Electronic Supplementary Information (ESI)

Enhancing Average Thermoelectric Figure of Merit of Elemental Te by Suppressing the Grain Boundary Scattering

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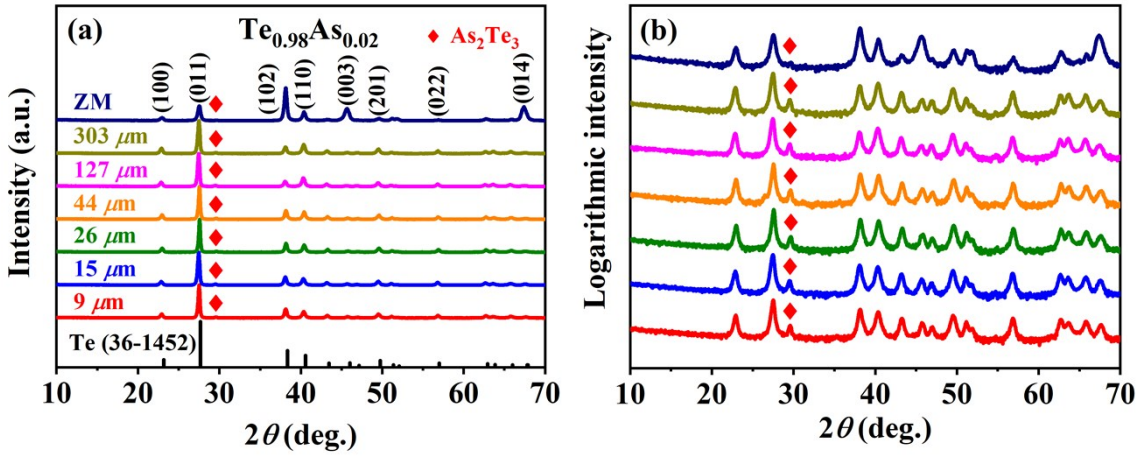

Fig. S1 (a) Bulk XRD patterns for $Te_{0.98}As_{0.02}$ samples. (b) Bulk XRD patterns with a logarithmic intensity axis for $Te_{0.98}As_{0.02}$ samples, in which the impurity peaks are more readily to be recognized.

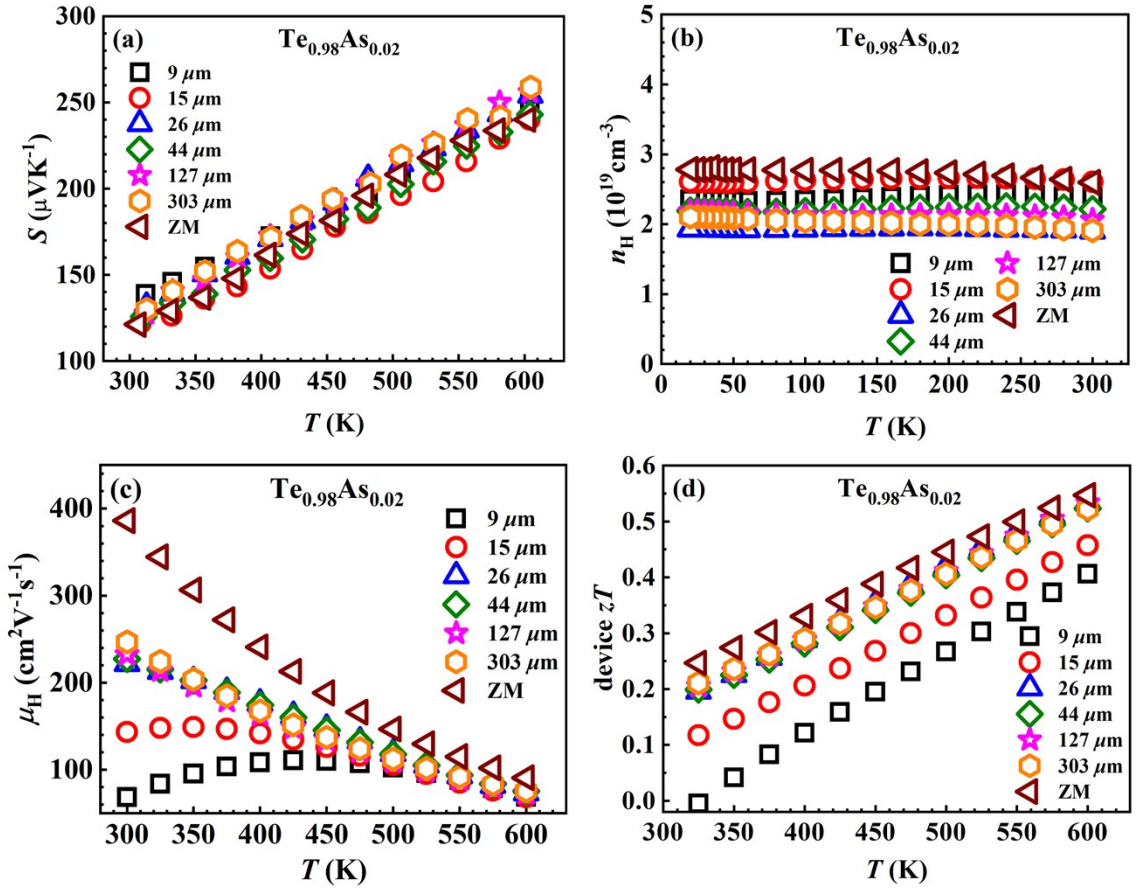

Fig. S2 Temperature dependences of (a) Seebeck coefficient, (b) carrier concentration, (c) carrier mobility and (d) device zT for $Te_{0.98}As_{0.02}$ samples. According to (a), the intrinsic conduction is not

obvious between 300 and 600 K for all Te samples, hence the carrier mobility in (c) is calculated by the formula $\sigma/n_{H}e$, where n_{H} is assumed to be constant. The cold-side temperature in (d) is fixed at 300 K.

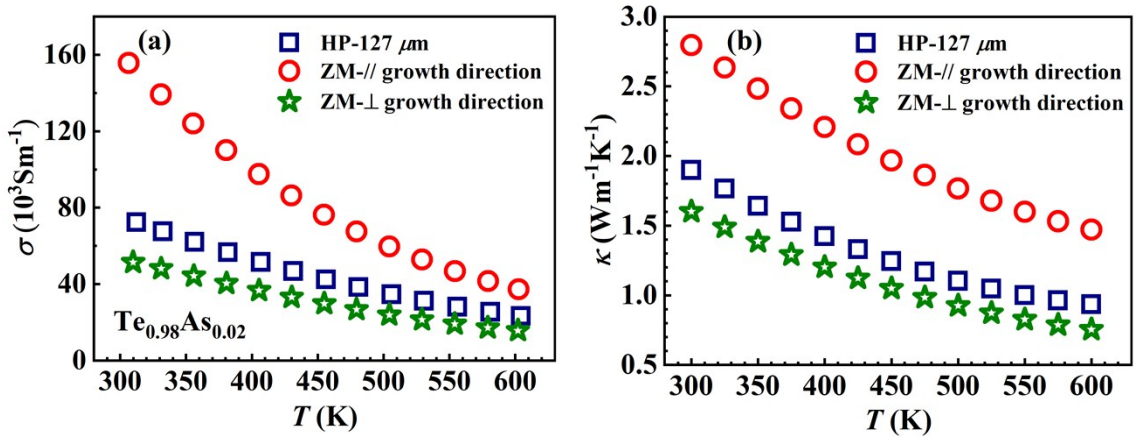

Fig. S3 Temperature dependences of (a) electrical conductivity and (b) thermal conductivity for HP and ZM $Te_{0.98}As_{0.02}$ samples.

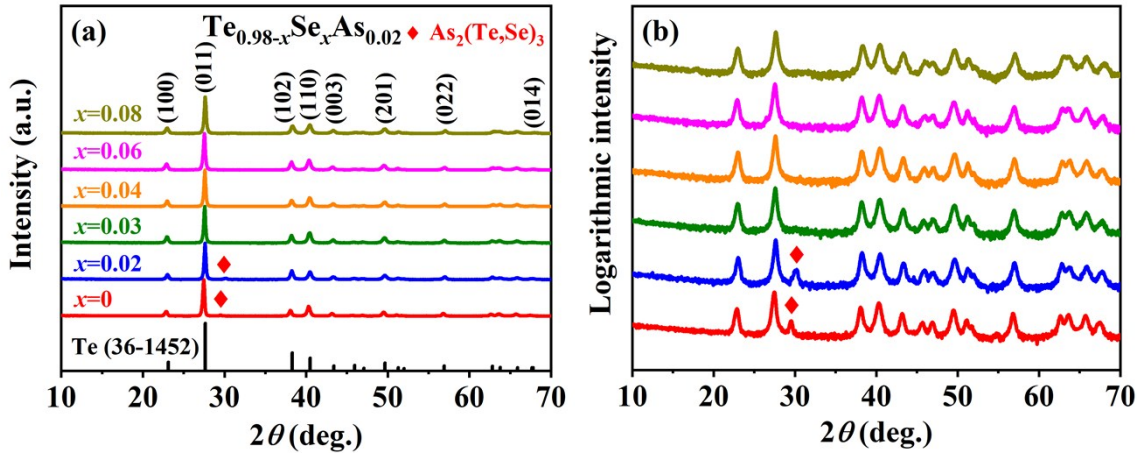

Fig. S4 (a) Bulk XRD patterns for $Te_{0.98-x}Se_{x}As_{0.02}$ samples. (b) Bulk XRD patterns with a logarithmic intensity axis for $Te_{0.98-x}Se_{x}As_{0.02}$ samples, in which the impurity peaks are more readily to be recognized.

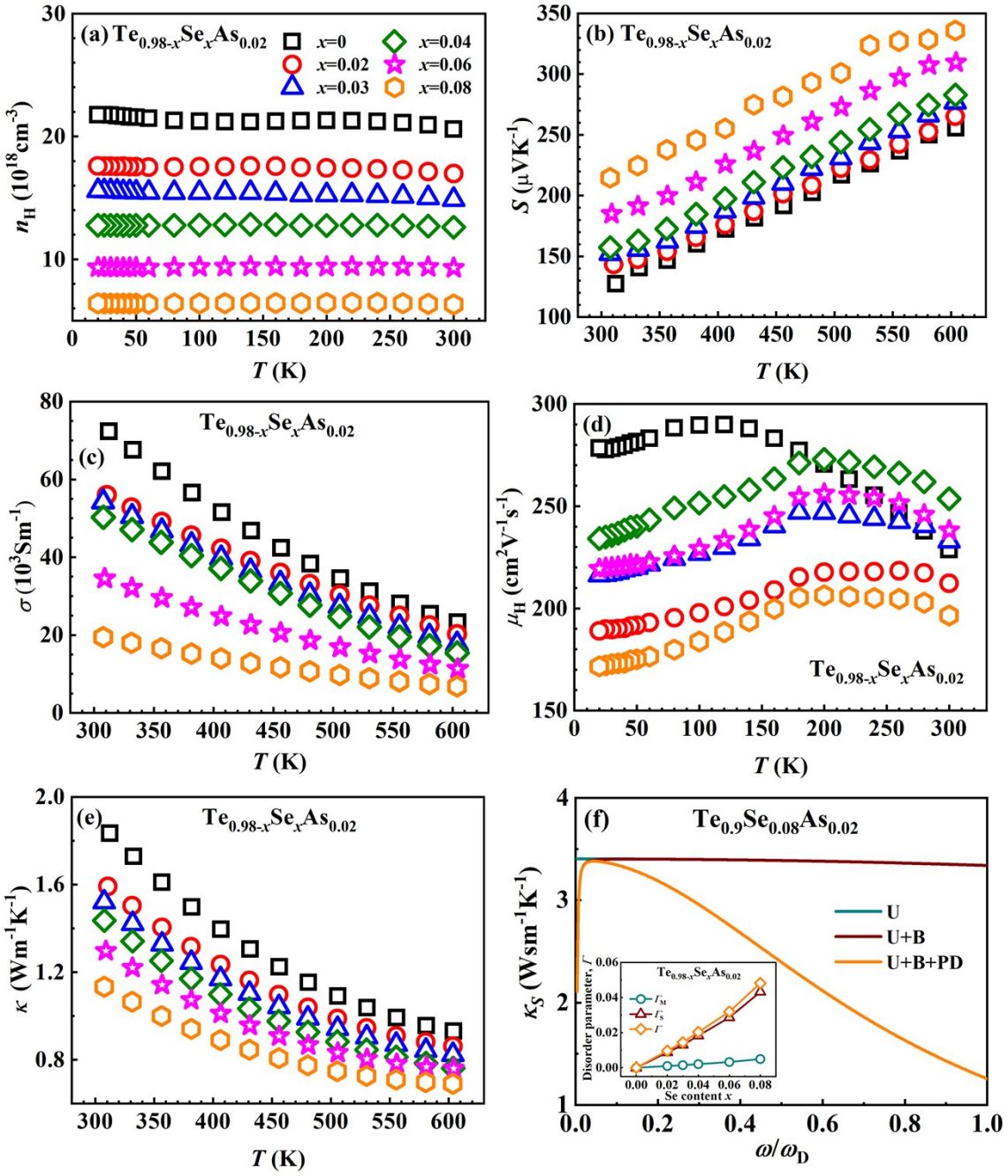

Fig. S5 Temperature dependences of (a) carrier concentration, (b) Seebeck coefficient, (c) electrical conductivity, (d) carrier mobility and (e) thermal conductivity for $Te_{0.98-x}Se_xAs_{0.02}$ samples. (f) Phonon frequency dependence of spectral lattice thermal conductivity at 300 K for $Te_{0.9}Se_{0.08}As_{0.02}$ alloys. The inset is the calculated disorder parameter Γ as a function of Se content for $Te_{0.98-x}Se_xAs_{0.02}$ samples. Γ consists of contribution from mass fluctuations Γ_M and strain field fluctuations Γ_S: $\Gamma = \Gamma_M + \Gamma_S$.

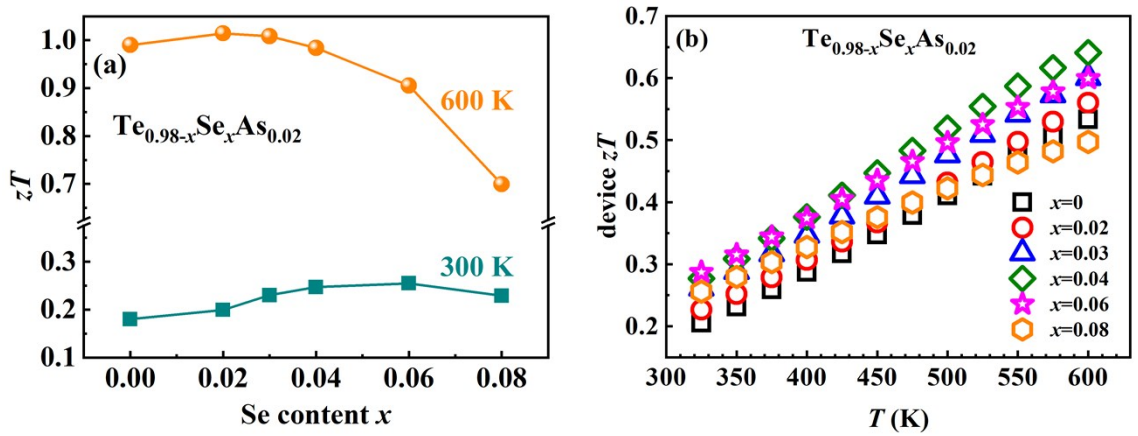

Fig. S6 (a) zT as a function of Se content for $Te_{0.98-x}Se_xAs_{0.02}$ samples (300 and 600 K). (b) Temperature dependence of device zT for $Te_{0.98-x}Se_xAs_{0.02}$ samples. The cold-side temperature is fixed at 300 K.

Calculation of lattice thermal conductivity based on the Debye-Callaway model

In the Debye-Callaway model,[2-4] the lattice thermal conductivity κ_L can be calculated according to the following equations:

$$\kappa_L = \frac{k_B}{2\pi^2 v_s}\left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{\tau_{tot}^{-1}\left(e^x-1\right)^2} dx, x = \frac{\hbar\omega}{k_B T} \quad \text{(S1)}$$

$$\tau_{tot}^{-1} = \tau_B^{-1} + \tau_P^{-1} + \tau_U^{-1} = \frac{v_s}{d} + A\omega^4 + B\omega^2 T exp\left(-\frac{\theta_D}{3T}\right) \quad \text{(S2)}$$

where k_B is the Boltzmann constant, $\hbar$ is the reduced Planck's constant, v_s is the average sound velocity, T is the absolute temperature, θ_D is the Debye temperature, τ_{tot} is the total relaxation time, ω is the phonon frequency, d is the grain size and roughly taken as the initial powder median size. v_s/d represents the grain boundary scattering. A, B are the pre-exponential factors for point defects scattering and Umklapp process scattering, respectively. To be noted, B is obtained by fitting the temperature dependence of κ_L for the HP-303μm $Te_{0.98}As_{0.02}$ sample. The calculating parameters

used in the Debye-Callaway model are summarized in Table S1. Other parameters obtained from our previous work[5] are listed in Table S2. More calculation details can also be found in our previous work.[5]

Table S1 The calculating parameters used in the Debye-Callaway model. Due to the small atom mass and tiny doping content, the As content in Te is hard to be detected.

Nominal composition	d (μm)	Actual composition	v/d ($10^7 s^{-1}$)	A ($10^{-41} s^3$)	B ($10^{-17} sK^{-1}$)
$Te_{0.98}As_{0.02}$	9	Te	17.6	0	2.2
$Te_{0.98}As_{0.02}$	15	Te	10.6	0	2.2
$Te_{0.98}As_{0.02}$	26	Te	6.1	0	2.2
$Te_{0.98}As_{0.02}$	44	Te	3.6	0	2.2
$Te_{0.98}As_{0.02}$	127	Te	1.3	0	2.2
$Te_{0.98}As_{0.02}$	303	Te	0.5	0	2.2
$Te_{0.96}Se_{0.02}As_{0.02}$	136	$Te_{0.993}Se_{0.007}$	1.2	0.7	2.2
$Te_{0.95}Se_{0.03}As_{0.02}$	141	$Te_{0.990}Se_{0.010}$	1.1	1.0	2.2
$Te_{0.94}Se_{0.04}As_{0.02}$	142	$Te_{0.986}Se_{0.014}$	1.1	1.4	2.2
$Te_{0.92}Se_{0.06}As_{0.02}$	137	$Te_{0.977}Se_{0.023}$	1.2	2.1	2.2

[2]					
$Te_{0.9}Se_{0.08}As_{0.02}$	122	$Te_{0.966}Se_{0.034}$	1.3	3.2	2.2

Table S2 The parameters used to calculate the lattice thermal conductivity, taken from our previous work.[5]

Parameters	Sign [unit]	Value
Average sound velocity	v_s [m.s^{-1}]	1588
Atomic volume	V [m^3]	3.38×10^{-29}
Debye temperature	θ_D [K]	146
Grüneisen parameter	γ	1.57
Poisson ratio	r	0.26
Density of mass	ρ [kg.m^{-3}]	5.89×10^3

References

[S1] J. Yang, G. P. Meisner and L. Chen, *Appl. Phys. Lett.*, 2004, **85**, 1140-1142.

[S2] J. Callaway and H. C. von Baeyer, *Phys. Rev.*, 1960, **120**, 1149-1154.

[S3] E. F. Steigmeier and B. Abeles, *Phy. Rev.*, 1964, **136**, A1149-A1155.

[S4] T. J. Zhu, C. G. Fu, H. H. Xie, Y. T. Liu, B. Feng, J. Xie and X. B. Zhao, *Europhys. Lett.*, 2013, **104**, 46003.

[S5] Y. H. Wu, Q. Zhang, F. Liu, T. Fang, T. J. Zhu and X. B. Zhao, *Adv. Electron. Mater.*, 2020, 2000038.