

## **Establishing microscopic photophysics of local cation and anion phase segregation in hybrid perovskite solar cells**

Dr. Masaru Kuno, University of Notre Dame (Principal Investigator)

Dr. Prashant Kamat, University of Notre Dame (Co-Investigator)

Dr. Luca Gavioli, Università Cattolica (Co-Investigator)

Hybrid perovskites such as MAPbI<sub>3</sub> (MA=CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>) and mixed halide perovskites such as MAPb(I<sub>1-x</sub>Cl<sub>x</sub>)<sub>3</sub> and MAPb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub> represent a potential paradigm shift for creating low-cost solar cells. Intriguing aspects of these materials include large carrier mobilities, large power conversion efficiencies (PCEs), the ability to tune bandgap with halide composition, and the potential to manufacture these materials at low cost.

Despite power conversion efficiencies that now exceed 22%, record PCEs are still far from their theoretical Shockley-Queisser limit of 31%. Hindering the realization of perovskite solar cells are a number of outstanding issues. The first is the lack of microscopic insight into solar cell performance beyond simple device-level metrics such as open circuit voltages ( $V_{oc}$ ), short circuit currents ( $i_{sc}$ ), fill factors (FFs) and PCEs. The fact that hybrid perovskite solar cells are fully solution-processed means that spatial heterogeneities in device performance likely exist. Consequently, it is critical to understand local hybrid perovskite photophysics and their ultimate impact on device performance –for example, to see whether reported PCEs are representative of the cell or if instead they reflect the behavior of a small subregion of the active absorber layer. Doing so requires utilizing spatially-resolved analytical techniques that have heretofore been underdeveloped.

An added hindrance preventing the realization of hybrid perovskite solar cells is their long-term stability. Intrinsic problems exist with hybrid perovskites wherein they undergo dynamic transformations linked to ion migration. Well known hysteretic behavior in MAPbI<sub>3</sub> solar cells is now attributed to both charge and cation migration followed by accumulation at MAPbI<sub>3</sub>/contact interfaces. Anion migration followed by subsequent accumulation at hybrid perovskite/contact interfaces is also suggested to be the source of unwanted charge injection barriers. In mixed halide perovskites, analogous transformations stem from light-induced anion migration.

In this proposal, we therefore seek to conduct detailed measurements that will elucidate and quantify limiting factors of hybrid perovskite solar cell performance, stemming from local electronic disorder linked to cation/anion phase segregation. We will address the origin of local variations in mixed anion/mixed cation perovskite photophysics and will provide quantitative (spatially-resolved) modeling for the fate of photogenerated carriers in working devices. More broadly, we will address how exactly cation and/or anion phase segregation impacts solar cell performance through changes to underlying charge recombination processes. These studies take advantage of recent measurements we have conducted to microscopically establish hybrid perovskite photophysics in thin films and perovskite solar cells. They also take advantage of work we have done to understand the origin of phase segregation in mixed halide perovskites, wherein we have recently developed a model to describe anion phase segregation in MAPb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub> under optical illumination.