EILERS GRADUATE STUDENT FELLOWSHIP
FINAL REPORT

EILERS FELLOW:	Anthony Kipkorir
FACULTY ADVISOR:	Prashant Kamat
REPORT PERIOD:	Jan 2022 – Dec 2022
PROJECT TITLE:	Photoinduced Electron Transfer Across Polymer-Capped $CsPbBr_3$ Interface in Polar Medium
CONNECTION TO ND ENERGY'S RESEARCH AREAS (CHECK ALL THAT APPLY):	**(x) Energy Conversion and Efficiency ( ) Sustainable and Secure Nuclear ( ) Smart Storage and Distribution (x) Transformation Solar ( ) Sustainable Bio/Fossil Fuels ( ) 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
Design $CsPbBr_3$ nanocrystals that are tolerant to polar solvents	Managed to collaborate with another group working on polymers to design a polymer for passivating the surfaces of the nanocrystals.	100%
Study electron transfer mechanisms	Utilized ultrafast transient absorption spectroscopy and stead-state photolysis to characterize forward and back electron transfer processes.	100%
Write and submit a paper to peer-reviewed journal.	The experiments were concluded, and the article was drafted and submitted. It is currently under review by Journal of Chemical Physics (JCP).	90%

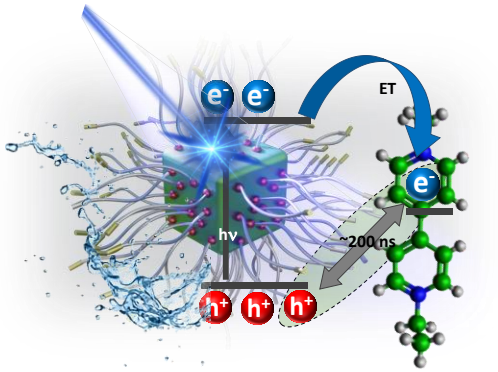
RESEARCH OUTPUT:
Please provide detailed information below regarding any output resulting from your research project.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS	(Sponsor, Project Title, PIs, Submission Date, Proposal Amount)
EXTERNAL AWARDS	(Sponsor, Project Title, PIs, Award Date, Award Amount)
JOURNAL ARTICLES	(Journal Name, Title, Authors, Submission Date, Publication Date, Volume #, Page #s) Journal of Chemical Physics, Photoinduced Electron Transfer Across Polymer-Capped $CsPbBr_3$ Interface in Polar Medium, Anthony Kipkorir, Xiuyu Jin, Haifeng Gao and Prashant V. Kamat, Jan 27, 2023, Under review
BOOKS AND CHAPTERS	(Book Title, Chapter Title, Authors, Submission Date, Publication Date, Volume #, Page #s)
PUBLIC PRESENTATIONS, SEMINARS, LECTURES	(Event, Presentation Title, Presentation Date, Location)
AWARDS, PRIZES, RECOGNITIONS	(Purpose, Title, Date Received)
INTERNAL COLLABORATIONS FOSTERED	(Collaborator Name, Organization, Purpose of Affiliation) Xiuyu Jin and Haifeng Gao, Gao Lab, to utilize the polymer synthesized by their lab to passivate/cap the nanocrystal surfaces.
EXTERNAL COLLABORATIONS FOSTERED	(Collaborator Name, Organization, Purpose of Affiliation)

WEBSITE(S) FEATURING RESEARCH PROJECT	(URL)
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	(Please describe each item in detail)

MAJOR GOALS AND ACCOMPLISHMENTS
(Additional Details, Technical Results, Charts and Graphics)

In-situ polymer capping of cesium lead bromide ($CsPbBr_3$) nanocrystals with polymethyl acrylate (PMA) is an effective approach to improve the stability of the nanocrystal in polar medium. This polymer capping extends the application of $CsPbBr_3$ in photocatalysis in otherwise 'harsh' polar environments (Fig. 1). The photoinduced electron transfer properties of PMA-capped $CsPbBr_3$ nanocrystals were probed using surface bound viologen molecules with different alkyl chains as redox-couples (Scheme 1). The apparent association constant (K_{app}) obtained for the binding of viologen molecules with PMA-capped $CsPbBr_3$ was 2.3×10^7 M^{-1}. This value is an order of magnitude greater than that obtained with oleic acid/oleylamine-capped $CsPbBr_3$. Although the length of the alkyl chain of the viologen molecule did not show any impact on the electron transfer rate constant, it influenced the charge separation efficiency and net electron transfer quantum yield. Viologen moieties with shorter alkyl chain length exhibited charge separation efficiency of 72% as compared to 50% for the longer chain alkyl chain length viologens.



Scheme 1. Photoinduced electron transfer between PMA-capped CsPbBr3 nanocrystals and viologen.

The key take home was that in photocatalytic studies it is not sufficient to demonstrate just the forward electron transfer. It is equally important to estimate various back electron transfer steps that ultimately determine the effectiveness of a photocatalyst for photoinduced electron transfer (Scheme 2).

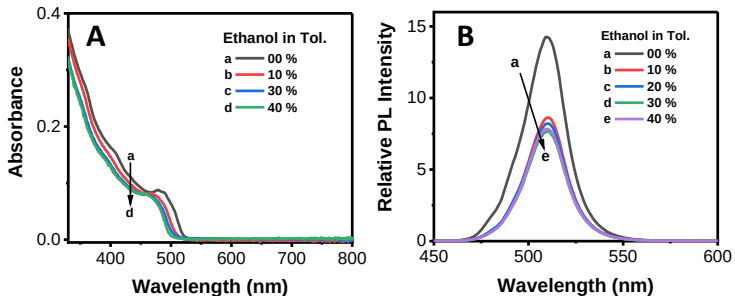
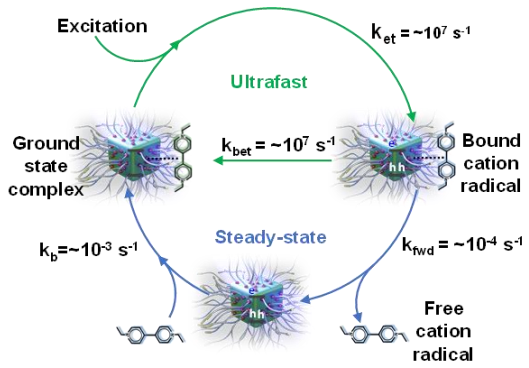


Figure 1. (A) Absorption spectra of PMA-capped $CsPbBr_3$ nanocrystals in different ratios of toluene/ethanol. (B) Changes in emission intensity of the PMA-capped $CsPbBr_3$ nanocrystals as a function of increasing ethanol percentage in toluene. No significant change in absorbance seen at higher concentration of ethanol confirms the protection provided by PMA capping in a medium with increased polarity.



Scheme 2. Summary of electron transfer events between PMA-capped $CsPbBr_3$ and viologen in ultrafast spectroscopy and steady-state photolysis.