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# Slow cooling and efficient extraction of hot carriers in perovskite films *via* engineering trap-mediated relaxation channels

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Long-lived hot carriers (HCs) are highly desired for HC photovoltaics, but achieving slow HC relaxation is challenging because strong electron-phonon interaction typically drives rapid thermalization. Herein, we investigate the influence of excess  $\text{PbI}_2$  on HC relaxation in formamidinium lead iodide (FAPbI<sub>3</sub>) perovskite films using femtosecond transient absorption spectroscopy. Our results show that excess  $\text{PbI}_2$  significantly slows down the HC relaxation at high excitation densities, extending their lifetime to hundreds of picoseconds. This effect arises from intraband trap states (ITSs) introduced by excess  $\text{PbI}_2$ , enabling an ITS-mediated channel that suppresses direct HC relaxation under high densities due to a hot phonon bottleneck. Owing to the remarkably suppressed HC relaxation, efficient HC extraction was successfully achieved in  $\text{PbI}_2$ -rich perovskite films by incorporating electron acceptors. Our findings suggest an effective approach to prolong the HC lifetime in perovskite films *via* engineering ITSs, offering valuable guidance for the rational design of high-efficiency HC photovoltaic devices.

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## Introduction

Due to the presence of the Shockley–Queisser (S–Q) limit, the power conversion efficiency (PCE) of single-junction solar cells is fundamentally constrained.<sup>1–3</sup> This limitation primarily results from the rapid dissipation of excess energy in the form of heat during carrier thermalization. To overcome this limit, the concept of hot-carrier solar cells has been proposed, aiming to extract hot carriers (HCs) before thermalization and achieve efficiencies beyond the S–Q limit.<sup>4,5</sup> Recently, lead halide perovskites have emerged as a promising candidate for solar energy conversion owing to their strong and broad absorption, large diffusion coefficient, long carrier lifetimes, and tunable bandgaps.<sup>6–11</sup> In particular, under high excitation densities, this class of materials exhibit a significant hot phonon bottleneck (HPB) effect due to their large electron-phonon interaction, which greatly slows down the HC relaxation process and thereby extends their lifetime to tens of ps.<sup>12–15</sup> This feature enables perovskite materials to show great potential for efficient HC extraction, offering a new opportunity to break the S–Q limit for high-efficiency photovoltaic applications.

Recently, it has been discovered that incorporating polarizations into perovskite films can introduce new intraband

intermediate states, thereby significantly slowing down the HC relaxation process *via* altering their relaxation pathway, which provides another effective way to extend the lifetime of HCs.<sup>16</sup> As is well known, for perovskite solar cells with relatively high efficiency ( $\geq 20\%$ ), excess  $\text{PbI}_2$  is often found to aggregate at the grain boundaries and interfaces of perovskite films, indicating that residual  $\text{PbI}_2$  might play an important role in affecting their carrier dynamics and device performance.<sup>17–19</sup> A lot of experimental studies have confirmed that an appropriate excess of  $\text{PbI}_2$  can passivate grain-boundary defects, improve crystallinity, and enhance device performance;<sup>20,21</sup> however, excessive  $\text{PbI}_2$  may also lead to the increase of nonradiative recombination centres and the reduction of photovoltaic efficiency.<sup>22–24</sup> Meanwhile, some theoretical studies have also shown that excess  $\text{PbI}_2$  may easily lead to the formation of some defects, such as iodine vacancies and interstitial iodine, due to their low formation energies.<sup>25,26</sup> These defect levels are even found to be likely higher than the conduction band minimum (CBM) or valence band maximum (VBM),<sup>27</sup> suggesting that excess  $\text{PbI}_2$  might affect the lifetime of HCs by modifying their relaxation pathway. Although the impact of excess  $\text{PbI}_2$  on defect formation and band-edge carrier kinetics in perovskite films, as well as their device performances, has been widely reported,<sup>28–30</sup> it is still unclear how it influences the HC relaxation dynamics.

Formamidinium perovskite (FAPbI<sub>3</sub>) has garnered broad attention due to its narrower bandgap and better stability.<sup>31–34</sup> Herein, we take FAPbI<sub>3</sub> films as an example to investigate the influence of excess  $\text{PbI}_2$  on their HC relaxation by using femtosecond transient absorption (TA) spectroscopy. The

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results show that under high excitation intensities, the relaxation process of HCs in FAPbI<sub>3</sub> films with excess PbI<sub>2</sub> can be greatly slowed down, leading to their lifetime of up to hundreds of ps. It is because excess PbI<sub>2</sub> can introduce new intraband trap states (ITSSs), thereby enabling an ITS-mediated HC relaxation pathway at high excitation densities, which, however, is absent at low excitation densities. This discrepancy is mainly a result of the competition between the direct and ITS-mediated relaxation channels of HCs under different densities. By incorporating appropriate acceptors, we successfully achieved the efficient extraction of HCs in FAPbI<sub>3</sub> films containing excess PbI<sub>2</sub> due to the prolonged HC lifetime. Our findings demonstrate a practical way to suppress HC relaxation in perovskite films *via* precise control of PbI<sub>2</sub> content, which might be of great significance for improving the performance of HC photovoltaic devices.

## Results and discussion

In this work, in order to study the effect of excess PbI<sub>2</sub> on carrier dynamics in perovskite films, we prepared five batches of FAPbI<sub>3</sub> films with different PbI<sub>2</sub> contents using a previously reported two-step method,<sup>35</sup> in which the PbI<sub>2</sub> content was controlled by adjusting the PbI<sub>2</sub> concentration in their precursors (more details about material preparation can be found in the SI). For convenience, these as-prepared perovskite films are denoted as FAPbI<sub>3</sub>-*x*, where *x* represents the PbI<sub>2</sub> concentration in their precursors (*i.e.*, FAPbI<sub>3</sub>-1 M, FAPbI<sub>3</sub>-1.25 M, FAPbI<sub>3</sub>-1.5 M, FAPbI<sub>3</sub>-1.75 M and FAPbI<sub>3</sub>-2 M). The representative SEM images of these samples are presented in Fig. S1, showing pronounced segregation along grain boundaries. As shown in Fig. 1a and S2, the UV-vis absorption spectra of these samples exhibit the same characteristic peaks at ~785 nm, while the peak positions of their photoluminescence (PL) spectra are located at ~803 nm, both consistent with previous reports.<sup>36</sup> The crystal structure and crystallinity of these films were further examined by X-ray diffraction (XRD). As shown in Fig. 1b, all as-

prepared FAPbI<sub>3</sub> films display diffraction peaks at 14° and 28.1°, corresponding to the (100) and (200) planes of  $\alpha$ -phase FAPbI<sub>3</sub>, respectively.<sup>37,38</sup> With the increase of PbI<sub>2</sub> content, another diffraction peak at 12.5° (corresponding to the (001) plane of PbI<sub>2</sub>) begins to appear from PbI<sub>2</sub> concentration >1.5 M, and its intensity gradually increases.<sup>39</sup> These observations strongly confirm the coexistence of perovskite and PbI<sub>2</sub> phases in these films and also demonstrate that PbI<sub>2</sub> contents in the films can be effectively tuned by controlling the PbI<sub>2</sub> concentration in the precursors.

We first investigated the carrier dynamics in these samples under low excitation intensities by using femtosecond TA spectroscopy (see the SI for more details). Fig. 1c presents the representative two-dimensional (2D) pseudo-color TA maps of FAPbI<sub>3</sub>-1.5 M sample under 400 nm excitation with a low fluence of 0.1  $\mu\text{J cm}^{-2}$ , and its corresponding TA spectra at different delays are shown in Fig. S3. The TA spectra exhibit a pronounced exciton bleaching (XB) peak centered at 793 nm,<sup>40</sup> consistent with its steady-state absorption spectrum (Fig. 1a). The XB signal originates from the state filling of band-edge carriers, and thus its kinetics exactly represents the time evolution of band-edge carriers after photoexcitation.<sup>41</sup> Fig. S4 plots the 2D pseudo-color TA images of other samples with different PbI<sub>2</sub> contents, and their corresponding XB kinetics are also compared in Fig. 1d, showing similar spectral features and kinetic behavior. These similar spectra, as well as their similar XRD patterns, between various samples indicate that excess PbI<sub>2</sub> hardly alters the bandgap and crystal structure of perovskite films. We note that the XB kinetics in all samples exhibit ultrafast rise (<1 ps) (see the inset of Fig. 1d), indicating that their HCs undergo rapid relaxation to the band edge under low excitation intensities.

To study the effect of excess PbI<sub>2</sub> on HC relaxation, we next performed TA measurements on two typical FAPbI<sub>3</sub> films with different PbI<sub>2</sub> contents under 400 nm excitation with a high fluence of 33  $\mu\text{J cm}^{-2}$ . Fig. 2a shows the 2D pseudo-color TA spectra of FAPbI<sub>3</sub>-1 M with the lowest PbI<sub>2</sub> content. Except for a similar XB peak, the TA spectra under high excitation fluence exhibit a distinct feature compared to the low-fluence case. The TA spectrum at early delays exhibits a broad bleach signal extending into the high-energy region (to ~630 nm) due to the rapid evolution of initial nonequilibrium carriers into a Fermi-Dirac distribution.<sup>42,43</sup> As the delay time increases, this high-energy tail gradually narrows, which evolves over ~100 ps towards a symmetric XB peak centered at 783 nm (Fig. 2a), clearly reflecting the slowing down of the HC relaxation process. The significantly slowed down HC relaxation under high excitation intensity has already been widely observed in many perovskite films,<sup>13,15</sup> which is attributable to the remarkable HPB effect at high carrier densities. Fig. 2b presents the 2D pseudo-color TA image of FAPbI<sub>3</sub>-1.5 M. Similarly, the TA spectra at early delays also show an obviously broadened bleach signal, indicating the presence of HPB in the sample. However, compared to FAPbI<sub>3</sub>-1 M, FAPbI<sub>3</sub>-1.5 M shows obviously narrower high-energy tails at initial delays (Fig. 2b and S5), suggesting the reduced HPB effect observed in the sample with excess PbI<sub>2</sub>.

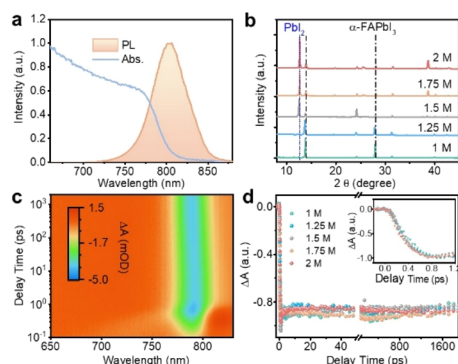


Fig. 1 Optical properties of FAPbI<sub>3</sub> films with different PbI<sub>2</sub> contents. (a) UV-vis absorption and PL spectra of FAPbI<sub>3</sub>-1.5 M. (b) XRD patterns of FAPbI<sub>3</sub> films with different PbI<sub>2</sub> contents. (c) 2D pseudo-color image of TA spectra of FAPbI<sub>3</sub>-1.5 M under 400 nm excitation at a low fluence of 0.1  $\mu\text{J cm}^{-2}$ . (d) Comparison of XB kinetics of five kinds of FAPbI<sub>3</sub> films under 400 nm excitation at a fluence of 0.1  $\mu\text{J cm}^{-2}$ .



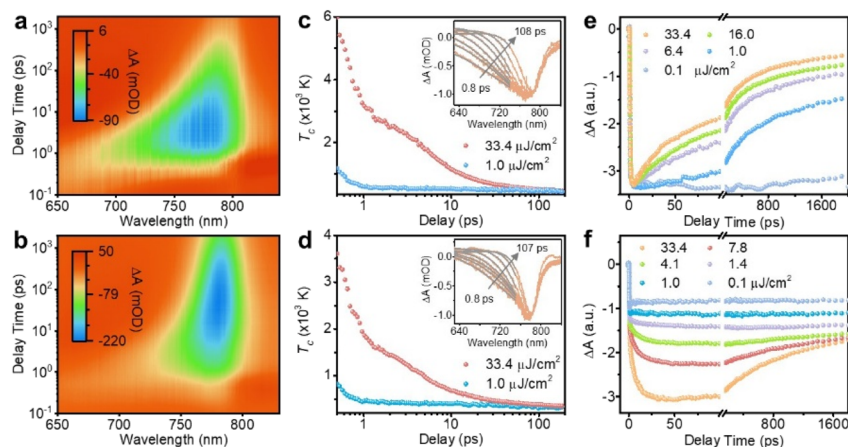


Fig. 2 Carrier dynamics of FAPbI<sub>3</sub>-1 M and FAPbI<sub>3</sub>-1.5 M. 2D pseudo-color images of TA spectra under 400 nm excitation at 33.4 μJ cm<sup>-2</sup> for (a) FAPbI<sub>3</sub>-1 M and (b) FAPbI<sub>3</sub>-1.5 M. Temporal evolution of the carrier temperature  $T_c$  of (c) FAPbI<sub>3</sub>-1 M and (d) FAPbI<sub>3</sub>-1.5 M under 400 nm excitation at indicated excitation fluences. The insets show their fitted high energy tails at a higher fluence using the Maxwell–Boltzmann distribution function. Comparison of XB kinetics normalized at 1 ps delay of (e) FAPbI<sub>3</sub>-1 M and (f) FAPbI<sub>3</sub>-1.5 M under indicated excitation intensities.

In order to further compare the HPB effect, we extracted the carrier temperature ( $T_c$ ) in the two samples by fitting the high-energy tail of TA spectra using a modified Maxwell–Boltzmann distribution (see the SI for a detailed description).<sup>38</sup> To ensure that HCs have reached a quasi-equilibrium temperature, the HC cooling kinetics was analyzed starting from 0.5 ps delay. Fig. 2c and d, respectively, compare the cooling curves of HCs in FAPbI<sub>3</sub>-1 M and FAPbI<sub>3</sub>-1.5 M under 400 nm excitation at two different excitation fluences. The insets show their TA spectral fitting at a high fluence, while those at a low fluence are shown in Fig. S6. At low excitation densities, HCs undergo rapid relaxation and  $T_c$  drops to room temperature within 1 ps, consistent with the ultrafast rise kinetics of the XB signal (see the insert in Fig. 1d), while under high excitation densities, the HCs exhibit a slower cooling rate, which even slows down to tens of ps, especially at later delays. Such slow HC cooling at high densities strongly confirms the presence of the HPB effect, which mainly originates from their large electron-phonon interaction, leading to the more rapid build-up of hot LO-phonon population and slower conversion rate from LO-phonons to acoustic phonons.<sup>13,44</sup> Compared with FAPbI<sub>3</sub>-1 M, the initial  $T_c$  value of FAPbI<sub>3</sub>-1.5 M is substantially lower, again confirming that the HPB effect is indeed reduced in the FAPbI<sub>3</sub>-1.5 M film with a higher PbI<sub>2</sub> content, consistent with the observed narrower high-energy tail in the sample (Fig. 2b).

Compared with FAPbI<sub>3</sub>-1 M, in addition to the reduced HPB effect, another more significant difference can be clearly observed in FAPbI<sub>3</sub>-1.5 M, where its XB signal still shows a remarkable growth trend within a hundred ps at high excitation densities. To elucidate this strange behavior, we further examined the excitation-fluence dependence of XB kinetics in the two samples (Fig. 2e and f). Their pseudo-color TA maps under other excitation fluences are provided in Fig. S7 and S8. For the FAPbI<sub>3</sub>-1 M film, although HC relaxation is remarkably slowed down at high excitation densities due to the HPB effect,

its XB signal still reaches its maximum within a few ps due to the presence of stronger higher-order recombination, leading to its faster decay rate at higher densities. In stark contrast, for FAPbI<sub>3</sub>-1.5 M, despite the weakened HPB effect, its XB signal rises very slowly and does not reach its maximum until ~100 ps under high excitation densities (Fig. 2f), suggesting a slow HC relaxation process. A similar slow-rising XB kinetic behavior has recently been observed in mixed-cation FAPbI<sub>3</sub> films and was attributed to the HC relaxation mediated by a polar cation induced intraband intermediate state.<sup>16</sup> However, unlike the above report, in which the slow-rising behavior also appeared at low excitation densities, our observation occurs specifically in FAPbI<sub>3</sub>-1.5 M under high excitation fluences and is absent in FAPbI<sub>3</sub>-1 M or at low fluences. This distinct dependence on the composition and excitation intensity suggests that the underlying HC relaxation mechanism in our system may differ subtly from the one previously reported.

Recent reports confirm that excess PbI<sub>2</sub> might create defect states higher than that of the CBM or VBM.<sup>26,27</sup> In order to confirm this, we conducted first-principles density functional theory (DFT) calculations to explore the electronic states of iodine vacancies ( $V_I$ ) and interstitial iodine ( $I_I$ ) in FAPbI<sub>3</sub> perovskite films. The results indicate that iodine-related defects introduce some localized electronic states above the CBM (Fig. S9), confirming the existence of intraband trap states (ITSS) induced by excess PbI<sub>2</sub>. To explain the slow rising behavior of the XB signal in FAPbI<sub>3</sub>-1.5 M, we presented a three-level kinetic model, in which the ITS above the lowest excited state ( $ES_1$ ) is introduced to mediate HC relaxation (Fig. 3a). In FAPbI<sub>3</sub>-1 M without ITSS, the photogenerated HCs relax directly to the  $ES_1$  only *via* electron-phonon scattering, and thus no slow-rising XB kinetics is observed even at high densities. In contrast, in FAPbI<sub>3</sub>-1.5 M with many ITSS, the photogenerated HCs may relax to the  $ES_1$  through two different channels: (1) directly relaxing to the  $ES_1$  *via* electron-phonon scattering at a rate of  $k_1$ ; (2) first relaxing to the



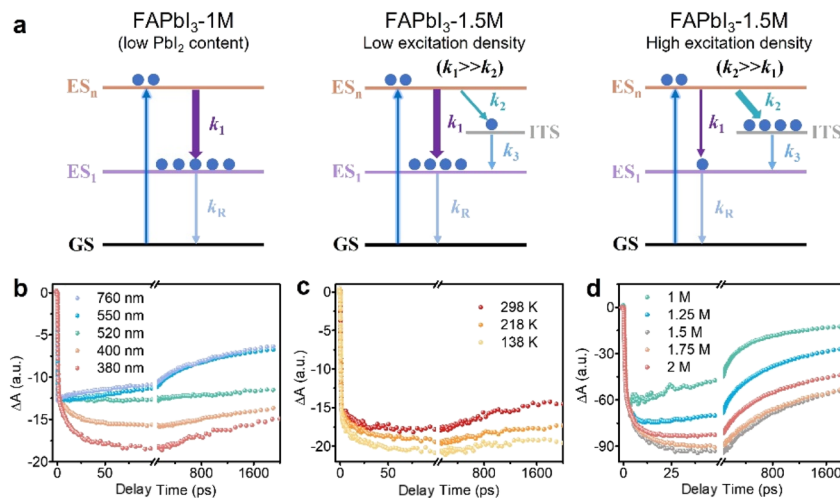


Fig. 3 Competition between direct and ITS-mediated HC relaxation pathways in FAPbI<sub>3</sub> films. (a) Schematic illustration of the HC relaxation process. ES, excited state; ITS, intraband trap state; GS, ground state. (b) XB kinetics of FAPbI<sub>3</sub>-1.5 M under various excitation wavelengths with an initial carrier density of  $\sim 3.3 \times 10^{18} \text{ cm}^{-3}$ . (c) XB kinetics of FAPbI<sub>3</sub>-1.5 M under 400 nm excitation at a high fluence of  $33.4 \mu\text{J cm}^{-2}$  at different temperatures. (d) XB kinetics of various FAPbI<sub>3</sub> films with different PbI<sub>2</sub> contents under 400 nm excitation at a fluence of  $33.4 \mu\text{J cm}^{-2}$ .

ITS at a rate of  $k_2$  and then transferring from the ITS to the ES<sub>1</sub> at a relatively slow rate of  $k_3$ . At low excitation fluences,  $k_1 \gg k_2$ , resulting in an inefficient ITS-mediated channel, and thus most carriers in FAPbI<sub>3</sub>-1.5 M can directly relax rapidly to the ES<sub>1</sub>, leading to the absence of a slow rising component, similar to the case of FAPbI<sub>3</sub>-1 M. However, at high densities, the presence of a HPB can remarkably slow down the direct relaxation rate, resulting in  $k_2 \gg k_1$ , which leads to most carriers first relaxing to the ITS and then transferring to the ES<sub>1</sub>. Therefore, the slow-rising XB kinetics observed at high densities actually reflects the carrier transfer process from the ITS to the ES<sub>1</sub>.

To verify the above mechanism, we next performed an excitation-wavelength-dependent TA measurement under relatively high excitation fluences (Fig. 3b). Note that, for comparability, the excitation fluence at different wavelengths was adjusted to ensure the same initial carrier density ( $\sim 3.3 \times 10^{18} \text{ cm}^{-3}$ ) generated in the sample. As expected, the slow-rising XB kinetics is only observed under short-wavelength excitation, while it disappears when the excitation wavelength exceeds 520 nm. This indicates that photogenerated carriers require sufficient energy to populate into the ITS, confirming that the ITS level is higher than the ES<sub>1</sub>. According to the excitation wavelength threshold, the ITS is estimated to be about 0.80 eV higher than the ES<sub>1</sub>. To further understand the two relaxation channels, we conducted a temperature-dependent TA measurement under high excitation fluences (Fig. 3c). As the temperature decreases, both the rise time and amplitude of the slow component increase, suggesting a larger initial carrier population into the ITS. Since the HPB effect becomes more severe at lower temperatures due to less efficient phonon scattering,<sup>14</sup> the direct cooling channel will inevitably slow down, thereby enhancing the contribution from the ITS-mediated channel. These temperature-dependent results indicate that the slow-rising XB kinetics does stem from the ITS-mediated relaxation and can also be engineered by controlling the competition between the above two relaxation channels.

To further understand the role of excess PbI<sub>2</sub>, we examined the HC relaxation kinetics in more FAPbI<sub>3</sub> films with different PbI<sub>2</sub> contents under high excitation densities (Fig. S10). The comparison of their XB kinetics is shown in Fig. 3d. For FAPbI<sub>3</sub>-1 M with the lowest PbI<sub>2</sub> content, its XB kinetics does not show the slow-rising component after 1 ps, suggesting the negligible formation of ITs likely due to insufficient PbI<sub>2</sub>. With the increase of PbI<sub>2</sub> concentration from 1.25 M to 1.5 M, the amplitude of the slow-rising XB kinetics in these samples does remarkably increase, strongly confirming the formation of more ITs. This results in more carriers populating into ITs and thus less contribution from the direct relaxation channel, leading to a weaker HPB effect observed in the samples with higher PbI<sub>2</sub> contents (Fig. 2a, b and S10). We also note that, when the PbI<sub>2</sub> concentration exceeds 1.5 M, the amplitude of the slow-rising component shows a slight decrease, which might be related to the weakening of the HPB effect caused by material properties. Compared with FAPbI<sub>3</sub>-1.5 M, the films containing more PbI<sub>2</sub> exhibit a smaller heat capacity (Fig. S11), which suggests faster heat conduction and a weaker HPB effect, leading to faster direct relaxation and less population into ITs.

Slow cooling of HCs is highly desired for their effective extraction, but hard to realize because of the presence of strong electron-phonon interaction. Introducing an ITS *via* incorporating excess PbI<sub>2</sub> or other means might be an effective method to slow down the HC cooling and promote their extraction. To verify this idea, we fabricated three batches of FAPbI<sub>3</sub>-1.5 M films *via* incorporating different electron acceptors, selected based on their band alignment with FAPbI<sub>3</sub> films (see the SI for detailed fabrication procedures).<sup>45</sup> Here, two kinds of SnO<sub>2</sub> were prepared *via* different methods (*i.e.*, commercial and ALD-deposited), resulting in slightly different bandgaps and are labeled as SnO<sub>2</sub>(com.) and SnO<sub>2</sub>(ALD), respectively. Fig. 4a–c show the band alignments of FAPbI<sub>3</sub> film and various acceptors, determined by ultraviolet photoelectron spectroscopy (Fig. S12 and S13). In principle, for ZnSe and SnO<sub>2</sub>(com.), due to their



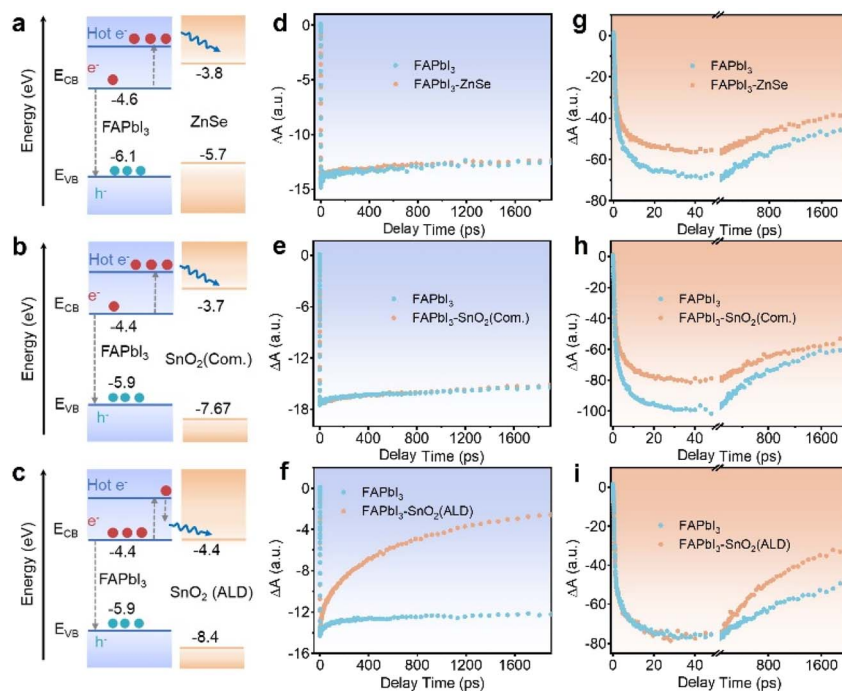


Fig. 4 Band alignment and HC extraction dynamics in FAPbI<sub>3</sub> films. (a–c) Energy level alignment of FAPbI<sub>3</sub>-1.5 M interfaced with different electron acceptors: (a) ZnSe, (b) SnO<sub>2</sub>(com.), and (c) SnO<sub>2</sub>(ALD). (d–f) Comparison of XB kinetics in three sets of samples with and without (d) ZnSe, (e) SnO<sub>2</sub>(com.) and (f) SnO<sub>2</sub>(ALD) acceptors under near-bandgap excitation (760 nm, 2.7 μJ cm<sup>-2</sup>). (g–i) Comparison of XB kinetics in three sets of samples with and without (g) ZnSe, (h) SnO<sub>2</sub>(com.), and (i) SnO<sub>2</sub>(ALD) acceptors under high-energy excitation (400 nm, 33.4 μJ cm<sup>-2</sup>).

higher CBM levels than FAPbI<sub>3</sub>, it is not possible to extract band-edge electrons, but it is possible to extract hot electrons, which is exactly opposite to SnO<sub>2</sub>(ALD). Their abilities to extract band-edge carriers can also be directly reflected in the XB kinetic differences between the samples with and without acceptors under near-bandgap excitation at 760 nm (Fig. 4d–f). As expected, the dramatically faster recovery kinetics was observed in FAPbI<sub>3</sub>-SnO<sub>2</sub>(ALD) than in FAPbI<sub>3</sub>, while for ZnSe and SnO<sub>2</sub>(com.), no difference in their XB kinetics was observed between the samples with and without acceptors. On this basis, we further compared the XB kinetics in the samples with and without acceptors under 400 nm excitation at a high fluence of 33.4 μJ cm<sup>-2</sup> (Fig. 4g–i). For the FAPbI<sub>3</sub>-SnO<sub>2</sub>(ALD) sample, no change was observed in the initial slow-rise kinetics (within 50 ps), suggesting that no hot electrons were extracted. In contrast, FAPbI<sub>3</sub>-ZnSe and FAPbI<sub>3</sub>-SnO<sub>2</sub>(com.) exhibit a noticeable reduction in the amplitude of slow-rising component of XB kinetics, confirming that a fraction of hot electrons was successfully extracted into acceptors. These results strongly demonstrate the synergistic advantage of doping excess PbI<sub>2</sub> into perovskite films in conjunction with suitable electron acceptors, thereby retarding the HC relaxation and promoting their extraction. Based on this, we further fabricated two kinds of PSCs using FAPbI<sub>3</sub>-1 M and FAPbI<sub>3</sub>-1.5 M films and measured their *J*-*V* characteristics (Fig. S14). The results show that the PSC with a high PbI<sub>2</sub> content exhibits a higher PCE and a larger open-circuit voltage (*V*<sub>oc</sub>) due to the excess energy of HC, demonstrating the positive influence of HC extraction on PCE.

## Conclusions

In summary, we have investigated the influence of excess PbI<sub>2</sub> on the HC relaxation process in FAPbI<sub>3</sub> perovskite films by using femtosecond TA spectroscopy. The results show that excess PbI<sub>2</sub> in FAPbI<sub>3</sub> films significantly slows down the HC relaxation at high excitation densities by introducing an ITS-mediated channel, leading to the occurrence of a slow-rising component (extending to hundreds of ps) in their XB kinetics. Through engineering the competition between the direct relaxation and the ITS-mediated channel of HCs, this slow HC relaxation process can be controlled through adjusting the PbI<sub>2</sub> content, excitation density or temperature. Leveraging the prolonged HC lifetime, we successfully achieved the effective extraction of HCs in FAPbI<sub>3</sub> films containing excess PbI<sub>2</sub> by using an appropriate electron acceptor. Our findings suggest an effective method to slow down HC relaxation by creating ITSs, which might be beneficial for the development of next-generation HC devices.

## Author contributions

W. T., J. L., Y. X. and S. J. conceived the project. X. Z. performed the sample preparation and characterization measurements. X. Z. conducted TA experiments with the assistance of X. T. X. Z. carried out the electron acceptor tests with the help of Q. S. and Q. D. Y. S. conducted DFT calculations. The manuscript was drafted by X. Z. and revised by J. L., Y. X., S. J. and W. T. All the authors discussed the results and contributed to the manuscript.



## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: experimental details about sample preparation and TA measurements, additional TA data and other characterization results. See DOI: <https://doi.org/10.1039/d6sc01780k>.

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