

EILERS GRADUATE STUDENT FELLOWSHIP FINAL REPORT

EILERS FELLOW:	Rebecca Scheidt
FACULTY ADVISOR:	Prashant Kamat
REPORT PERIOD:	January 2018 – December 2018
PROJECT TITLE:	Charge Carrier Migration and Halide Ion Movement in All-Inorganic Perovskite Films for Photovoltaic Applications And Interfacial Charge Transfer between Excited CsPbBr ₃ Nanocrystals and TiO ₂ : Charge Injection versus Photodegradation
CONNECTION TO ND ENERGY'S RESEARCH AREAS (CHECK ALL THAT APPLY):	<input checked="" type="checkbox"/> Energy Conversion and Efficiency <input type="checkbox"/> Sustainable and Secure Nuclear <input type="checkbox"/> Smart Storage and Distribution <input checked="" type="checkbox"/> Transformation Solar <input type="checkbox"/> Sustainable Bio/Fossil Fuels <input type="checkbox"/> Transformative Wind

MAJOR GOALS AND ACCOMPLISHMENTS:

List your major research goals and provide a brief description of your accomplishments (1-2 sentences). Indicate the percentage completed for each goal. Please use a separate sheet to share additional details, technical results, charts, and graphics.

MAJOR RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Study gradient perovskite film stability under heat both optically and physically	The heat induced effects on the stability of gradient anion perovskite films was studied using <i>in situ</i> absorbance spectroscopy. Various temperatures were employed in order to find a relationship between heat and homogenization of the films which was then used to find the energy of activation of halide ion movement throughout the film.	85%
Study gradient perovskite film stability under irradiation both optically and physically	Irradiation induced effects have been widely reported in perovskite materials. Elucidating the effect of irradiation on the stability of gradient halide ion perovskites was completed by irradiating films with different white light power densities and using <i>in situ</i> UV-Vis absorbance spectroscopy.	30%
Elucidate the interfacial interactions between excited CsPbBr ₃ nanocrystals and TiO ₂	Interfacial electron transfer between excited CsPbBr ₃ perovskite nanocrystals and metal oxide electron transport layers was elucidated using transient absorption spectroscopy. Atmospheric effects on the system was also studied and it was found that atmospheric oxygen acts as an electron scavenger, leading to perovskite degradation	100%

RESEARCH OUTPUT:

Please provide detailed information below regarding any output resulting from your research project.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS	
EXTERNAL AWARDS	
JOURNAL ARTICLES	"Interfacial Charge Transfer between Excited CsPbBr ₃ Nanocrystals and TiO ₂ : Charge Injection versus Photodegradation"; Scheidt, R. A., Kerns, E., Kamat, P. V.; <i>Journal of Physical Chemistry Letters</i> ; 2018 , 9 (20), pp 5962-5969
BOOKS AND CHAPTERS	
PUBLIC PRESENTATIONS, SEMINARS, LECTURES	
AWARDS, PRIZES, RECOGNITIONS	
INTERNAL COLLABORATIONS FOSTERED	
EXTERNAL COLLABORATIONS FOSTERED	

WEBSITE(S) FEATURING RESEARCH PROJECT	
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	https://pubs.acs.org/doi/suppl/10.1021/acs.jpcllett.8b02690/suppl_file/jz8b02690_liveslides.mp4 (Live Slides audio/visual presentation discussing a summary of the project)

MAJOR GOALS AND ACCOMPLISHMENTS

Gradient halide ion perovskite films show promise as a material to be utilized in tandem photovoltaic devices that can maximize light collection efficiency. In order to elucidate whether devices of this materials are feasible, their stability under operating conditions must be assessed.

One strain on the material comes from the elevated temperatures associated with operating conditions. In order to study this effect, gradient perovskite films were subjected to heat while *in situ* UV-Vis absorbance measurements were taken throughout the annealing process. Optically probing the films with UV-Vis absorbance spectroscopy is a facile method to study the internal structure of the film since film absorbance acts as a spectral fingerprint.

It was found that gradient perovskites films homogenize to form mixed halide perovskites. Additionally, it was observed that the rate of homogenization was temperature dependent, with high temperatures completing the annealing process much faster than room temperature. This relationship is known as an Arrhenius relationship. Using the Arrhenius equation, which relates the rate of change of concentration of a species to temperature, the energy of activation can easily be found. It was found that the energy of activation for halide ions to move through a CsPbX₃ film is 74.5 kJ/mol.

HOMO PIC PLUS ARRHENIUS PLOT

Progress was also made in physically quantifying the movement of the anions using physical characterization techniques. Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) allows for the relative amounts of elemental species to be found in different regions of a material. The first steps in using this technique to find the elemental composition of gradient films at various points during the annealing process has begun. Future work will finish these measurements at the intermediate time points and find a suitable model to describe the diffusion of halide ions throughout the film.

Heat is not the only strain perovskites undergo during operating conditions. Irradiation has also been widely reported to cause the segregation of halide ions throughout mixed halide perovskite films. Using this information, it was postulated that irradiation can cause segregation in gradient halide perovskite films, allowing the material to maintain stability in operating conditions.

By irradiating gradient perovskite films and taking *in situ* UV-Vis absorbance measurements, the stability of the gradient film can be assessed. This work has already shown the effect of white light irradiation (of varying power densities) on gradient halide perovskite films. This light allows for the gradient structure to be maintained over time. Further studies are needed to look at below band gap excitation (preferentially exciting the materials with monochromatic light) as well the physical studies discussed above.

LIGHT OVER TIME GRAPH

Finally, a separate project was begun and completed with money from the Eilers Fellowship. Metal oxide electron transport layers are used in the most efficient solar cells. Despite the extensive use of these metal oxides (MOs), the interaction between (MOs) and perovskites has not been fully explored. Semiconducting MOs such as TiO₂, SnO₂, and ZnO are excellent photocatalysts that can initiate the degradation of adsorbed molecules. The obvious question is whether such sensitized degradation prevails in the case of perovskite nanocrystals deposited on semiconducting oxides.

To investigate the role of the metal oxide substrate on the photostability of perovskite layers, we have probed the interfacial charge-transfer processes using transient absorption spectroscopy. We have also studied the effect of environmental conditions and concluded that atmospheric oxygen scavenges excited state electrons from the CsPbBr₃/MO system, inducing anodic corrosion. We have identified PbO as the major photodegraded product. The importance of surrounding atmosphere and the supporting metal oxide in governing the stability of perovskite nanocrystals was discussed.

For relevant data please find the attached published article that this research yielded.