Collaborative Research: A Blueprint for Photocatalytic Water Splitting: Mapping Multidimensional Compositional Space to Simultaneously Optimize Thermodynamics and Kinetics

David Watson, University at Buffalo; Sarbajit Banerjee, Texas A&M University; Louis Piper, Binghamton University

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DMREF/EMN Kick-Off Meeting

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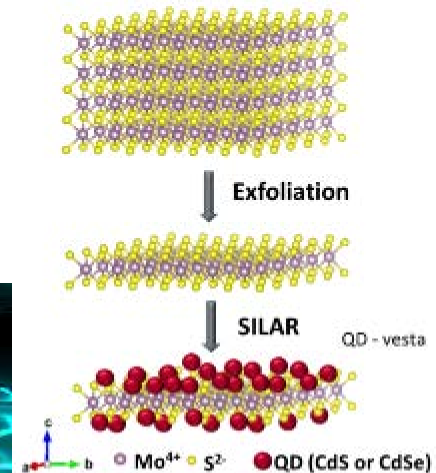
Collaborative Research: A Blueprint for Photocatalytic Water Splitting: Mapping Multidimensional Compositional Space to Simultaneously Optimize

Award #	**Supplements to DMREF #: 1626967, 1627197, 1627583**
Year 1 Funding	$100K

PI's: Sarbajit Banerjee, Louis Piper, David Watson
Partners: Lawrence Berkeley National Laboratory

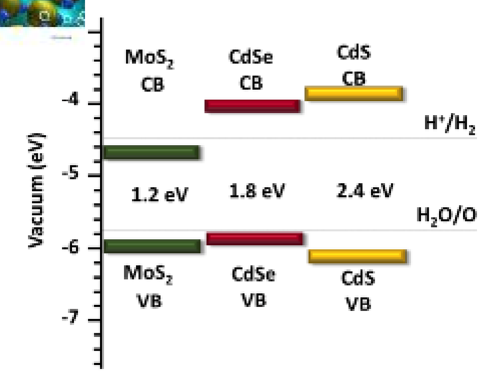
Project Vision

In our collaboration with HydroGEN partners, we will engineer improved hydrogen evolution by tethering MoS_2 nanosheets to II-VI quantum dot solar harvesters of our rationally-designed photocatalysts. This project will combine expertise in synthesis, computational modeling, and sophisticated *in-situ* x-ray spectroscopy to accelerate our understanding of this promising class of ternary photocatalysts



Project Impact

In two generations of catalyst development within our DMREF project, we've arrived upon high-performance binary hetero-structured catalysts for photocatalytic water splitting. We have also separately identified active edge sites of MoS_2 thought to mediate hydrogen evolution. The proposed effort with HydroGEN will rapidly accelerate our progress to commercially viable earth-abundant catalysts for hydrogen evolution by providing an additional interface to optimize.



Innovation and Objectives

Project history

The team developed a topochemical "etch-a-sketch" intercalation approach for facile installation of p-block cations in metastable polymorphs of V_2O_5 nanowires. This prompted our teams' novel hypothesis that mid-gap states in the nanowires could be rationally tuned to facilitate charge extraction from attached photoactive II-VI quantum dots (QDs), thereby separating photogenerated charges and minimizing photoanodic corrosion. High-throughput synthesis and characterization in conjunction with machine learning have enabled rapid screening of material compositions, recently resulting in β-$Sn_xV_2O_5$/CdSe architectures capable of efficacious hydrogen evolution. Further enhancement is anticipated by tethering MoS_2 nanosheets to the QDs.

Proposed targets

Metric	State of the Art	Proposed
Dynamics of charge extraction from light-harvesting QDs	*<1 ps*	*<100 fs*
Faradaic efficiency and longevity of photocatalytic hydrogen evolution	*>80%; >10 h*	*>95%; >100 h*
Solar-to-hydrogen conversion efficiency in a single junction device	*<3%*	*3-5%*

Barriers

- *in-situ* measurements of the photo-catalysts
- Interpretation of *in-situ* spectra
- Mitigation of deleterious recombination and photoanodic corrosion pathways
- Effective utilization of entire solar spectrum

Partnerships

We have identified partnerships at LBNL, specifically:

- Dr Guo (ALS) is an expert in in-situ x-ray spectroscopy of catalysts
- Dr Prendergast (Molecular Foundry) is an expert in x-ray simulation
- providing the expertize of *in-situ* cells and modeling required

Technology Innovation

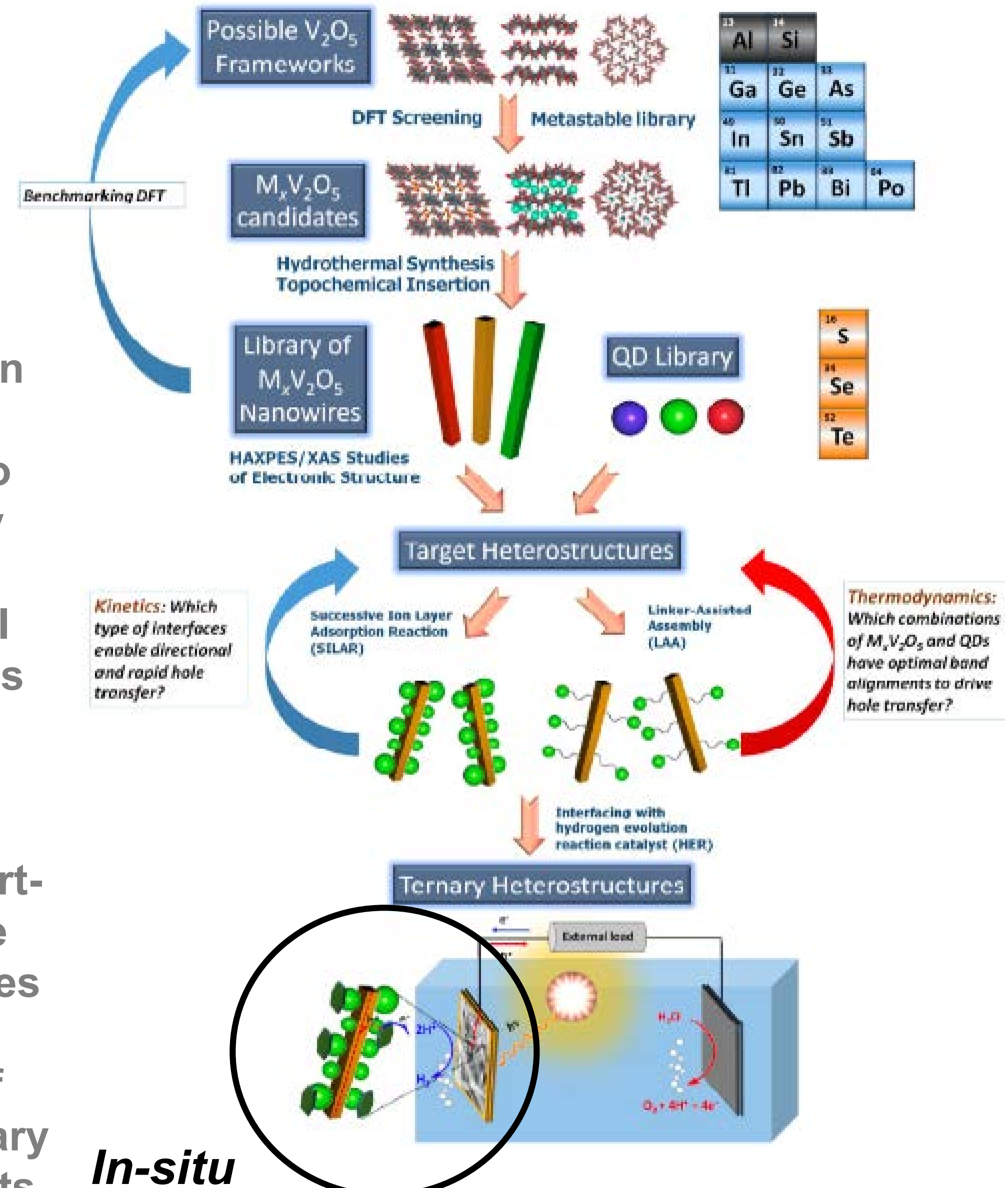
Photo-catalysts by design

1. Enable a Paradigm Shift in Culture

At the heart of our rational design of photo-catalysts is the ability to band engineer efficient charge-separation at interfaces to induce photo-catalytic activity in inert systems. This DMREF-EMN project extends the activities within our existing DMREF project by utilizing the tools developed within HydroGEN to develop an entirely new class of ternary heterostructures, where hydrogen evolution is further enhanced at the II-VI QD/MoS_2 interface. Ongoing discussions with large oil company for *in situ H_2 generation in difficult terrains*.

2. Integrate Experiments and Modeling

In-situ XAS/RIXS experiments using start-of-the-art wet cells configurations at the ALS will be combined with first principles x-ray simulations to understand the buried interfacial electronic structure of this new class of nano-engineered ternary photo catalysts in aqueous environments.



***In-situ* Characterization**

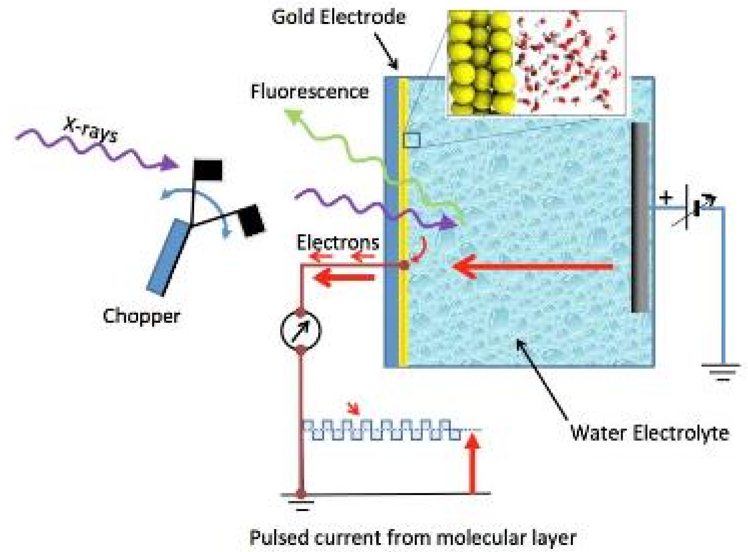
Effective Leveraging of the EMN Resource Nodes

Identified EMN Partner Partnership:

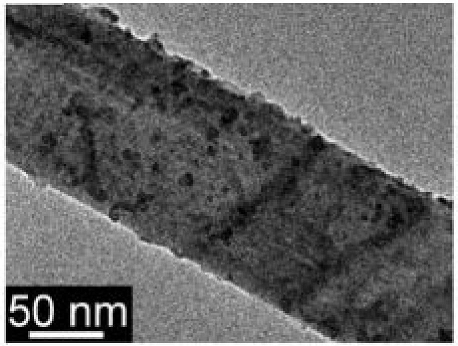
HydroGEN: *Photoelectrochemical Device In Situ and Operando Testing Using X-Rays.*

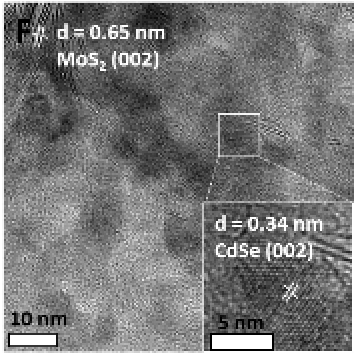
Lawrence Berkeley National Laboratory.

- The HydroGEN node has developed unique capabilities for *in-situ* soft x-ray studies of catalysts at LBNL, including electrochemical cells (Dr Jinghua Guo) and first-principles x-ray simulations (Dr David Prendergast).
- Profs. Banerjee and Piper have long-standing collaborations with Drs Guo and Prendergast, along with personnel embedded within the ALS and Molecular Foundry research facilities at LBNL
- The proposed *in-situ* XAS/RIXS effort will focus on a newly engineered ternary photo-catalysts generated from our DMREF project and will maximize direct interactions on this project between the DMREF PhD and Post-Doctoral researchers with the HydroGEN staff.



***In-situ* wet cell at ALS developed by HydroGEN**





TEM images of $M_xV_2O_5$/CdSe (left) and MoS_2/CdSe (right) nanostructures developed for this project