Tracking Photo-Induced Halide Segregation in Mixed-Halide Perovskite Solar Cells

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Introduction

Organic-inorganic perovskite semiconductors are a promising new material in the world of solar cell technology. Though these materials show promising photoconversion efficiencies (over 29% in perovskite-silicon tandem cells), they present numerous difficulties when facing real-world application. In mixed-halide perovskites, a phenomenon known as halide segregation occurs upon photoexcitation of the material, which can hinder the efficiency of the cell. Here, our lab looks at perovskite samples of various compositions made with the intent of boosting efficiencies and reducing defects that can lead to processes like halide segregation. We hope to use time-resolved terahertz spectroscopy to track electron mobility and lifetime within cells, as well as cathodal luminescence, scanning electron microscopy (SEM), and confocal microscopy to track halide segregation and determine the effectiveness of various defect mitigation techniques.

Halide Segregation as a Process

When charge-carriers are excited by the light absorbed by a solar cell, there is a chance that defects at the material's surface will trap the carriers at energy levels below the conduction band, preventing them from moving freely through the material. An eventual build-up of trapped electrons will generate a charge gradient that drives the migration of negatively charged ions within the material. In a methylammonium lead-based perovskite cell with the composition $CH_3NH_3Pb(Br_xI_{1-x})_3$, a mix of bromide and iodide ions act as the anion in the perovskite crystal structure, with the value of x ranging from 0 to 1. Since iodide ions migrate slower than bromide ions, when a mixed-halide cell experiences a charge gradient, iodide-rich regions will form as bromide ions disperse (Fig. 1). These regions have a higher valence band edge and lower conduction band edge than the general material, so it is energetically favorable for electrons to travel there and recombine non radiatively, meaning they cannot be used to drive a current through the device, cutting back on photoconversion efficiencies.[1]
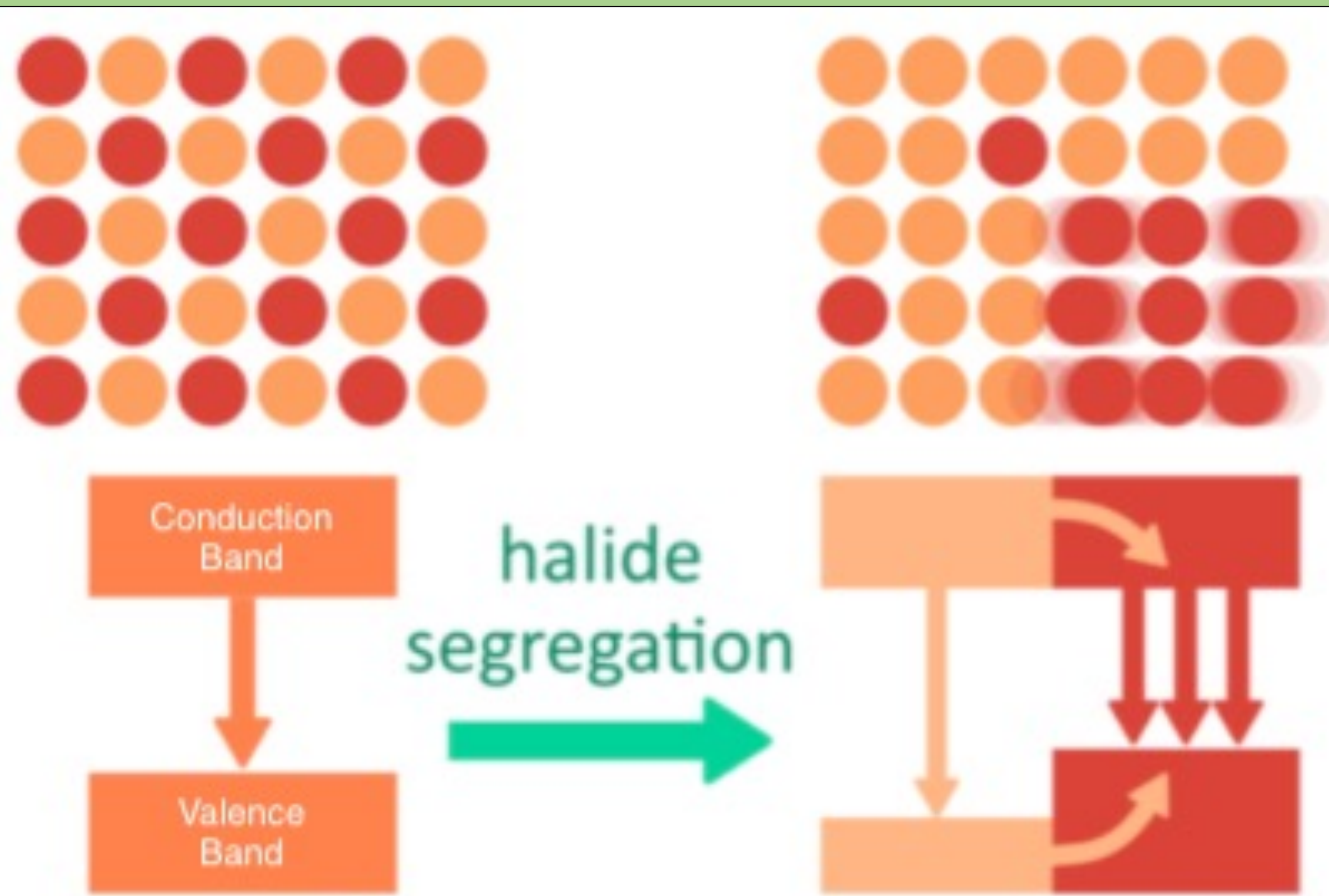

Fig. 1: A smaller bandgap energy in I-rich regions (red) makes the non-radiative recombination of electrons more favorable than staying excited within the conduction band of the perovskite (peach). Figure adapted from Ref. 2.

Time-Resolved Terahertz Spectroscopy (TRTS)

Charge-carrier lifetimes and mobilities are measured using a femtosecond pulse laser. Since lifetime and mobility are both indicators of cell efficiency, we can use TRTS as a means of showing the extent of defects within a material that would lead to halide segregation.
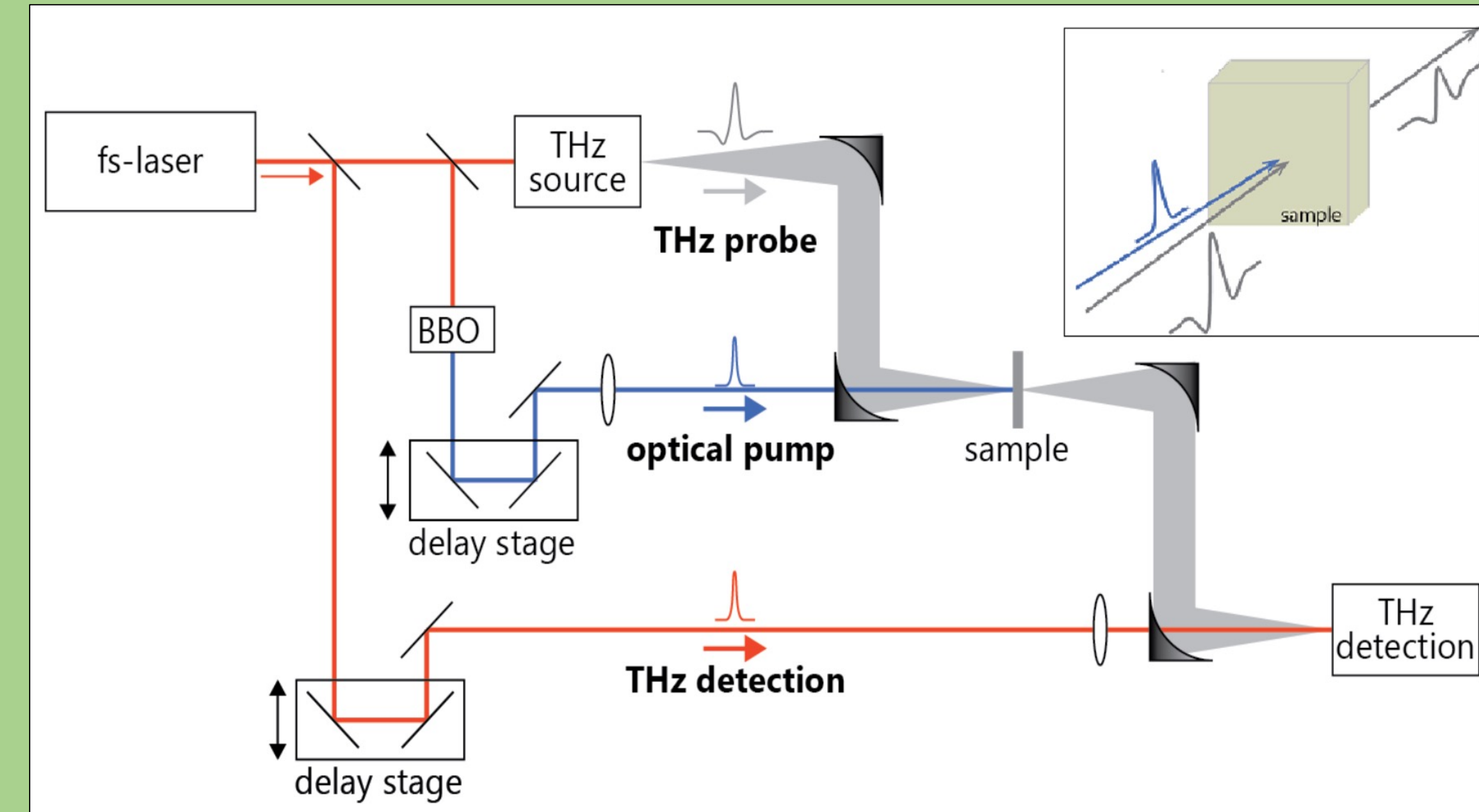

Fig. 2: Our TRTS setup includes a 400 nm pump pulse to excite the solar cell material, a THz probe pulse absorbed by the excited charge carriers, and an 800 nm detection pulse which is polarized to a degree depending on the presence of THz after passing through the sample. Charge carrier mobility is calculated from the amount of THz absorbed by the material, and lifetime from how the THz transmission changes as a function of pump pulse arrival time.

Preliminary Results & Future Work

We've started by testing the material properties of single-halide perovskite samples provided by the Belisle Lab at Wellesley College, which contain only bromide ions and no iodide. Using TRTS and SEM, we were able to capture the electron behavior and crystal structure within a $CH_3NH_3PbBr_3$ sample. We found that the sample exhibited shorter lifetimes under greater pump powers (Fig. 3). We were also able to capture SEM images that show regions of luminescence within the same material (Fig. 4). Our plan for future experimentation is to pair TRTS measurements tracking lifetime and mobility with SEM images tracking luminescent I-rich regions within mixed-halide perovskites. Also, we plan to use confocal microscopy to track the movement of luminescent regions within a cell over time. We hope to reach conclusions about how different chemical compositions and passivation techniques decrease the extent of segregation and increase photoconversion efficiencies.
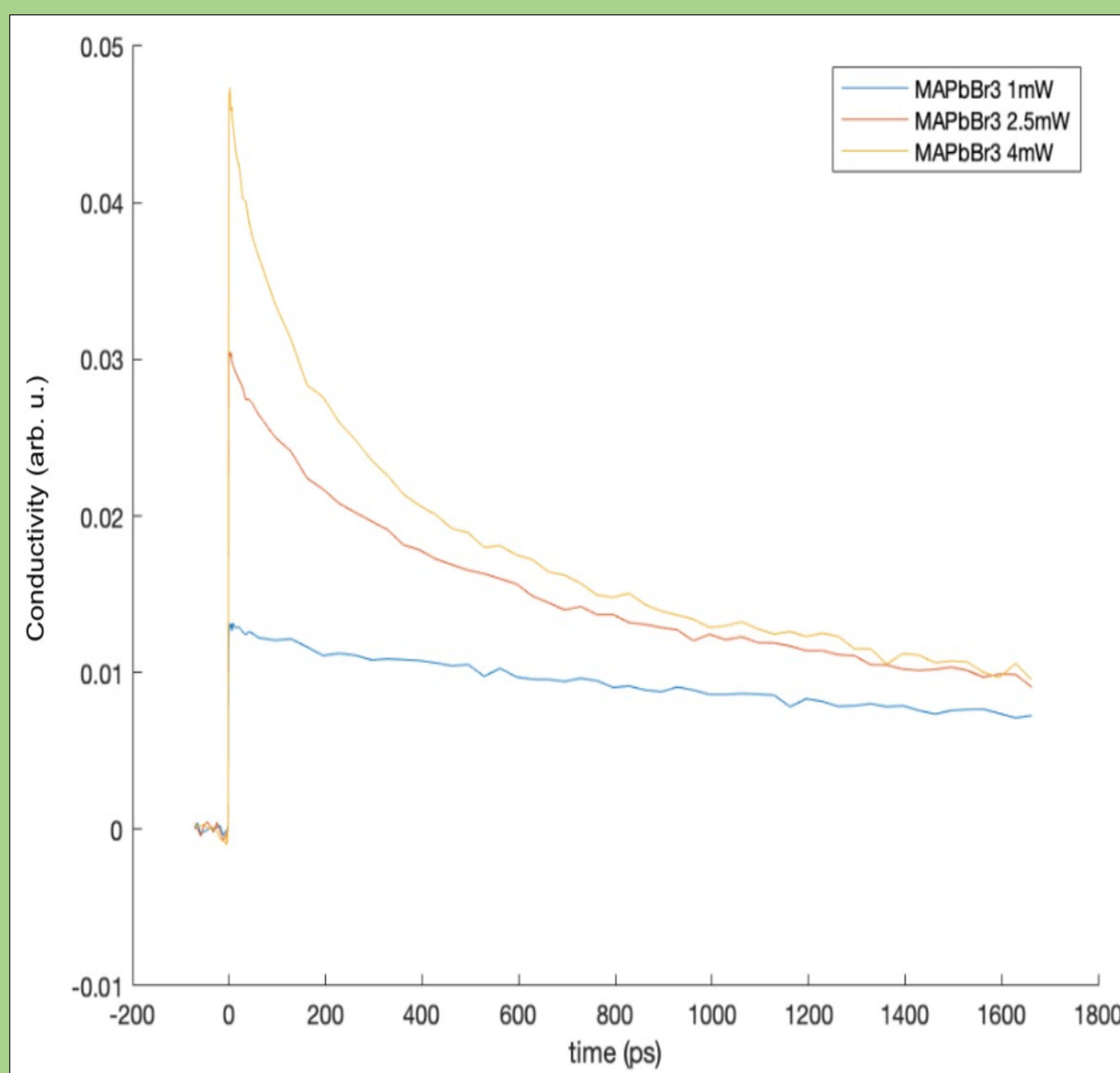

Fig. 3: TRTS data from the same perovskite sample at 3 different pump powers. A more pronounced decay in conductivity over time correlates to a shorter lifetime of excited charge carriers within the material.
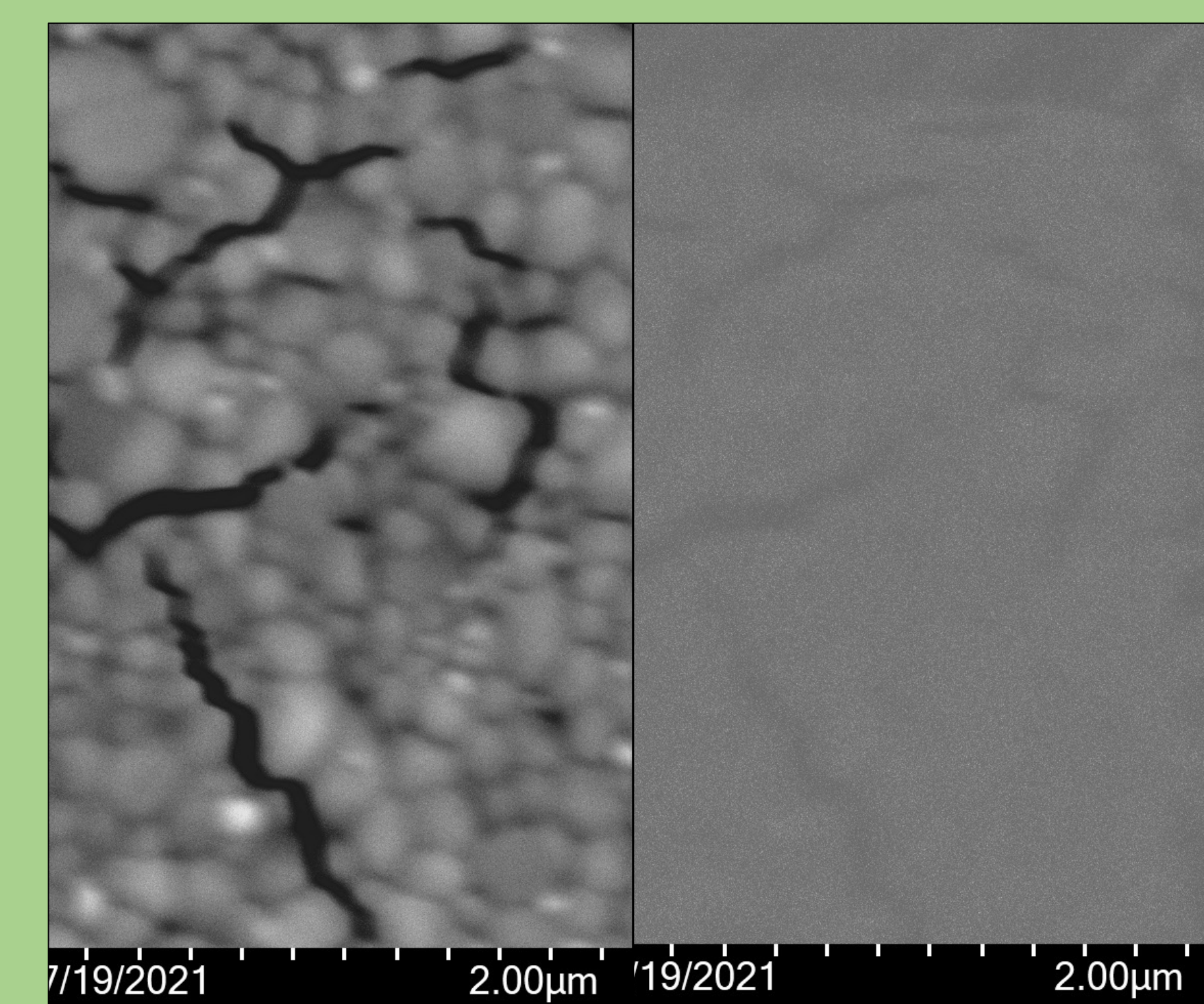

Fig. 4: Standard secondary electron SEM image of a perovskite solar cell (left) with a luminescence image of the same area (right). For a mixed-halide perovskite, SEM imaging can be used to identify I-rich regions that result from photo-induced halide segregation

References

1. R.E. Beal et al., Structural Origins of Light-Induced Phase Segregation in Organic-Inorganic Halide Perovskite Photovoltaic Materials, Matter, 2, 207, (2020)

2. Motti et al., The impact of phase segregation in mixed halide perovskites: a matter of charge recombination rather than transport, Proceedings of 13th Conference on Hybrid and Organic Photovoltaics (HOPV21), 2021