

## Research Update: Luminescence in lead halide perovskites

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## Research Update: Luminescence in lead halide perovskites

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Efficiency and dynamics of radiative recombination of carriers are crucial figures of merit for optoelectronic materials. Following the recent success of lead halide perovskites in efficient photovoltaic and light emitting technologies, here we review some of the noted literature on the luminescence of this emerging class of materials. After outlining the theoretical formalism that is currently used to explain the carrier recombination dynamics, we review a few significant works which use photoluminescence as a tool to understand and optimize the operation of perovskite based optoelectronic devices. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4962144>]

### INTRODUCTION

Complementarity of photovoltaic (PV) and light emitting device (LED) operation leads to the reciprocity theorem that correlates the efficiency of electroluminescence (EL) to the PV external quantum efficiency.<sup>1,2</sup> Then, the obvious correlation between electro-luminescence and photoluminescence (PL) established via the mechanism of radiative carrier recombination<sup>3</sup> makes PL spectroscopy an easy and versatile tool for elaborating and optimizing efficient optoelectronic materials. Given the recent success of hybrid organic-inorganic metal halide perovskites as active materials for efficient PV devices,<sup>4,5</sup> LEDs,<sup>6,7</sup> and lasers,<sup>8–10</sup> it is of no surprise that PL spectroscopy is used extensively to probe the photo-physical mechanisms and to estimate figures of merit for the material's optoelectronic capabilities. Besides, PL/EL measurements can be used as insightful probes to comprehend and tackle the pertinent issues of stability and reliability marring the perovskite based technologies.<sup>11–13</sup>

In a simplistic description, hybrid perovskites are direct bandgap semiconductors<sup>14,15</sup> where the absorption of light leads to an excitation of an electron from the valence band to the conduction band, leaving behind a hole. The Coulomb correlations between the photo-generated carriers and the binding energy of the resultant exciton have been intensely investigated and debated recently. In the case of methyl ammonium lead iodide (MAPbI<sub>3</sub>), a wide range of binding energies from 2 meV to 50 meV<sup>16–18,43</sup> have been reported, obtained from different experimental techniques. This variability can partly be attributed to the wide variance in the dielectric response induced by the material's microstructure.<sup>19</sup> In spite of the ambiguity over precise value of the exciton binding energies, it has been shown for the range of reported values that free electrons and holes form the majority of the photo-excited population,<sup>16,20–22</sup> at excitation densities below 10<sup>17</sup> cm<sup>-3</sup>. Bimolecular recombination of such photo-generated free carriers leads to photoluminescence close to the band-edge.

Here we outline the theoretical formalism that is currently used to explain the recombination dynamics in these materials and highlight the aspects within the model that have to be fully comprehended with possible refinements. Then, we describe the instabilities observed in PL from these materials subject to various external stimuli and discuss the implications of such results on the

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device stability. Finally we mention the nascent but swiftly growing field of nanostructures made of lead halide perovskites and their defect-free PL dynamics.

## RADIATIVE RECOMBINATION

In the simple case where radiative recombination of electrons and holes is the only recombination mechanism, the general rate equation describing the dynamics of carriers can be written as

$$\frac{dn}{dt} = G - B_{rad}n^2, \quad (1)$$

where  $G$  is the charge photo-generation rate, and  $B_{rad}$  is the bimolecular recombination coefficient. Under steady-state conditions, the carrier evolution can be equated to zero, which leads to a steady-state carrier density of  $n = \sqrt{G/B}$  and a steady-state PL intensity of  $I_{PL} = B_{rad}n^2 = G$ . Since the charge generation rate scales linearly with the intensity of the exciting light, in the pure radiative regime, integrated PL intensity under steady-state also scales linearly with the excitation density. The non-equilibrium PL dynamics under pulsed excitation also show strong intensity dependence owing to the relationship:  $I_{PL}(t) \propto B_{rad}n^2(t) = \frac{B_{rad}n_0^2}{(B_{rad}n_0t+1)^2}$ , where  $n_0$  is the initial excitation density.

$B_{rad}$  is an intrinsic material property that fundamentally dictates the carrier lifetime and thus crucial for the device optimization.<sup>23</sup> Small  $B_{rad}$  would ensure long carrier lifetimes and thus long carrier diffusion lengths enabling effective carrier collection in PV devices. This would also result in substantial steady-state carrier density under illumination that can lead to large open-circuit voltages.<sup>24</sup> One of the most exciting characteristics of the hybrid perovskites, particularly in the case of lead iodides, has been the long carrier diffusion lengths<sup>25-27</sup> as evidenced by the small  $B_{rad}$  that ranges at around  $10^{-9}$ – $10^{-10}$  cm<sup>3</sup> s<sup>-1</sup> with minor variability depending on the processing conditions or the experimental technique employed for the estimation.<sup>16,28-30</sup>

In the case of inorganic semiconductors, as detailed by Roobroeck and Shockley,<sup>31</sup>  $B_{rad}$  can be defined as the ratio  $R_{rad}/n_i^2$  where  $R_{rad}$  is the radiative recombination rate that represents the number of electron-hole recombination events per unit volume and time and is directly proportional to the absorption cross section and the photon density of states; and  $n_i$  is the intrinsic carrier population achieved by thermal excitation above the Fermi-energy. For efficient light harvesting in the PV devices, it is imperative to have high absorption cross sections that automatically results in high radiative rates.  $B_{rad}$  can, on the contrary, be tuned to lower values by controlling the intrinsic carrier concentration. One of the possible ways to achieve it is to design materials with smaller bandgaps. As suggested by Filippetti *et al.*,<sup>23</sup> both  $R_{rad}$  and  $n_i$  increase exponentially with reducing  $E_g$ , but due to the quadratic dependence of the denominator ( $n_i^2$ ), the reduction in the bandgap on the whole results in a smaller value for the bimolecular recombination coefficient leading to longer lifetimes. This is also substantiated by D'Innocenzo *et al.*<sup>32</sup> who attributed the increasing lifetimes observed in films of MAPbI<sub>3</sub> with reducing polycrystallinity to the effective tuning of the bandgap to lower values. In fact, the ideal bandgap of lead iodide perovskites is possibly the primary reason to achieve long diffusion lengths apart from higher spectral sensitivity of the PV cell and large  $V_{oc}$ . These values are strikingly similar to those of GaAs with comparable bandgaps and doping densities, at about  $4 \times 10^{-9}$  cm<sup>3</sup> s<sup>-1</sup>. The remarkable feature of perovskites is that they exhibit some of the characteristics of highly crystalline semiconductors, even though they are solution processed with high degree of polycrystallinity.

Despite the fact that MAPbI<sub>3</sub> shows a similar  $B_{rad}$  to that of GaAs, it exhibits comparatively low carrier mobilities<sup>28,33</sup> ( $\mu = 1$ – $100$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in MAPbI<sub>3</sub>;  $\sim 10^5$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for electrons<sup>34</sup> and  $\sim 800$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for holes<sup>35</sup> in GaAs at room temperature). Often in the case of low mobility semiconductors, Langevin type models are employed to describe the recombination process, in which case  $B_{rad}$  can be written as  $\mu(e/\epsilon_0\epsilon_r)$ <sup>36,37</sup> and can be evaluated as at least four orders of magnitude lower than the experimental value, as discussed by Herz.<sup>30</sup> This apparent disparity calls for a detailed investigation on the mechanism of radiative recombination.

Recently, Zhu and coworkers have observed that acoustic phonon scattering has a primary role in the mobility, thus postulating formation of large polarons in the material.<sup>38,39</sup> They have also suggested that the dynamics of polaron interactions might result in the observed slower recombination rates,<sup>39</sup> though more detailed investigations must be carried out to substantiate such a hypothesis. In a contrasting report, Wright *et al.*<sup>40</sup> have recently postulated that the carrier scattering primarily arises from optical phonons indicating the need for a thorough investigation of the relevance of electron-phonon coupling in the carrier recombination.

The role of dielectric response of the material within the Langevin like formalism is another important concern. The dielectric permittivity in hybrid perovskites shows a strong frequency dependence going from 9 at optical frequencies to about 100 at static conditions.<sup>41</sup> Such large variability induces uncertainty over the choice of the frequency of the dielectric response relevant for coulomb interactions among photo-carriers.<sup>19,42</sup> When the carriers are far apart, all the vibrational/rotational contributions have to be included to the material polarizability in order to reduce the strength of Coulomb interaction, while when they approach each other, the relevant dielectric constant dynamically shifts to that at optical frequencies. Similar ambiguity is also seen in the evaluation of the exciton binding energy. Interestingly, Leijtens *et al.*<sup>43</sup> have observed an increase in the radiative recombination rate under a static electric field, at 170 K, which is accompanied by the alignment and locking of the methyl ammonium cations within the lattice. Due to their dipolar nature, the MA<sup>+</sup> cations contribute strongly to the electrostatic response of the material and thus their relative degree of freedom and disorder can modulate the dielectric response. Any external perturbation that can affect the dipolar alignment can thus strongly affect the recombination rates. Therefore, an additional contribution from the dielectric screening between carriers to the radiative mechanism may not be completely ruled out although with possible deviations from the conventional Langevin like scenario, as suggested in other low-mobility semiconductors.<sup>44,45</sup> Similar modulation of the radiative rates can also be achieved by varying the sample temperature<sup>28</sup> or the microstructure,<sup>32</sup> again suggesting a non-negligible contribution of the dielectric screening to the carrier recombination mechanism.

## TRAP LIMITED RECOMBINATION

Radiative recombination is often hindered by the presence of non-radiative decay channels, either induced by trapping of the photo-generated carriers within intra-gap defect states or by multi-particle Auger-like interactions. While the former is the dominant channel at excitation densities lower than the available defect density, and thus relevant for photovoltaic and LED applications, the latter is the primary limiting mechanism for lasing action at high excitation densities. The trap limited recombination dynamics in hybrid perovskites have been largely described within the simplified Shockley-Read-Hall (SRH) formalism<sup>46</sup> as

$$\frac{dn}{dt} = G - \gamma_t(N_t - n_t)n - B_{rad}n^2, \quad (2)$$

where  $\gamma_t$  is the trapping rate,  $N_t$  is the total trap density, and  $n_t$  is the filled trap density. Within this formalism, the traps are assumed to be deep ( $\gg 25$  meV) within the bandgap such that thermal energy is insufficient to de-trap the carrier. For a better description of the PL dynamics, one must consider the coupled dynamics of carriers and the traps, the latter described by

$$\frac{dn_t}{dt} = \gamma_t(N_t - n_t)n - \gamma_r n_t p, \quad (3)$$

where  $\gamma_r$  represents the non-radiative recombination of the trapped carrier with the hole in the valence band (see Figure 1(a)). It can be shown here that the steady state PL scales as  $I^{3/2}$  with the pump intensity ( $I$ ). Intuitively this implies greater probability of radiative recombination at higher excitation densities due to an increased occupation of the available traps, quenching the trapping rate. This can be experimentally observed as an increase in the relative PL quantum yield with the excitation density, as shown in Figure 1(b), up to an excitation density of  $10^{18}$  cm<sup>-3</sup> where radiative

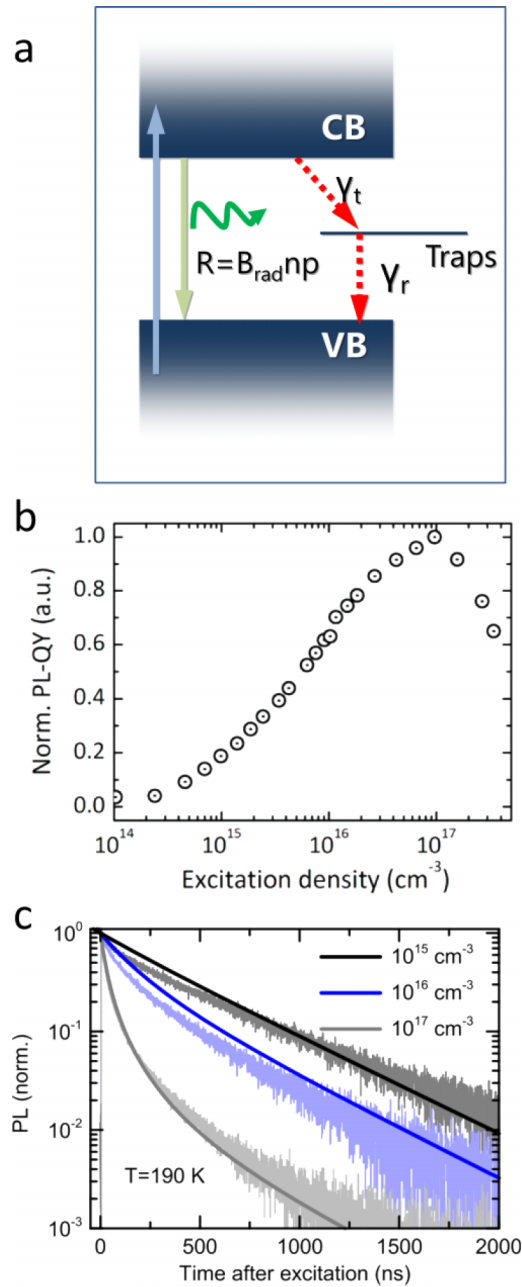


FIG. 1. (a) Schematic of trap limited recombination scenario. VB and CB represent valence and conduction bands. Radiative recombination (represented as  $R$ ) of free carriers leads to PL. The electrons can also be trapped within defects and subsequently recombine non-radiatively with free holes in the VB. (b) Excitation density dependence of the PLQY in MAPbI<sub>3</sub>. (Reproduced with permission from D'Innocenzo *et al.*, *J. Am. Chem. Soc.* **136**, 17730 (2014). Copyright American Chemical Society.) (c) PL dynamics at different excitation densities. (Reproduced with permission from Stranks *et al.*, *Phys. Rev. Appl.* **2**, 034007 (2014). Copyright American Physical Society.)

recombination is the most dominant process and beyond which other higher order non-radiative channels open up.<sup>20</sup>

Under the assumption that the available trap states density is much larger than the excitation density, one can also estimate the effective recombination rate that follows a mono-exponential behavior with minimum intensity dependence<sup>20,21</sup> (see the dynamics at  $10^{15} \text{ cm}^{-3}$  excitation density in Figure 1(c)). When the excitation density becomes comparable to the available trap states

density, the recombination lifetime gets stretched due to the dispersive trapping dynamics,<sup>30</sup> apart from acquiring an intensity dependence due to greater contribution from the radiative recombination dynamics (Figure 1(c)).

Often the carrier dynamics are described by a simple rate equation:  $\frac{dn}{dt} = G - k_1n - k_2n^2$  ( $k_1$  and  $k_2$  are the monomolecular trapping and bimolecular radiative recombination rates, respectively),<sup>22,28,29,32</sup> instead of invoking the complete set of coupled rate equations containing electron, hole, and trap densities as described earlier. Such a simplistic description however assumes deep trapping of the carriers and loss of the trapped carriers due to the non-radiative recombination with the hole immediately after the trapping event. However, given the different nature of defects that the perovskite films are prone to, such formalism may not necessarily be comprehensive enough to describe the recombination dynamics in these materials.

Recent theoretical works have highlighted the peculiar defect physics in hybrid perovskites.<sup>47</sup> The major consensus has been that most of the intrinsic point defects, vacancies (V), interstitials (I), as well as anti-sites, form shallow carrier traps.<sup>47-50</sup> As argued by Yin *et al.*,<sup>47</sup> given the high formation energies for deep trap states, SRH recombination can be ruled out, at least within the context of point defects. However, possible deviations have been pointed out by Du<sup>51</sup> and Agiorgousis *et al.*,<sup>52</sup> induced predominantly due to defects associated with the halogen. In addition, single crystals have shown to exhibit much lower defect densities<sup>53,54</sup> ( $\sim 10^{10} \text{ cm}^{-3}$ ) with respect to the polycrystalline films ( $\sim 10^{16} \text{ cm}^{-3}$ ), suggesting a major role of surfaces and grain boundaries as carrier traps. In such a case with inhomogeneous spatial distribution of defects, diffusion related arguments need to be considered to effectively describe the recombination dynamics. Different fabrication conditions as well as specific precursor chemistry can affect the nature and energetics of the defects, thus preventing the classification of the trap-limited recombination with the standard SRH formalism. Instead, crucial refinements of the model are to be considered by including the presence of shallow defects, surface, and doping effects. Importantly, the trap-limited dynamics need to be always correlated with the fabrication route without generalization of the formalism to the entire hybrid perovskite material library.

PL lifetime is often taken as a standard figure of merit for the optoelectronic efficiency of the material. In fact, long lifetimes are used as indicators for long diffusion lengths, a prerequisite for a good PV material. Whilst this is valid within pure radiative regime, under trap-limited conditions, it is not trivial to directly associate the PL lifetimes to the material quality. As described earlier, the monoexponential lifetime is indicative of carrier trapping, especially at low excitation densities and not necessarily for long diffusion lengths in the material. Thus attention must be paid while using PL dynamics for evaluating material quality or comparing samples. Measurement of intensity dependent PL quantum yields as well as dynamics is absolutely essential to properly assess the regime under which the measurement is performed and thus to correctly interpret the dynamics.

## EXTRINSIC INSTABILITIES IN PL

One of the primary drawbacks of the opto-electronic technologies embodying hybrid perovskites is the device instability, primarily attributed to the diffusion of mobile ions under operating conditions.<sup>11,12,55-59</sup> The effect of such ion diffusion processes has also been observed in photo-luminescence experiments under applied electric field, under light soaking, and under varied atmospheric conditions. Leijtens *et al.*<sup>43</sup> have shown that under static electric field of tens of kV/cm<sup>2</sup> and at low excitation densities where one explores the trap-limited dynamics, the monomolecular PL lifetime increases with electric field (see Figure 2(a)). This suggests a reduction of available trap density that in turn reduces the trapping probability and increases the lifetime. Based on previous works on ion diffusion,<sup>55-57</sup> they have suggested that the mobile ions act as carrier traps and that with electric field, the defects are cleared from the bulk of the film. Upon removal of the electric field, the ions that have accumulated at the electrodes form a strong electric field and collect the photo-generated carriers, followed by non-radiative carrier trapping.

Modulation of PL yields and lifetimes has also been observed by Stranks and co-workers,<sup>60</sup> but under light soaking conditions. They report an activation energy of about  $\sim 200$  meV for the ion diffusion provided by the photo-excitation gradient. The resultant diffusion of ions enables effective

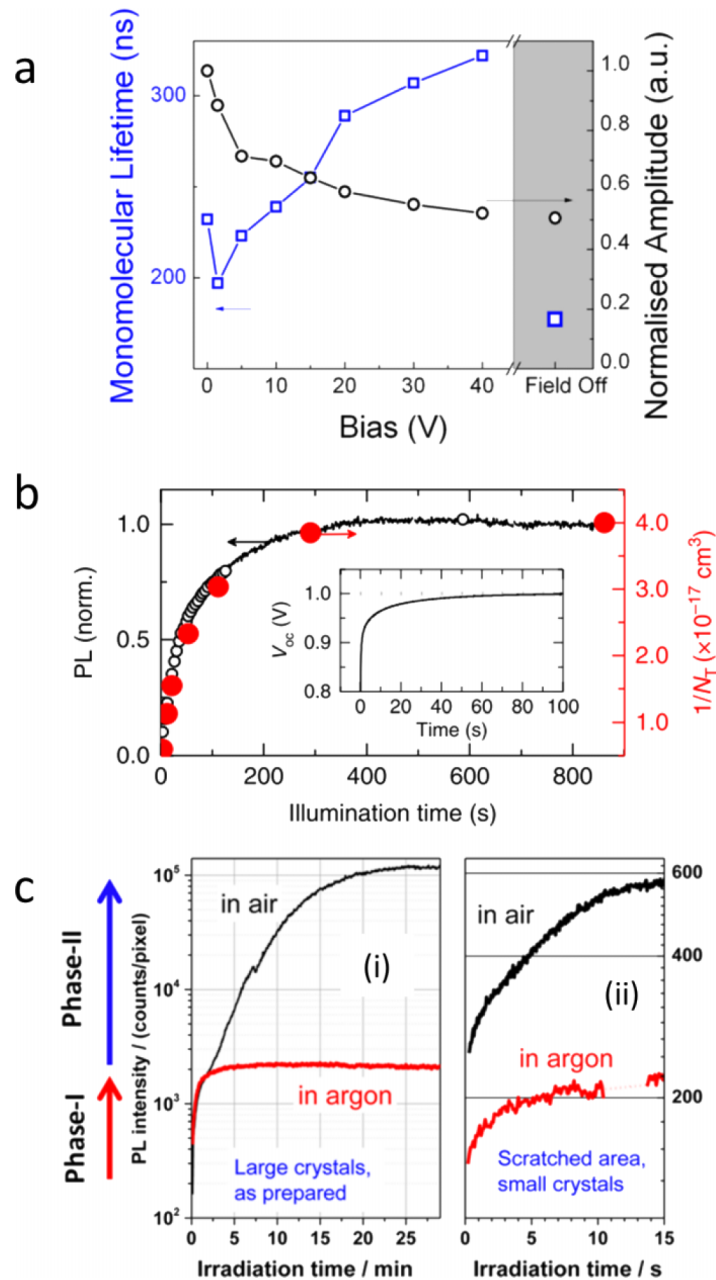


FIG. 2. (a) Monomolecular PL lifetime plotted as a function of applied bias on a MAPbI<sub>3</sub> film, suggesting reduction in trap density induced by ion drift. When the field is switched off, the lifetime reduces due to the opening of the non-radiative quenching at the electrodes due to accumulated ions. Reproduced with permission from Leijtens *et al.*, J. Am. Chem. Soc. **137**, 15451 (2015). Copyright American Chemical Society. (b) Normalized PL intensity and the trap density changing in slow time scales under illumination. Reproduced with permission from DeQuillettes *et al.*, Nat. Commun. **7**, 11683 (2016). Copyright Macmillan Publishers Limited. (c) Enhancement of PL under illumination and in the presence of air and argon. Reproduced with permission from Tian *et al.*, J. Phys. Chem. Lett. **6**, 4171 (2015). Copyright American Chemical Society.

passivation of the defects, thus enhancing the PL from the film in the time scales of seconds under illumination (see Figure 2(b)). Ion diffusion was also proposed by Hoke *et al.*<sup>61</sup> to explain the spectral shift of the PL to lower energies under illumination in the case of mixed halide perovskite films.

Independently, Tian *et al.*<sup>62</sup> have reported both enhancement of PL and increase in the PL lifetimes in MAPbI<sub>3</sub> under illumination consistent with reduction of the trap density. However they see the PL enhancement only in the presence of ambient air (see Figure 2(c)) and have suggested

oxygen induced defect passivation rather than by diffusing ions. In another work,<sup>63</sup> the authors report a dependence of the “light curing” of the defects on the effective size of the crystal with efficient and faster curing in the case of smaller crystallites ( $\sim 100$  nm, see Figure 2(c), (ii)) substantiating the role of oxygen diffusion. Tachikawa *et al.*<sup>64</sup> observe a primary role of surface states in the carrier trapping process, which are effectively passivated by oxygen. In a complete contrast Fang *et al.*<sup>65</sup> attribute the PL enhancement to moisture based on their investigations under various atmospheric conditions, but under UV illumination. They observe a suppression of a residual and defective  $\text{PbI}_2$  phase within the perovskite film in the presence of moisture, which leads to the overall PL enhancement. The varied reported reasons for the PL modulation can partly be related to the distinct fabrication conditions that can strongly influence the nature of the defects and their subsequent passivation/creation mechanisms. Detailed investigations of each of the hypothesized processes have to be performed under systematic variation of the fabrication protocols to fully comprehend and negate or exploit the observed instabilities.

### DEFECT-FREE NANOCRYSTALS

In contrast to the case of thin films and single crystals of perovskites, the effect of defects was shown to be completely absent when they are made as colloidal suspensions. With sizes ranging to about 10 nm and thus reasonably immune to strong quantum confinement effects, Akkerman *et al.*<sup>66</sup> and Yakunin *et al.*<sup>10</sup> have demonstrated that the PLQY can reach as high as 90%. Though the exact reason for the complete quenching of defects in these systems is unknown, it can be tentatively attributed to the more controlled crystallization dynamics in the suspension or to the surface passivation effects.

Akkerman *et al.*<sup>67</sup> have shown in the case of cesium lead bromide ( $\text{CsPbBr}_3$ ) nanocrystals that the PL dynamics are characterized by intensity independent monoexponential lifetimes (Figure 3(a)). This, unlike the cases of thin films and single crystals, suggests pure excitonic emission. The recombination dynamics of the exciton can be described by  $\frac{dn_{exc}}{dt} = G - kn_{exc}$ , which explains both high quantum yields in the absence of non-radiative channels and monoexponential PL decays. The excitonic character of the emission can be attributed to the greater overlap between electron and hole densities within the nanocrystal.<sup>67</sup> Moving from cubic nanocrystals to two dimensional nanosheets with perceivable confinement effects, the authors have observed similar trends of the relative PLQY and lifetimes (Figure 3(a)) with excitation fluence, albeit with lower absolute quantum yields. The reduction of the absolute PLQY can also be seen in the nanocrystals with

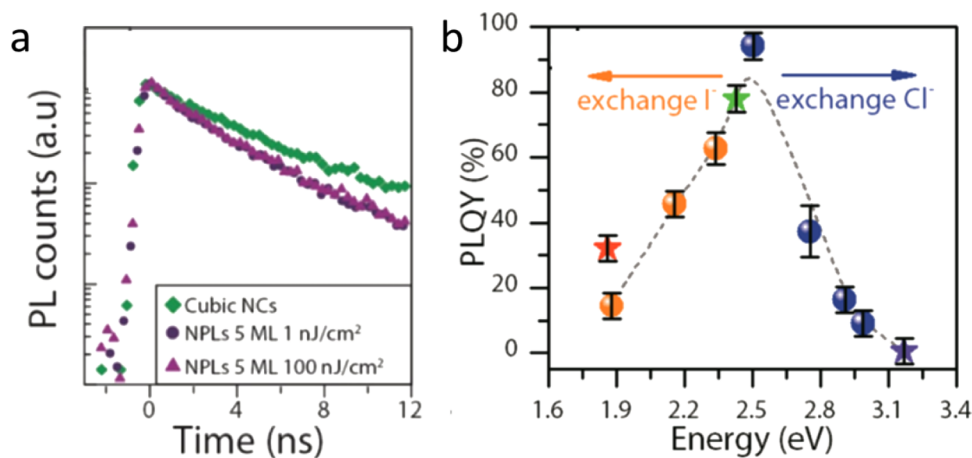


FIG. 3. (a) Intensity independent PL dynamics from colloidal suspensions of  $\text{CsPbBr}_3$  nanocrystals (8.5 nm) and nanosheets with 5 monolayers. Reproduced with permission from Akkerman *et al.*, *J. Am. Chem. Soc.* **138**, 1010 (2016). Copyright American Chemical Society. (b) Absolute PLQY from nanocrystals with different halide stoichiometries and thus different band-gaps. Reproduced with permission from Akkerman *et al.*, *J. Am. Chem. Soc.* **137**, 10276 (2015). Copyright American Chemical Society.



mixed halide composition with the maximum achieved in the case of bromides (Figure 3(c)).<sup>66</sup> The nature of the small but significant non-radiative channel that is modulated either by effective size of the nanocrystal or chemical composition might represent fundamental limitation for the PL yields in these systems and needs to be further investigated.

## COMPETING MECHANISMS FOR LASING ACTION

With reported values for the threshold of amplified spontaneous emission lying at excitation densities greater than  $10^{18} \text{ cm}^{-3}$ , the primary competing channel for the lasing action is the multi-particle Auger like interaction.<sup>8,9,20,68</sup> Auger recombination is a three particle process in which two carriers of the same kind undergo an elastic scattering event resulting in the excitation of one of them to higher energy, and the non-radiative recombination of the other with an available carrier of the opposite sign, thus reducing the density of carrier population available for radiative recombination. In the case of band-like semiconductors, Auger recombination involves either two electrons and one hole or two holes and one electron, thus giving rise to a well-known cubic behavior of the Auger rate:  $R_{Aug} = \gamma_{Auger} n^3$ . The reported value for  $\gamma_{Auger}$  for MAPbI<sub>3</sub> in the literature<sup>20,28</sup> varies around  $10^{-27}$ – $10^{-28} \text{ cm}^6 \text{ s}^{-1}$ . Taking a hint from established quantum well lasers, we recently have proposed a multi-phase architecture within the film to counter the Auger interactions.<sup>69</sup> We have shown in the case of MAPbI<sub>3</sub>, a co-existence of two distinct phases close to the phase transition temperature and an efficient picosecond population transfer from the high energy phase to the low energy one. Importantly, such a transfer enables a spatial redistribution of the carrier population that reduces inter-carrier interaction which results in a reduction of the threshold for amplified spontaneous emission (ASE). While such architecture might provide design principles for achieving cw-lasing with these materials, the specific nature of Auger interactions is yet to be systematically investigated to effectively counter them. More specifically, the effect of the peculiar band structure on the Auger process and the role of defect scattering centers are to be explored.

## SUMMARY AND OUTLOOK

We provided a birds-eye view of the current trends in the luminescence spectroscopy on lead halide perovskites. At the outset, the observed recombination dynamics in PL measurements seem to be well explained within the standard SRH formalism. However, there are some striking deviations that are yet to be fully understood. The nature of the bimolecular radiative recombination process and the role of dielectric response and polaronic effects are yet to be investigated. Being processed from solution, these materials are prone to defects of different nature with each of them having distinct but grave effects on the carrier recombination. Independent experimental determination of the nature and energetics of defects and the assessment of their role in the PL dynamics is to be carried out in conjecture with systematic variation of the fabrication conditions. While ion migration is viewed as the major contributor for the observed instabilities in the PL, the actual mechanism is to be elaborated further. On the other hand, colloidal suspensions of nanocrystals appear to be the route for the fabrication of defect free system, though the origin of other non-radiative channels is to be understood. Whilst lead halide perovskites are also seen as potential candidates for electrically pumped cw-lasers, Auger like population quenching processes pose a major hurdle and are to be systematically addressed.

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