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

EE0008838

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Project ID #P192

DOE Hydrogen Program 2021 Annual Merit Review and Peer Evaluation Meeting

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Project Overview

Project Partners

Lead PI, Shane Ardo (University of California Irvine)
Co-PI, Rohini Bala Chandran (University of Michigan)
Co-PI, Dan Esposito (Columbia University)

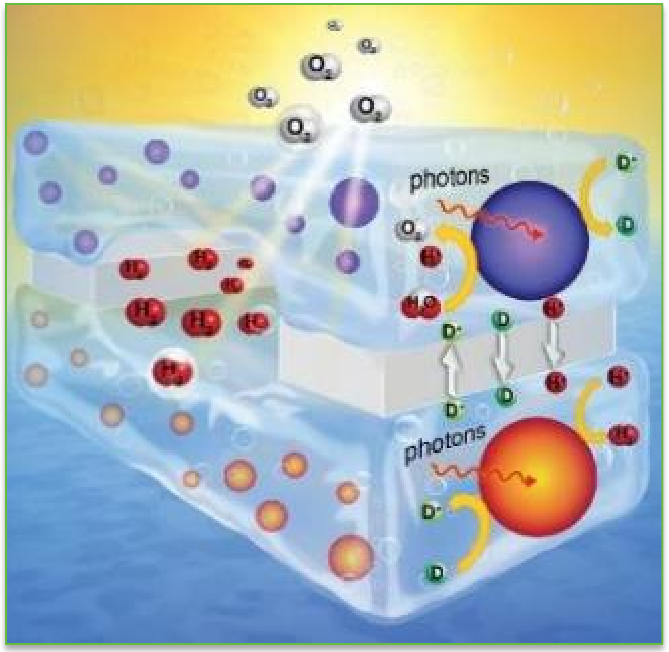
Project Vision

We are solving the key challenges of reaction selectivity and low-cost redox shuttle mixing in particle-based Z-scheme (Type 2) solar water splitting reactors, by engineering ultrathin *coatings*, that are measured to be *selective* and numerically simulated to be *effective*, and depositing them *conformally on visible-light-absorbing nanoparticles*, and *evaluating use of natural convection*

Project Impact

We anticipate validation of high efficiency and techno-economically viable Type 2 photocatalyst reactors for solar water splitting

Award #	EE0008838
Start/End Date	10/01/2019 – 03/31/2023
Project Funding*	$1.25M



* this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)

Approach – Summary

Project Motivation

Results from numerical simulations performed as part of a prior DOE EERE FCTO Incubator project (Lead PI Ardo, Co-PI Weber, PD Bala Chandran) suggest that solar water splitting with photocatalyst particles can be as efficient as with photoelectrodes, when reactions are highly selective for H_2 and O_2 evolution and redox shuttle species are well mixed

Keene, **Bala Chandran** & **Ardo**, *Energy & Environmental Science*, 2019, *12*, 261

Barriers

- Few composite particles are known that selectively evolve H_2 and O_2 instead of performing undesired redox shuttle back reactions
- Empirical and numerical results guide our design of ultrathin coatings for selective reactivity, and reactor dimensions for natural convective mixing

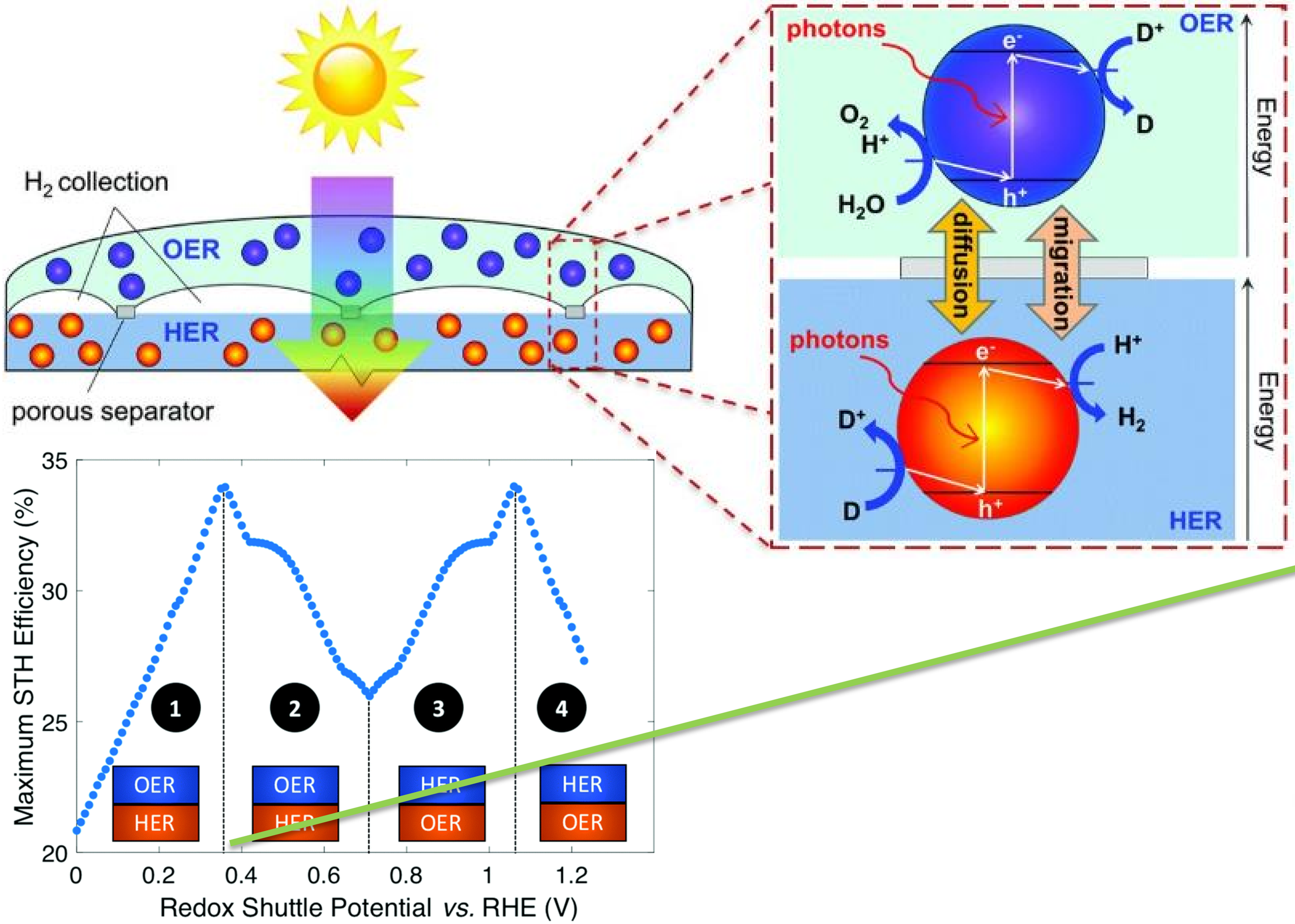
Key Impact

Metric	State of the Art	Expected Advance
Y1: H_2 from Ir-doped $SrTiO_3$ Particles	Apparent quantum yield (AQY) < 0.1% (>750nm)	$AQY_{\geq 750nm} \geq 0.1\%$, >90% stability for 1 day
Y2: H_2 from Coated Planar Electrodes	SiO_x|Pt is selective for H_2 over Cu(II) reduction	≥95% selectivity for H_2 & O_2 over Fe(III) or IO_3^-
Y3: H_2 from Coated $SrTiO_3$ Particles	Internal quantum yield (IQY) = x	IQY ≥ 10x

Partnerships

Katie Hurst (NREL): atomic layer deposition of coatings on particles
Tadashi Ogitsu (LLNL): simulations of transport through coatings
Alec Talin (SNL): nanoprobe measurements of single particles
Genevieve Saur (NREL) & Strategic Analysis Inc.: TEA
Hanna Breunig (LBNL): lifecycle assessment
Akihiko Kudo (Tokyo Univ. Science): syntheses of ABO_3 particles
John Gregoire (Caltech): combinatorial deposition of codoped ABO_3
Takashi Hisatomi (Shinshu Univ.): syntheses of $MO_xN_yS_z$ particles

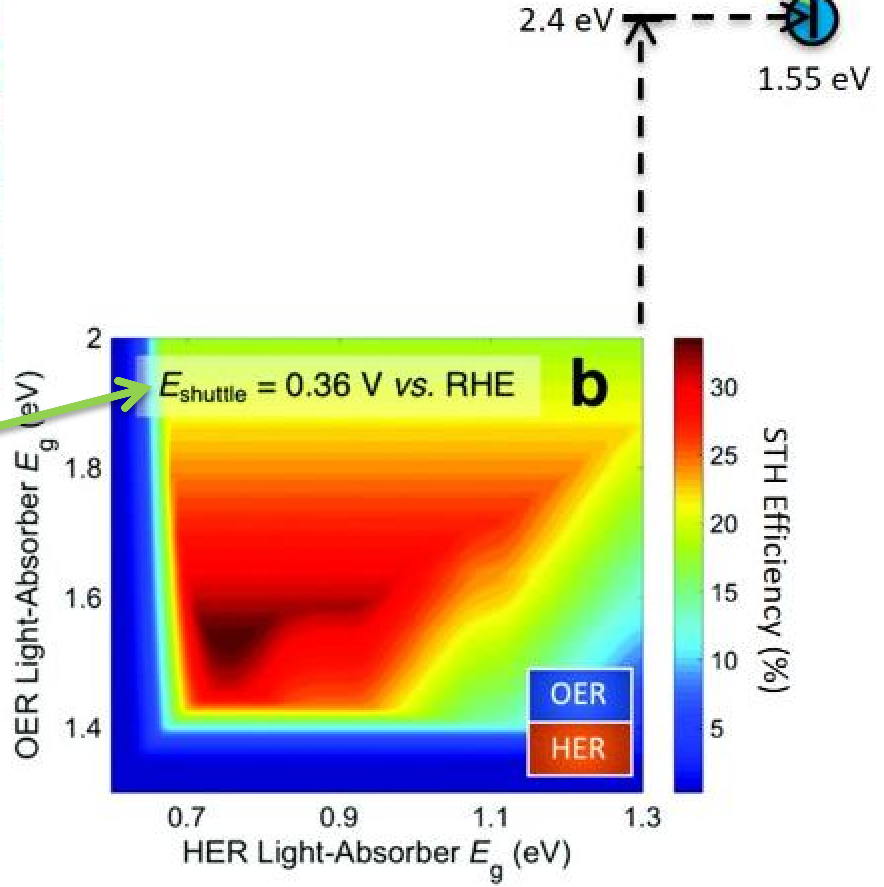
Approach – Innovation (Prior DOE EERE Work)



Ir-doped $SrTiO_3$ ($E_g \approx 1.55$ eV)

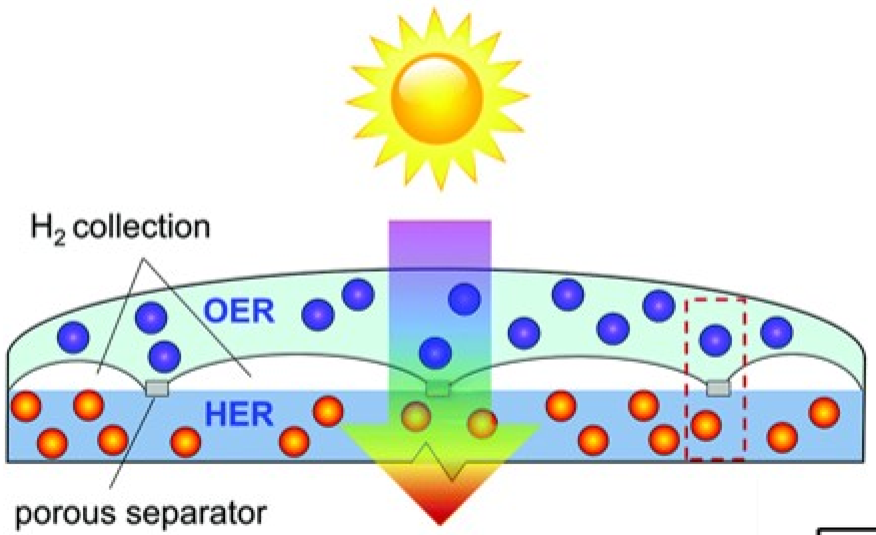
with $BiVO_4$ ($E_g \approx 2.4$ eV)

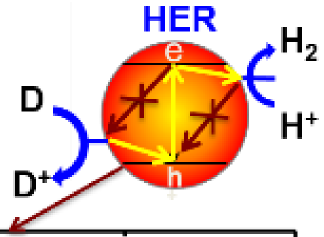
Predicted η_{STH} > 10%

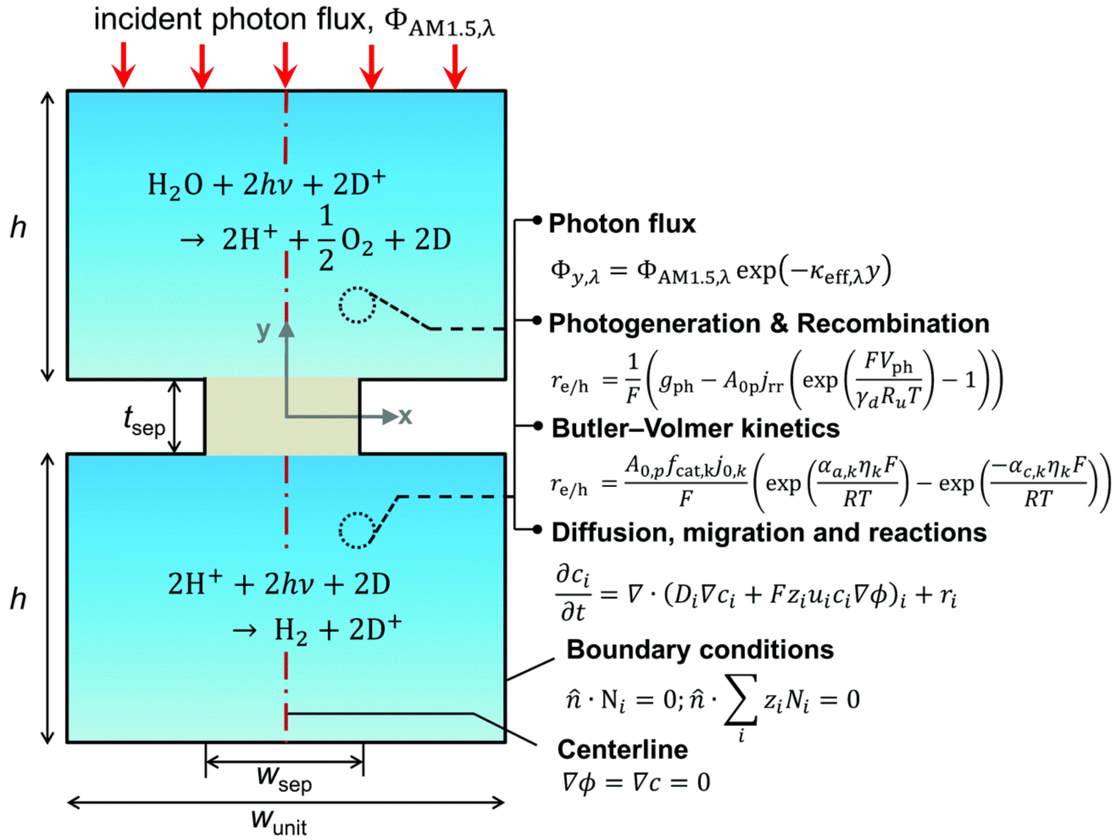


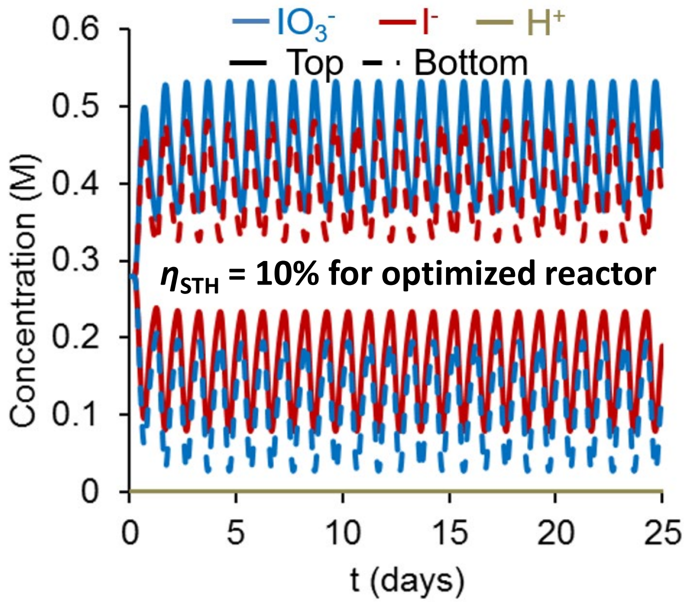
Keene, **Bala Chandran** & **Ardo**, *Energy & Environmental Science*, 2019, *12*, 261

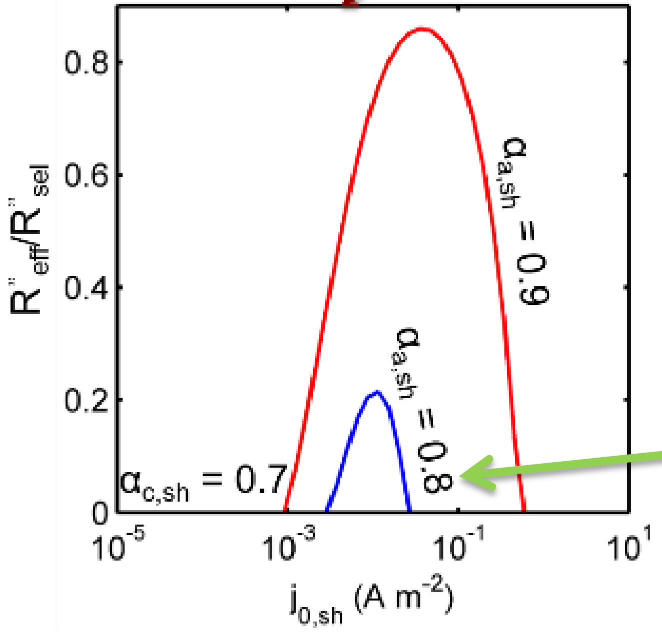
Approach – Innovation (Prior DOE EERE Work)











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

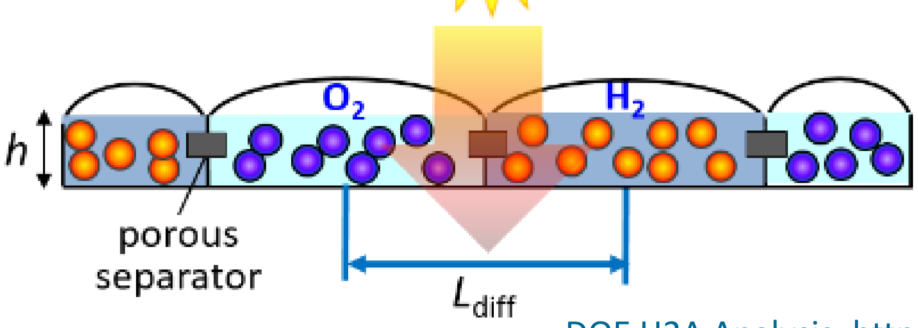
Bala Chandran, **Breen**, **Shao**, **Ardo** & **Weber**, *Energy & Environmental Science*, 2018, *11*, 115

Approach – Innovation (Summary of Scope of Work)

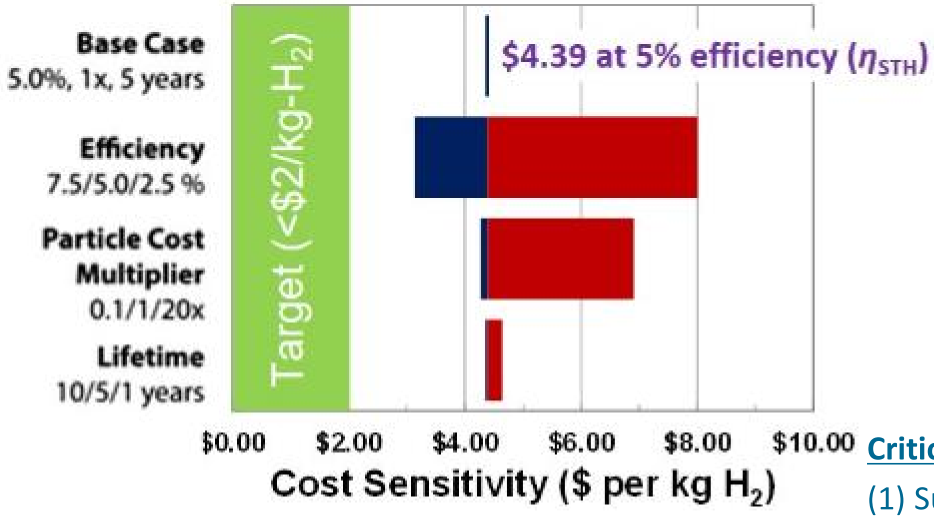
- **Few ultrathin coatings with controlled deposition protocols have been shown to result in selective reactivity for desired H_2 and O_2 evolution over undesired redox shuttle back reactions on photocatalyst particles.** By developing general protocols for the controlled synthesis, deposition, and characterization of ultrathin coatings **(AI)** on planar electrodes and photocatalyst particles **(AG)**, we will better understand how to controllably engineer interfaces for selective desired reactivity, e.g., the HER and redox shuttle oxidation over the opposite undesired reactions of the HOR and redox shuttle reduction. Our protocol development is synergist with studies of stability (PEC, STCH) and control of catalyst placement (LTE, Fuel Cells), and we leverage EMN HydroGEN Consortium expertise in ALD (NREL), theory (LLNL), and single-particle measurements (SNL).
- **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)**. Our model development is synergist with models being developed for other solar hydrogen technologies (PEC, STCH), and we leverage EMN HydroGEN Consortium expertise in techno-economics (NREL) and life cycle assessment (LBNL).
- **A stable state-of-the-art particle for visible-light-driven photocatalytic H_2 production is Ir-doped $SrTiO_3$.** Through evaluation of Ir-doped $SrTiO_3$ photocatalyst particles and related multiply-doped ABO_3 perovskite materials **(AE)**, we are advancing the efficiency and selectivity of composite photocatalyst particles for solar H_2 production **(AG)**. Our materials discovery and development is synergistic with efforts for other solar hydrogen technologies that use similar materials (STCH), and our efforts support the Materials Genome Initiative (MGI).

Relevance and Impact

Initial "Type 2" Design

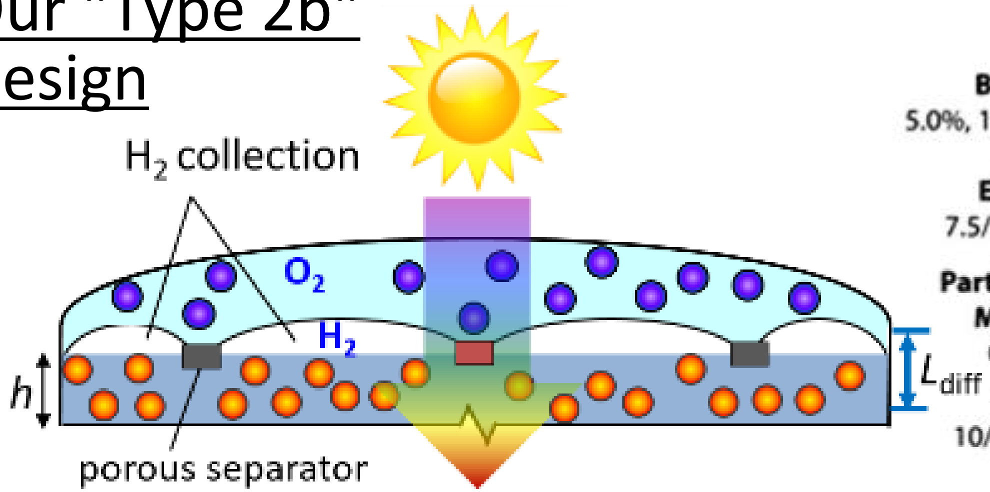


Type 2

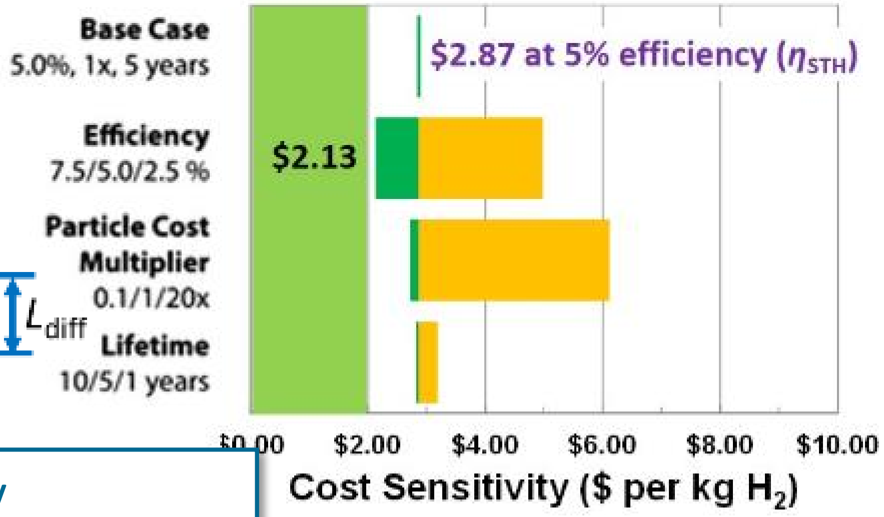


DOE H2A Analysis, https://www.hydrogen.energy.gov/h2a_production.html

Our "Type 2b" Design



Type 2b



- Serial light absorption increases efficiency
- Smaller mass transport distances require less mixing

Critical EMN Nodes to Enable R&D

(1) Surface Modifications for Catalysis (Coatings)
(2) Modeling of EChem Interfaces (Coatings)
(3) Electron/Photon Characterization (Particles)
(4) TEA of H_2 Production (Reactors)
(5) Prospective LCA Model for Plant (Reactors)

- *Coatings for selectivity and corrosion mitigation are cross-cutting* within the HydroGEN Consortium
- *Reactor-level modeling and experiments* are also relevant to all programs within the HydroGEN Consortium
- *Ultrafast spectroscopy expertise and capabilities* would be valuable resources to include in the HydroGEN Consortium

* *potentially addresses climate change, creates US jobs, and builds US clean energy infrastructure*

Accomplishments (Milestones and Year 1 Go/No-Go)

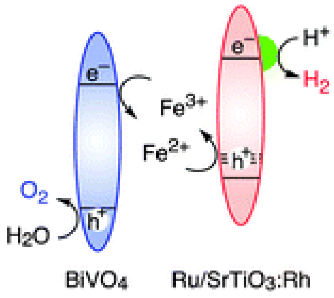
Subtask	Milestone	Milestone Description	Verification Process	Qtr
Numeric Models	M4.2.1	Quantify time-dependent and spatially-dependent temperature profiles and concentrations of redox shuttle species for ≥3 fluence conditions.	**Bala Chandran (UM)** Heat Maps, IR Camera *100% complete*	**Q3**
Numeric 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)** Properties, Numerical *>90% complete*	**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 H_2 evolution reaction and for the O_2 evolution reaction.	**Esposito (CU)[1]** Images, Ellipsometry *100% complete*	**Q4**
New Particles	**D1.1.1 (Go/No-Go)**	Quantum yield (QY) of ≥0.1% for H_2 evolution and >90% stability for 1 day from suspensions of Ir-doped $SrTiO_3$ particles in the presence of sacrificial electron donors and near-infrared-light excitation.	**Ardo (UCI)[2]** QY, Inline Mass Spec *100% complete*	**Q4**
Numeric Models	M4.2.2	Simulate effects due to light absorption and natural convection on quantum yield (QY) for H_2 evolution and solar-to-hydrogen (STH) conversion efficiency	**Bala Chandran (UM)** QY/STH, Numerical *100% complete*	**Q5**
New Particles	M1.2.1	Deposit an array of ABO_3 particles with ≥1000 dopant compositions	**Ardo (UCI)[3]** Visual Inspection *100% complete*	**Q6**

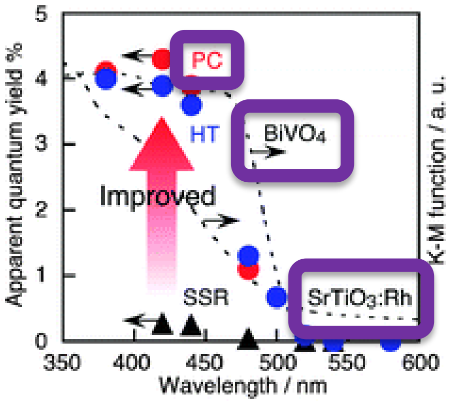
[1]Hurst, Katie (NREL) – atomic layer deposition of coatings
[2]Kudo, Akihiko (Tokyo University of Science) – syntheses of photocatalyst particles
[3]Gregoire, John (California Institute of Technology) – combinatorial materials deposition

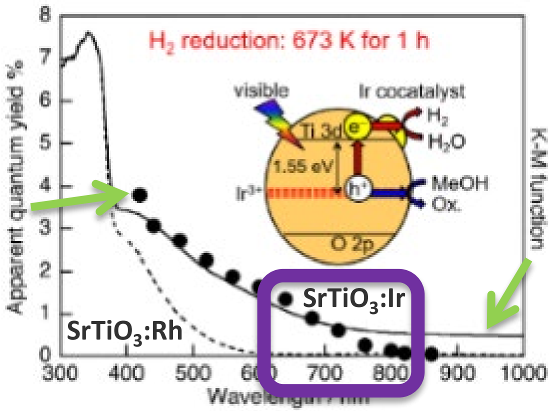
Accomplishments (Photocatalyst Particle Suspensions)

Motivation: Kato, Sasaki, Shirakura & Kudo, *J. Mater. Chem. A*, 2013, *1*, 12327
Suzuki, Matsumoto, Iwase & Kudo, *Chem. Comm.*, 2018, *54*, 10606

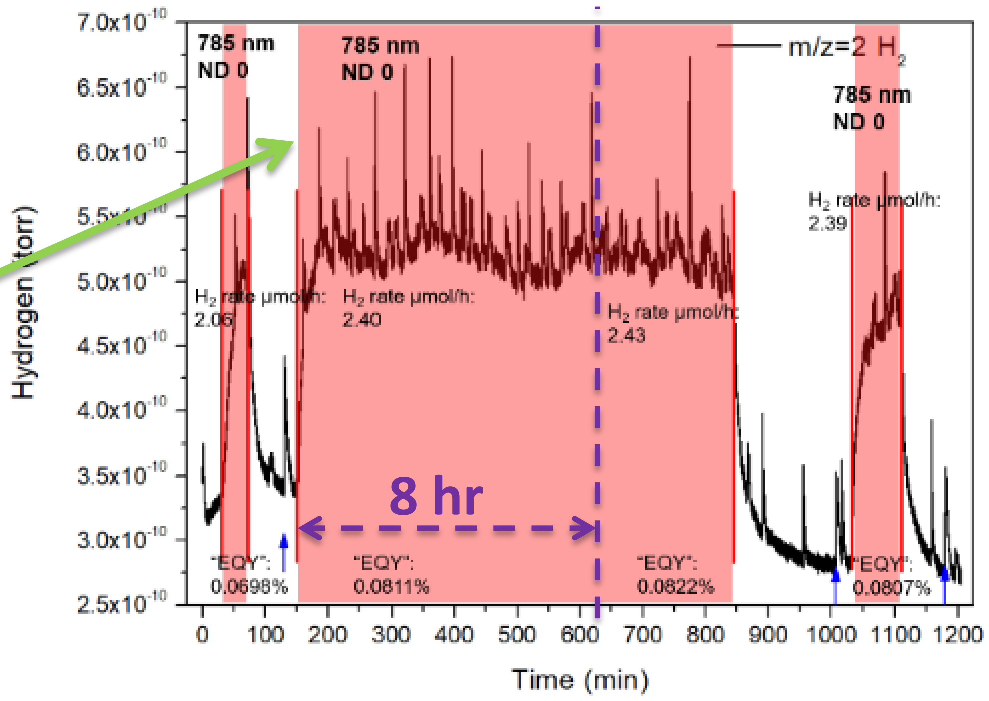
Z-scheme type photocatalysis system





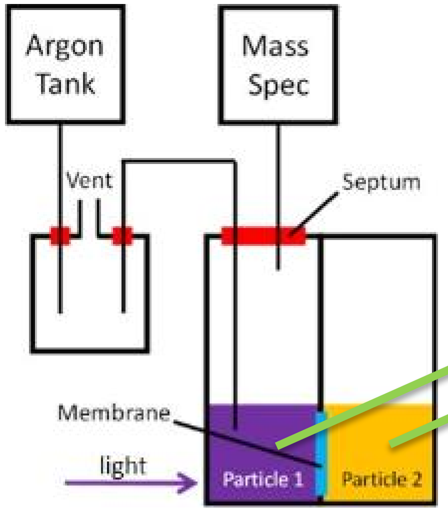


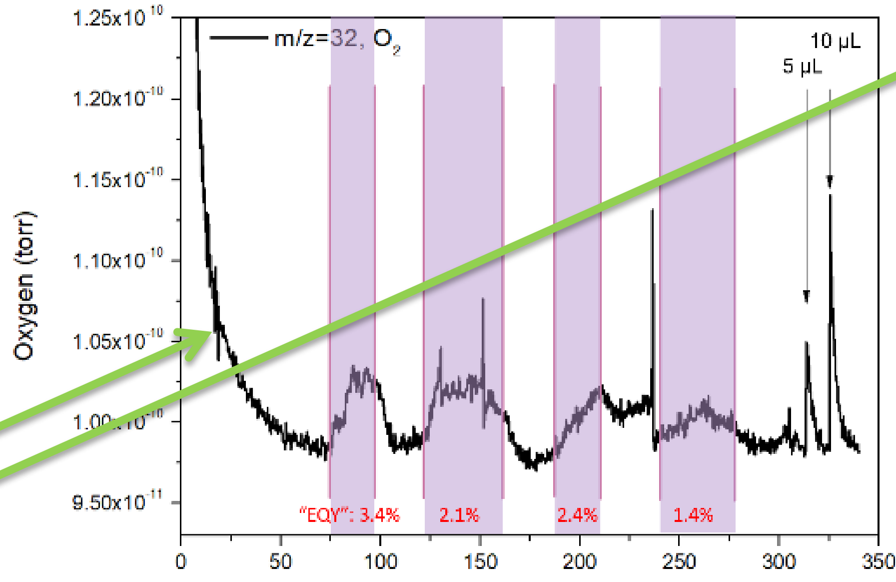
For Past M1.1.1: EQY_{405nm} > 1.0% for OER from 3x $BiVO_4$
For Current D1.1.1: IQY_{785nm} > 2.0% for HER from 3x Ir-doped $SrTiO_3$ and >90% stable over 8 hr



Ir/$SrTiO_3$:Ir (ID22) (1.8 mg/mL) with 0.3wt% Ir cocatalyst in aq 10 vol% CH_3OH under 785 nm LED illumination

Experiment:

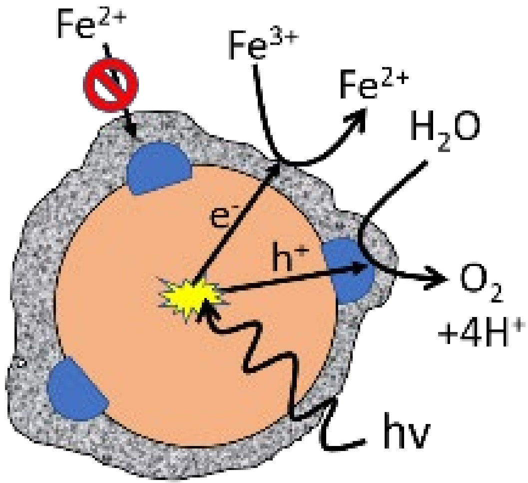


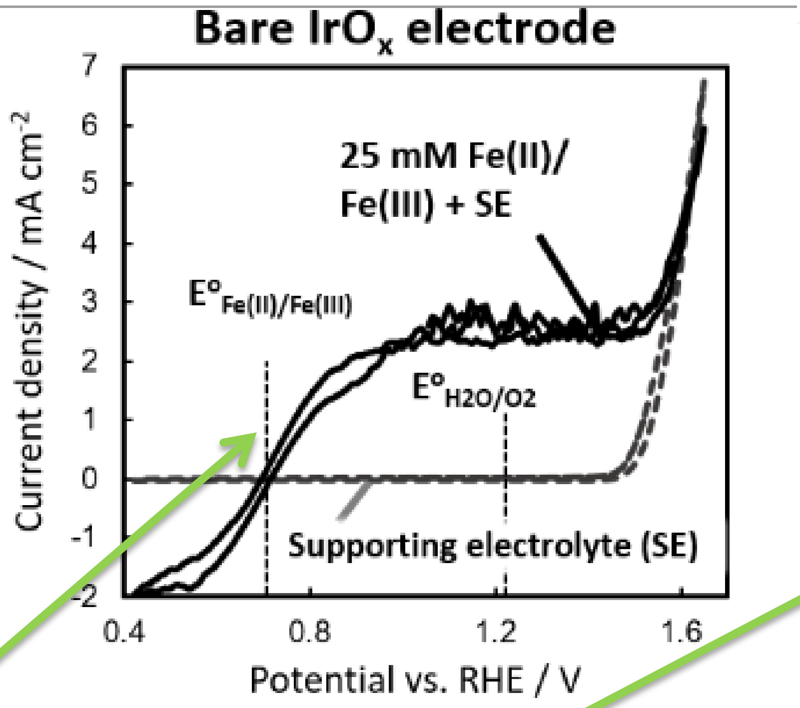


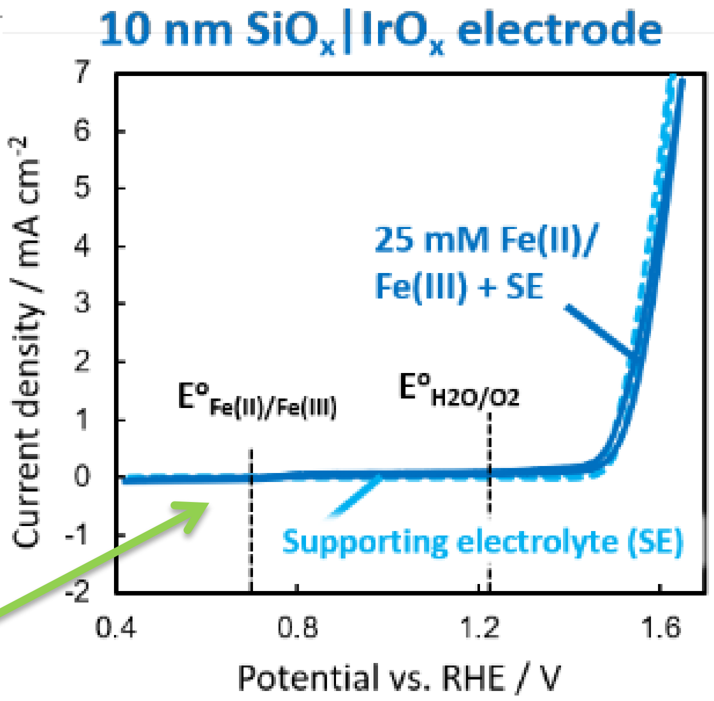
Time (min) **$BiVO_4$** (ID27) (5.1 mg/mL) in aq 50 mM $AgNO_3$ under 405 nm LED illumination

Accomplishments (Selective Coatings – Experiments)

Motivation:

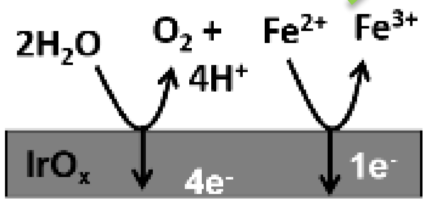


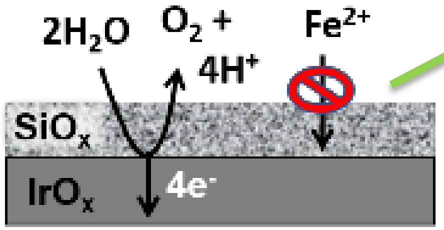




CVs (20 mV/s) in pH 1.5 aqueous Na_2SO_4(100 mM)–$Fe(SO_4)_n$(25 mM, 1:1 Fe(III):Fe(II))

Experiment:

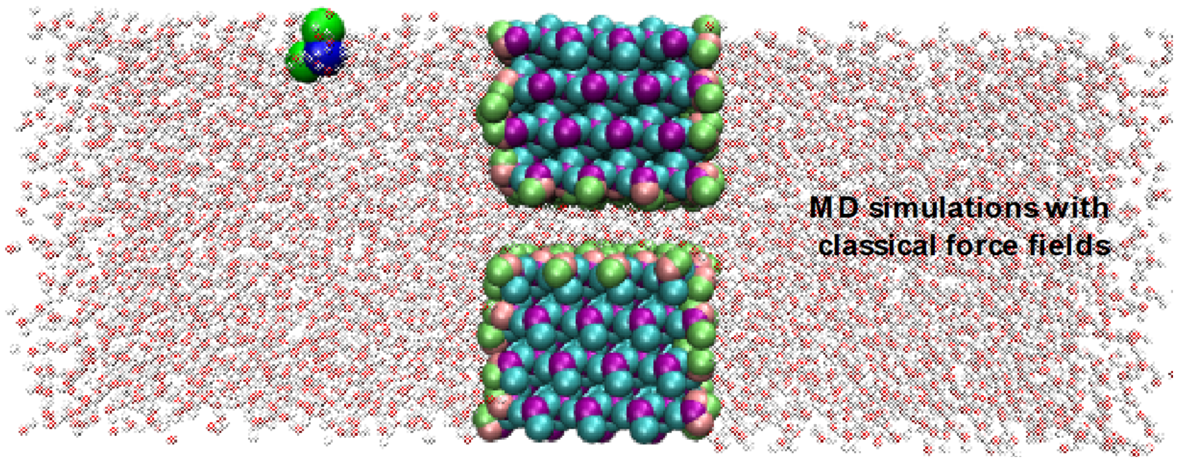


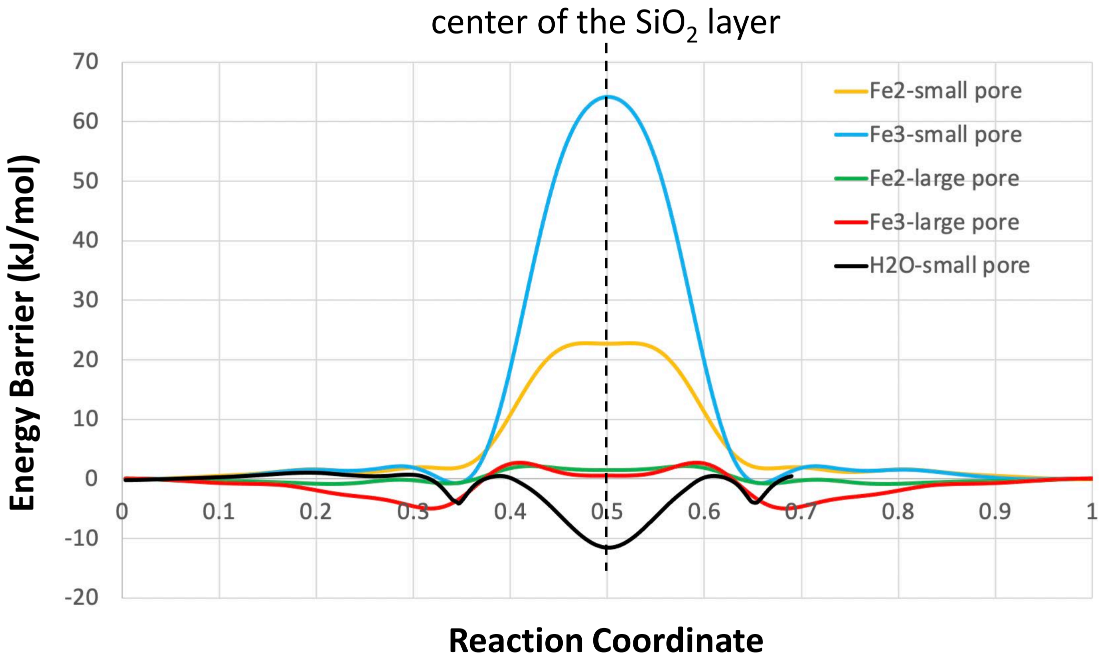


AMR 2020: ~5 nm thick SiO_x attenuates Fe(III) redox by ~10x, yet does not attenuate HER

Toward Future D2.1.1: ~10 nm thick SiO_x attenuates Fe(II) oxidation by ~97%, yet does not significantly attenuate OER; **very close to meeting Year 2 Go/No-Go**

Accomplishments (Selective Coatings – Theory)





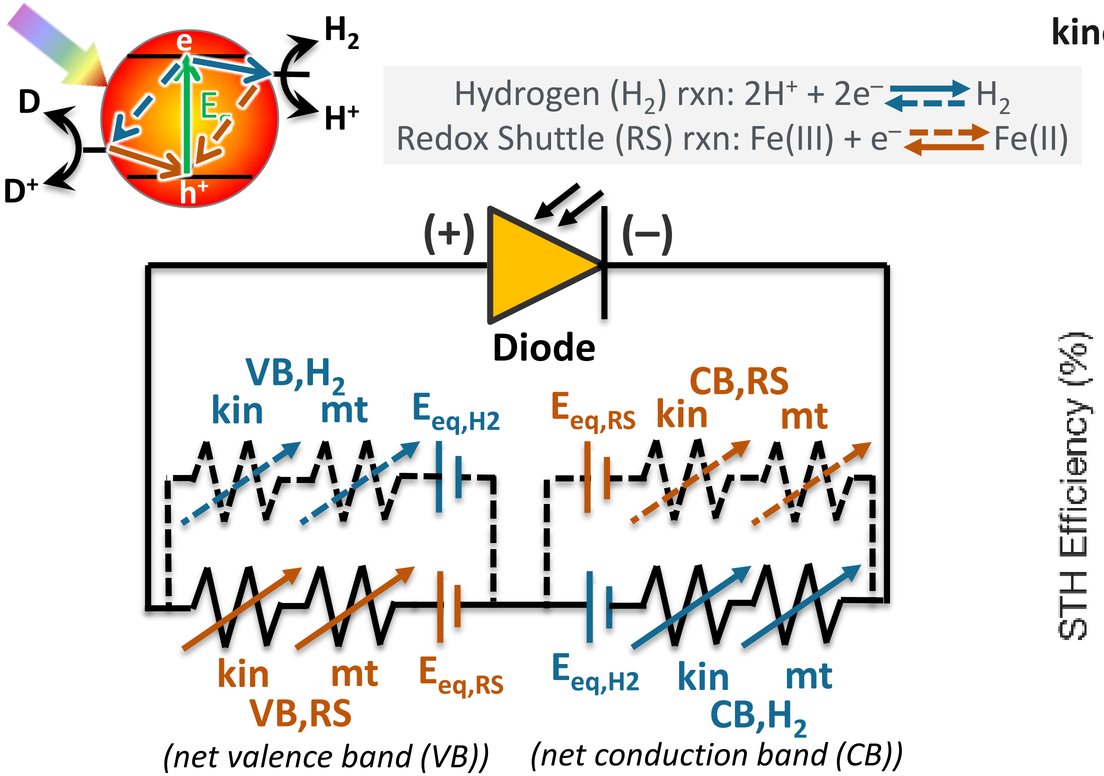
Questions that we aim to answer

- What surface interactions influence ion transport?
- How does coating composition and structure impact water and ion permeabilities?
- What are ion transport mechanisms?

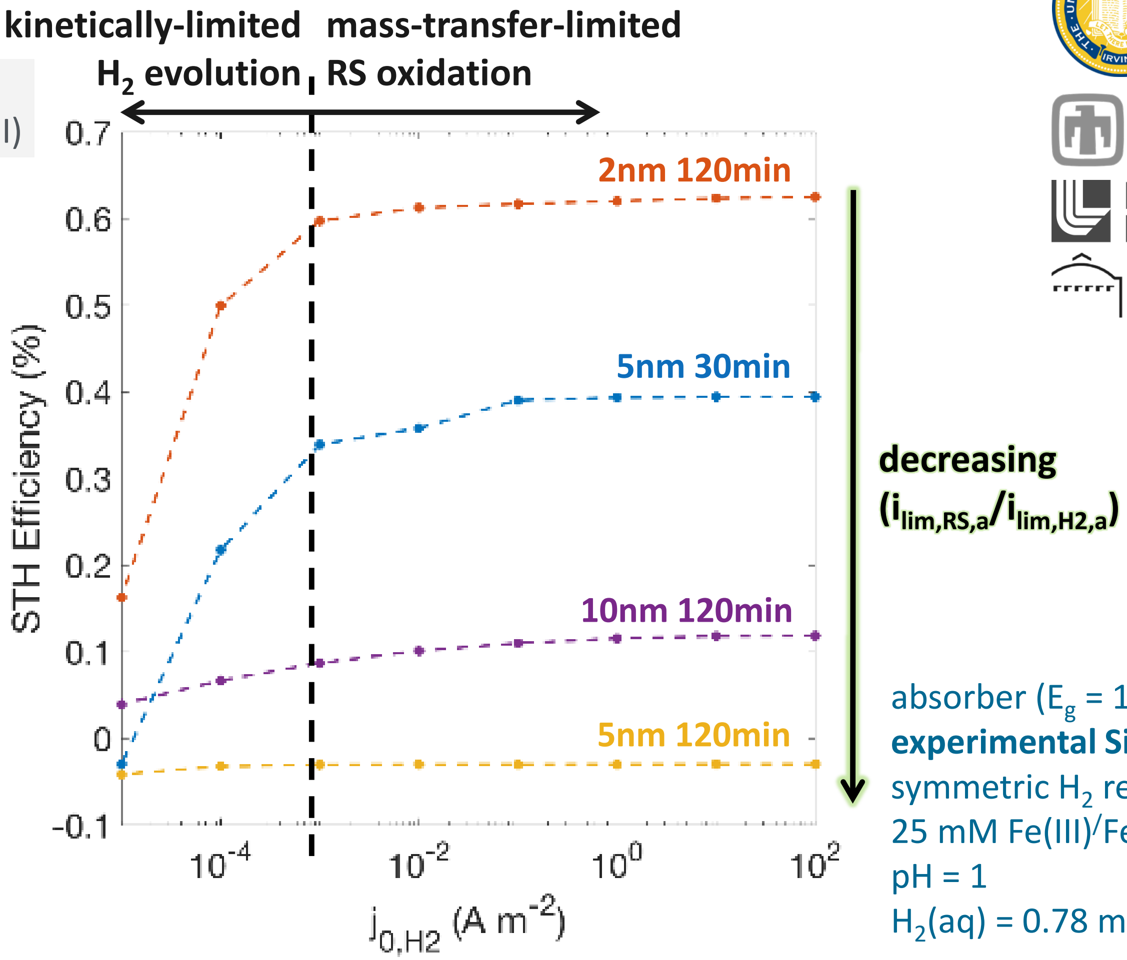
Meta-dynamics simulations for two pore sizes in SiO_2

- Pore sizes as Si–Si distances were 0.95 nm (small) and 1.35 nm (large)
- Suppressed transport of Fe(III), compared to Fe(II) and water, due to ion sieving
- Favorable water transport through even small pores in the SiO_2 layer

Accomplishments (Selective Coatings – Simulations)



Experimental SiO_x Coatings (Columbia U.)	**$i_{lim,RS,a}$ (mA cm⁻²)**	$i_{lim,RS,c}$ (mA cm⁻²)	**$i_{lim,H2,a}$ (mA cm⁻²)**	$j_{0,RS}$ (mA cm⁻²)	$\alpha_{RS,a}$	$\alpha_{RS,c}$
5nm 30min	**0.626**	-0.305	**0.392**	0.119	1.05	0.76
2nm 120min	**0.797**	-0.460	**0.278**	0.451	0.89	0.01
5nm 120min	**0.053**	-0.077	**0.122**	0.013	0.9	0.26
10nm 120min	**0.145**	-0.045	**0.067**	0.068	0.37	1.1



absorber (E_g = 1.6 eV, Abs = 100%)
experimental SiO_x ultrathin coating
symmetric H_2 redox ($\alpha_{H2,c} = \alpha_{H2,a} = 0.5$)
25 mM Fe(III)/Fe(II)
pH = 1
H_2(aq) = 0.78 mM (sat'd)

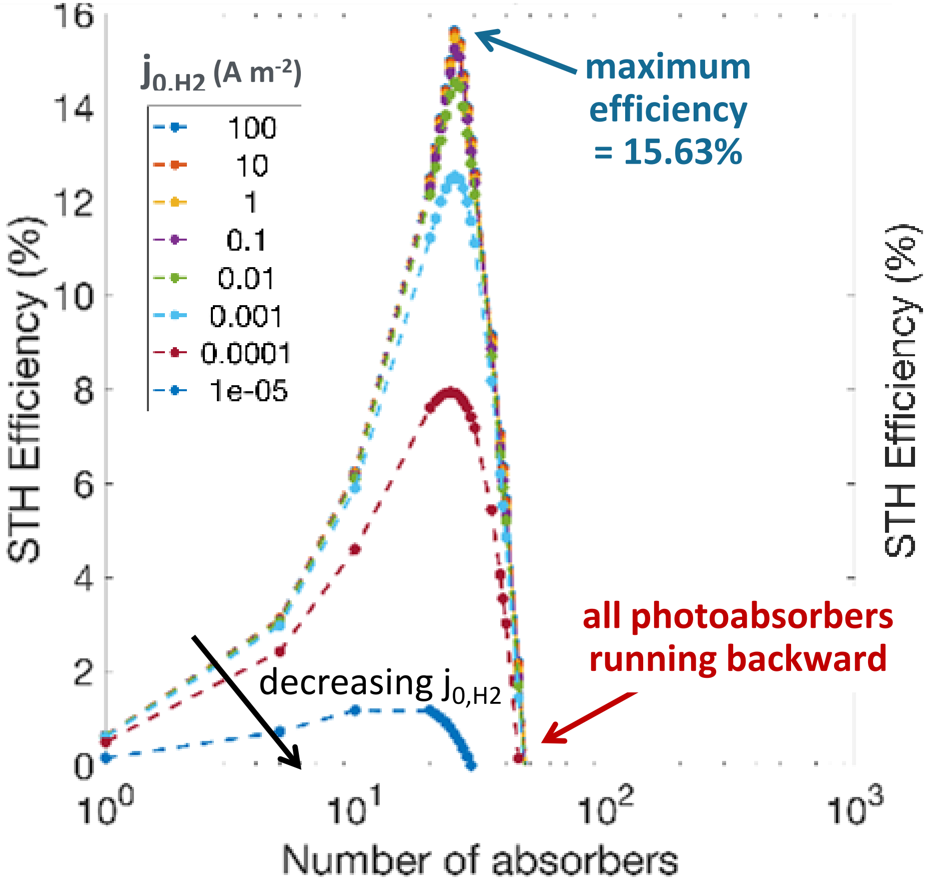
Toward Current M4.1.2: Assuming a single photoabsorber slab, solar-to-H_2 (STH) efficiencies are limited by low limiting redox shuttle oxidation current densities

Accomplishments (Selective Coatings – Simulations)

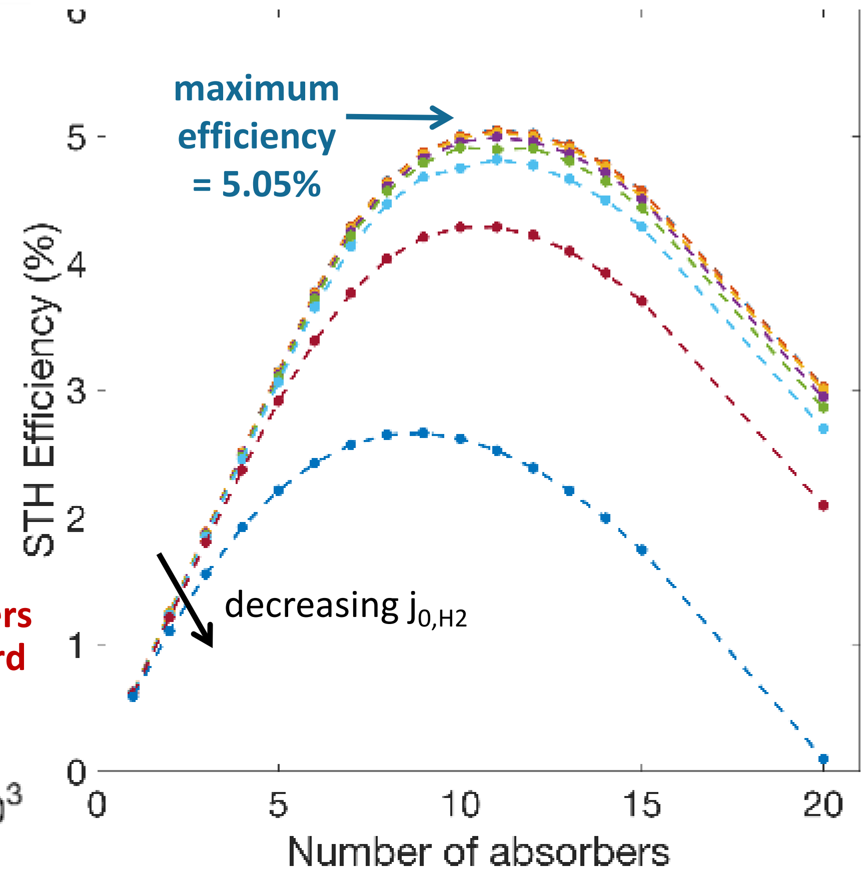
How does the solar-to-H_2 (STH) efficiency change if we have *N* light absorbers instead of just 1?

$$\eta_{STH} = \frac{\Delta G^o_{O_2/H_2O}}{I_{AM1.5}} \sum_{i=1}^{N} \frac{|j_{CB,H2,i}| - j_{VB,H2,i}}{n_e F}$$

"Best Case": light intensity split evenly over *N*



Beer's Law: light intensity decreases exponentially



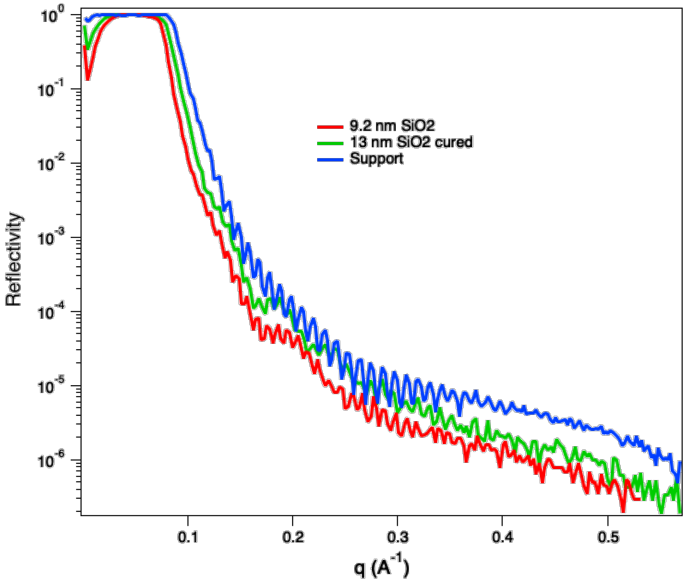
$$j_{0,BB} \propto \frac{I_{AM\,1.5}}{N}$$

absorber (E_g = 1.6 eV, Abs_{total} = 100% (BC), 68% (BL))
experimental SiO_x ultrathin coating (2nm 120min)
symmetric H_2 redox ($\alpha_{H2,c} = \alpha_{H2,a} = 0.5$)
25 mM Fe(III)/Fe(II)
pH = 1
H_2(aq) = 0.78 mM (sat'd)

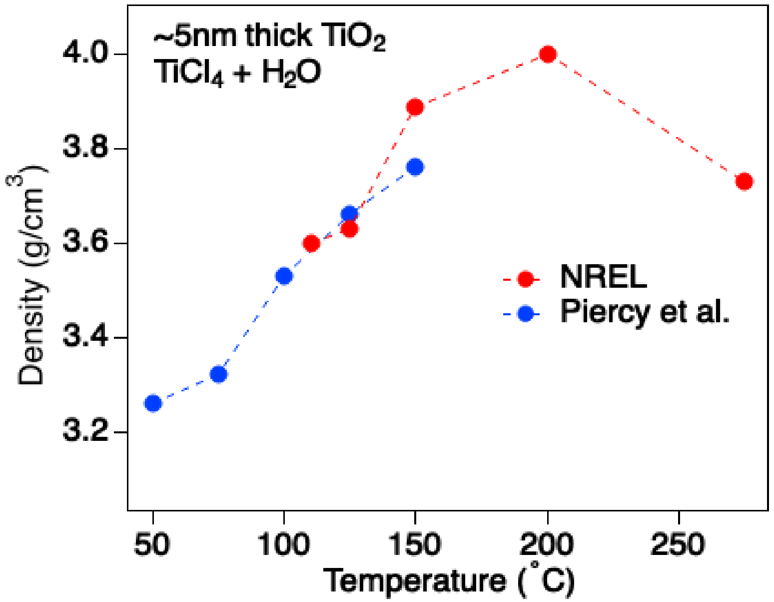
For Current M4.1.2, *Toward Future M4.1.3*: Solar-to-H_2 (STH) efficiencies depend on both limiting current densities and absorbed photon fluxes summed over all photoabsorbers

Accomplishments (Selective Coatings – ALD on Particles)

CU grown SiO_x films



NREL grown TiO_x films

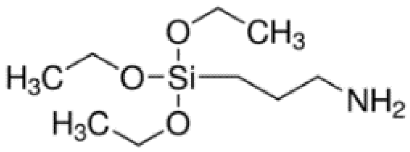


* Analysis of these X-ray reflectivity (XRR) data in progress

Developing ALD process for SiO_x ultrathin coatings

((3-aminopropyl)triethoxysilane (APTES) + H_2O + O_3)

* O_3 generator recently installed in ALD system



Toward Future M2.2.1, G2.2.1: Control of thickness and density of SiO_x and TiO_x ultrathin coatings

Cocatalyst/ABO_3(method): Dopant (ID)	Aqueous Electrolyte	EQY (%)
Pt/$SrTiO_3$(Solid State):Rh (Kudo: ID34)	10 v/v% CH_3OH	<3.57
	12 mM Fe(III)/Fe(II), pH 1.5	<2.2
+ 160 cycles ALD TiO_x (NREL)	10 v/v% CH_3OH	<0.059
	12 mM Fe(III)/Fe(II), pH 1.5	0
Ir/$SrTiO_3$(Polymerizable Complex):Ir (Kudo: ID35)	10 v/v% CH_3OH	<0.76

* TEM analysis of TiO_x coating thickness/conformality in progress

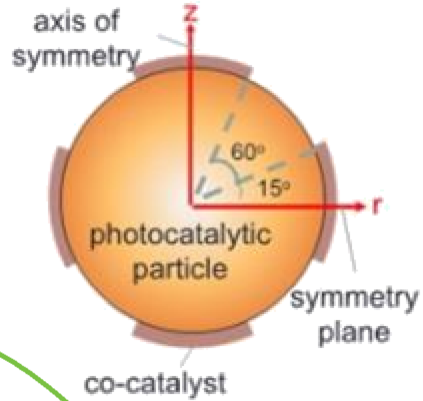
Accomplishments (Single Particles – Numerical Model)

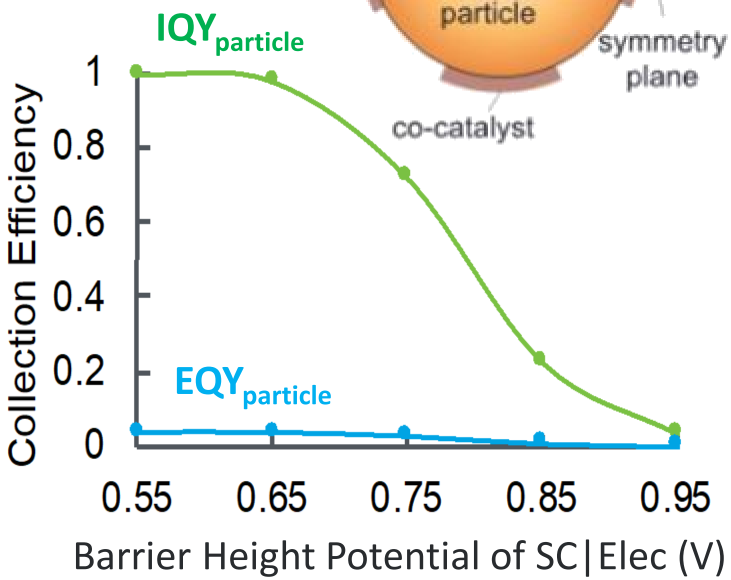
Motivation: Effects of particle size, optical, transport and interfacial parameters on quantum efficiencies

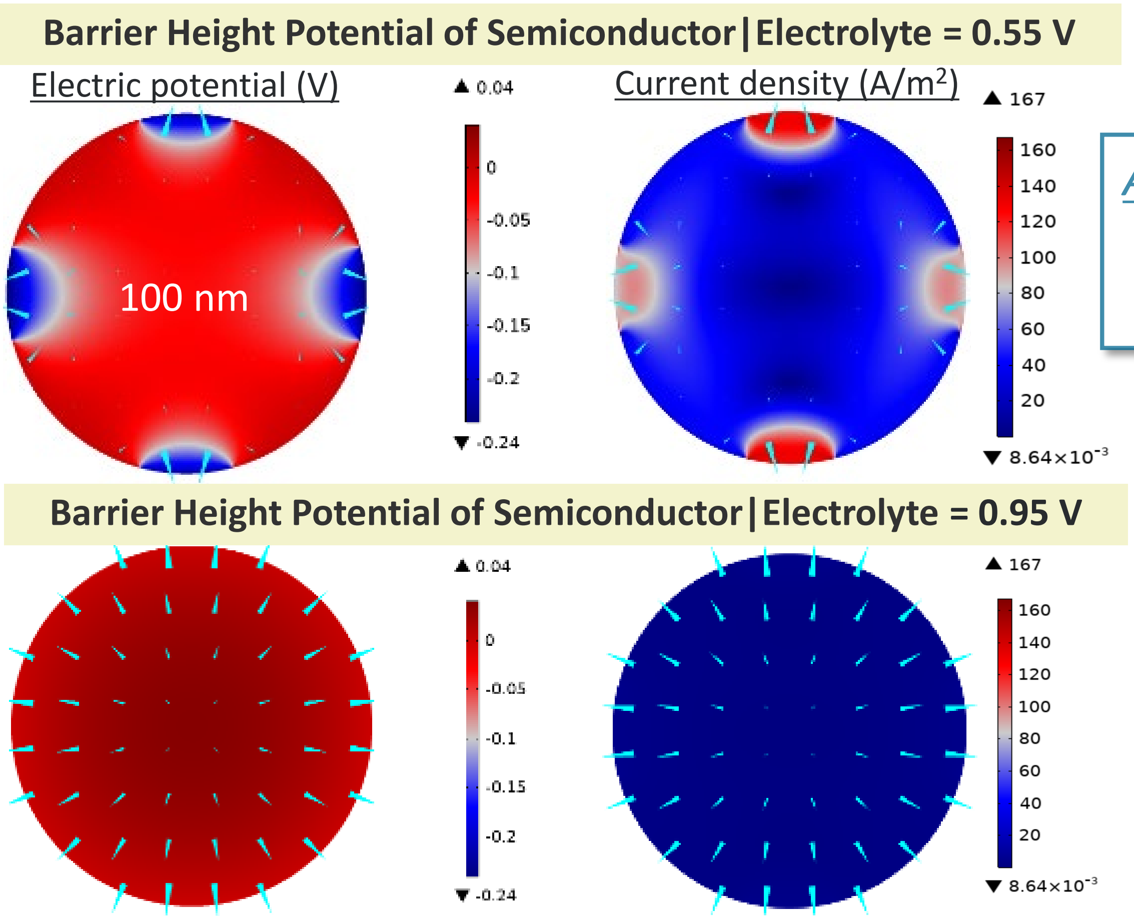
Model: 2D axisymmetric; drift–diffusion transport; bulk-limited generation/recombination; E_g = 2 eV; n-type dopant density = 6 x 10^{16} cm^{-3}; metallic and dense cocatalysts each with $\phi_{B,metal}$ = 1 V

$$\text{IQY}_{\text{particle}} = \frac{\text{Rate of } h^+/e^- \text{ leaving surface}}{\text{Rate of absorption of above bandgap photons}}$$

$$\text{EQY}_{\text{particle}} = \frac{\text{Rate of } h^+/e^- \text{ leaving surface}}{\text{Rate of incident AM1.5 photons}}$$



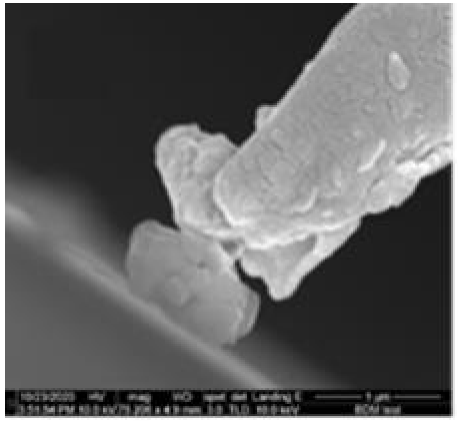


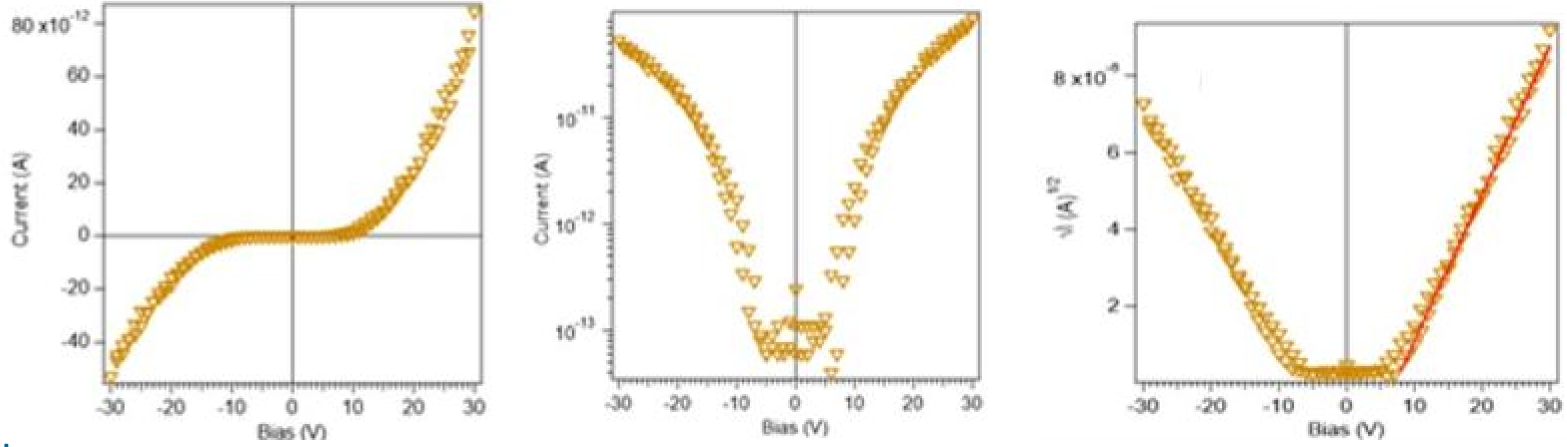


AMR 2020: Internal quantum yield (IQY) is affected by particle diameter

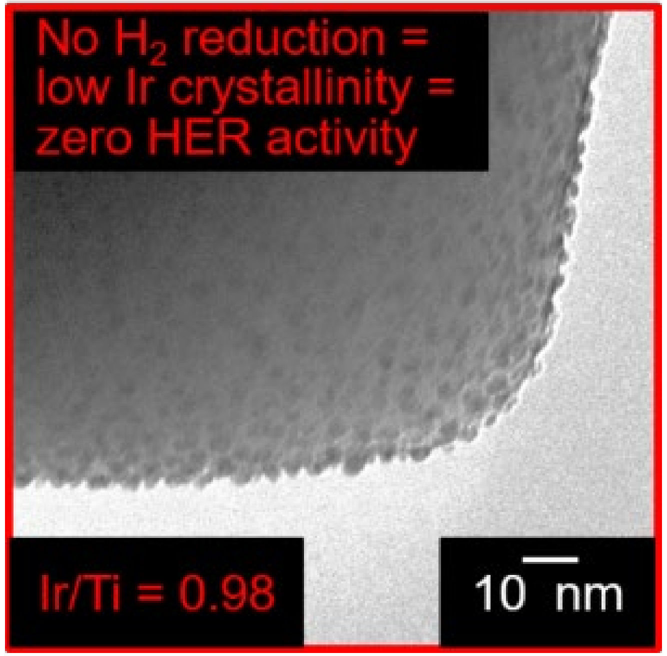
Toward Current M4.1.2: Assuming a single spherical photoabsorber particle, barrier height potential substantially influences charge-carrier separation

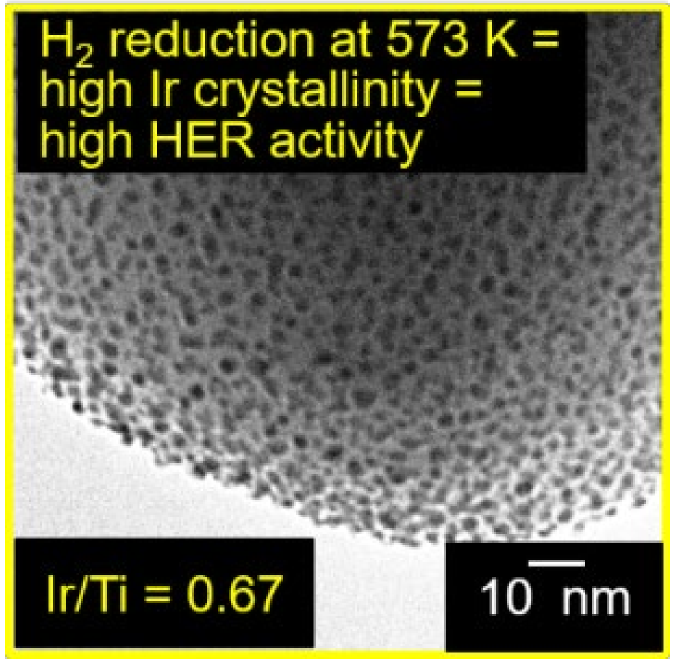
Accomplishments (Single Particles – Characterization)

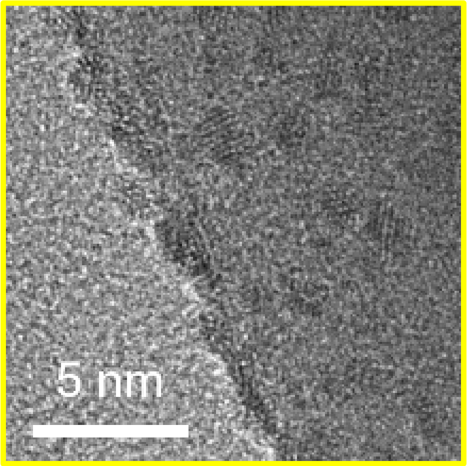




Single particle nano-probe electrical characterization *(EBIC and PEC (not shown))*: results on Rh-doped $SrTiO_3$ nanoparticles are consistent with space–charge-limited conduction (linear $I^{1/2}$–V behavior), and not Schottky-barrier-limited conduction (which would exhibit linear log(I)–V behavior)







TEMs indicate that photocatalytic activity correlates with Ir cocatalyst crystallinity

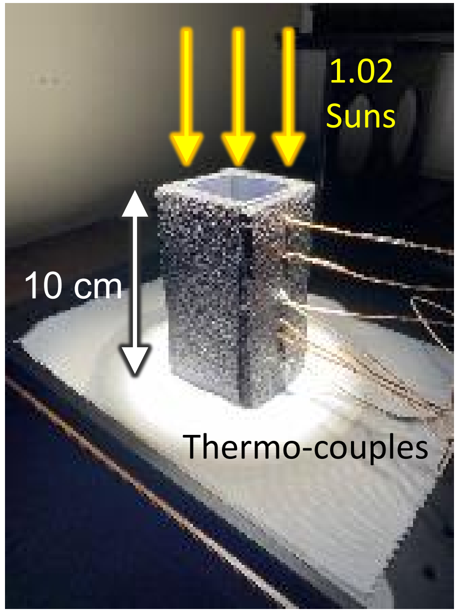
Accomplishments (Natural Convection – Experiments)

Motivation:

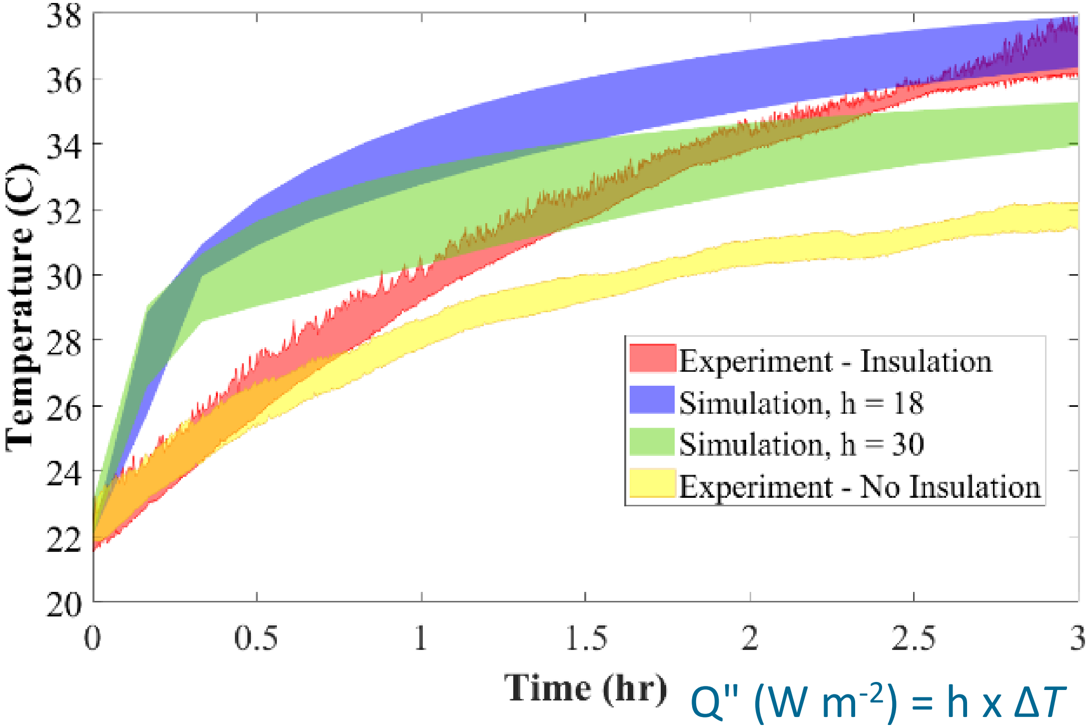
Original techno-economic analyses (DTI, 2009) predict that PVC piping required for forced convection is the largest capital cost of the reactor

Experiment:

Solar Simulator
Newport Oriel Sol3A
Xe lamp + AM 1.5G filter

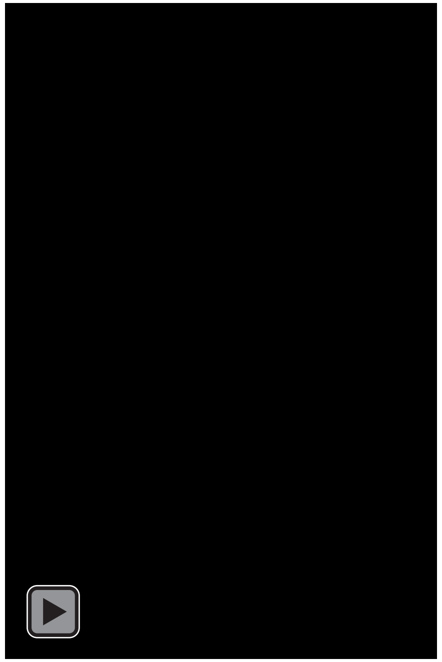


Prototype Reactor
10 cm polycarbonate tube
Acrylic base, painted black



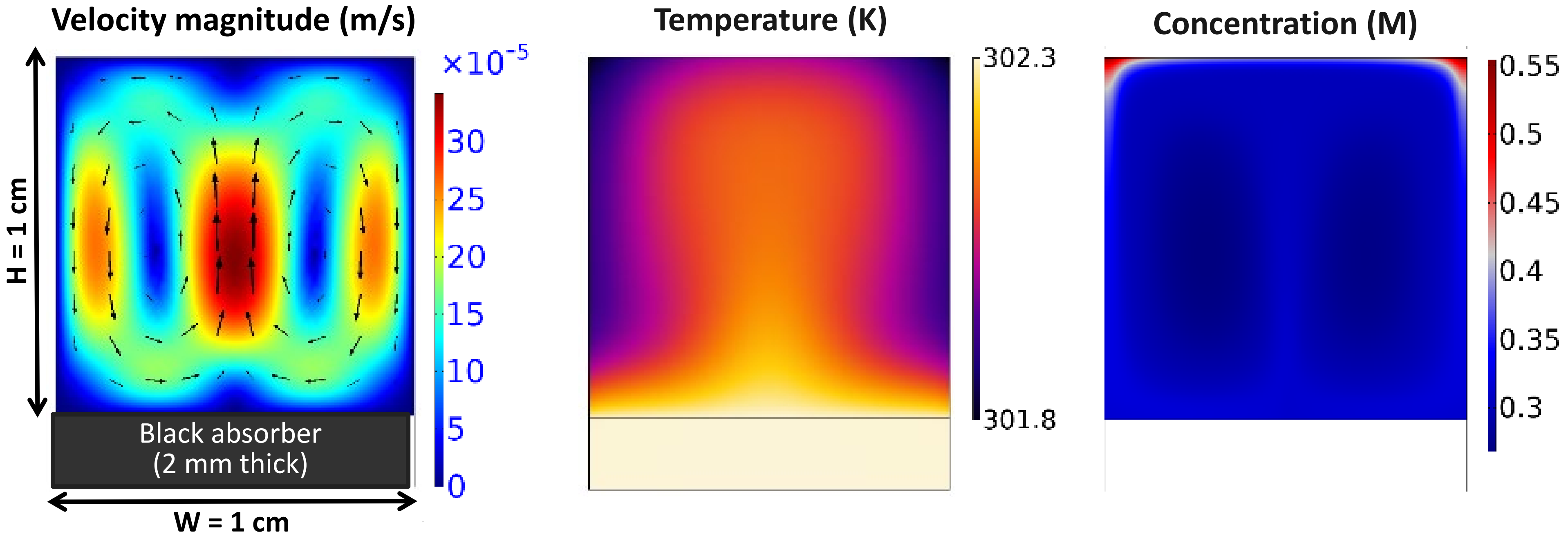
Q'' (W m^{-2}) = $h \times \Delta T$

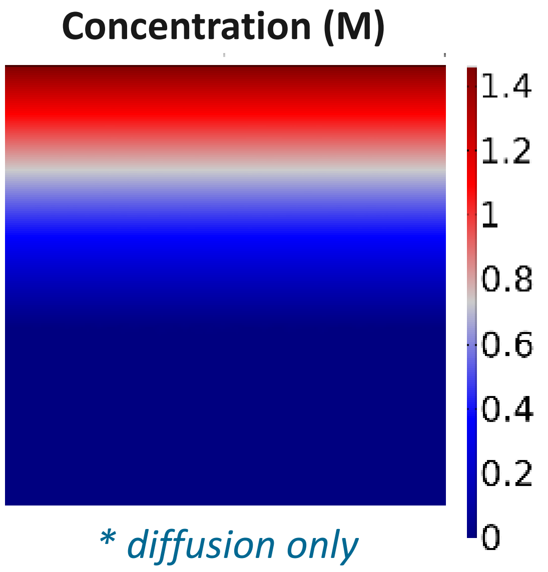
For Current M4.2.1: Illumination of a simple prototype reactor using a solar simulator results in mixing due to natural convection



VIDEO: Convective mixing after exposure to ~1 Sun irradiance (dye in water, 5x speed)

Accomplishments (Natural Convection – Simulations)





- coupled mass, momentum, energy, species transport in bottom compartment (redox shuttle species influx from the top)
- quasi-steady-state model (incident light intensity scaled using 8 hr of 1 Sun AM1.5 spectrum)
- uniform absorption of visible light (400 – 700 nm) and volumetric consumption of redox species at 10% STH efficiency
- infrared light is absorbed by water and follows Beer's law
- walls modeled with heat loss to the surroundings (h = 12 W m^{-2} K^{-1})
- no surface evaporation (h = 0)

For Current M4.2.2, *Toward Future M4.2.3*: Sunlight absorption results in natural convection, which results in much faster mixing than from diffusion alone

Collaboration: Effectiveness

Critical interactions with EMN project node experts

- Core science and engineering node collaborators attend every biweekly All Hands Team Meeting
- Katie Hurst (NREL), Surface Modifications for Catalysis and Corrosion Mitigation Node: ALD protocol development for SiO_x (and TiO_x) to coat planar electrodes and particles for assessment of redox selectivity; XRR measurements to determine coating density
- Tadashi Ogitsu (LLNL), Ab Initio Modeling of Electrochemical Interfaces Node: *ab initio* simulations of the pore size dependence of water and hydrated iron ion transport through graphite and SiO_x to inform desired coating properties
- Alec Talin (SNL), Electron Beam and In Situ Photon Beam Characterization of PEC Materials and Devices Node: SEM, electrical transport, EBIC and PEC measurements on various composite single particles to inform about non-ensemble behavior
- Genevieve Saur (NREL), Techno-Economic Analysis of Hydrogen Production Node, and Strategic Analysis, Inc.: discussions of design considerations for a cost and resource efficient "Type 2b" photocatalyst plant to re-assess reactor design feasibility
- Hanna Breunig (LBNL), Prospective LCA Model for 1-GW Scale PEC Hydrogen Plant Node: discussions of design considerations for a cost and resource efficient "Type 2b" photocatalyst plant to re-assess reactor design feasibility

Interactions with the broader HydroGEN research community

- Cross-cutting "2b" benchmarking/protocols project team: Lead PI Ardo and Co-PI Esposito were 2 of 7 PEC session leads at the March workshop; developing redox shuttle protocol paper and perspective paper on particle-based Z-scheme photocatalysis
- Developed photocatalyst activity metadata for global data repository; training and discussions with HydroGEN Data Hub experts scheduled for 4/30
- Akihiko Kudo (Tokyo University of Science): synthesis of doped and cocatalyst-modified $SrTiO_3$ and ABO_3 particles to provide particle libraries for deposition of coatings and assessment of H_2 and/or O_2 evolution activity
- John Gregoire (California Institute of Technology): combinatorial deposition and high-throughput spectroscopic characterization of several arrays of doped $SrTiO_3$ materials to discover dopant combinations that result in efficient photocatalytic performance
- Takashi Hisatomi (Shinshu University): synthesis of mixed metal-oxide/nitride/sulfide particles to provide (historically unstable) particle libraries for deposition of coatings, assessment of H_2 and/or O_2 evolution activity, assessment of materials stability
- Xiaoqing Pan, Ruqian Wu, Nien-Hui Ge (University of California Irvine): synergistic UCI Seed Funding
- Senior Undergraduate Design Project (University of Michigan): synergistic prototype design and development

Proposed Future Work (Milestones and Y2 Go/No-Go)

Subtask	Milestone	Milestone Description	Verification Process	Qtr
Numeric Models	M4.2.3	Quantify minimum redox shuttle concentration for sustained reactor operation at 3 – 10% efficiency with natural convection – **use current models, to support feasibility of our reactor designs**	**Bala Chandran (UM)** Conc., Numerical *>90% complete*	**Q7**
Tech-niques	M3.1.1	Quantify H_2 evolution activity and materials properties of a single wetted photocatalyst particle – **microscopy images taken and activity measured for <10-particle clusters, thus sonicate them more, to bridge single particle to reactor scale performance**	**Ardo/Esposito (UCI/CU)[1]** Activity, EChem/TEM *>90% complete*	**Q8**
Selective Coatings	**D2.1.1 (Go/No-Go)**	Demonstrate a selective ultrathin oxide coating on a thin-film electrode that exhibits ≥95% selectivity for the desired H_2 and also O_2 evolution reactions – **nearly fully achieved, which will support pathways to high-efficiency solar photocatalytic water splitting**	**Esposito (CU)[2]** LSV, Potentiostat *>90% complete*	**Q8**
Tech-niques	M3.2.1	Quantify the H_2 evolution activity of an array of ABO_3 materials in ≤1 day – **leverage prior expertise in screening arrays of materials, in order to discover new efficient dopant combinations**	**Ardo/Esposito (UCI/CU)[3]** H_2 Activity, HTE Method *Year 3*	**Q9**
Selective Coatings	M2.2.1	Demonstrate a selective ultrathin oxide coating on particles that results in a ≥2 times larger H_2 evolution quantum yield (QY) – **continue work, to support paths to high-efficiency photocatalysis**	**Ardo (UCI)[2]** QY, Inline Mass Spec *Year 3*	**Q10**
Numeric Models	M4.1.3	Determine optimal coating thickness and coverage of electro-catalysts on a single particle that result in 3 – 10% efficiency – **use and update single particle model, to inform materials parameters**	**Bala Chandran (UM)** Loading, Numerical *Year 3*	**Q10**

Tokyo University of Science; California Institute of Technology; Shinshu University; University of California, Irvine; Columbia University; University of Michigan; Sandia National Laboratories; NREL Transforming ENERGY; Lawrence Livermore National Laboratory; Berkeley Lab – Bringing Science Solutions to the World

** All Co-PI have plans to reopen their labs to full capacity shortly*

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

[1]Talin, Alec (SNL) – nanoprobe measurements of single particles
[2]Hurst, Katie (NREL) – atomic layer deposition of coatings
[3]Gregoire, John (California Institute of Technology) – combinatorial materials deposition

Proposed Future Work

- **<u>End of Project Goal</u>: Demonstrate a selective ultrathin oxide coating on particles that results in a ≥10 times larger H_2 evolution quantum yield than for uncoated particles**
- *For the past year, all three Co-PI's labs operated at a reduced capacity*
  - *Labs at UC Irvine and Univ. of Michigan recently regained full working capacity*
- Experimental efforts have been ahead of schedule and so it is likely that remaining experimental milestones can be met according to the SOPO, although the End of Project Goal is more ambitious
- Numerical modeling and simulation efforts were slightly behind schedule for most of the project, due to the breadth of physics proposed for each milestone, but those efforts are now on schedule

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

Technology Transfer Activities

- Our technology-to-market strategy involves occasional conversations with major chemical and gas companies
- Follow-on funding opportunities will be considered as they become available, with an eye toward center-scale funding opportunities
- The current TRL of our technology is somewhat too low to engage in detailed marketing strategies
- To-date, there no intellectual property filings from this project
- Prior related 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.*

Project Summary

- Cost effective particle-based Z-scheme (Type 2) solar water splitting reactors require innovations in reaction selectivity and low-cost redox shuttle mixing
- Our team consists of >10 senior personnel and >10 junior personnel that together are designing, developing, and characterizing new composite photocatalyst particles for solar water splitting
- We reproducibly demonstrated H_2 evolution from Ir-doped $SrTiO_3$ particles using near-infrared light excitation and with >90% stability for >1 day
- We reproducibly demonstrated that a <10 nm thick SiO_x or TiO_x coating results in >95% selectivity for the H_2 evolution reaction over undesired redox shuttle reduction and the O_2 evolution reaction over undesired redox shuttle oxidation
- We have developed a modeling framework that spans multiple length scales and can simulate species transport through ultrathin coatings, single photocatalyst particle behavior, efficiencies for ensembles of photocatalyst particles, and reactor-scale natural convection

Presentations

(1) Invited Talk (virtual), Solar Energy Systems Conference, **August 12, 2020**, W. Gaieck, S. Keene, Z. Chen, K. Watanabe, R. Stinson, L. Barrera, M. Xu, X. Pan, A. Kudo, D. V. Esposito, R. Bala Chandran, S. Ardo,* “Design guidelines for photocatalyst reactors for solar fuels production based on numerical simulations and composite materials engineering”

(2) Invited Presentation (virtual), DOE-EERE-FCTO HydroGEN Go/No-Go Annual Review Meeting, **September 23, 2020**, S. Ardo,* “Development of Composite Photocatalyst Materials that are Highly Selective for Solar Hydrogen Production and their Evaluation in Z-Scheme Reactor Designs”

(3) Invited Seminar (virtual), Department of Materials Science & Engineering, Rutgers University, **September 29, 2020**, D. Esposito,* “Electrocatalysis at Buried Interfaces”

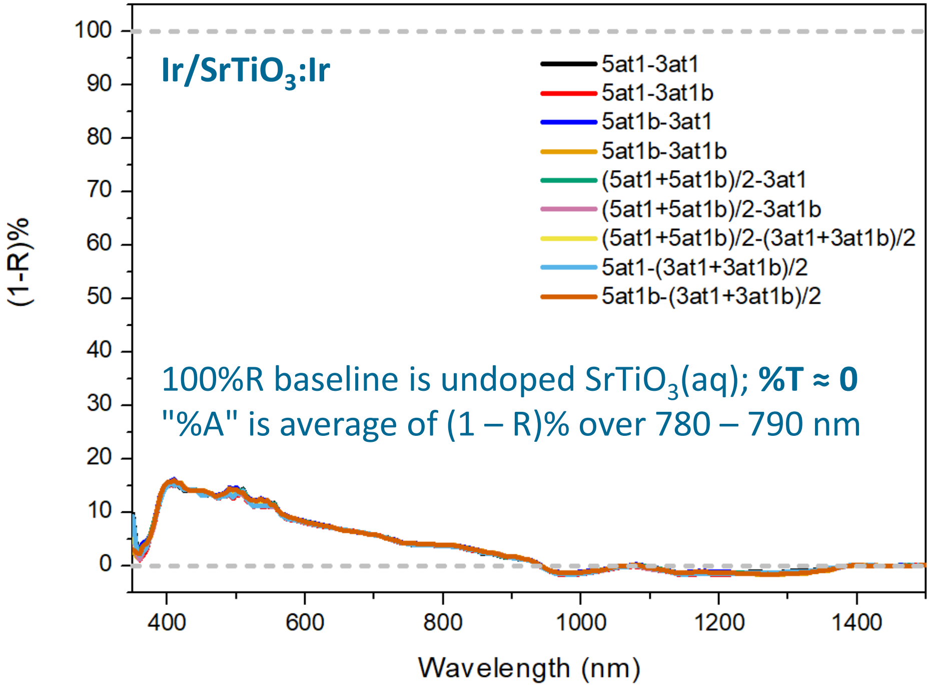
(4) Invited Seminar (virtual), Department of Mechanical Engineering, University of Waterloo, **October 8, 2020**, R. Bala Chandran,* “Understanding Transport and Chemical Phenomena in Solar Fuel Generators, Thermal Energy Storage & Wastewater Nutrient Recovery”

(5) Invited Seminar (virtual), Department of Chemical Engineering, University of Cantabera, Spain, **November 19, 2020**, D. Esposito,* “Electrocatalysis at Buried Interfaces”

Technical Backup Slides

Accomplishments (Photocatalyst Particle Suspensions)

Reactor cell



	"Abt_{785nm}" (%)	$IQY_{\geq 8hr}$ (%) (n = 3)
EQY	(assumed 100)	0.0808 ± 0.0009
IQY*	90.0 ± 0.6	0.090 ± 0.001
IQY**	81.2 ± 0.3	0.099 ± 0.001
IQY***	5.4 ± 0.5	1.5 ± 0.1
IQY******	**3.90 ± 0.08**	**2.07 ± 0.05**

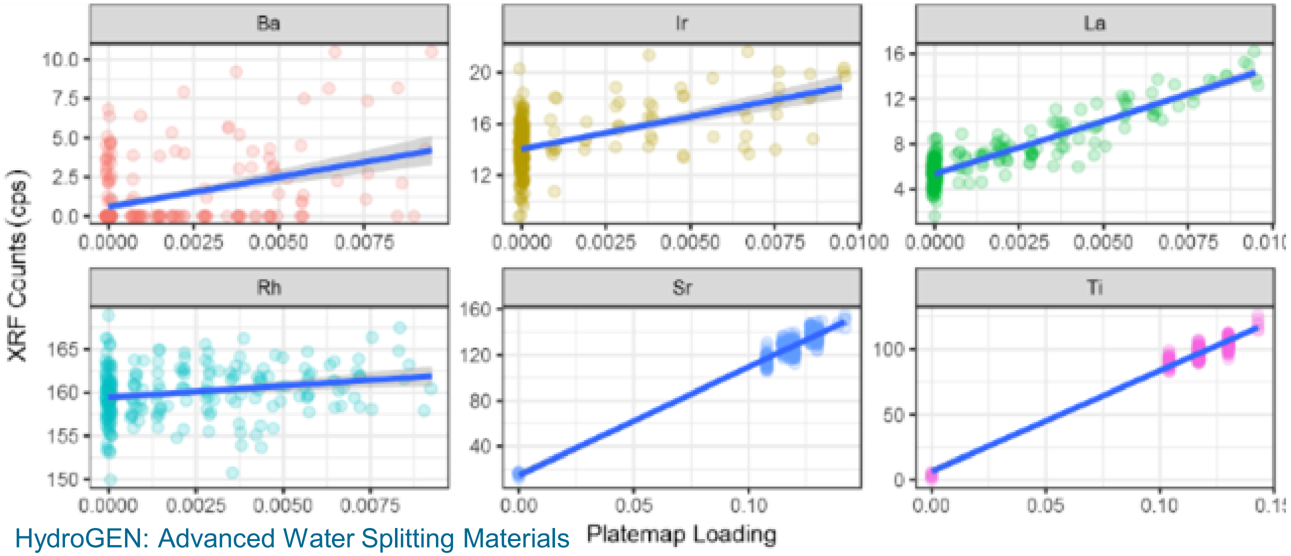
EQY = External Quantum Yield = rate H_2 / incident photon flux
IQY = Internal Quantum Yield = rate H_2 / absorbed photon flux
Abt = Absorptance = 1 – Reflectance = (1 – %R)

- IQY* is calculated as EQY/%A, assuming that the only light lost is that of specular reflection due to refractive index mismatches between 10% v/v CH_3OH(aq), quartz, and air
- IQY** is calculated as EQY/%A, assuming that the main loss of light is due to imperfect cell design, with (1 – %R) reported referenced to a baseline on a standard reflective material
- IQY*** is calculated as EQY/%A, assuming that the main loss of light is due to imperfect cell design, with (1 – %R) reported referenced to a baseline of 10% v/v CH_3OH(aq), and zeroed based on offset of signals at 1400 – 1500 nm
- IQY**** is calculated as EQY/%A, assuming that the main loss of light is due to imperfect cell design, with (1 – %R) reported referenced to a baseline of undoped $SrTiO_3$(aq), and zeroed based on offset of signals at 1400 – 1500 nm (see figure)

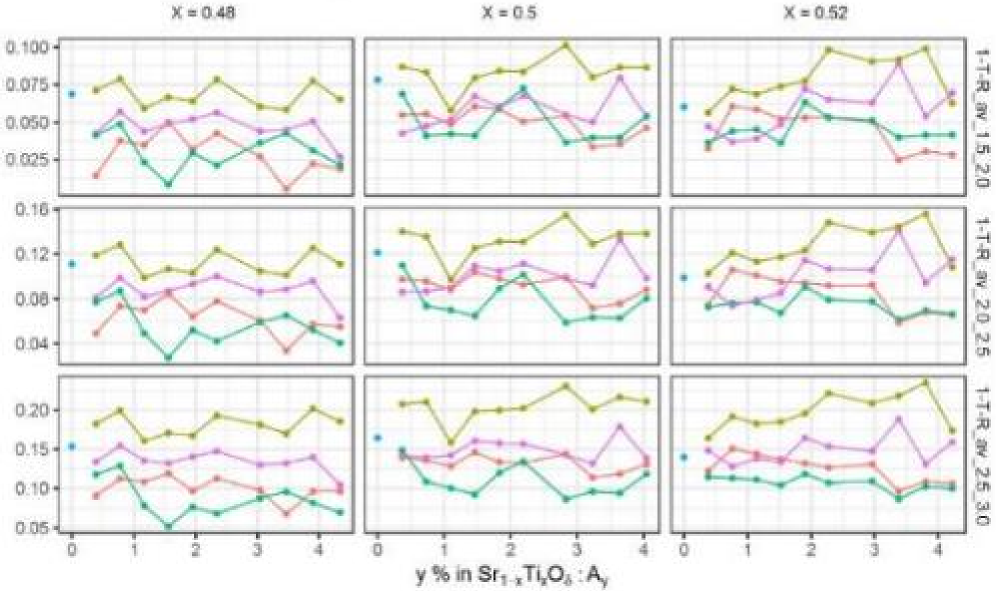
Accomplishments (Combinatorial Deposition of $SrTiO_3$)

~1800 doped $SrTiO_3$ materials, containing various amounts of Rh, La, Ir and/or Ba dopants, deposited using ink-jet printing on a quartz plate

X-Ray Fluorescence



Absorptance (1 – %T – %R)



1.5 – 2.0 eV spectral range

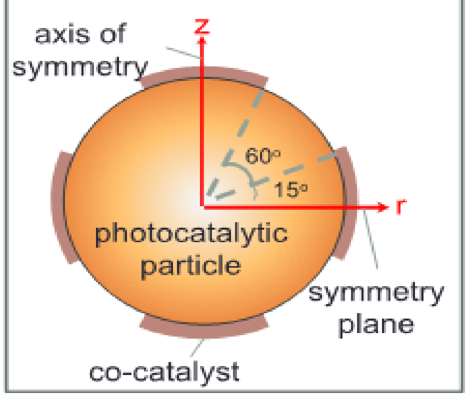
2.0 – 2.5 eV

2.5 – 3.0 eV spectral range

Accomplishments (Single Particles – Numerical Model)

Parameter	Value
Band gap energy, E_g	2 eV
Above-bandgap absorption coefficient, α	1.2 x 10^7 m^{-1}
Semiconductor|Electrolyte Barrier Height: $\phi_{B,sem}$	varies
Semiconductor|Cocatalyst Barrier Height: $\phi_{B,metal}$	1 V
Bulk recombination rate constant	10^{-14} m^3/s
Mobility of charge carriers, μ	0.01 m^2/s
Relative permittivity of semiconductor, ε_r	12
Density of states, N_C and N_V	10^{21} cm^{-3}
Donor dopant density, N_D	6 x 10^{16} cm^{-3}

Modeling Domain



Governing Equations

Poisson's equation

$$\nabla.(\epsilon_r \nabla\phi) = \frac{q}{\epsilon_0}(N_D + p - n)$$

Drift-Diffusion Equation

$$\nabla\cdot\Big(\underbrace{D_e\nabla n - \mu_e n\nabla\phi}_{J_n/q_e}\Big) = (G_{np} - R_{np})$$

$$\nabla\cdot\Big(\underbrace{D_h\nabla p + \mu_e p\nabla\phi}_{-J_p/q_e}\Big) = (G_{np} - R_{np})$$

$$G_{np} = \alpha G_{ph}\exp\left(-\alpha\left(r_p - \sqrt{r^2 + z^2}\right)\right)$$

$$G_{ph} = \int_0^{\lambda_{bg}=\frac{hc}{E_{bg}}} \phi_{AM1.5}(\lambda)d\lambda$$

$$R_{np} = \beta(np - n_i^2)$$

Boundary Conditions

Electrostatic Potential:

Semiconductor | Electrolyte: $\phi = -\psi_{el} = -(\phi_{B,sem-el} + \chi_{sem})$

Semiconductor | Co-catalyst: $\phi = \eta - \psi_{metal} = \eta - (\phi_{B,metal-el} + \chi_{sem})$

Flux of h+/e-:

$$J_n = -q_e v_{s,n}(n - n_0); J_p = q_e v_{s,p}(p - p_0)$$

$$n_0 = N_c \exp\left(-\frac{q_e\phi_B}{k_B T}\right); p_0 = N_v \exp\left(-\frac{q_e(E_g - \phi_B)}{k_B T}\right)$$

Cocatalyst-electrolyte Interface:

$$J_{tot} = J_n - J_p = j_{0,cat}\left(\exp\left(\frac{\alpha_a\eta}{V_{th}}\right) - \exp\left(\frac{-\alpha_c\eta}{V_{th}}\right)\right)$$

Accomplishments (Single Particles – Numerical Model)

Tokyo University of Science, California Institute of Technology, Shinshu University, University of California Irvine, Columbia University, University of Michigan, Sandia National Laboratories, NREL, Lawrence Livermore National Laboratory, Berkeley Lab

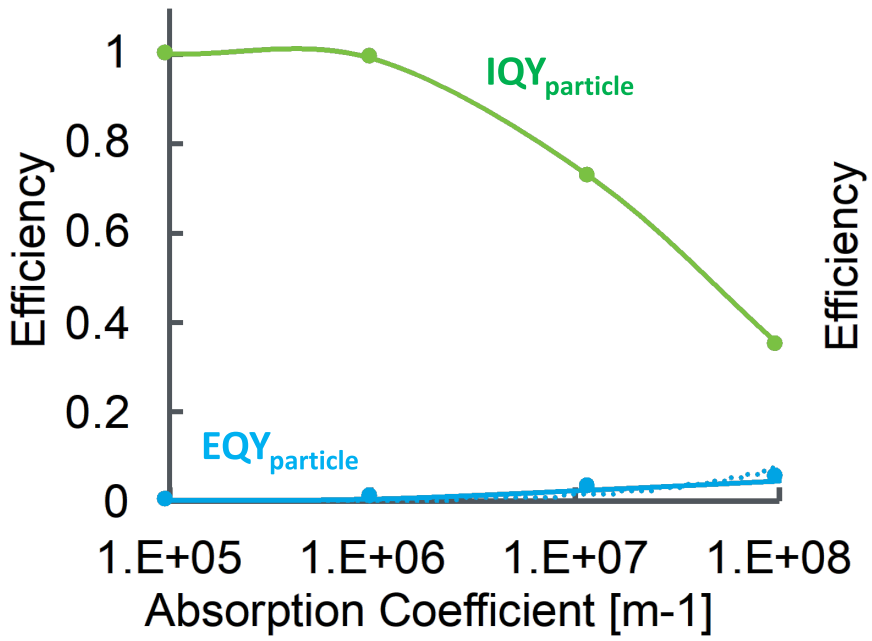
Motivation: Effects of particle size, optical, transport and interfacial parameters on quantum efficiencies

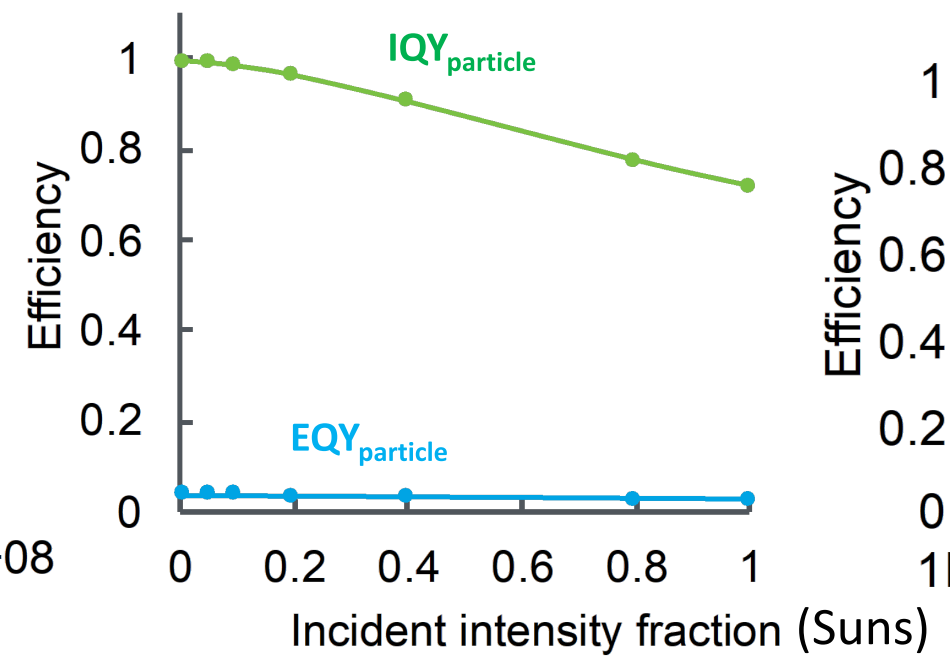
Model: 2D axisymmetric; drift–diffusion transport; bulk-limited generation/recombination; E_g = 2 eV; n-type dopant density = 6 x 10^{16} cm^{-3}; metallic and dense cocatalysts each with $\phi_{B,metal}$ = 1 V

$$IQY_{particle} = \frac{\text{Rate of } h^+/e^- \text{ leaving surface}}{\text{Rate of absorption of above bandgap photons}}$$

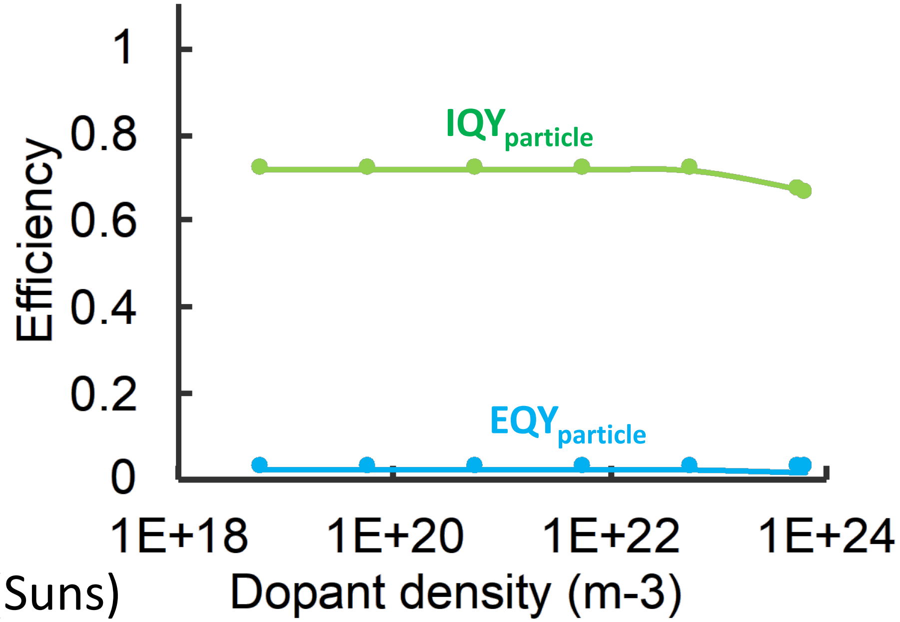
$$EQY_{particle} = \frac{\text{Rate of } h^+/e^- \text{ leaving surface}}{\text{Rate of incident AM1.5 photons}}$$

Effects of Optical Properties





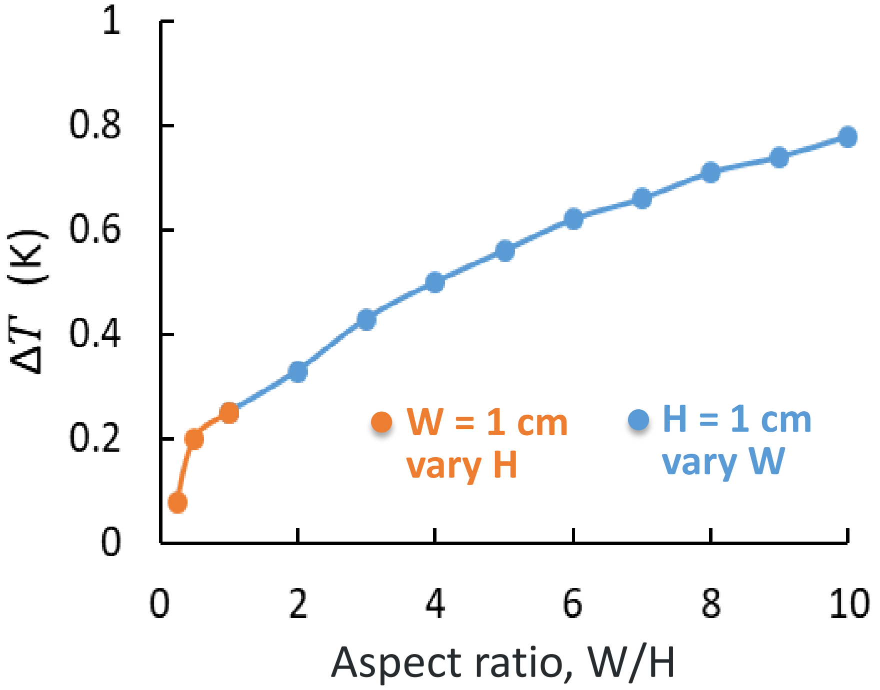
Effects of Materials Properties



Accomplishments (Natural Convection – Simulations)

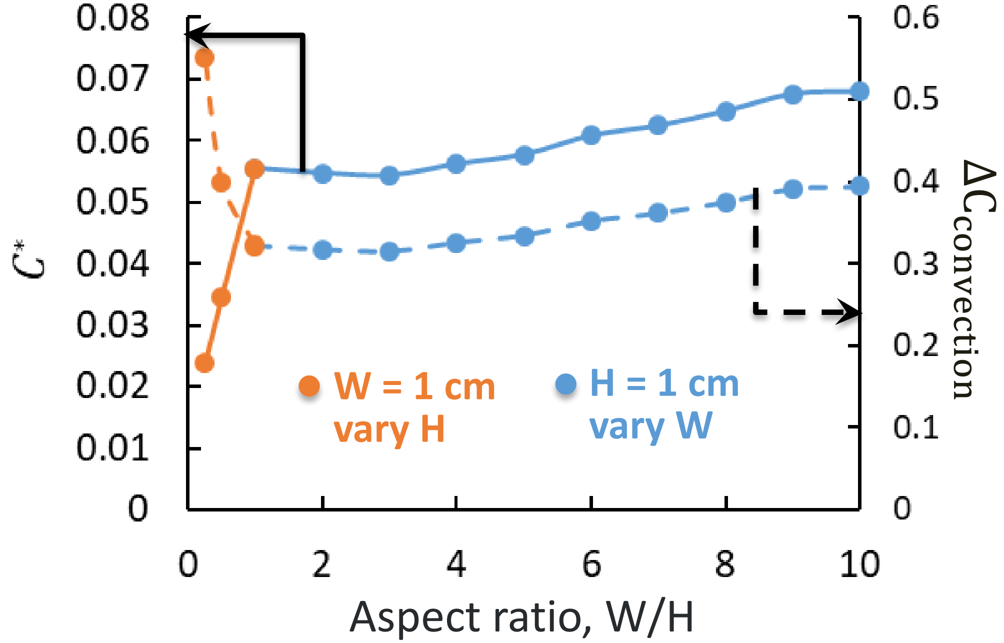
Average temperature difference

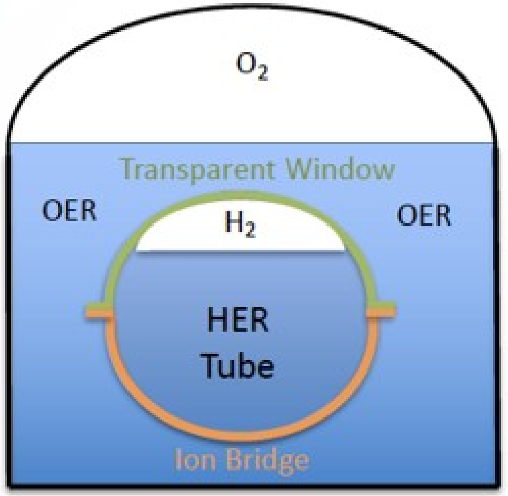
$$\Delta T = \left(T_{\mathrm{bottom,avg}} - T_{\mathrm{top,avg}}\right)$$



Non-dimensional concentration difference

$$C^* = \frac{\Delta C_{\mathrm{convection}}}{\Delta C_{\mathrm{diffusion}}}$$





- $\Delta T > 0$ favorable for natural convection; smaller C^* indicates better mixing
- Species mixing with convection, as compared to diffusion, is enhanced by at least 15 times
- Shallow reactor heights result in more favorable ΔT, which reduces absorption of infrared light by water
- Changing W and H results in different impacts on $\Delta C_{\mathrm{convection}}$, which changes infrared absorption profiles

* one of several new proposed designs for TEA (from Strategic Analysis, Inc.)