Carrier Dynamics in Upconverting Thin Film Perovskite/Rubrene Bilayers Studied by Combined Surface Photovoltage and Photoluminescence

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A typical perovskite-driven photon upconverter consists of lead halide perovskite thin film layered with a small molecule semiconductor annihilator, such as rubrene. These systems exhibit triplet-triplet annihilation upconversion from the near-infrared to the visible spectrum, with the perovskite film acting as a triplet sensitizer while the rubrene layer functions as the annihilator and emitter [1, 2]. A key feature of this style of upconverter, which removes the conventional excitonic triplet sensitizer and replaces it with the interface of a bulk semiconductor film, is the conversion of free electrons and holes in the perovskite into strongly-bound electron-hole pairs (i.e. excitons) within the organic annihilator film. The process is an emerging application of lead halide perovskite beyond the photovoltaics space, and is interesting both in a photonics role, and as a fundamental investigation into energy transduction at hybrid semiconductor interfaces.

This study aims to generate new insights into these perovskite upconverter systems using a combination of transient surface photovoltage and photoluminescence methods. Transient surface photovoltage measures the transient electrical polarization across a semiconductor film stack resulting from carrier diffusion, trapping and recombination following excitation by a short laser pulse. As such, it offers insight into the net charge distribution throughout the sample as well as the rates of various carrier transfer and recombination processes. Photoluminescence, conversely, probes specifically radiative carrier recombination in the perovskite layer and, analogously, bright exciton relaxation in the annihilator layer.

We measured density-dependent SPV and photoluminescence transients under similar excitation conditions, allowing us to make a like-for-like comparison of the internal processes telegraphed by both measurements and compare with the performance under steady state excitation. Modifications introduced to the perovskite synthesis allowed us to exert a degree of control over the carrier density throughout the sample stack, and observe the subsequent impacts on the carrier-driven excitonic processes. These modifications yielded an increased upconversion efficiency at high carrier densities compared to a control sample. The results suggest that radiative recombination in the perovskite bulk limits exciton formation efficiency at high carrier densities.

1. Nienhaus, L., et al., *Triplet-Sensitization by Lead Halide Perovskite Thin Films for Near-Infrared-to-Visible Upconversion.* ACS Energy Letters, 2019: p. 888-895.
2. Prashanthan, K., et al., *Interdependence of photon upconversion performance and antisolvent processing in thin-film halide perovskite-sensitized triplet–triplet annihilators.* The Journal of Chemical Physics, 2020. **153**(16): p. 164711.