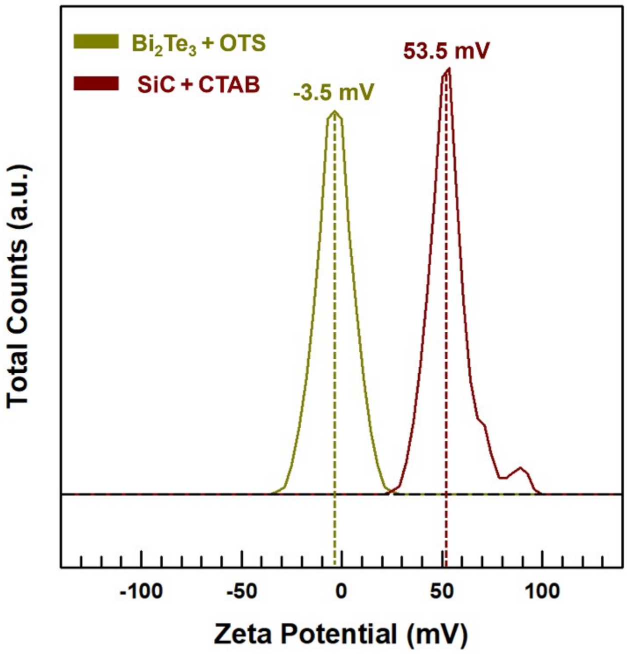

Fig. S5. Zeta potential value of surface-modified Bi2Te3 and SiC.

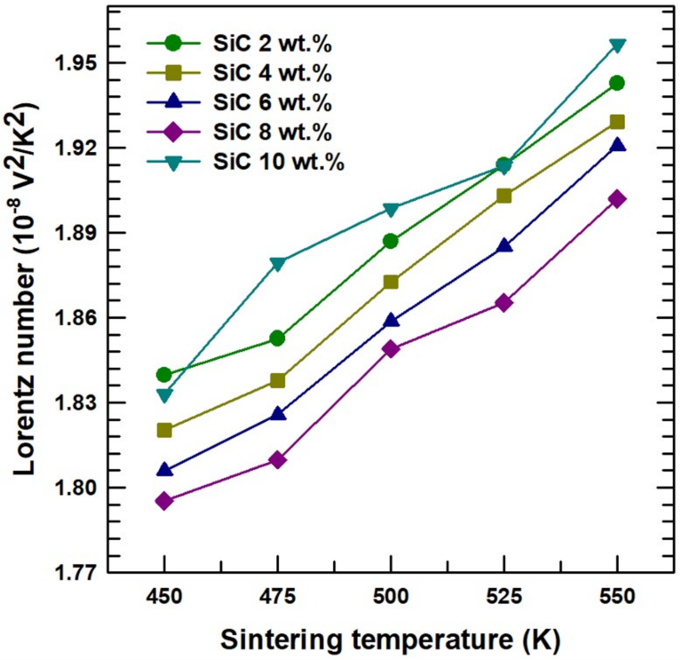

Fig. S6. Calculated Lorentz number of each final composite at 300 K depending on sintering-temperature.

3. Table

Sintering T = 450 K (measured at 300 K)	2 wt.% SiC	4 wt.% SiC	6 wt.% SiC	8 wt.% SiC
Carrier concentration (n) [$10^{18}cm^{-3}$]	5.75	5.31	5.00	4.79
Carrier mobility (μ) [$cm^2/V\cdot sec$]	305.61	273.26	251.70	223.29

Table. S1. Carrier concentration and mobility values of each Bi_2Te_3/SiC composite at 300 K when the sintering temperature is 450 K.

SiC content	2 wt.%	4 wt.%	6 wt.%	8 wt.%	10 wt.%
Specific surface area (m^2/g)	16.34	25.91	37.11	68.72	8.43

Table. S2. BET analysis results with various SiC content.