Supplementary Materials for:

Ultrahigh thermoelectric performance in Cu_2Se-based hybrid materials with highly dispersed molecular CNTs

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DFT Calculation

Density-functional theory (DFT) calculations were performed with the projector-augmented wave (PAW) method as implemented in the highly efficient Vienna Ab Initio Simulation Package (VASP). Regular Monkhorst-Pack k-point meshes (where k is the electron wavevector) of 1 × 1 × 10 in Cu-CNT(4,4) and 3 × 3 × 1 in Cu-graphene(7×7 supercell) were used. The cutoff energies are 400 eV. An energy convergence criterion of 10 E^{-5} eV implemented by the Perdew-Becke-Ernzerhof (PBE) is used.

Details about the κ_{min} predication for Cu_2Se

Using the *diffuson* picture of Allen and Feldman[1,2] where diffusons are non-localized, non-propagating oscillations that can carry heat, an estimation of the minimum κ_L, κ_{min}, can be determined phenomenologically by modifying the Einstein model of thermal conductivity (to be reported elsewhere). The result, in the high

temperature limit, gives the minimum thermal conductivity in terms of the number density of atoms, n, and the average frequency of the vibrational density of states, ω_{avg}:

$$\kappa_{min} = \frac{n^{\frac{1}{3}} k_B}{\pi} \omega_{avg} \qquad (1)$$

Using the phonon density of states reported by[3], $\omega_{avg} = 16\ meV$, and taking $n = 6.024 \times 10^{28}\ atoms/m^3$ from ICSD data, $\kappa_{min} = 0.42\ W/mK$ for Cu_2Se. Additionally, it was found empirically that ω_{avg} is highly correlated with the speed of sound through the maximum Debye frequency[4]. Making the appropriate substitutions, Eq. 1 can be reduced to:

$$\kappa_{min} \approx 0.77\, n^{2/3} k_B\, v_s \qquad (2)$$

Keeping n the same as above and using $v_s = \frac{1}{3}(v_L + 2v_T) \approx 1726\ m/s$ gives the estimation for the minimum κ_L of the Cu_2Se/CNT composites reported in the main text. We note that this estimation ($\kappa_{min} = 0.28\ W/mK$) is much lower than the value predicted by the Cahill-Pohl equation ($\kappa_{min} = 0.44\ W/mK$).

Details about the X_d calculation for Cu_2Se

The thickness of the fully depleted layer (X_d) in Cu_2Se/CNTs hybrid materials can be calculated by the depletion approximation[5]

$$X_d = \left(\frac{2\varepsilon \Delta V}{q N_d 3} \right)^{1/2}, \qquad (3)$$

where ε is the dielectric constant of nearly stoichiometric Cu_2Se[6], $\varepsilon = 11$, ΔV is the built-in potential in the interfacial area, equaling to the difference in work functions between Cu_2Se and CNT, q is elementary charge, and N_d is the carrier concentration in Cu_2Se.

References

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5. D. A. Neamen, Semiconductor Physics and Devices, Basic Principles, New York: The McGraw-Hill Companies, Inc.
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Figure S1 to S4

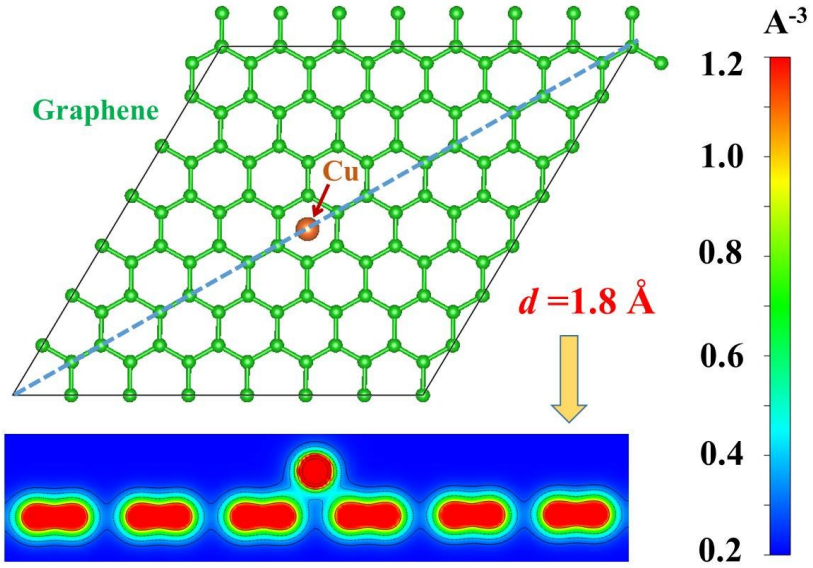

Fig. S1 Charge density of the Cu-graphene system when putting a Cu atom on the surface of graphene with a vertical distance d = 1.8 Å.

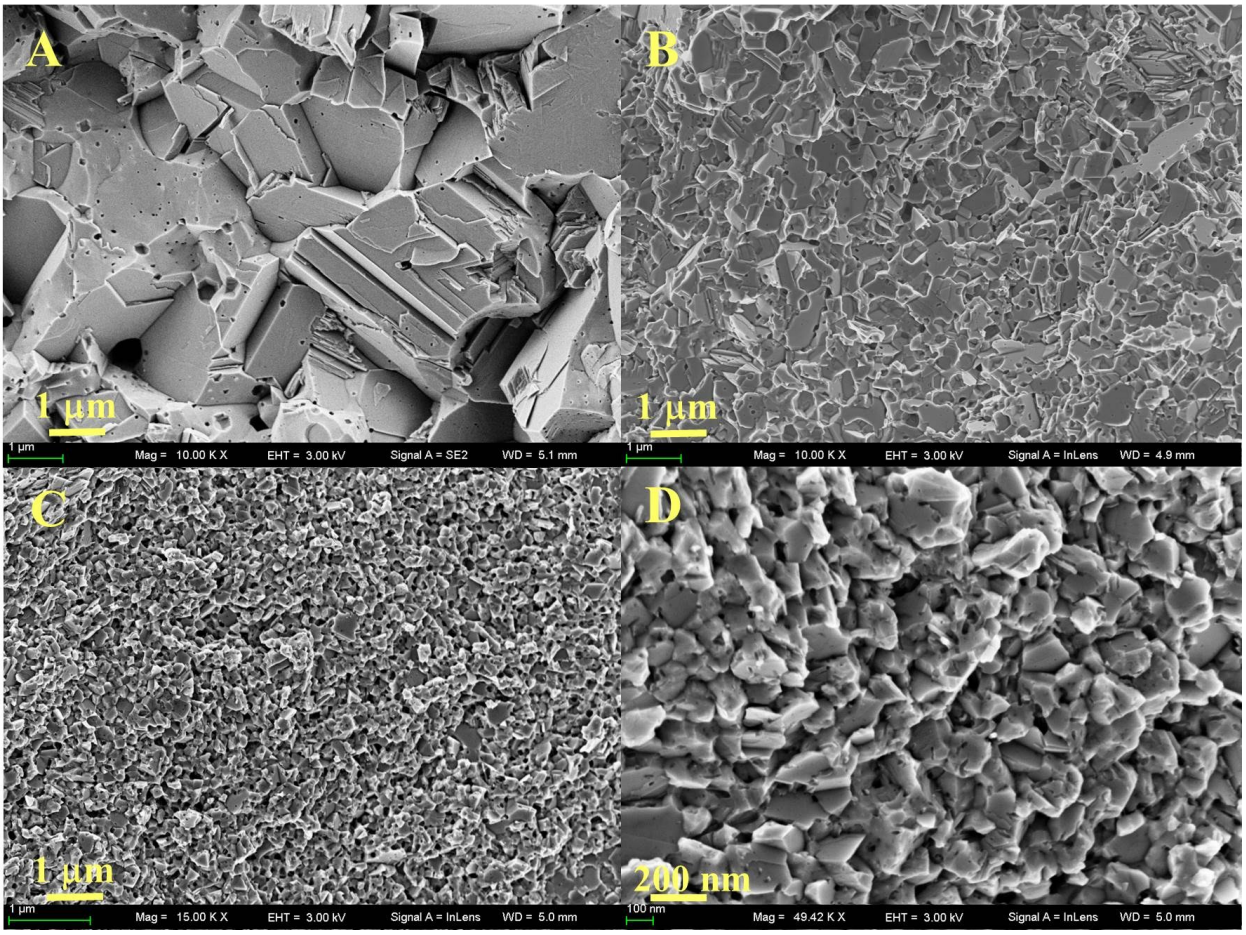

Fig. S2 Fractured secondary electron images of the SPS-sintered Cu_2Se/CNTs hybrid materials. (**A**) Cu_2Se; (**B**) Cu_2Se/0.25% *wt* CNTs; (**C**) Cu_2Se/0.75% *wt* CNTs. (**D**) is the high-magnification image of (**C**).

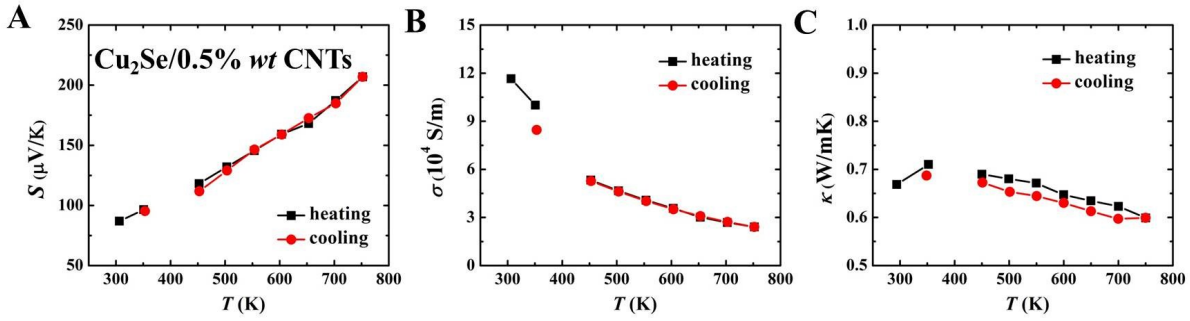

Fig. S3 TE properties of Cu_2Se/*x*% *wt* CNTs hybrid materials measured in the heating and cooling processes. (**A**) Seebeck coefficient, (**B**) electrical conductivity, and (**C**) thermal conductivity for Cu_2Se/0.5% *wt* CNTs.

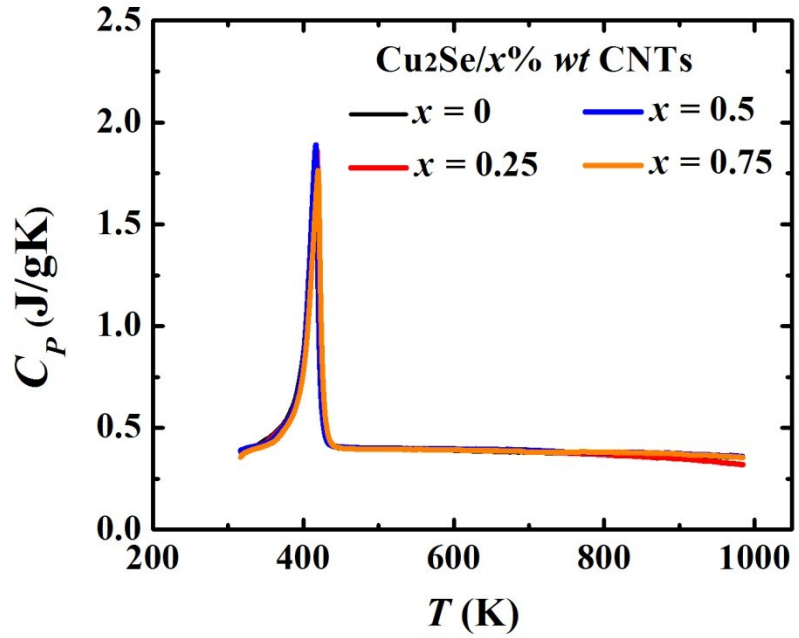

Fig. S4 Temperature dependence of heat capacity (C_P) for Cu_2Se/x% *wt* CNTs (x = 0, 0.25, 0.5 and 0.75) hybrid materials.