

Research Progress on Ultrafast Dynamics of Hot Carriers in Halide Perovskites: A Review

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Abstract. Halide perovskites are promising for solar cells, photodetectors, and other optoelectronic devices due to their optoelectronic properties. Hot-carrier relaxation critically governs energy conversion efficiency. While slow hot-carrier cooling was traditionally ascribed to hot and quantum phonon bottlenecks, recent ultrafast spectroscopy studies challenge this view. This review synthesizes new experimental insights into hot-carrier relaxation in perovskite nanocrystals and two-dimensional (2D) perovskites, focusing on three key aspects: (1) Auger processes that bypass the phonon bottleneck; (2) A-site cation-dependent cooling rates (e.g., CsPbBr₃, MAPbBr₃, and FAPbBr₃), reflecting varying carrier-phonon coupling; and (3) slower surface vs. faster bulk cooling in 2D perovskites. Notably, conventional transient absorption may overestimate hot-carrier cooling times; state-resolved and time-resolved photoluminescence reveal sub-picosecond cooling in weakly confined nanocrystals. This paper clarifies characterization methods, underlying mechanisms, and control strategies; highlights unresolved debates; and outlines future research directions.

Keywords: Halide perovskites, Phonon bottleneck, Auger process, Hot carriers, Cation engineering

1. Introduction

As a new generation of optoelectronic semiconductor materials, halide perovskites have become a research hotspot in photovoltaics, photodetection, and related fields. They exhibit high absorption coefficients, solution processability, long carrier diffusion lengths, and tunable band gaps. Photoexcitation with above-bandgap photons generates hot carriers, whose relaxation rate directly determines energy conversion efficiency. Unlike conventional semiconductors, where rapid phonon-mediated cooling causes large thermal losses, perovskites show slower hot-carrier cooling, enabling potential breakthrough of the Shockley–Queisser limit in single-junction solar cells and establishing this as a central research focus.

Early studies attributed slow hot-carrier cooling in perovskites to the hot phonon bottleneck: rapid emission of longitudinal optical (LO) phonons by hot carriers, coupled with inefficient LO-to-acoustic phonon relaxation, leads to LO phonon accumulation and suppressed energy dissipation. Quantum confinement in nanocrystals further restricts phonon propagation, enhancing this effect. However, high-precision ultrafast techniques, especially state-resolved pump–probe and time-

resolved photoluminescence, reveal that conventional transient absorption overestimates cooling times due to artifacts from bandgap renormalization, biexciton effects, and other overlapping signals. Thus, hot-carrier relaxation is more complex than the traditional bottleneck picture suggested.

Recent studies show that hot-carrier relaxation is governed by three key factors: efficient Auger processes, bypassing the phonon bottleneck in weakly confined nanocrystals; A-site cation selection, tuning carrier–phonon coupling and cooling rates; and quantum confinement plus surface effects in 2D perovskites, yielding distinct surface versus bulk relaxation dynamics. This review systematically summarizes the underlying mechanisms, regulation strategies, and characterization methods for hot carriers in perovskites, aiming to guide the design and scalable fabrication of high-performance hot-carrier optoelectronic devices.

2. Hot-carrier relaxation fundamentals and limitations of the traditional phonon-bottleneck picture

Hot-carrier relaxation in perovskites proceeds in three sequential stages: (1) ultrafast Coulomb scattering (< 100 femtoseconds (fs)), establishing quasi-thermal distributions; (2) LO phonon emission (100–400 fs), transferring energy to the lattice; and (3) slower lattice cooling (sub-ps to several ps), whose rate governs hot-carrier lifetime and extraction efficiency. Stage durations vary with material composition and excitation conditions.

Transient absorption (TA) spectroscopy—widely used for its simplicity and femtosecond resolution—traditionally estimated hot-carrier cooling times of 1–10 ps by fitting the high-energy bleach tail, attributing slow cooling to the phonon bottleneck. However, TA signals conflate multiple contributions: bandgap renormalization, biexciton dynamics, defect states, and other artifacts. This interferences overestimate cooling times and obscure true relaxation physics [1].

In contrast, state-resolved pump–probe (SRPP) and time-resolved photoluminescence (TRPL) isolate carrier dynamics with minimal spectral overlap. Under weak confinement, CsPbBr₃ and FAPbBr₃ nanocrystals exhibit actual hot-carrier cooling in ~ 400 fs, nearly an order of magnitude faster than TA-derived values [1]. This suggests that the apparent phonon bottleneck at low excitation is largely an artifact of TA methodology, fundamentally reshaping our understanding of hot-carrier relaxation and redirecting the field towards more accurate probing and mechanism-driven design.

3. Core mechanisms of hot carrier relaxation

3.1. Modulation of phonon bottlenecks by auger processes

In weakly confined perovskite nanocrystals, Auger process dominates hot-carrier cooling under certain conditions. As a non-radiative, carrier-carrier energy transfer process, it enables hot-carriers to rapidly relax to the band edge while exciting secondary carriers—bypassing carrier-phonon coupling entirely and thus breaking the phonon bottleneck [1]. First-principles simulations and experiments confirm sub-picosecond Auger-driven cooling, orders of magnitude faster than phonon-mediated relaxation. This challenges the phonon-bottleneck paradigm and opens new pathways for hot-carrier regulation.

3.2. Synergistic effects of hot phonon bottleneck and auger heating

The hot phonon bottleneck effect still exists under certain conditions, especially at high excitation densities (usually higher than 10^{18} cm^{-3}) [2]. At this time, a large number of hot carriers emit LO phonons rapidly, and the rate of phonon generation is much higher than the relaxation rate. The accumulation of non-equilibrium LO phonons forms a hot phonon bottleneck. At the same time, frequent Auger recombination occurs between high-concentration carriers, and the energy released by this recombination reheats the cooled carriers, further prolonging the slow cooling process. At low excitation densities (lower than 10^{17} cm^{-3} , close to the operating conditions of actual devices), the carrier concentration is low, and the generation and relaxation rates of LO phonons reach a balance, so the hot phonon bottleneck can be ignored. At this time, the cooling of hot carriers is jointly determined by carrier–phonon coupling and Auger processes, with the Auger process playing a dominant role. This indicates that the relaxation of hot carriers has an obvious dependence on excitation density [2].

3.3. Effects of polarons and lattice distortion

Perovskites have a flexible ionic lattice structure, and the movement of carriers is likely to cause local lattice distortion, forming large polarons. Polarons are quasiparticles formed by the interaction between carriers and the lattice polarization field. Their screening effect can weaken the strength of carrier–phonon coupling, slowing down the cooling rate of hot carriers, which is an important factor affecting hot carrier dynamics at low excitation densities [3]. Femtosecond electron diffraction (FED) has directly observed the ultrafast lattice distortion during exciton–polaron formation, clearly seeing the elongation of Pb–Br bonds and changes in lattice constants within 380–1200 fs, which directly confirms the formation characteristics of polarons [3]. Studies also found that the softer the lattice and the fewer the defects, the more significant the polaron effect, and the slower the cooling of hot carriers. This provides a new way to regulate the lifetime of hot carriers through lattice engineering.

In summary, the relaxation of hot carriers in perovskites is the result of the competition and synergy between Auger processes, hot phonon effects, and polaron screening. The dominant mechanism changes with the excitation density, dimensionality, and lattice environment of the material.

4. Regulation of hot carrier cooling by A-Site cations

A-site cations are one of the most direct and effective structural parameters for regulating the dynamics of hot carriers in perovskites. They regulate the strength of carrier–phonon coupling by changing the lattice dynamics and dielectric environment of the inorganic Pb–Br framework, thereby affecting the phonon scattering cooling channels mentioned in Chapter 3.

In the three typical nanocrystal systems of CsPbBr₃, MAPbBr₃, and FAPbBr₃, the cooling rate of hot carriers shows a clear rule: CsPbBr₃ is the slowest, MAPbBr₃ is in the middle, and FAPbBr₃ is the fastest [4]. Experiments have measured that their cooling times are about 390 fs, 270 fs, and 210 fs, respectively, with a difference of nearly double in rate. This rule is stable at low excitation densities and is not affected by factors such as excitation intensity and sample size, laying a foundation for the screening of hot carrier materials and the regulation of cation engineering.

The core reason for this cation dependence is the difference in the coupling strength between cations and the inorganic Pb–Br framework [4]. The inorganic Cs⁺ has a small ionic radius and weak

polarity, so its interaction with the Pb–Br framework is weak, resulting in low carrier–phonon coupling strength. Hot carriers release energy through phonon scattering at a low efficiency, leading to slow cooling. The organic MA⁺ (methyammonium ion) and FA⁺ (formamidinium ion) have strong polarity and large molecular sizes, forming stronger hydrogen bonds and van der Waals interactions with the Pb–Br framework, which enhances carrier–phonon coupling and accelerates cooling. Among them, FA⁺ has a larger molecular size, stronger interaction with the Pb–Br framework, a softer lattice, and the strongest carrier–phonon coupling, so it has the fastest cooling rate. This structure-activity relationship provides theoretical support for regulating the cooling rate of hot carriers through cation doping [4].

5. Dimensionality and surface effects: unique properties of 2D perovskites

Two-dimensional layered perovskites have a unique Ruddlesden-Popper phase quantum well structure, with weak van der Waals interactions between layers and restricted phonon propagation. Their hot carrier dynamics are significantly different from those of three-dimensional systems [5]. Combined studies of TA and two-photon photoemission spectroscopy (2PPE) show that the cooling of hot carriers in 2D perovskites has two stages: the fast cooling within 100–200 fs is dominated by the scattering between hot carriers and LO phonons, with rapid energy release; the slow cooling within 3–4 ps is dominated by the relaxation of LO phonons to acoustic phonons. The quantum confinement effect slows down the relaxation of LO phonons, leading to the accumulation of non-equilibrium LO phonons and the formation of an obvious hot phonon bottleneck [5]. Compared with three-dimensional perovskites, the slow cooling stage of two-dimensional systems is more significant, and the effective lifetime of hot carriers is longer, which has unique advantages in device applications.

Two-dimensional perovskites have obvious differences in hot carrier dynamics between the surface and bulk, a feature that three-dimensional perovskites do not have [5]. 2PPE can only detect the surface area of about 3 nm, while TA can detect the entire bulk. Comparative results show that surface hot carriers cool significantly slower than bulk carriers. This is because surface lattice strain relaxes more easily, weakening surface carrier–phonon coupling relative to the strained bulk, slowing surface cooling [5]. Since real devices extract hot carriers primarily at surfaces and interfaces, this slower surface cooling directly limits extraction efficiency. The finding thus guides device optimization via surface modification and interface engineering.

6. Ultrafast characterization techniques for hot carrier dynamics

The study of hot carrier dynamics in perovskites mainly relies on various ultrafast spectroscopy techniques, which have different detection principles and advantages and are suitable for different research scenarios [6, 7]. TA spectroscopy is simple to operate, widely used, and has a time resolution of femtoseconds, which can quickly obtain the temporal evolution information of hot carriers. However, it cannot distinguish between hot carriers and cold carriers and is easily interfered with various factors, leading to misjudgment. SRPP technology can eliminate interference by differentially measuring carriers in different energy states, and the measurement results are more reliable, making it one of the core technologies for accurate characterization of hot carrier cooling [1]. Time-resolved photoluminescence (TRPL) technology directly observes the luminescence behavior of hot carriers, with no ambiguity in signals, and is regarded as the "gold standard" for judging the phonon bottleneck effect [1].

Terahertz spectroscopy (THz) and 2PPE are key tools for probing hot-carrier dynamics. THz spectroscopy tracks ultrafast changes in carrier mobility, a direct indicator of carrier–phonon coupling strength, and thus indirectly reveals hot carrier-lattice interactions [7]. 2PPE offers exceptional surface sensitivity, enabling clear separation of surface and bulk hot carrier dynamics, making it essential for studying surface effects in 2D perovskites [5]. Emerging ultrafast technologies, including time-resolved photoemission spectroscopy and two-dimensional electronic spectroscopy (2DES), now complement these methods. They directly resolve transient processes like polaron formation and phonon-mode evolution, yielding richer experimental insight into relaxation mechanism [8].

At the device level, in-situ ultrafast characterization—such as bias- or illumination-dependent TA or TRPL—captures carrier relaxation and transport under realistic operating conditions (e.g., electric fields and interfacial effects), offering more relevant guidance for device optimization [9]. No single technique fully resolves hot carrier relaxation. Combining multiple methods cross-validate results, mitigates measurement artifacts, and delivers more accurate, comprehensive dynamics [6, 8, 9].

7. Current challenges in research

Despite significant progress in studying hot carrier dynamics in perovskites, three key challenges remain. First, no consensus exists on the dominant relaxation mechanism. Auger processes, polaron formation, and hot phonon bottlenecks each prevail under different excitation conditions or material systems, yet no universal theoretical model unifies these observations, and experimental reports often conflict [1-3].

Second, measured hot carrier cooling times vary widely across techniques, sometimes by over an order of magnitude, due to differences in detection principles and susceptibility to artifacts. Standardized measurement protocols and data analysis methods are still lacking [1, 5].

Third, most fundamental studies use high-quality nanocrystals and single-crystal thin films: low-defect, idealized systems that poorly represent real devices. Actual devices contain abundant defects and interface states and operate in complex environments, all of which strongly influence hot carrier relaxation, yet systematic investigation under such conditions remains limited [5, 6].

Finally, the intrinsic relaxation behavior of hot carriers under low excitation density of standard solar illumination is not clear. Actual devices work under this condition, and the relaxation mechanism at this time is significantly different from that at high excitation density. The lack of related research restricts the transformation of basic research to practical applications [2, 4]. In addition, the competitive process between hot carrier migration and relaxation within sub-picoseconds still needs more precise experiments and theoretical explanations [10].

8. Conclusion

Based on existing research, it can be seen that the relaxation of hot carriers in halide perovskites is the result of the combined action of Auger processes, hot phonon bottlenecks, polaron effects, and material structures and has obvious dependence on the system and excitation conditions. Conventional transient absorption spectroscopy tends to overestimate the cooling time. High-precision spectroscopy has confirmed that efficient Auger processes in weakly confined nanocrystals can break the phonon bottleneck and achieve sub-picosecond cooling; A-site cations follow the regulation rule of $\text{Cs} < \text{MA} < \text{FA}$, which is directly related to the coupling strength with the inorganic framework; 2D perovskites have obvious surface-bulk differences, with slower surface

cooling. These findings refine the physical understanding of hot carrier relaxation and provide a foundation for optoelectronic device design.

Future work should prioritize four directions: (1) study intrinsic relaxation under low-excitation, device-relevant conditions to clarify how multiple mechanisms synergize; (2) use surface and interface engineering to modulate strain and defects, enhancing hot carrier extraction efficiency; (3) develop a unified theoretical model integrating multiple physical mechanisms to enable predictive capability; (4) Advance low-cost, high-sensitivity, standardized ultrafast characterization techniques. As mechanistic insight deepens regulation strategies improve, perovskite hot-carrier devices will achieve breakthroughs in high-efficiency photovoltaics and ultrafast photodetection, accelerating the development of new-generation optoelectronics.

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