FORGASH STUDENT FELLOWSHIP
FINAL REPORT

FORGASH SCHOLAR:	Jishnudas Chakkamalayath
FACULTY ADVISOR:	Dr. Prashant Kamat
REPORT PERIOD:	CY 2022
PROJECT TITLE:	Interfacial Processes in Perovskite-Metal Hybrid Structure for Photocatalytic Applications
CONNECTION TO ND ENERGY'S RESEARCH AREAS (CHECK ALL THAT APPLY):	**(✓) Energy Conversion and Efficiency** **( ) Sustainable and Secure Nuclear** **( ) Smart Storage and Distribution** **(✓) 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
Cascading energy transfer in lead halide perovskite-molecular hybrid assemblies	We demonstrated the energy flow in perovskite-molecular assemblies occurs through singlet energy transfer event, which opens new doors for photon upconversion in these systems. Further studies to be done to hamper singlet energy transfer and force the perovskite to sensitize triplet state of the chromophore.	40%
Transient chemistry of organic dyes	We elucidated the excited and transient features of the organic dyes rubrene and DBP using pulse radiolysis which is crucial for understanding the mechanisms of photon upconversion systems. This research led to the publications in *The Journal of Physical Chemistry A*	100%
Investigate the interfacial processes in perovskite-metal hybrid structure	We demonstrated that the metal nanoparticles are efficient in capturing and storing photogenerated electrons from the semiconductor but the accumulation of electrons caused ejection and aggregation of metal nanoparticles from the surface of semiconductor. Design of stable semiconductor- metal hybrid structure is still a challenge. This research led to the publications in *The Journal of Physical Chemistry C* and *The Journal of Physical Chemistry Letters*	75%
Elucidating the stability of 2D/3D interface of metal halide perovskites	We probed the light and heat induced changes in 2D/3D interface and found the migration of organic cations from 2D to 3D phase proving the increased stability is due to the reformed phase through not the 2D/3D interface. This research led to the publications in *ACS Energy Letters*	95%

RESEARCH OUTPUT:

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

CATEGORY	INFORMATION
EXTERNAL PROPOSALS	N/A
EXTERNAL AWARDS	N/A
JOURNAL ARTICLES	• Chakkamalayath, J., Hiott, N., & Kamat, P. V. (**2022**). How Stable Is the 2D/3D Interface of Metal Halide Perovskite under Light and Heat?. ACS Energy Letters, 8, 169-171. • Chakkamalayath, J., Szabó, G., DuBose, J. T., & Kamat, P. V. (**2022**). Excited State and Transient Chemistry of a Perylene Derivative (DBP). An Untold Story. The Journal of Physical Chemistry A. • DuBose, J. T., Szabó, G., Chakkamalayath, J., & Kamat, P. V. (**2022**). Excited-State Transient Chemistry of Rubrene: A Whole Story. The Journal of Physical Chemistry A, 126(40), 7147-7158. • Jin, X., Ma, K., Chakkamalayath, J., Morsby, J., & Gao, H. (**2022**). In situ photocatalyzed polymerization to stabilize perovskite nanocrystals in protic solvents. ACS Energy Letters, 7(2), 610-616. • Chakkamalayath, J., Hartland, G. V., & Kamat, P. V. (**2022**). Photoinduced Transformation of $Cs_2Au_2Br_6$ into $CsPbBr_3$ Nanocrystals. The Journal of Physical Chemistry Letters, 13(13), 2921-2927.

BOOKS AND CHAPTERS	N/A
PUBLIC PRESENTATIONS, SEMINARS, LECTURES	Jishnudas Chakkamalayath, Prashant V. Kamat Energy Cascading from Perovskite Nanocrystals ND Energy Post-Doctoral & Graduate Student Luncheon, September 21, 2022 Jishnudas Chakkamalayath, Prashant V. Kamat Cascading Energy Transfer in Lead Halide Perovskite-Molecular Hybrid Assemblies PINDU Conference, November 12, 2022 Jishnudas Chakkamalayath, Prashant V. Kamat Dynamic nature of Au within the halide perovskite lattice ACS Fall Meeting, August 21-22, 2022 Jishnudas Chakkamalayath, Prashant V. Kamat Dynamic nature of Au within the halide perovskite lattice 5th Annual ND Energy Research Symposium, March 31, 2022
AWARDS, PRIZES, RECOGNITIONS	N/A
INTERNAL COLLABORATIONS FOSTERED	N/A
EXTERNAL COLLABORATIONS FOSTERED	N/A
WEBSITE(S) FEATURING RESEARCH PROJECT	N/A
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	N/A

MAJOR GOALS AND ACCOMPLISHMENTS

In recent years, significant research effort has been expended on funneling energy from semiconductor nanocrystals to sensitizing dyes by designing hybrid assemblies that can capture photons over a wide range of visible and near-infrared region. A significant advancement in the field is tailoring such assemblies to initiate nonlinear optoelectronic processes like triplet-triplet annihilation (TTA) and singlet fission (SF) which theoretically overcome the limitation of power conversion efficiency in conventional photovoltaic devices.

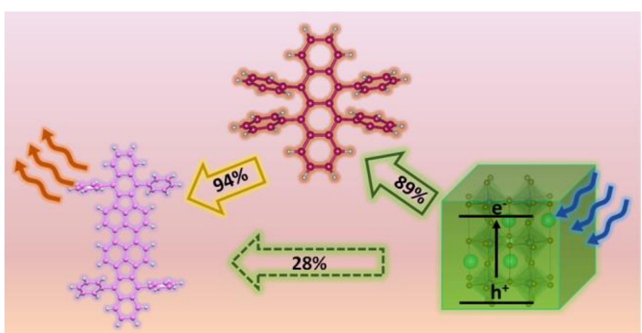

Figure 1. Scheme showing energy transfer from perovskite nanocrystals to rubrene and then to DBP. The efficiency of energy transfer are also noted. The direct energy transfer between perovskite and DBP has very low efficiency.

Lead halide perovskites are a new class of synthetic material that have only been studied for solar applications within the last decade. Their inexpensive and low temperature processing, high efficiency, and ease of incorporation into existing technologies make them one of the most promising and exciting materials for solar energy conversion. With the support of the *The Forgash Fellowship for Solar Energy Research* we were able to investigate the use of perovskites as the sensitizer, and rubrene and perylene derivative (DBP) as the sensitizing molecules (Figure 1).

We demonstrated singlet energy transfer at the perovskite nanocrystal-rubrene interface and rubrene-DBP interface. The favorable energetics in these systems resulted in the cascading singlet energy transfer. The intimate knowledge of transients of the species employed is crucial in understanding the mechanism of energy transfer. We elucidated the spectral features of singlet, triplet, radical cation, and radical anion of rubrene and DBP and they show fingerprint characteristics that can be resolved spectroscopically. The primary results from the study about the dyes have been published in *The Journal of Physical Chemistry A*.

In general, the mechanistic insights gained from this research will help scientists and engineers utilize perovskites in a variety of renewable energy-related applications. This will undoubtedly open up new avenues for photon upconversion, photocatalysis, and possibly biomedical imaging.