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

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?
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.

Electron transfer bridge
*Electrons and holes recombine also pumps protons driving ATP synthesis*

**Adapted from Photosystem II (Springer, 2005)**

**Photosystem II**
- pumps 4 holes to a water splitting catalyst
  - “Oxygen evolving complex”

**Photosystem I**
- pumps electrons to reduce NADP+ to NADP
  - NADP reduces $CO_2$ in the Calvin cycle to make sugars etc.
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…

Water splitting half reactions
Reduction: 2H⁺ + 2e⁻ → 2H₂
Oxidation: H₂O + 2h⁺ → 1/2O₂ + 2H⁺
Overall: H₂O → 1/2O₂ + H₂
ΔG = +237 kJ/mol, 1.23 eV/electron

CO₂ energetics are similar

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔG°  (kJ mol⁻¹)</th>
<th>n</th>
<th>ΔE°  (eV)</th>
<th>λmax (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O → H₂ + ½ O₂</td>
<td>237</td>
<td>2</td>
<td>1.23</td>
<td>611</td>
</tr>
<tr>
<td>CO₂ + H₂O → HCOOH + ½ O₂</td>
<td>270</td>
<td>2</td>
<td>1.40</td>
<td>564</td>
</tr>
<tr>
<td>CO₂ + H₂O → HCHO + O₂</td>
<td>519</td>
<td>4</td>
<td>1.34</td>
<td>579</td>
</tr>
<tr>
<td>CO₂ + 2H₂O → CH₃OH + 3/2 O₂</td>
<td>702</td>
<td>6</td>
<td>1.21</td>
<td>617</td>
</tr>
<tr>
<td>CO₂ + 2H₂O → CH₄ + 2O₂</td>
<td>818</td>
<td>8</td>
<td>1.06</td>
<td>667</td>
</tr>
</tbody>
</table>

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

$\Delta G = +237$ 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

![Graph showing cell voltage versus current density with 0.6 V overpotential](image)

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.

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…

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

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.
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.

"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)
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 CO$_2$RR) as inputs (no wires)

• Products are separated
  – produced fuel is kept away from oxidation site
Recent Discoveries in JCAP

- Electrochemical environments of oxygen catalysts
- Efficient photocathodes for hydrogen evolution
- First standardized benchmarking of solar-fuels catalysts
- World’s fastest high-throughput electrochemical screening system
- Mechanism of oxygen evolution on an active catalyst
- Computed energies of semiconductor/molecular linker interfaces
- Optimal band gaps for water-splitting solar-fuel devices
- First sustainability analysis for solar-fuel generation
- Active molecular catalyst-coupled semiconductor
- Efficient light-capture nanowire architecture
- Underpinning Discovery Science
- Accelerated Materials Discovery
- Scale-up and System Integration
- Component Assembly and Optimization
- Microfluidic test best for rapid materials scale-up
- Fundamental properties of ion conducting membranes
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/TiO₂ electrode  
Unstable against oxidation

Ok for oxidation, unstable against reduction

Stable for both

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.
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)

Example: water oxidation catalysis

- User: Michal Bajdich
- JCAP Sub-Project: Heterogeneous catalysis (Alex Bell, PI)
- Program Used: GPAW ($E_{\text{TOT}}$, surfaces) Quantum Espresso (spectra)
- Purpose: To identify phase, surface and limiting step of heterogeneous catalysts
- Conclusion: $\beta$-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
CoO$_x$ integration into stable water oxidation system

High current density, stable

CoO$_x$ on Si

In the expected oxidation state

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\textsubscript{Zn} antisites causes the n-type filling
- Computation: hundreds of processors for tens of hours (on Hopper)
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


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

Synthesis of single phase epitaxial ZnSn$_x$Ge$_{1-x}$N$_2$ with continuously tunable bandgap

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?

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

# Integration, multiscale modeling

## The vision

<table>
<thead>
<tr>
<th>Light absorption</th>
<th>1-D Model</th>
<th>Multidimensional Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beer-Lambert law</td>
<td>✓</td>
<td>✓ Maxwell’s equations</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Waveguiding/plasmonic effects</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Semiconductor transport</th>
<th>1-D Model</th>
<th>Multidimensional Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drift/diffusion (Nernst-Planck) Poisson</td>
<td>✓</td>
<td>Drift/diffusion (Nernst-Planck) Poisson</td>
</tr>
<tr>
<td>All relevant recombination models Advanced handling of surface states</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Catalysis, membrane/solution transport</th>
<th>1-D Model</th>
<th>Multidimensional Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butler-Volmer Kinetic model for charge transfer Ohm’s law</td>
<td>✓</td>
<td>Butler-Volmer Ohm’s law (Nernst-Planck)</td>
</tr>
</tbody>
</table>
Thank you
JCAP Approach and recent discoveries

**UNDERPINNING DISCOVERY SCIENCE**
- Mechanism of oxygen evolution on an active catalyst
- Computed energies of semiconductor/molecular linker interfaces
- Efficient photocathodes for hydrogen evolution
- First standardized benchmarking of solar-fuels catalysts
- World’s fastest high-throughput electrochemical screening system

**ACCELERATED MATERIALS DISCOVERY**
- Optimal band gaps for water-splitting solar-fuel devices
- First sustainability analysis for solar-fuel generation
- Active molecular catalyst-coupled semiconductor
- Efficient light-capture nanowire architecture

**SCALE-UP AND SYSTEM INTEGRATION**
- Microfluidic test best for rapid materials scale-up
- Electrochemical environments of oxygen catalysts

**COMPONENT ASSEMBLY AND OPTIMIZATION**
- Computed energies of semiconductor/molecular linker interfaces
- Fundamental properties of ion conducting membranes
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 \(V_{\text{OC}}\), 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\(_4\)