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Enhanced Radiative Recombination of Excitons and Free Charges Due to Local Deformations in the Band Structure of $MAPbBr_3$ Perovskite Crystals

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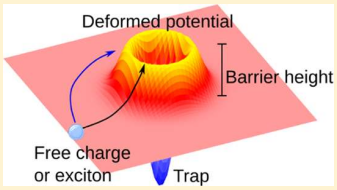
Supporting Information

ABSTRACT: We have imaged the emissions from excitons and free charges in a methylammonium lead bromide perovskite ($MAPbBr_3$) crystal. In a direct band gap semiconductor, dynamics of excited electrons and holes in hybrid lead-halide perovskites is rather complex because of the formation of excitons and the presence of traps and structural inhomogeneities. A recent report by Nah et al. (Nah, S.; Spokoyny, B.; Stoumpos, C.; Soe, C. M. M.; Kanatzidis, M.; Harel, E. *Nat. Photonics* **2017**, *11*, 285−288) has identified spatially segregated populations of excitons and free charges in perovskites. Understanding the cause of segregation and how such distributions contribute to the photoresponse has remained a challenge. Here, we have used phase-modulated two-photon photoluminescence microspectroscopy to separately quantify the emissions from excitons and free charges in a $MAPbBr_3$ crystal. Our results show that while most of the emission at room temperature is from the recombination of free charges, there are also localized spots where the emissions from excitons dominate. By analyzing the enhancement of the emissions at low temperatures, we show that the trap-mediated nonradiative recombinations are suppressed by local deformations in the band structure. The deformations that are induced by local strains in the crystal prevent excitons and free charges from reaching the traps. Our results indicate that strain engineering through structural designs can improve the performance of perovskite light-emitting diodes.



INTRODUCTION

Halide-based organic−inorganic hybrid perovskites have emerged as the most promising photoactive materials for photovoltaics,[1−6] light-emitting devices,[7−11] and optically pumped lasers.[12,13] This noticeable progress is attributed to the excellent optoelectronic properties, such as high absorption coefficients,[14,15] direct band-to-band recombination,[16,17] low exciton binding energies,[18] and attractive charge-transport properties.[19] Among them, bromide-based perovskites have been used in tandem solar cells to efficiently harvest visible light.[20−22] As a mid-band gap semiconductor, they are also suitable for green light-emitting diodes[23−25] and high-performance photodetectors.[26] Optical excitations in perovskites create electrons and holes, which either form bound electron−hole pairs known as excitons or remain as independent, free charges. A higher population of free charges improves the photoconversion efficiency (PCE) in a solar cell. The excitons, on the other hand, lower the PCE but increase the photoluminescence (PL).[27−29] Thus, quantification of the population of excitons and free charges in perovskites is crucial for understanding the bottlenecks in their intrinsic performance in solar cells and light-emitting devices.[30−32]

The PL spectra from different regions in a thin film of $MAPbBr_3$ show large variations owing to the presence of different phases and defects.[18,33] Because the spectra from different phases overlap with the excitonic emission,[18,32,34] a simple spectral imaging cannot be used to quantify the spatial variation of excitons and free charges. Nevertheless, as excitons are highly emissive and have shorter lifetimes compared to free charges, time-resolved PL spectroscopy at different excitation densities has been used to differentiate their populations in $MAPbBr_3$.[27,35] Similarly, pump-probe spectroscopy has been used to locate regions where the excitons are prevalent[36] and for direct visualization of long-range carrier transport in solution-processed $CH_3NH_3PbI_3$ thin films.[37] However, these measurements are time-consuming and impractical for imaging and quantifying the spatial distributions of the different populations.

The exciton and free carriers that coexist within the perovskite films[38,39] can be identified based on their recombination kinetics.[40,41] The recombination of excitons that are directly formed after the excitation follows a monomolecular recombination dynamics where the rate is proportional to the number of paired electrons and holes, $R_{ex} \propto n_e$ or n_h. On the other hand, the recombination of free charges is a bimolecular process in which the rate is proportional to the product of electron and hole populations, $R_{ex} \propto n_e\, n_h$ (see Figure 1a). Here, we have used two-photon excitation with two phase-modulated beams to investigate the different recombination dynamics and quantify the spatial distributions of excitons and free charges. When two beams, whose phases are modulated at frequencies ϕ_1 and ϕ_2, excite a

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