

Photoinduced Transformations in Hybrid Metal Halide Perovskite Nanostructures.

Jacob B. Hoffman, Jara, Seog J. Yoon, M. K. Kuno and **Prashant V. Kamat**

Radiation Laboratory, and Department of Chemistry and Biochemistry

University of Notre Dame, Notre Dame, IN 46556

The simple fabrication techniques and lower carbon footprint makes the organic metal halide perovskite system attractive candidate for designing next generation solar cells. These cells have already delivered solar cell efficiencies greater than 22%. By using transient absorption and emission spectroscopy we have succeeded in elucidating the excited state behavior of $\text{CH}_3\text{NH}_3\text{PbI}_3$ as well as the nature of the charge separation responsible photocurrent generation.

The hybrid perovskite exhibits halide ion composition dependent photochemistry and enables bandgap tuning for selective visible light response. By varying the ratio of Br:I in the mixed halide perovskite ($\text{CH}_3\text{NH}_3\text{PbBr}_x\text{I}_{3-x}$) it was possible to tune the bandgap between 1.55 -2.43 eV. When subjected to visible light irradiation such mixed halide perovskites exhibit migration of halide ions to create iodide-rich and bromide-rich regions. This intriguing aspect of halide ion movement in mixed halide films can be probed through

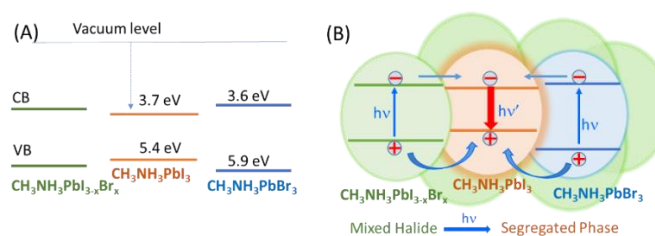


Figure 1. (A) Energy band diagram for mixed halide and phase segregated pairs. (B) Charge separation in phase segregated pairs and transfer of charge carriers to $\text{CH}_3\text{NH}_3\text{PbI}_3$ sites.

emission and transient absorption spectroscopy. These spectroscopy measurements have allowed us to establish the time scale with which such segregation occurs under laser (405 nm, 25 mW/cm^2 –1.7 W/cm^2) irradiation as well as dark recovery. While the phase segregation occurs with a rate constant of 0.1-0.3 s^{-1} , the recovery occurs over a time period of several minutes-hour. The kinetics of the photoinduced segregation and dark recovery becomes slower in halide deficient films suggesting the involvement of halide defects in the phase segregation. The relative photoluminescence quantum yield for I-rich region (em. max. 760 nm) is nearly two orders of magnitude greater than that of Br-rich region (em. max. 530 nm), thus indicating the dominance of I-rich region to serve as charge recombination centers (Figure 1). Understanding such cascading charge transfer from Br-rich region to localized I-rich region is important for designing gradient halide structures in mixed halide systems.

References

1. Manser, J. S.; Saidaminov, M. I.; Christians, J. A.; Bakr, O. M.; Kamat, P. V., Making and Breaking of Lead Halide Perovskites. *Accounts of Chemical Research* **2016**, *49*, 330-338.
2. Manser, J. S.; Christians, J. A.; Kamat, P. V., Intriguing Optoelectronic Properties of Metal Halide Perovskites. *Chem. Rev.* **2016**, *116*, 12956–13008.
3. Yoon, S. J.; Draguta, S.; Manser, J. S.; Sharia, O.; Schneider, W. F.; Kuno, M.; Kamat, P. V., Tracking Iodide and Bromide Ion Segregation in Mixed Halide Lead Perovskites during Photoirradiation. *ACS Energy Letters* **2016**, 290-296.