Revealing Ultrafast Carrier Dynamics of Hybrid Perovskites at Various Stages of Nucleation and Growth Kinetics

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1. Introduction

Hybrid organic–inorganic perovskites (hybrid perovskites) are rapidly being deployed in various devices, ranging from light-harvesting solar cells to light-emitting diodes and detectors. More recently, hybrid perovskites have been implemented in planar-heterojunction field-effect transistors, and other light-based applications like optically-pumped nanoscale lasers, low-threshold nonlinear switches, phase shifters, and electro-optical modulators. Besides the commonly stated high absorption coefficient and long carrier diffusion lengths that hybrid perovskites offer, another key feature is their ability to operate in various devices over a wide range of carrier densities. Therefore, it is critical to understand how carrier densities and their associated dynamics are modified when the morphology of thin film or micro-structuring impact the dynamics of carriers, and thus impact the overall optoelectronic properties.

The performance of hybrid perovskite devices depends critically on their growth conditions. For example, varying the solution-processed methods for thin-film fabrication dictate grain size, local crystalline heterogeneity, film morphology, and dimensionality (quantum dots, nanowires and bulk crystals). These structural and morphological changes have a profound impact on fundamental processes such as absorption coefficient, photoluminescence efficiency, carrier mobility, optical bandgap, and recombination dynamics.[3–7] In general, the crystallization process in the hybrid perovskites dictate their overall morphology. Supersaturation of the perovskite precursor is the driving force in the crystallization process, with the perovskite organic and inorganics components that diffuse and reach size greater than the critical radius that initiate the nucleation process. To elicit supersaturation, many methods have been developed, such as i) increasing solute concentration, ii) cooling the solution, iii) increasing solvent evaporation, iv) alteration in solvent composition, and v) decreasing solubility of the solute. Implementing techniques such as hot casting[8–10] anti-solvent treatment,[11–13] vacuum quenching,[14,15] gas blowing,[16] use of additives in precursor solution,[17,18] solvent annealing,[19] non-stoichiometric composition,[20,21] and solvent additives[22] rely on these approaches to control supersaturation and crystallization. In all techniques described, the growth of hybrid perovskite crystals involved three processes: i) the solution reaches supersaturation, ii) nucleation, and iii) subsequent growth toward a large crystal.[23] While the community of hybrid perovskites has intensely investigated how to control the structure and morphology of thin films to improve photovoltaics, little work has relied on controlling nucleating crystals to render high quality films. In fact, only recently has this idea been demonstrated by Sidhik et al., who use nucleating seeds of hybrid perovskites to create high-quality 2D-layered hybrid perovskite thin films with...
increased device performance. While few reports of in situ structural studies connect the properties of thin films to their parent nucleating crystals, more research is needed to determine how the electronic properties and carrier dynamics of the hybrid perovskites evolve during the growth process.

In this Letter, we quantify how the ultrafast electronic properties of prototypical lead halide perovskites evolve during its nucleation and growth kinetic process. We devise a new simple fabrication strategy to reduce the broad phase space of the solution precursors that dictate thin film formation; this allows us to “freeze” various phases of hybrid perovskites growth on the same substrate (Figure 1). This type of phase-gradient sample enables us to probe, in a systematic way, the ultrafast broadband optical response of hybrid perovskites at different growth stages. This demonstration is the first report, to the best of our knowledge, of ultrafast spectroscopy conducted on such nucleating microcrystals. Surprisingly, our results reveal that the microcrystals share similar optoelectronic properties and carrier dynamics with the end product, that is, the large-grain thin films. With the different phases of hybrid perovskite on the same substrate, we systematically study the carrier dynamics displaying a broad complex optical response. The similarity in dynamics underscores how quickly the electronic and optical properties of hybrid perovskites emerge during the nucleation and crystal growth stages. While thin film of large grains is always desirable for technological applications because of a reduced density of trap states, this work shows that isolated microstructures confine the excited carriers and modify the dynamics locally. Consequently, a thorough knowledge of bimolecular and Auger recombination dynamics is critical when higher injected carrier densities are required for use in perovskite-based light management and lasing applications.

2. Results

Samples of hybrid perovskites (methyl ammonium lead iodide, CH$_3$NH$_3$PbI$_3$) were prepared on glass substrates using a
modified hot-casting, spin coated solution-processed method. Detailed synthesis process is discussed in the Methods section. Briefly, since the precursor phase can guide the final hybrid perovskite film morphology,[31] we use spin-coating to first uniformly distribute nucleating seeds on the substrate. Following this spin-coating step, we employ a temperature-assisted crystallization that yield three different hybrid perovskite phases on the same sample: i) nucleating microcrystals (dots), ii) needle-like crystals (wires), and iii) large-grain thin films (grains). Each phase is easily identified using either optical and scanning electron microscopy, and importantly for ultrafast microscopy, are visually well separated spatially from each other (Figure 1).

Higher and lower temperature regions on the substrate yielded large grains and nucleating microcrystals, respectively, while the intermediate zone on the temperature-gradient substrate yielded needle-like structures. At the intermediate temperature, the nucleating seeds undergo a 1D growth to form long needles that can grow to hundreds of microns in length within few seconds.[26,27] Such growth, if allowed to proceed, generates a thin film with stacked-needle morphology which contains many pinholes with low hybrid perovskite coverage.[23,28,29] We further characterize each hybrid perovskite phase using X-ray diffraction (XRD), scanning electron and optical microscopy. We found that the dot, wire, and grain phases all had signatures associated with bulk hybrid perovskites (denoted by asterisks in Figure 1b). X-ray diffraction result for PbI₂ spin-coated on glass substrate is also included in Figure 1b for comparison (shaded grey plot). We note that because we intentionally “freeze” the various stages of growth (on the same substrate), residual PbI₂ is expected to be locally present in all phases. For our purpose, however, broadband transient absorption microscopy allows to selectively probe the dynamics of hybrid perovskites by selectively filtering the relevant kinetics (e.g., near optical band gap of hybrid perovskites at ν ≈ 750 nm). For the case of dots, we see the presence of PbI₂ signatures near 2θ = 12°. Unexpectedly, the PbI₂ signature, albeit still present, is drastically reduced in the wire case. We attribute this effect to the evaporation process of the solute and fast needle-like growth dynamics that creates highly crystalline material, albeit with poor substrate coverage.

At higher substrate temperature, typically >125 °C, spherulitic growth takes place radially from the nucleating seeds which leads to large grains being formed (10–100 μm). This growth pattern is confined to a 2D plane, results in films with thickness of ≈ 1 μm, and terminates within few seconds. The growth stops when two domains meet, creating a grain boundary, with a film morphology defined by a Voronoi diagram.[30] This growth habit and the resultant grain morphology is reminiscent of “flash infrared annealing,” which uses high-power infrared light to crystallize hybrid perovskites within few seconds.[31]

While it is not feasible to probe the ultrafast carrier dynamics of hybrid perovskites during the crystallization process (i.e., while spin-coating), our strategy of phase-gradient fabrication enables us to probe indirectly various stages of their growth. To assess the intrinsic carrier dynamics of the various microstructures of hybrid perovskites, we conduct broadband near-infrared femtosecond pump-probe spectroscopy. Briefly, a high-repetition-rate diode-pumped Yb:KGW femtosecond laser system based on chirped-pulse amplification (PHAROS from Light Conversion) is used to pump a hybrid optical parametric amplifier to produce light pulses centered at 840 nm which are subsequently frequency doubled to 420 nm (pump). Changes in transmission of a spectrally dispersed broadband probe pulse beam is recorded when the sample is excited (pump on) and when it is in its ground state (pump off) at varying pump-probe delays and at a repetition rate of 1 kHz. Further details of our ultrafast pump-probe setup are found in the Methods section. We conducted ultrafast transient spectroscopy at room temperature for optical fluences between 75–65 μJ cm⁻² in order to evaluate a broad range of carrier processes including trapping, bimolecular and Auger recombination. Representative datasets of these broadband ultrafast transient absorption measurements at a low pump fluence of ≈ 7.5 μJ cm⁻² are shown in Figure 2. The main signal (λ ≈ 750 nm) corresponds to an electromagnetic induced transparency (bleach) near the bandedge of the hybrid perovskite. Such ground state bleach is caused by the transition between valence-band maxima and conduction-band minima at the R point.[32,33] Specifically, for each phase, we note only a slight wavelength-dependent variation in differential absorption minima for the case of grains (749 nm), wires (746 nm), and dots (756 nm). Normalized temporal slices for λ = 750 ± 5 nm and spectral slices at τ = 5 ps are shown for the dot, wire, and grain phases (Figure 2b,c). While there are visible differences in their kinetics, the similarity in spectra and kinetics between the nucleating microcrystals and large-grain films is remarkable. The differences in kinetics will be further investigated in subsequent paragraphs.

To quantify the carrier dynamics most pertinent to our system, near the bandedge, we examine the population term within the χ(3) formalism.[34,35] We perform fits on all transient data acquired on each hybrid perovskite phase at the relevant spectral slice (λ = 750 ± 5 nm) with a fitting procedure that corresponds to a convolution of the system response with the cross-correlation of the pump and probe pulses; this fitting equation probes time-dependent changes in carrier density n(t) in halide perovskites and is given by:[36,37]

\[
\Delta \alpha (\lambda, t) \propto \frac{dn(t)}{dt} = \phi(t) - k_n(t) - k_1n(t)^2 - k_p(t)^3
\]

(1)

where, \(\phi(t) = \frac{1}{h \nu_p} \left(1 - e^{-\alpha t}\right) \left(\frac{1}{d} \left(1 - R\right) \frac{F}{\tau_{\text{pulse}}} \right) e^{-\frac{2\alpha d}{\lambda}}\)

(2)

Here, \(\phi(t)\) is the carrier generation process. The rate coefficients \(k_i = 1, 2, 3\) corresponds to first-order (monomolecular) recombination caused by trap-assisted processes, second-order (bimolecular) caused by intrinsic electron-hole pair recombination, and third-order (Auger) which is a many-body recombination process of an electron-hole pair that transfer its energy and momentum to a third participant, that is, either a hole or an electron. The process involves a phonon absorption or emission that assist this recombination process.

Other terms in this equation are: \(h\) is the Planck’s constant, \(\nu_p\) is the pump pulse frequency, \(\alpha\) is the absorption coefficient, \(d\) is the thickness of the thin film, \(R\) is the reflectance of the thin film, \(F\) is the fluence per pulse, \(\tau_{\text{pulse}}\) is the pulse duration as measured by autocorrelation measurement. For such fitting, we assume the ideal case that \(k_i = 1, 2, 3\) are constants and that the densities of both electrons and holes.
are similar. Representative fits of the kinetics are overlaid on the experimental data of Figure 2b, and highlights the excellent quality of the fits. With pump excitation fluences in the $7.5\, \mu \text{J cm}^{-2}$ range, corresponding to $(1 - 10) \times 10^{17}$ carriers/cm$^3$, bimolecular recombination ($k_2$) processes are known to dominate the kinetics.$^{[32,38,39]}$ Using the total recombination rate $r(n, t) = k_1 + nk_2 + n^2k_3$, we find indeed that the bimolecular recombination rate contribute to $>90\%$ of the kinetic trace for all phases. For the large-grain thin film, we retrieve $k_2$ values in the range of $(15 - 60) \times 10^{-10}$ cm$^3$ s$^{-1}$. These fluence-dependent values are within typical range, as measured by various other spectroscopic techniques.$^{[32]}$ A similar fitting procedure is applied to the other hybrid perovskite phases, and at an excitation fluence of $\approx 26\, \mu \text{J cm}^{-2}$, we obtain $k_2$ recombination rates which is about an order of magnitude larger, that is, $290 \times 10^{-10}$ cm$^3$ s$^{-1}$ for the dot phase and $470 \times 10^{-10}$ cm$^3$ s$^{-1}$ for the wire phase. At longer time delays, that is, for $\tau > 1$ ns when excited carrier densities are reduced to the $10^{13} - 10^{16}$ cm$^{-3}$ range,$^{[39,40]}$ trapping processes among the various phases of hybrid perovskites can also be evaluated, as shown below.

3. Discussions

The pseudo-color representation of transient absorption spectra as a function of probe wavelength and pump-probe delay clearly highlight that the electronic and optical properties of hybrid perovskites are established within the first few seconds of nucleation and crystal growth. In all three phases, we observe a pronounced bleaching feature near the optical bandgap of $\approx 750$ nm ($E_g \approx 1.65$ eV) caused by state-filling$^{[41]}$ that is when the excited carriers (or excitons) block the optical transition near the optical band gap. The above-bandgap positive differential absorption signatures ($\Delta \alpha$ for $\lambda < 725$ nm) correspond to photoinduced intraband absorption (PIA) of the excited charge carriers. The other positive $\Delta \alpha$ signature at longer wavelength (i.e., lower energy side of the bandgap), is assigned to hot carrier cooling dynamics and correlate with the buildup of ground state bleaching.$^{[42,43]}$ These signatures, present in all three phases, last less than a picosecond and attest to the excellent electronic properties of hybrid perovskites when benchmarked to dynamics of bulk single crystals.$^{[33]}$ Combined with the negative differential absorption at the optical bandgap, the overall
response resembles a derivative-like signature that redshifts as a function of time. This transient feature is in sharp contrast to dynamical Burstein–Moss effect, which is a blue-shift of the optical bandgap transition caused by band filling and screening of the excitonic resonance.\(^{44–46}\) Therefore, this feature arises from renormalization of the bandgap caused by the presence of free charge carriers. A comprehensive study of this phenomenon in hybrid perovskite thin films conducted by Trinh et al. has attributed this red shift to transient Stark effect initiated by hot carriers, and further estimates the energy-loss rate process to be \(\approx 5 \, \text{eV/ps}.\)\(^{42}\) This derivative-like signature is present in all phases, and once more attest to the great electronic properties of nascent hybrid perovskites even in the nucleating microcrystal phase.

The overall carrier dynamics of hybrid perovskites is predominantly attributed to bimolecular recombination at the optically injected carrier densities we studied. This interpretation of the experimental dataset is based on the fundamental assumption that the radiative recombination is proportional the product of the electron and holes concentrations.\(^{47–49}\) Furthermore, much insight can also be gained by examining timescales which are most relevant for the different recombination processes — for example, Auger (\(k_i\)) which occurs within the first tens of picoseconds, and trapping (\(k_j\)) which occurs at longer time delays when the carrier concentration has decreased.\(^{50}\) In Figure 3, we show plots of i) \(1/(\Delta \text{Abs})^2\), ii) \(1/\Delta \text{Abs}\), and iii) \(-\ln(\Delta \text{Abs})\) versus time delays. These plots are linear in the case of pure i) Auger, ii) bimolecular, and iii) trapping behavior within the time frame most relevant to those mechanisms. Their slopes can further inform us on the mechanistic detail at play and provides a methodology to compare the efficiency of the recombination process among the various phases. For example, to evaluate trapping mechanism in the large grain phase (Figure 3, bottom), we examine the longer timescale signatures (typically, \(\tau > 1 \, \text{ns}\)).\(^{39}\) For all pump excitation fluence studied, we find slopes which are independent of excitation density as it should be, with \(k_j\) calculated to be \(\approx 4 \times 10^{-8} \, \text{s}^{-1}\). Hence, doubling the excitation density doubles the recombination rate for this mechanism. Once trap-assisted recombination channels are suppressed, bimolecular recombination sets in. Using a similar plotting strategy, now for \(1/\Delta \text{Abs}\) versus time, we find bimolecular rates of \((14 - 25) \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1}\). These values agree with past studies which found \(k_j = 0.2 - 20 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1}\), reflecting on the intrinsic nature of bimolecular recombination in prototypical CH\(_3\)NH\(_3\)PbI\(_3\). In Figure 3 (top), we also quantify the potential contribution of Auger recombination that could occur during its characteristic short timescale (\(\tau < 50 \, \text{ps}\)). For the grain phase, there is a negligible change in the slope for all the range of optical excitation studied, confirming that the Auger mechanism plays a lesser role in our study. Again, this observation agrees with our global fit which finds that bimolecular recombination to be dominant.

We now quantitatively summarize carrier dynamics of hybrid perovskites among all three phases, as depicted in Figure 4. For the case of trapping, we plot \(-\ln(\Delta \text{Abs})\) versus time delay and examine the different slopes at longer time delays; Figure 4 (bottom) readily highlights that the grain phase has a lower \(k_j\) monomolecular-trapping rate \((2 \times 10^8 \, \text{s}^{-1})\) as compared to the wire \((4.5 \times 10^8 \, \text{s}^{-1})\) and dot \((4 \times 10^8 \, \text{s}^{-1})\) phases. These values agree with our understanding of the wire and dot phases having more trap-related charge-carrier recombination since their growth have not been fully realized, attributed to the non-optimum growth temperature. To understand the higher-order recombination processes, we plot in Figure 4 the \(1/\Delta \text{Abs}\) and \(1/\Delta \text{Abs}^2\) transient data which corresponds to bimolecular and Auger recombination, respectively. While it is not strictly feasible to distinguish between second- and third-order, we note that our plots provide a method to comparing how dynamics in various microstructured phases of hybrid perovskites are modified. For example, at a fluence of 26 \(\mu \text{j/cm}^2\), the bimolecular
recombination rate shows an order of magnitude increase from the grain ($k_g = 45 \times 10^{-18} \text{ cm}^3 \text{s}^{-1}$) to either the dot or wire phases ($k_d = 250 - 400 \times 10^{-18} \text{ cm}^3 \text{s}^{-1}$). The increase in rate is attributed to the confining microstructure that enhances carrier–carrier recombination. The fact that the wire phase has a more confined geometry than the dot phase and therefore has a higher $k_w$ value validates this argument. For timescales relevant to Auger recombination, that is, $\tau < 50$ ps, we again see an increase of Auger recombination rate of about an order in magnitude.

While we emphasize that for fluences studied here, bimolecular recombination dominates, increase in $k_r$ recombination rates is potentially related to size effects, which can increase carrier–carrier interaction. Two possible reasons for a higher $k_r$ recombination are: i) a change in confinement that equates to lessening the requirement of momentum conservation that can lead to increase carrier interactions in isolated micron-scale crystals and wires; ii) a change in structure can create nonuniform electromagnetic fields and nonuniform carrier distribution, which can boost Auger recombination rate due to Coulomb enhancement effects.

To further validate our quantitative analysis of carrier dynamics in the various phases of hybrid perovskite, we performed complementary time-resolved photoluminescence (TRPL) measurement. We use the same excitation pulse characteristics ($\lambda = 420 \text{ nm}$ and pulse duration of 40 fs) and similar fluence range as in our TA studies above. To make sure complete depopulation of carriers occur before the next pulse re-excite the material (i.e., to avoid build-up of excited carriers), we conduct TRPL at a low repetition rate of 100 kHz, compared to using laser repetition rate exceeding 10 MHz. More details of our setup are found in the Methods section. We summarize the key features of emission decay kinetics in Figure 5. Evident from Figure 5a, we see that the emission dynamics of the grain and dot phases are similar. This similarity in kinetics is seen at all fluences and stems from the fact that trap-states are mostly suppressed in the excitation range where we expect bimolecular recombination to dominate as discussed above. As for the wire phase, the emission dynamics is different for both short ($\tau < 50$ ns) and long timescales ($\tau > 100$ ns) caused by the additional monomolecular trapping channel (Figure 4, bottom; blue curve). Moreover, another reason that the dot phase respond similarly to the grain phase could be the finite, micron-scale size of the dots, which have a lower effective number of trap states when compared to the extended geometry of the wires. Furthermore, since we spatially filter the collected emission at the excitation region using our Fourier Imaging setup, we do not expect carrier diffusion within the probed volume to play a major role in expect the carrier distribution to homogenize within the first few hundred picoseconds and.

To quantify the emission dynamics, within the framework of normalized emission kinetics at $\tau = 0$ ns (Figure 5), we fit the photoluminescence decay curves with a modified stretching exponential line shape:

$$I(t) = I_0 \exp -\left(\frac{x}{\tau_1}\right)^\beta + (1-I_0) \exp -\left(\frac{x}{\tau_2}\right)^\beta$$

(3)

where $\tau_1, \tau_2$ are the decay times and $I_0$ and $(1-I_0)$ are the weight factor of each decay mechanism. This equation fits well to all TRPL data acquired at all fluences and for all phases, as shown in Figure 5. Other fitting curves such as a mono-exponential, two exponentials, or a single stretched-exponential decay did not fit the data well. In our case, the rationale for using the stretched exponential is to capture the distribution of decay channels potentially caused by i) the various phases having various defect states and shallow trap states, and ii) the increased complexity of carrier dynamics as the density of carriers...
increases with higher laser fluences. This distribution of decay channels is parametrized by the parameter $\beta$, and together with the retrieved slower emission lifetime ($\tau_2$), we can calculate the average lifetime of this decay mechanism using the equation $\tau = \frac{\tau_1}{\beta} \int_0^\infty \frac{1}{\tau_2} e^{-\beta x} dx$. For this stretched exponential function, also known as the Kohlrausch decay function, a $\beta$ close to 1 corresponds to single mono-exponential decay with a narrow distribution of decay channels. The former exponential term in this equation is used to capture the fast emission lifetime ($\tau_1$) which corresponds to geminate-like recombination, in our experimental framework of normalized emission. This “geminate recombination” corresponds to electron-hole pairs correlation stemming from dissociated excitons (but still near lattice site) or exciton-like species, as well described and modeled by Manger et al. Other works in TRPL depict similar rapid decrease of this fast lifetime component as the optical fluence is increased. In our analysis, we see that for both the dot and grain, the range that $\beta$ value takes with increasing fluence are similar: from 0.64 to 0.46 (dot) and 0.63 to 0.45 (grain), as the fluence is increased from 6.4 to 47.7 $\mu$J cm$^{-2}$. This decrease in $\beta$ corresponds to an increase in the distribution of decay channels. The stretched exponential function thus captures the faster emission dynamics resulting from an increase in excited carrier density, with associated average lifetimes dropping from $\tau = 25$ ns to $\tau = 1.68$ ns for the dot, and from $\tau = 27$ ns to $\tau = 1.75$ ns for the grain. The $\beta$ value, for the wire phase, ranges from 0.86 to 0.59 and has lower corresponding average lifetimes, that is, $\tau = 15$ ns to $\tau = 0.9$ ns as fluence increases. We find that the fast lifetime component ($\tau_1$) for the dots and grains to decrease as we increase fluence: from 0.56 to 0.38 to 0.79 to 0.36 ns. These values are below typical IRF for TRPL using single-photon counting system, and further studies using for example femtosecond optical Kerr gating are necessary to fully resolved the emission dynamics. Here, our main finding is that in the fluence range studied, the dot and grain phase share similar emission dynamics, originating from the fact that nucleating micron-scale seeds that create the large-grain thin film have similar composition and structure.

4. Conclusion

Taken together, we see that the large-grain phase provides superior optoelectronic properties, with its reduced trap states (Figure 2a.). For the fluences studied in this work, where trap recombination dynamics are suppressed, the grain phase displays an order of magnitude longer bimolecular recombination dynamics compared to the wire and dot phases. However, the finite size of the dots, and reduced trap states compared to the wire phase, allows the dot and grain phase to share similar emission dynamics. These changes in recombination rate for the three microstructured film clearly highlights that for -applications in nanophotonics (LEDs and LASERs), further systematic studies of size-dependent carrier dynamics is necessary using the same base phase (i.e., film of large-grain phase that are then milled or etched to the relevant critical size). Importantly, our work also shows that trap-related dynamics of these phases can be compared at longer timescales (>1 ns, Figure 4 bottom) by plotting $-\ln$(ΔAbs) versus time delay, where we see that monomolecular recombination is larger for the wire and dot phases. Here again, this indicates the higher quality of the large-grain phase.

Our study details the ultrafast dynamics of charge carriers in hybrid perovskites at various stages of nucleation and growth kinetics, enabled by the development of a phase-gradient fabrication strategy. With the various phases of hybrid perovskite on the same substrate, we are able to systematically study the
carrier dynamics over a broad spectral and temporal range. The similarity in broadband dynamics highlight how quickly the electronic and optical properties of hybrid perovskites develop during the nucleation and crystal growth stages. Our research also points out that for future applications in micron-scale LEDs and lasers, that is when higher injected carrier densities are required, the contribution of Auger recombination can be markedly different to thin films, highly sensitive to changes in the size and morphology. Thus, research to further our understanding of carrier dynamics in confined, isolated microstructures is critical to help drive hybrid perovskites toward applications that necessitate higher carrier densities.

5. Experimental Section

Sample Fabrication: Thin films of hybrid perovskites were synthesized via a temperature-assisted crystallization process.[67] Synthesis of hybrid perovskites microstructured thin films were performed in two steps. The first step involved preparing the substrate and the second step comprises the growth of the thin films on the preprocessed substrate. The entire fabrication process was performed in a nitrogen-filled glovebox. In a typical preparation method, 0.2 g methyl ammonium iodide (CH$_3$NH$_3$I, Sigma Aldrich, 98%) and 0.578 g lead iodide (PbI$_2$, Sigma Aldrich, 99%) were mixed with 1.0 mL of anhydrous N,N-dimethylformamide (DMF, Sigma Aldrich, 99%) in a glass vial. The mixture solution was ultrasonicated and then kept on a first heating plate at 80 °C for 2 h. This ensures the homogeneous mixing of all the constituent compounds in DMF. Next, the microscopic glass coverslip (2.5 cm × 2.5 cm, Fisherbrand) was processed. Glass coverslips were cleaned using an ultrasonicator for 10 min using acetone (Sigma Aldrich, 99.7%), followed with isopropanol (Sigma Aldrich, 99%) and deionized water. The treated glass coverslips were then coated with ZnO nanospheres solution (Sigma Aldrich, size < 130 nm, 40 wt % in ethanol,) and then baked on a second heating plate at 210°C to evaporate the ethanol residue. The ZnO coating ensured uniform heating throughout the glass coverslips. Following the preparation of the substrate, the heated solution of hybrid perovskites was spin coated on the pre-heated substrate at 4000 rpm for 5 s and transferred immediately back onto the heating plate, which was maintained at a temperature of 210°C. To introduce the temperature gradient, the substrate with the precursor solutions was held at an angle of 45° for 5 s, which enabled to obtain three growth phases that were spatially well separated, distinct, and can be probed optically. Using 1D heat transfer modeling, the temperatures on the glass substrate (at 5 s) was estimated where the grain, wire, and dots were formed to be ≈210,160, and 120 °C, respectively.

Ultrafast Spectroscopy: Time-resolved absorption data of the samples were obtained using transient femtosecond pump-probe spectroscopy. These spectra were acquired by exciting samples with 420 nm pulse from optical parametric amplifier having pulse duration of 40 fs, beam spot size of 150 µm at varying pump fluences relevant to the pump-probe experiments, that is, < 100 µJ cm$^{-2}$. Broadband femtosecond pump-probe spectroscopy was conducted using a high repetition rate diode-pumped Yb: KGW femtosecond laser system based on chirped-pulse amplification (PHAROS from Light Conversion) to pump a hybrid optical parametric amplifier and produce light pulses centered at 840 nm that are subsequently frequency doubled to 420 nm (pump). The pulses were frequency doubled using a barium-beta-borurate crystal (BBO: Type I, θ = 29.2° and φ = 90.0°, 0.5 mm thick) to produce pulses at 420 nm (i.e., pump), pass through the chopper to block every other pulse, and is focused on the region of interest with a spot size of 150 µm in diameter (1/e$^2$). As probe, this work focused 7 µJ/pulse from the amplifier (λ = 1030 nm) on a sapphire crystal to generate a vertically polarized white-light supercontinuum. Using a pair of spherical parabolic mirrors, the supercontinuum probe pulses were overlapped spatially with the pump beam on the sample (probe beam diameter of 35 µm), and synchronized temporally using a mechanical stage. To vary the time delay between probe and pump pulse, the pulse generated by OPA was sent through optical delay line consisting of retroreflector mounted on high precision motorized translational stage. This work noted that the delay of the probe pulse was too weak that no appreciable population was excited from ground to excited states or vice versa. It was then focused on the sample spatially overlapped with pump, re-collimated, and focused onto a multimode fiber for wavelength sensitive detection.

Time-Resolved Photoluminescence Spectroscopy: Time-resolved emission was performed on the home-built microscopy setup with Fourier Imaging and spatial filtering capabilities. The phase-gradient sample was mounted a translation stage and the region of interest (dot, wire, and grain) was positioned with respect to the exciting pulse (λ = 420 nm, 40 fs, 100 kHz). The pulse was focused to a 20 µm spot using a 3.8 mm focal spot lens. The broadband emission was collected using a Mitutoyo objective (NA 0.7, 100x) from the transmission side, and was spatially filtered using a mechanical iris at the conjugate plane. The emission was then spectrally filtered a with long pass filter (λ > 650 nm, OD 6) and then filtered further using bandpass centered at 750 nm (λ = 750 ± 25 nm, OD 4) before being directed to the time-correlated single-photon counting setup. The emission was directed to a Micro Photon Device (MPD) PDM series single photon avalanche photodiode with a 50 µm active area. The binning size was set to be 32 ps. Additionally, a flip mirror was positioned in the beam line to direct the light to the spectrometer for PL measurement.

Acknowledgements
B.S.D. and R.P.N.T. contributed equally to this work. Support for this project was provided by NASA EPSCoR R&D (award number 80NSSC19M0051) and UAB startup funds. B.S.D. acknowledges financial support from the Alabama Graduate Research Scholars Program (GRSP) funded through the Alabama Commission for Higher Education and administered by the Alabama EPSCoR.

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
charge-carrier dynamics, growth kinetics, hybrid organic–inorganic perovskites, nucleation

Received: August 18, 2022
Revised: January 15, 2023
Published online: March 22, 2023
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