The extensive combustion of fossil fuels has induced serious global warming and environmental pollution. Consequently, it is urgent to develop new economical and environmentally friendly energy sources to reduce the emission of greenhouse gases. As an alternative approach, thermoelectric (TE) materials have drawn wide interests recently, which can provide low temperature electricity efficiently. However, these strategies sometimes lead to a degradation of the electronic transport properties. Thus, exploring compounds with intrinsic low $\kappa_L$ has been of great interest because the electronic transport properties can be optimized with a small effect on the $\kappa_L$. Compounds with high atomic mass usually lead to low $\kappa_L$. The bonding heterogeneity also can significantly suppress the transport of phonons. Moreover, the bonding heterogeneity in Cu$_3$SbSe$_5$ and BaAgYTe$_3$ was observed to induce rattle-like vibrations and dominantly controlled by the phonon transport property. Thus, a reduced $\kappa_L$ can effectively improve thermoelectric performance. Defect engineering or nanostructuring is usually used to increase phonon scattering, inducing low thermal transport properties. However, these strategies sometimes lead to a degradation of the electronic transport properties. Thus, exploring compounds with intrinsic low $\kappa_L$ has been of great interest because the electronic transport properties can be optimized with a small effect on the $\kappa_L$. Compounds with high atomic mass usually lead to low $\kappa_L$. The bonding heterogeneity also can significantly suppress the transport of phonons. Moreover, the bonding heterogeneity in Cu$_3$SbSe$_5$ and BaAgYTe$_3$ was observed to induce rattle-like vibrations and
Two-dimensional (2D) materials are promising candidates for thermoelectric materials because of the quantum confinement effect, which can break the interwoven relation between S and $\sigma$. Diverse advanced 2D thermoelectric materials with low $\kappa$ and high electronic transport properties have been reported in recent years, such as the 2D pentagonal TMM$_2$ (TM = Pd, Pt; M = S, Se, Te),$^{21,22}$ triphosphides (e.g., In$_2$P$_3$, Ga$_3$P$_3$, and SnP$_3$),$^{23,24}$ transition metal chalcogenides M$_2$X$_2$ (M = metal and X = O, S, Se, and Te),$^{25,26}$ SnSe,$^{27}$ and InSe.$^{30}$ Among them, the 2D Te-based materials have attracted tremendous interest due to the heavy atomic mass, which can suppress the transport of phonons. In 2018, Liu et al.$^{31}$ fabricated a hexagonal monolayer PdTe$_2$ with superconducting behavior. Afterward, a theoretical study by Marfoua et al. reported the hexagonal and pentagonal PdTe$_2$ with $zT = 0.8$ at 300 K, using the Boltzmann transport equation.$^{32}$ A similar phenomenon was also observed in 2D PtTe$_2$.$^{33}$ Other 2D Te-based materials such as the group IIIA/IVA-Te (e.g., In$_2$Te$_3$, SnTe$_2$, and GaTe$_3$) have also been extensively investigated as promising thermoelectric materials. Bulk CdTe$^{34}$ and CdTe$_2$ are semiconductors with band gaps of 1.50 (direct) and 1.08 eV (indirect), respectively. CdTe thin films have been widely used in solar cell prototyping.$^{38}$ In 2017, researchers predicted a $\alpha$-CdTe (tetragonal-PbO structure) monolayer with low formation enthalpy and excellent dynamic stability. The novel electronic structure endows 2D $\alpha$-CdTe with a promising application potential in optoelectronic devices.$^{39}$ In 2020, Naseri et al. built a planar 2D CdTe$_2$ with the use of the predicted CdS honeycomb structure.$^{40}$ Afterward, Kolobov et al. reported a two-monolayer-thick CdTe slab (cleaved from bulk CdTe) that has extremely low formation enthalpies and a direct band gap of 1.03 eV.$^{41}$ However, the structure configuration, phase stability, and thermoelectric performance of diverse 2D CdTe$_2$ still lack a full investigation.

In this work, we carried out extensive structural searches to explore 2D CdTe$_2$ materials (i.e., CdTe, CdTe$_2$, and CdTe$_3$), using the particle swarm optimization (PSO) method. 2D CdTe and CdTe$_2$ were verified to be stable 2D materials with low formation enthalpies and excellent dynamic stability. Through bonding analysis, CdTe$_2$ exhibits strong bonding heterogeneity, originating from weak Cd–Te ionic bonding and strong Te–Te covalent bonding. The loosely bound Cd atoms and quasi-sandwich structure in CdTe$_2$ give rise to low group velocities of the acoustic modes. The bonding heterogeneity in CdTe$_2$ introduces lattice anharmonicity, which is manifested in the larger mode Grüneisen parameters. Moreover, the different bonding strengths render CdTe$_2$ quite localized optical phonons with low frequency, leading to weaker coupling between acoustic and optical phonon modes, which can significantly suppress the transport of phonons. On the other hand, the occupied $\pi^*\sigma_p$, $\sigma_p\sigma$ and $\sigma_p\pi$ bondings in covalent Te–Te pairs give rise to a superior p-type electronic conductivity and high Seebeck coefficient of p-type CdTe$_2$, making it a promising thermoelectric material at room temperature.

## COMPUTATIONAL APPROACH

The structural searches of 2D CdTe, CdTe$_2$ and CdTe$_3$ were carried out in crystal structure analysis by particle swarm optimization (CALYPSO) methodology,$^{42,43}$ whose validity has been verified by correctly predicting many bulk and 2D materials.$^{44,45}$ In the structural search process, 40 generations were searched, each generation containing 40 structures. The chemical formula of the generated CdTe structures was set as $1\overline{8}$. Beyond the structural searches, the frequently reported 2D crystal structures, such as InP$_{33}$ and penta-PdTe$_2$,$^{2}$ were also considered. However, the 2D CdTe with the structure prototypes was significantly distorted after full structure relaxation. *Ab initio* calculations were performed in the Vienna Ab Initio Simulation Package (VASP) code.$^{46}$ The electron–ion interaction was described using the projector augmented wave potential (PAW) method and applying the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional.$^{47,48}$ To ensure that all the enthalpy calculations were well converged to 1 meV/atom, the kinetic energy cutoff was set at 500 eV. Also, 11 $\times$ 11 $\times$ 1 and 7 $\times$ 7 $\times$ 1 Monkhorst–Pack $k$-point meshes were used for 2D CdTe and CdTe$_2$, respectively. Since the 2D Te has been experimentally synthesized,$^{49}$ we select bulk Cd and the most stable 2D Te ($\alpha$-Te)$^{50}$ as references to calculate the formation enthalpies and access the experimental feasibility.

$$\Delta H(CdTe) = \frac{[H(CdTe) - H(Cd) - xH(Te) + xH(\alpha-Te)]}{1 + x}$$

where $H$ denotes the enthalpy per chemical unit for CdTe$_2$, Cd, and Te. The Heyd–Scuseria–Ernzerhof (HSE06) exchange–correlation functional was used to calculate the electronic band structures.$^{51}$ The band structure with the HSE06 + SOC correction was calculated separately and is plotted in Figure S1. Since the HSE06+SOC correction is much time-consuming, we only consider the HSE06 correction in our article. Considering that the density functional theory calculations were performed at 0 K, *ab initio* molecular dynamics (AIMD) simulations were done at 300 K to evaluate the thermal stability of 2D CdTe at room temperature. A canonical ensemble (NVT) with a Nose–Hoover heat bath scheme was used,$^{52}$ and 20,000 steps were calculated with a time step of 2 fs. To minimize the constraint induced by periodicity, the lattice vector of CdTe was converted to a rectangle, and then, a 5 $\times$ 5 $\times$ 1 supercell (100 atoms) was created, while for the 2D CdTe$_2$, a 4 $\times$ 4 $\times$ 1 supercell (96 atoms) was created. The crystal orbital Hamiltonian population (COHP) analyses were performed using the LOBSTER code to uncover the bonding characters of CdTe and Te–Te pairs.$^{53}$

The electronic transport properties of $S$, $\sigma$, and $\kappa$ were calculated using semiclassical Boltzmann theory within the constant scattering time approximation using the BoltzTraP code.$^{54,55}$ The reliability of this method has been verified by many studies.$^{22,56}$ Denser 25 $\times$ 25 $\times$ 1 and 20 $\times$ 20 $\times$ 1 $k$-point meshes were used for 2D CdTe and CdTe$_2$, respectively. The $\kappa_{ij}$ was calculated based on the phonon Boltzmann transport equation, as implemented in the ShengBTE code.$^{56}$ Phonon dispersions and second-order interatomic force constants (2nd IFCs) were calculated using Phonopy packages$^{57}$ with a supercell of 5 $\times$ 5 $\times$ 1 both for 2D CdTe and CdTe$_2$. The third-order interatomic force constants (3rd IFCs) were calculated using the same supercell. The cutoff radius was set to 5.53 Å (up to the fifth nearest neighbors) for CdTe and 6.38 Å (up to the fifth nearest neighbors) for CdTe$_2$ under the consideration of accuracy and cost. The $\kappa_{ij}$ convergence test is shown in Figure S2. A dense phonon q-grid of 101 $\times$ 101 $\times$ 1 was used to calculate the $\kappa_{ij}$ of 2D CdTe and CdTe$_2$. During the electronic and thermal property calculations, the effective
thicknesses for the CdTe and CdTe$_2$ were considered to be 8.13 and 7.64 Å, respectively.

## RESULTS AND DISCUSSION

### Structure and Phase Stability

Extensive unbiased structure searches were carried out for CdTe, CdTe$_2$, and CdTe$_3$. To access the experimental feasibility, the phase stability of most stable 2D CdTe materials was verified by the calculation of formation enthalpies ($\Delta H$) with the use of bulk Cd and the most stable 2D Te ($\alpha$-Te) as references. The calculated formation enthalpies of CdTe, CdTe$_2$, and CdTe$_3$ are $-0.417$, $-0.283$, and $-0.185$ eV/atom, respectively. Based on the formation enthalpies, we constructed the convex hull. As shown in Figure 1a, phases on the convex hull are stable against decomposing into the nearest compositions. Both the 2D CdTe and CdTe$_2$ are on the convex hull; however, the CdTe$_3$ is above the convex hull and can decompose into CdTe$_2$ and Te monolayers. Thus, we only discuss the 2D CdTe and CdTe$_2$ in the following section. Considering that the calculations were carried out at 0 K, we performed the AIMD simulations at 300 K for 2D CdTe (Figure 1b) and CdTe$_2$ (Figure 1c). During the AIMD simulations, the total energy is nearly constant. After a 40 ps simulation, the crystal...
structures of CdTe and CdTe$_2$ monolayers remained intact, suggesting that both the 2D CdTe and CdTe$_2$ are stable at ambient temperature.

Detailed top and side views of CdTe and CdTe$_2$ monolayer structures are shown in Figure 1d,e, respectively. Other metastable 2D CdTe, CdTe$_2$, and CdTe$_3$ are shown in Figure S3. Consistent with the investigation of Kolobov et al.,$^{21}$ the CdTe monolayer adopts a honeycomb prototype with the space group $P\bar{6}m1$ and lattice constants $a = b = 4.67$ Å. In CdTe$_2$, each Cd atom is coordinated by four Te atoms in CdTe with two distinct distances of 2.86 and 3.06 Å. The CdTe$_2$ adopts a typical penta-structure with the symmetry group $P4_2/m$ and lattice constants $a = b = 6.06$ Å. Unlike the 2D PdTe$_2$ and PtTe$_2$ penta-structures, the CdTe$_2$ adopts a quasi-sandwich structure with Te−Cd−Te stacking. Similar to CdTe, all the Cd atoms are coordinated by four Te atoms with a uniform distance, 2.88 Å. The Cd−Te distances in both CdTe and CdTe$_2$ are comparable to those of bulk CdTe (2.86 Å). Considering the large electronegativity difference, it can be speculated that the Cd−Te bonding is coupled primarily through ionic bonding. The higher Te concentration in 2D α−Te (3.04 Å), which is shorter than that of 2D α−Te (3.04 Å),$^{50}$ indicating a strong covalent bonding character. The detailed atom positions are listed in Table S1.

**Bonding Analysis.** To unambiguously reveal the bonding character of the Cd−Te and Te−Te−Te pairs, we calculated the crystal orbital Hamilton population (COHP, −COHP plotted here) curves for 2D CdTe (Figure 2a) and CdTe$_2$ (Figure 2b). COHP is an efficient way to investigate bonding characters, which partitions the band structure energy into orbital pair interactions, and stronger bonding can lead to higher −COHP peaks. As shown in Figure 2a,b, Te−Te pairs exhibit much higher −COHP curves than Cd−Te pairs in both 2D CdTe and CdTe$_2$, suggesting a stronger bonding strength in Te−Te−Te pairs. The −COHP integration (−ICOHP, dashed line in Figure 2a,b) at the Fermi level can quantitatively determine the bonding strength; Cd−Te pairs have low −ICOHP values of 1.0 eV/pair both in CdTe and CdTe$_2$, while the −ICOHP for Te−Te pairs in CdTe$_2$ is 3.16 eV/pair, confirming their much stronger bonding strength and a potential covalent bonding character. The inserts in the figure are the electron localization function (ELF)$^{50}$ maps around Cd−Te and Te−Te pairs. The ELF between Cd and Te atoms is nearly zero both in CdTe and CdTe$_2$, revealing the ionic bonding nature. High ELF values (approximately 0.76) can be observed in the Te dimers, suggesting a strong covalent bonding character. Noteworthily, the negative −COHP values within −1.6 and 0.0 eV represent that strong antibonding states exist in Te−Te pairs. Such antibonding states originated from the $\pi^*$ bonding of p orbitals, which have also been observed in other chalcogenides, e.g., Na$_2$S$_3$,$^{15}$ and Ag$_2$Te$_{1-x}$$^{19}$ Considering the atomic arrangement of Cd and Te atoms, CdTe$_2$ can be viewed as a quasi-bonding hierarchy structure with covalent−ionic−covalent stacking.

To investigate the influence of bonding heterogeneity on the atomic-level dynamics of CdTe$_2$, we calculated the potential energy curves of Cd and Te atoms by displacing them along $x$/$y$ directions from their equilibrium positions (Figure 2c). In the 2D CdTe, the Cd and Te atoms are located in similar potential wells caused by the uniform ionic bonding. In the CdTe$_2$, Cd atoms lay in shallower potential wells compared with CdTe, whereas Te atoms lay in much deeper energy wells. This showed that the Cd atoms in CdTe$_2$ can vibrate more easily than in CdTe, and the vibrations of the Te atoms are damped in CdTe$_2$. This phenomenon was also verified by the velocity autocorrelation function (VACF).$^{60,61}$ As shown in Figure 2d, the oscillations of Cd and Te atoms are similar in CdTe but sharply different in CdTe$_2$. In CdTe$_2$, the oscillations of Cd atoms are more substantial than those of CdTe; however, the Te atoms are damped significantly, confirming the strong chemical bonding heterogeneity in CdTe$_2$. Similar with Cu$_{19}$Sb$_3$S$_{13}$ and BaAgYTe$_{19}$, the bonding heterogeneity in CdTe$_2$ may significantly enhance the scattering of the heat-carrying phonon and suppress the lattice thermal conductivity.

**Figure 3.** Phophon dispersion and phonon density of states of CdTe (a) and CdTe$_2$ (b). Lattice thermal conductivity $\kappa_l$ as a function of temperature (c). Branch contribution to $\kappa_l$ as a function of temperature (d). Frequency-resolved $\kappa_l$ at 300 K (e). Cumulative $\kappa_l$ as a function of the phonon mean free path at 300 K (f).
Lattice Thermal Conductivity. Phonon dispersion analyses can effectively assess the $\kappa_L$. Thus, we calculated the phonon dispersion for CdTe (Figure 3a) and CdTe$_2$ (Figure 3b). The three acoustic phonon branches which correspond to an out-of-plane flexural acoustic mode, an in-plane transverse acoustic mode, and an in-plane longitudinal acoustic mode are marked as ZA, TA, and LA, respectively. There is no negative frequency observed in the entire Brillouin zone for either CdTe or CdTe$_2$, confirming their dynamic stability. Generally, higher cutoff frequencies of an acoustic branch can lead to higher $\kappa_L$. Both the CdTe and CdTe$_2$ monolayers show low cutoff frequencies of ZA, TA, and LA branches, i.e., 1.23, 1.29, and 1.46 THz in CdTe and 0.76, 0.78, and 1.36 THz in CdTe$_2$, respectively, which are comparable to those of 2D Cu$_2$S$^{25}$ and InP$^{24}$. Such low acoustic branch frequencies are dominantly contributed by the high atomic mass of Cd and Te atoms. Moreover, there is no phonon gap between acoustic and optical branches in either CdTe or CdTe$_2$, suggesting a strong optical--acoustic phonon scattering, which can further suppress the $\kappa_L$. $^{50}$

Notably, the CdTe$_2$ possesses much lower cutoff frequencies of acoustic branches, contributed by the loosely bound Cd atoms and the quasi-sandwich structure with covalent–ionic–covalent stacking, which is similar to that of BaAu$_2$P$_4$ $^{43}$ and AgBiTeO$^{63}$ with bonding hierarchy. As shown in Figure S4, compared with CdTe, the lower cutoff frequencies of acoustic branches induced small group velocities in CdTe$_2$. The relatively larger mode Grünisen parameters of acoustic branches in CdTe$_2$ suggested that the bonding heterogeneity induced larger lattice anharmonicity. Moreover, there is one phonon gap in the optical branches of CdTe$_2$ located at around 2.4 THz, whereas five gaps exist in CdTe$_2$, located at around 1.5, 2.0, 3.0, 4.0, and 4.3 THz. We calculated the phonon DOS to uncover such a phenomenon (Figure 3a,b). The Cd and Te atoms are strongly hybridized both in CdTe and CdTe$_2$, which arises from their similar atomic mass values. For CdTe$_2$, strong covalent bonding in Te–Te pairs leading to stiffer elastic constants and higher frequencies of optical branches gives rise to a weaker hybridization, quasi-localized phonon branches, and multiple gaps in optical branches. These localized optical phonons with low frequencies induce multiple scattering channels, which can significantly suppress the transport of phonons. $^{19}$ Moreover, the higher frequencies of optical branches in CdTe$_2$ give rise to a weaker coupling between acoustic and optical phonon modes, indicating a higher optical--acoustic phonon scattering and leading to a lower $\kappa_L$. $^{19}$

The $\kappa_L$ values of CdTe and CdTe$_2$ were obtained from the iterative solution of the linearized Boltzmann transport equation. The calculated $\kappa_L$ values for CdTe and CdTe$_2$ in the range of 300–700 K are plotted in Figure 3c. The $\kappa_L$ decreased with increasing temperature. Both the CdTe and CdTe$_2$ monolayers exhibit an ultralow $\kappa_L$ at 300 K, 0.94 and 0.33 Wm$^{-1}$K$^{-1}$, respectively, much lower than that of 2D $\kappa$-Te (9.85 Wm$^{-1}$K$^{-1}$ at 300 K) $^{10}$ and comparable to that of In$_4$S$_3$ doped Cu$_2$S (0.95 Wm$^{-1}$K$^{-1}$ at 850 K). $^{64}$ Consistent with the chemical bonding and phonon dispersion analysis, the $\kappa_L$ of CdTe$_2$ is almost half as large as that of CdTe in the entire temperature range. Thus, bonding heterogeneity induced by the coexistence of ionic and covalent bondings can significantly suppress the $\kappa_L$. These phenomena were further clarified, and the influence of the Te concentration was excluded, by reviewing the previously reported 2D PdTe$_2$. $^{32}$ The $\kappa_L$ of P-PdTe$_2$ with the coexistence of Pd–Te and Te–Te bonding is almost half as large as that of H-PdTe$_2$ with uniform Pd–Te bonding. $^{32}$

The normalized contributions of acoustic and optical branches to $\kappa_L$ are shown in Figure 3d. The contribution of ZA branches dominates the $\kappa_L$ in both CdTe and CdTe$_2$ monolayers. The proportions of contributions of ZA, TA, LA, and optical branches to the total $\kappa_L$ are 36.7, 18.6, 25.2, and 19.5%, respectively, in CdTe and 54.2, 9.7, 17.1, and 19.0%, respectively, in CdTe$_2$. Consistently, the frequency-resolved $\kappa_L$ at 300 K in CdTe (Figure 3e) shows that phonons with frequencies lower than 1.8 THz are the primary contributors to...
total $k_{ij}$ whereas the optical branches with high frequencies show small contributions. For CdTe$_2$, the main contribution to $k_i$ comes from ZA branches with frequencies lower than 0.8 THz and the optical branch with frequencies around 3 Hz (originating from Te atoms as shown in Figure 3b).

The $k_i$ as a function of the phonon mean free path (MFP) is an important parameter to estimate the size effects and design nanostructures with optimized $k_i$.

As shown in Figure 3f, almost all phonons have an MFP below 1 μm in 2D CdTe. Notably, phonons in CdTe with MFPs below 20 nm contribute 3/4 of the $k_{ij}$ implying that the $k_i$ of CdTe can decrease sharply with a sample of less than 20 nm.

### Electronic Structure

The band structure and density of states (DOS) were calculated using the HSE06 hybrid functional. The 2D CdTe possesses a direct band gap of 1.82 eV with the valence band maximum (VBM) and conduction band minimum (CBM) located at Γ points. Our predicted band gap is higher than the previously reported value (1.03 eV), obtained using the PBESol method.

The highly dispersive CBM and relatively flat VBM in CdTe suggest a low electronic and high hole effective mass. Similar to the pentagonal PtS$_2$, the 2D CdTe$_2$ has an indirect band gap of 1.96 eV with the VBM located at M points and the CBM located between M and Γ points. In CdTe$_2$, both the CBM and VBM are highly dispersive, indicating a low electron and hole effective mass. Moreover, the valence bands are localized and highly degenerate around the Fermi level, which can significantly enhance the electrical conductivity and Seebeck coefficient, resulting in a high thermoelectric power factor.

To investigate the origin of such degenerated valence bands, we calculated the partial charge densities of these bands. As shown in the inset of Figure 4d, based on the partial charge density and COHP analyses (Figure 2b), these degenerated valence bands originate from the strong covalent Te–Te π* bonding. Furthermore, the $\pi$ and $\sigma$ bandings formed by Te–Sp orbitals are also distributed around the Fermi level, whereas the unoccupied $\sigma^*$ bonding dominantly contributes to the conduction bands. Thus, the Te–Te covalent bonding induced a high DOS with sharp peaks around the Fermi level, which can significantly enhance the power factor of p-type CdTe$_2$.

### Electronic Transport Coefficients

To explore the electronic transport coefficients of the CdTe and CdTe$_2$ monolayers, we first explore the relaxation time $\tau$, which is proportional to the electronic conductivity. The relaxation time $\tau$ was calculated through the well-known model

$$\tau = \frac{m^* \mu}{e}$$

where $m^*$ is the effective mass of electrons and holes, $\mu$ is the carrier mobility, and $e$ is the electron charge. For 2D materials, the $\mu$ can be derived using Bardeen–Shockley deformation potential (DP) theory, given by

$$\mu_{2D} = \frac{2e\hbar^2 C_{2D}}{3k_B T m^* E_d}$$

where $\hbar$ is the reduced Planck constant, $C_{2D}$ is the two-dimensional elastic modulus, which can be calculated through applying stress under uniaxial strain, $k_B$ is the Boltzmann constant, $T$ is the temperature (in K), and $E_d$ is the deformation potential, which can be calculated by

$$E_d = \frac{\partial E_{\text{edge}}}{\partial l}$$

where $E_{\text{edge}}$ is the maximum (minimum) energy value of the VBM (CBM) under small compression and expansion, $l_0$ is the lattice parameter, and $\partial l$ is the variation of the lattice parameter. The energy of core electrons is considered as the energy reference.

Table 1 lists the calculated carrier mobilities and relaxation time for electrons and holes for CdTe and CdTe$_2$. Consistent with the bonding and electronic structure analysis, p-type CdTe$_2$ shows superior carrier mobility. The strong anisotropy in CdTe$_2$ was also observed in pentagonal PtM$_2$ ($M = S$, Se, Te), ZrS$_2$, and As$_2$Te$_3$.

Boltzmann transport theory (BTE) was used to evaluate $\sigma$, $S$, and $k_i$. The Seebeck coefficients and electrical conductivities of CdTe and CdTe$_2$ as a function of the carrier concentration at 300, 500, and 700 K are shown in Figure 5a,b,d,e. Based on the single-parabolic band (SPB) model, the $S$ and $\sigma$ are usually interwoven, as described by

$$S = \frac{8\pi^2 K_T^2}{3e^2} m^* \left( \frac{\mu}{3n} \right)^{1/3}$$

and

$$\sigma = \frac{n e^2 \tau}{m^*}$$

where $n$ is the carrier concentration. The existence of occupied Te–Te π*, $\pi$, and $\sigma$ bandings significantly enhanced the p-type electrical conductivity, which is comparable to the 2D α–Te (uniform covalent bonding) and much higher than that of the 2D CdTe. The high electrical concentration in p-type CdTe$_2$ also induces high electronic thermal conductivity. As shown in Figure 5S, the total thermal conductivity of p-type CdTe$_2$ at 300 K is much higher than that of CdTe and n-type CdTe$_2$. However, the p-type CdTe$_2$ still exhibits high $S$, comparable to that of CdTe. Such an abnormal character is dominantly contributed by the highly degenerated band structure as discussed above. On the basis of the calculated $S$ and $\sigma$, we calculated the PF ($S^2\sigma$) for CdTe and CdTe$_2$. The maximum PFs at 300 K are 2.8 and 1.5 mW m$^{-1}$K$^{-2}$ for p- and n-types, respectively of CdTe. The superior $S$ and $\sigma$ lead to the largest PF in the p-type CdTe$_2$, which is 38.3 mW m$^{-1}$K$^{-2}$.

### Figure of Merit

On the basis of the above-mentioned results, we calculated the figure of merit $zT = S^2\sigma T/(\kappa_e + \kappa_l)$. Figure 6a,b shows the results for 2D CdTe and CdTe$_2$ at 300, 500, and 700 K. The $zT$ values are strongly correlated with temperature and carrier concentration. For CdTe, the $zT_{\text{max}}$ is 0.69 for the p-type and 0.60 for the n-type system at 300 K. The high power factor and low $\kappa_l$ give rise to a substantially
larger $zT_{\text{max}}$ of p-type CdTe$_2$, i.e., 0.85, 0.90, and 0.92 at 300, 500, and 700 K, respectively, which is higher than that of α-Te (0.54 at 300 K)\textsuperscript{10} and H-PdTe$_2$ (0.8 at 300 K).\textsuperscript{32} The high $zT_{\text{max}}$ suggests that CdTe$_2$ is a promising room temperature thermometric material. Moreover, the $zT_{\text{max}}$ for p-type CdTe$_2$ is almost unchanged in a wide range of carrier concentrations ($3 \times 10^{10} - 1 \times 10^{13}$ cm$^{-2}$). Such a character is important, since the high band gaps of CdTe and CdTe$_2$ indicate that a sufficient carrier concentration is difficult to achieve. The low thermal conductivity also renders CdTe$_2$ a promising candidate in low-thermal conductivity applications.

**CONCLUSIONS**

In conclusion, through the extensive structural search method, we explored the potential 2D CdTe compounds. The most stable 2D CdTe and CdTe$_2$ crystalize in the space groups $P\bar{6}m1$ and $P42_1m$, respectively. Both the 2D CdTe and CdTe$_2$ show low formation enthalpies and excellent dynamic stability, making them promising for synthesis. In CdTe, all the atoms are coupled through ionic bonding. CdTe$_2$ exhibits strong bonding heterogeneity, originating from the weak Cd–Te ionic bonding and strong Te–Te covalent bonding. The quasi-localized phonon branches, low group velocities of the acoustic modes, and high lattice anharmonicity in CdTe$_2$ induced a low $\kappa_L$ of 0.33 W m$^{-1}$ K$^{-1}$ at 300 K. The occupied $\pi^*_{5p} \sigma_{5p}$ and $\sigma_{5p}$ bondings in Te–Te pairs facilitate the electronic conductivity and enhance the Seebeck coefficient of p-type CdTe$_2$. The low lattice thermal conductivity and high electronic conductivity endow CdTe$_2$ with a considerably larger maximum $zT$~0.85 for the p-type system, making it a promising room temperature thermometric material.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.2c01176.

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