Changes in generated carrier recombination dynamics upon photodegradation of $MAPbI_3$ perovskite

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Hybrid perovskites are an exemplary material, synthesizable using solution processing methods, only similar in their fabrication to one more group of active media – organic semiconductors. Despite promising parameters, these perovskites suffer from various sources of degradation, such as oxygen [1] and water [2] [3] aided perovskite decomposition and defect formation, impeding the longevity of this class of materials. In particular, the degradation induced by high intensity light is still poorly understood in how it affects the photodynamics of charge carriers (only a few works try systematic investigation, such as [4]). However, light exposure is the factor most straightforward to control (t_{exp}, W etc.) and was chosen for this work.

To study the photoluminescence (PL) properties of the chosen solution processed $MAPbI_3$ multigrain film on a glass substrate, a custom-built photoluminescence microscopy setup [5] was used to measure PLQY(f, P) maps and PL decays. A pulsed 485 nm laser (150ps) was used to excite the sample through an objective lens of a wide-field fluorescence microscope. Five different pulse fluences P were used, ranging from $P_1 = 4.1\cdot10^8$ to $P_5 = 4.9\cdot10^{12}$ photons/cm^2, while the frequency $f \in$ [100Hz, 80MHz]. Employing the modified Shockley-Read-Hall model (SRH+) [5], analysis of the resulting PL decays and PLQY(f, P) maps (dubbed HORSEs) yielded detailed information on perovskite photodynamics through parameters such as defect density and non-fluorescent rates.

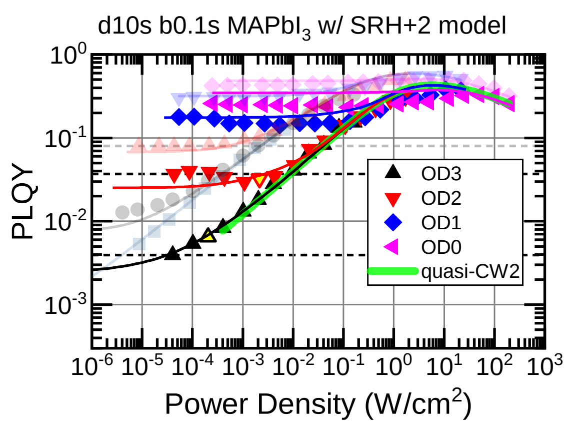

Fig. 1. Photodegraded $MAPbI_3$ PLQY(f, P) map – HORSE, fitted according to SRH+ and compared with a fresh $MAPbI_3$ HORSE.

Investigation of a $MAPbI_3$ film region in the photodegraded state required the use of the programming capabilities of the experimental setup, allowing to repeatedly bleach (for t_{bleach} = 0.1–1s) the initially degraded region (for t_{degr}(80MHz, P_5) = 10, 30s) during the HORSE data sequence or PL decay measurements, to prevent intentionally degraded $MAPbI_3$ dark recovery and photobrightening. Comparing SRH+ model fitting parameters for fresh and photodegraded perovskite region HORSEs, we report an increase in trap-mediated PL loss processes as well as emergence of rapid PL decay components. This points to an appearance of a second type of defects in the $MAPbI_3$ sample after high intensity light exposure. Furthermore, it can be speculated that the temporary induced defects are caused by reversible photochemical reactions within the perovskite at high light intensity and/or photo-assisted ion diffusion, since the timescale for dark recovery ~ 1 min – 10 h, agreeing with ion diffusion lifetimes [6].

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