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Supplementary Information

Electron-phonon coupling, bipolar effect, and thermoelectric performance of the $CuSbS_2$ monolayer

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1. Lattice thermal conductivity and intrinsic carrier concentration

The lattice thermal conductivity of the $CuSbS_2$ monolayer was calculated by using the ShengBTE code[1] based on the phonon Boltzmann transport theory. Using 6×4×1 and 3× 2×1 supercells, the second-order (harmonic) and the third-order (anharmonic) interatomic force constants (IFCs) are calculated by VASP with input files prepared by the Phonopy and the thirdorder.py in ShengBTE, respectively. The $\kappa_{lat}^{\alpha\beta}$ is:

$$\kappa_{lat}^{\alpha\beta} = \frac{1}{\kappa_B T^2 \Omega N} \sum f_0(f_0+1) v_\lambda^\alpha v_\lambda^\beta \tau^\lambda \quad \text{(S1)}$$

Where κ_B represents the Boltzmann constant, N, Ω, ω_λ, τ_λ and υ_λ are the number of phonon wave vectors, the volume of the unit cell, the phonon frequency, the phonon lifetime, and the phonon group velocity. λ, α/β, and f_0 stand for the phonon mode, the cartesian components, and the Bose-Einstein distribution function. It should be noted that, in order to avoid the interaction between layers, the existence of the vacuum space of the supercell is essential. However, the existence of vacuum space will increase the value of Ω in Eq. (S1), which will affect the calculation result of lattice thermal conductivity. Therefore, we calculated the true thickness of the $CuSbS_2$ monolayer and thus obtained the volume of the monolayer. Then use Eq. (S2) to correct the result obtained by Eq. (S1).

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$$\kappa_{l2D}^{\alpha\beta} = \kappa_l^{\alpha\beta} \frac{h}{d} \quad \text{(S2)}$$

Here, h is the height of the supercell containing the vacuum space. d is the thickness of the $CuSbS_2$ monolayer excluding the vacuum space, which can be obtained by optimizing a supercell including two monolayers without vacuum space.

Based on the Fermi-Dirac distribution[2] and density of states (DOS), we calculated the intrinsic carrier concentration of the $CuSbS_2$ monolayer with the following expression：

$$n_0 = \int \rho_c(E) f(E) dE \quad \text{（S3）}$$

$$p_0 = \int \rho_v(E)[1 - f(E)] dE \quad \text{（S4）}$$

$$f(E) = \frac{1}{e^{\frac{(E-E_F)}{kT}} + 1} \quad \text{（S5）}$$

Where E_F is Fermi level, k is the Boltzmann constant, $f(E)$ stands for the appearance probability of electron, and $1 - f(E)$ is the appearance probability of hole. Meanwhile, $\rho_c(E)$ and $\rho_v(E)$ stand for the DOSs of conduction and valence bands, respectively.

2. Transport coefficients under the bipolar effect

The bipolar effect should be considered because both electron and hole occur in the semiconductor $CuSbS_2$. Because both holes and electrons can contribute to the electrical conductivity with the same sign, the electric conductivity containing the bipolar effect can be simply obtained by $\sigma = n_h e|\mu_h| + n_e e|\mu_e|$. However, we use the more accurate results from the ones by solving the Boltzmann transport equation as follows:

$$\sigma_{bp} = \sigma_n + \sigma_p \quad \text{(S6)}$$

Where σ_n and σ_p are thermal conductivities corresponding to the n and p-type carriers, respectively.

The Seebeck coefficient is dramatically affected because the two charge carriers

add opposite sign Seebeck voltage. The contribution of each charge carrier to the total Seebeck coefficient is weighted by the electrical conductivity. Representing the Seebeck coefficient corresponding to the *n* and *p*-type carriers by S_n and S_p and setting $S_n<0$ and $S_p>0$, one can obtain the Seebeck coefficient including bipolar effect by

$$S_{bp} = \frac{S_n\sigma_n + S_p\sigma_p}{\sigma_n + \sigma_p} \quad \text{(S7)}$$

The electronic thermal conductivity of including bipolar effect is also given with the combination of the two types of carriers. If Lorenz's classical relationship is used, one can approximately be obtained $\kappa_{bp} = L\sigma_p T + L\sigma_n T + \left(S_p - S_n\right)^2 \frac{\sigma_p\sigma_n T}{(\sigma_p+\sigma_n)}$. We use the data from solving the Boltzmann transport equation as the σ_{bp} to give more accurate results. So, the following expression is used to calculate κ_{bp}.

$$\kappa_{bp} = \kappa_n + \kappa_p + (S_n + S_p)^2 \frac{\sigma_n\sigma_p T}{\sigma_n+\sigma_p} \quad \text{(S8)}$$

According to Eq (1), the *ZT* free of carrier types and concentrations can be obtained by

$$ZT_{bp} = \frac{S_{bp}^2\sigma_{bp}T}{\kappa_l+\kappa_{bp}} \quad \text{(S9)}$$

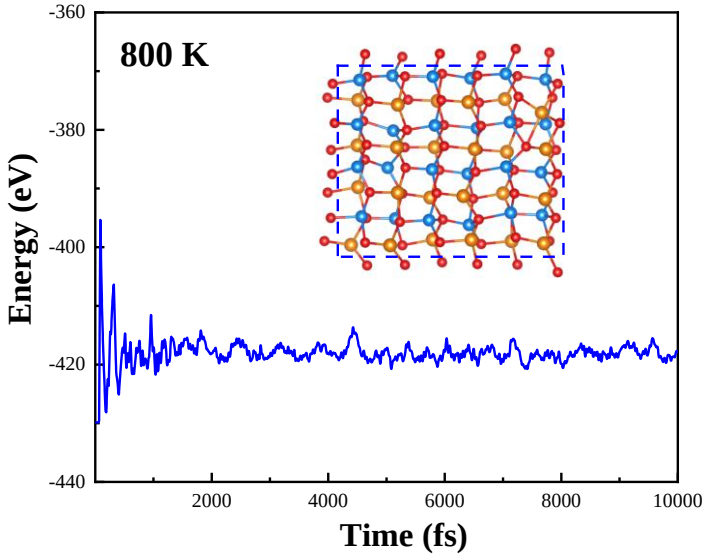

Fig S1. The energy of the $CuSbS_2$ monolayer by AIMD simulation at 800 K.

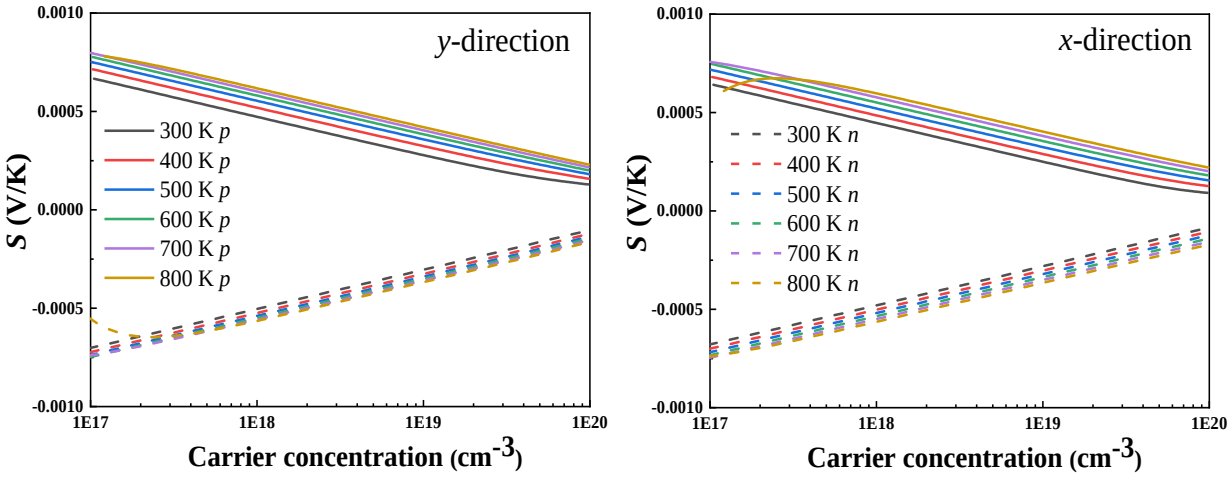

Fig S2. The Seebeck coefficient (S) with different carrier types and concentrations along x and y directions of the $CuSbS_2$ monolayer. The solid line represents the p carrier, and the dotted line represents the n carrier.

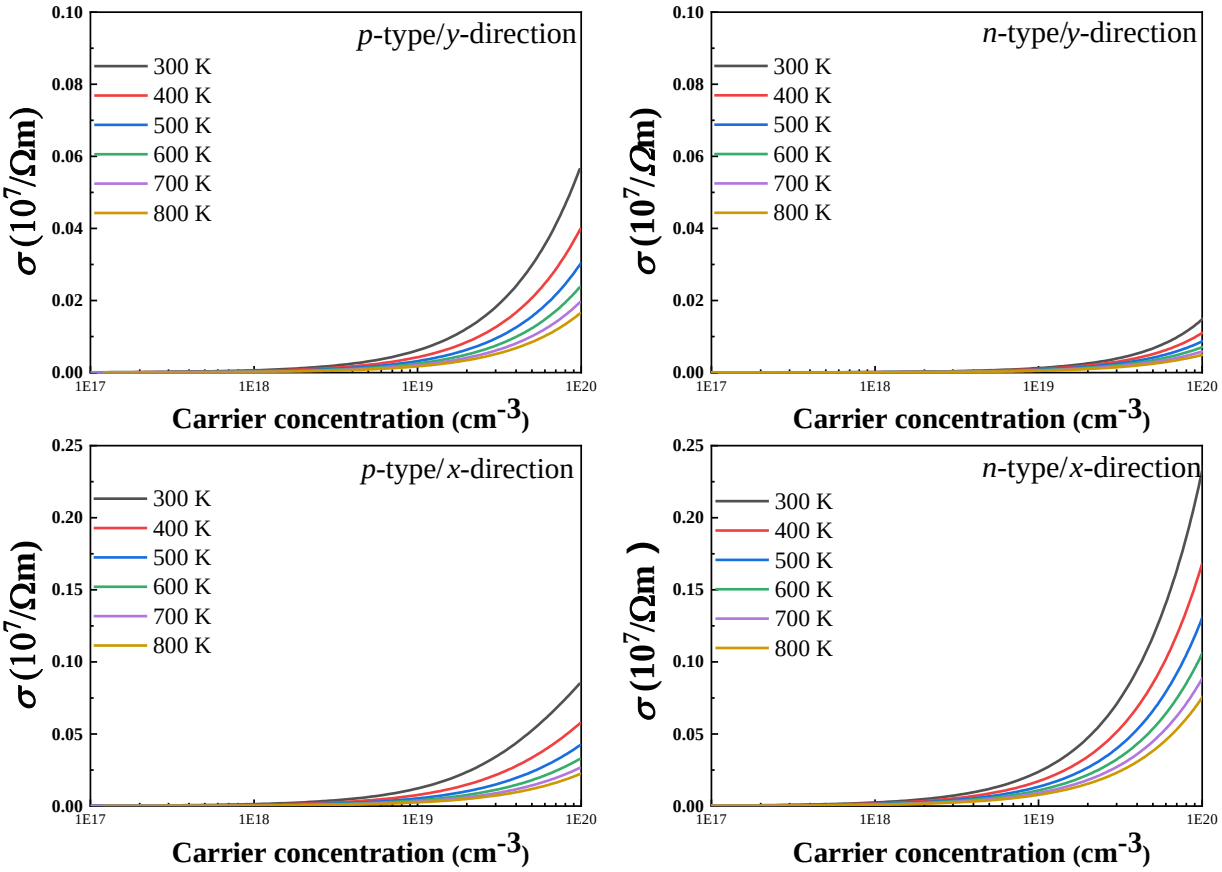

Fig S3. The electrical conductivity(σ) of the $CuSbS_2$ monolayer along with the *x* and *y* directions under different concentrations of the *p* and *n* carriers.

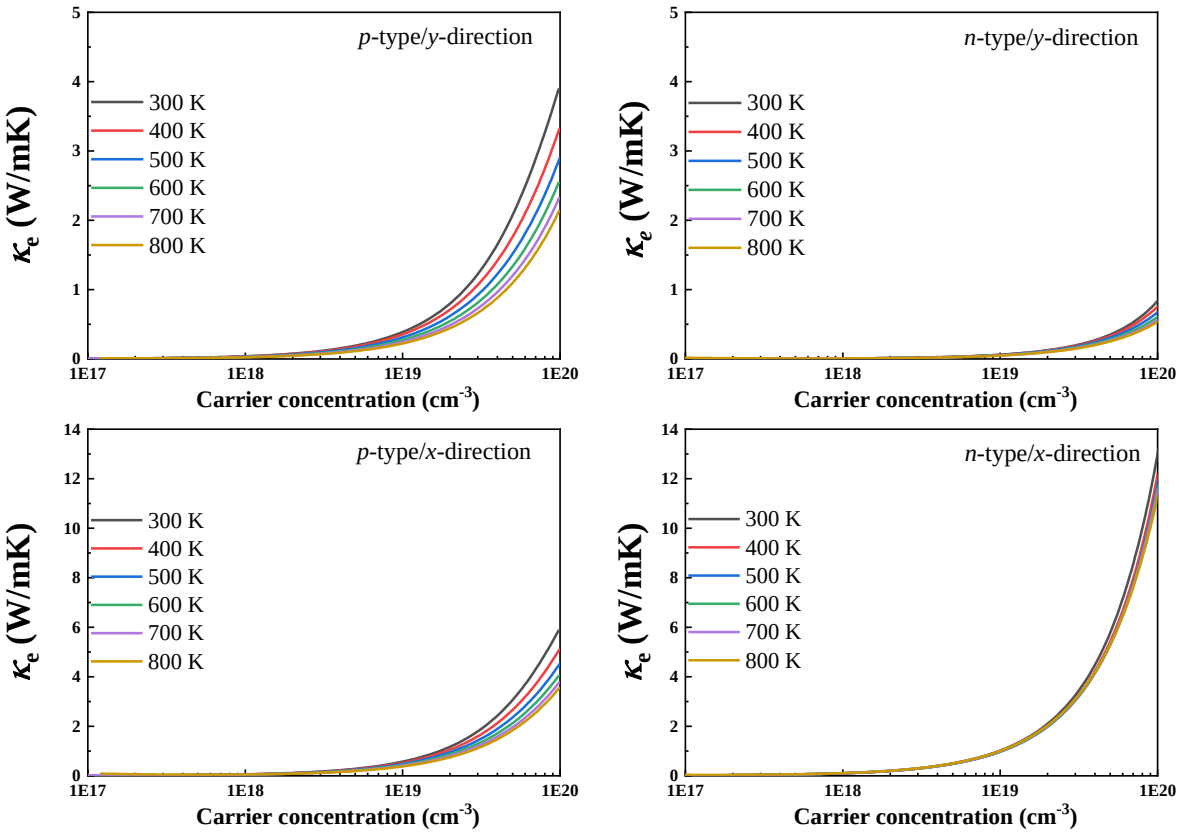

Fig S4. The electronic thermal conductivity along x and y directions of the $CuSbS_2$ monolayer under different concentrations of the *p* and *n* carriers.

Table S1. The intrinsic carrier concentration, transport coefficients and ZT (σ_{bp}, S_{bp}, κ_{ebp}, and ZT_{bp}) with the bipolar effect of the $CuSbS_2$ monolayer at different temperatures.

T(K)			300K	400K	500K	600K	700K	800K
Intrinsic carrier concentration		n	1.868×10^{18}	3.173×10^{18}	4.269×10^{18}	5.143×10^{18}	5.835×10^{18}	6.386×10^{18}
		p	3.352×10^{19}	4.579×10^{19}	5.993×10^{19}	7.581×10^{19}	9.320×10^{19}	1.120×10^{20}
σ（1/Ωm）	x	n	4.418×10^{4}	5.433×10^{4}	5.677×10^{4}	5.549×10^{4}	5.264×10^{4}	4.915×10^{4}
		p	3.749×10^{5}	3.102×10^{5}	2.769×10^{5}	2.600×10^{5}	2.519×10^{5}	2.489×10^{5}
		bp	4.190×10^{5}	3.645×10^{5}	3.336×10^{5}	3.155×10^{5}	3.046×10^{5}	2.981×10^{5}
	y	n	2.259×10^{3}	3.009×10^{3}	3.324×10^{3}	3.369×10^{3}	3.262×10^{3}	3.070×10^{3}
		p	2.022×10^{5}	1.899×10^{5}	1.855×10^{5}	1.845×10^{5}	1.848×10^{5}	1.857×10^{5}
		bp	2.044×10^{5}	1.929×10^{5}	1.888×10^{5}	1.879×10^{5}	1.880×10^{5}	1.887×10^{5}
S (V/K)	x	n	-4.268×10^{-4}	-4.029×10^{-4}	-3.949×10^{-4}	-3.945×10^{-4}	-3.983×10^{-4}	-4.046×10^{-4}
		p	1.520×10^{-4}	1.703×10^{-4}	1.860×10^{-4}	1.975×10^{-4}	2.057×10^{-4}	2.116×10^{-4}
		bp	9.102×10^{-5}	8.489×10^{-5}	8.712×10^{-5}	9.339×10^{-5}	1.013×10^{-4}	1.100×10^{-4}
	y	n	-4.503×10^{-4}	-4.255×10^{-4}	-4.142×10^{-4}	-4.087×10^{-4}	-4.065×10^{-4}	-4.067×10^{-4}
		p	1.858×10^{-4}	2.065×10^{-4}	2.164×10^{-4}	2.201×10^{-4}	2.206×10^{-4}	2.195×10^{-4}
		bp	1.787×10^{-4}	1.966×10^{-4}	2.053×10^{-4}	2.088×10^{-4}	2.097×10^{-4}	2.093×10^{-4}
κ_e (W/mK)	x	n	0.183	0.302	0.405	0.496	0.573	0.634
		p	2.010	2.431	2.805	3.169	3.558	3.986
		bp	6.165	8.810	11.158	13.282	15.251	17.087
	y	n	0.011	0.018	0.023	0.027	0.029	0.031
		p	1.374	1.618	1.804	1.993	2.196	2.414
		bp	1.656	2.109	2.477	2.804	3.107	3.392
ZT	x	n	0.478	0.896	1.339	1.780	2.213	2.634
		p	0.378	0.594	0.839	1.090	1.327	1.538
		bp	0.094	0.084	0.090	0.105	0.126	0.153
	y	n	0.034	0.073	0.119	0.168	0.218	0.268
		p	0.390	0.704	1.037	1.348	1.616	1.835
		bp	0.347	0.586	0.819	1.026	1.205	1.356

Reference

1. W. Li, J. Carrete, N. A. Katcho and N. Mingo, *Computer Physics Communications*, 2014, **185**, 1747-1758.
2. L. Coldren, S. Corzine and M. Mašanović, *Diode Lasers and Photonic Integrated Circuits*, 2012, 529-544.