

## **NDnano Summer Undergraduate Research 2016 Project Summary**

**1. Student name:** Charles Marchant

**2. Faculty mentor name:** Prof. Prashant V. Kamat

**3. Project title:** The Role of Methylammonium Cations in Perovskite Solar Cells

**4. Briefly describe any new skills you acquired during your summer research:**

Working in a research lab for the first time, I acquired many new skills and techniques. These include how to work in a glove box and how to manufacture solar cells by spin coating solutions onto glass. I also learned about how solar cells work and how to test their performances a lamp and filter to simulate solar light and a potentiostat to measure current and voltage. The experience was a fantastic chance to get to know life in a research environment and helped prepare me for the future.

**5. Briefly share a practical application/end use of your research:**

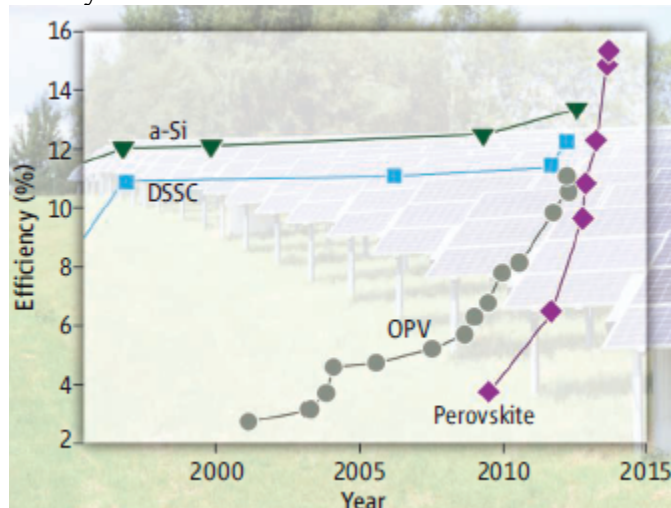
Perovskite solar cells are a promising type of solar cell which has a high rate of light to energy conversion, with a power conversion efficiency only 3% below standard silicon based solar cells in use today. As such it is expected that perovskite solar cells will be available commercially within the next decade. The research I have conducted here at Notre Dame is being continued after my departure.

**Begin two-paragraph project summary here (~ one type-written page) to describe problem and project goal and your activities / results:**

Over the past seven years, perovskite solar cells have emerged as one of the most exciting developments in solar cell technology. Since the first publication on the subject being published in 2009, with a power conversion efficiency of 3.8%, the technology has made a huge advancement, with a record of 22.1% power conversion efficiency being reported earlier in 2016. To put this in perspective, current commercial silicon based solar cells have a record of 25.2% power conversion efficiency, however that technology has been in development since the 1950s. such a large leap in efficiency in such a short time is truly superb.

Despite this, perovskite solar cells face significant challenges to commercial use. Firstly, they exhibit low stability under atmospheric conditions and degrade rapidly in the presence of water. Secondly, there is a lack of understanding of the fundamental processes taking place during the photoconversion process. The project I undertook sought to investigate the role that methylammonium cations play in  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite. This was achieved by varying the amount of methylammonium iodide used in the synthesis of perovskite precursor solutions, and replacing lost iodide using LiI. The two most important findings were that the solar cell performance is affected dramatically by a change in methylammonium concentration, varying by as much as 10% power conversion efficiency, while a sharp increase in emission intensity is observed when the Pb:methylammonium ratio drops below 1:1. One possible reason for this is

that the Li cation from the LiI used to replace iodide is being incorporated into the structure somehow, as a colleague of mine has repeated the experiment without using LiI, removing the increase in emission intensity.



Graph of advancement of different types of solar cells.

**Publications (papers/posters/presentations):**



**The Role of Methylammonium Cations in Perovskite Solar Cells**

Charles Marchant, Anselme Mucunguzi, Prashant V. Kamat  
Dept. of Chemistry and Biochemistry, Radiation Laboratory, and Dept. of Chemical & Biomolecular Engr., University of Notre Dame



### Abstract

Organic inorganic hybrid perovskites emerged as a promising photoconverting material for use in solar cells in 2009, when Kojima et al.<sup>1</sup> fabricated a dye-sensitized perovskite solar cell with 3.8% power conversion efficiency. Since then, peak power conversion efficiency has reached over 20% in a short period of time, a remarkable rise which is hugely promising in the search for a clean, efficient energy source.

Organic inorganic hybrids have the general formula AB<sub>3</sub>X<sub>3</sub>, where A is an organic cation, B is an inorganic cation and X is a halide. Methylammonium lead iodide, CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, is the most commonly used compound in perovskite solar cells. However, so far little is known about the role played by the organic cation CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>. This work attempts to investigate the role of the methylammonium cation by studying the photophysical properties of perovskite thin films with varying stoichiometric amounts of the methylammonium cation and the effect on the performance of perovskite solar cells.

### Absorption and Emission

- UV-Vis absorption and emission data of perovskite films on a micro glass slide.

Figure 2: Optical characterization of prepared samples. (A) Absorption spectra (A) spectra of PL intensity, (B) normalized PL intensity, (C) PL intensity of films.

- Absorption spectra show little change with varying CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>, with only a slight increase in intensity between 600nm and 800 nm for the 1:1:0 sample observed.
- Emission spectra also show increasing intensity of photoluminescence with decreasing CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> for the range of stoichiometries tested.
- No appreciable emission peak shift observed, slight redshift with decreasing CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>.
- By looking at the films, one can see that they all have an identical appearance.

### Solar Cell Performance

PbI <sub>2</sub> :MAI	V <sub>oc</sub>	J <sub>sc</sub>	ff	η
1:1.0	1.03	18.1	0.7	13.1
1:1.1	0.93	6.9	0.48	3.1

Figure 3: (A) Current density vs. voltage of two best performing cells fabricated using 1:1.00 and 1:1.10 ratio of PbI<sub>2</sub>:MAI. (B) Picture of sample cells from front and back. (C) Summary of results from 3 best cells of each ratio: Maximum open-circuit voltage (V<sub>oc</sub>), short-circuit current density (J<sub>sc</sub>), fill factor (ff), and PCE (η).

- Cells were fabricated on FTO (fluorine-doped tin oxide) coated glass with a TiO<sub>2</sub> compact layer, mesoporous TiO<sub>2</sub> electron transfer layer, perovskite layer, spiro-OMeTAD hole transfer layer and gold cathode.
- Perovskite precursor solution was prepared by dissolving PbI<sub>2</sub> and MAI in DMF (1:1 PbI<sub>2</sub>:DMF stoichiometric ratio) and diluting in DMAc.
- Fabricated cells were tested using a Xenon lamp (Power output=0.1mW/cm<sup>2</sup>, average power output from the sun) and a potentiostat to acquire current density vs. voltage plots.
- Fill factor was calculated as  $FF = \frac{V_{oc} J_{sc}}{P_{max}}$ . PCE was calculated as  $PCE = \frac{V_{oc} J_{sc} FF}{P_{in}}$ .
- There was a noticeable decrease in values for all parameters for the cells fabricated using 1:1.10 PbI<sub>2</sub>:MAI.

### Introduction

Figure 1: Diagram of the perovskite crystal structure. (For our purposes, A=CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>, B=Pb<sup>2+</sup>, X=I<sup>-</sup>).

- To probe the role of CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>, the quantity of methylammonium iodide (MAI) has been varied during synthesis of the perovskite precursor solution.
- Ultrahigh iodide was used to replace iodide.
- Synthetic methods developed by the Park group will be used.<sup>21</sup>

### Transient Absorption Spectra

Figure 4: Delayed state properties of prepared perovskite films. (A) to (D) show time-resolved transient absorption spectra of the films with a laser excitation at 380nm and a pump power of 500μW. (E) kinetic profiles of the bleach recovery at 380nm. (F) Arrhenius plot of kinetic profiles of films. Kinetic profiles indicate second order recombination dynamics of the perovskite films.

- Transient Absorption Spectroscopy has been an efficient method to investigate the excited state properties of semiconductors. It uses a pulsed laser (pump) to excite the ground state population, followed by a probe some very short time later to take an absorption spectrum.
- Results are recorded in ΔA, where ΔA=Absorption after probe - Absorption after pump. Higher absorption after probe indicates more species in the ground state at that time, i.e. more charge carriers have recombined.
- All of our samples exhibit similar time-resolved transient absorption spectra, and the kinetic profile of each sample follows second order recombination dynamics. This implies that the mechanism of recombination of charge carriers is the same for each sample.<sup>21</sup>

### Conclusions

- No significant change in absorption was observed, however a reduction in photoluminescence could signify higher quality films.
- Method of recombination of charge carriers appears to be the same for each sample in the range tested.
- V<sub>oc</sub> is not significantly reduced with an increase in MAI, which implies good charge separation. However, the flow of current is significantly impaired, causing low performance.
- Further work is required to explore trap density and grain size, and to collect quantitative data on charge separation and recombination processes.

### Kamat Lab

Visit [KamatLab.com](http://KamatLab.com) to learn more information about our group!

**References**

- [1] Kojima, Y. et al. Nat. Mater. 8, 478-481 (2009).
- [2] Park, N. et al. J. Am. Chem. Soc. 132, 6962-6968 (2010).
- [3] Marchant, C. S., Kamat, P. V. Nature Materials 8, 913-914 (2009).