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A Perspective on Hot Carrier Solar Cells

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Carrier Cooling in Lead Halide Perovskites: A Perspective on Hot Carrier Solar Cells

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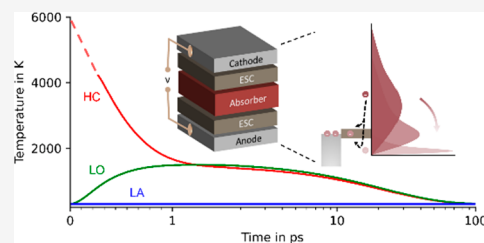


Article Recommendations



Supporting Information

ABSTRACT: The concept of hot carrier solar cells (HCSCs) has been proposed as a promising yet elusive path toward high-performance photovoltaics (PV), capable of surpassing the Shockley–Queisser limit by recycling energy that would otherwise be lost during thermalization. Lead halide perovskites (LHPs) have emerged as highly promising materials for PV applications. The reports of slow hot carrier (HC) cooling in these materials have ignited discussions of their potential in realizing HCSCs. Here we summarize the key findings regarding HC dynamics in LHPs, as revealed by numerous studies using advanced time-resolved spectroscopies. We also emphasize the interconnected mechanisms involved in HC cooling. In addition, we discuss the influence of nanostructuring on HC cooling dynamics in LHPs and suggest that two-dimensional LHPs, with their inherent quantum well structure, might exhibit modified phononic features and altered carrier–phonon coupling strength. We conclude by critically discussing the prospects for HCSCs, taking into account our current understanding of HC cooling and excitation conditions under sunlight.



Extensive research has been conducted on renewable energy sources to pave the way for a more sustainable future, with photovoltaics (PV) emerging as a realistic long-term solution.^{1,2} The power conversion efficiency (PCE) plays a vital role in assessing the PV device quality and has exhibited steady improvement over decades.^{3,4} However, according to the Shockley–Queisser (SQ) limit the maximum efficiency that conventional single-junction solar cells can achieve is around 33%.⁵ Therefore, numerous strategies have been proposed to overcome the SQ limit,^{6,7} including multijunction cells,^{8–11} carrier multiplication processes^{12,13} (e.g., multiple exciton generation,^{14,15} singlet exciton fission,¹⁶ and quantum-cutting¹⁷), and hot carrier solar cells (HCSCs).¹⁸

From all possible loss mechanisms in the SQ model,¹⁹ a significant share is related to the blue part of the solar spectrum which excites significantly higher-energy charge carriers compared to the optical band gap. The overflow of energy is dissipated as heat in the material when these hot carriers (HCs) relax to the band edge. One third of the energy is lost in this way in the SQ model.⁷ Therefore, the fundamental idea of HCSCs^{20–23} is to make use of this additional energy and to extract photogenerated electrons and holes at energy higher than the band gap. In this way, less energy is converted to heat. In HCSCs this is achieved via the “heat” “warming up” of the cold carriers. These are the carriers that are “cooled” down below the extraction energy and the carriers that are excited by the lower energy part of the spectrum below the extraction energy. In this way, one is not only making use of the excess energy of the blue solar photons but can also lower the bandgap

to harvest lower energy photons than what would otherwise be possible. In addition, in the pursuit of optimal absorber material with low bandgap, leveraging materials with high two-photon absorption coefficient aligns with maximizing photon utilization from radiation and enriches the HCSC possibilities. The general structure of HCSCs can be simplified as a light absorber layer sandwiched between two energy selective contacts (ESCs), as shown in Figure 1.²⁴ The extraction energy window needs to be suitably narrow for minimizing the energy loss within the contacts, as shown in the energy diagram in Figure 1. The idea of HCSCs was first proposed by Ross and Nozik in 1982,¹⁸ and the PCE calculations in the case of different loss mechanisms in HCSCs have been developed over decades.^{24–27} For example, theoretical calculations indicate that an HCSC device has the potential to achieve 50% PCE under concentrated solar radiation (1000 times), provided that certain conditions are met: sufficiently long cooling time of 1 ns, fast HC equilibration time (heat exchange) of 1 ps, and narrow extraction energy window of ESC of 0.1 eV.²⁸

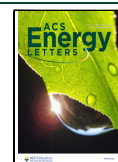
The theoretical maximum conversion efficiency of an ideal HCSC is near 66% under 1 sun illumination, aligning closely with the efficiency attained by tandem cells employing an infinite

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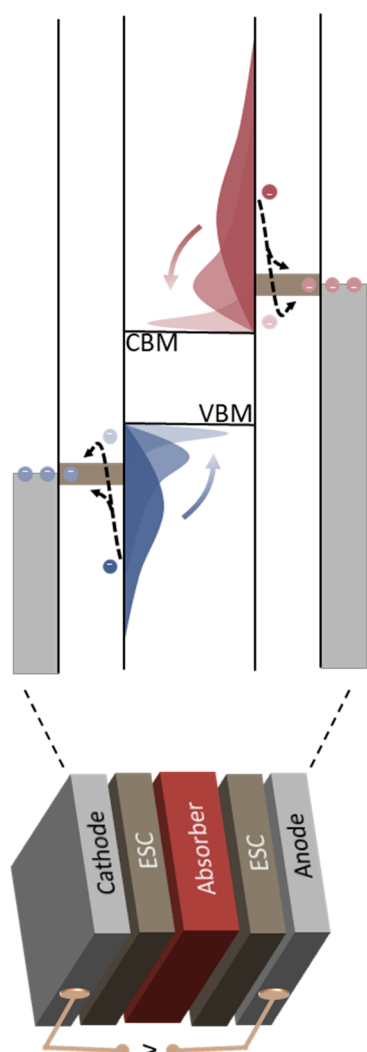


Figure 1. Schematic of hot carrier solar cell device, where ESC represents energy selective contact, and the corresponding energy schematic of an HCSC, where conduction band minimum (CBM) and valence band maximum (VBM) are marked.

number of junctions.¹⁸ This equivalence holds because both aim to minimize thermalization losses. The infinite-junction device achieves this by perfectly matching the bandgap of materials to each photon energy, while the HCSC maximizes efficiency by recycling the energy released during thermalization in a single-junction system.

In recent years, lead halide perovskites (LHPs) have garnered significant attention for their numerous attractive properties in PV applications, including HCSCs. Upon analyzing the loss channels within MAPbI₃ across the solar spectrum, the theoretical maximum PCE of perovskite-based HCSCs is found to be approximately 57%,²³ indicating its high potential in surpassing the SQ limit. Remarkably, the giant two-photon absorption coefficient observed in perovskite nanostructures, including quantum dots (QDs) and 2D perovskites, makes them interesting also for harnessing low-energy photons.^{29,30} An important characteristic that determines the potential of a material as a candidate for HCSCs is the HC lifetime, which should be long enough for carriers with excess energy to be extracted. The HC lifetime of LHPs with different compositions have been extensively studied.²³ Figure 2 shows the number of publications during the past decade related to HCSCs and the part which is using LHP as target material.^{31–33} We point out that a significant number of these papers published around 2017 are highly cited. The possible reason for the “special year” may lie in the fact that the high-quality bulk LHP layers leading to solar cells with respectable PCE were achieved by that time allowing the exploration of additional possibilities.³⁴ While hot carrier extraction has been achieved,³¹ no real-life improvement of the solar cell performance owing to the hot carriers has been reported. Most likely, the necessary conditions for HCSCs have not been achieved so far. Theoretical analyses considering the thermodynamic balance of HC relaxation, equilibration, and extraction rates have suggested a range of the possible limiting parameters, the most important of which are the hot carrier lifetime and temperature.^{18,22,25,26,28} The long-range HC transport observed in perovskite (up to 600 nm) also suggests the potential of LHP in HCSC applications.³⁵ The other key element, ESC, can be achieved via the resonant tunneling effect in double-barrier nanosystems, which can improve the HC extraction efficiency.^{36–38} Various studies have been conducted on the application of quantum well (QW) structure as a potential final form of HCSCs.^{39,40} The QW structure enriches

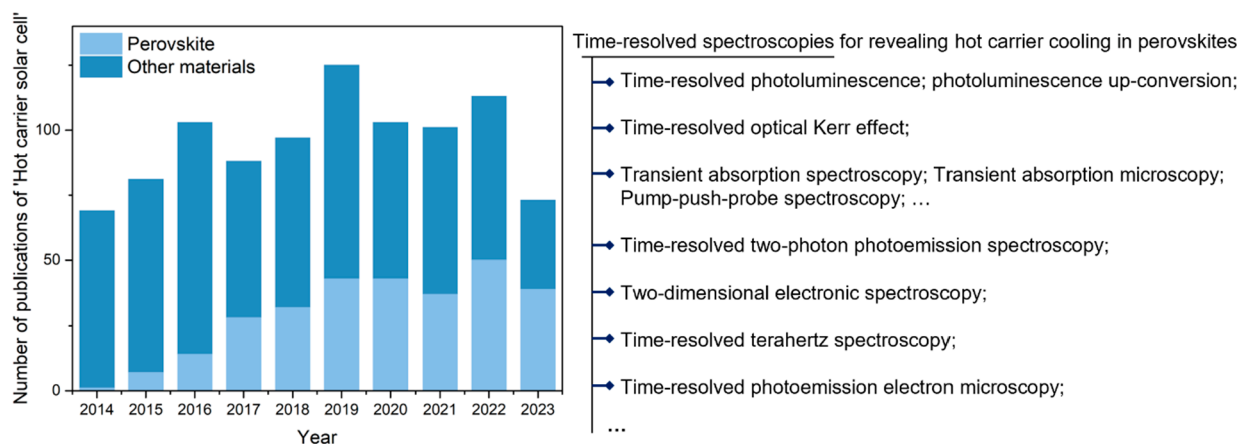


Figure 2. Publications in the field of hot carrier solar cells and using perovskite as absorber material based on the search results from Web of Science (from 2014 to 2023, accessed November 2023) and a list of advanced time-resolved spectroscopies used for investigating hot carrier cooling in perovskites.

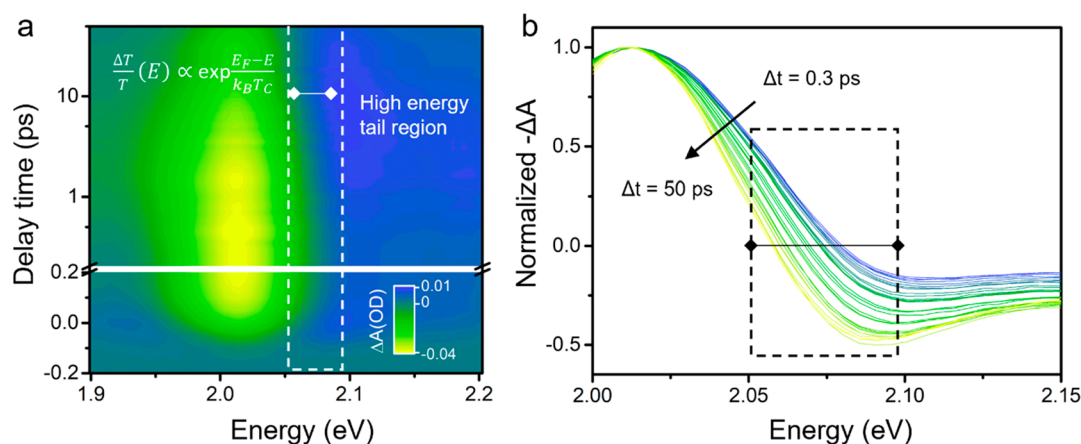


Figure 3. Transient absorption spectra for demonstrating the extraction of HC temperatures (a) and the normalized spectra (b) extracted from panel a with the delay time range from 0.3 to 50 ps. The highlighted section denotes the high-energy tail region used for Boltzmann fitting, with the equation integrated into the figure for reference. The data adapted from ref 46.

the possibilities for future device fabrication by selectively combining different materials and adjusting the phononic features. While the mechanisms remain elusive, slower HC cooling rates have been reported in multiple quantum well (MQW) systems compared to bulk materials.^{20,41,42}

To target the best material composition and device configuration for efficient HCSCs, understanding the relaxation pathways of HC in LHP is pivotal. Various advanced time-resolved spectroscopic techniques have been utilized to study the HC cooling dynamics in LHPs, as shown in Figure 2. Since the late 1960s, optical techniques have been employed to directly measure the HC relaxation in semiconductors.⁴³ The development of ultrafast lasers, with pulse duration being well below 100 fs, has enabled us to investigate the important carrier scattering processes in materials including LHPs. Transient absorption spectroscopy is extensively utilized to investigate the HC cooling dynamics in perovskites, with the carrier temperature being extracted by fitting the high-energy tail of the photobleaching signal to the Boltzmann distribution (approximation to the Fermi–Dirac distribution). However, this fitting method presents uncertainties related to the density of states which is difficult to quantify and is usually simplified to be a constant value in the investigated spectral region, as shown in Figure 3. There is also possible spectral overlap between the bleach and the excited state absorption signals, which can complicate the analyses. These uncertainties can significantly influence the accuracy of the results.⁴⁴ Even though two-dimensional electronic spectroscopy (2DES) is not free from such difficulties, it allows superb simultaneous time and energy resolution.³⁹ As a powerful alternative, in time-resolved two-photon photoemission (TR-2PPE) spectroscopy, the system is excited by a short pump pulse and the hot electrons are ionized by a delayed probe pulse.^{45,46} In this way, the emitted photoelectrons directly map out the energy distribution of hot electrons in the conduction band as a function of delay time, although the energy resolution of the method is currently not very high. Extra caution should be exercised regarding sample degradation, e.g., conduct measurements at low environmental temperatures, especially when mapping the hot electrons with high excitation fluence for a better signal-to-noise ratio.

Time-resolved hot luminescence is another method to investigate the HC cooling dynamics by fitting the emission tail region at the high-energy side to a Boltzmann distribution.⁴⁷

No practically viable perovskite-based hot carrier solar cell exists. Nevertheless, the long diffusion length and extended lifetime of hot carriers high-light perovskites' promising potential for such applications.

However, only materials with emissive hot states are suitable for this technique, and the hot photoluminescence signal becomes very weak on the longer time scales. Given that hot luminescence occurs at higher energies, there is a risk of reabsorption, particularly in optically thick samples, which can affect the accurate detection of HCs. Furthermore, carrier population dynamics within a broad energetic disorder can also appear as a slow decrease in carrier temperature, which can complicate the assessment of HC dynamics.⁴⁸

Regardless of the signal source and setup configuration, the measurements listed in Figure 2 have been used to understand the HC cooling dynamics in perovskites directly or indirectly. Since analyses of the experimental results and interpretations typically involve approximations and assumptions, combining information from multiple techniques can provide a more complete picture of the HC cooling dynamics in LHPs.⁴⁶ The reported time scales of HC cooling cover a broad range depending on the material and the measurement. In Table 1 we summarize the typical times for carrier cooling to 600 K in the perovskite materials under different excitation conditions. A detailed list can be found in the Supporting Information.

The HC relaxation process generally consists of four stages, as shown in Figure 4. In the first stage, initial excited HCs lose their energy via carrier–carrier and carrier–phonon scattering in the time scale of 100 fs, which is named HC thermalization. Only after the quasi-equilibrium is reached can the “temperature of the HC system” be assigned, and the HCs follow the Fermi–Dirac distribution. In the next stage, HCs further lose their energy mainly by interacting with the lattice to emit longitudinal-optical (LO) phonons with small k -value (momentum). The equilibrium between HC and LO phonons is reached within the time scale of a few picoseconds. In the third stage, acoustic phonon emission is involved, and the equilibrium among HC, LO phonons, and acoustic phonons is reached on

Table 1. Time Scale of HC Cooling down to 600 K under Different Excitation Conditions and with Applying Different Techniques in Different LHPs

Compositions	Excitation conditions		Delay time to 600 K (ps)	ref
	Excitation energy	Excitation density n_0 ($\times 10^{17} \text{ cm}^{-3}$)		
APbI ₃ film (A = MA, FA, Cs) E_g : 1.3–1.7 eV	Above bandgap (~ 3.1 eV)	28–60	12–60	49–51
		5–15	0.5–0.9	49,51
	Near bandedge (~ 2.2 eV)	65–270	0.8–1	49,52,53
APbBr ₃ film (A = MA, FA, Cs) E_g : 2.2–2.4 eV	Above bandgap (~ 3.1 eV)	1–40	0.1–0.5	49,52–55
		30	~ 3.6	56
	Near bandedge (~ 2.7 eV)	70–85	0.75–1	52
APbX ₃ film (A = MA, FA, Cs, or mixture) (X = mixture of I, Br)		18–20	~ 0.35	52
	Above bandgap (3.1 eV)	30–40	0.4–0.5	51,57
		3–4	<0.1	51,57
APbX ₃ film (A = MA, FA, Cs) (X = mixture of Br, Cl)	Above bandgap (3.1 eV)	30	2.4–2.8	56
Low-Dimensionality Samples				
APbI ₃ QDs (A = MA, FA, Cs)	~ 2.64	4–8	0.2–0.4	58
A'PbI ₃ QDs (A = mixture of MA, FA, Cs)	~ 2.64	4–6	0.3–0.4	58
APbI ₃ NCs film (A = MA, FA, Cs)	3.1 eV	10–70	30–40	59,60
APbBr ₃ NCs film (A = MA, FA, Cs)		2–4	2–9	59,60
	3.1 eV	10–170	2–40	31,61,62
		1–5	0.2–0.7	31,61–63
2D Perovskites: (B)(MA) _{n-1} PbI _{n-3n+1}				
$n = 1$ (B = (ACA)(MA), PEA, (3AMP) ₂ , (4AMP) ₂)	3.1–3.9 eV	65	1–2	64
		4 $\mu\text{J}/\text{cm}^2$		65
		6–20	<0.5	64
$n = 2$ (B = (BA) ₂)	3.1 eV	2 $\mu\text{J}/\text{cm}^2$		65
		30 $\mu\text{J}/\text{cm}^2$	~ 2	66
		<15 $\mu\text{J}/\text{cm}^2$	<0.3	66
$n = 3$ (B = (BA) ₂)	3.1 eV	30 $\mu\text{J}/\text{cm}^2$	~ 9	66
		120–240	1.5–2.5	46
		30–60	0.3	46
$n = 4$ (B = (BA) ₂)	3.1 eV	<15 $\mu\text{J}/\text{cm}^2$	<0.3	66
		<30 $\mu\text{J}/\text{cm}^2$	<0.3	66
				66

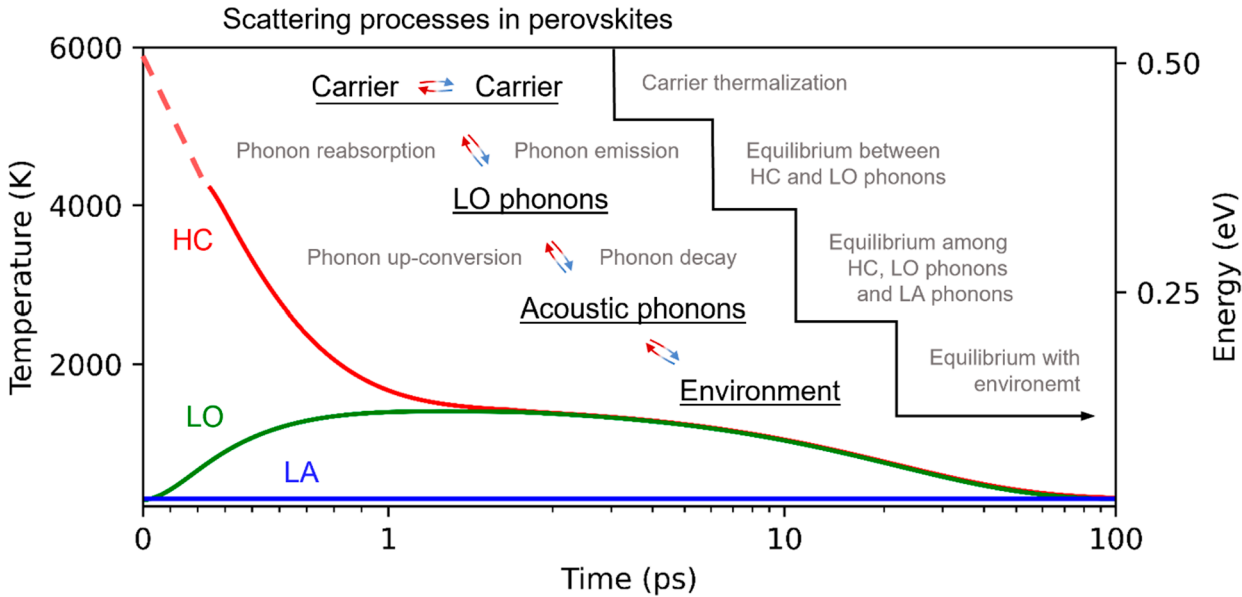


Figure 4. Schematic of the time-dependent temperature of the hot carrier, LO phonons, and LA phonons.

the 100 ps time scale. Thereby, the HC cooling involves a cascade of processes in which reaching equilibrium between different phonon modes is one of the key elements. This can be used for prolonging the carrier cooling via the so-called hot

phonon bottleneck by engineering the phononic band gap with the help of nanostructures.⁶⁷

The most efficient channel of phonon decay in LHPs is called Klemens decay, where one LO phonon decays into two

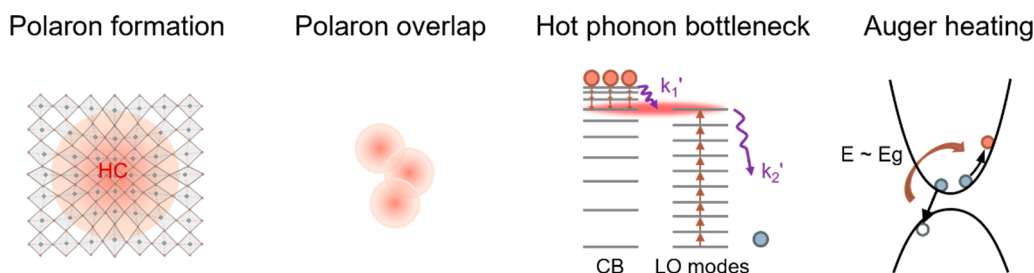


Figure 5. Schematics of polaron formation, polaron overlap, hot phonon bottleneck effect, and Auger heating.

longitudinal-acoustic (LA) phonons.⁶⁸ The possibility of other LO phonon decay channels should not be completely ruled out, e.g., by emitting transverse acoustic (TA) phonons. Further cooling of the system involves heat dissipation to the environment or carrier recombination on the nanosecond time scale, which will not be discussed here since the carriers are no longer in a “hot” state. The cooling dynamics of HC, LO phonons, and LA phonons after carrier thermalization, as shown in Figure 4, can be deduced based on the three-temperature model⁶⁹ and the HC cooling dynamics model.⁴⁹

Several mechanisms have been proposed to play a role in prolonging the HC lifetime in LHPs, including polaron formation, hot phonon bottlenecks, and Auger recombination (also known as Auger heating). These mechanisms have shown distinct excitation intensity thresholds, with typical characteristic carrier densities of 10^{16} – 10^{17} , 10^{17} – 10^{19} , and higher than 10^{19} cm⁻³, respectively. The schematics of these mechanisms as well as the polaron overlap are shown in Figure 5. Also acoustic phonon–optical phonon up-conversion, Rashba splitting, trapping of HCs, and changes in the near-bandgap density of states (DOS) have been suggested to prolong HC lifetime in LHPs.^{47,51,59} We will not further discuss these possibilities here.

Polaron formation occurs when a charge carrier interacts with the crystal lattice, leading to the formation of a quasiparticle consisting of the carrier and the surrounding lattice deformations. In LHPs, the dominant driving force for polaron formation is long-range (Fröhlich) interaction between self-trapped carriers and a displaceable inorganic sublattice, with a minor contribution from an A-site cation.⁷⁰ The formation of the polaron was first proposed to explain the long carrier diffusion length, and low recombination rate, with relatively modest mobility in LHPs.³² Although there has been a long-standing debate over the size of the formed polaron in LHPs, recent studies have provided evidence that large polarons may be formed; that is, the polaron transportation is coherent and the mobility decreases with increasing temperature in typical (three-dimension) LHPs.^{71–74} The “large” in the name means that the polarization cloud can extend over several unit cells, instead of being confined to a single site as for a small polaron.⁷⁵ It is generally accepted that polarons are formed in LHPs on the time scale of ~ 100 fs, while the polaron stabilization energy and the polaron size can be altered by chemical composition and particle size.^{76–78} The picture for the composition dependence is straightforward. Since the lattice distortion is significantly altered when changing the B-site cation or the X-site anion, the optical phonons participating in polaron formation can be different.^{70,79–81} For LHP building blocks that have quantum confined nanostructures, e.g., LHP nanocrystals (NCs) or quantum dots, the polaron formation is also observed, with possible influences from the degree of size confinement and dielectric confinement.^{82–84} In the HC cooling scenario, the

presence of a polaron serves as a protective shield, screening hot carriers from scattering with charged defects and optical phonons. As a result, HC cooling can be significantly decelerated, with the slowdown commencing on the time scale of the formation of large polarons (~ 100 fs).

The hot phonon bottleneck is another effect that can explain the prolonged lifetime of HCs in LHPs under a high excitation intensity. As mentioned above, when an excited carrier is generated in a polar material, it quickly thermalizes with other carriers and the lattice via LO phonon emission. Further, the LO phonon can decay to acoustic phonons, and the most efficient decay channel in polar material (Klemens decay) is hindered in LHPs due to the large energy separation ($E_{LO} > 2E_{LA}$).⁵⁵ Considering the strong Fröhlich interaction between carrier and LO phonons and the inefficient LO phonon decay, it is expected that an equilibrium status between HC and LO phonons can be reached before the final equilibrium between the carrier and lattice (acoustic phonons). The hot phonon bottleneck happens when the dissipation of the excess energy of the LO phonons is significantly slower than the time that it takes to reach the HC–LO phonon equilibrium. This means that the LO phonon emission and reabsorption are governed by the detailed balance at the HC temperature, while the LO phonons are in strong nonequilibrium with respect to the other modes. The energy of the system (HC–LO phonon) during phonon emission is not necessarily dissipated if the efficiency of phonon reabsorption is sufficiently high. Given that the hot phonon bottleneck effect occurs under strong excitation with efficient phonon reabsorption and less efficient phonon decay, it is natural to expect that the effect is dependent on carrier density (as it involves the electron–phonon scattering rate) and environmental temperature (as it relates to phonon occupancy).

In addition to the hot carrier relaxation dynamics, it is important to understand the elementary unit where heat exchange from a hot to a cold carrier can take place, possibly with hot phonons as mediators.

It should be noted that it is possible to observe two stages in HC cooling in LHPs under moderate excitation without the pronounced hot phonon bottleneck effect. After carrier thermalization, the HC system loses energy via LO phonon emission (resulting in HC–LO phonon equilibrium) and phonon decay (leading to equilibrium among HC, LO phonons, and acoustic phonons). Therefore, the emergence of two stages is dependent on the coupling strength of the HC–LO phonon and the efficiency of the phonon decay rate in dissipating the

excess energy of the carrier–LO phonon system. Conversely, in the presence of the hot phonon bottleneck effect under high excitation, the initial system temperature of the second stage may be significantly elevated. For LHPs, the hot phonon bottleneck effect is considered to be enhanced compared to conventional inorganic semiconductors, due to the relatively small LO phonon energy and possibly the low DOS in the electronic structure of LHPs.^{85,86}

Auger heating, or nonradiative interband Auger recombination, is another mechanism that plays an important role in prolonging HC lifetime in LHPs under intense excitation.⁵⁵ In this process, the energy released from interband carrier recombination is effectively transferred to another excited carrier, causing it to undergo a transition from a relatively cold state to a hot state above the band edge by the amount of the energy of recombination, at least the bandgap. Thus, the lifetime of the HC system can be prolonged due to the energy redistribution within the carrier population. Furthermore, the impact of Auger heating is particularly pronounced at high carrier densities, due to the enhanced three-body scattering, and in materials characterized with a small band gap or those exhibiting nanostructures.^{55,87} The latter (nanostructure) increases the Auger heating in two ways. First, the Coulomb interaction between charge carriers is enhanced by spatial confinement, which increases the possibility of Auger heating. Second, the conservation rule for translational momentum is less strict in NCs, and the excess carrier in the Auger heating process can accept the recombination energy, leading to transition to higher excited states. Thus the Auger processes are more efficient in NCs compare to bulk semiconductors.⁸⁸

We point out that the process of Auger heating is different from the Auger-type energy transfer, where the additional energy of the electron is given to the hole (or the other way around). Such a process has been discussed as a possible explanation of an accelerated relaxation rate in small inorganic semiconductor NCs (e.g., CdSe NCs) under low excitation fluence.⁸⁹ Interestingly, in LHP NCs, the HC lifetime is significantly longer compared to conventional NCs.⁶² These phenomena suggest the suppression of Auger-type energy transfer in LHP NCs, likely attributed to factors such as the symmetric energy dispersion, smaller carrier effective mass, and other related characteristics of LHPs.⁹⁰

Developing a comprehensive model that includes all of these mechanisms would offer a thorough perspective on the HC cooling process in LHPs. The transition of dominant mechanisms for slowing down HC cooling, from the polaron to hot phonon bottleneck effect, is proposed to occur at a critical Mott density. The large polarons begin to spatially overlap at higher excitation intensities, leading to mutual repulsive interactions that destabilize the large polarons.^{52,72,91} With a further increase in the carrier density, the possibility of the cold carrier absorbing energy released from carrier recombination is increased and the HC lifetime can be significantly prolonged, as suggested in the Auger heating process. The cooling dynamics of the HC system under different excitation densities is not ruled by one mechanism, but the collective influence from multiple factors and the significance of each mechanism are not yet clear. Quantitative investigations are needed to complete the picture, e.g., the relation between transition temperature and the material composition, to which percentage the usage of these mechanisms can be most beneficial for HCSC applications, how to balance the material stability, and how to judge which

operation condition (e.g., excitation fluence) is most practical for LHP-based HCSCs in the future.

In conclusion, extensive research has been conducted on HC cooling and electron–phonon coupling in LHP materials for the development of HCSCs. The HC cooling processes in LHPs involve several stages, including HC thermalization, LO phonon emission, and phonon decay. Mechanisms such as polaron formation, hot phonon bottleneck, and Auger heating have been proposed to contribute to the extended HC lifetimes observed in LHPs. These mechanisms are interconnected, and a comprehensive model encompassing all of them would provide a thorough understanding of HC cooling in LHPs.

However, important challenges remain. What is the required time scale of hot carrier cooling for practical perovskite-based HCSCs? What are the other criteria? So far, no solar cell that benefits from hot carrier extraction has been demonstrated. Does this mean that the time scale of HC cooling is not sufficiently long for making a real device? It has been argued that for making a meaningful contribution, the cooling time needs to be comparable to radiative recombination, and 1 ns was named as a guideline for achieving 50% efficiency.²⁶ In the studies where hot carrier injection has been demonstrated, so far the focus has been on fast injection,⁶² clearly motivated by the short lifetime of hot carriers. In the following discussion, we approach the issue from a different angle so far overlooked in the literature. As explained in the original suggestion by Ross and Nozik,¹⁸ for the HCSC to work efficiently, both hot and cold carriers need to be taken care of—the surplus energy of hot carriers is used to “warm up” the cold carriers originating from the band-edge transitions initiated by the red side of the solar spectrum. This means that the thermal energy of the hot carriers excited by the blue photons needs to be able to meet the cold carriers excited by the red photons. We point out that the hot carriers do not need to meet themselves with the cold carriers. It would be enough that the hot phonons (see the hot phonon bottleneck) meet the cold carriers and warm them up. If we consider as “blue” all the photons with wavelength shorter than 500 nm, we can estimate from the AM 1.5 solar spectrum that each second 2×10^{20} blue photons from the Sun fall on an Earth area of a square meter. We argue that for the maximum HCSC performance, every carrier excited by a blue photon needs to be able to provide energy to a cold carrier excited by a red photon. This means that the blue photons need to be coming to the elementary unit where the heat exchange can take place at a rate that is not smaller than the cooling rate. Otherwise the likelihood that the heat exchange can take place would be reduced. Let us consider a square of $100 \times 100 \text{ nm}^2$. A blue photon from the Sun falls at such a square once per $0.5 \mu\text{s}$, on average. Using a high-end solar concentrator (can reach 1000 times), this number can be reduced to a subnanosecond scale. If the unit is smaller, the necessary time scale would be correspondingly longer. The question of what should be considered as the elementary unit of the heat exchange in HCSCs has not been addressed in the scientific literature so far. We point out that for the heat exchange to take place, the hot and cold carriers do not need to necessarily meet. In the context of the hot phonon bottleneck, the charge carriers reach thermal equilibrium with the subset of phonons. It is enough that the cold carriers would be interacting with these hot phonons and warm up in this way. As a word of warning, the optical experiments of hot carrier cooling typically use light intensities many orders of magnitude higher than what can be achieved with solar concentrators. In summary, we emphasize the

significance of the hot phonon bottleneck which not only extends the HC lifetime but also facilitates heat exchange between hot and cold carriers, even if the carriers themselves do not meet.

To understand the expectation of the HC lifetime and the involved mechanisms in LHPs, it is crucial to investigate HC cooling dynamics, which can be achieved through spectroscopic techniques. Transient absorption spectroscopy and time-resolved photoluminescence spectroscopy are powerful tools for accessing the transient change in the HC population, but extra cautiousness is needed since the fitting method can have a significant impact on determining the HC cooling rate and potentially provide misleading results. To reduce the risks, we recommend simultaneous use of several ultrafast spectroscopic techniques and combining their information for a more comprehensive understanding of HC cooling processes in LHPs. Furthermore, it can facilitate a clearer assessment of which compositions or structures of LHPs hold the best promise for HCSC applications.

Nanostructures and quantum well structures have been explored to manipulate the HC lifetime and enhance the efficiency of HC extraction in HCSC. For example, two-dimensional LHPs,^{92–95} with their inherent quantum well structure, hold great potential as a material candidate for HCSC applications.^{65,96} These materials have already demonstrated numerous advantages in LHP-based photovoltaic applications. Along these lines, further investigations of the HC cooling dynamics of 2D LHPs with varying “n-values” (referring to the number of octahedral layers in one unit cell) would be highly needed. For example, the exciton binding energy of 2D perovskites, depending on the n-values and compositions,⁹⁷ ranges from 30 to 120 meV, and even up to 200 meV.^{98–101} Additional investigation and comprehensive studies are required to fully understand the interplay between exciton binding energy, n-value, and the observed variations in the HC cooling dynamics among different 2D perovskite structures. The existing investigations into HC cooling in 2D perovskites, as outlined in Table 1, have yet to yield a definitive conclusion on this aspect. Such studies would provide valuable insights into the behavior of HCs in these materials and help to assess their potential for HCSC applications. Further research and development in this field are essential for the realization of high-efficiency LHP-based HCSCs and the advancement of renewable energy technologies toward a more sustainable future.

In this Perspective, we provide an overview of the intriguing field of hot carrier cooling in LHPs from our personal standpoint, fully aware that our perspective cannot encompass the entirety of this extensive body of research. We apologize if we have not mentioned your important work. Given the wealth of studies available, we had to be selective in our approach, inevitably introducing a subjective element into our selection.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenergylett.3c02359>.

Comprehensive table of hot carrier cooling time scales in different perovskites (PDF)

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■ REFERENCES

- (1) Green, M. A.; Bremner, S. P. Energy conversion approaches and materials for high-efficiency photovoltaics. *Nat. Mater.* **2017**, *16*, 23–34.
- (2) Nozik, A. J. Utilizing hot electrons. *Nat. Energy* **2018**, *3* (3), 170–171.
- (3) NREL. Best Research-Cell Efficiency Chart. <https://www.nrel.gov/pv/cell-efficiency.html> (accessed 2023-11-30).

- (4) Jena, A. K.; Kulkarni, A.; Miyasaka, T. Halide Perovskite Photovoltaics: Background, Status, and Future Prospects. *Chem. Rev.* **2019**, *119* (5), 3036–3103.
- (5) Shockley, W.; Queisser, H. J. Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. *J. Appl. Phys.* **1961**, *32* (3), 510–519.
- (6) Ehrler, B.; Alarcón-Lladó, E.; Tabernig, S. W.; Veecken, T.; Garnett, E. C.; Polman, A. Photovoltaics Reaching for the Shockley–Queisser Limit. *ACS Energy Lett.* **2020**, *5* (9), 3029–3033.
- (7) Rao, A.; Friend, R. H. Harnessing singlet exciton fission to break the Shockley–Queisser limit. *Nat. Rev. Mater.* **2017**, *2*, 17063.
- (8) Tanabe, K. A Review of Ultrahigh Efficiency III-V Semiconductor Compound Solar Cells: Multijunction Tandem, Lower Dimensional, Photonic Up/Down Conversion and Plasmonic Nanometallic Structures. *Energies* **2009**, *2* (3), 504–530.
- (9) Polman, A.; Atwater, H. A. Photonic design principles for ultrahigh-efficiency photovoltaics. *Nat. Mater.* **2012**, *11* (3), 174–177.
- (10) Lewis, N. S. Research opportunities to advance solar energy utilization. *Science* **2016**, *351* (6271), No. aad1920.
- (11) Vos, A. D. Detailed balance limit of the efficiency of tandem solar cells. *J. Phys. D* **1980**, *13*, 839–846.
- (12) Tauc, J. Electron impact ionization in semiconductors. *J. Phys. Chem. Solids* **1959**, *8*, 219–223.
- (13) Queisser, H. J. Multiple carrier generation in solar cells. *Sol. Energy Mater. Sol. Cells* **2010**, *94* (11), 1927–1930.
- (14) Semonin, O. E.; Luther, J. M.; Choi, S.; Chen, H. Y.; Gao, J.; Nozik, A. J.; Beard, M. C. Peak External Photocurrent Quantum Efficiency Exceeding 100% via MEG in a Quantum Dot Solar Cell. *Science* **2011**, *334* (6062), 1530–1533.
- (15) Beard, M. C.; Luther, J. M.; Semonin, O. E.; Nozik, A. J. Third Generation Photovoltaics based on Multiple Exciton Generation in Quantum Confined Semiconductors. *Acc. Chem. Res.* **2013**, *46* (6), 1252–1260.
- (16) Ehrler, B.; Wilson, M. W. B.; Rao, A.; Friend, R. H.; Greenham, N. C. Singlet Exciton Fission-Sensitized Infrared Quantum Dot Solar Cells. *Nano Lett.* **2012**, *12* (2), 1053–1057.
- (17) Ferro, S. M.; Wobben, M.; Ehrler, B. Rare-earth quantum cutting in metal halide perovskites – a review. *Mater. Horiz.* **2021**, *8* (4), 1072–1083.
- (18) Ross, R. T.; Nozik, A. J. Efficiency of hot-carrier solar energy converters. *J. Appl. Phys.* **1982**, *53* (5), 3813–3818.
- (19) Nelson, C. A.; Monahan, N. R.; Zhu, X. Y. Exceeding the Shockley–Queisser limit in solar energy conversion. *Energy Environ. Sci.* **2013**, *6* (12), 3508–3519.
- (20) Conibeer, G.; Shrestha, S.; Huang, S.; Patterson, R.; Xia, H.; Feng, Y.; Zhang, P.; Gupta, N.; Tayebjee, M.; Smyth, S.; Liao, Y.; Zhang, Z.; Chung, S.; Lin, S.; Wang, P.; Dai, X. Hot carrier solar cell absorbers: materials, mechanisms and nanostructures. In *Next Generation Technologies for Solar Energy Conversion V*; San Diego, California, United States, **2014**; Vol. 9178, 917802.
- (21) Conibeer, G.; Shrestha, S.; Huang, S.; Patterson, R.; Xia, H.; Feng, Y.; Zhang, P.; Gupta, N.; Tayebjee, M.; Smyth, S.; Liao, Y.; Lin, S.; Wang, P.; Dai, X.; Chung, S. Hot carrier solar cell absorber prerequisites and candidate material systems. *Sol. Energy Mater. Sol. Cells* **2015**, *135*, 124–129.
- (22) Hirst, L. C.; Lumb, M. P.; Hoheisel, R.; Bailey, C. G.; Philipps, S. P.; Bett, A. W.; Walters, R. J. Spectral sensitivity of hot carrier solar cells. *Sol. Energy Mater. Sol. Cells* **2014**, *120*, 610–615.
- (23) Li, M.; Fu, J.; Xu, Q.; Sum, T. C. Slow Hot-Carrier Cooling in Halide Perovskites: Prospects for Hot-Carrier Solar Cells. *Adv. Mater.* **2019**, *31* (47), 1802486.
- (24) Würfel, P. Solar energy conversion with hot electrons from impact ionisation. *Sol. Energy Mater. Sol. Cells* **1997**, *46* (1), 43–52.
- (25) Takeda, Y.; Ito, T.; Motohiro, T.; König, D.; Shrestha, S.; Conibeer, G. Hot carrier solar cells operating under practical conditions. *J. Appl. Phys.* **2009**, *105* (7), 074905.
- (26) Kahmann, S.; Loi, M. A. Hot carrier solar cells and the potential of perovskites for breaking the Shockley–Queisser limit. *J. Mater. Chem. C* **2019**, *7* (9), 2471–2486.
- (27) Gibelli, F.; Lombez, L.; Guillemoles, J.-F. Hot-Carrier Solar Cells: Modeling Carrier Transport. In *Advanced Micro- and Nanomaterials for Photovoltaics*; Elsevier, **2019**; pp 53–92.
- (28) Takeda, Y.; Motohiro, T.; König, D.; Aliberti, P.; Feng, Y.; Shrestha, S.; Conibeer, G. Practical Factors Lowering Conversion Efficiency of Hot Carrier Solar Cells. *Appl. Phys. Express* **2010**, *3* (10), 104301.
- (29) Liu, W.; Xing, J.; Zhao, J.; Wen, X.; Wang, K.; Lu, P.; Xiong, Q. Giant Two-Photon Absorption and Its Saturation in 2D Organic-Inorganic Perovskite. *Adv. Optical Mater.* **2017**, *5* (7), 1601045.
- (30) Chen, J.; Zhang, W.; Pullerits, T. Two-photon absorption in halide perovskites and their applications. *Mater. Horiz.* **2022**, *9* (9), 2255–2287.
- (31) Chen, J.; Messing, M. E.; Zheng, K.; Pullerits, T. Cation-Dependent Hot Carrier Cooling in Halide Perovskite Nanocrystals. *J. Am. Chem. Soc.* **2019**, *141* (8), 3532–3540.
- (32) Zhu, H.; Miyata, K.; Fu, Y.; Wang, J.; Joshi, P. P.; Niesner, D.; Williams, K. W.; Jin, S.; Zhu, X.-Y. Screening in crystalline liquids protects energetic carriers in hybrid perovskites. *Science* **2016**, *353* (6306), 1409–1413.
- (33) Niesner, D.; Zhu, H.; Miyata, K.; Joshi, P. P.; Evans, T. J.; Kudisch, B. J.; Trinh, M. T.; Marks, M.; Zhu, X. Y. Persistent Energetic Electrons in Methylammonium Lead Iodide Perovskite Thin Films. *J. Am. Chem. Soc.* **2016**, *138* (48), 15717–15726.
- (34) Yoo, J. J.; Shin, S. S.; Seo, J. Toward Efficient Perovskite Solar Cells: Progress, Strategies, and Perspectives. *ACS Energy Lett.* **2022**, *7* (6), 2084–2091.
- (35) Guo, Z.; Wan, Y.; Yang, M.; Snider, J.; Zhu, K.; Huang, L. Long-range hot-carrier transport in hybrid perovskites visualized by ultrafast microscopy. *Science* **2017**, *356* (6333), 59–62.
- (36) Liao, Y.; Zhang, P.; Bremner, S.; Shrestha, S.; Huang, S.; Conibeer, G. Resonant Tunneling through Monolayer Si Colloidal Quantum Dots and Ge Nanocrystals. *Adv. Funct. Mater.* **2017**, *27* (21), 1605348.
- (37) Takeda, Y.; Ichiki, A.; Kusano, Y.; Sugimoto, N.; Motohiro, T. Resonant tunneling diodes as energy-selective contacts used in hot-carrier solar cells. *J. Appl. Phys.* **2015**, *118* (12), 124510.
- (38) Yang, Z.; Peng, W.; Su, S.; Lin, G.; Chen, J. Performance assessment and optimization of a hot carrier solar cell with double energy selective contacts. *Phys. Scr.* **2018**, *93* (9), 095002.
- (39) Rosenwaks, Y.; Hanna, M. C.; Levi, D. H.; Szymid, D. M.; Ahrenkiel, R. K.; Nozik, A. J. Hot-carrier cooling in GaAs: Quantum wells versus bulk. *Phys. Rev. B* **1993**, *48* (19), 14675–14678.
- (40) Pelouch, W. S.; Ellingson, R. J.; Powers, P. E.; Tang, C. L.; Szymid, D. M.; Nozik, A. J. Comparison of hot-carrier relaxation in quantum wells and bulk GaAs at high carrier densities. *Phys. Rev. B* **1992**, *45* (3), 1450–1453.
- (41) Conibeer, G. J.; Guillemoles, J. F.; Green, M. A. Phononic band gap engineering for hot carrier solar cell absorbers. In *Proc. 20th Eur. Photovolt. Sol. Energy Conf.*, Barcelona, Espagne, **2005**.
- (42) Guillemoles, J.-F.; Conibeer, G.; Green, M. Phononic engineering with nanostructures for hot carrier solar cells. In *Proc. 15th Eur. Photovolt. Sol. Energy Conf.*, Shanghai, China, **2005**.
- (43) Shah, J.; Leite, R. C. C. Radiative Recombination from Photoexcited Hot Carriers in GaAs. *Phys. Rev. Lett.* **1969**, *22* (24), 1304–1307.
- (44) Lim, J. W. M.; Giovanni, D.; Righetto, M.; Feng, M.; Mhaisalkar, S. G.; Mathews, N.; Sum, T. C. Hot Carriers in Halide Perovskites: How Hot Truly? *J. Phys. Chem. Lett.* **2020**, *11* (7), 2743–2750.
- (45) Richter, J. M.; Branchi, F.; Valduga de Almeida Camargo, F.; Zhao, B.; Friend, R. H.; Cerullo, G.; Deschler, F. Ultrafast carrier thermalization in lead iodide perovskite probed with two-dimensional electronic spectroscopy. *Nat. Commun.* **2017**, *8*, 376.
- (46) Lin, W.; Liang, M.; Niu, Y.; Chen, Z.; Cherasse, M.; Meng, J.; Zou, X.; Zhao, Q.; Geng, H.; Papalazarou, E.; Marsi, M.; Perfetti, L.; Canton, S. E.; Zheng, K.; Pullerits, T. Combining two-photon photoemission and transient absorption spectroscopy to resolve hot carrier cooling in 2D perovskite single crystals: the effect of surface layer. *J. Mater. Chem. C* **2022**, *10*, 16751–16760.

- (47) Fang, H.-H.; Adjokatse, S.; Shao, S.; Even, J.; Loi, M. A. Long-lived hot-carrier light emission and large blue shift in formamidinium tin triiodide perovskites. *Nat. Commun.* **2018**, *9*, 243.
- (48) Savill, K. J.; Klug, M. T.; Milot, R. L.; Snaith, H. J.; Herz, L. M. Charge-Carrier Cooling and Polarization Memory Loss in Formamidinium Tin Triiodide. *J. Phys. Chem. Lett.* **2019**, *10* (20), 6038–6047.
- (49) Yang, Y.; Ostrowski, D. P.; France, R. M.; Zhu, K.; van de Lagemaat, J.; Luther, J. M.; Beard, M. C. Observation of a hot-phonon bottleneck in lead-iodide perovskites. *Nat. Photonics* **2016**, *10*, 53–59.
- (50) Chen, B. A.; Pang, G. T.; Lan, X. Q.; He, Z. B.; Chen, R. Strong band filling induced significant excited state absorption in MAPbI₃ under high pump power. *Mater. Today Phys.* **2020**, *14*, 100228.
- (51) Yang, J.; Wen, X.; Xia, H.; Sheng, R.; Ma, Q.; Kim, J.; Tapping, P.; Harada, T.; Kee, T. W.; Huang, F.; Cheng, Y. B.; Green, M.; Ho-Baillie, A.; Huang, S.; Shrestha, S.; Patterson, R.; Conibeer, G. Acoustic-optical phonon up-conversion and hot-phonon bottleneck in lead-halide perovskites. *Nat. Commun.* **2017**, *8*, 14120.
- (52) Chan, C. C. S.; Fan, K.; Wang, H.; Huang, Z.; Novko, D.; Yan, K.; Xu, J.; Choy, W. C. H.; Lončarić, I.; Wong, K. S. Uncovering the Electron-Phonon Interplay and Dynamical Energy-Dissipation Mechanisms of Hot Carriers in Hybrid Lead Halide Perovskites. *Adv. Energy Mater.* **2021**, *11* (9), 2003071.
- (53) Price, M. B.; Butkus, J.; Jellicoe, T. C.; Sadhanala, A.; Briane, A.; Halpert, J. E.; Broch, K.; Hodgkiss, J. M.; Friend, R. H.; Deschler, F. Hot-carrier cooling and photoinduced refractive index changes in organic-inorganic lead halide perovskites. *Nat. Commun.* **2015**, *6*, 8420.
- (54) Wang, X.; Huo, D.; Wang, X.; Li, M.; Wang, Y.; Wan, Y. Hot Carrier Dynamics and Charge Trapping in Surface Passivated beta-CsPbI₃ Inorganic Perovskite. *J. Phys. Chem. Lett.* **2021**, *12* (29), 6907–6913.
- (55) Fu, J.; Xu, Q.; Han, G.; Wu, B.; Huan, C. H. A.; Leek, M. L.; Sum, T. C. Hot carrier cooling mechanisms in halide perovskites. *Nat. Commun.* **2017**, *8*, 1300.
- (56) Mix, L. T.; Ghosh, D.; Tisdale, J.; Lee, M. C.; O'Neal, K. R.; Sirica, N.; Neukirch, A. J.; Nie, W.; Taylor, A. J.; Prasankumar, R. P.; Tretiak, S.; Yarotski, D. A. Hot Carrier Cooling and Recombination Dynamics of Chlorine-Doped Hybrid Perovskite Single Crystals. *J. Phys. Chem. Lett.* **2020**, *11* (19), 8430–8436.
- (57) Wang, T.; Jin, L.; Hidalgo, J.; Chu, W.; Snaith, J. M.; Deng, S.; Zhu, T.; Lai, B.; Prezhdov, O.; Correa-Baena, J.-P.; Huang, L. Protecting hot carriers by tuning hybrid perovskite structures with alkali cations. *Sci. Adv.* **2020**, *6* (43), eabb1336.
- (58) Li, H.; Wang, Q.; Oteki, Y.; Ding, C.; Liu, D.; Guo, Y.; Li, Y.; Wei, Y.; Wang, D.; Yang, Y.; Masuda, T.; Chen, M.; Zhang, Z.; Sogabe, T.; Hayase, S.; Okada, Y.; Iikubo, S.; Shen, Q. Enhanced Hot-Phonon Bottleneck Effect on Slowing Hot Carrier Cooling in Metal Halide Perovskite Quantum Dots with Alloyed A-Site. *Adv. Mater.* **2023**, *35* (38), 2301834.
- (59) Papagiorgis, P.; Protesescu, L.; Kovalenko, M. V.; Othonos, A.; Itskos, G. Long-Lived Hot Carriers in Formamidinium Lead Iodide Nanocrystals. *J. Phys. Chem. C* **2017**, *121* (22), 12434–12440.
- (60) Meng, J.; Lan, Z.; Lin, W.; Liang, M.; Zou, X.; Zhao, Q.; Geng, H.; Castelli, I. E.; Canton, S. E.; Pullerits, T.; Zheng, K. Optimizing the quasi-equilibrium state of hot carriers in all-inorganic lead halide perovskite nanocrystals through Mn doping: fundamental dynamics and device perspectives. *Chem. Sci.* **2022**, *13* (6), 1734–1745.
- (61) Ghosh, G.; Biswas, R. K.; Marjit, K.; Ghosh, S.; Ghosh, A.; Pati, S. K.; Patra, A. Impacts of CsPbBr₃/PbSe Heterostructures on Carrier Cooling Dynamics at Low Carrier Density. *Adv. Opt. Mater.* **2022**, *10* (9), 2200030.
- (62) Li, M.; Bhaumik, S.; Goh, T. W.; Kumar, M. S.; Yantara, N.; Gratzel, M.; Mhaisalkar, S.; Mathews, N.; Sum, T. C. Slow cooling and highly efficient extraction of hot carriers in colloidal perovskite nanocrystals. *Nat. Commun.* **2017**, *8*, 14350.
- (63) Ghosh, G.; Marjit, K.; Ghosh, S.; Ghosh, D.; Patra, A. Evidence of Hot Charge Carrier Transfer in Hybrid CsPbBr₃/Functionalized Graphene. *ChemNanoMat* **2022**, *8* (8), No. e202200172.
- (64) Wei, Q.; Ren, H.; Liu, J.; Liu, Q.; Wang, C.; Lau, T. W.; Zhou, L.; Bian, T.; Zhou, Y.; Wang, P.; Lei, Q.; Mohammed, O. F.; Li, M.; Yin, J. Long-Lived Hot Carriers in Two-Dimensional Perovskites: The Role of Alternating Cations in Interlayer Space. *ACS Energy Lett.* **2023**, *8* (10), 4315–4322.
- (65) Yin, J.; Naphade, R.; Maity, P.; Gutiérrez-Arzaluz, L.; Almalawi, D.; Roqan, I. S.; Brédas, J.-L.; Bakr, O. M.; Mohammed, O. F. Manipulation of hot carrier cooling dynamics in two-dimensional Dion–Jacobson hybrid perovskites via Rashba band splitting. *Nat. Commun.* **2021**, *12* (1), 3995.
- (66) Jia, X.; Jiang, J.; Zhang, Y.; Qiu, J.; Wang, S.; Chen, Z.; Yuan, N.; Ding, J. Observation of enhanced hot phonon bottleneck effect in 2D perovskites. *Appl. Phys. Lett.* **2018**, *112* (14), 143903.
- (67) Esmailpour, H.; Whiteside, V. R.; Piyathilaka, H. P.; Vijayaragunathan, S.; Wang, B.; Adcock-Smith, E.; Roberts, K. P.; Mishima, T. D.; Santos, M. B.; Bristow, A. D.; Sellers, I. R. Enhanced hot electron lifetimes in quantum wells with inhibited phonon coupling. *Sci. Rep.* **2018**, *8*, 12473.
- (68) Klemens, P. G. Anharmonic Decay of Optical Phonons. *Phys. Rev.* **1966**, *148* (2), 845–848.
- (69) Alber, L.; Scalera, V.; Unikandanunni, V.; Schick, D.; Bonetti, S. NTMpy: An open source package for solving coupled parabolic differential equations in the framework of the three-temperature model. *Comput. Phys. Commun.* **2021**, *265*, 107990.
- (70) Poncé, S.; Schlipf, M.; Giustino, F. Origin of Low Carrier Mobilities in Halide Perovskites. *ACS Energy Lett.* **2019**, *4* (2), 456–463.
- (71) Puppini, M.; Polishchuk, S.; Colonna, N.; Crepaldi, A.; Dirin, D. N.; Nazarenko, O.; De Gennaro, R.; Gatti, G.; Roth, S.; Barillot, T.; Poletto, L.; Xian, R. P.; Rettig, L.; Wolf, M.; Ernstorfer, R.; Kovalenko, M. V.; Marzari, N.; Grioni, M.; Chergui, M. Evidence of Large Polarons in Photoemission Band Mapping of the Perovskite Semiconductor CsPbBr₃. *Phys. Rev. Lett.* **2020**, *124* (20), 206402.
- (72) Miyata, K.; Atallah, T. L.; Zhu, X.-Y. Lead halide perovskites: Crystal-liquid duality, phononglass electron crystals, and large polaron formation. *Sci. Adv.* **2017**, *3* (10), e1701469.
- (73) Zhu, X. Y.; Podzorov, V. Charge Carriers in Hybrid Organic-Inorganic Lead Halide Perovskites Might Be Protected as Large Polarons. *J. Phys. Chem. Lett.* **2015**, *6* (23), 4758–4761.
- (74) Milot, R. L.; Eperon, G. E.; Snaith, H. J.; Johnston, M. B.; Herz, L. M. Temperature-Dependent Charge-Carrier Dynamics in CH₃NH₃PbI₃ Perovskite Thin Films. *Adv. Funct. Mater.* **2015**, *25* (39), 6218–6227.
- (75) Zheng, F.; Wang, L.-W. Large polaron formation and its effect on electron transport in hybrid perovskites. *Energy Environ. Sci.* **2019**, *12* (4), 1219–1230.
- (76) Mahata, A.; Meggiolaro, D.; De Angelis, F. From Large to Small Polarons in Lead, Tin, and Mixed Lead–Tin Halide Perovskites. *J. Phys. Chem. Lett.* **2019**, *10* (8), 1790–1798.
- (77) Hintermayr, V. A.; Polavarapu, L.; Urban, A. S.; Feldmann, J. Accelerated Carrier Relaxation through Reduced Coulomb Screening in Two-Dimensional Halide Perovskite Nanoplatelets. *ACS Nano* **2018**, *12* (10), 10151–10158.
- (78) Miyata, K.; Meggiolaro, D.; Trinh, M. T.; Joshi, P. P.; Mosconi, E.; Jones, S. C.; De Angelis, F.; Zhu, X. Y. Large polarons in lead halide perovskites. *Sci. Adv.* **2017**, *3* (8), e1701217.
- (79) Wright, A. D.; Verdi, C.; Milot, R. L.; Eperon, G. E.; Perez-Osorio, M. A.; Snaith, H. J.; Giustino, F.; Johnston, M. B.; Herz, L. M. Electron-phonon coupling in hybrid lead halide perovskites. *Nat. Commun.* **2016**, *7*, 11755.
- (80) Sendner, M.; Nayak, P. K.; Egger, D. A.; Beck, S.; Müller, C.; Epping, B.; Kowalsky, W.; Kronik, L.; Snaith, H. J.; Pucci, A.; Lovrinčić, R. Optical phonons in methylammonium lead halide perovskites and implications for charge transport. *Mater. Horiz.* **2016**, *3* (6), 613–620.
- (81) Milot, R. L.; Klug, M. T.; Davies, C. L.; Wang, Z.; Kraus, H.; Snaith, H. J.; Johnston, M. B.; Herz, L. M. The Effects of Doping Density and Temperature on the Optoelectronic Properties of Formamidinium Tin Triiodide Thin Films. *Adv. Mater.* **2018**, *30* (44), 1804506.
- (82) Zheng, K.; Abdellah, M.; Zhu, Q.; Kong, Q.; Jennings, G.; Kurtz, C. A.; Messing, M. E.; Niu, Y.; Gosztola, D. J.; Al-Marri, M. J.; Zhang,

X.; Pullerits, T.; Canton, S. E. Direct Experimental Evidence for Photoinduced Strong-Coupling Polarons in Organolead Halide Perovskite Nanoparticles. *J. Phys. Chem. Lett.* **2016**, *7* (22), 4535–4539.

(83) Nuber, M.; Tan, Q. Y.; Sandner, D.; Yin, J.; Kienberger, R.; Soci, C.; Iglev, H. Accelerated polaron formation in perovskite quantum dots monitored via picosecond infrared spectroscopy. *J. Mater. Chem. C* **2023**, *11* (10), 3581–3587.

(84) Cannelli, O.; Colonna, N.; Puppini, M.; Rossi, T. C.; Kinschel, D.; Leroy, L. M. D.; Löffler, J.; Budarz, J. M.; March, A. M.; Doumy, G.; Al Haddad, A.; Tu, M.-F.; Kumagai, Y.; Walko, D.; Smolentsev, G.; Krieg, F.; Boehme, S. C.; Kovalenko, M. V.; Chergui, M.; Mancini, G. F. Quantifying Photoinduced Polaronic Distortions in Inorganic Lead Halide Perovskite Nanocrystals. *J. Am. Chem. Soc.* **2021**, *143* (24), 9048–9059.

(85) Pérez-Osorio, M. A.; Milot, R. L.; Filip, M. R.; Patel, J. B.; Herz, L. M.; Johnston, M. B.; Giustino, F. Vibrational Properties of the Organic–Inorganic Halide Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ from Theory and Experiment: Factor Group Analysis, First-Principles Calculations, and Low-Temperature Infrared Spectra. *J. Phys. Chem. C* **2015**, *119* (46), 25703–25718.

(86) Kawai, H.; Giorgi, G.; Marini, A.; Yamashita, K. The mechanism of slow hot-hole cooling in lead-iodide perovskite: first-principles calculation on carrier lifetime from electron-phonon interaction. *Nano Lett.* **2015**, *15* (5), 3103–3108.

(87) Achermann, M.; Bartko, A. P.; Hollingsworth, J. A.; Klimov, V. I. The effect of Auger heating on intraband carrier relaxation in semiconductor quantum rods. *Nat. Phys.* **2006**, *2*, 557–561.

(88) Rabouw, F. T.; De Mello Donega, C. Excited-State Dynamics in Colloidal Semiconductor Nanocrystals. *Top. Curr. Chem.* **2016**, *374* (5), 58.

(89) Klimov, V. I.; McBranch, D. W. Femtosecond IP-to-1S Electron Relaxation in Strongly Confined Semiconductor Nanocrystals. *Phys. Rev. Lett.* **1998**, *80* (18), 4028–4031.

(90) Yin, W.-J.; Yang, J.-H.; Kang, J.; Yan, Y.; Wei, S.-H. Halide perovskite materials for solar cells: a theoretical review. *J. Mater. Chem. A* **2015**, *3* (17), 8926–8942.

(91) Frost, J. M.; Whalley, L. D.; Walsh, A. Slow Cooling of Hot Polarons in Halide Perovskite Solar Cells. *ACS Energy Lett.* **2017**, *2* (12), 2647–2652.

(92) Liang, M.; Lin, W.; Lan, Z.; Meng, J.; Zhao, Q.; Zou, X.; Castelli, I. E.; Pullerits, T.; Canton, S. E.; Zheng, K. Electronic Structure and Trap States of Two-Dimensional Ruddlesden–Popper Perovskites with the Relaxed Goldschmidt Tolerance Factor. *ACS Appl. Electron. Mater.* **2020**, *2* (5), 1402–1412.

(93) Yu, S.; Yan, Y.; Chen, Y.; Chábera, P.; Zheng, K.; Liang, Z. Enabling room-temperature processed highly efficient and stable 2D Ruddlesden–Popper perovskite solar cells with eliminated hysteresis by synergistic exploitation of additives and solvents. *J. Mater. Chem. A* **2019**, *7* (5), 2015–2021.

(94) Mao, L.; Stoumpos, C. C.; Kanatzidis, M. G. Two-Dimensional Hybrid Halide Perovskites: Principles and Promises. *J. Am. Chem. Soc.* **2019**, *141* (3), 1171–1190.

(95) Metcalf, I.; Sidhik, S.; Zhang, H.; Agrawal, A.; Persaud, J.; Hou, J.; Even, J.; Mohite, A. D. Synergy of 3D and 2D Perovskites for Durable, Efficient Solar Cells and Beyond. *Chem. Rev.* **2023**, *123* (15), 9565–9652.

(96) Hu, S.; Huang, Y.; Zhang, Y.; Yan, P.; Li, H.; Sheng, C. Slow Hot-Carrier-Cooling in a 2D Lead-Iodide Perovskite Film and Its Photovoltaic Device. *J. Phys. Chem. C* **2022**, *126* (5), 2374–2382.

(97) Blancon, J. C.; Stier, A. V.; Tsai, H.; Nie, W.; Stoumpos, C. C.; Traore, B.; Pedesseau, L.; Kepenekian, M.; Katsutani, F.; Noe, G. T.; Kono, J.; Tretiak, S.; Crooker, S. A.; Katan, C.; Kanatzidis, M. G.; Crochet, J. J.; Even, J.; Mohite, A. D. Scaling law for excitons in 2D perovskite quantum wells. *Nat. Commun.* **2018**, *9*, 2254.

(98) Gao, Y.; Zhang, M.; Zhang, X.; Lu, G. Decreasing Exciton Binding Energy in Two-Dimensional Halide Perovskites by Lead Vacancies. *J. Phys. Chem. Lett.* **2019**, *10* (14), 3820–3827.

(99) Gelvez-Rueda, M. C.; Hutter, E. M.; Cao, D. H.; Renaud, N.; Stoumpos, C. C.; Hupp, J. T.; Savenije, T. J.; Kanatzidis, M. G.;

Grozema, F. C. Interconversion between Free Charges and Bound Excitons in 2D Hybrid Lead Halide Perovskites. *J. Phys. Chem. C* **2017**, *121* (47), 26566–26574.

(100) Blancon, J. C.; Tsai, H.; Nie, W.; Stoumpos, C. C.; Pedesseau, L.; Katan, C.; Kepenekian, M.; Soe, C. M.; Appavoo, K.; Sfeir, M. Y.; Tretiak, S.; Ajayan, P. M.; Kanatzidis, M. G.; Even, J.; Crochet, J. J.; Mohite, A. D. Extremely efficient internal exciton dissociation through edge states in layered 2D perovskites. *Science* **2017**, *355* (6331), 1288–1292.

(101) Sun, Q.; Zhao, C.; Yin, Z.; Wang, S.; Leng, J.; Tian, W.; Jin, S. Ultrafast and High-Yield Polaronic Exciton Dissociation in Two-Dimensional Perovskites. *J. Am. Chem. Soc.* **2021**, *143* (45), 19128–19136.