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Light-Induced Defect Healing and Strong Many-Body Interactions in Formamidinium Lead Bromide Perovskite Nanocrystals

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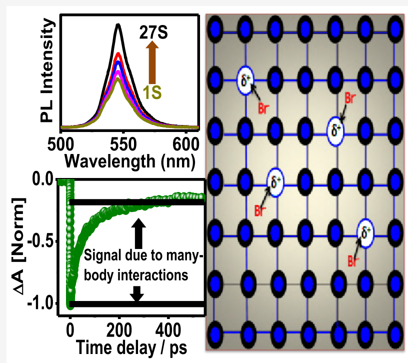
ABSTRACT: Organic lead halide perovskite (OLHP) nanocrystals (NCs) have paved the way to advanced optoelectronic devices through their extraordinary electrical and optical properties. However, understanding of the light-induced complex dynamic phenomena in OLHP NCs remains a subject of debate. Here we used wide field microscopy and time-resolved spectroscopy to correlate the local changes in photophysics and the dynamical behavior of photocarriers. We demonstrate that light-induced brightening of the photoluminescence from the formamidinium lead bromide NC films is related to the film preparation condition and reduction of trap density. The density of trap states is reduced via halide ion migration from interstitial position. Our femtosecond transient absorption study identifies transient Stark effect due to the generation of hot carriers. Because of slow carrier trapping, Auger recombination through many-body carrier−carrier interactions dominates over trion recombination. This work presents unprecedented insights into the light-driven processes enabling better device design in the future.



Organic−inorganic hybrid perovskites have attracted significant attention due to their incredible performance in optoelectronic devices.[1−6] These materials possess favorable properties such as a high absorption coefficient,[7] slow recombination rate,[8−11] direct band-to-band transition,[12,13] long-range diffusion length,[14,15] and high photoluminescence (PL) quantum yield (QY).[16,17] A high PL QY when nonradiative recombination is almost eliminated is particularly important for the development of efficient light-emitting diodes (LEDs).[18] In general, perovskite nanocrystals (NCs) exhibit a high PL QY and a low amplified stimulated emission (ASE) threshold down to 7.5 μJ/cm^2 under femtosecond laser excitation.[16] The reason for the higher PL QY in NCs compared with their bulk counterparts is the formation of bright excitons, which has been explained by the Rashba effect due to the combination of strong spin−orbit coupling and inversion asymmetry.[19] The high exciton binding energy due to the confinement also contributes to the efficient emission. The strain-induced lattice compression and the concurrent reduction of the stereochemical activity of the s^2 lone pair of the Pb^{2+} ion, which results in the enhanced localization of s^2 electron density,[20] are responsible for the high exciton binding energy of perovskite NCs.

The PL intensity of OLHP depends on many factors like the excitation intensity, chemical treatment, and sample preparation technique.[21−24] The method of sample preparation controls the nano- and microstructures of the sample, the surface-to-volume ratio of the material, and the concentration of defects.[1,25] The previous studies on perovskite bulk crystals (BCs) suggested that the concentration of defects can be reduced under light illumination over time, and this reduction corresponds to the healing of defect states due to ion migration from interstitial positions to defect centers.[21,26] Cahen and coworkers reported healing of the photodamaged part in perovskite single crystals and proposed that the self-healing mechanism does not necessarily involve defect or ion migration phenomena.[27] However, the dynamics of photo-brightening in perovskite NCs is not yet fully understood.

Furthermore, the fundamental properties on a short time scale such as fast carrier trapping, corresponding charge-carrier recombination, and many-body interactions should be studied because perovskite NCs are used in light-emitting devices. Among the different NCs, the formamidinium-based $FAPbBr_3$ perovskite NCs show excellent PL properties (QY above 70%) with a low lasing threshold value (>7.5 μJ/cm^2), which makes them a promising candidate for LEDs.[28,29] These crystals exhibit higher thermal stability than the corresponding methylammonium (MA)- and cesium (Cs)-based perovskites.[16] The operational stability and luminescence efficiency of perovskite NC LEDs can be significantly affected by both the dynamical behavior of charge carriers and the ion

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