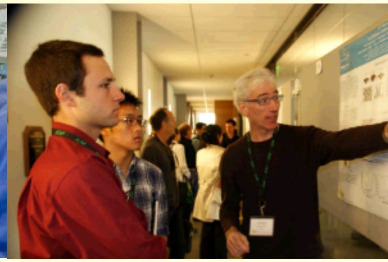
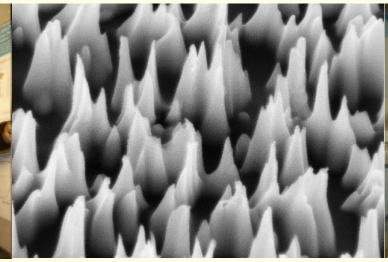
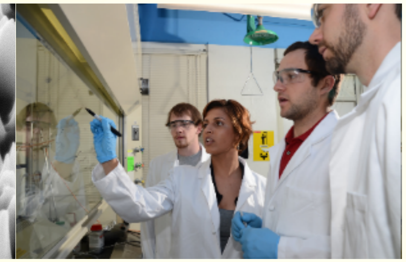





Fundamental Challenges in Solar to Fuel Conversion aka *Improving on Photosynthesis*

Joel Ager
Joint Center for Artificial Photosynthesis
Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA

February 4, 2014
NERSC User Meeting
Berkeley, CA

JCAP
JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

The Joint Center for Artificial Photosynthesis is a DOE Energy Innovation Hub, supported by the Office of Science of the U.S. Department of Energy

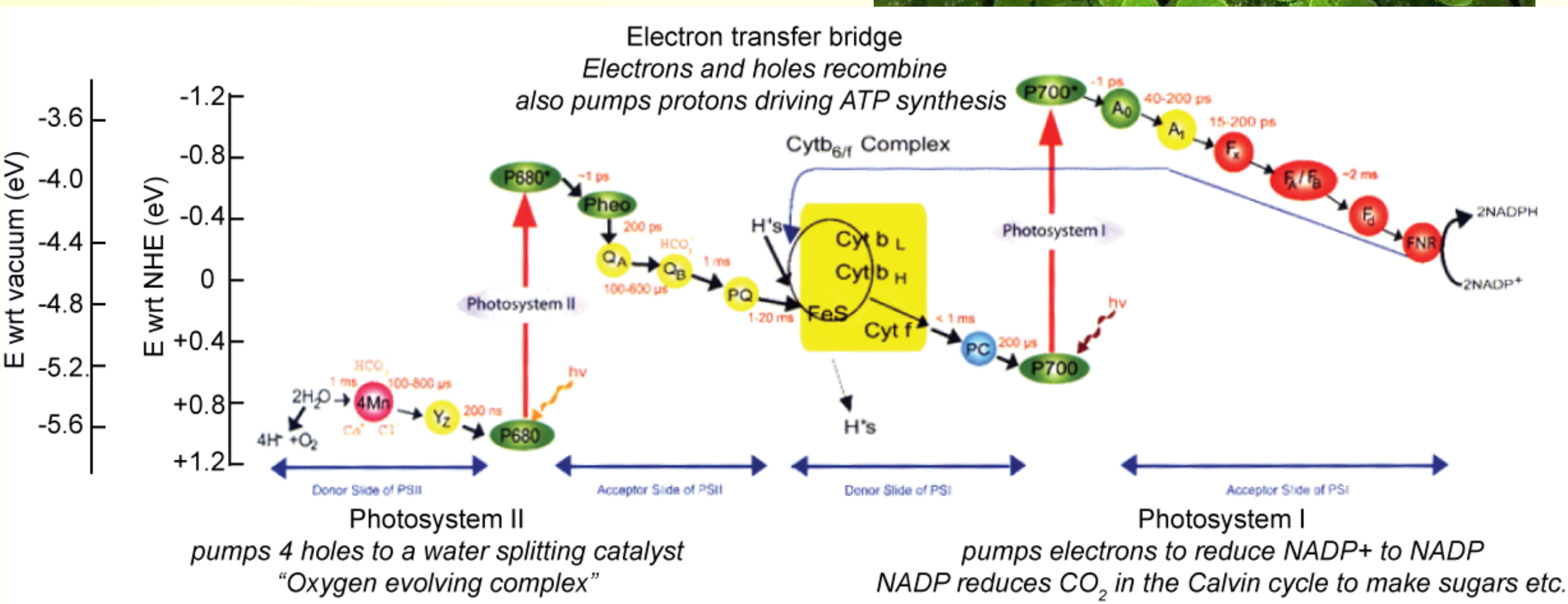
What is “artificial photosynthesis”?

What is photosynthesis?

Natural photosynthesis

with an energy level diagram

Plants (also algae and cyanobacteria) perform synthetic redox chemistry with two red photons, using the reduction products to build plant mass and releasing the oxidation product (O_2) into the air



Adapted from *Photosystem II* (Springer, 2005)

What is “artificial photosynthesis?

- Same basic idea as natural photosynthesis
  - Use sunlight
  - Synthesize a (useful) chemical product

Is it hard to do?
Solar to fuel energetics do not look too difficult…

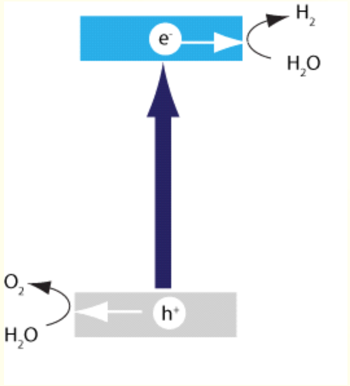
<u>Water splitting half reactions</u>

Reduction: $2H^+ + 2e^- \rightarrow 2H_2$

Oxidation: $H_2O + 2h^+ \rightarrow 1/2O_2 + 2H^+$

Overall: $H_2O \rightarrow 1/2O_2 + H_2$

ΔG = +237 kJ/mol, 1.23 eV/electron



CO_2 energetics are similar

Reaction			ΔG^o (kJ mol^{-1})	n	ΔE^o (eV)	λmax (nm)
H_2O	→	$H_2 + ½ O_2$	237	2	1.23	611
$CO_2 + H_2O$	→	$HCOOH + ½ O_2$	270	2	1.40	564
$CO_2 + H_2O$	→	$HCHO + O_2$	519	4	1.34	579
$CO_2 + 2H_2O$	→	$CH_3OH + 3/2 O_2$	702	6	1.21	617
$CO_2 + 2H_2O$	→	$CH_4 + 2O_2$	818	8	1.06	667

- Observation
  - The money making reaction is reduction
- So why are oxidizing water?
  - *Where else are we going to get Gt-equivalents of electrons?*

The voltage requirements are a little tougher than one might think

Thermodynamics vs. Kinetics

Use water splitting as a model system, CO_2 reduction is similar

Reduction: $2H^+ + 2e^- \rightarrow 2H_2$

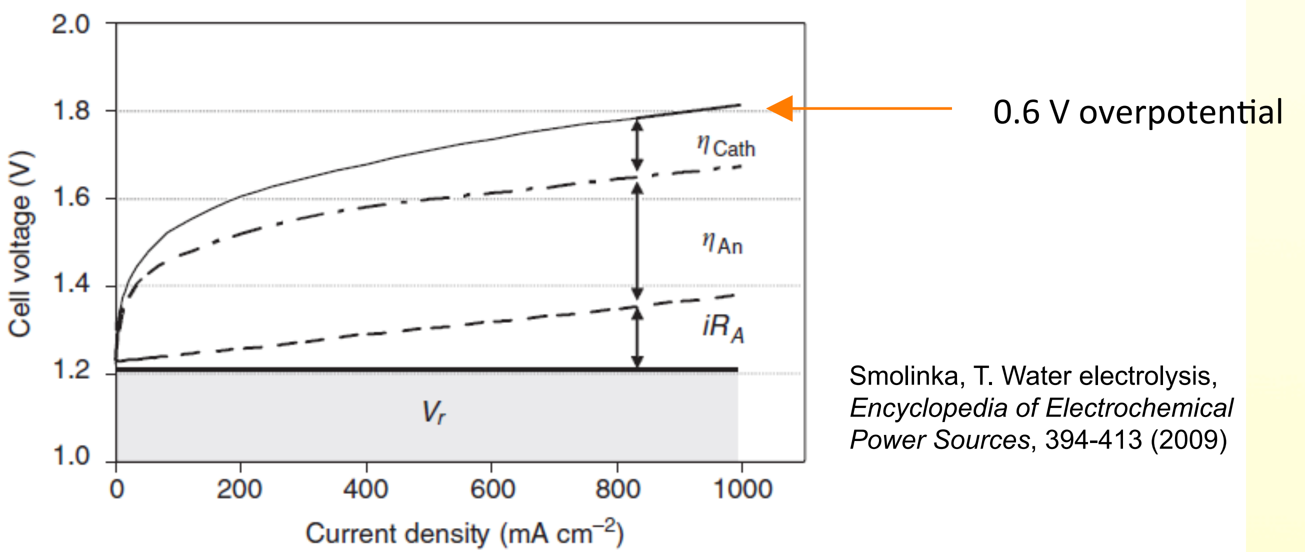
Oxidation: $H_2O + 2h^+ \rightarrow 1/2O_2 + 2H^+$

Overall: $H_2O \rightarrow 1/2O_2 + H_2$

ΔG = +237 kJ/mol, 1.23 eV/electron,

at 1.23 V *the forward and reverse rates are equal*

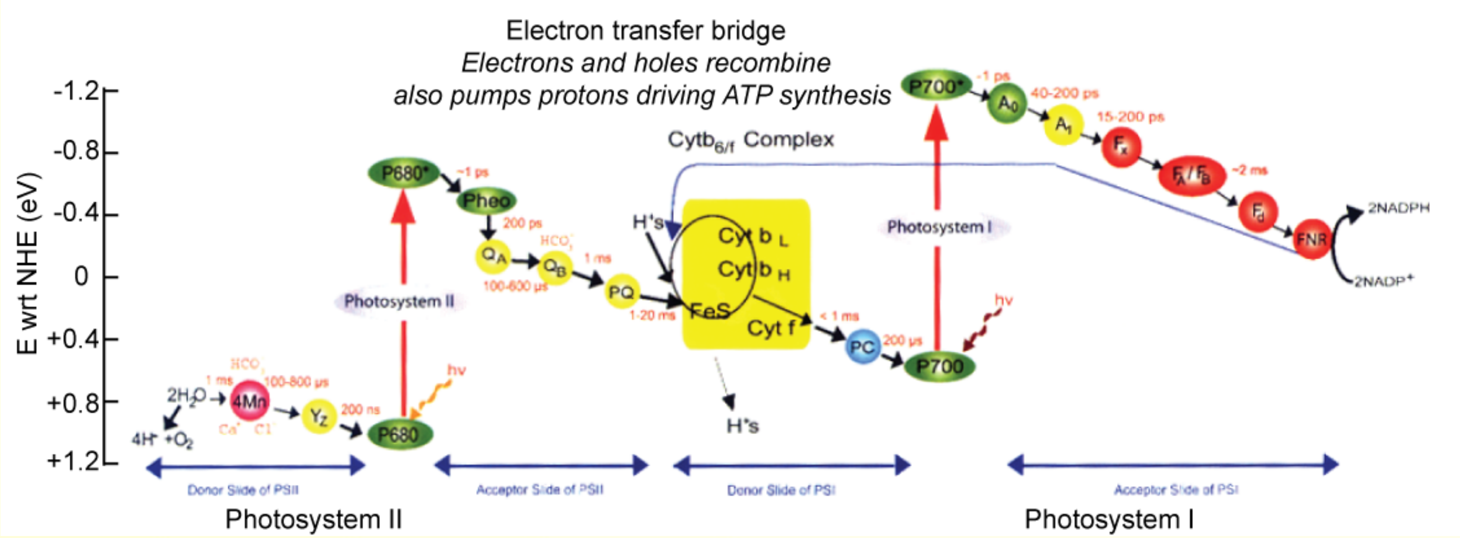
Therefore "Overpotentials" needed to drive reaction at an appreciable rate

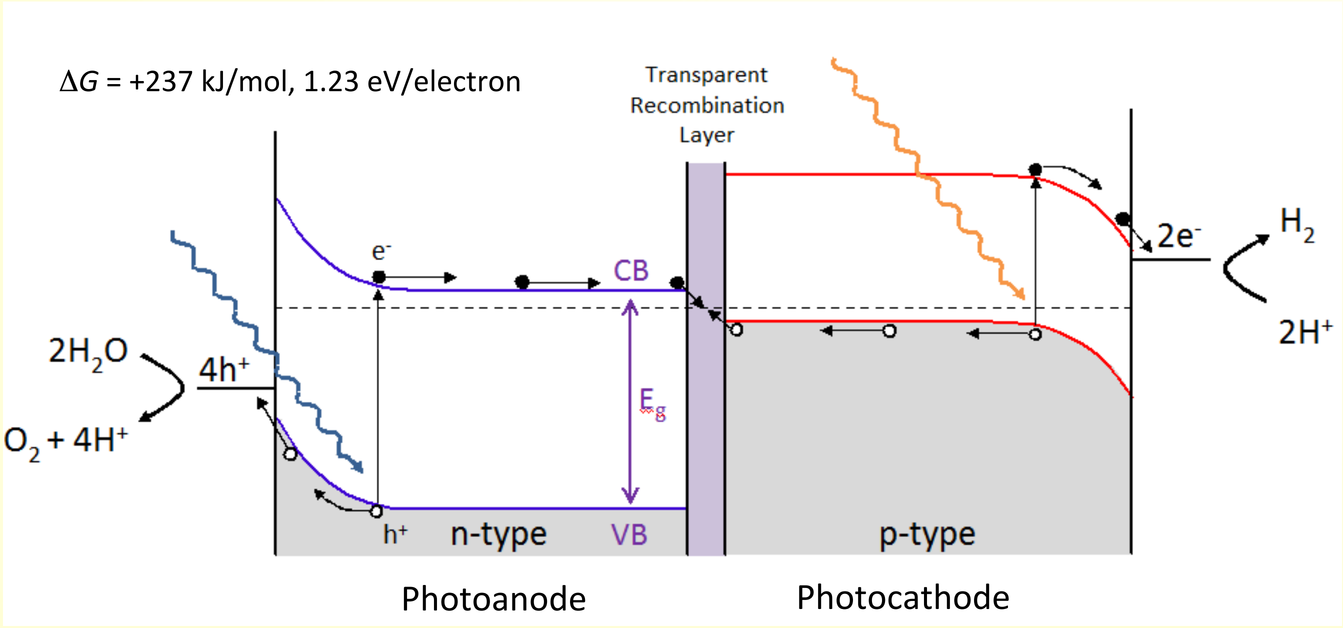


Smolinka, T. Water electrolysis, *Encyclopedia of Electrochemical Power Sources*, 394-413 (2009)

Figure 3 Typical cell voltage versus current density characteristic of a polymer electrolyte membrane (PEM) electrolysis cell with illustration of the contribution of different potential losses during operation.

Approach





A photocathode and photoanode linked in series analogous to Photosystem I and Photosystem II of natural photosynthesis

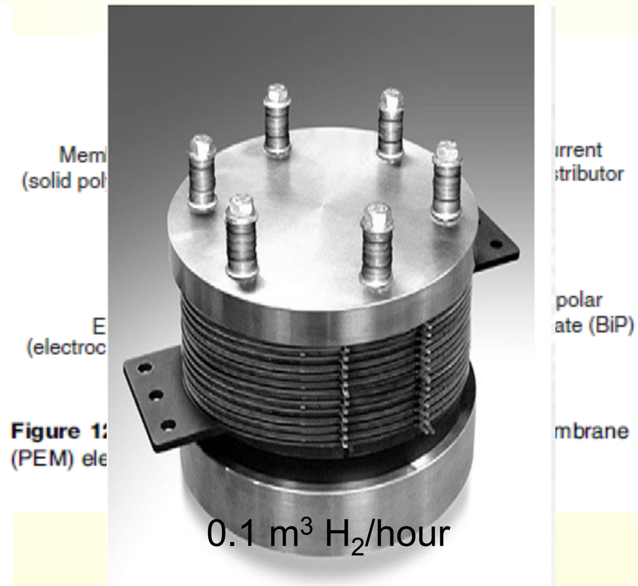
Why aren't we doing artificial photosynthesis on a large scale right now?

The individual components exist…

PV power getting close to grid parity

Alkali-based H_2 generator

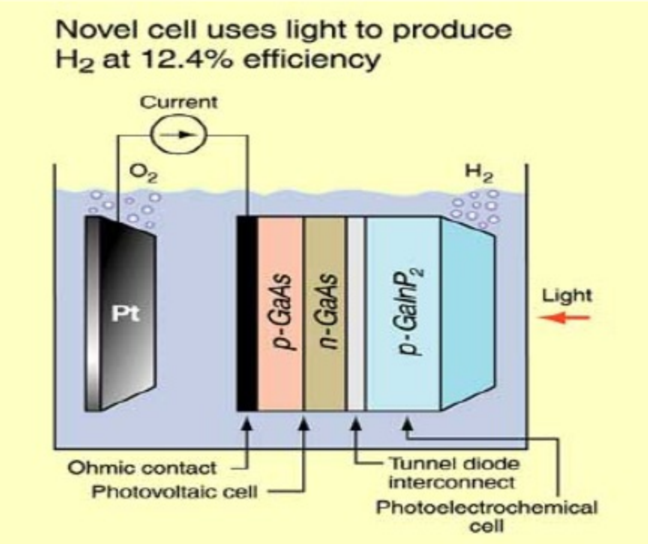
PEM-based system

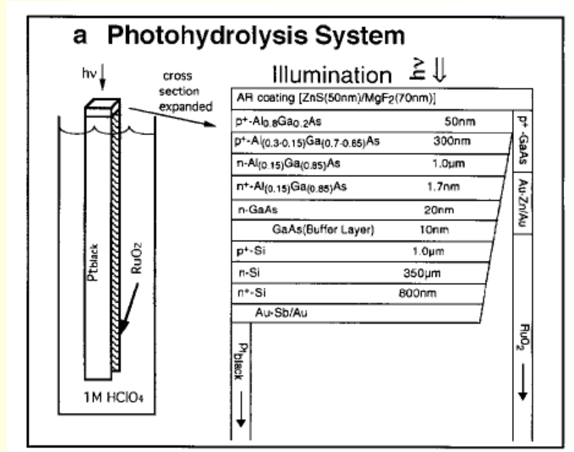


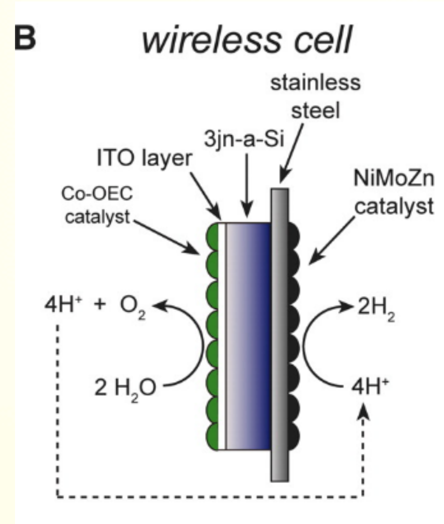
Smolinka, T. Water electrolysis, *Encyclopedia of Electrochemical Power Sources*, 394-413 (2009)

But…
Not the cheapest way to make H_2
H_2 is not used in our current energy cycle
So…
Solar to H_2 not practical (yet) on any commercially interesting or ecologically relevant scale

There are lab-scale demos



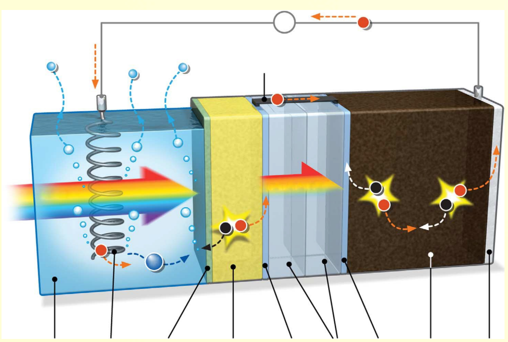




12% STH
Turner *et al*. (1998)
Pt/pn-GaAs//p-GaInP/Pt

18% STH
Licht *et al*. (2000)
RuO_2/pn-AlGaAs//pn-Si/Pt black

~3% STH
Nocera *et al*. (2011)
Co-Pi/3J-a-Si/NiMoZn

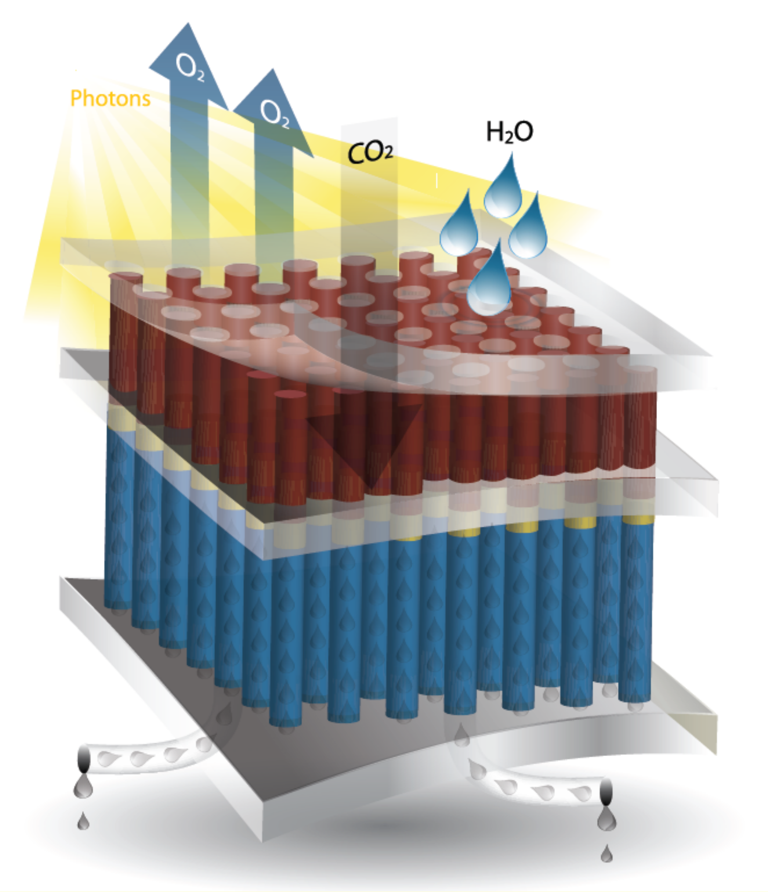


~5% STH
van de Krol *et al*. (2013)
Co-Pi/$BiVO_4$//2J-a-Si/Pt wire

But…
A really attractive and integrated combination of efficiency, stability, and scalability has yet to be demonstrated

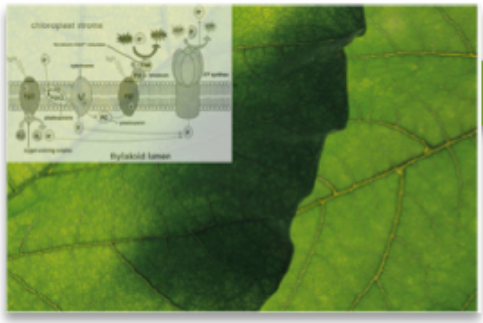
What will it take to change this picture?

Combine photovoltaics and water electrolysis in a way that is cheaper than either of them individually



JCAP Mission

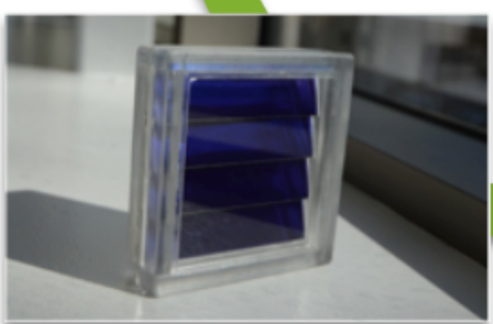
The JCAP Mission is to demonstrate a scalably manufacturable solar-fuels generator, which uses Earth-abundant elements and (with no wires) robustly produces fuel from the sun 10 times more efficiently than (current) crops.



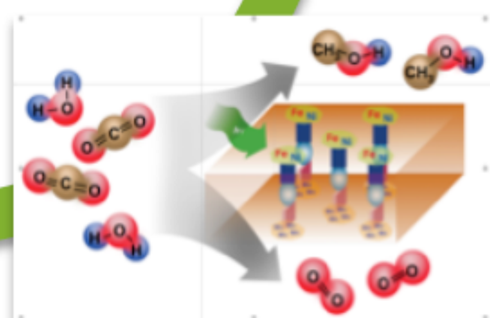
Photosynthesis

"It is time to build an actual artificial photosynthetic system, to learn what works and what does not work, and thereby set the stage for making it work better"

Melvin Calvin (1961 Nobel Prize Laureate)



1st Generation JCAP Solar-Fuels Generator

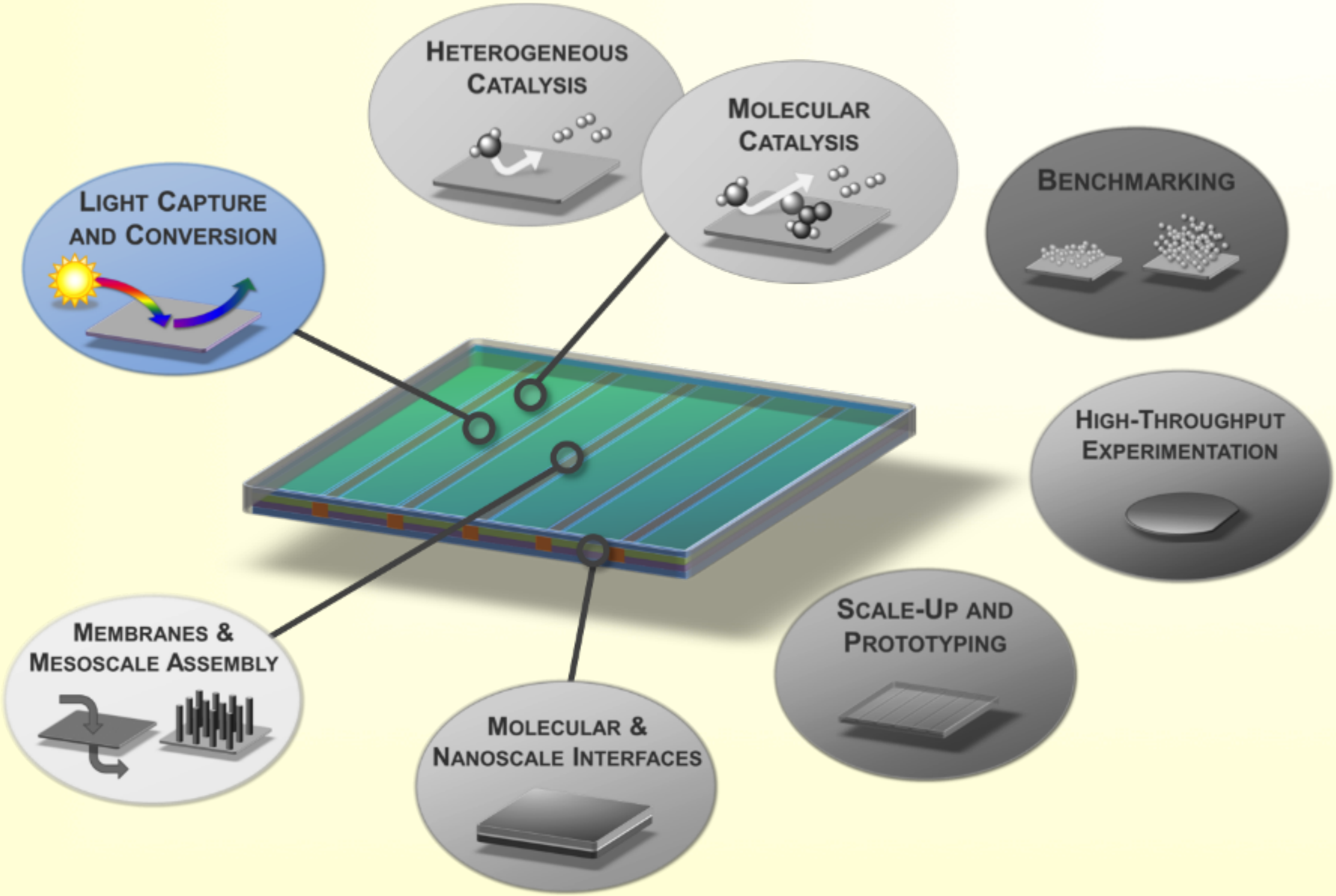


Artificial Photosynthesis

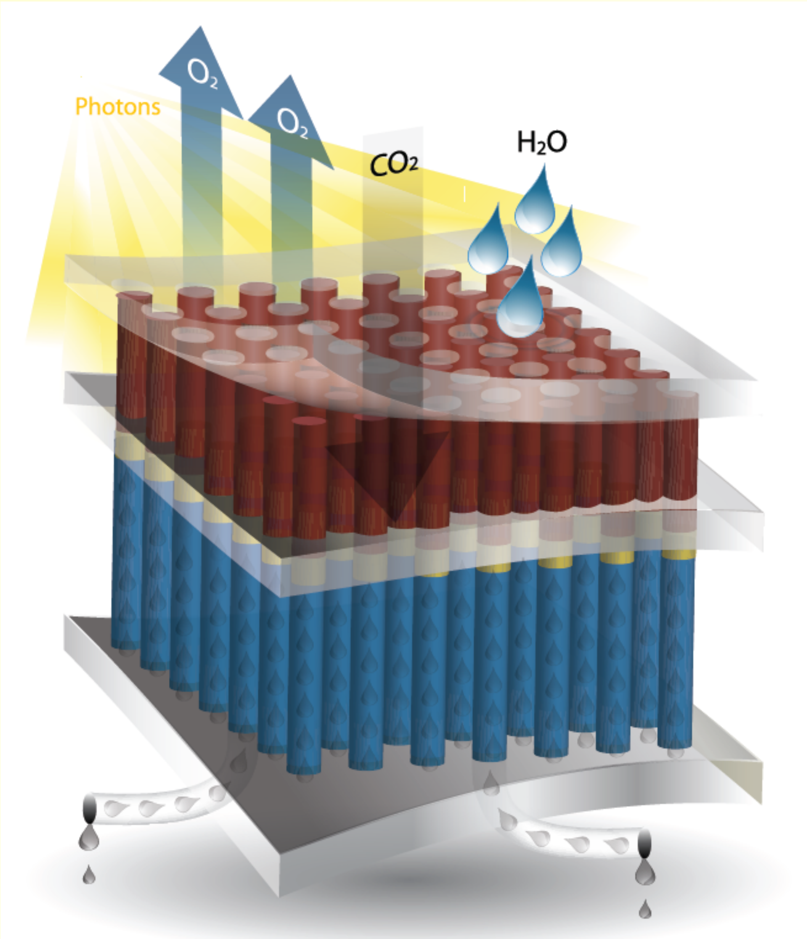
Joint Center for Artificial Photosynthesis (JCAP)

JCAP staff, March, 2013

JCAP R&D structure

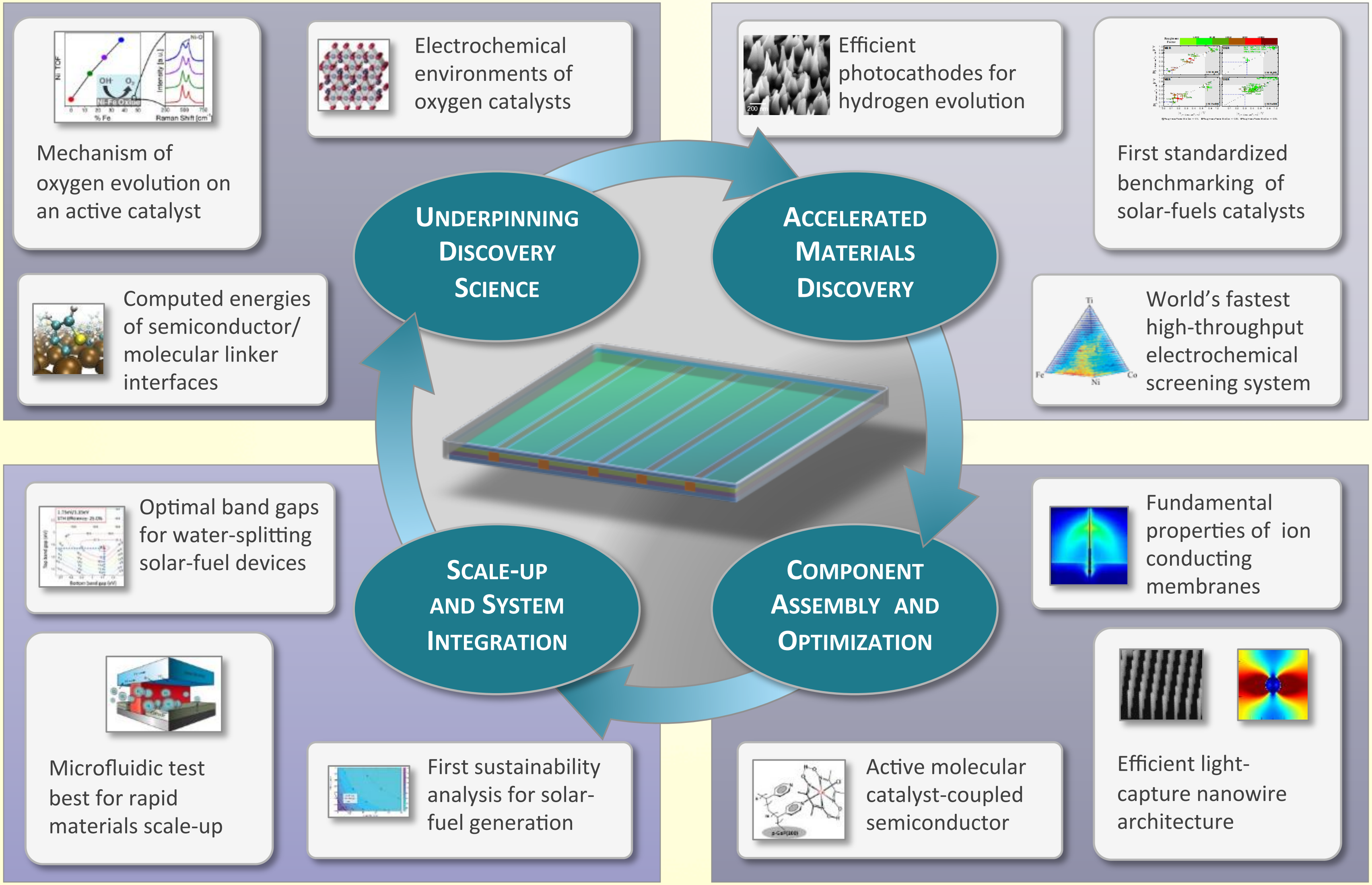


Principles of integration



- Operates with just sunlight, water, and CO_2 (for CO2RR) as inputs (no wires)
- Products are separated
  - produced fuel is kept away from oxidation site

Recent Discoveries in JCAP



Role of and Opportunities for Advanced Computation

Access:

JCAP allocation was 2013 is **3.3M hours**.

Contact is Lin-Wang Wang, PI in JCAP Light Capture and Conversion and in Theory Cross-cutting Team

Let's start with a few illustrations of what we have been doing

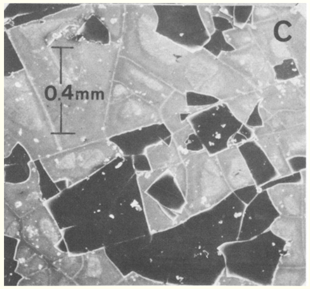
Example:
Ab-initio calculations of materials stability under HER and OER conditions

User: Shiyou Chen
JCAP Sub-Project: Light Capture (Lin-Wang Wang, PI)

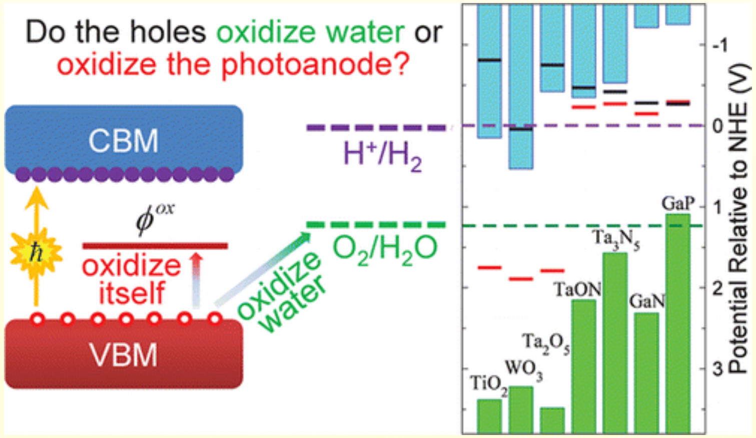
Context: corrosion of materials, especially of photoanodes under OER conditions, is an unsolved challenge in solar to fuels research since decades

The advance: general, accurate, and predictive method to calculate, *ab-initio*, whether a material is stable or not

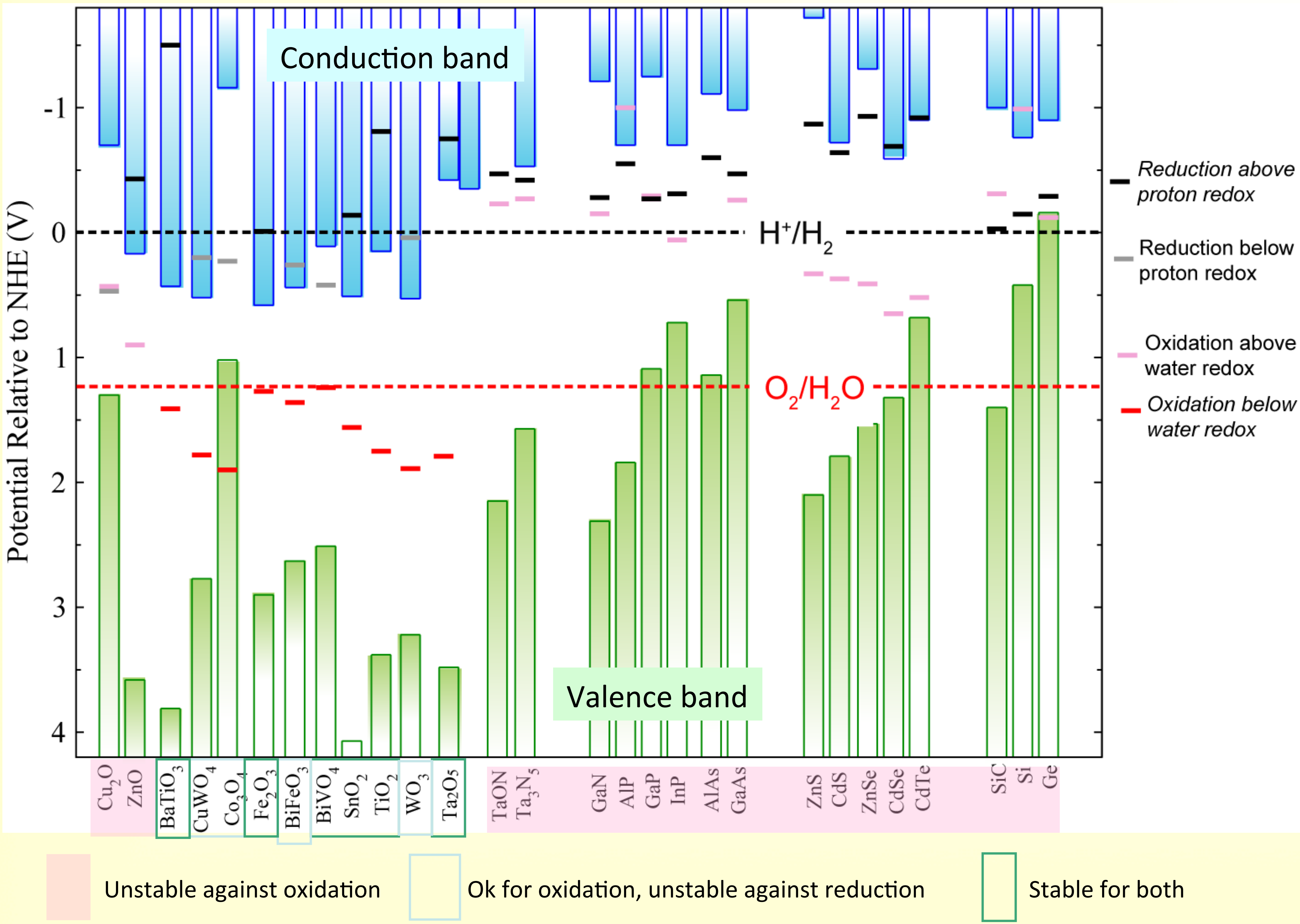
The key science: combination of a new *ab initio* calculation method for compound formation energy and band alignment allows the prediction of the stability of almost any compound semiconductor in aqueous solution



Corroded n-CdS/TiO_2 electrode
P. A. Kohl, S. N. Frank and A. J. Bard, *JECS* **124**, 225 (1977).



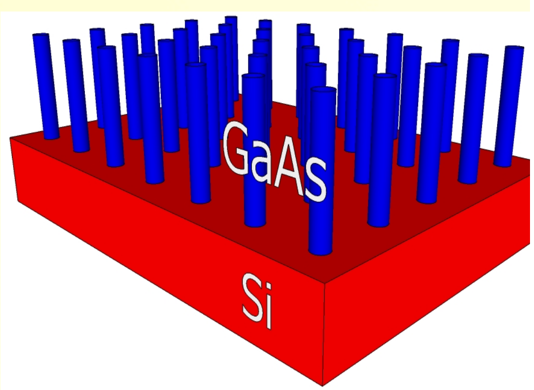
Shiyou Chen and Lin-Wang Wang, [Chem. Mater., 2012, 24 (18), pp 3659–3666]. **DOI:** 10.1021/cm302533s

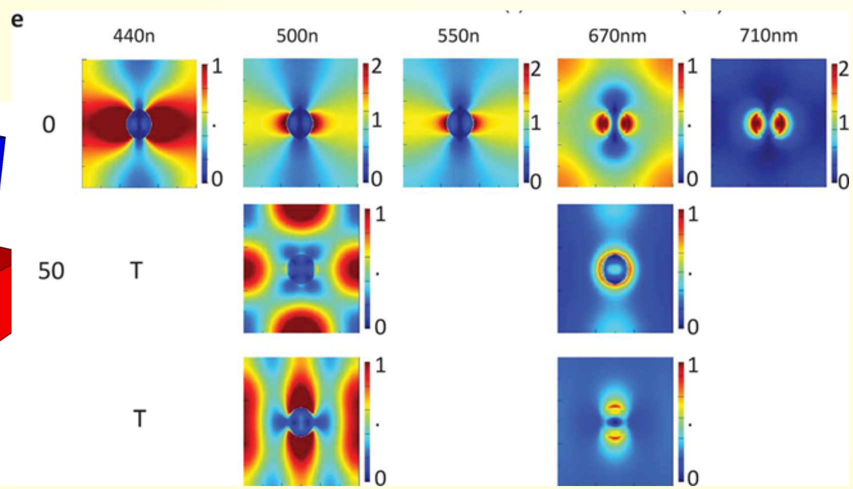


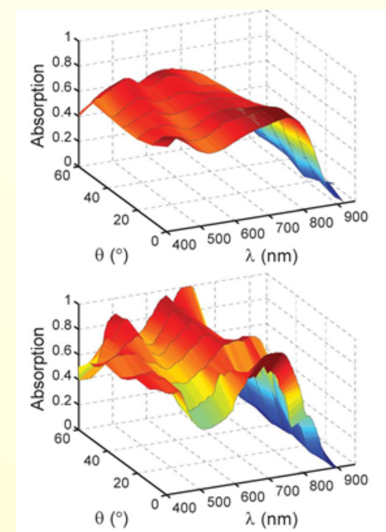
Shiyou Chen and Lin-Wang Wang, *Chem. Mater.*, 2012, 24, 3659.

Example: Light Management

- User: Kate Fountaine
- JCAP Sub-Project: Mesoscale and Membranes (Harry Atwater, PI)
- Program Used: Lumerical FDTD
- Purpose: To explain the super-absorption in sparse GaAs nanowire arrays
- Conclusion: Area fill fraction of 4% lead to absorption of 80%
- Computation: 64 core for 10 hours, many calculations, many jobs running in parallel





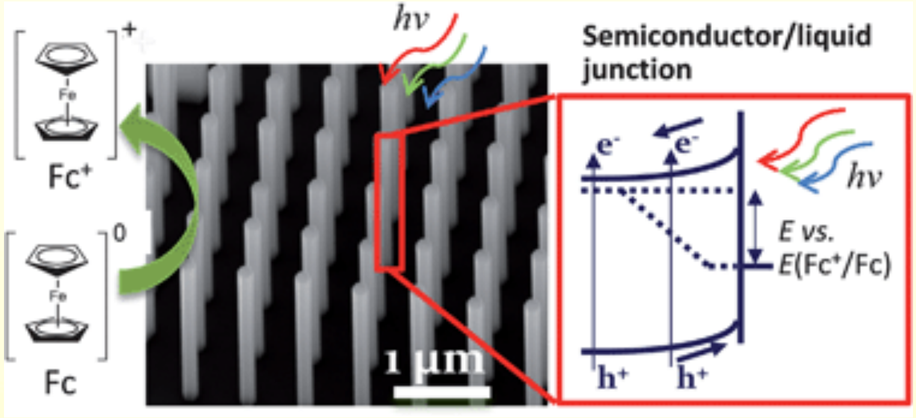


Efficient photoelectrochemical charge conversion from sparse arrays of light absorbing nanowires

Context: III-V materials can be used to make efficient PV and PEC devices but are expensive

The advance: A sparse array GaAs nanowires (<10% areal coverage) has nearly 100% EQE for light to charge conversion

The key science: Understanding of sub-wavelength plasmonic effects enables predict design. Advanced nanofabrication allows realization of the design.



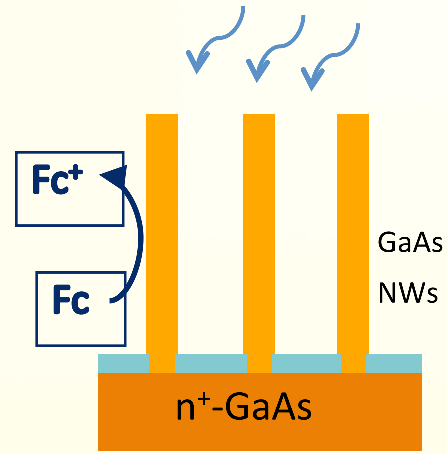
Shu Hu, Chun-Yung Chi, Katherine T. Fountaine, Maoqing Yao, Harry A. Atwater, P. Daniel Dapkus, Nathan S. Lewis, and Chongwu Zhou,

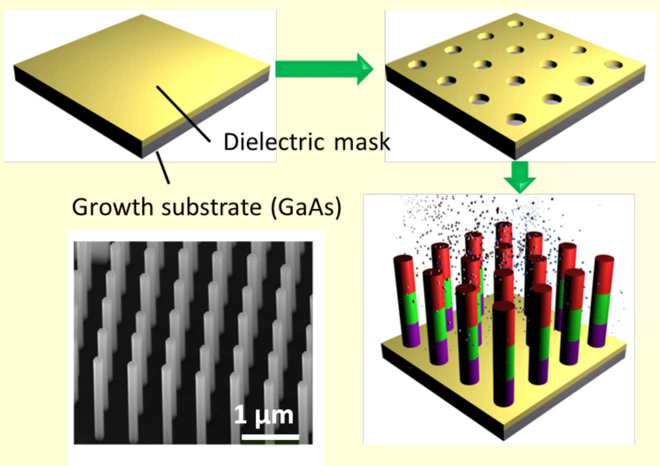
Energy Environ. Sci. **6** 1879, 2013, Advance Article. DOI: 10.1039/C3EE40243F.

Efficient photoelectrochemical charge conversion from sparse arrays of light absorbing nanowires

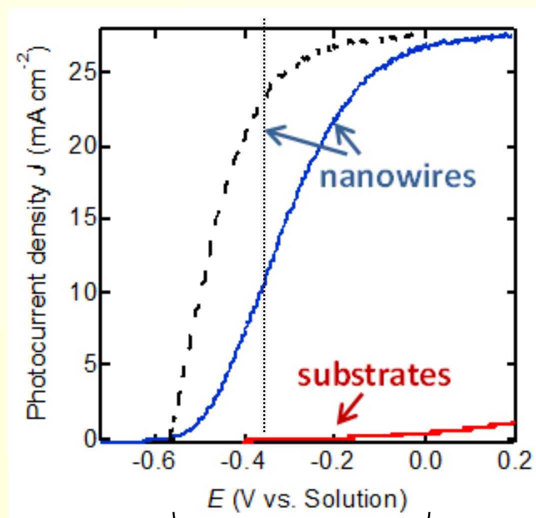
Achievements

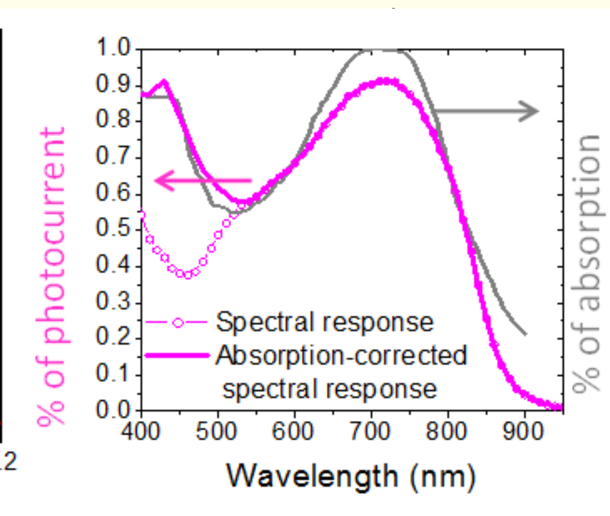
- Short-circuit current density: 25 mA cm^{-2}
- Open-circuit potential for $FeCp_2^{0/+}$
590 mV, highest reported for GaAs NW arrays.
- Energy conversion efficiency ~ 8%





GaAs nanowire growth: P. D. Dapkus *et al.*, USC, Center for Energy Nanoscience (EFRC)





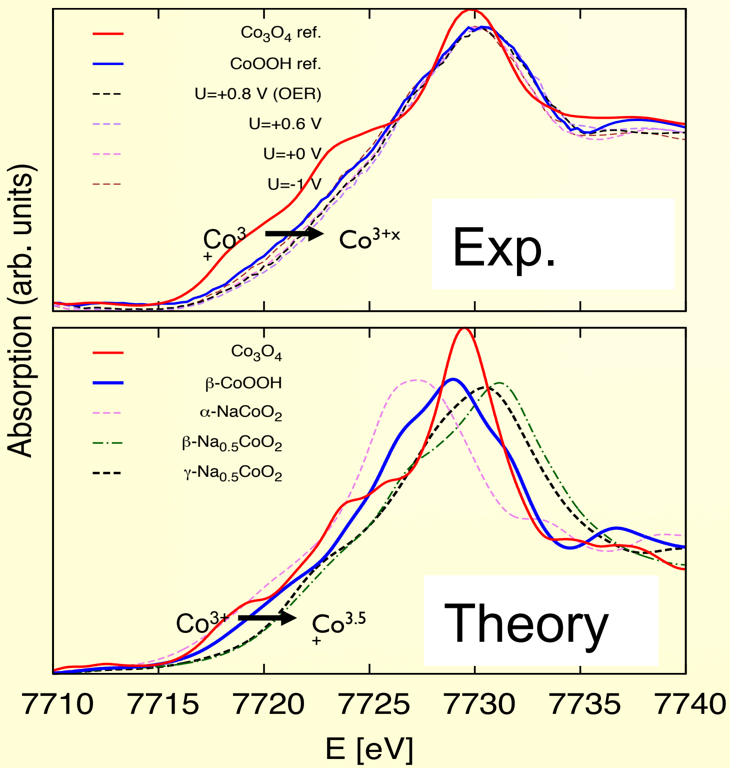
590 mV onset potential

Shu Hu, Chun-Yung Chi, Katherine T. Fountaine, Maoqing Yao, Harry A. Atwater, P. Daniel Dapkus, Nathan S. Lewis, and Chongwu Zhou, [*Energy Environ. Sci.* **6** 1879, 2013, Advance Article. DOI: 10.1039/C3EE40243]F.

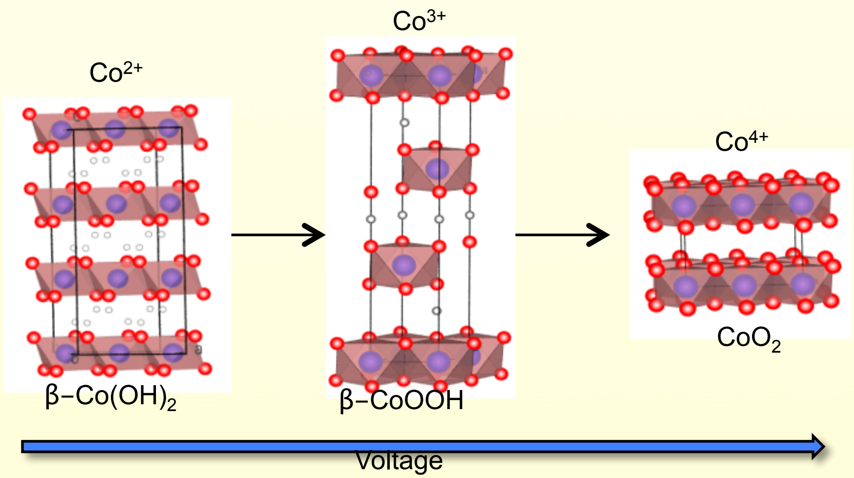
Example: water oxidation catalysis

- User: Michal Bajdich
- JCAP Sub-Project: Heterogeneous catalysis (Alex Bell, PI)
- Program Used: GPAW (E_{TOT}, surfaces) Quantum Espresso (spectra)
- Purpose: To identify phase, surface and limiting step of heterogeneous catalysts
- Conclusion: β-CoOOH is the intermediate step for 1.23 V in large pH value
- Computation: ~300 electrons, 128 processors for 48 hours on Carver for each job

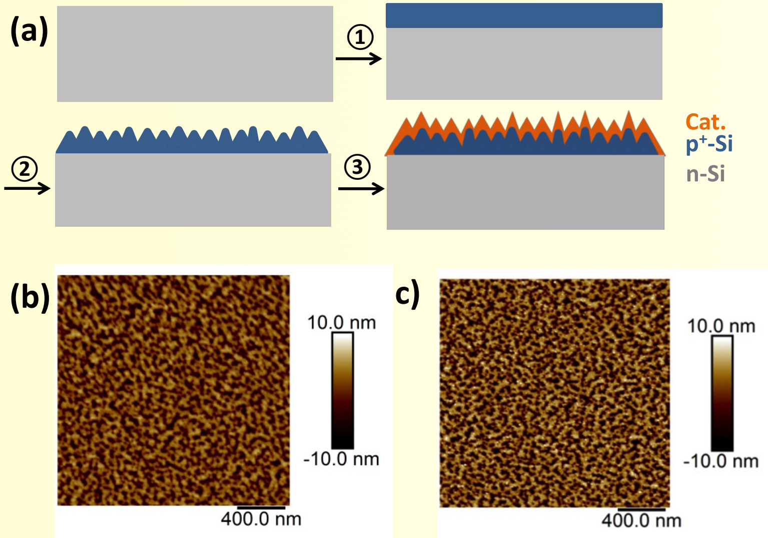
Co K-edge of CoO_x (in-situ OER)



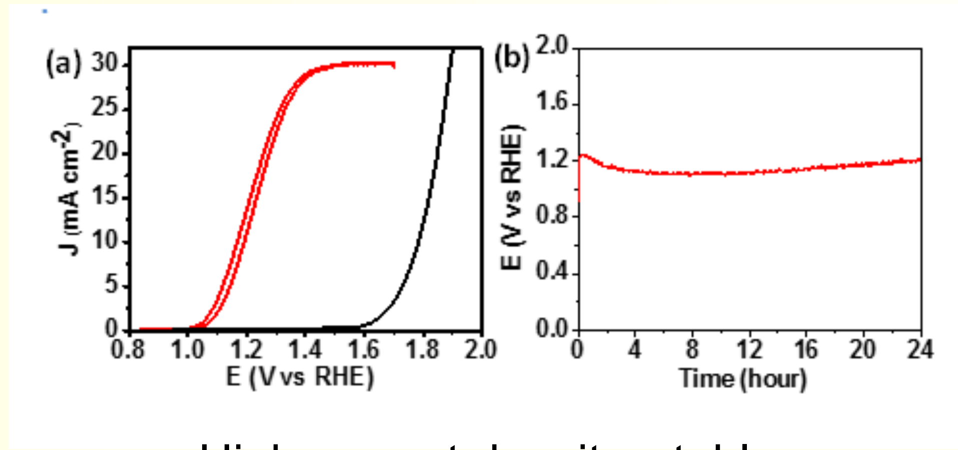
β-CoOOH: OER active phase of CoO_x



CoO_x integration into stable water oxidation system



CoO_x on Si



High current density, stable

In the expected oxidation state

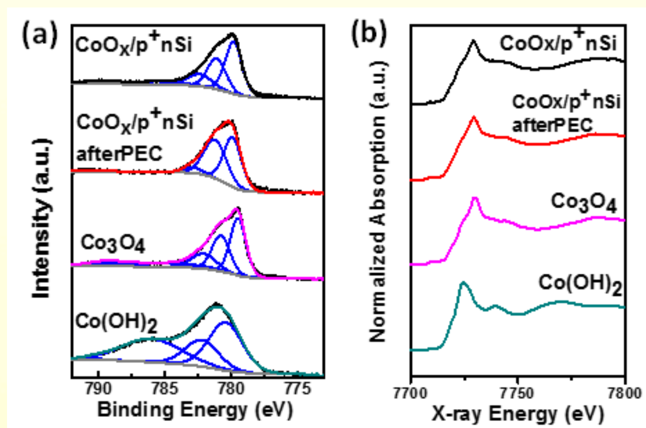
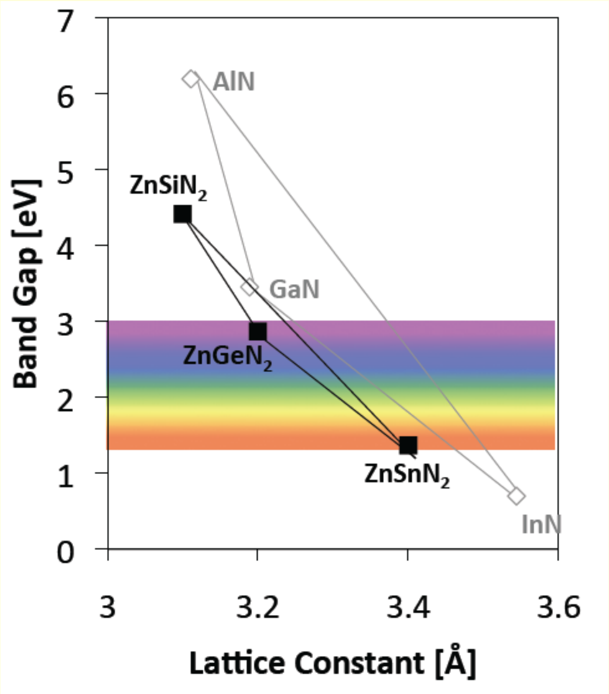


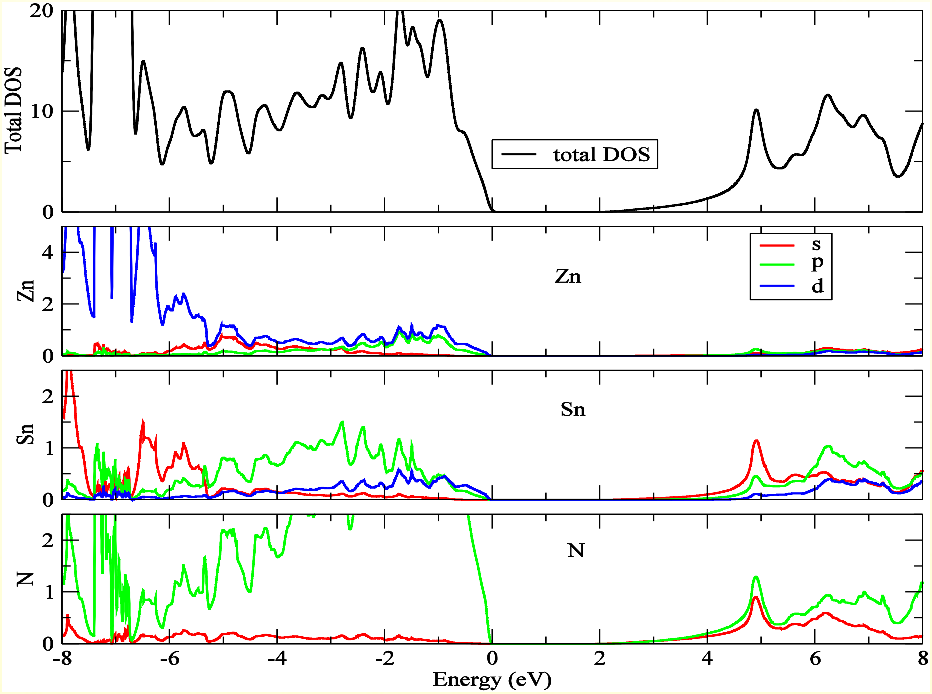
Figure 4. (a) XPS ($Co\ 2p_{3/2}$) and (b) XANES (Co K-edge) spectra of CoO_x/p^+n-Si samples: as-deposited and after PEC stability testing for 1 h at an overpotential of 400 mV in 1M NaOH (pH 13.6), as well as Co_3O_4 and $Co(OH)_2$ standards.

J. Yang, Walczak, Anzenberg, Yuan, Beeman, Schwartzberg, Lin, Hettick, Javey, Ager, Yano, Frei, Sharp, submitted

Example: Accurate Band Structure calculations

- User: Shiyou Chen
- JCAP Sub-Project: Light absorber
- Program Used: VASP
- Purpose: To calculate defect formation energy and effects in band structure
- Conclusion: Sn_{Zn} antisites causes the n-type filling
- Computation: hundreds of processors for tens of hours (on Hopper)





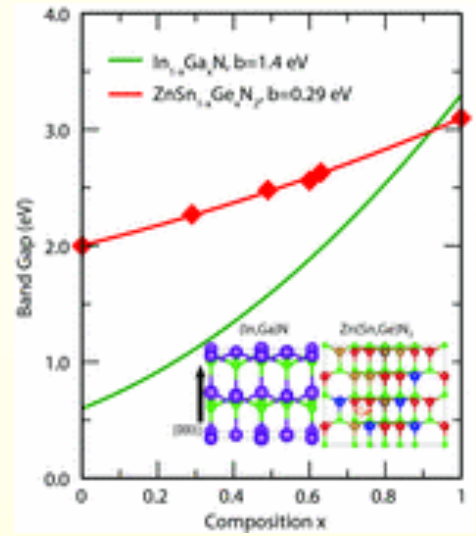
ZnSnN total and partial density of states

Discovery of new Earth-Abundant light absorber

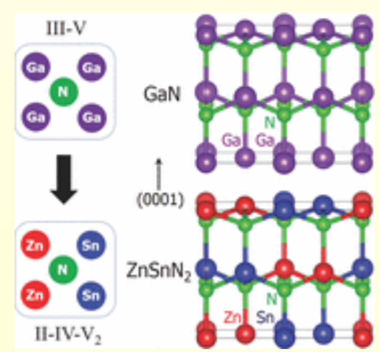
Context: Producing a high efficiency and scalable PEC device requires an earth-abundant light absorber with a band gap in the range of 1.8 to 2.2 eV.

The advance: II-IV-V2 alloys are deposited by a scalable thin film method and shown to have a tunable band gap in the range of interest for high efficiency solar to hydrogen.

The key science: accurate band structure and defect formation energy calculations, thin film heteroepitaxy using a scalable deposition method



Prineha Narang, Shiyou Chen, Naomi C. Coronel, Sheraz Gul, Junko Yano, Lin-Wang Wang, Nathan S. Lewis, Harry A. Atwater "Band Gap Tunability in Zn(Sn,Ge)N2 Semiconductor Alloys" *Adv. Mater.*, on-line 12/5/13 DOI: 10.1002/adma.201304473.

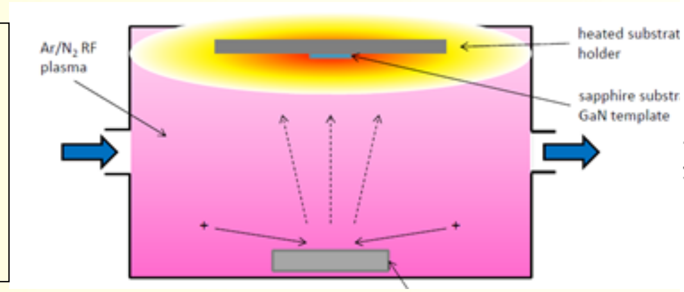


Shiyou Chen, Prineha Narang, Harry A. Atwater, and Lin-Wang Wang "Phase Stability and Defect Physics of Ternary ZnSnN2 Semiconductor: First Principles Insights" *Adv. Mater.*, DOI: 10.1002/adma.201302727

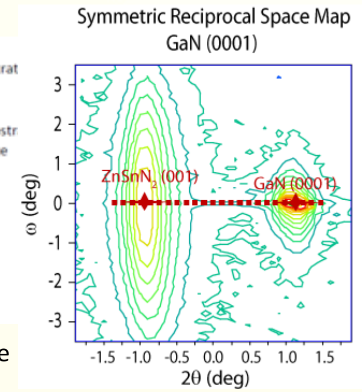
Zn-IV-Nitrides: Earth Abundant Light Capture Materials

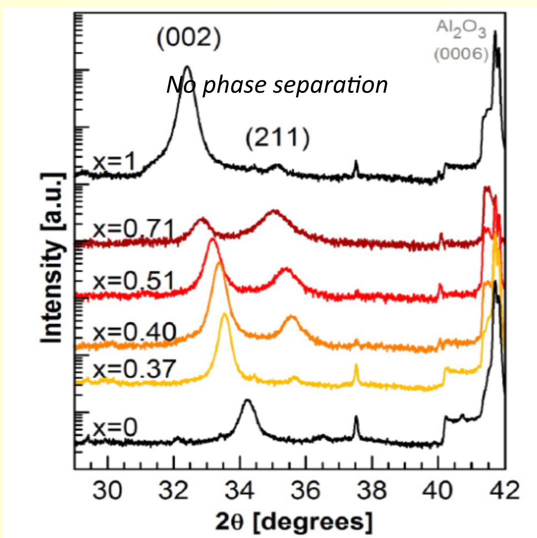
Achievements

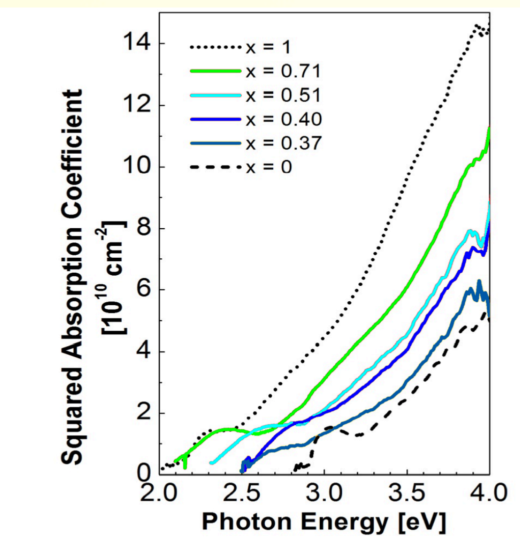
- Epitaxial, single-phase Zn-IV-N_2 alloys were synthesized (IV = Sn, Ge)
- Band gap is direct and tunable in the JCAP range of interest

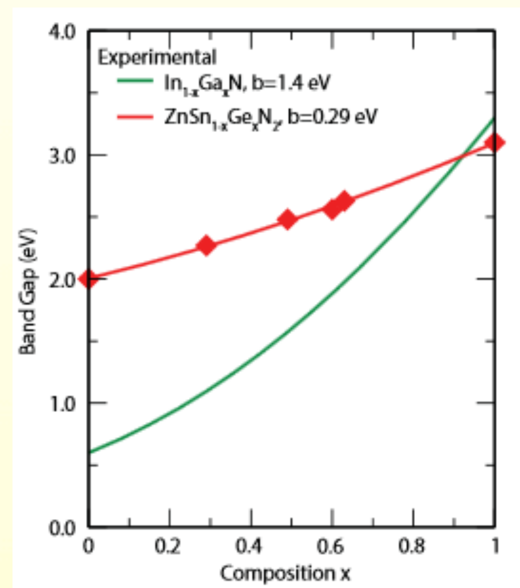


single-phase, stoichiometric, oxygen-free films by reactive sputtering grown epitaxially on GaN/sapphire







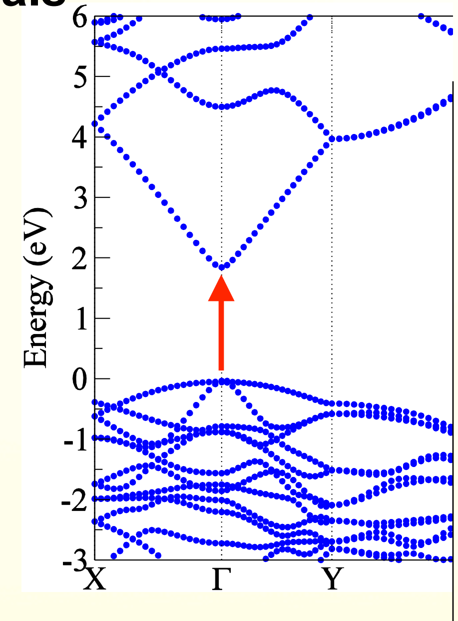


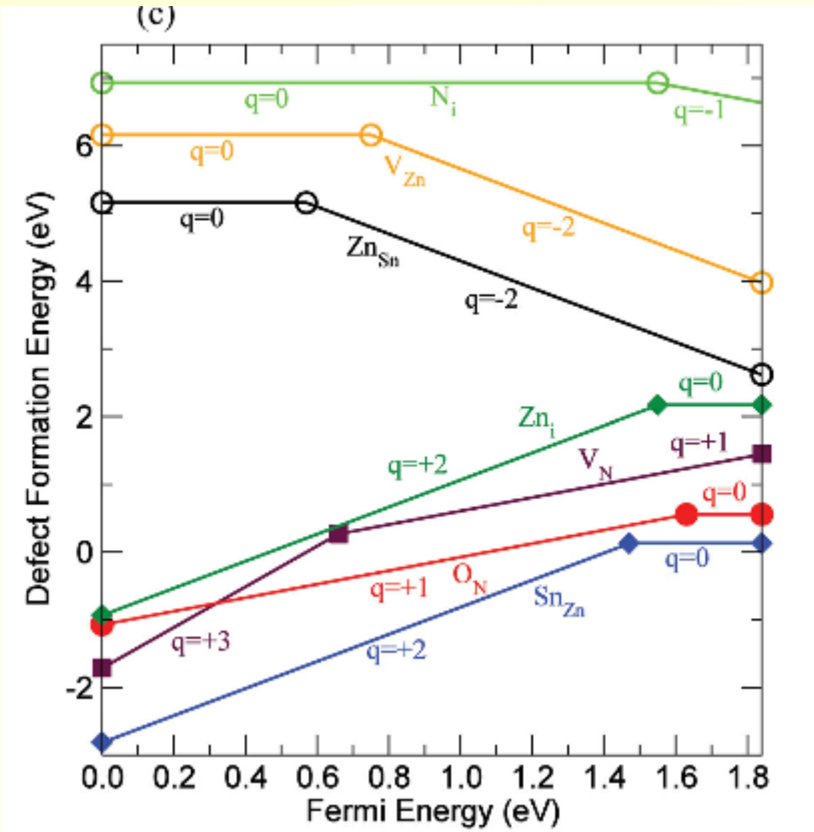
Synthesis of single phase epitaxial $ZnSn_xGe_{1-x}N_2$ with continuously tunable bandgap

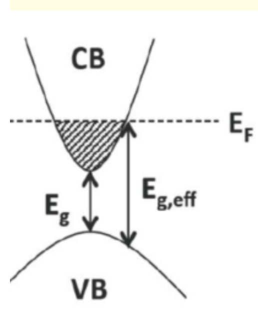
Prineha Narang, Shiyou Chen, Naomi C. Coronel, Sheraz Gul, Junko Yano, Lin-Wang Wang, Nathan S. Lewis, Harry A. Atwater "Band Gap Tunability in Zn(Sn,Ge)N2 Semiconductor Alloys" *Adv. Mater.*, on-line 12/5/13 DOI: 10.1002/adma.201304473.

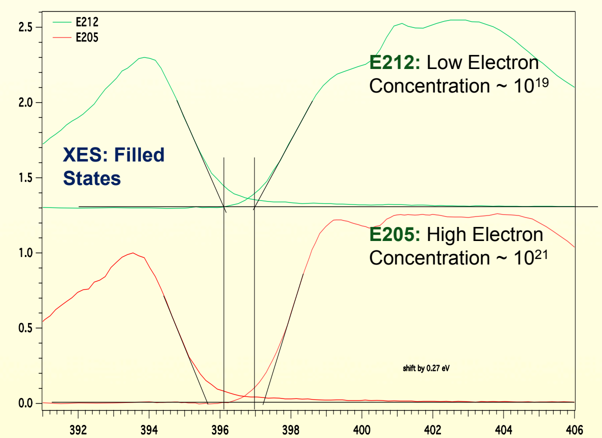
$ZnSnN_2$: Earth Abundant Light Capture Materials

- It is heavily n-type
- Band gap is larger than expected
- Band filling effect
- What causes the n-type ?



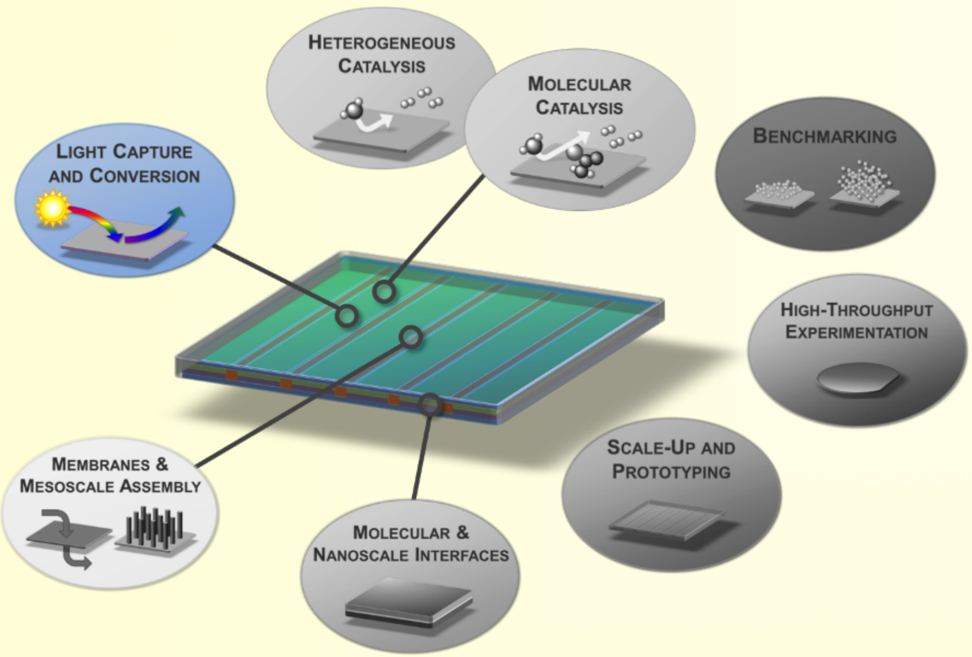




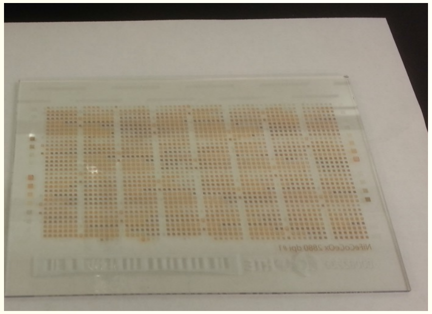


Shiyou Chen, Prineha Narang, Harry A. Atwater, and Lin-Wang Wang "Phase Stability and Defect Physics of Ternary ZnSnN2 Semiconductor: First Principles Insights" *Adv. Mater.*, DOI: 10.1002/adma.201302727

Opportunities

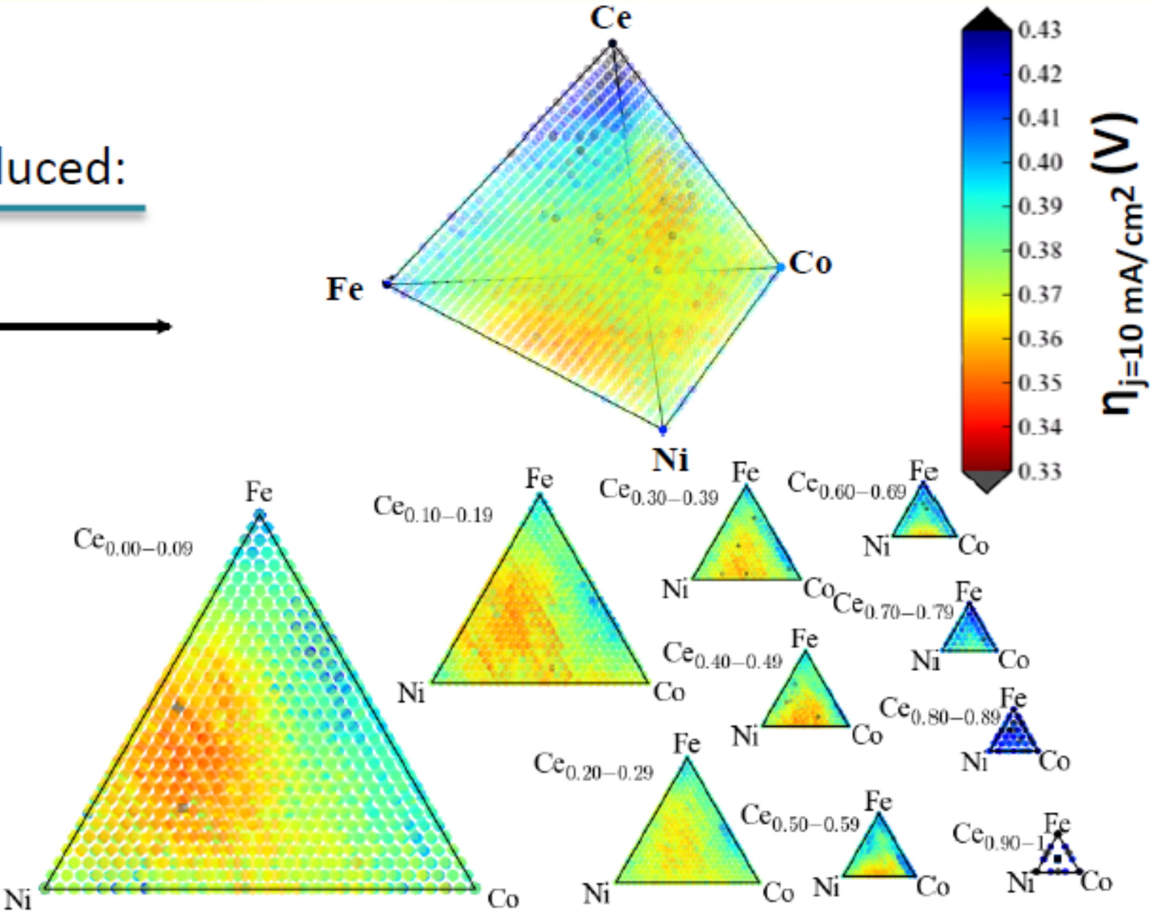


Connections to high throughput experimentation



Ni-Fe-A-B-O_x
Libraries produced:

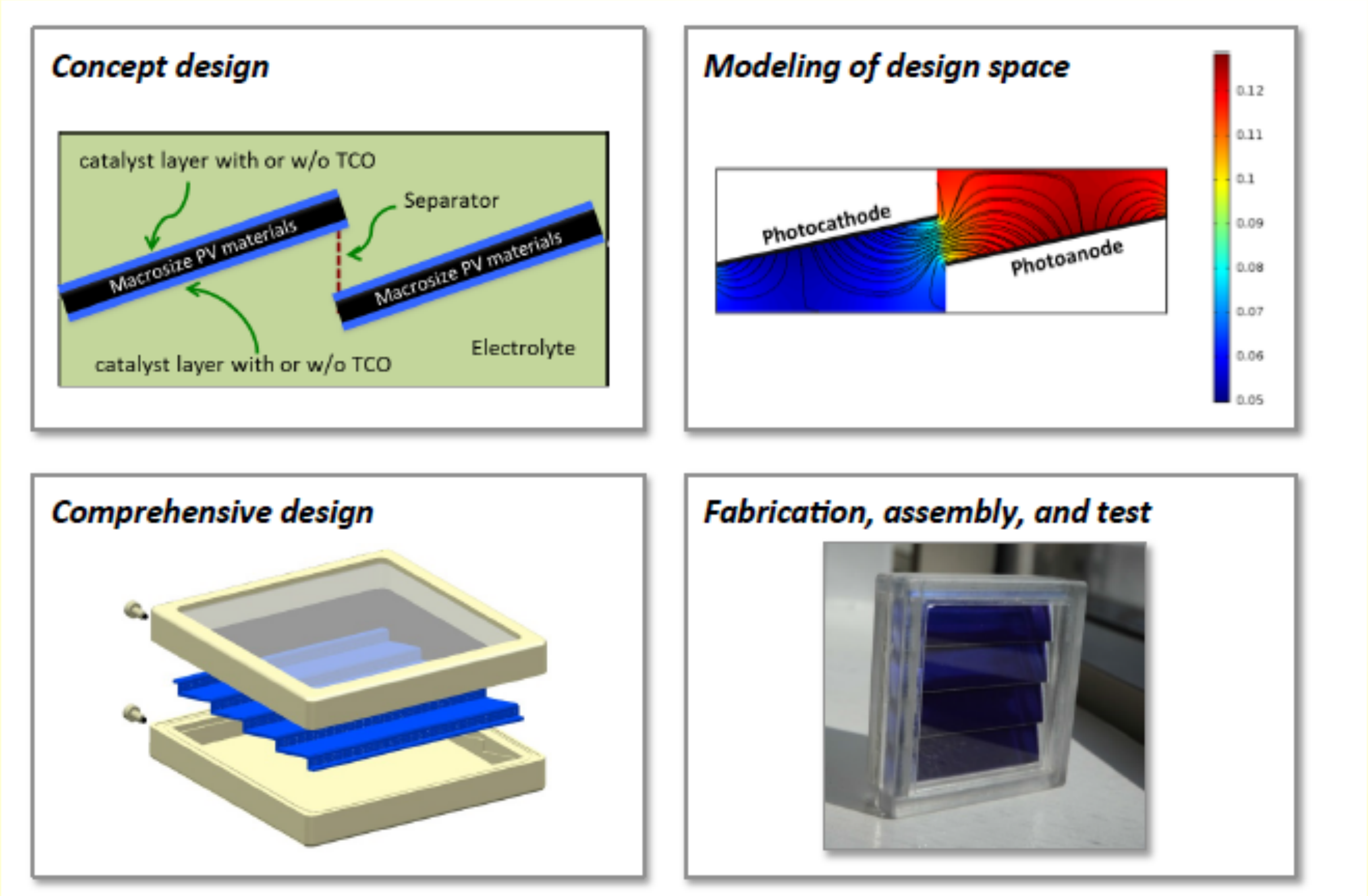
- Ni-Fe-Co-Ti
- Ni-Fe-Co-Ce
- Ni-Fe-Mg-Zr
- Ni-Fe-Mg-Mo
- Ni-Fe-Co-Al
- Ni-Fe-Bi-V
- Ni-Fe-Cu-W
- Ni-Fe-Ga-Zr
- Ni-Fe-Ga-Mo
- Ni-Fe-Mo-Zr



Rapid identification of compositions with relatively high catalyst activity.

Integration, multiscale modeling

Possible now

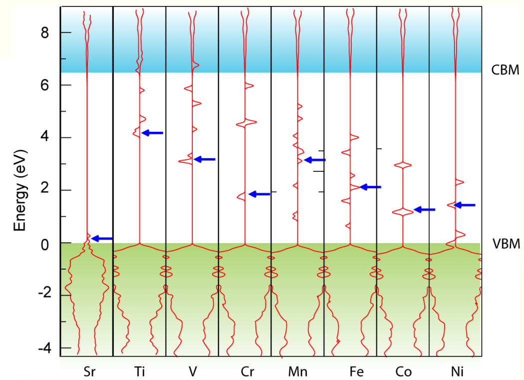


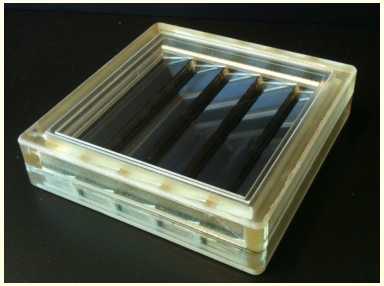
S. Haussener, C. Xiang, J. M. Spurgeon, S. Ardo, N. S. Lewis and A. Z. Weber, Modeling, simulation, and design criteria for photoelectrochemical water-splitting systems, *Energy Environ. Sci.* **5**, 9922 (2012).

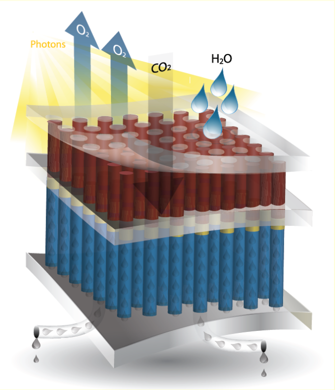
Integration, multiscale modeling

The vision

	1-D Model	Multidimensional Model
Light absorption	☑ Beer-Lambert law	☑ Maxwell's equations Waveguiding/plasmonic effects
Semiconductor transport	☑ Drift/diffusion (Nernst-Planck) Poisson	P Drift/diffusion (Nernst-Planck) Poisson All relevant recombination models Advanced handling of surface states
Catalysis, membrane/ solution transport	☑ Butler-Volmer Kinetic model for charge transfer Ohm's law	P Butler-Volmer Ohm's law (Nernst-Planck)

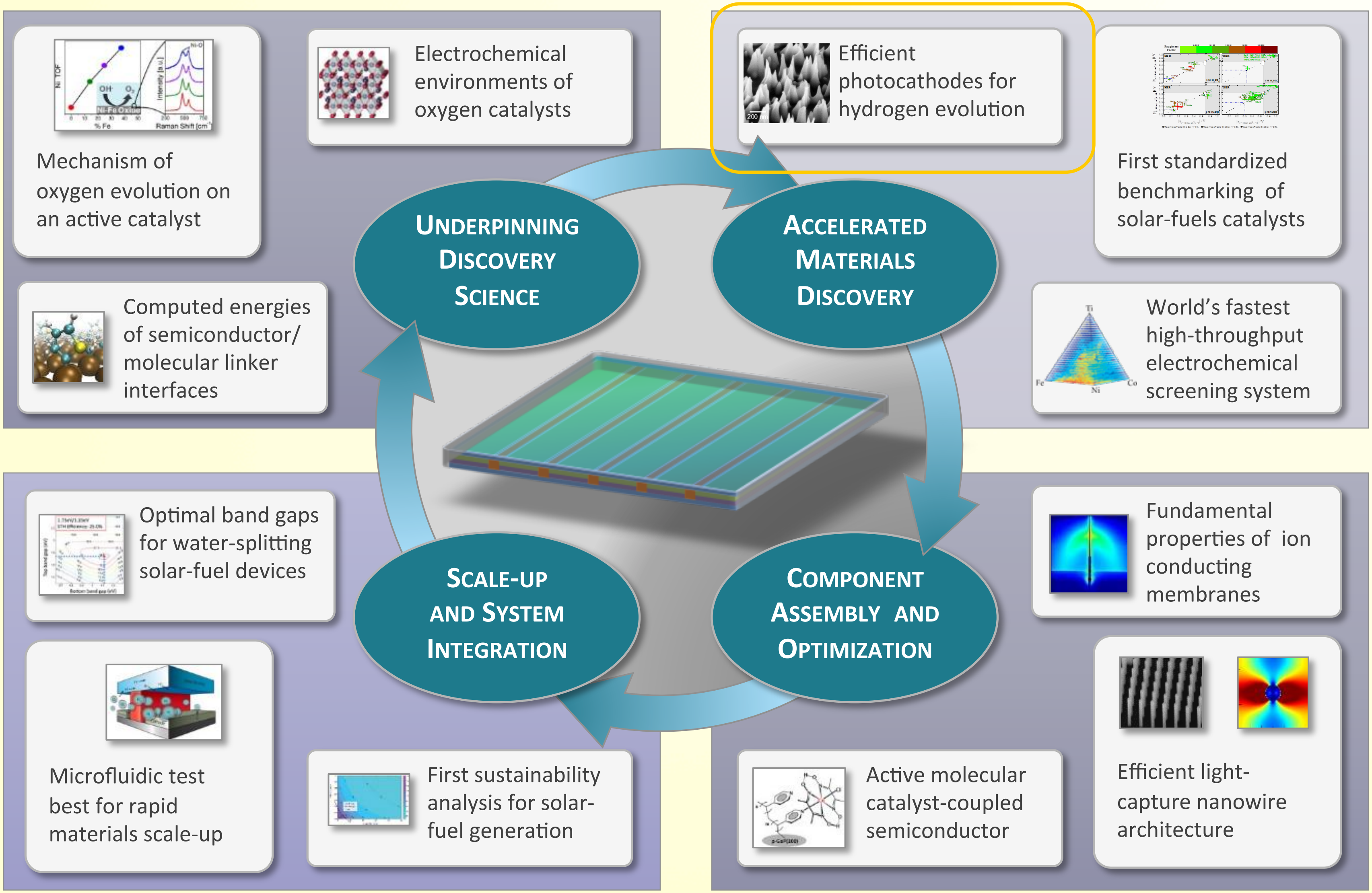







Thank you

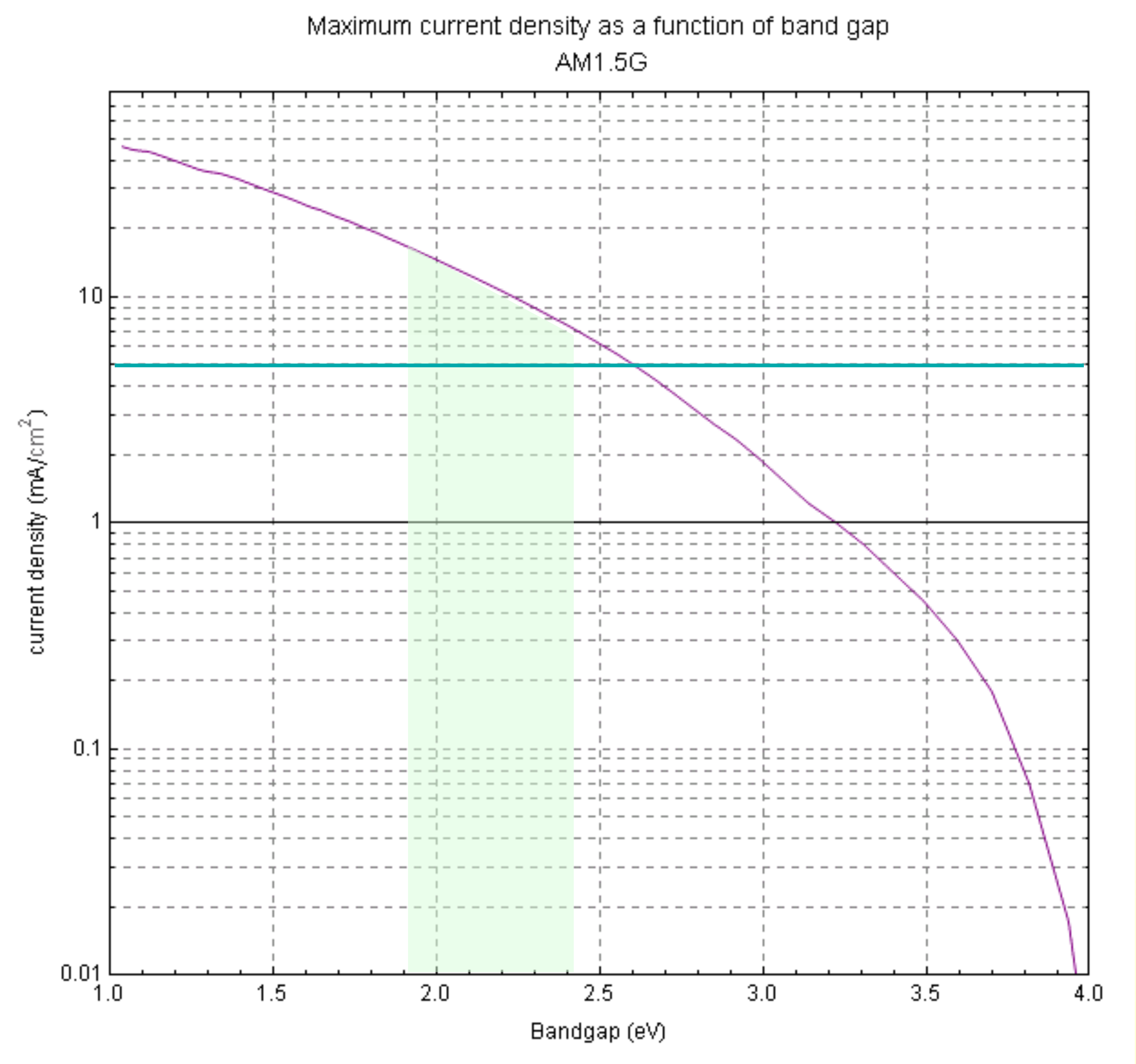
JCAP Approach and recent discoveries



If we can get 75% EQE and half the band gap as V_{OC}

And the photocathode does half the work

Then photoanode target range is 1.9-2.4 eV for a 5 mA cm^{-2} system



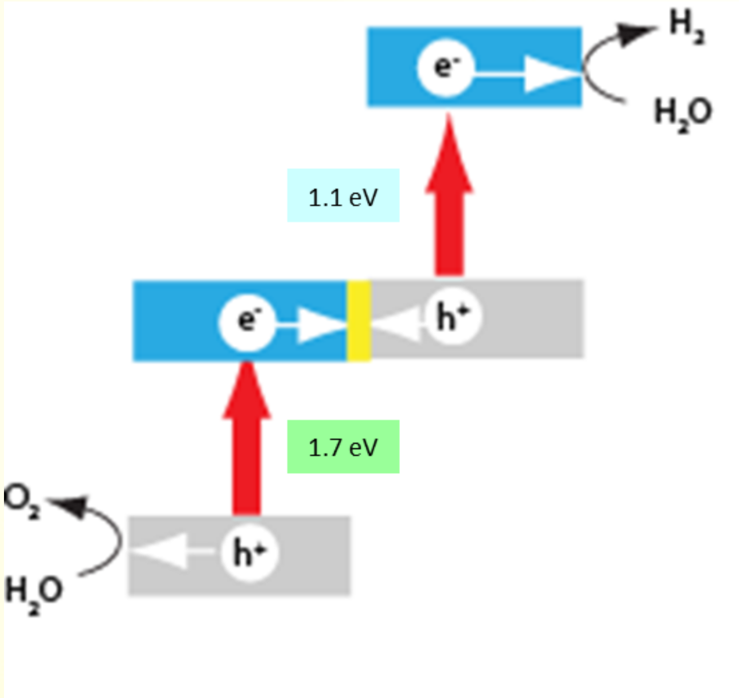
Fundamental Science Challenges in Light Capture

Earth abundant light absorbers with 1.7- 2.4 eV band gap

and with

current density, voltage, and stability which can sustain economical water splitting

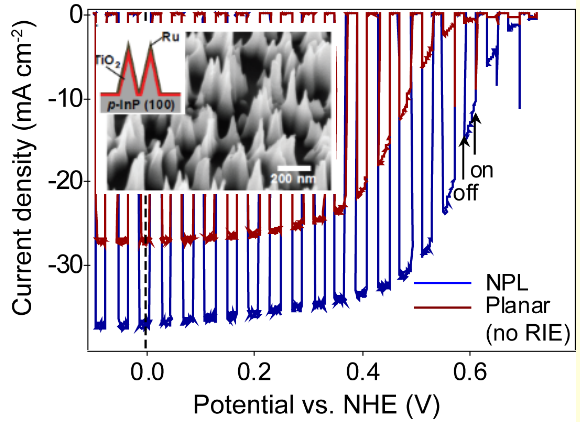
> If the band gap is too high – insufficient absorption of solar photons
>
> If too low, insufficient driving force for the desired redox chemistry



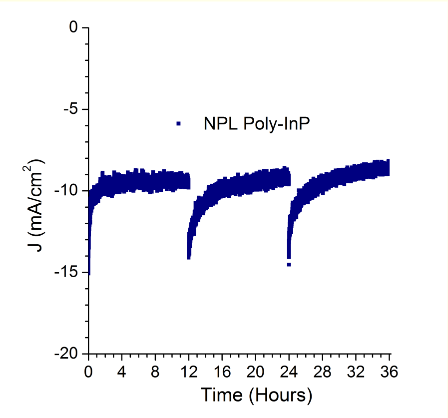
A combination of a 1.1 eV bandgap cathode with 1.7 eV anode would yield maximum conversion efficiency under ideal conditions.

Summary

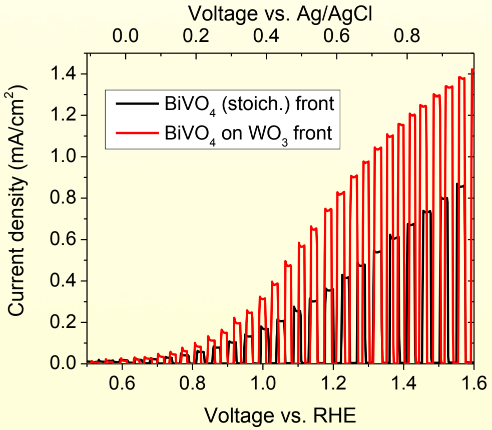
- Photocathodes
  >10 mA cm^{-2} current densities, large V_{OC}, STH up to 15% (p-InP with bias), stability with conformal TiO_2 protection
- Photoanodes
  Fundamental study of synthesis, native defects, and electron/hole transport in $BiVO_4$
- Integration
  Spontaneous water splitting shown



InP nanopillars make a high performance photocathode for H_2 generation



3 nm of TiO_2 enables stable photocathode operation for days



Native defect and hole transport control in $BiVO_4$