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Perovskite Excitonics: Primary Exciton Creation and Crossover from Free Carriers to a Secondary Exciton Phase

Valerio Sarritzu, Nicola Sestu, Daniela Marongiu, Xueqing Chang, Qingqian Wang, Maria Antonietta Loi, Francesco Quochi, Michele Saba,* Andrea Mura, and Giovanni Bongiovanni*

Understanding exciton formation is of fundamental importance for emerging optoelectronic materials, like hybrid organic–inorganic perovskites, as excitons are the lowest-energy photoexcitations in semiconductors, are electrically neutral, and do not directly contribute to charge transport, but can emit light more efficiently than free carriers. However, despite the increasing attention toward these materials, experimental results on the processes of formation of an exciton population in perovskites are still elusive. Here, an ultrafast differential photoluminescence technique is presented that is able to track the kinetics of exciton formation and dissociation in $\text{CH}_3\text{NH}_3\text{PbBr}_3$. Data show the presence of geminate excitons, i.e., primary excitons directly created upon photon absorption, and their dissociation into free electron–hole pairs. The formation is demonstrated of a secondary exciton phase through pairing of the initial population of free carriers. The analysis of the generation of secondary excitons provides an estimate of the Langevin factor, the parameter governing the charge-pairing rate. Understanding and controlling the formation of a bright exciton population instead of a highly conductive free carrier population may help to design new hybrid perovskite materials with tailored optoelectronic functionalities.

1. Introduction

The photophysics of hybrid organic–inorganic lead halide perovskites is an interesting blend of some of the best features of organic and inorganic semiconductors. One of the most remarkable is that the majority of optical excitations are highly mobile and conductive free carriers under the typical operating conditions of optoelectronics devices.^[1–11] In contrast with having insulating, bound excitons, this is a desirable feature in solar cells, where the scope of photoconversion is to guide

opposite charges toward opposite electrodes. On the other hand, light-emitting diodes (LEDs) require high rates of radiative recombination at low injection levels, in order to operate efficiently. This condition is best satisfied if the emitting species are excitons, as their radiative recombination rate is proportional to the exciton density. Conversely, light emission from free charges is quite inefficient at low carrier concentrations, since radiative decay is a second order process in the carrier density. Understanding exciton formation processes is therefore of importance to design perovskite materials that bolster light emission.

However, exciton formation in hybrid perovskites has been elusive so far. The mass-action law, known as Saha equation,^[12] foresees an equilibrium with predominance of free carriers for excited state densities relevant to devices, despite the fact that the measured exciton binding

energy is larger than the ambient thermal energy, as for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ ($E_b = 60$ meV).^[13] Saha equation also predicts the formation of a majority population of excitons at large excitation densities, but such crossover has not been observed yet, hinting that thermodynamic equilibrium between bound and unbound states may not be assumed. In order to identify the exciton formation processes, the determination of the photoexcitation kinetics becomes the central issue. The task has been pursued using an array of time-resolved optical spectroscopy techniques. Many reports investigated the photoexcitation dynamics by differential femtosecond transmission or reflection spectroscopy.^[5,14–24] This technique detects small changes in the linear absorption/reflection spectrum near the optical gap induced by a population of photoexcitations, but it is not very selective to the nature of photoexcitations. Terahertz (THz) pump-probe spectroscopy overcomes this limitation and directly measures the absorption spectrum due the internal quantum transitions of the exciton population ($1s \rightarrow 2p, 3p$, and so on) and free electron–hole plasma. In hybrid perovskites, the THz absorption spectrum also contains interfering contributions from phonon modes. Most experiments reported to date agree that free carriers are the only photoexcitations in hybrid perovskites;^[3,25–27] however, two recent studies suggest that transitions between excitonic Rydberg states are also observed in $\text{CH}_3\text{NH}_3\text{PbI}_3$; yet, the ensuing estimates of

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the exciton binding energy at room temperature are different in the two experiments—17 meV and less than 2 meV, respectively.^[28,29] A further complication arises from the fact that THz experiments were performed under pump fluences as high as $10^2 \mu\text{J cm}^{-2}$, corresponding to electron and hole injection levels above 10^{19} cm^{-3} . In this regime, the average particle separation is close to the exciton Bohr radius and the kinetics between free carriers and excitons is strongly altered by unavoidable and complicated many-body effects, so much so that the very existence of excitons becomes questionable. Transient photoluminescence experiments and the combination of this technique with differential transmission spectroscopy corroborate the early findings of THz spectroscopy that the majority of photoexcitations are free carriers at room temperature in 3D hybrid perovskites.^[4,15,30–34] Yet, all these results do not provide any comprehensive answer to several crucial aspects of the exciton-plasma dynamics: are primary photoexcitations, that is the species directly excited by photon absorption, only free carriers? How fast do excitons form or dissociate? Are the kinetics of exciton formation and dissociation fast enough to produce an equilibrium distribution within the excited state lifetime? To which extent are exciton formation and dissociation kinetics influenced by extrinsic factors, such as intragap defect states and disorder? Can a bright excitonic phase form at low carrier injection levels and room temperature?

To address all these issues and provide a comprehensive picture, the experiment reported in this work probes the population of the excited states in a wide range of concentrations, at various temperatures and under both transient and stationary regimes. To this aim, photoluminescence experiments are particularly suitable as spontaneous emission is the result of the electron-hole two-particle correlation and therefore directly probes the excited state population and its statistics.^[35,36] Here, a train of short laser pulses is used as excitation, both at high and low repetition rates. Specifically, the differential photoluminescence technique employed with high repetition excitation rates is able to monitor

photoexcitations down to very faint charge injection levels, corresponding to electron-hole densities lower than 10^{11} cm^{-3} , and to reveal the transient and quasi steady-state response in the same experiment. The optical measurements were performed on $\text{CH}_3\text{NH}_3\text{PbBr}_3$ single crystals, as this material is more suitable than $\text{CH}_3\text{NH}_3\text{PbI}_3$ to explore excitonic effects thanks to its higher exciton binding energy—even at room temperature. Data show the luminescence of geminate excitons, i.e., primary excitons created in a single, coherent optical absorption process of one photon with quantum energy well above the band edge. Dissociation of geminate excitons is ultrafast at room temperature, while it slows down for decreasing temperature, and turns out to be determined by trapping mechanisms. At room temperature geminate excitons are, however, always a tiny fraction of the overall density of photoexcited electron-hole pairs, as expected in inorganic semiconductors supporting Wannier-like excitons. At low temperature, we managed to detect the formation of secondary excitons through the incoherent bimolecular pairing of free electrons and holes. This reveals that excitons outnumber free carriers and become the majority population at excitation densities high enough to ensure a fast pairing process, but still below the critical density for exciton dissociation by screening (Mott criterion). The experimental observation of both primary and secondary excitons, the relative abundance with respect to free carriers as well as the dependence on temperature and carrier photoinjection intensity provide a unified and coherent framework for the photophysics of band-edge excitations in hybrid halide perovskites.

2. Results

2.1. Geminate Exciton Formation in $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Perovskites

As illustrated in **Figure 1** the UV-vis absorption spectrum of lead halide perovskites is characterized by an exciton peak at the

Figure 1. Sketch of the outcomes of optical absorption in a semiconductor. The black line on each panel depicts the perovskite absorption spectrum, while the blue line represent the exciton dispersion. Free electron-hole pair states are represented by the blue shading. A two-particle representation is employed to show together in the same dispersion curve excitons and free carriers; for unbound pairs, the wavevector k is therefore the sum of electron and hole wavevectors. Resonant excitation just below the bandgap creates excitons (left panel), while nonresonant excitation in the continuum as a direct process can only lead to free electron hole couples, because of momentum conservation (centre panel). Geminate excitons may be created with an indirect process assisted by a phonon (right panel).

absorption onset: resonant optical excitation of this peak may lead to the direct creation of excitons with virtually zero momentum. On the other hand, nonresonant excitation well above the bandgap energy produces free electron–hole pairs, but cannot create excitons in a direct process because photon and exciton dispersions are mismatched, meaning that the photon does not carry enough momentum for the creation of a high-energy exciton. The geminate, nonresonant, creation of an exciton is only possible as an indirect process through the contribution of a phonon providing the needed extra momentum.^[37,38] The ratio between the two processes is determined by the strength of the coupling of electronic states to phonons and the relative density of states between excitons and free pairs, which in turn depends on the exciton binding energy and electron–hole effective masses. In perovskites, as in most inorganic semiconductors, direct creation of free carriers is expected to be the most probable of the processes, while in organic semiconductors geminate creation of exciton is the outcome of optical absorption well above the band edge.

Geminate excitons may be a tiny fraction of direct photoexcitations in perovskites, but the photoluminescence they generate is linearly proportional to their concentration, while electron–hole pairs emit an intensity quadratic in their concentration. At very low photoexcitation densities therefore signatures of geminate excitons may appear in the emitted photoluminescence signal, even under nonresonant photoexcitation conditions when primary excitations are free carriers.

This photoluminescence experiment employs 100-fs pulsed laser excitation above the bandgap (≈ 3 eV photon energy) on a wide range of carrier photoinjection levels, from a 5×10^{10} to 4×10^{19} cm⁻³. At the lowest carrier density, the mean interparticle distance is $\approx 10^3$ times the exciton Bohr radius ($r_B = \frac{\hbar}{\sqrt{2\mu_x E_b}} \approx 2.5$ nm, where $\hbar$ is the Planck's constant and $\mu_x \approx 0.1 m_e$ the electron–hole reduced mass). On the other hand, the highest pair concentration corresponded to an interparticle spacing comparable to r_B . The lowest injection levels were performed at high repetition rate (80 MHz), creating a transient excess of photoexcitations on top of a background population in a quasi-stationary regime. As shown in the cartoon in the top left inset in **Figure 2** the optical response results from the fact that the overshooting population triggered by each laser pulse decayed nonexponentially, with tails long enough to overlap with the following pulse and cause a population build up. To single out the prompt transient and its spectrogram, we analysed the differential photoluminescence intensity $\Delta PL(t, \lambda) = PL(t, \lambda) - PL_{<0}(\lambda)$, where $PL(t, \lambda)$ represents the light intensity emitted from the sample in a narrow temporal interval centred at time t , while $PL_{<0}(\lambda)$ stands for the photoluminescence

Figure 2. Time resolved differential photoluminescence decays from CH₃NH₃PbBr₃. Top left panel: sketch of the experimental set-up, with the photoluminescence signal consisting of two contributions, the transient emission triggered by the arrival of each laser pulse, and the quasi-stationary signal due to the long-lived population of photoexcitations. This latter contribution becomes more and more intense for increasing repetition rate. Laser pulses, 100 fs in duration and 400 nm in wavelength, are provided by a frequency-doubled Ti:sapphire oscillator with 80 MHz repetition rate. Main panel: normalized photoluminescence decays are shown in different colours corresponding to different excitation fluence; red and orange decays are produced with excitation by the MHz source, cyan and blue decays instead with the larger fluence from the kHz excitation source; at low excitation, the characteristic decay time is shorter than the temporal resolution of the apparatus, but it becomes longer for higher excitation fluence, as emission from geminate excitons is overcome by emission due to bimolecular recombination of free carriers; when the fluence exceeds $0.3 \mu\text{J cm}^{-2}$, the decay time again decreases due to faster higher-order recombination. Top right inset: absorption (black) and photoluminescence spectra taken at $t = 0$, $\Delta PL_0(\lambda)$, (red at low excitation, blue at high excitation).

intensity in a window of the same duration but centred at times just before each laser pulse was absorbed by the sample ($t = 0$).

The light emission properties at $T = 300$ K are reported in **Figure 2**. The main panel shows the emission transients $\Delta PL(t)$ for several pulse fluences, ϕ , detected with a streak camera and integrated over the exciton line. At very low laser intensities, emission is dominated by a fast (resolution-limited) contribution (< 15 ps). The fast transient is replaced by a long-lived, nonexponential signal for increasing pulse fluence. Further increasing the fluence was possible by switching the excitation source to a kHz repetition rate femtosecond regenerative amplifier. At the highest fluences, the large densities of photoexcitations produced the well-known decrease of the photoluminescence decay time due to the activation of nonradiative Auger processes.^[39,40] The raw photoluminescence curves including the pulse-to-pulse build up are shown in the **Figure S1** in the Supporting Information, together with the ratio of build-up offset to total photoluminescence intensity as a function of laser fluence (**Figure S2**, Supporting Information). The top right inset in **Figure 2** shows the spectra of the light emitted within a small temporal window centred at $t = 0$, i.e., right after the excitation pulse arrival. Spectra of the fast and slow signals are all peaked close to the edge of the optical absorption, indicating that both are due to intrinsic photoexcitations of the

crystal. The anomalous dependence of the photoluminescence lifetime on the excitation intensity is summarized in the upper panel of Figure 3.

The crucial quantity that discriminates the emitting species is the differential photoluminescence intensity emitted at $t = 0$, ΔPL_0 , shown in the main panel of Figure 3 as a function of the pulse fluence. ΔPL_0 follows a linear behavior for $\phi < \bar{\phi} = 10^{-2} \mu\text{J cm}^{-2}$ ($n_0 < \bar{n}_0 = 4 \times 10^{15} \text{ cm}^{-3}$), while it scales quadratically for $\phi > \bar{\phi}$ ($n_0 > \bar{n}_0$). The observed behavior suggests the formation of two excitation species with different formation and decay dynamics. We interpret the fast photoluminescence signal, whose initial intensity scales linearly with ϕ ($\Delta\text{PL}_0 \propto \phi$, $\phi < \bar{\phi}$), as due to radiative recombination of geminate excitons. Directly excited excitons quickly dissociated (< 15 ps) into unbound charged pairs, yielding the observed fast light emission transient. On the other hand, in the excitation regime where ΔPL_0 scales quadratically with pulse fluence ($\Delta\text{PL}_0 \propto \phi^2$, $\phi > \bar{\phi}$; $\Delta\text{PL}_{t>0}$, $\phi \leq \bar{\phi}$), a dependence we attribute to the emission to the bimolecular recombination of free carriers.^[13,30]

The detection of geminate exciton photoluminescence does not imply that excitons are a large fraction of optical excitations, but only that they emit more efficiently than free carriers. In fact the branching ratio between excitons and free carriers

upon optical excitation should not depend on the excitation fluence, meaning that geminate excitons always represent a small fraction of created excitations, though their relative populations may change at later times due to different kinetics. A quantitative estimate of such a fraction would require knowing the relative radiative oscillator strength between excitons and free carriers and is at present not possible.

Figure 3 also reports the photoluminescence intensity detected 1 ns after laser pulse excitation (empty markers). The ΔPL_0 intensity measured after the delay scaled quadratically with the pulse fluence (power law with exponent $m = 2$), which is the signature of bimolecular recombination of free electron-hole pairs that were left after geminate excitons had disappeared. Deviations from the quadratic dependence only appear at pulse fluences large enough to induce faster population decay than in the low excitation regime.

2.2. Free Carrier-Exciton Crossover in $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Perovskites at Low Temperature

Measurements at room temperature confirm that unbound carriers are the majority photoexcitation species in $\text{CH}_3\text{NH}_3\text{PbBr}_3$. Yet, the mass action law forecasts an equilibrium exists for the overall photoexcitation density, $2n_{\text{eq}}$, above which excitons

outnumber free electron-hole pairs: $n_{\text{eq}}(T) = \left(\frac{\mu_x k_B T}{2\pi\hbar^2} \right)^{\frac{3}{2}} e^{-\frac{E_b}{k_B T}}$.

Plugging in the values for temperature, exciton binding energy, and effective mass, the crossover density is $2n_{\text{eq}}(T = 300\text{K}) \approx 8 \times 10^{16} \text{ cm}^{-3}$. Above such density, a majority population of excitons should spontaneously form through incoherent pairing of free electrons and holes. Detecting exciton formation from photoluminescence decays is however challenging, as the decays depend on both radiative and nonradiative recombination channels, with bimolecular and monomolecular kinetics, and are also affected by spatial inhomogeneities, and carrier and light diffusion.

The way to unambiguously detect the exciton photoluminescence is to focus on ΔPL_0 , which is however only affected by excitons that form within the temporal resolution of the streak camera, and no later than that. The fact that no secondary exciton emission is detected in ΔPL_0 at room temperature, even for excitation densities well above the predicted crossover, implies that the formation of a majority population of secondary excitons does not occur within our temporal resolution ($t_r \approx 50$ and 15 ps for 1 kHz and 80 MHz lasers, respectively). In order to favour this process, the measurements presented below were carried out at temperatures as low as 15 K, moving the crossover density to a negligible value, $2n_{\text{eq}}(T = 15\text{K}) \approx 6 \times 10^{-5} \text{ cm}^{-3}$.

At low temperature, the instantaneous photoluminescence intensity ΔPL_0 measured at $t = 0$ (shown in Figure 4) undergoes a similar evolution as at room temperature. For low excitation fluences, it grows linearly because of geminate excitons. In this regime the time decay (inset in Figure 4) is longer than at room temperature, and becomes slightly faster at higher fluences because of the activation of nonlinear decay processes.

According to Saha equation, excitons at such temperatures and densities should not dissociate into free carriers, and

Figure 3. Instantaneous photoluminescence as a monitor for geminate exciton creation. Main panel: log-log plot of the instantaneous intensity of photoluminescence ΔPL_0 (filled markers, at time $t = 0$, empty markers at $t = 1$ ns) as a function of the pulse fluence; the circle markers refer to excitation with a 80 MHz Ti:sapphire oscillator (100 fs, 400 nm), the squares to the excitation with a larger fluence, 1 kHz regenerative amplifier (130 fs, 392 nm); the dashed lines represent power dependences with exponents $m = 1$ and $m = 2$, as marked. Top panel: photoluminescence decay time, defined as the time to reach $1/e$ reduction from initial value, as a function of pulse fluence (bottom axis) or corresponding injected photoexcitation density (top axis); the decay time is the for injected carrier densities below $5 \times 10^{14} \text{ cm}^{-3}$, the decay time values are limited to ≈ 20 ps by the temporal resolution of the detection apparatus.

Figure 4. Exciton crossover at 15 K. Main panel: log–log plot of the instantaneous photoluminescence intensity ΔPL_0 as a function of the injected carrier density (proportional to laser fluence); solid black dots represent measurements at 15 K temperature under MHz excitation, while the black square refer to KHz excitation, still at 15 K temperature; data collected at 80 K at the highest fluences have been added for comparison (blue squares, KHz excitation). Upper left inset: emission spectra in three excitation regimes are shown for comparison, i.e., free carrier regime, where geminate excitons are detected ($m = 1$, $n < 10^{15} \text{ cm}^{-3}$); free carrier regime where only free carriers are detected ($m = 2$, $n \approx 10^{16} \text{ cm}^{-3}$); exciton regime ($n > 10^{17} \text{ cm}^{-3}$). Lower right inset: time decay of photoluminescence in three excitation regimes, i.e., where geminate excitons are detected (blue trace, $m = 1$, $n = 10^{13} \text{ cm}^{-3}$), where free carriers prevail (black trace, $m = 2$, $n = 5 \times 10^{16} \text{ cm}^{-3}$) and finally when secondary excitons take over free carriers (red trace, $m = 1$, $n = 1.1 \times 10^{18} \text{ cm}^{-3}$).

therefore we interpret the decay of geminate excitons as due to extrinsic nonradiative decay processes, like trapping into defect states. For injected photoexcitation densities in excess of 10^{15} cm^{-3} , ΔPL_0 grows quadratically, a sign that recombination requires a bimolecular pairing and therefore involves a majority of free carriers. Around photoexcitation densities of 10^{17} cm^{-3} , however, the slope of ΔPL_0 reverts to 1, as expected if a majority population of secondary excitons are formed after excitation in the time window of our time resolution. A hint of crossover also appears at 80 K, although at larger excitation fluences.

2.3. Photoexcitations in $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Perovskites Under a Quasi-stationary Excitation Regime

Figure 5 shows the quasi-stationary time-integrated photoluminescence intensity detected with a CCD camera. The perovskite film was excited by a high-repetition rate laser at low and room temperature; the time-integrated detection measured predominantly the long-lived population of photoexcitations in a quasi-stationary regime, accumulated because the

temporal decay was much longer than the delay between subsequent pulses. At low temperature, the emission spectrum of perovskite films is complicated by the appearance of sub-gap emissive states, as shown in the inset in Figure 5. Such extrinsic emission however saturates with growing excitation intensity. On the other hand, the intrinsic emission peak is always present and in time-integrated detection follows a power-law dependence on the pulse fluence with fractional exponent $m = \frac{3}{2}$ at both low and room temperature (see main panel in Figure 5). This exponent in a free-carrier semiconductor arises, according to the Shockley–Read–Hall model, when nonradiative recombinations of unbound electrons and holes involve intragap states that, being completely empty or completely filled, preferentially trap only one kind of carrier, either electrons or holes.^[41] Whether traps are to be ascribed to bulk or surface states depends on sample conditions and it is still a debated question, particularly relevant for device performance optimization.^[18,41–47] Whatever the nature of the traps, our observation implies that a majority population of excitons is never formed during the lifetime of the photoexcitations under steady-state excitation, and this holds even at the lowest temperatures. Finally, we mention that a low doping level of the semiconductor as an alternate explanation is not compatible with our observations, since it could explain the observed linear dependence of ΔPL_0 versus the pulse fluence, but would also give a linear dependence of the time integrated

photoluminescence, in contrast with the fractional exponent we have found experimentally. In addition, the ultrafast decay time of the geminate excitons and the increase in decay time for growing excitation densities observed at room temperature is also inconsistent with the assumption of residual doping. Other possible scenarios not involving free carriers and traps have been discussed and ruled out in previous work.^[30,41]

3. Discussion

The observation of the crossover from free carriers to excitons at low temperature gives the opportunity to estimate the bimolecular exciton formation rate, known as the Langevin factor (B_L) in the organic semiconductor community. Since we have established that the fraction of geminate excitons directly created by nonresonant laser excitation is small with respect to the amount of free carriers, in order for the photoluminescence ΔPL_0 to scale linearly, excitons need to form by pairing of free carriers within the temporal resolution of our apparatus, i.e., $t_r \approx 50 \text{ ps}$. The bimolecular formation rate is given by $B_L n_c$,

Figure 5. Quasi-cw photoluminescence. Main panel: log–log plot of the time-integrated photoluminescence intensity as a function of laser fluence; the power law dependence as an exponent close to 1.5, meaning that free electron–hole pairs are the majority photoexcitations in steady state. Inset: PL spectra recorded by a CCD with a grating spectrometer, at various excitation fluences, as marked.

assuming that both free electrons and holes have density n_c , so that the condition that excitons form within the temporal resolution translates to $B_L \sim \frac{1}{n_c \tau_r}$. The crossover in Figure 4 occurs for $n_c \approx 2 \times 10^{17} \text{ cm}^{-3}$, corresponding to an mean interparticle distance (Wigner–Seitz radius) $r_{ws} = \sqrt[3]{\frac{3}{4\pi n}} \approx 11 \text{ nm}$ or ≈ 4 times the exciton Bohr radius, and yielding $B_L \approx 10^{-7} \text{ cm}^3 \text{ s}^{-1}$.

According to the Langevin theory, exciton formation is related to the probability of encounter between moving electrons and holes, treated as classical particles, and reads $B_L = \frac{\mu e}{\epsilon}$, where μ is the mobility, e the electron charge, and ϵ the dielectric constant. The exciton formation rate takes into account the actual strength of the Coulomb interaction in the semiconductor, a measure of which is provided by the exciton binding energy.

The Langevin factor can be therefore rewritten as $B_L = \frac{2^{\frac{3}{2}} h \mu}{e \sqrt{\mu_x}} \sqrt{E_b}$, meaning that a larger binding energy not only moves the equilibrium towards bound states but also makes exciton formation faster. In hybrid perovskites, the free carrier mobility increases with decreasing temperature,^[39] and so should do the Langevin factor and the rate of electron–hole pairing. The crossover density n_c is therefore expected to decrease with decreasing temperature, as found in the experiments. At $T = 15 \text{ K}$, the Langevin theory allows assessing the carrier mobility $\mu \approx 0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ from the knowledge of B_L . This value is lower than what reported in literature for hybrid perovskites,^[48] but it should be taken with a grain of salt as it is the outcome of a classical theory applied to a quantum phenomenon. Exciton formation should actually be addressed

within the full quantum treatment introduced in inorganic semiconductors by Piermarocchi et al.^[38]

The estimation $B_L \approx 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ for the exciton formation rate coefficient is greater than the bimolecular radiative recombination rate coefficient in hybrid perovskites, which can be estimated by various means, but for which $B \approx 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ is an upper limit. This fact implies that the encounter of free electrons and holes is more likely to generate a bound exciton than the emission of a photon, as also happens in GaAs quantum wells.^[38,49] In our samples however free carriers may recombine nonradiatively before forming excitons because nonradiative recombination represented the fastest rate, as demonstrated by the fact that the total photoluminescence intensity emitted by the stationary photoexcitations scaled with a 3/2 power law with respect to excitation fluence, instead of being linear, as expected in the radiative regime. Recently, very long photoluminescence decay times and quantum yields close to unity have been demonstrated in lead halide perovskites by saturating traps and making non-radiative recombination much slower.^[50–53] In such samples approaching the radiative regime exciton formation through pairing

of free carriers should be achieved within the photoexcitation lifetime.^[34]

The photoluminescence spectrum is the same in the low-density monomolecular regime of geminate excitons, in the free carrier bimolecular regime and again after crossover into the monomolecular regime of excitons. Two scenarios are compatible with such finding. The first one is that photoluminescence always stems from radiative decay of exciton states, even when free carriers are the large majority, because exciton emission is much more efficient than that from free carriers; the main radiative decay channel in the free carrier regime would therefore be that excitons form slowly by bimolecular pairing of free carriers and then rapidly emit. An increase in laser fluence would cause a quadratic increase of the number of excitons ($X_0 \propto n_0^2 \propto \phi^2$) and therefore of the differential photoluminescence intensity ΔPL_0 , provided that the exciton decay is faster than its formation time.^[13] In the quasi-stationary regime studied and achieved under high repetition rate, the actual steady-state electron and hole populations are determined by nonradiative trapping mechanisms. According to the Shockley–Read–Hall model applied to an intrinsic semiconductor,^[41] the product of the electron and hole populations scales as $n_e n_h \propto \phi^{3/2} \propto I^{3/2}$, and so does the stationary exciton population and cw-photoluminescence intensity ($\text{PL} \propto X \propto n_e n_h$). The second scenario is that free carriers emit photoluminescence with the exact same energy as excitons because of Coulomb correlation contributing the missing binding energy.^[54] At present, experiments do not distinguish among such scenarios, which have however been debated at length in the

community studying optical properties of III-V inorganic semiconductors.^[49,55,56]

4. Conclusion

Our spectroscopic data provide an overall, coherent picture of the kinetics of excitons in hybrid perovskites. By means of a differential photoluminescence technique, primary (geminate) excitons are unveiled; they represent a minority population of photoexcitations in 3D hybrid perovskites. An insulating excitonic regime in $\text{CH}_3\text{NH}_3\text{PbBr}_3$ is demonstrated, but only at cryogenic temperatures under a transient regime and photoexcitation concentrations larger than $2 \times 10^{17} \text{ cm}^{-3}$. The Langevin factor, which determines the rate of charge pairing out of a free carrier population, was estimated to be $B_L \approx 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ ($T = 15 \text{ K}$). Under a quasi-stationary excitation regime and for temperatures as low as 15 K , a majority population of excitons is, however, not observed, because the rate of bimolecular exciton formation ($B_L n$) at low carrier densities is too slow with respect to trapping. Since excitons emit much more brightly than free carriers at low injection levels, realizing an exciton population in device working condition may be very beneficial for light emitting devices. Trap saturation strategies may allow longer excited state lifetime and therefore more time for exciton formation.^[50–53] Quantum confinement strategies on the other hand may produce materials with increased exciton formation rates, such as 2D layered perovskite materials, dot-in-matrix or nanocrystalline composites, by enhancing the exciton binding energy E_b , and therefore the Langevin coefficient B_L which is proportional to E_b , and at the same time increase local concentration by funnelling optical excitations.^[57–61]

5. Experimental Section

Perovskite Preparation and Characterization: $\text{CH}_3\text{NH}_3\text{PbBr}_3$ single crystals were prepared by an antisolvent vapor-assisted crystallization that allows to obtain high quality, smooth, and crack-free crystals. A solution of $\text{CH}_3\text{NH}_3\text{Br}$ and PbBr_2 0.2 M with 1:1 molar ratio in *N,N*-Dimethylformamide was prepared and poured in a small beaker. The beaker was placed inside another bigger beaker containing dichloromethane, in which perovskite precursors are completely insoluble, and sealed. The slow diffusion of dichloromethane into the precursor's solution led to the crystals precipitation and growth. The crystals were left to grow for 5 d prior to dry and wash them with isopropyl alcohol. All the chemicals were purchased from Sigma Aldrich apart from $\text{CH}_3\text{NH}_3\text{Br}$ that was synthesized by reacting a proper amount of HBr 48% in water and methylamine, 33 wt % in ethanol as described elsewhere.^[7]

Time-Resolved Photoluminescence: Samples were mounted to a cold finger in a closed-cycle helium cryostat (CTI-Cryogenics Model 22) and excited with two different laser sources depending on the excitation range of interest. Differential time-resolved photoluminescence measurements were carried out using a Ti:sapphire oscillator (Spectra-Physics Tsunami) delivering 100-fs-long pulses at a repetition rate of 80 MHz in the range of 0.1–100 pJ of energy per pulse. Fluences up to 1 mJ per pulse were achieved with a regenerative amplifier laser (Quantronix Integra-I) delivering 130-fs-long pulses at a repetition rate of 1 KHz. In both experiments, the photoluminescence was dispersed with a grating spectrometer (Princeton Instruments Acton SpectraPro 2300i equipped with a 50 g mm^{-1} grating blazed at 600 nm) and detected by a streak camera (Hamamatsu C5640).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

excitons, hybrid perovskites, light-emitting diodes, ultrafast spectroscopy

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