Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Development of Composite Photocatalyst Materials that are Highly Selective for Solar Hydrogen Production and their Evaluation in Z-Scheme Reactor Designs

Shane Ardo
University of California Irvine

Project ID: P192

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Summer 2020

US DOE, EERE, FCTO, Annual Merit Review

Project Overview

Partners

- **Lead PI, Shane Ardo (University of California Irvine):** composite photocatalyst materials
- **Co-PI, Rohini Bala Chandran (University of Michigan):** numerical modeling and simulations
- **Co-PI, Dan Esposito (Columbia University):** ultrathin selective coatings

University Collaborators

- **John Gregoire (California Institute of Technology, Y2-3):** combinatorial deposition and high-throughput screening of photocatalysts and composite materials
- **Takashi Hisatomi (Shinshu University, Y2-3):** mixed metal-oxide/nitride/sulfide photocatalysts
- **Akihiko Kudo (Tokyo University of Science, Y2-3):** doped $SrTiO_3$ composite photocatalysts

HydroGEN Node Collaborators

- **Katie Hurst (NREL, Y1+):** particle ALD
- **Tadashi Ogitsu (LLNL, Y1+):** coating models
- **Alec Talin (SNL, Y1+):** scanning nanoprobes
- **Hanna Breunig (LBNL, >Y1):** LCA
- **Genevieve Saur (NREL, >Y1):** TEA

Barriers Addressed

(AE) Materials Efficiency – Bulk and Interface
(AG) Integrated Device Configurations
(AI) Auxiliary Materials

Project ID	**P192**
Project Start Date	**10/01/19**
Project End Date	**03/31/23**
Total Project Budget *	**$1,250,000**
Recipient Share	$250,001
Federal Share	$999,999
DOE Funds Spent	$0k *(by 05/01/20)*

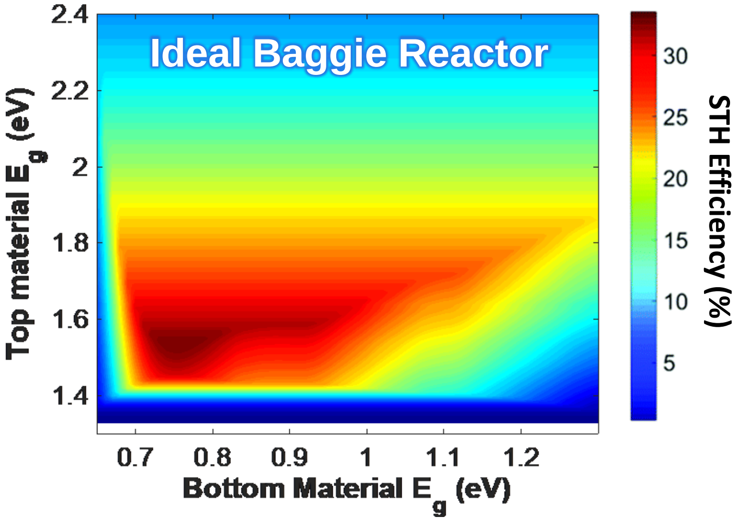
** This amount does not include cost share or support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

Project Relevance

Motivation

Results from prior a DOE EERE FCTO Incubator project (Lead PI Ardo and Co-PI Weber (PD: Bala Chandran)) demonstrated that Type 2 photocatalyst reactors for solar H_2 production can be as efficient as wafer-based reactors, ***assuming perfect reaction selectivity for H_2 evolution and O_2 evolution***.

Keene, **Bala Chandran** & **Ardo**, *Energy Environ. Sci.*, 2019, *12*, 261



Objectives

<u>Life of the Project</u>: Solve the remaining major challenge toward realization of efficient and techno-economically viable photocatalyst reactors for solar H_2 production of ***reaction selectivity for visible-light-driven H_2 evolution*** over redox shuttle reduction. We aim to do this by depositing engineered ultrathin coatings on visible-light-absorbing Ir-doped $SrTiO_3$ photocatalyst particles.

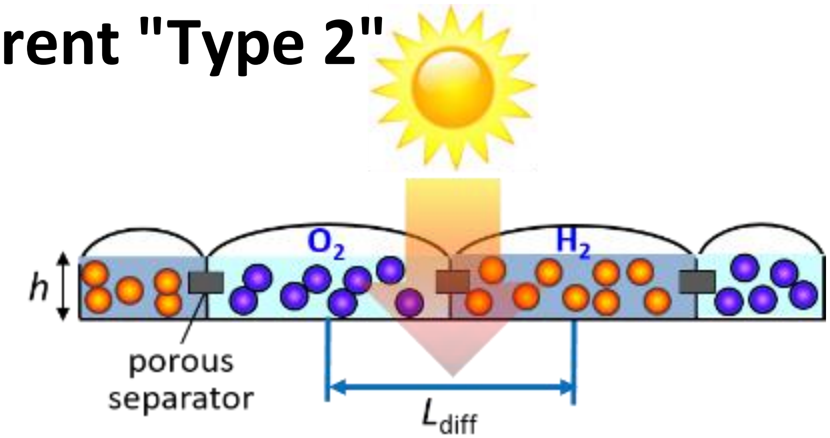
<u>Current Project Year</u>: Demonstrate efficient doped metal-oxide photocatalyst particles and selective ultrathin oxide coatings for the H_2 evolution reaction and the O_2 evolution reaction.

Impact

By experimentally demonstrating H_2 evolution from illuminated Ir-doped $SrTiO_3$ photocatalyst particles with Ir cocatalysts, as well as ultrathin coatings that are selective toward H_2 evolution over redox shuttle reduction that are supported by numerical simulations, we are advancing the efficiency and selectivity of integrated composite materials for solar H_2 production.

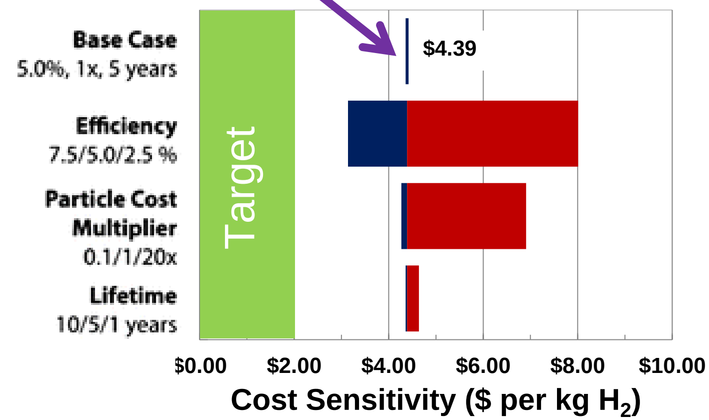
Approach – Innovation (Prior DOE EERE Work)

Current "Type 2"



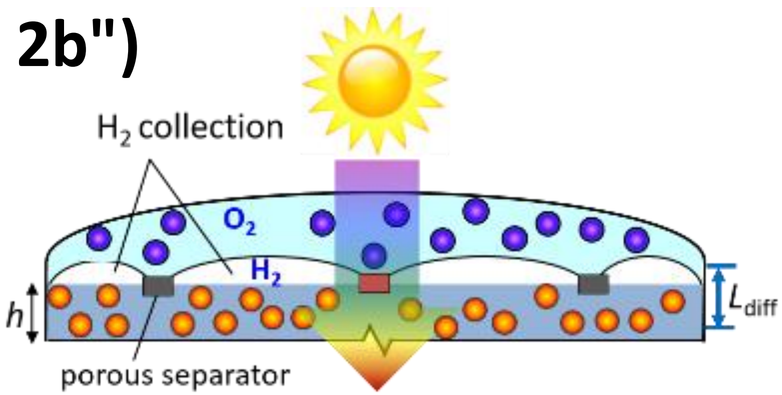
$4.39 at 5%

Type 2



Our Stacked-Reactor Design

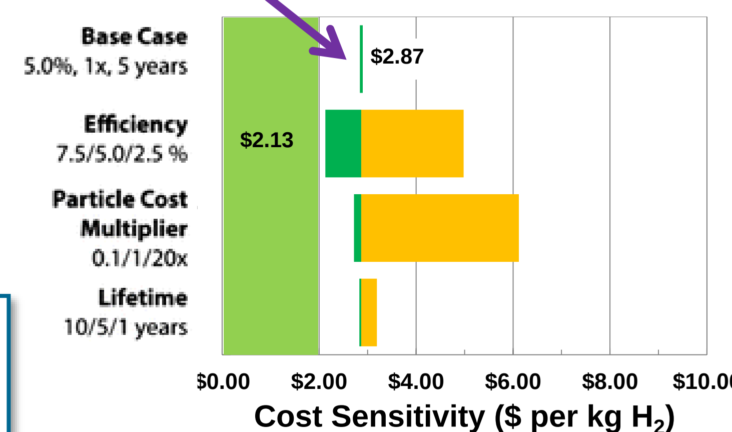
("Type 2b")



- Serial light absorption increases efficiency
- Much smaller mass transport distances

$2.87 at 5%

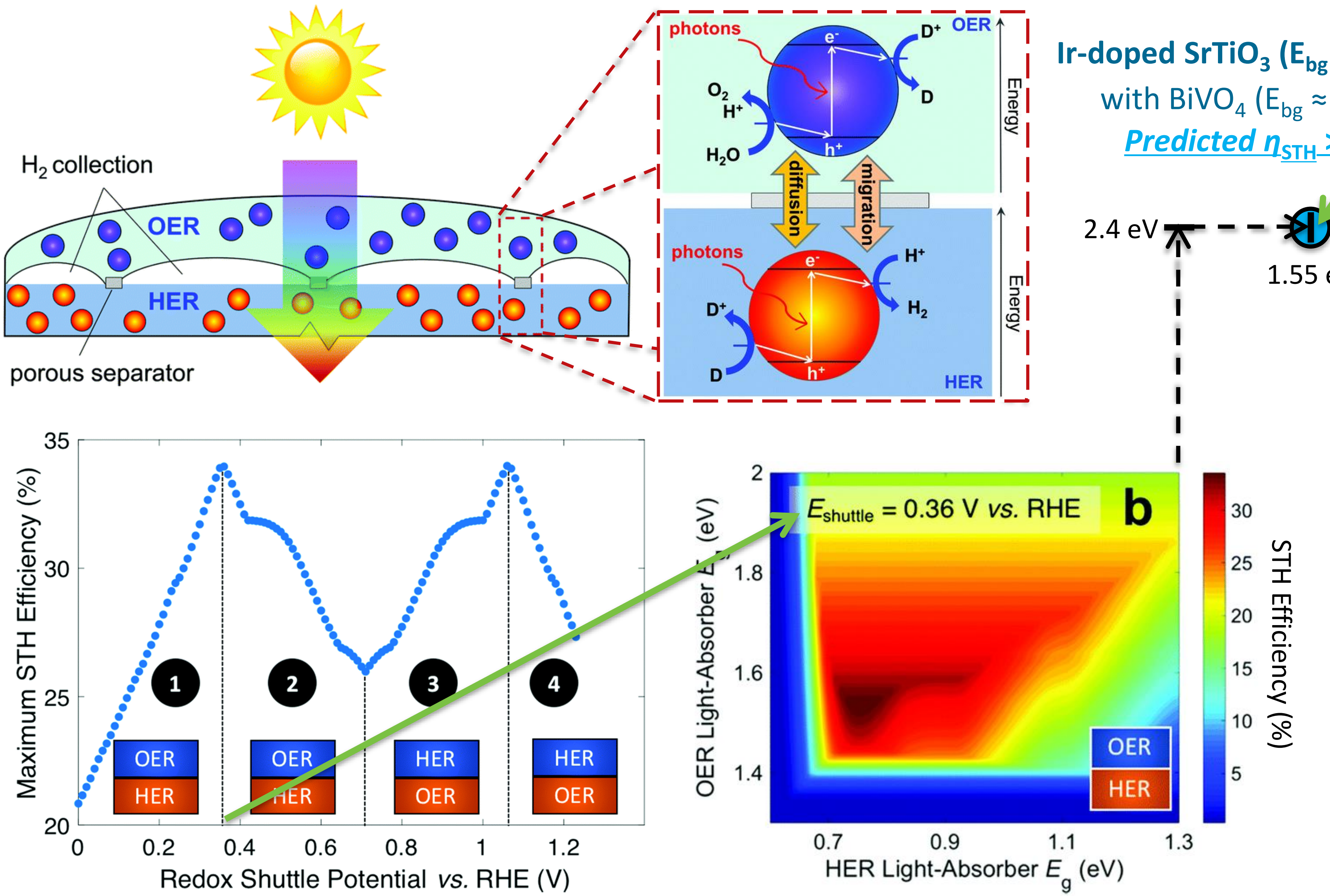
Type 2b



DOE H2A Analysis, https://www.hydrogen.energy.gov/h2a_production.html

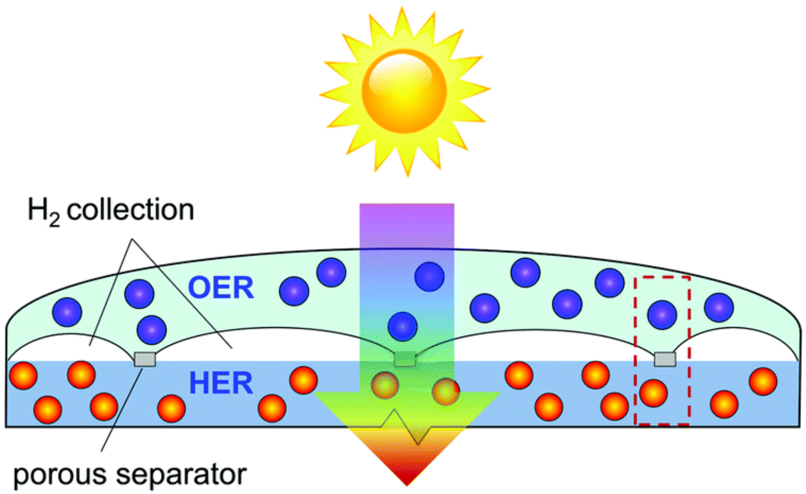
Approach – Background (Prior DOE EERE Work)

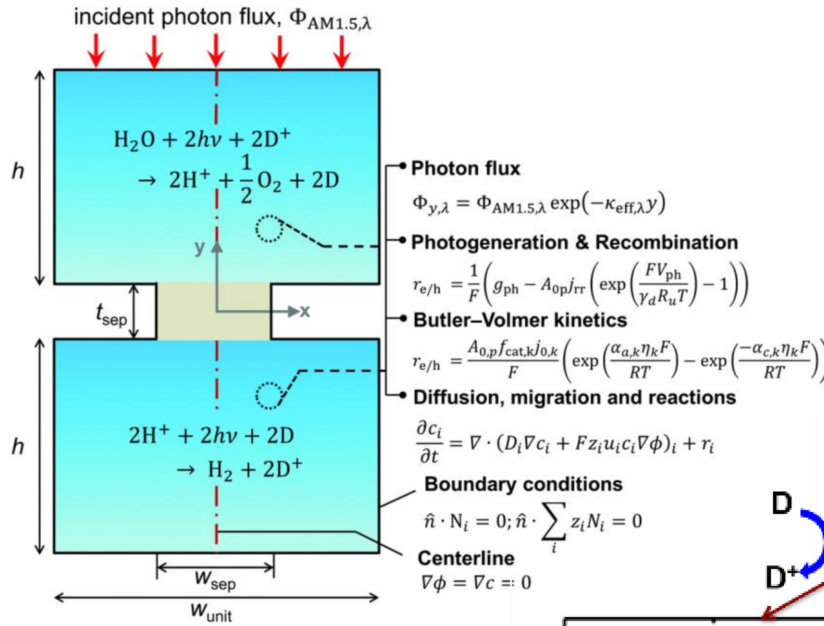
Ir-doped $SrTiO_3$ (E_{bg} ≈ 1.55 eV)
with $BiVO_4$ (E_{bg} ≈ 2.4 eV)
Predicted η_{STH} > 10%

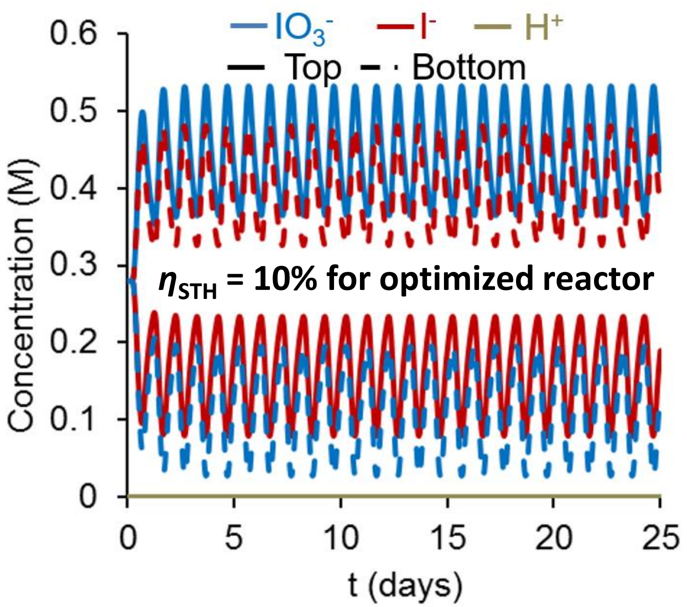


Keene, **Bala Chandran** & **Ardo**, *Energy Environ. Sci.*, 2019, *12*, 261

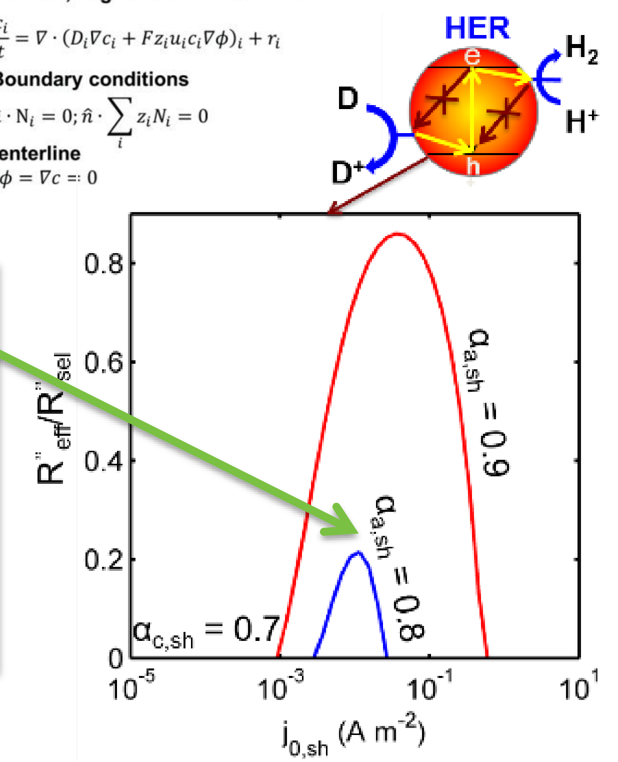
Approach – Background (Prior DOE EERE Work)







The rate of non-selective HER (R''_{eff}), relative to the rate of selective HER (R''_{sel}), depends greatly on redox selectivity ($\alpha_{a,sh}$)



Bala Chandran, **Breen**, **Shao**, **Ardo** & **Weber**, *Energy Environ. Sci.*, 2018, *11*, 115

Approach – Technical Summary

- **A very small number of ultrathin coatings with specific deposition protocols have been shown to enable selective reactivity for desired reactions using photocatalyst particles.** By developing general protocols for the controlled synthesis, deposition, and characterization of ultrathin coatings **(AI)** on planar electrodes and photocatalyst particles **(AG)**, we will better understand how to controllably engineer interfaces for selective desired reactivity, like the HER and redox shuttle oxidation, over the opposite undesired reactions, like the HOR and redox shuttle reduction. *This protocol development is synergist with studies of stability (PEC, STCH) and control of catalyst placement (LTE, Fuel Cells).*
- **Our team is pioneering the development of accurate models of photocatalyst reactors for solar H_2 production.** Through numerical models and simulations of a broad range of relevant device physics, we are gaining better predictive capabilities for optimal spatial and temporal properties of composite photocatalyst particles **(AE)**, their components **(AI)**, and their reactors **(AG)**. *This model development is synergist with models being developed for other solar hydrogen technologies (PEC, STCH).*
- **The state-of-the-art material for stable visible-light-driven photocatalytic H_2 production is Ir-doped $SrTiO_3$.** Through evaluation of Ir-doped $SrTiO_3$ photocatalyst particles and related perovskite materials **(AE)**, we are advancing the efficiency and selectivity of composite photocatalyst particles for solar H_2 production **(AG)**. *This materials development is synergistic with technologies that use similar materials (STCH).*

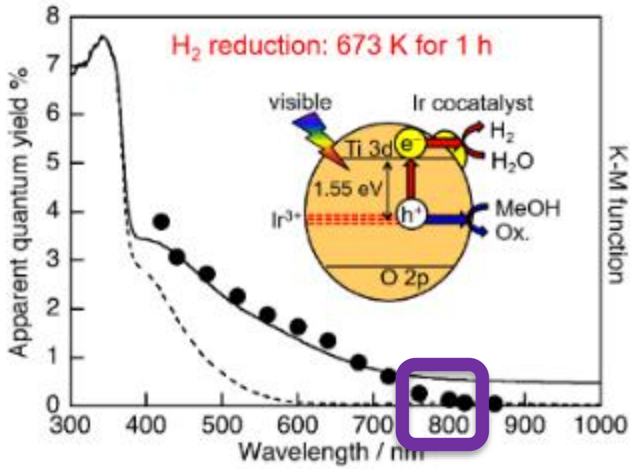
Approach – Relevant Milestones and Go/No-Go

Subtask	Milestone	Milestone Description	Verification Process	Qtr
Photocat Particles	**M1.1.1**	**Quantum yield (QY) of ≥1% for the OER from suspensions of $BiVO_4$ particles in the presence of sacrificial electron acceptors and under visible-light illumination.**	**Ardo (UCI)[1] QY, Inline Mass Spec *<u>100% complete</u>***	**Q1**
Numeric Models	**M4.1.1**	**Determine semiconductor optical, transport, and recombination properties that are needed to attain a solar-to-hydrogen conver-sion efficiency of ≥3% with 100% selectivity for desired reactions.**	**Bala Chandran (UM)[2] Properties, Numerical *<u>75% complete</u>***	**Q2**
Numeric Models	**M4.2.1**	**Quantify time-dependent and spatially-dependent temperature profiles and concentrations of redox mediator species for ≥3 fluence conditions.**	**Bala Chandran (UM) Heat Maps, IR Camera *<u>25% complete</u>***	**Q3**
Numeric Models	M4.1.2	Determine semiconductor optical, transport, and recombination properties that are needed to attain a solar-to-hydrogen conversion efficiency of ≥3% for an H_2 evolution selectivity of 5% – 100%.	**Bala Chandran (UM)[2]** Properties, Numerical *<u>75% complete</u>*	Q4
Selective Coatings	M2.1.1	Deposit ultrathin coatings of <10 nm of SiO_x and TiO_x onto well-defined state-of-the-art metallic or metal-oxide cocatalyst thin films for the HER and the OER.	**Esposito (CU)[3,4]** Images, Ellipsometry *<u>25% complete</u>*	Q4
Photocat Particles	**<u>D1.1.1</u>** **<u>(Go/No-Go)</u>**	Quantum yield of ≥0.1% for the HER and a >90% stability over 1 day from suspensions of Ir-doped $SrTiO_3$ particles in the presence of sacrificial electron donors and under near-infrared-light excitation.	**Ardo (UCI)[1]** QY, Inline Mass Spec *<u>25% complete</u>*	Q4

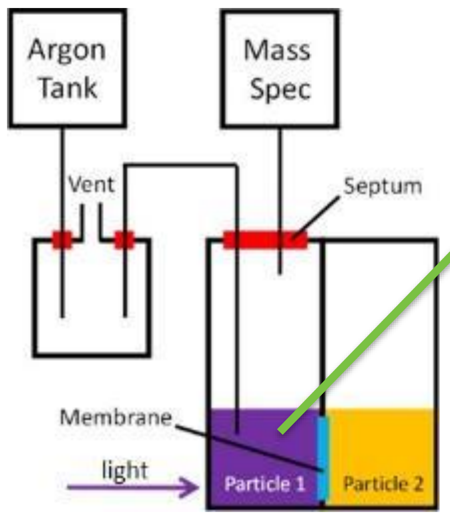
[1]Kudo, Akihiko (Tokyo University of Science) – photocatalyst particles
[2]Ogitsu, Tadashi (LLNL) – ab initio modeling of coatings
[3]Hurst, Katie (NREL) – particle-scale ALD development
[4]Talin, Alec (SNL) – scanning nanoprobe microscopies

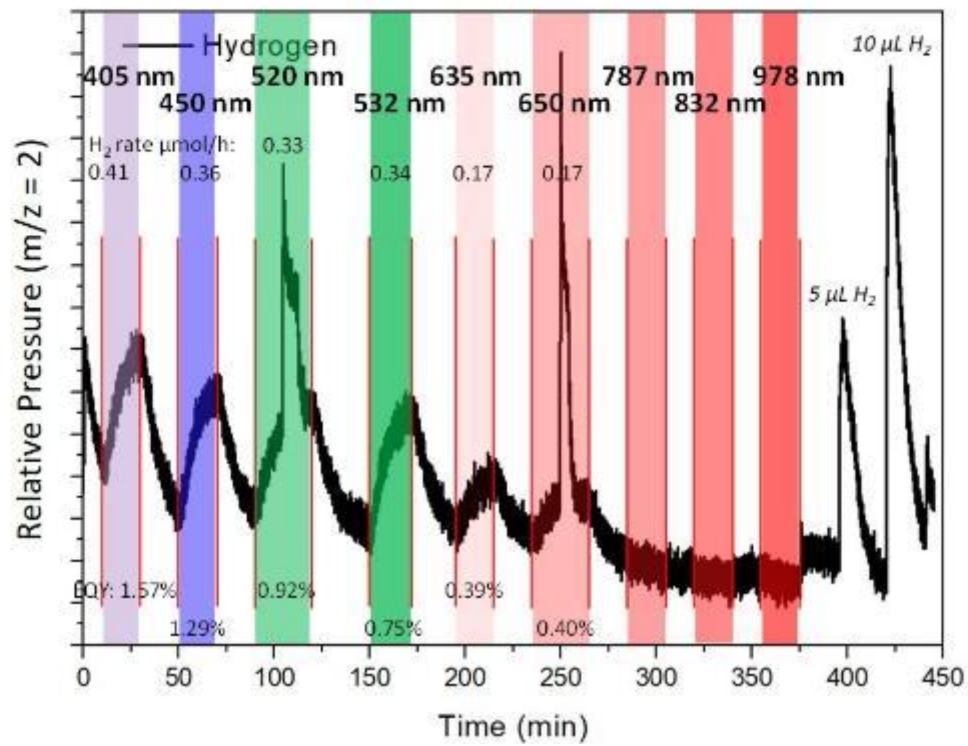
Accomplishments (Photocatalysts by UC Irvine)

Motivation: Suzuki, Matsumoto, Iwase & Kudo, *Chem. Comm.*, 2018, *54*, 10606



Experiment:

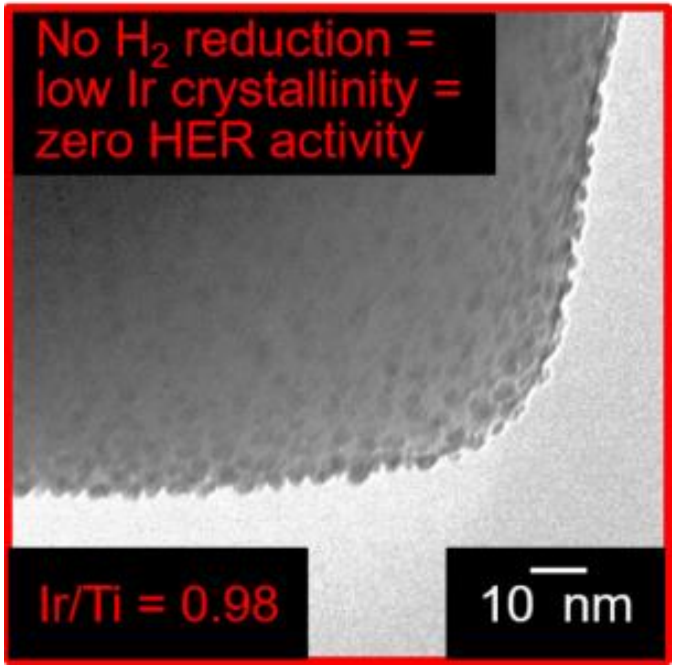


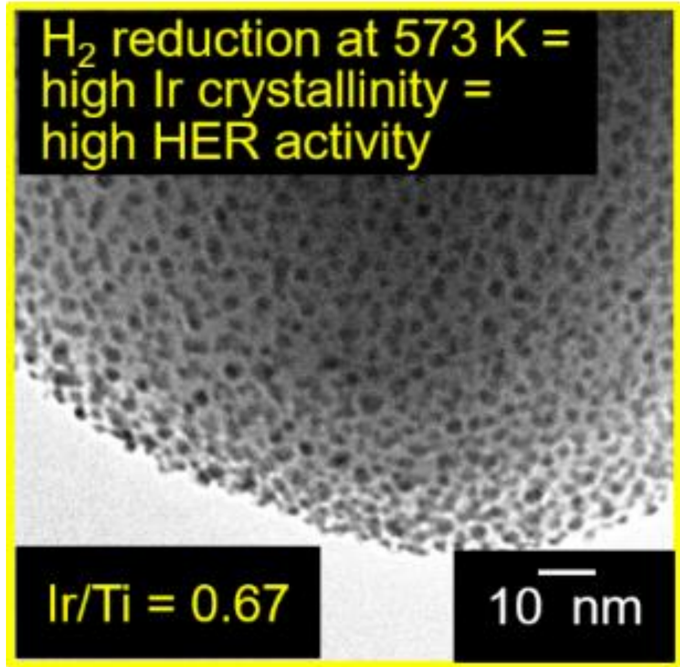


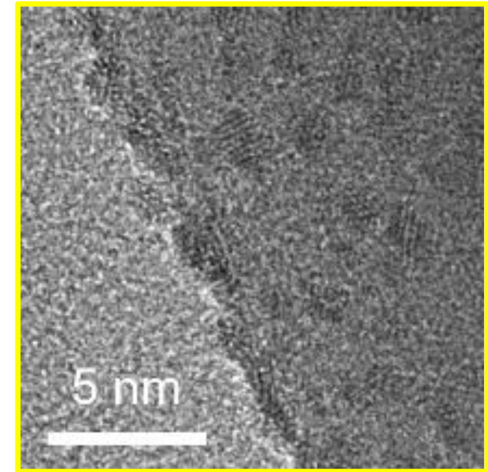
Ir/$SrTiO_3$:Ir (1 mg/mL) with 0.3wt% Ir cocatalyst (impregnated @ 673 K for 2 h, H_2 anneal @ 673 K for 1 h) in 10 vol% aq CH_3OH

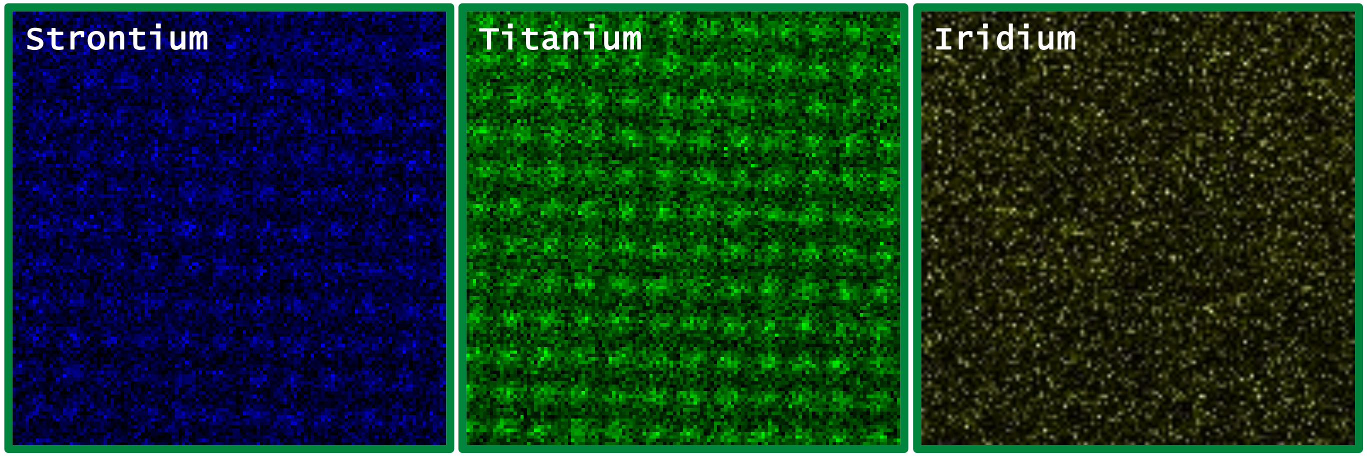
Toward D1.1.1: An external quantum yield (EQY) for HER from Ir-doped $SrTiO_3$ of >0.39% using ≤650 nm light

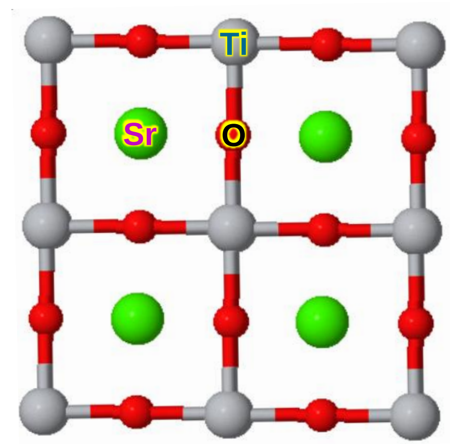
Accomplishments (Photocatalysts by UC Irvine)



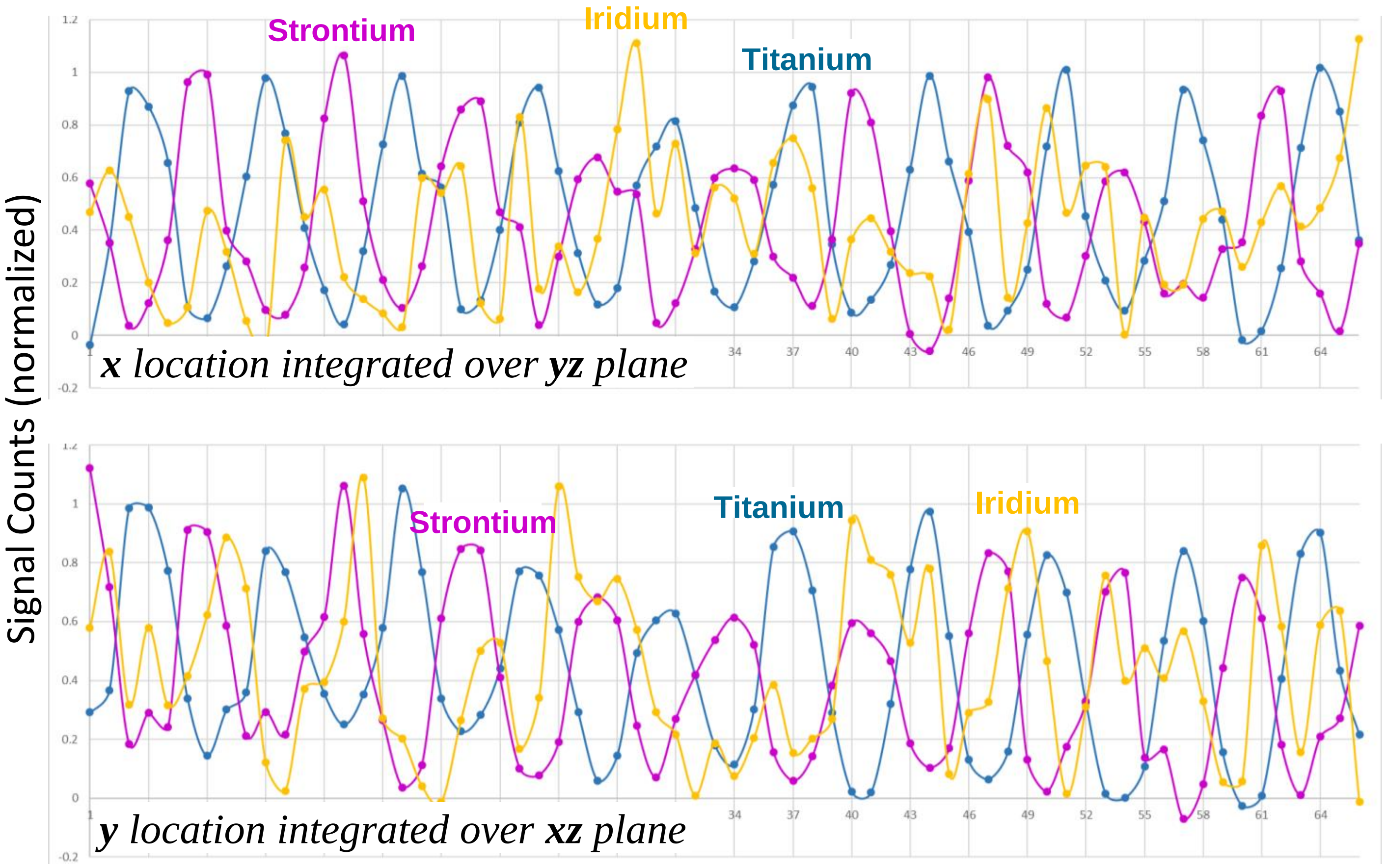


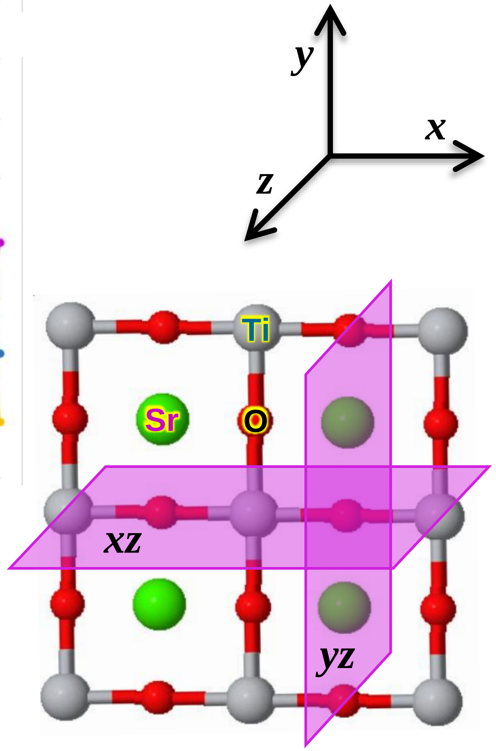






Accomplishments (Photocatalysts by UC Irvine)

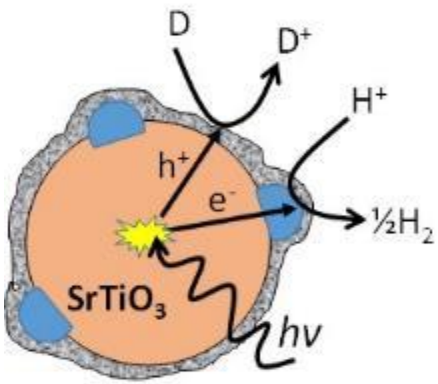


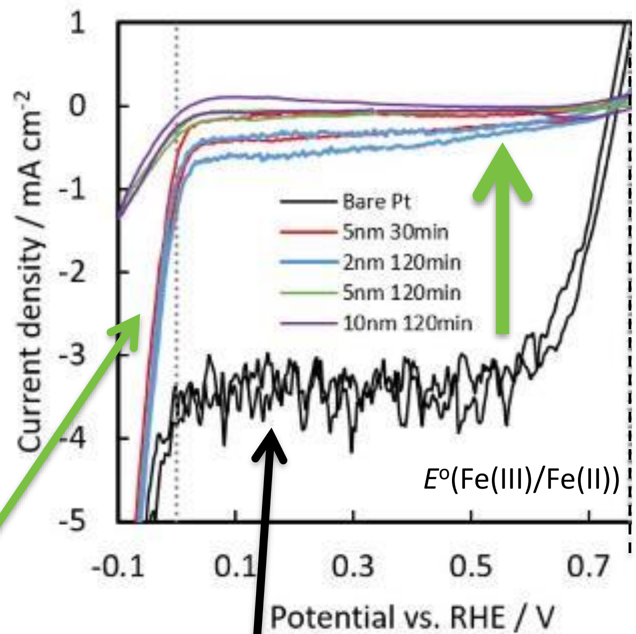


Toward D1.1.1: Expected A/B locations are observed for Sr/Ti, yet the specific locations for Ir dopants are less clear

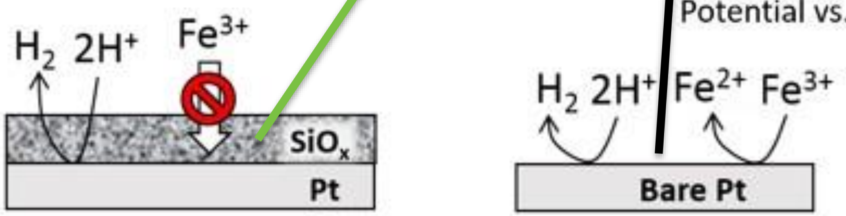
Accomplishments (Coatings by Columbia U.)

Motivation:

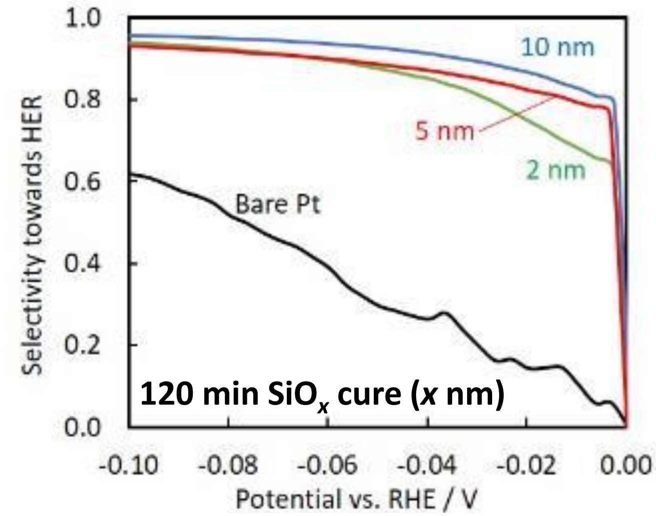


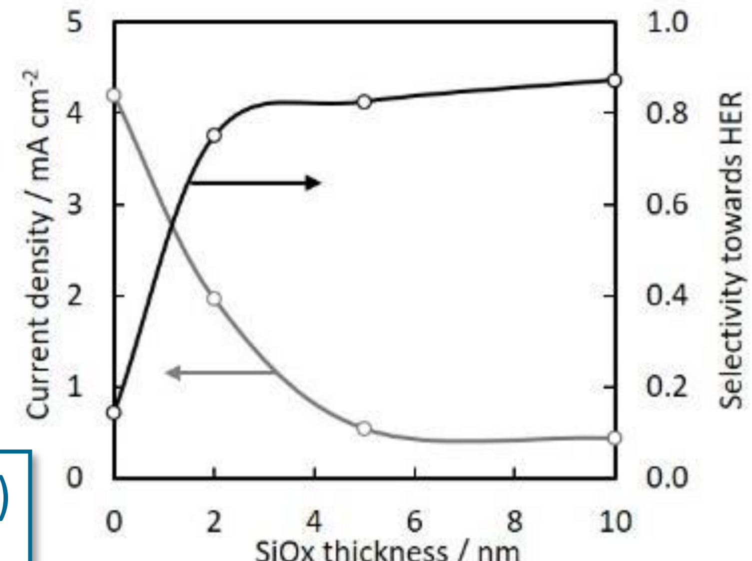


Experiment:



CVs (20 mV/s) at Pt electrodes immersed in pH 1.5 aqueous Na_2SO_4(100 mM)–$Fe(SO_4)_n$(25 mM, 1:1 Fe(II):Fe(III))



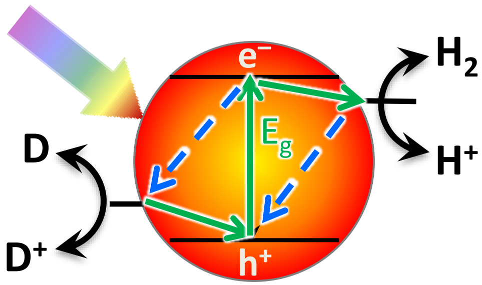


* *Selectivity =* j_{HER}/j_{total} *at -0.02 V vs. RHE*

Toward M2.1.1: ~5 nm thick SiO_x attenuates Fe(III) redox by ~10x, yet does not attenuate HER

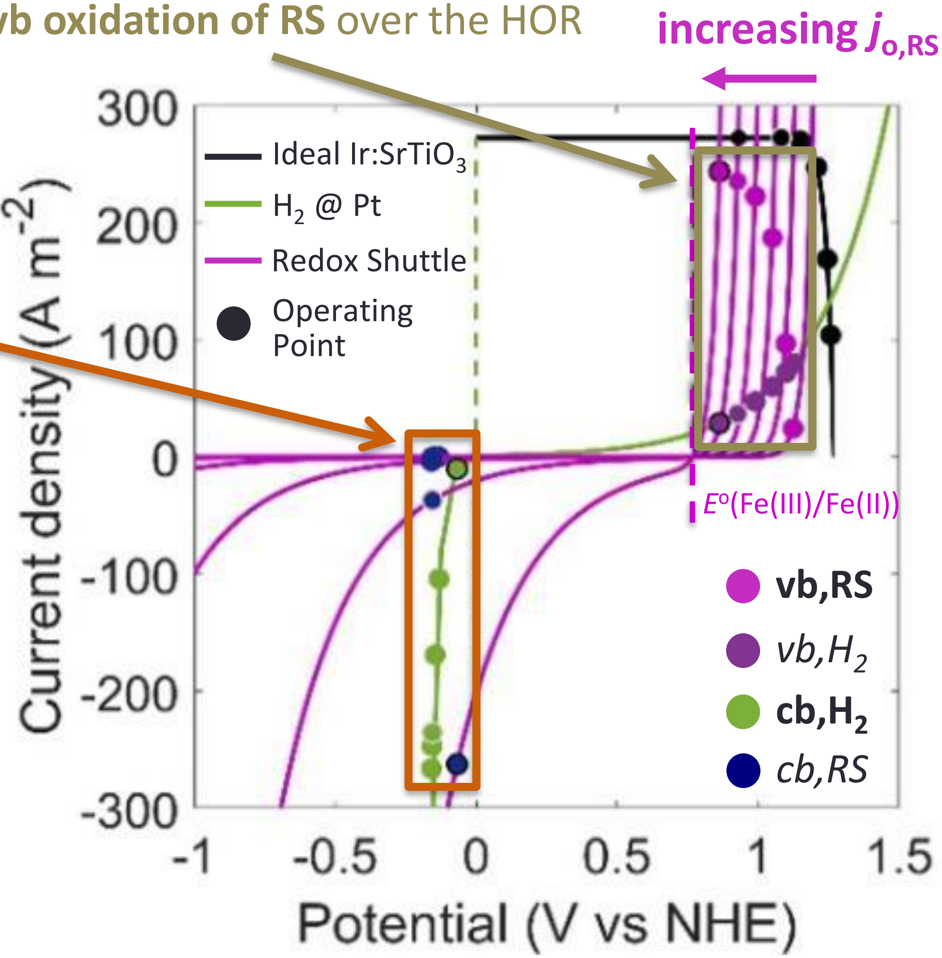
Accomplishments (Simulations by U. Michigan)

Motivation:



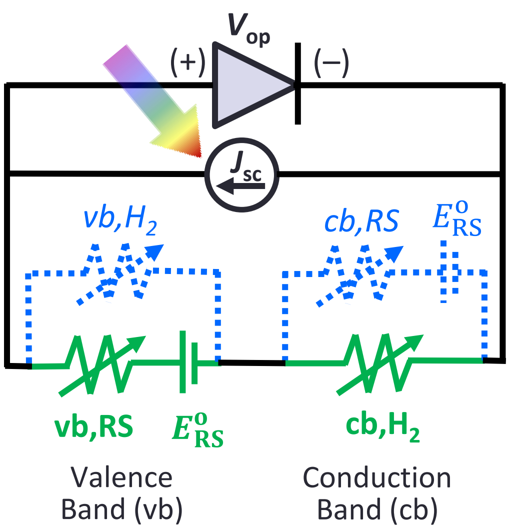
Larger $j_{o,RS}$ results in more **desired vb oxidation of RS** over the HOR

Larger $j_{o,RS}$ results in more **undesired cb reduction of RS** over the HER



Model:

Non-selective detailed-balance: conduction band (cb) e⁻/h⁺ and valence band (vb) e⁻/h⁺ can each do H_2 redox and shuttle (RS) redox; $j_{o,RS} = [10^{-5}, 10^{0}]$ mA/cm², $\alpha_{a,RS} = 0.9$, $\alpha_{c,RS} = 0.1$



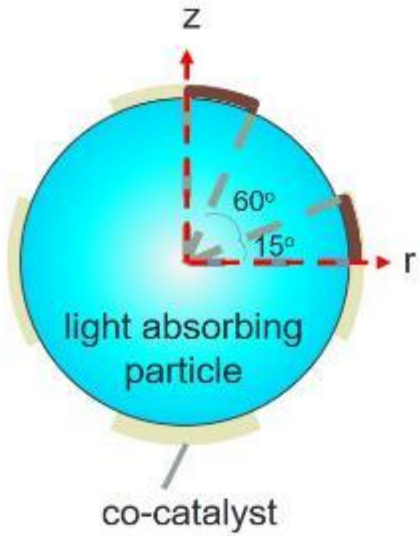
Toward M4.1.2: Reaction selectivity depends on j_o, and on limiting j due to solubility of H_2 and coatings *(not shown)*

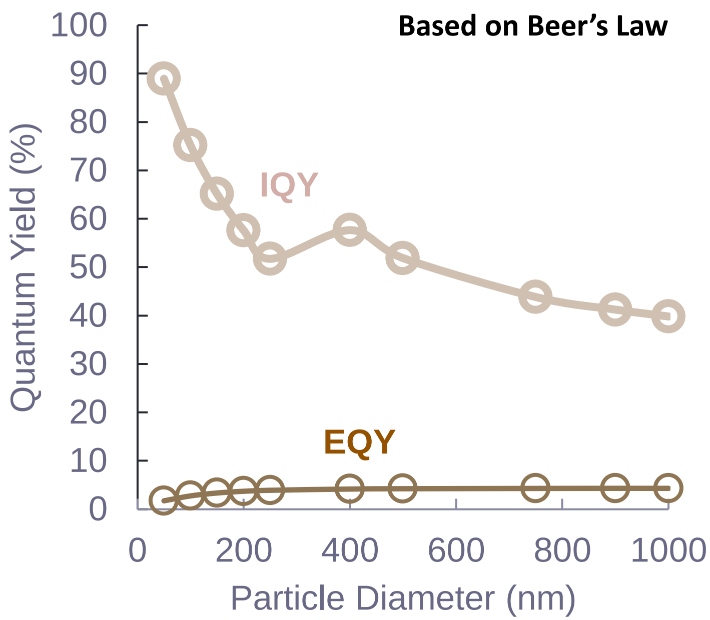
Bala Chandran, **Breen**, **Shao**, **Ardo** & **Weber**, *Energy Environ. Sci.*, 2018, *11*, 115

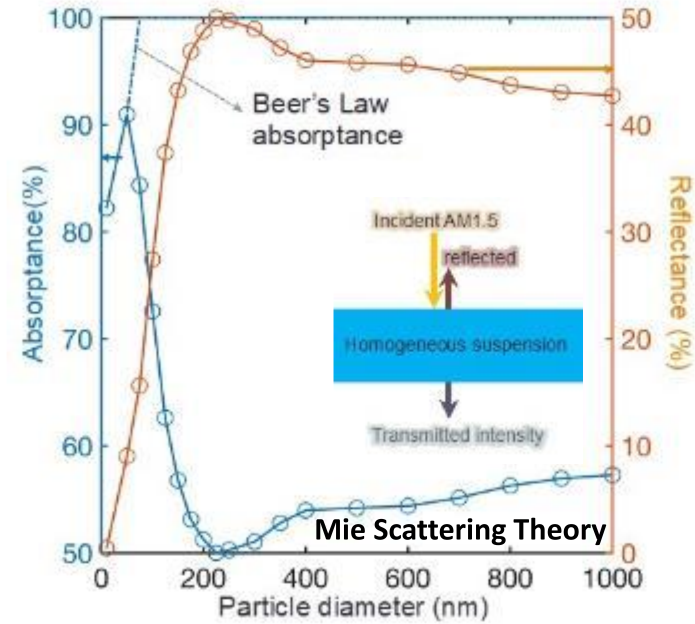
Accomplishments (Simulations by U. Michigan)

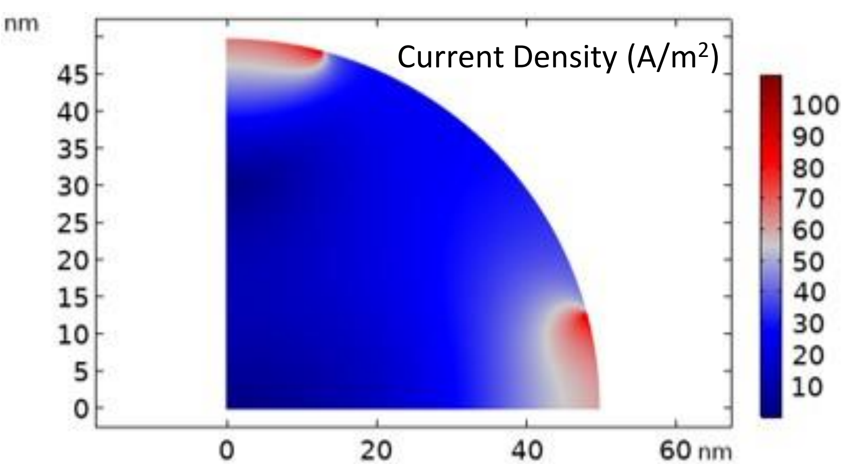
Model:

Continuity of mass









Toward M4.1.1:

- Single particle transport model with Beer's Law absorption indicate that nanoparticles can be effective at the HER
- Internal quantum yield (IQY) is affected by particle diameter
- Scattering of light must be considered

Responses to Reviewers' Comments

This project was not reviewed last year.

Collaboration and Coordination

HydroGEN Node Collaborations

- Katie Hurst (NREL), Surface Modifications for Catalysis and Corrosion Mitigation Node: enable reaction selectivity via particle ALD on photocatalyst particles
- Tadashi Ogitsu (LLNL), Ab Initio Modeling of Electrochemical Interfaces Node: understand selectivity and transport processes in coatings
- Alec Talin (SNL), Electron Beam and In Situ Photon Beam Characterization of PEC Materials and Devices Node: provide nanoscale details of photocatalyst particle function
- Hanna Breunig (LBNL), Prospective LCA Model for 1-GW Scale PEC Hydrogen Plant Node: identify requirements for a feasible "Type 2b" photocatalyst plant
- Genevieve Saur (NREL), Techno-Economic Analysis of Hydrogen Production Node: identify requirements for a feasible "Type 2b" photocatalyst plant

University Vendor Collaborations

- John Gregoire (California Institute of Technology): identify new photocatalysts and composite materials using combinatorial deposition and high-throughput screening
- Takashi Hisatomi (Shinshu University): identify new visible-light-absorbing mixed metal-oxide/nitride/sulfide photocatalysts
- Akihiko Kudo (Tokyo University of Science): provide synthetic expertise on doped $SrTiO_3$ composite photocatalysts

Remaining Challenges and Barriers

- **<u>End of Project Goal</u>: Demonstrate a selective ultrathin oxide coating on particles that results in a ≥10 times larger HER quantum yield than for uncoated particles**
- *All three PI's labs were closed starting in March due to COVID-19, and have remained closed since that time*
  - *Biweekly team meetings remained via Zoom*
  - *All of the personnel on the project have shifted their research efforts to focus on numerical modeling and simulations*
  - *All labs have plans to begin the reopening process shortly*
- Experimental efforts were ahead of schedule and so it is likely that remaining experimental milestones can be met according to the SOPO
- Purely numerical modeling and simulation efforts are behind schedule due to the breadth of physics proposed for each milestone
  - <u>Reactor-scale model of transport properties</u>: *Complete*
  - <u>Equivalent-circuit model of reaction properties</u>: *Complete*
  - <u>Single-particle model of semiconductor optical properties</u>: *Near-Complete*
  - <u>Reactor-scale model of natural convection</u>: *Initial Model Generated*

Any proposed future work is subject to change based on funding levels.

Proposed Future Work

Subtask	Milestone	Milestone Description	Verification Process	Qtr
Numeric Models	M4.2.1	Quantify time-dependent and spatially-dependent temperature profiles and concentrations of redox mediator species – ***upon lab reopening,**** **use infrared camera to quantify these, in order to understand how natural convection can aid species transport**	**Bala Chandran (UM)** Heat Maps, IR Camera *25% complete*	**Q3**
Numeric Models	M4.1.2	Determine properties that are needed to attain a solar-to-hydrogen conversion efficiency of ≥3% for an H_2 evolution selectivity of 5% – 100% – **continue to develop models and perform simulations, in order to guide experimental synthetic work**	**Bala Chandran (UM)** Properties, Numerical *75% complete*	**Q4**
Selective Coatings	M2.1.1	Deposit ultrathin coatings of MO_x onto well-defined state-of-the-art metallic or metal-oxide cocatalyst thin films for the HER and the OER – ***upon lab reopening,**** **continue initial experiments, in order to identify coatings that result in optimal reaction selectivity**	**Esposito (CU)** Images, Ellipsometry *25% complete*	**Q4**
Photocat Particles	D1.1.1 (Go/No-Go)	Quantum yield of ≥0.1% for the HER and a >90% stability over 1 day from Ir-doped $SrTiO_3$ particles and near-infrared-light excitation – ***upon lab reopening,**** **re-synthesize and re-evaluate materials, in order to demonstrate feasibility of effective solar H_2 production**	**Ardo (UCI)** QY, Inline Mass Spec *25% complete*	**Q4**
Numeric Models	M4.2.2	Simulate effects due to light absorption and natural convection – **expand on previous models that included some of these processes**	**Bala Chandran (UM)** QY/STH, Numerical	**Q5**
Photocat Particles	M1.2.1	Deposit an array of ABO_3 particles with ≥1000 dopant compositions – ***upon lab reopening,**** **use state-of-the-art facilities to do this**	**Ardo (UCI)** ***and Gregoire (Caltech)*** Visual Inspection	**Q6**

Any proposed future work is subject to change based on funding levels.

** All labs have plans to begin the reopening process shortly*

Technology Transfer Activities

- Our technology-to-market strategy involves continued conversations with major chemical and gas companies
- Future funding opportunities will be explored when they present themselves, e.g. NSF DMREF
- The current TRL of this technology is a little too low to engage in detailed marketing strategies
- To-date, there no intellectual property filings from this project
- Prior intellectual property filings include: *Ardo, S.; Keene, S.; Phun, G. S. U.S. Patent Application and PCT International Patent Application, University of California Irvine, 2019, 16/673,680 (Provisional patent, 2018, 62/755,410). Optically Thin Light-Absorbers for Increasing Photochemical Energy-Conversion Efficiencies.*

Summary

- Demonstrated an external quantum yield for the HER from Ir-doped $SrTiO_3$ of >0.39% using ≤650 nm light and in the presence of sacrificial electron donors
- Showed that the atomic distributions and locations of Sr and Ti in Ir-doped $SrTiO_3$ are as expected based on the perovskite crystal structure; however, the specific locations for Ir dopants are less clear
- Demonstrated that a ~5 nm thick SiO_x layer attenuates Fe(III) reduction by factor of ten, yet does not attenuate the HER
- Simulations showed that reaction selectivity depends on the exchange current density of the redox shuttle and depends on limiting current densities due to the solubility of H_2 and the presence of ultrathin coatings
- Simulations show that the internal quantum yield for the HER and the extent of light scattering is affected by the diameter of photocatalyst nanoparticles

Subtask	Milestone	Milestone Description	Verification Process	Qtr
Photocat Particles	M1.1.1	Quantum yield (QY) of ≥1% for the OER from suspensions of $BiVO_4$ particles in the presence of sacrificial electron acceptors and under visible-light illumination.	**Ardo (UCI)**[1] QY, Inline Mass Spec *100% complete*	Q1
Numeric Models	M4.1.1	Determine semiconductor optical, transport, and recombination properties that are needed to attain a solar-to-hydrogen conversion efficiency of ≥3% with 100% selectivity for the desired reactions.	**Bala Chandran (UM)**[2] Properties, Numerical *75% complete*	Q2