Supplementary Information (SI) for Dalton Transactions.

Supporting Information

Enhanced Thermoelectric Performance of Flexible PEDOT:PSS/PEG Matrices Incorporating Hollow Ag@Ag_2Se Core–Shell Fillers

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Supporting Information:

Note 1. Experimental Methods

1.1. Materials

Sodium chloride (NaCl), anhydrous ethanol (C_2H_5OH, 99.8%), polyvinylpyrrolidone (PVP), and sodium borohydride ($NaBH_4$) powder were purchased from Sigma-Aldrich (USA). Silver(I) nitrate ($AgNO_3$), selenium (Se) powder, sodium sulfite (Na_2SO_3, anhydrous), diethylene glycol (DEG, $C_4H_{10}O_3$), sodium hydroxide (NaOH) pellets, and deionized (DI) water were obtained from Daejung Chemical & Metals Co. (Seoul, Korea). PEDOT:PSS (Clevios™ PH 1000) was purchased from Heraeus Clevios GmbH (Germany), and polyethylene glycol 1000 (PEG-1000, $H(CH_2CH_2O)_nOH$) was supplied by Daejung Chemical & Metals Co. (Seoul, Korea). All reagents were of analytical grade and used as received without further purification.

1.2. Synthesis of Hollow Ag Particles

Hollow Ag particles were synthesized using a water-soluble NaCl template method. In a typical procedure, 3.6 g of NaCl was dissolved in 10 mL of deionized (DI) water to form a saturated NaCl solution. Subsequently, 5 mL of this solution was rapidly injected into 200 mL of anhydrous ethanol at 263 K under stirring to induce antisolvent crystallization, resulting in the formation of cubic NaCl templates. Separately, 1.5 g of $AgNO_3$ and 1.5 g of PVP were dissolved in 50 mL of anhydrous ethanol under stirring to prepare an Ag precursor solution. The NaCl templates were then added into this $AgNO_3$–PVP solution and stirred in the dark for 24 h, allowing the formation of NaCl@AgCl composite particles. The obtained NaCl@AgCl particles were dispersed in ethanol, and $NaBH_4$ was added as a reducing agent. The reduction was carried out at 263 K for 3 h under continuous stirring to produce

NaCl@Ag particles. Finally, the products were repeatedly washed with ethanol and DI water, followed by vacuum filtration, to obtain the hollow Ag particles after the removal of NaCl templates.

1.3. Preparation of Hollow Ag@Ag_2Se Fillers

The hollow Ag@Ag_2Se core–shell fillers were synthesized via a solution-phase selenization process. Prior to the reaction, a 0.2 M Na_2SeSO_3 stock solution was prepared by dissolving 0.32 g of Se powder and 0.5 g of Na_2SO_3 in 40 mL of DI water, followed by stirring at 360 K for 1 h. Then, 5 mL of this stock solution was mixed with 15 mL of diethylene glycol (DEG) to obtain a 0.05 M Na_2SeSO_3/DEG precursor solution (20 mL).

For the selenization, 0.12 g of the as-prepared hollow Ag particles, 0.9 g of PVP, and 30 mL of DEG were mixed and stirred, and the pH was adjusted to 9 using 0.1 M NaOH. The mixture was then transferred to an oil bath maintained at 350 K. The 0.05 M Na_2SeSO_3/DEG solution (20 mL) was injected dropwise into the system at a rate of 0.5 mL min^{-1} under continuous stirring. After the complete addition, the reaction was maintained for an additional 1 h to ensure uniform shell growth. The resulting products were washed several times with ethanol and DI water, and finally collected by vacuum filtration to obtain the hollow Ag@Ag_2Se core–shell fillers.

1.4. Fabrication of Hollow Ag@Ag_2Se/PEDOT:PSS/PEG Composites

For the preparation of the final composites, a PEDOT:PSS/PEG matrix was first prepared. PEG 1000 was incorporated at a content of 10 wt.% in the PEDOT:PSS/PEG matrix. PEG 1000 was completely melted at 330 K, while PEDOT:PSS (Clevios PH 1000) was mixed with 5 mL of ethylene glycol (EG) and stirred for 1 h. The two solutions were then combined and stirred for an additional 3 h to form a homogeneous PEDOT:PSS/PEG matrix.

Subsequently, the hollow $Ag@Ag_2Se$ fillers were incorporated into the matrix at loadings of 2.5, 5, 7.5, and 10 wt%. The mixtures were stirred and ultrasonicated to achieve uniform filler dispersion. After thorough homogenization, the composite solutions were drop-cast onto smooth culture dishes and dried under vacuum at 330 K for 6 h. Finally, the dried films were peeled off from the substrates to yield free-standing, flexible composite films of hollow $Ag@Ag_2Se$/PEDOT:PSS/PEG.

1.5. Characterization

X-ray diffraction (XRD; New D8 Advance, Bruker AXS, TX, USA) was performed to confirm the crystalline structure of the NaCl template and prepared fillers. The measurements were conducted at an operating voltage of 40 kV and a current of 40 mA using Cu Kα radiation ($\lambda = 0.154056$ nm). Diffraction patterns were collected over a 2θ range of 10°–80° with a scan rate of 1°/min and a step size of 0.02°. 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). Particle size analysis (PSA) was performed using a laser diffraction particle size analyzer (SALD-2300, Shimadzu, Japan) to evaluate the size distribution of the NaCl templates. 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 chemical interactions between PEDOT:PSS and PEG. Using a custom-built device, the thermoelectric properties, including the Seebeck coefficient and electrical conductivity, were measured. Each thermoelectric property was measured on at least five independently prepared samples, and the reported values represent the average with standard deviation. Error bars in the figures indicate the standard deviation of the measured values. 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), with an estimated measurement uncertainty of ±5% arising from thermal diffusivity, density, and specific heat capacity. Latent heat and phase-change behavior of the matrix were measured by differential scanning calorimetry (DSC; Perkin-Elmer DSC-7) in the range of 300 - 370 K.

2. Figures

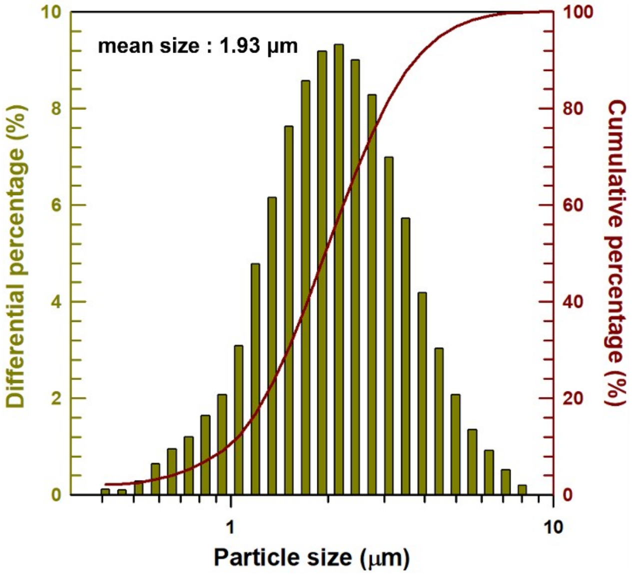

Fig. S1. Particle size distribution of NaCl templates.

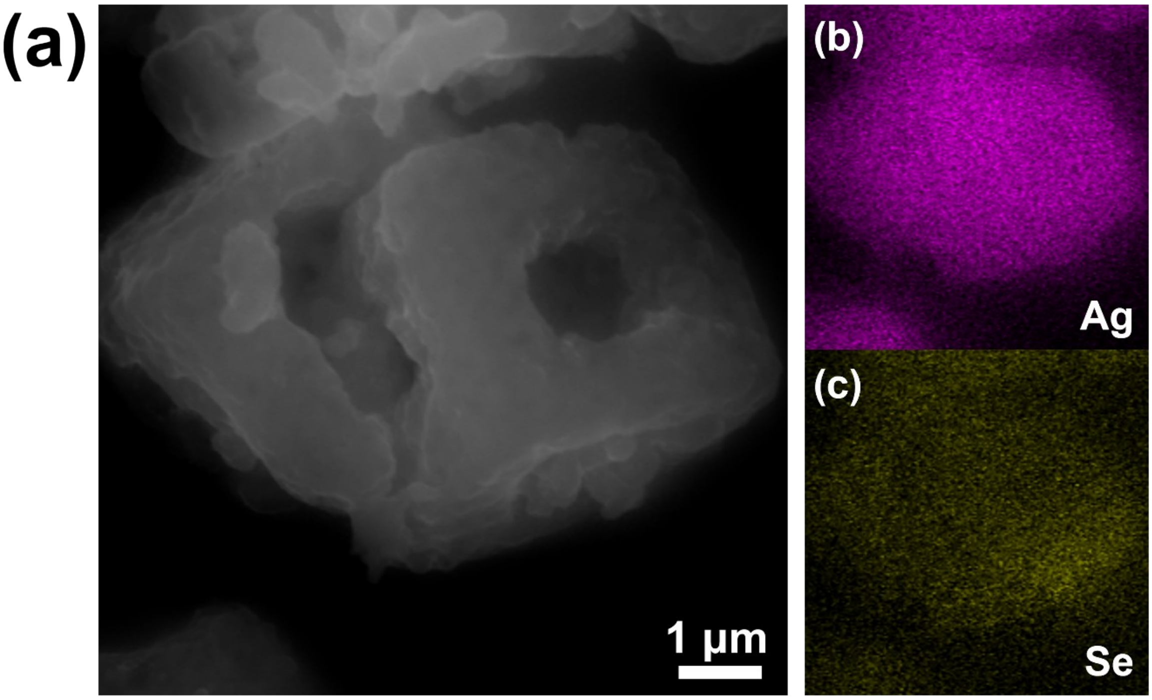

Fig. S2. (a) FE-SEM and (b-c) EDS elemental mapping images of hollow Ag@Ag_2Se.

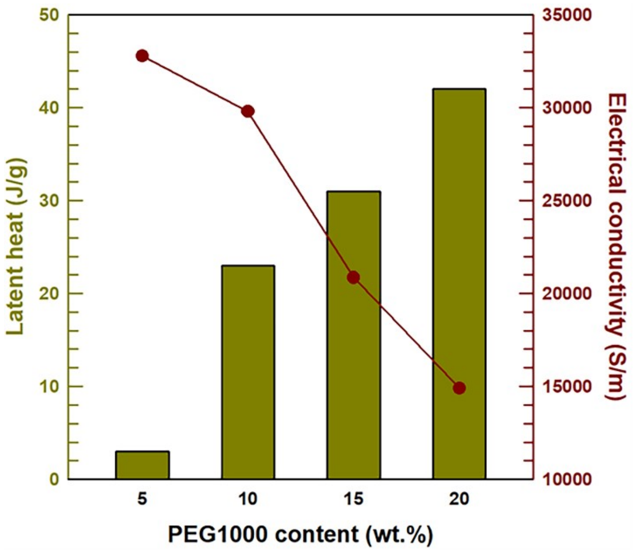

Fig. S3. Latent heat (yellow bars) and electrical conductivity (red line) of the PEDOT:PSS/PEG matrix as a function of PEG content.

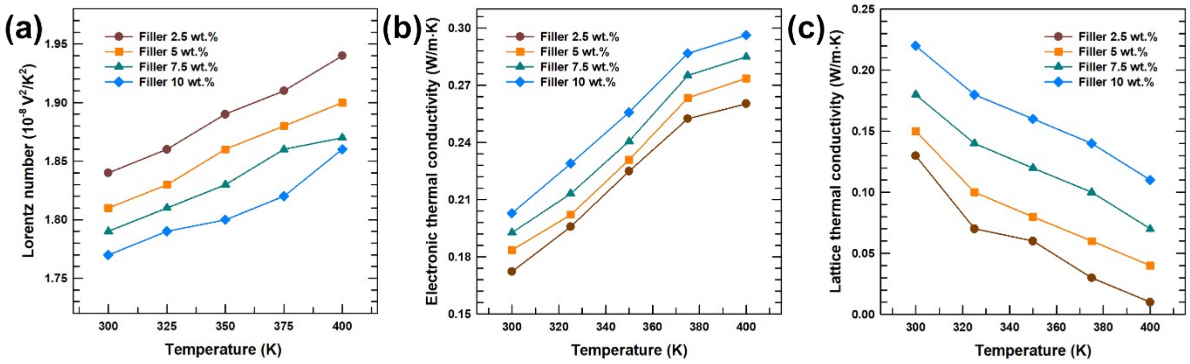

Fig. S4. Temperature-dependent (a) Lorentz number, (b-c) electronic and lattice thermal conductivity of each composite.

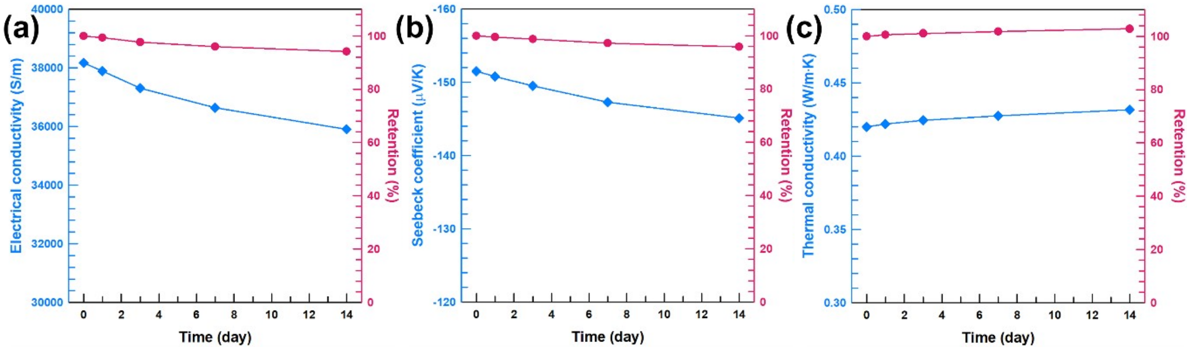

Fig. S5. Environmental stability of the 10 wt.% Ag@Ag_2Se composite under humid air conditions at 300 K, showing time-dependent changes in (a) electrical conductivity, (b) Seebeck coefficient, and (c) thermal conductivity, together with their retention ratios.

3. Tables

Temperature (K)	Seebeck coefficient (S) (μV/K)	Power factor (μW/m·K^2)	Figure of merit (ZT)
300	18.5	10.2	0.01
325	15.7	7.5	0.01
350	11.1	3.8	< 0.01
375	7.9	1.9	< 0.01
400	5.3	0.8	< 0.01

Table S1. Temperature-dependent Seebeck coefficient, power factor, and figure of merit of PEDOT:PSS/PEG matrix.

Heating-cooling cycles (count)	Electrical conductivity (S/m)	Seebeck coefficient (μV/K)	Thermal conductivity (W/m·K)
0	38174	-151.5	0.42
5	37791	-150.8	0.42
10	37128	-150.2	0.42
15	36543	-149.7	0.43
20	36019	-149.1	0.43

Table S2. Thermoelectric properties of the 10 wt.% Ag@Ag_2Se composite measured as a function of heating–cooling cycles at 300 K.