Supporting Information for

Enhancement of thermoelectric performance in non-toxic $CuInTe_2$/SnTe coated grain nanocomposite

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Seebeck coefficient calculation

The enhancement of the Seebeck coefficient by energy filtering was analyzed using the model of *A. Popescu*'s work.[1] The transmission probability is described in the main text(Eq. 2). Before applying the model to calculation, the Seebeck coefficient for uncoated SnTe should be calculated correctly. The SnTe has a narrow gap(~ 0.18 eV) at the non-parabolic light hole band maximum, and below that there is a heavy hole band with a band offset around 0.3 ~ 0.4 eV.[2] To consider the non-parabolicity and multi-band effect, we used following equations.[2, 3]

$$S_{lh} = \frac{k_B}{e}\left[\frac{{}^{1}F_{-2}^{1}(\eta,\alpha)}{{}^{0}F_{-2}^{1}(\eta,\alpha)} - \eta\right] \quad : \quad \text{light hole band}$$
$$S_{hh} = \frac{k_B}{e}\left[\frac{{}^{1}F_{-2}^{1}(\eta-\Delta_v,\alpha)}{{}^{0}F_{-2}^{1}(\eta-\Delta_v,\alpha)} - (\eta-\Delta_v)\right] \quad : \quad \text{heavy hole band} \qquad \text{Eq. S1}$$

Here, k_B, e, η, α, and Δ_v are the Boltzmann constant, electron charge, reduced Fermi level, non-parabolicity parameter(= k_BT/E_g), and band offset respectively. F is the Fermi-Dirac integral,[3, 4]

$${}^{n}F_{k}^{m} = \int_0^\infty \left(\frac{\partial f_0}{\partial x}\right) x^n \left(x+\alpha x^2\right)^m \left[\left(1+2\alpha x\right)^2 + 2\right]^{k/2} dx \qquad \text{Eq. S2}$$

where f is Fermi-Dirac distribution function and x is reduced energy(= E/k_BT). The electrical conductivities for both bands are,[2]

$$\sigma_{lh} = \frac{C}{m_{lh} D_{lh}^2}\,{}^{0}F_{-2}^{1}(\eta,\alpha)$$
$$\sigma_{hh} = \frac{C}{m_{hh} D_{hh}^2}\,{}^{0}F_{-2}^{1}(\eta-\Delta_v,\alpha) \qquad \text{Eq. S3}$$

where, C, m and D are the constant, effective mass and deformation potential respectively. Only the ratio of each conductivities is important, thus we used ratio

D_{hh}/D_{lh} = 0.5. The effective masses for both bands are obtained from the literatures[2], m_{lh} = 0.168m_e, m_{hh} = 1.92m_e. The total Seebeck coefficient can be obtained by following equation.

$$S_{total} = \frac{\sigma_{lh} S_{lh} + \sigma_{hh} S_{hh}}{\sigma_{lh} + \sigma_{hh}} \qquad \text{Eq. S4}$$

To fit our experimental data of uncoated SnTe, we used temperature dependent Fermi level position and band offset as shown in Figure S4.

To fit the data of coated grain $CuInTe_2$/SnTe nanocomposites we utilized a transmission factor which is described in main text Eq. 2. But the variation of Seebeck coefficient among various amounts of coating could not be explained by variation of the barrier thickness(w_B). Instead, we utilized fraction factor, f_v, to fit the experimental data. In the real experiment, some portion of SnTe particles could be coated because of the variation of Cu, In precursors' amounts. Therefore, to consider this factor we assumed that only some portion of the grains are coated, while the rest remain uncoated. The final transmission probability is described as following equations.

$$T_B = \frac{4E\left(E_B - E\right)}{E_B^2 \sinh^2\left(2w_B\sqrt{2m^*\left(E_B - E\right)}/\mathrm{h}\right) + 4E\left(E_B - E\right)}, \qquad \left(E < E_B\right)$$

$$= \frac{4E\left(E - E_B\right)}{E_B^2 \sinh^2\left(2w_B\sqrt{2m^*\left(E - E_B\right)}/\mathrm{h}\right) + 4E\left(E - E_B\right)}, \qquad \left(E > E_B\right) \qquad \text{Eq. S5}$$

Total transmission probability $T_{B\_total} = T_B f_v + 1 \cdot \left(1 - f_v\right)$

Modeling of coherent phonon scattering[5]

The theoretical model for coherent phonon scattering is based on our previous study.[5] The model assumes the coated grain media as close-packed core-shell spheres. The detailed derivations of scattering cross section and relaxation time are described in our previous study. Here, we briefly describe the derivation of model in our previous study.

The model is based on Mie scattering theory about light scattering by multiple particles. Due to the wave-like behavior of phonon, the scattering of phonon could be discussed using octics.[6-8] The light scattering in polycrystal transparent alumina had been discussed under assumption of transparent spheres.[9] Thus, our previous model[5] assumes the polycrystal coated grains as close-packed core-shell spheres which are transparent for phonon waves. The phase lag of a phonon passing through the coating layer as induced by the acoustic impedance difference had been discussed by approximated Mie scattering theory. The obtained scattering cross section is given as,

$$\sigma_M = 2\,\mathrm{Re}\left(\begin{array}{l} \int_0^{\alpha_c} \left\{ 1 - e^{2i\chi\cos\alpha\left[\frac{k'}{k}\left(1-\sqrt{t^2\cdot\sec^2\alpha-\tan^2\alpha}\right)+\sqrt{t^2\cdot\sec^2\alpha-\tan^2\alpha}-1\right]} \right\} 2\pi R\sin\alpha d\left(R\sin\alpha\right) \\ +\int_{\alpha_c}^{\pi/2}\left[1 - e^{2i\chi\cos\alpha\left(\frac{k'}{k}-1\right)} \right] 2\pi R\sin\alpha d\left(R\sin\alpha\right) \end{array} \right) \quad \text{Eq. S6}$$

where, *k, k', χ, α, and R* are the wavevector in matrix, wavevector in coating layer, size parameter, incident angle, and radius of grain with coating thickness respectively. The parameter *t* in Eq. S6 is *r/R*, where *r* is radius of grain without the coating thickness. To consider the dependent(correlated) scattering effect,[10, 11] the following formula was used.

$$Q_D = \underbrace{Q_M}_{=\frac{\sigma_M}{\pi R^2}} \int_0^{4\pi} G(\theta)\frac{\Phi(\theta)}{4\pi} d\Omega \qquad \text{Eq. S7}$$

Here, Q, G, Φ and Ω are the scattering efficiency, form factor, scattering phase function, and solid angle, respectively. Finally, the relaxation time for coherent phonon scattering by the coated grain structure is,

$$\tau_{CG} = \frac{1}{v_g \eta_{CG} \sigma_D \gamma} \qquad \text{Eq. S8}$$

where, v_g, η_{CG}, σ_D, and γ are the phonon group velocity, number density of coated grains, dependent scattering efficiency which is obtained from Eq. S7, and enskog factor which consider close-packing of scatterers, respectively. To calculate the lattice thermal conductivity, we utilized the Callaway model with relaxation time approximation.[12, 13]

$$\kappa_L = \frac{k_B}{2\pi^2 v_g}\left(\frac{k_B T}{\mathsf{h}}\right)^3 \left\{ \int_0^{\theta/T} \frac{\tau_c x^4 e^x}{(e^x-1)^2} dx + \frac{\left[\int_0^{\theta/T} \frac{\tau_c}{\tau_N} \frac{x^4 e^x}{\left(e^x-1\right)^2} dx\right]^2}{\int_0^{\theta/T} \frac{1}{\tau_N}\left(1-\frac{\tau_c}{\tau_N}\right) \frac{x^4 e^x}{\left(e^x-1\right)^2} dx} \right\} \qquad \text{Eq. S9}$$

Here, the combined relaxation time is,

$$\frac{1}{\tau_c} = \frac{1}{\tau_N} + \frac{1}{\tau_U} + \frac{1}{\tau_{e-ph}} + \frac{1}{\tau_A} + \frac{1}{\tau_B} + \frac{1}{\tau_{CG}} \qquad \text{Eq. S10}$$

where, τ_N, τ_U, $\tau_{e\text{-}ph}$, τ_A, τ_B, and τ_{CG} are the relaxation times for normal scattering, Umklapp scattering, electron-phonon scattering, alloy scattering, boundary scattering, and scattering caused by the coated grains, respectively. In the Eq. S9, the x, θ are

normalized energy of phonon(= $\hbar\omega/k_BT$), debye temperature respectively. The formulas for each scattering mechanisms in Eq. S10 was same with previous study.[5]

Lorenz number calculation

To estimate lattice thermal conductivity, we utilized Wiedemann Franz law. The Lorenz number could be obtained by a well-known formula which contains the Fermi integral.[3] In our analysis, we used following formula to consider non-parabolicity.[4]

$$L = \left[\frac{{}^{2}F_{-2}^{1}}{{}^{0}F_{-2}^{1}} - \left(\frac{{}^{1}F_{-2}^{1}}{{}^{0}F_{-2}^{1}} \right)^{2} \right] \quad \text{Eq. S11}$$

Here, F is calculated using Eq. S2. The obtained Lorenz number for uncoated SnTe is similar to that of our previous study.[5] *J.H. Bahk et al*,[14] had reported that, when there is potential barrier, the Lorenz number could be reduced to around 0.8×10^{-8} W/ΩK^2. If we use same Lorenz number of uncoated SnTe for coated grain nanocomposites, the lattice thermal conductivities of coated grain SnTe nanocomposites become unrealistically small. Thus, we utilized the transmission probability(Eq. S5) for the calculation of Lorenz number. The T_B obtained from Eq. S5 is also multiplied by the integrand in Fermi-Dirac integral. The results and electronic thermal conductivity are plotted on Figure S5.

Table S1. Solubility product(K_{sp}) table[15] for metal chalcogenides

solid	E = S	E =Se	E = Te
CuE	5×10^{-36}	2×10^{-40}	
In_2E_3	6×10^{-76}		
CdE	1×10^{-28}	4×10^{-35}	1×10^{-42}
SnE	1×10^{-26}	5×10^{-34}	
ZnE	3×10^{-25}	1×10^{-27}	

Table S2. Carrier concentration and mobility for $CuInTe_2$/SnTe coated grain nanocomposites

Samples	Carrier concentration(cm^{-3})	mobility (cm^2/Vs)
uncoated SnTe	4.781×10^{19}	6.976×10^2
CG-Cu:In/1:1	4.481×10^{19}	5.640×10^2
CG-Cu:In/3:3	3.147×10^{19}	6.933×10^2
CG-Cu:In/5:5	4.448×10^{19}	3.823×10^2
CG-Cu:In/7:7	3.504×10^{19}	3.270×10^2

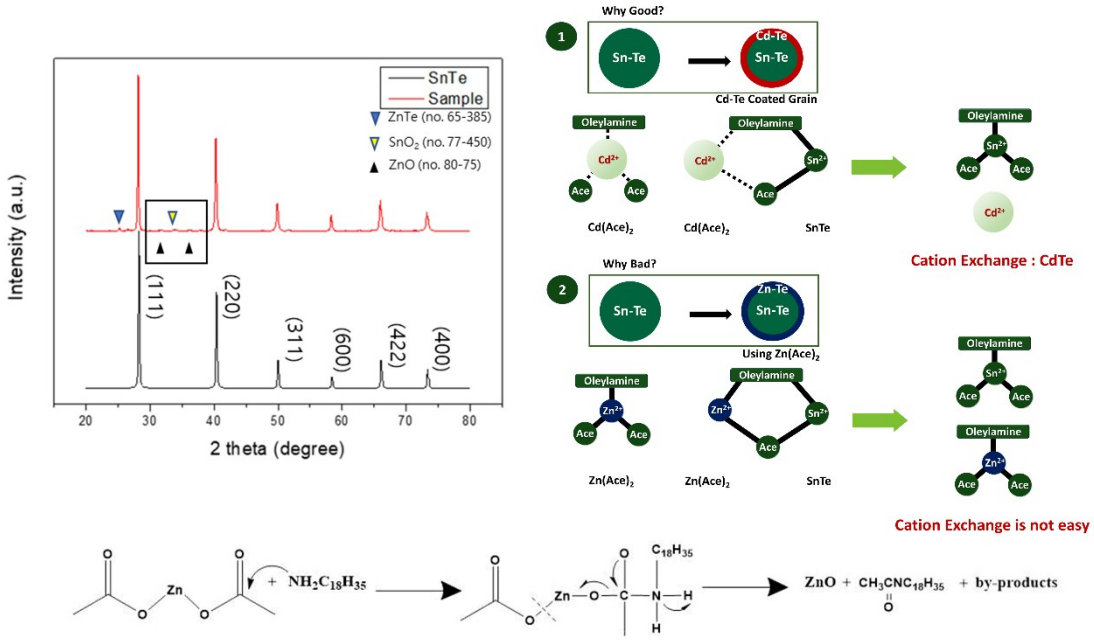


Figure S1. Result of cation exchange reaction with Zn precursor. The schematic shows why ZnTe is hardly formed by cation exchange with the host SnTe, rather ZnO is formed as by-product.

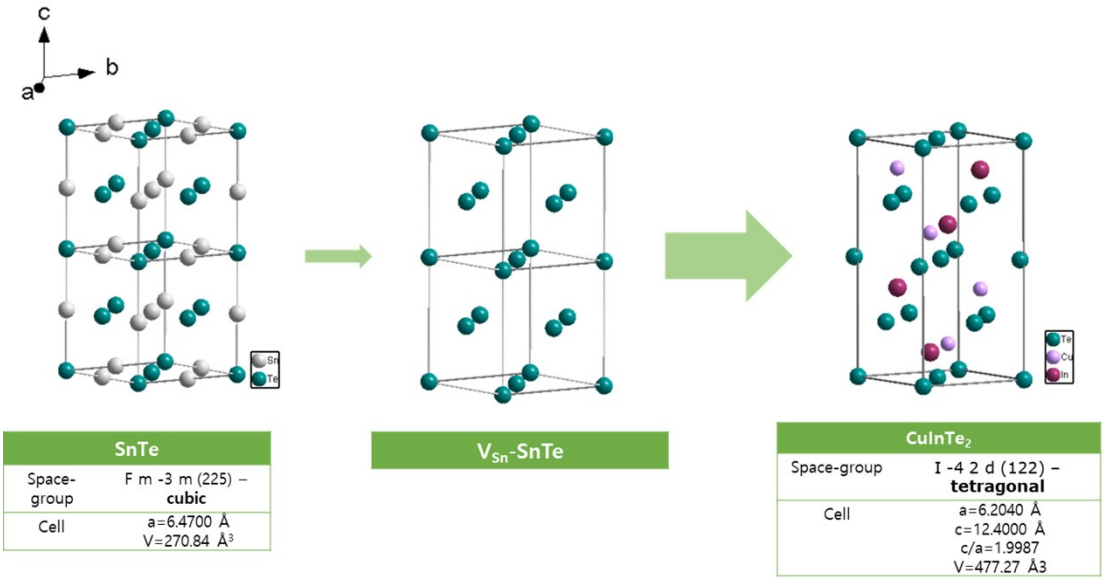
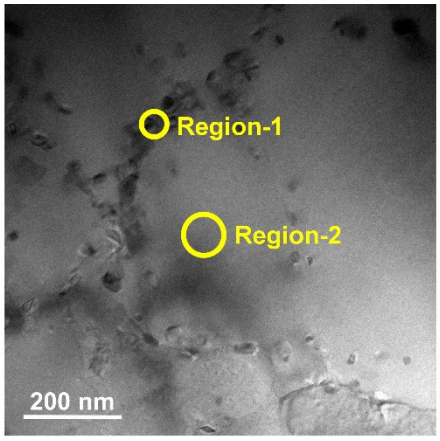
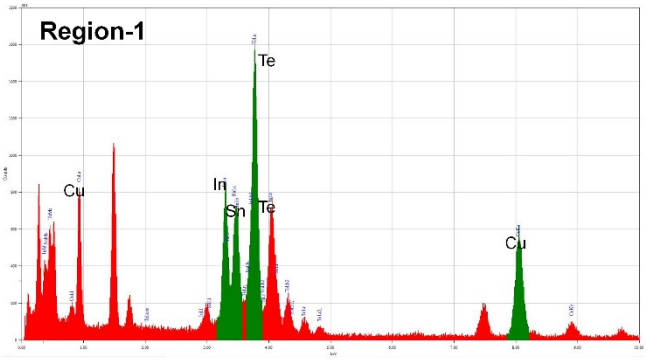
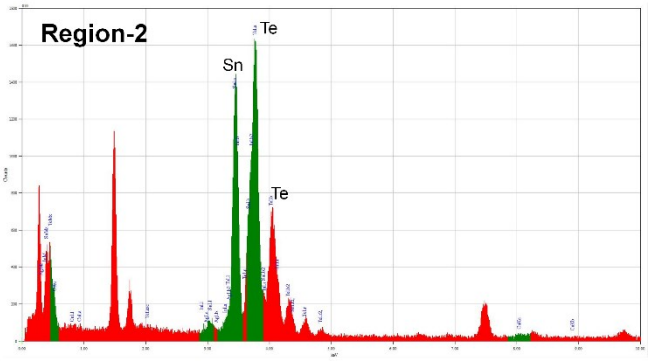


Figure S2. Similarity of crystal structure of SnTe and $CuInTe_2$







at%	Region-1	Region-2
Sn	8.16	45.98
Te	41.07	49.39
Cu	19.13	0.62
In	17.80	0.32
O	13.84	3.69

Figure S3. STEM-EDS results for coated grain boundary structure

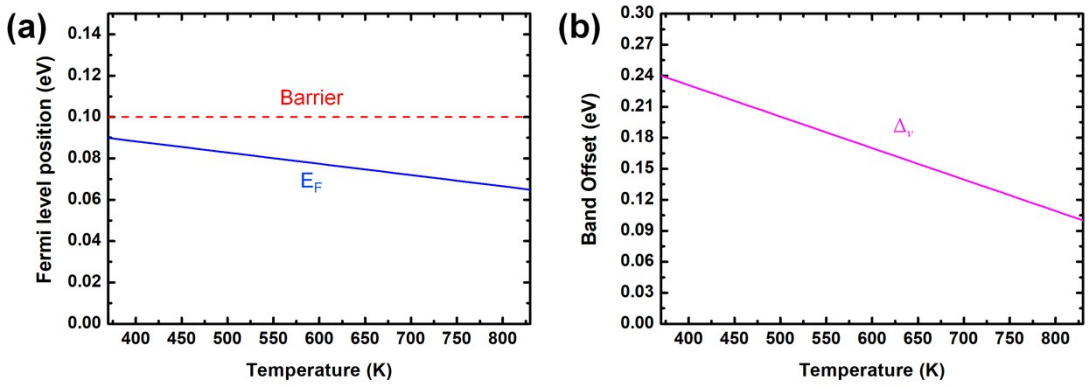


Figure S4. Fitting parameters((a): Fermi level position from valence band maximum, (b): band offset) used in our Seebeck coefficient calculation for uncoated SnTe and coated grain nanocomposites

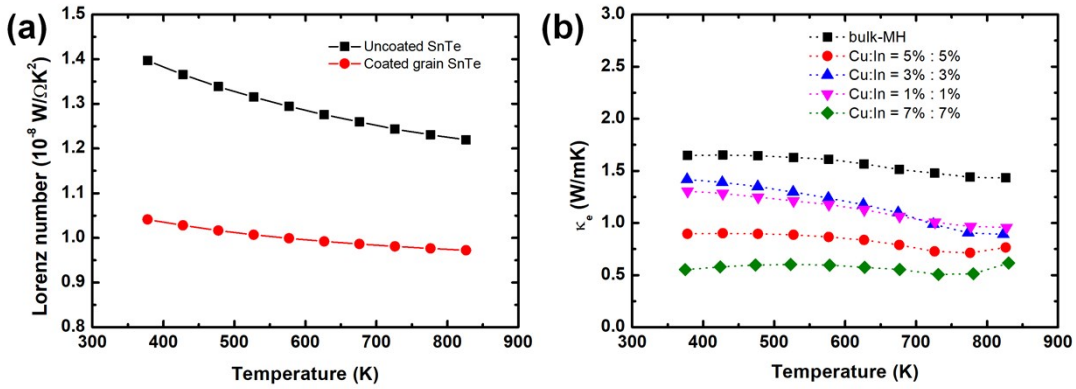


Figure S5. Calculated Lorenz number(a) and electron thermal conductivity(b).

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