NDnano Undergraduate Research Fellowship (NURF)  
2015 Project Summary

1. Student name: Tessa Ronan

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

3. Project title: Coordination Chemistry of the CH$_3$NH$_3$PbI$_3$ Perovskite Precursor Solution

4. Briefly describe any new skills you acquired during your summer research: As a physics graduate in a chemistry lab, there are many new skills that I have acquired during my research here. The other postgraduate students working in the lab were very helpful and at hand to show me anything I needed to know. I learned how to calculate and weigh out required volumes and concentrations of solutions as well as how to filter the solutions. I also learned how to deal with any waste in the lab, such as sharps and acids, or any toxic materials. The most useful techniques I learned were coordination chemistry, UV-vis spectroscopy and photolysis. I also learned how to make and test solar cells.

5. Briefly share a practical application/end use of your research: The studies carried out by me will be continued after I leave with the aim to understand the crystallization process of the CH$_3$NH$_3$PbI$_3$ perovskite structure and to subsequently improve the solar cell performance.

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

Metal-halide perovskites are emerging as top contenders for light absorption in solar cell technologies. In the past four years, the perovskite solar cell power conversion efficiencies have risen from 3% to over 20%, indicating their potential to overtake the silicon based solar technologies currently on the market. The perovskite crystal structure is made up of an organic halide cation (A), a metal halide cation (B), and a halide anion (X) in an ABX$_3$ structure. This work focuses primarily on the CH$_3$NH$_3$PbI$_3$ perovskite. The precursor solutions display inverse
solubility in gamma-Butyrolactone, which enables the rapid growth of single crystals. However, their exact growth mechanism from solution is still unknown. Through UV-vis absorption spectroscopy, my aim was to explore the complexation that occurs in CH$_3$NH$_3$PbI$_3$ precursor solutions and what the effect of temperature, stoichiometry, solvent, deaeration, and irradiation has on the crystallization process, and subsequently on the solar cell performance.

By measuring the absorption spectroscopy of the precursor solution at higher temperatures, it was found that increasing temperature weakens the complexation of lead iodide. By varying stoichiometries of iodide to lead, it was found that with excess ligand, the higher coordination complexes of lead iodide dominate. Samples of CH$_3$NH$_3$I were irradiated using a Xenon lamp, in which case the solution turned from clear to yellow to brown over time. Attributing this process to be the dissociation of iodide under UV light, further investigations were carried out on the effect of irradiation on different complexations of iodide and lead iodide. A pre-irradiated precursor CH$_3$NH$_3$PbI$_3$ solution was used in the fabrication of solar cell electrodes. These electrodes had, on average, a higher current density output than the control cells. If consistent, further studies will be required to analysis why, and to investigate what the optimal irradiation parameters will be to potentially improve the CH$_3$NH$_3$PbI$_3$ perovskite solar cell performance.

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Coordinating Chemistry of the CH$_3$NH$_3$PbI$_3$ Perovskite Precursor Solution

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Abstract

The perovskite crystal structure is made up of an organic cation (MA), a metal cation (Pb), and a halide anion (I$^-$) in an 8:1:3 ratio. This work focuses primarily on the CH$_3$NH$_3$PbI$_3$ perovskite. Through UV-visible absorption spectroscopy, this work helps to explore the composition that occurs in CH$_3$NH$_3$PbI$_3$ precursor solutions and how the effect of solution temperature, stoichiometry, and irradiation has on the crystallization process, and subsequently on the solar cell performance.

Introduction

- Metal-halide perovskites are emerging as top candidates for light absorption in solar cell technologies. In the past four years, the possible solar cell power conversion efficiencies have risen from 3% to over 20%, redirecting their potential to overtake the efficiencies based solar technologies currently on the market.
- The perovskite precursor solutions display inverse volatility in comparison to the halides, which inhibits the rapid growth of single crystals. However, their grain growth mechanisms from solution still unknown.

Absorbance Characteristics

- Absorbance spectroscopy shows the species that form in various stoichiometries of halide to lead halide form a similar concentration of 0.2 M.

Compensation in Different Solvents

- The compensation constant, Kc, decreases with the concentration of the halide. The value of Kc was found by increasing the concentration of CH$_3$NH$_3$I while keeping the concentration of CH$_3$NH$_3$PbI$_3$ constant at 0.2 M in DMF and DMSO.

Effect of Irradiation on the Precursor Solution

- Upon irradiation of CH$_3$NH$_3$I in DMF using a xenon lamp at 380 nm, the solution turns from clear to yellow over time. The solution turns to the dissociation of lead halide and the formation of lead halide in higher stoichiometric numbers.

Temperature Effect

- A higher temperature results in a higher concentration of lead halide, which increases the solar cell efficiency. The temperature is measured at room temperature and 300°C, respectively.

Conclusions and Future Work

- For varying compositions, the higher the concentration of lead halide, the higher the efficiency of the solar cell.
- Increasing temperature increases the complexity of the precursor solution.
- CH$_3$NH$_3$I and CH$_3$NH$_3$PbI$_3$ both dissociate upon irradiation in DMF, while CH$_3$NH$_3$I turns from clear to yellow over time. The precursor solution, which is the dissociation of lead halide, increases the efficiency of the solar cell.

The research work is ongoing to investigate further the effect of irradiation on the composition and lead halide in different solvents.

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