Artificial Photosynthesis: A photovoltaic perspective

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UCB EECS Solid State Seminar
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carboncycle2.0

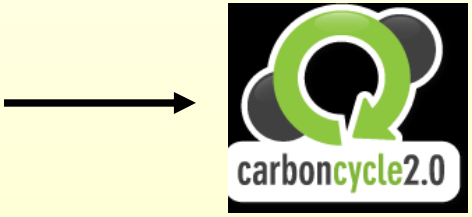
Acknowledgment and Disclaimer

Acknowledgment:

This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0004993.

What is “artificial photosynthesis”?

Why might it be of interest?

What does this logo mean? 

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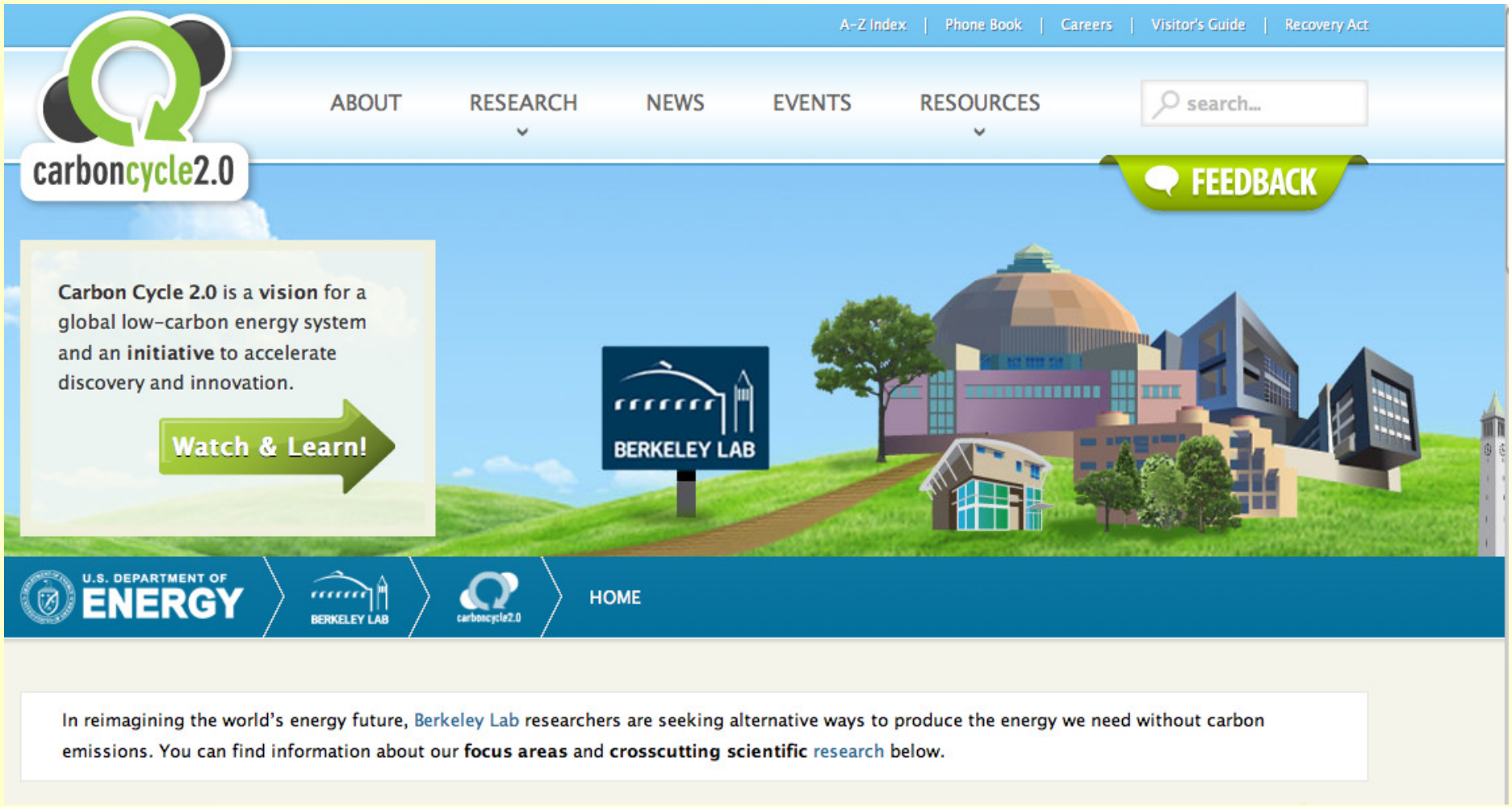
What is Carbon Cycle 2.0?



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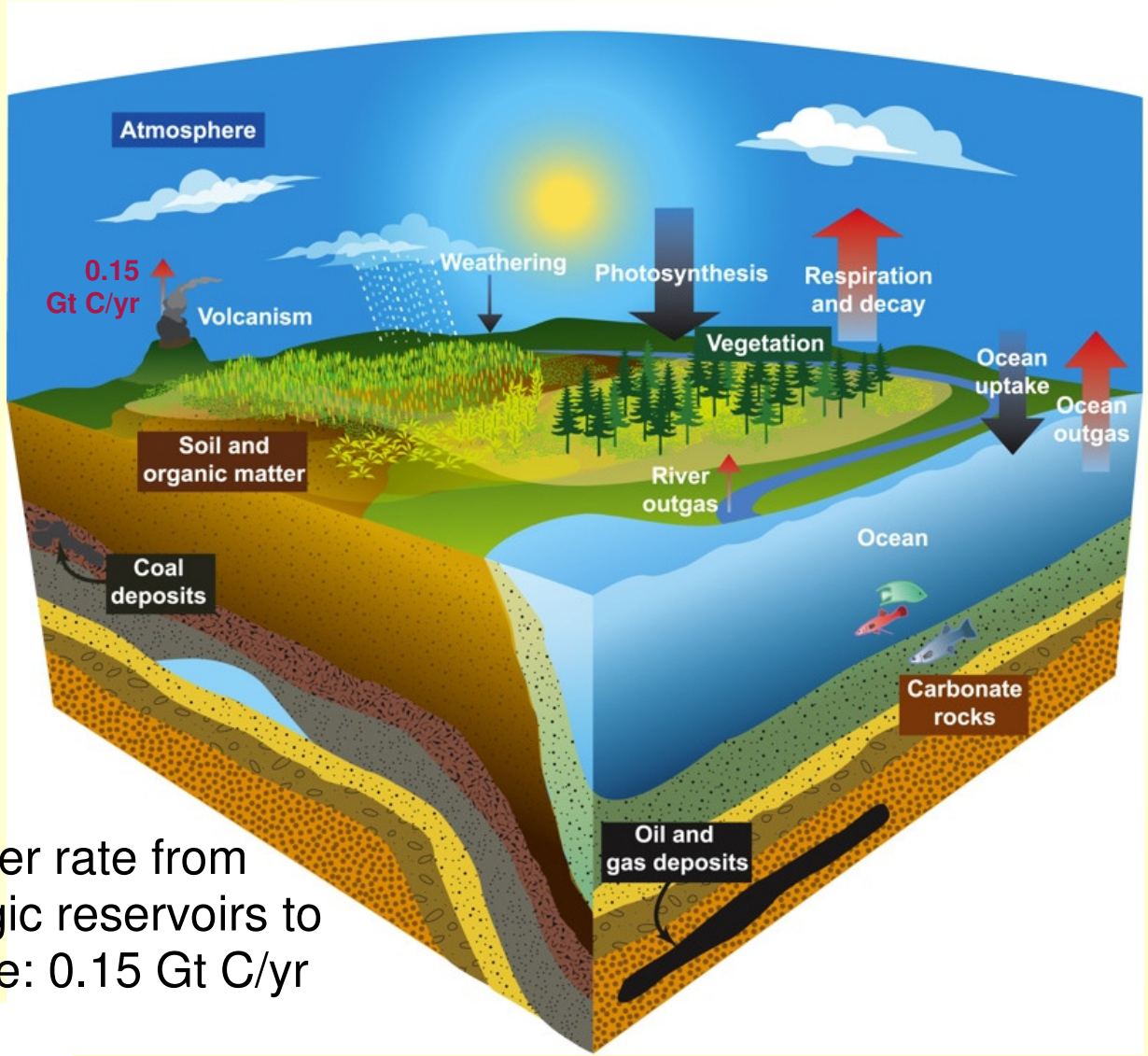
Carbon Cycle 1.0: Natural Carbon Cycle



Transfer rate from geologic reservoirs to surface: 0.15 Gt C/yr

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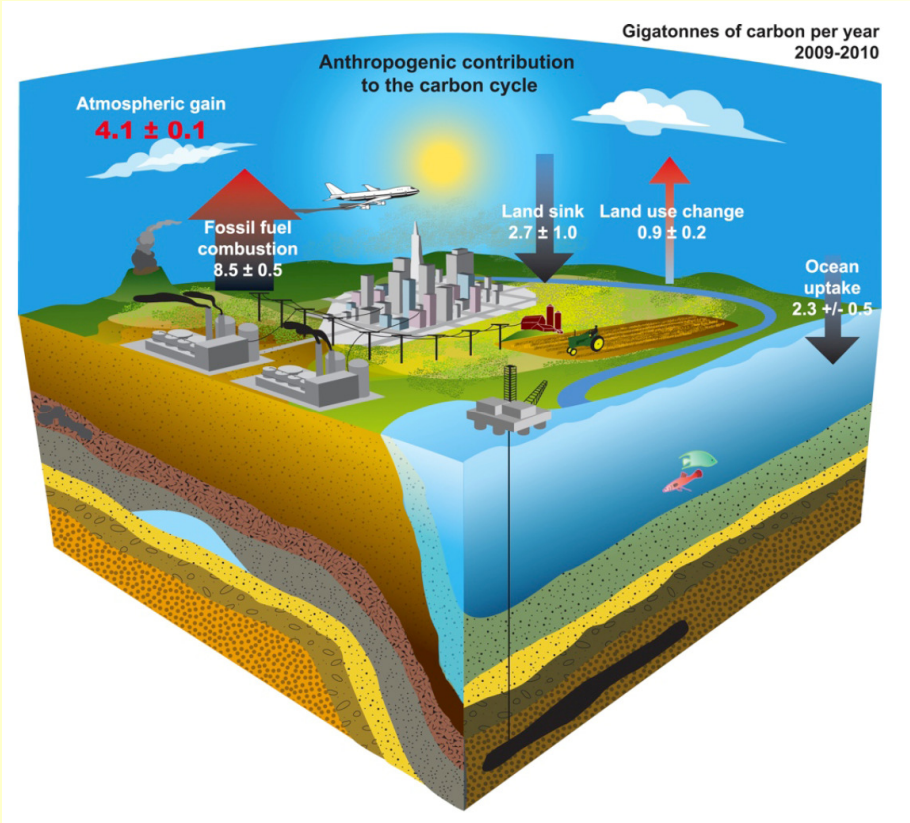
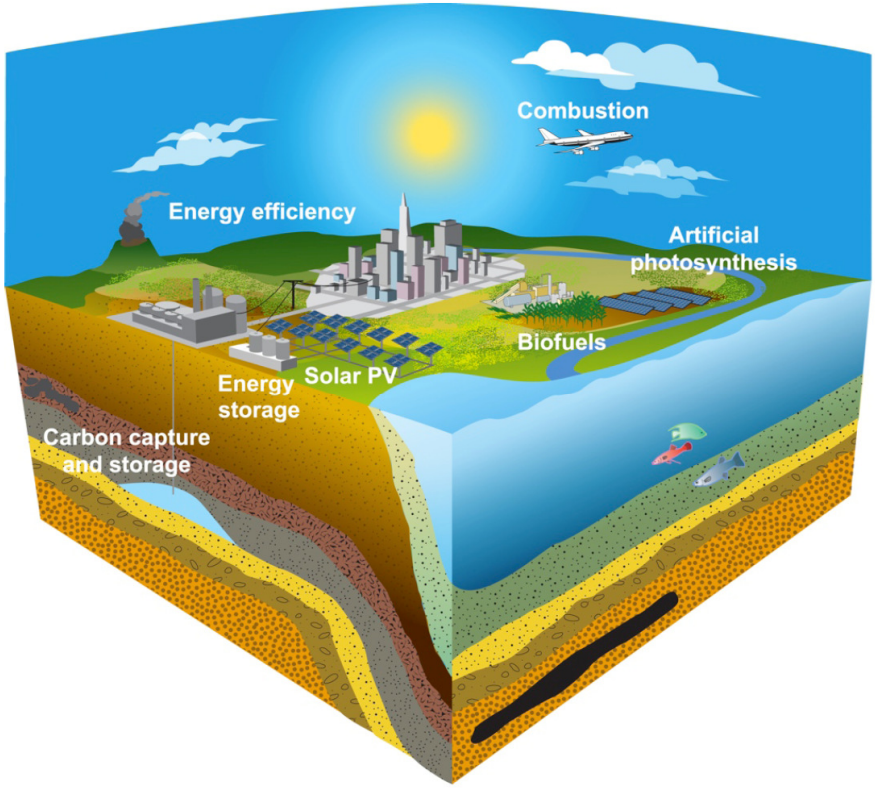
Current open-ended C cycle
Carbon Cycle 1.x (2011 AD)



Transfer rate from geologic reservoirs driven by burning fossil fuels = 9 Gt C/yr

Future balanced C cycle
Carbon Cycle 2.0 (2100 AD?)



Goal: 2x to 3x more energy production but with less than 1/3 of 2010 C emissions

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LBNL Research – Carbon Cycle 2.0 Initiative

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Let's look at the energy landscape

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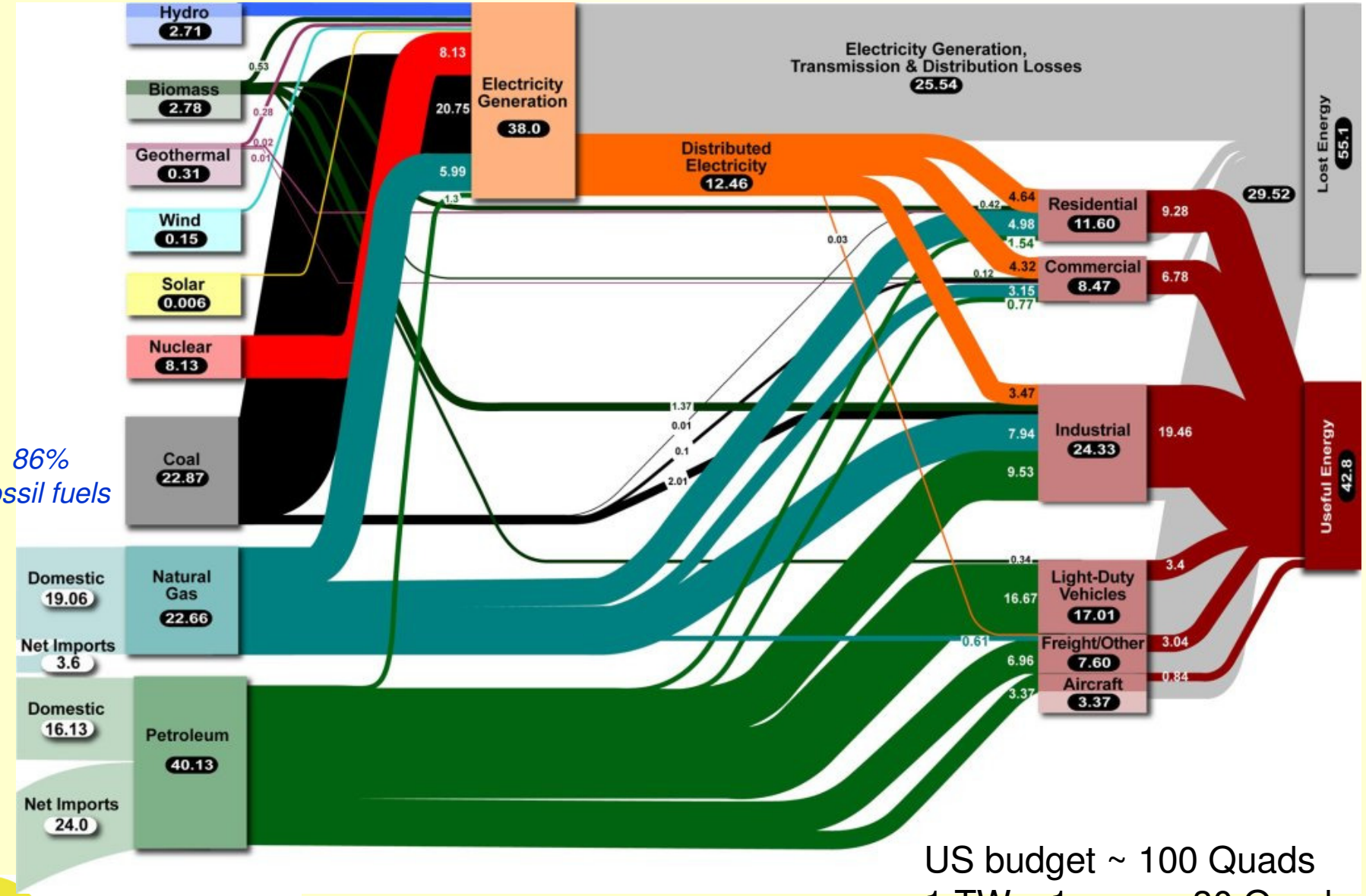
Look at all that "fossil fuel"



86% fossil fuels

US budget ~ 100 Quads
1 TW x 1 year = 30 Quads

Units are Quads = 10^{15} BTU ~ 10^{18} joule (EJ)

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Solar, in perspective

Solar
0.006 Quads = 1.7 TW-hr

5 MWp solar farm

Diablo Canyon Nuclear Power Plant
2 x 1100 MW reactors
Ran at 90% capacity in 2006:
18 TW-hr

Altamont Wind Turbines
576 MW capacity, 125 MW on average
1.1 TW-hr yearly average

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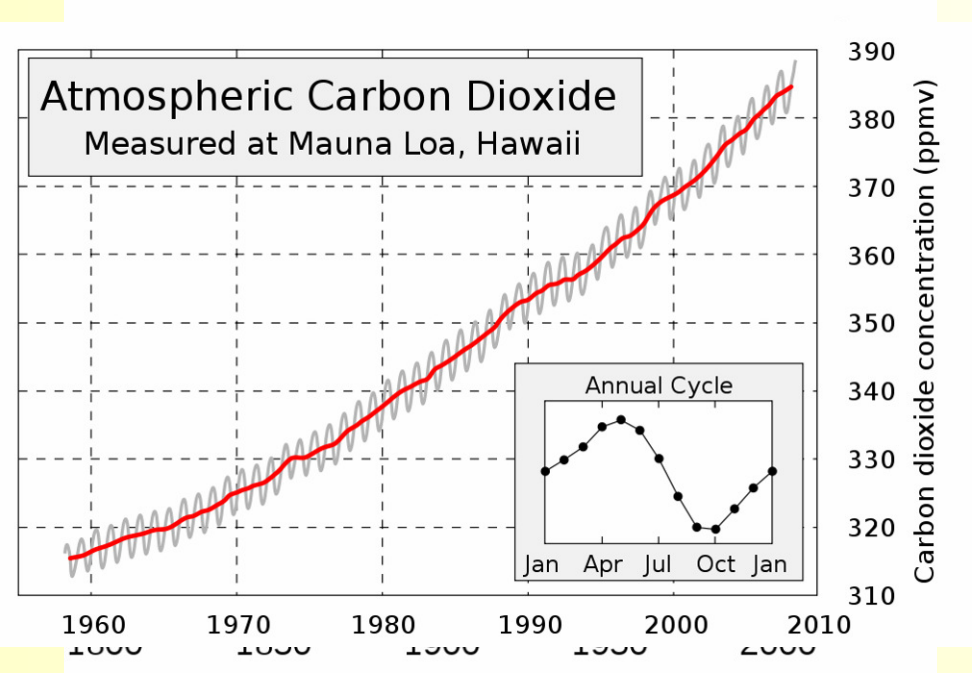
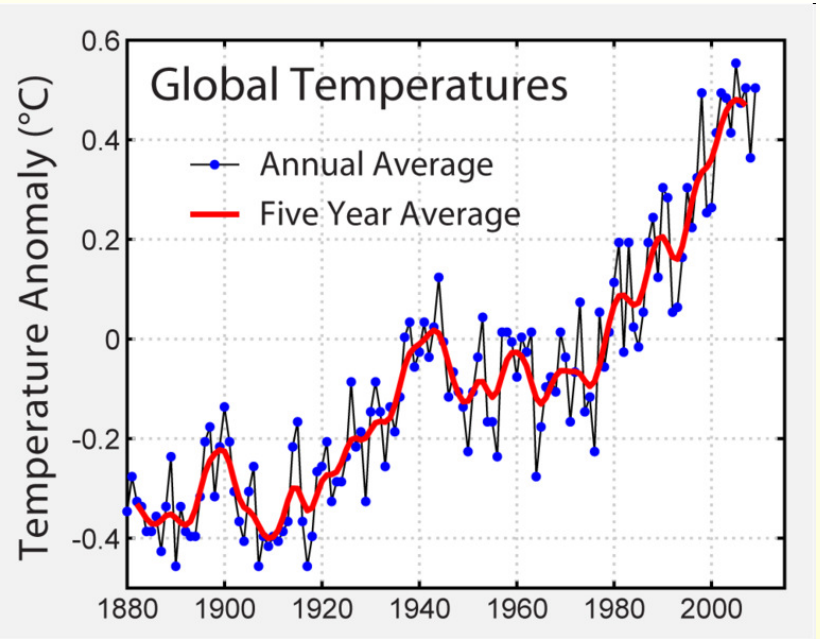
Fossil fuel use and consequences





- Photosynthesis fixed 3 gigatons carbon/year on average in 2000-2008

?

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Wikipedia
Global Carbon Project

Is there a particular fossil fuel which would be good to replace?

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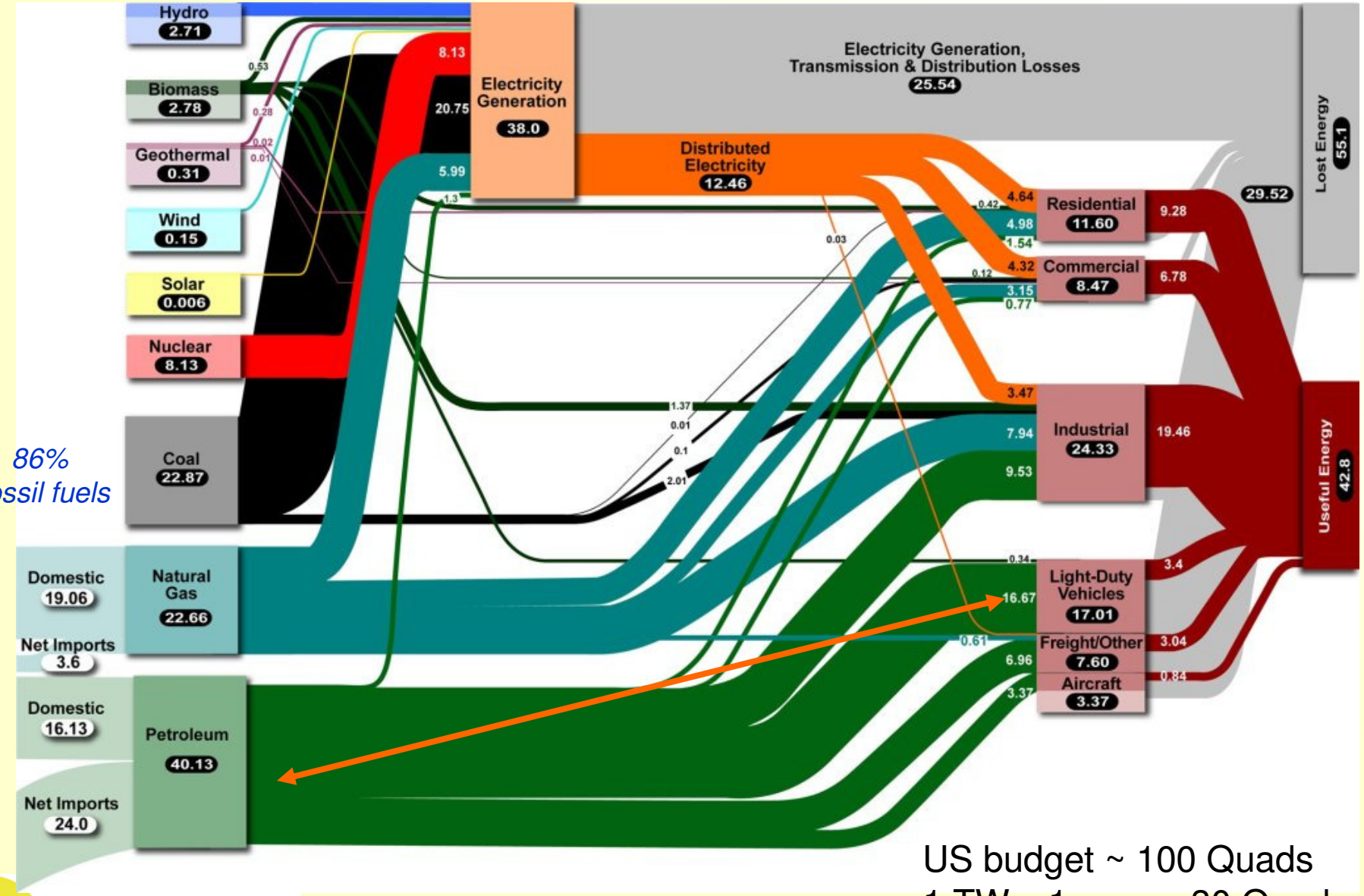
Which line is the fattest?



86%
fossil fuels

US budget ~ 100 Quads
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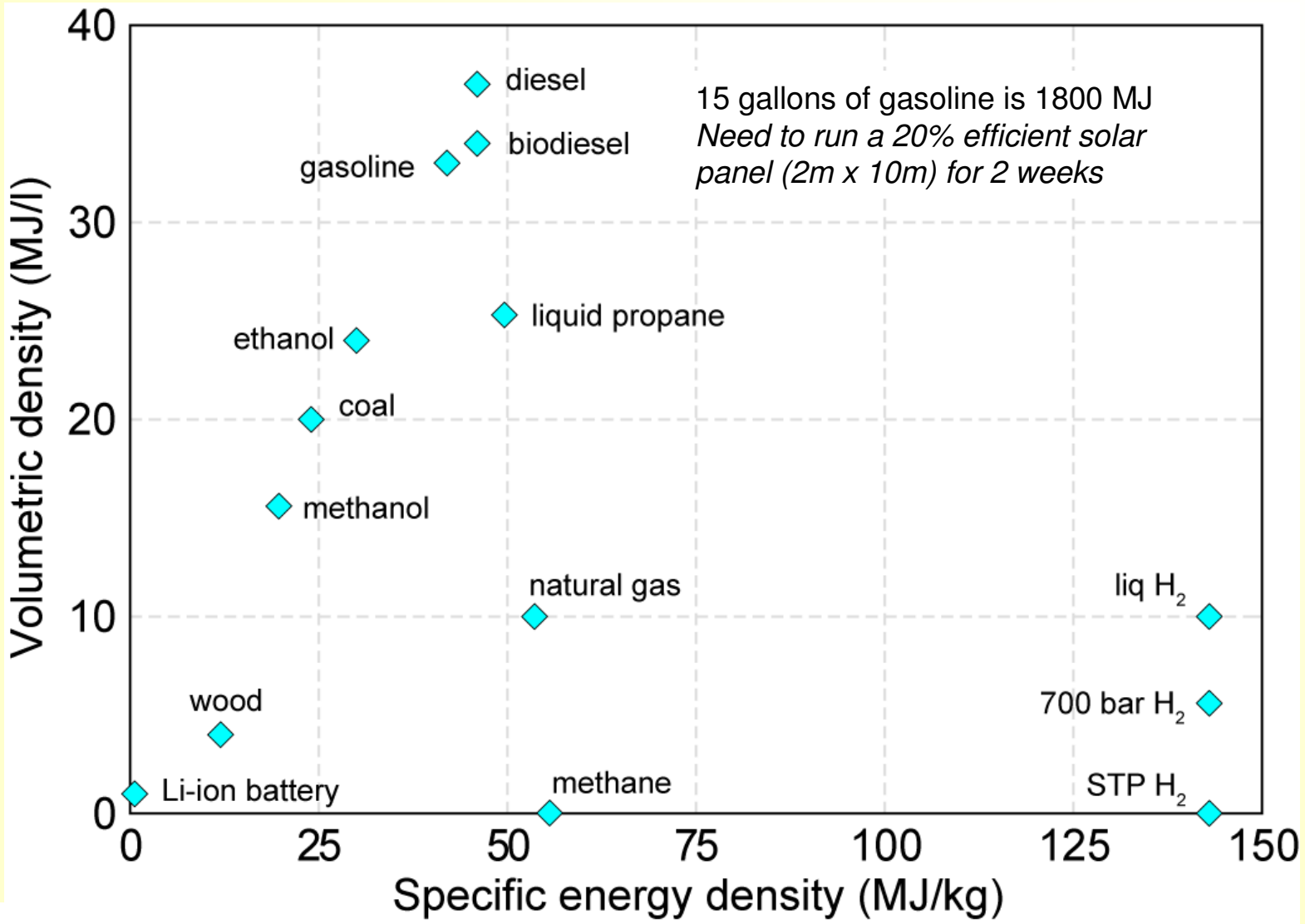
Why fossil fuels are so good for transportation



Less volume

Weighs less

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With the exception of nuclear and geothermal, the sun was the source of “our” energy

Natural Photosynthesis

- Old photosynthesis: fossil fuels
  - Convenient but finite
  - Impacts of CO_2 emission

- Current photosynthesis: biofuels
  - Scalable
  - Not as efficient as we would like
    - ca. 0.5% energy conversion efficiency
  - *How much fuel can we generate this way?*

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What is “artificial photosynthesis”?

Why might it be of interest?

What does this logo mean? →

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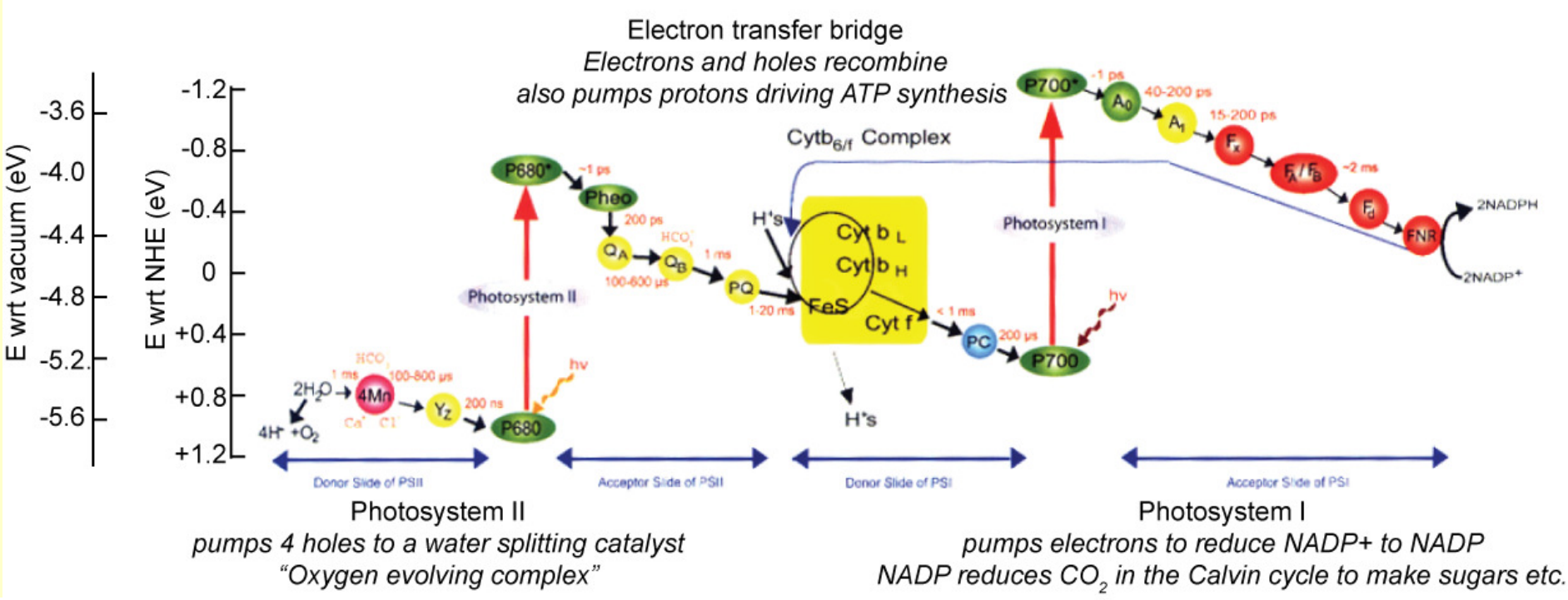
Simple picture of natural photosynthesis

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



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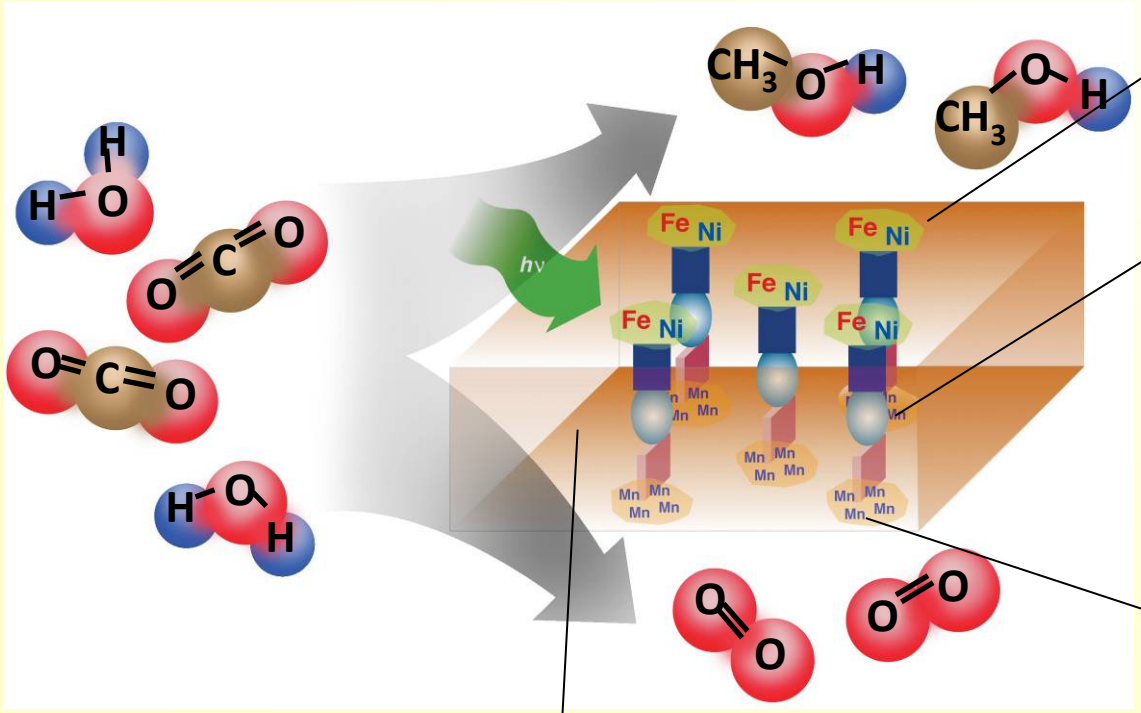
Adapted from *Photosystem II* (Springer, 2005)

In *artificial* photosynthesis we want to do the same thing as the natural system, but more efficiently



catalyst for the reduction reaction (Nature uses Fe complex for H_2 production)

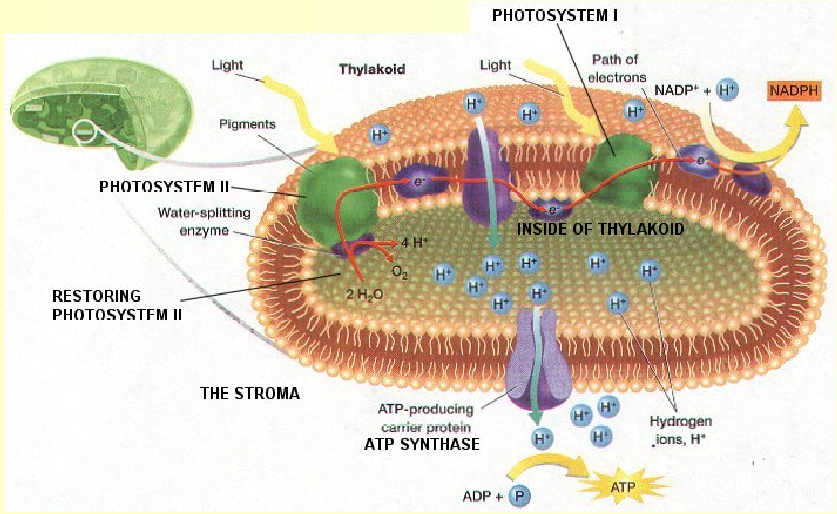
Light Capture
electron –hole pairs generated here with sufficient voltage (e.g. 1.23 eV + overpotential) to drive reactions.

catalyst for the oxidation reaction (plants use Mn complex)

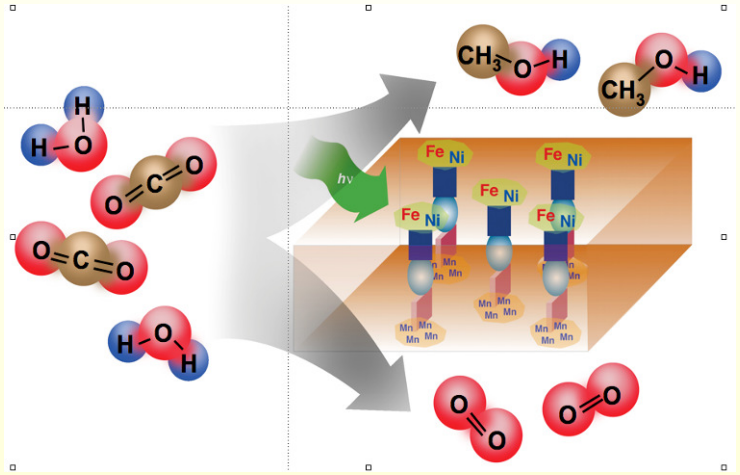
Membrane keeps oxidation and reduction products separated (to avoid reverse reactions) but allows H^+ transport

Melvin Calvin, 1982: It is time to build an actual artificial photosynthetic system, to learn what works and what doesn't work, and thereby set the stage for making it work better

Photosynthesis



Artificial Photosynthesis



There are some challenges – otherwise we would already be doing it

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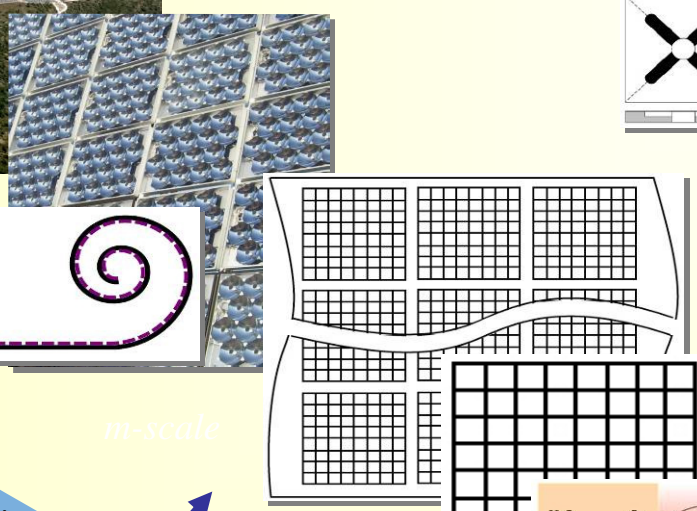
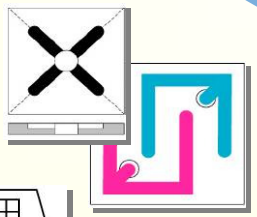
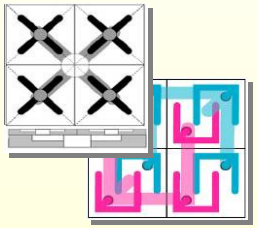
There are challenges at all length scales





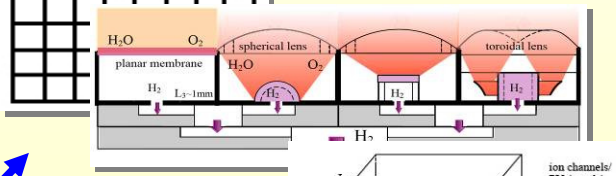


System/design/process level

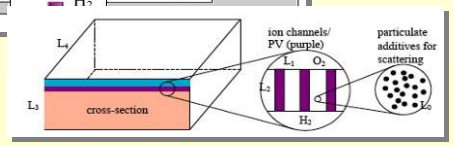
Flow chamber building blocks

m-scale

Device/physics level



cm-scale



mm-scale

Scalablility and Sustainability Analysis

Integration of Components

catalysts (Homogeneous; Heterogeneous; "Hybrid")

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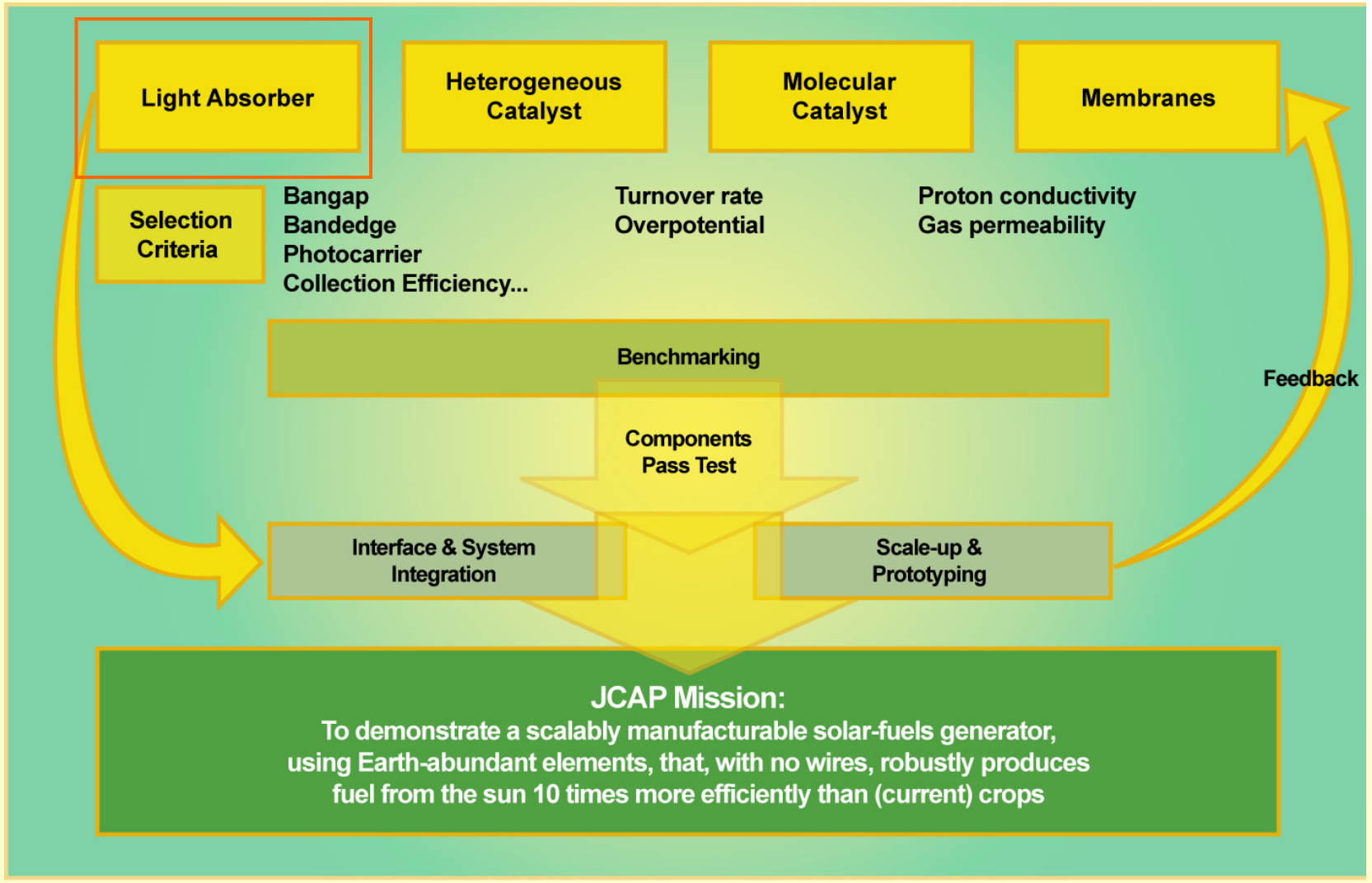
Joint Center for Artificial Photosynthesis

- Initiated July, 2010
- Eight Partners
  - Two DOE National Laboratories (**LBNL**, SLAC)
  - Six Research Universities (**Caltech**, UCB, Stanford, UCSB, UCI, UCSB)
- Start-up company approach with highly focused research agenda

JCAP Strategic Structure



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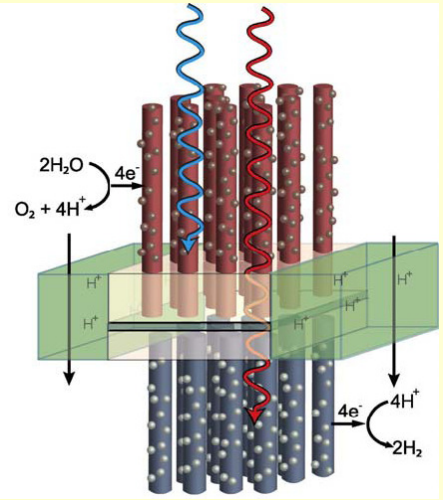
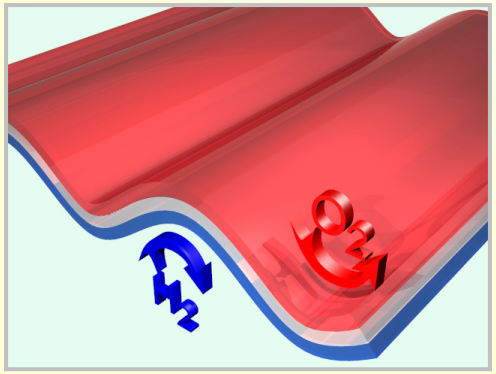
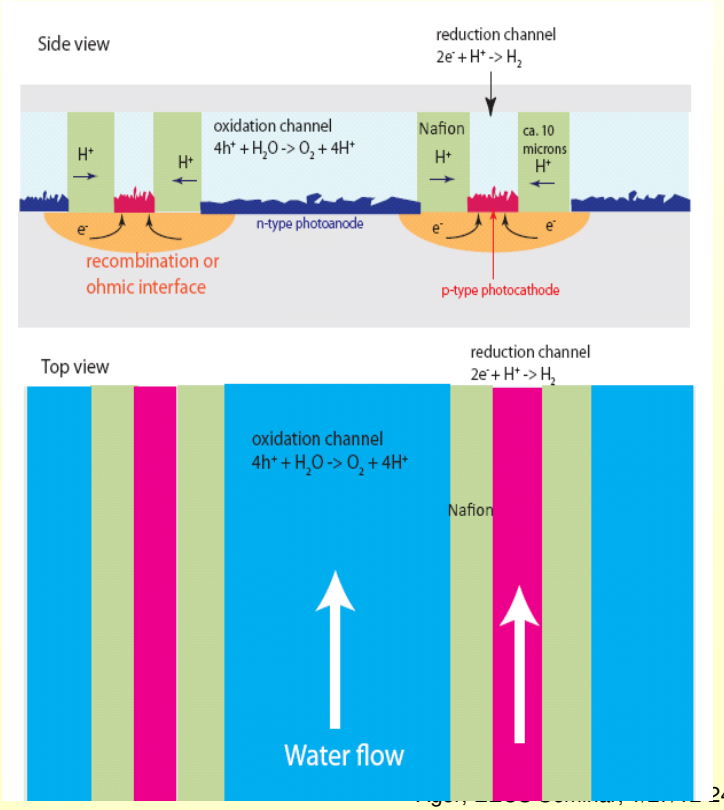
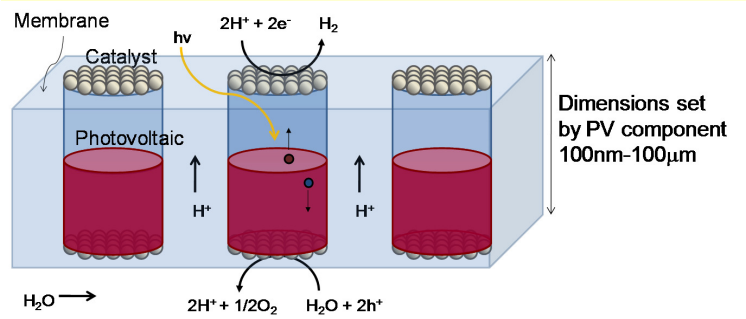
What is "Light Capture and Conversion"?

Answer: The photovoltaic heart of the fuel generating system, delivering photo-generated electrons and holes to the redox catalysts at the chemical potentials required to perform the desired synthetic chemistry









Redox chemistry and current continuity

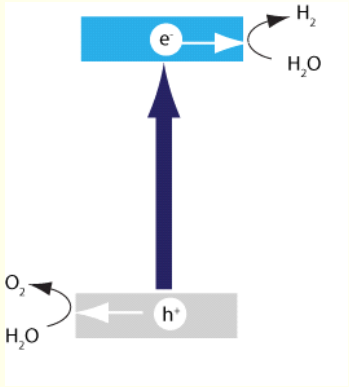
Water splitting half reactions

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?*

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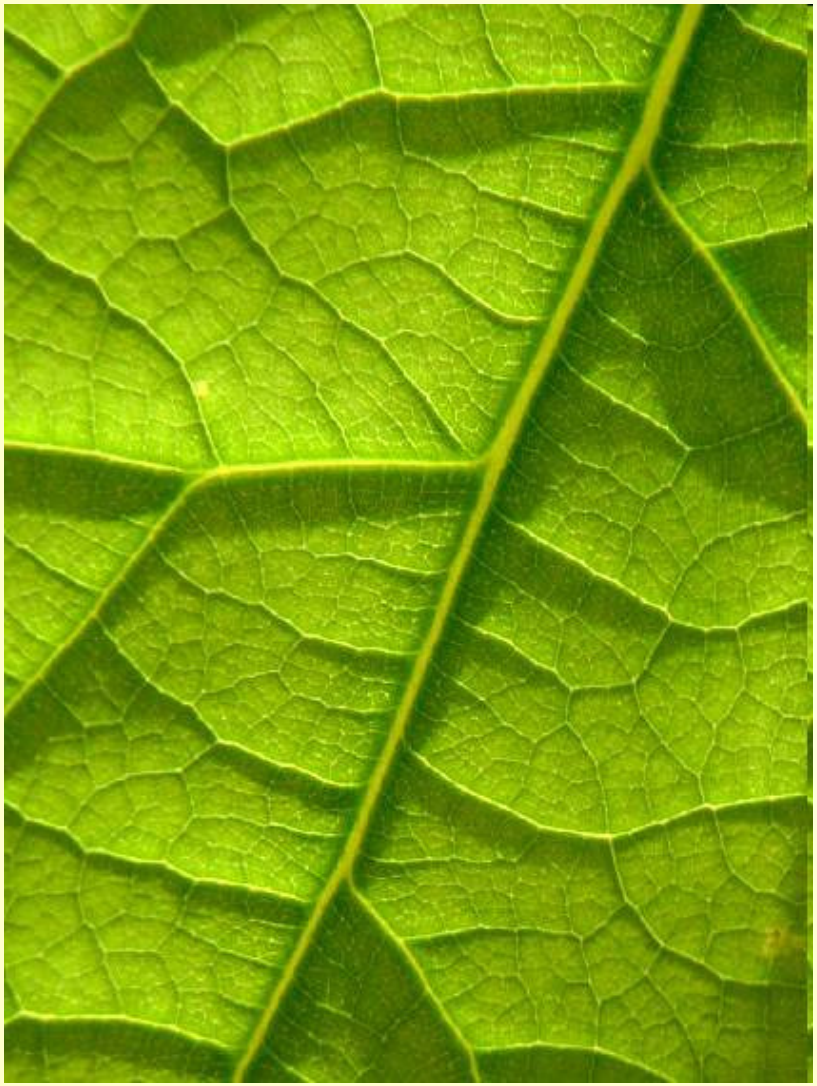

The voltage requirements are a little tougher than one might think

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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

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

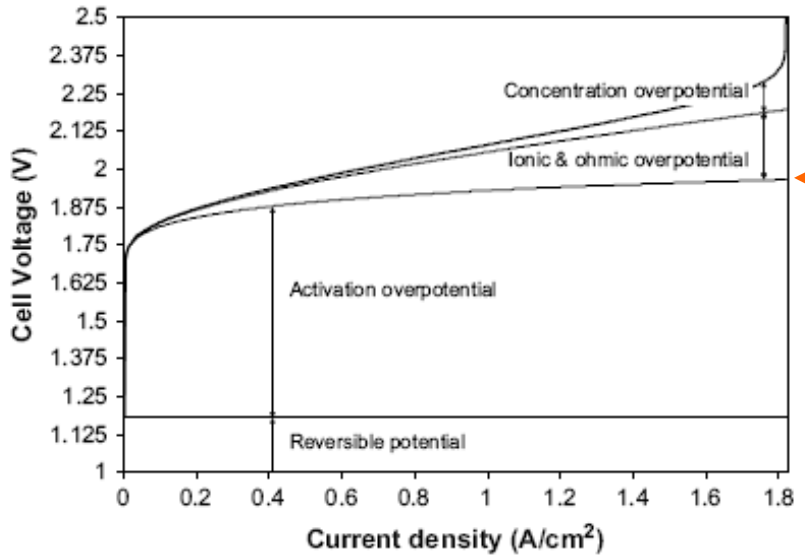


Fig. 4 – Simulated i–V curve of a PEM electrolytic cell with Pt electrodes (80 °C, 1 atm).

0.6 V overpotential for Pt

García-Valverde *et al.*, Int. J. Hydrogen Energy 33 5352 (2008)

The absolute band positions matter

Aligning with the redox potentials…

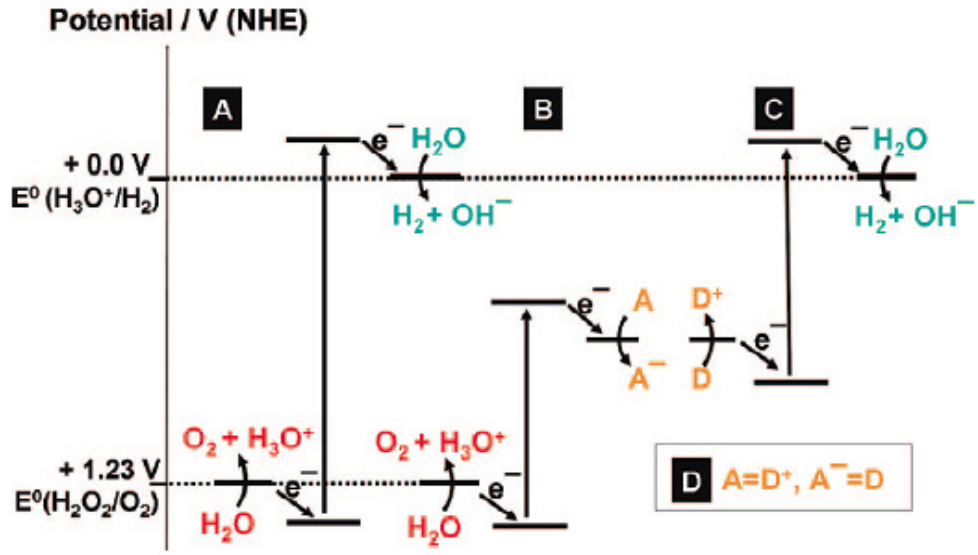


Figure 1. Potential energy diagrams for photochemical water splitting at pH = 0: (A) single semiconductor system; (B) with an electron acceptor; (C) with an electron donor; (D) dual semiconductor system (z scheme) employing a redox shuttle. Modified from ref 108.

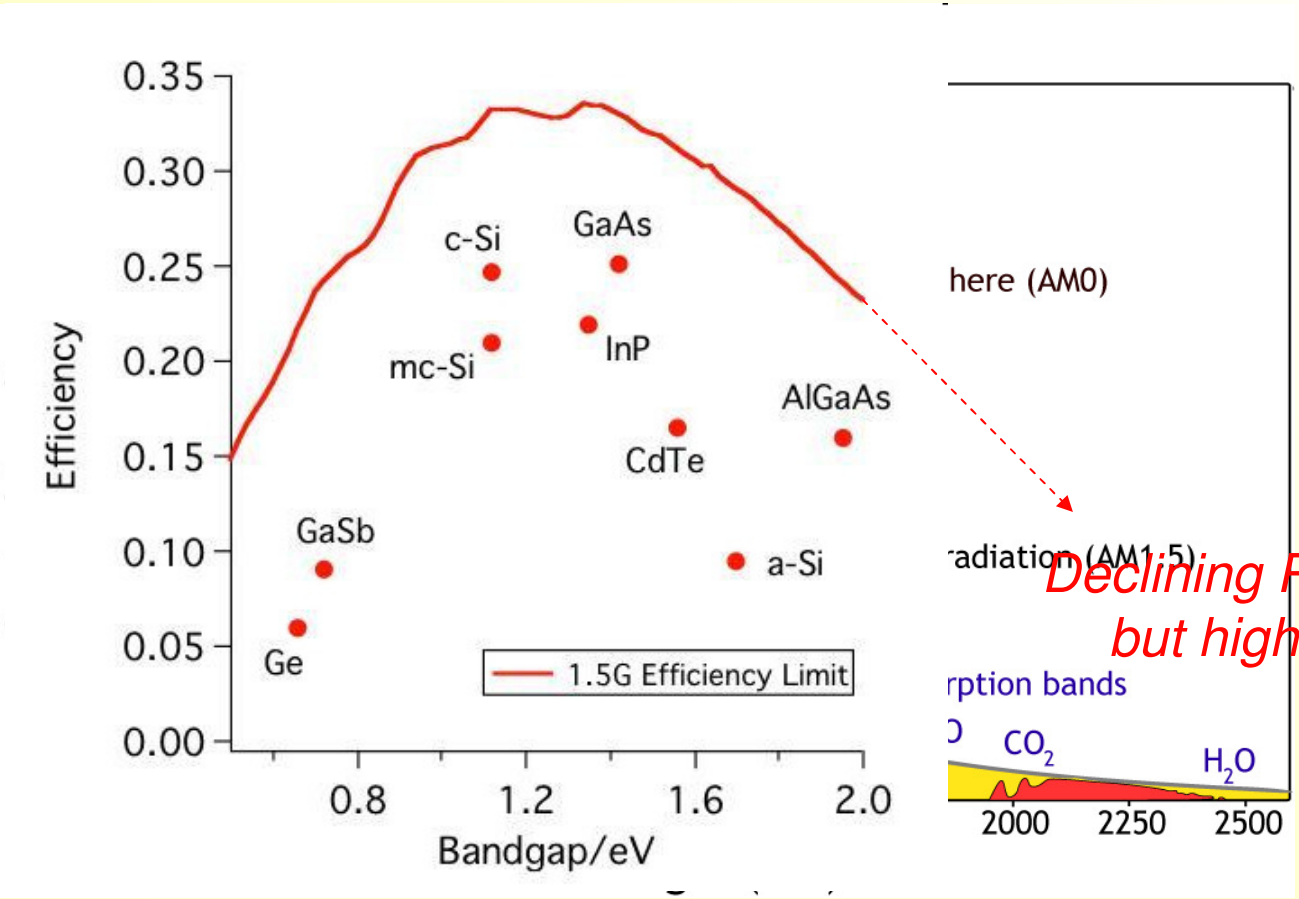
- Conduction band edge has to be higher than the potential for the reduction reaction
- Valence band edge has to be lower than the potential for the oxidation reaction

Very important: Stability, especially for the photoanode (holes)

Osterloh, Chem. Mater. 20 35 (2008)

Can regular solar cells do it?

PV technology is aimed at maximum efficiency



Declining PV efficiency but higher voltage

Shockley-Queisser limit, JAP 32 510-519 (1961)

Most single junction cells
Not enough voltage

Table I. Confirmed terrestrial cell and submodule efficiencies measured under the global AM1·5 spectrum (1000 W/m^2) at 25°C (IEC 60904-3: 2008, ASTM G-173-03 global)

Classification[a]	Effic[b] (%)	Area[c] (cm^2)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF[d] (%)	Test centre[e] (and date)	Description
Silicon							
Si (crystalline)	25·0 ± 0·5	4·00 (da)	0·706	42·7	82·8	Sandia (3/99)[f]	UNSW PERL[11]
Si (multicrystalline)	20·4 ± 0·5	1·002 (ap)	0·664	38·0	80·9	NREL (5/04)[f]	FhG-ISE[12]
Si (thin film transfer)	16·7 ± 0·4	4·017 (ap)	0·645	33·0	78·2	FhG-ISE (7/01)[f]	U. Stuttgart (45 μm thick)[13]
Si (thin film submodule)	10·5 ± 0·3	94·0 (ap)	0·492[g]	29·7[g]	72·1	FhG-ISE (8/07)[f]	CSG Solar (1–2 μm on glass; 20 cells)[14]
III-V Cells							
GaAs (thin film)	26·1 ± 0·8	1·001 (ap)	1·045	29·6	84·6	FhG-ISE (7/08)[f]	Radboud U. Nijmegen[15]
GaAs (multicrystalline)	18·4 ± 0·5	4·011 (t)	0·994	23·2	79·7	NREL (11/95)[f]	RTI, Ge substrate[16]
InP (crystalline)	22·1 ± 0·7	4·02 (t)	0·878	29·5	85·4	NREL (4/90)[f]	Spire, epitaxial[17]
Thin Film Chalcogenide							
CIGS (cell)	19·4 ± 0·6[h]	0·994(ap)	0·716	33·7	80·3	NREL (1/08)[f]	NREL, CIGS on glass[18]
CIGS (submodule)	16·7 ± 0·4	16·0 (ap)	0·661[g]	33·6[g]	75·1	FhG-ISE (3/00)[f]	U. Uppsala, 4 serial cells[19]
CdTe (cell)	16·7 ± 0·5[h]	1·032 (ap)	0·845	26·1	75·5	NREL (9/01)[f]	NREL, mesa on glass[20]
Amorphous/Nanocrystalline Si							
Si (amorphous)	9·5 ± 0·3[i]	1·070 (ap)	0·859	17·5	63·0	NREL (4/03)[f]	U. Neuchatel[21]
Si (nanocrystalline)	10·1 ± 0·2[j]	1·199 (ap)	0·539	24·4	76·6	JQA (12/97)	Kaneka (2 μm on glass)[22]
Photochemical							
Dye sensitised	10·4 ± 0·3[k]	1·004(ap)	0·729	22·0	65·2	AIST (8/05)[f]	Sharp[23]
Dye sensitised (submodule)	**8·4 ± 0·3[k]**	**17·11 (ap)**	**0·693[g]**	**18·3[g]**	**65·7**	**AIST (4/09)**	**Sony, 8 serial cells[3]**
Organic							
Organic polymer	5·15 ± 0·3[k]	1·021(ap)	0·876	9·39	62·5	NREL(12/06)[f]	Konarka[24]
Organic (submodule)	**2·05 ± 0·3[k]**	**223·5 (ap)**	**6·903**	**0·502**	**59·1**	**NREL (1/09)**	**Plextronics[4,25]**
Multijunction Devices							
GaInP/GaAs/Ge	32·0 ± 1·5[j]	3·989(t)	2·622	14·37	85·0	NREL (1/03)	Spectrolab (monolithic)
GaInP/GaAs	30·3[j]	4·0 (t)	2·488	14·22	85·6	JQA (4/96)	Japan Energy (monolithic)[26]
GaAs/CIS (thin film)	25·8 ± 1·3[j]	4·00 (t)	—	—	—	NREL (11/89)	Kopin/Boeing (4 terminal)[27]
a-Si/μc-Si (thin submodule)[j,l]	11·7 ± 0·4[j,l]	14·23(ap)	5·462	2·99	71·3	AIST (9/04)	Kaneka (thin film)[28]

These voltages look interesting…

Can a single photon do it?

Wide bandgap oxides work

But efficiency is poor

Chem. Mater. **2008,** *20,* 35–54

Reviews

260 references!

Inorganic Materials as Catalysts for Photochemical Splitting of Water

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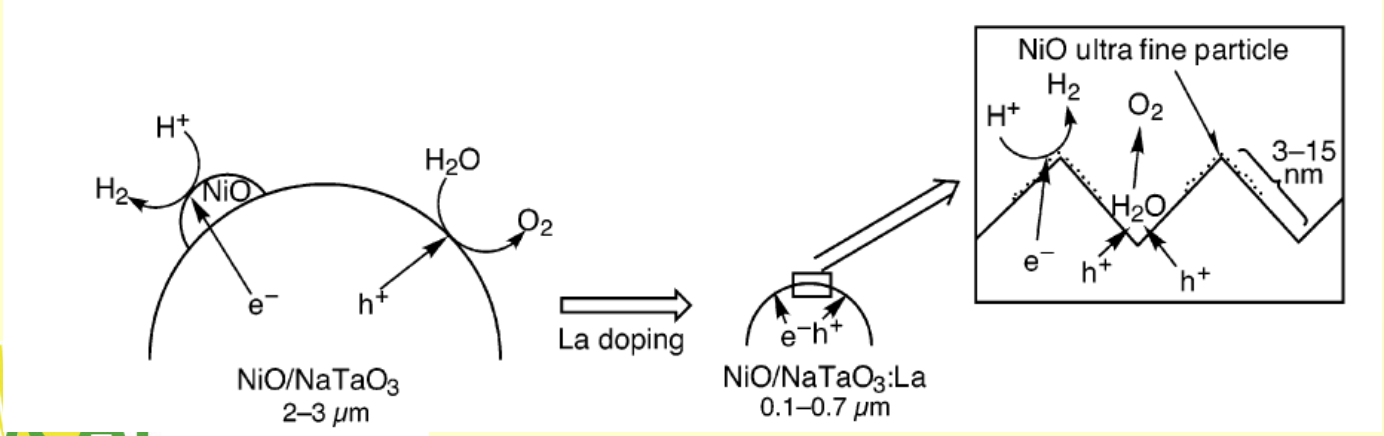
Received August 25, 2007. Revised Manuscript Received October 18, 2007

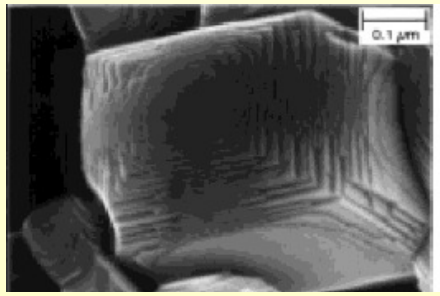
Photochemical splitting of water into H_2 and O_2 using solar energy is a process of great economic and environmental interest. Since the discovery of the first water splitting system based on TiO_2 and Pt in 1972 by Fujishima and Honda, over 130 inorganic materials have been discovered as catalysts for this reaction. This review discusses the known inorganic catalysts with a focus on structure–activity relationships.

Only some of these have stoiochiometric products without bias or other tricks

But TiO_2, $SrTiO_3$, etc. do work…

Highest quantum efficiency for $NaTaO_3$-based system
56% QE at 270 nm (E_g ~ 4.1 eV)
Kato *et al.*, JACS (2003)





Ok, what about two photons (like the natural system)?

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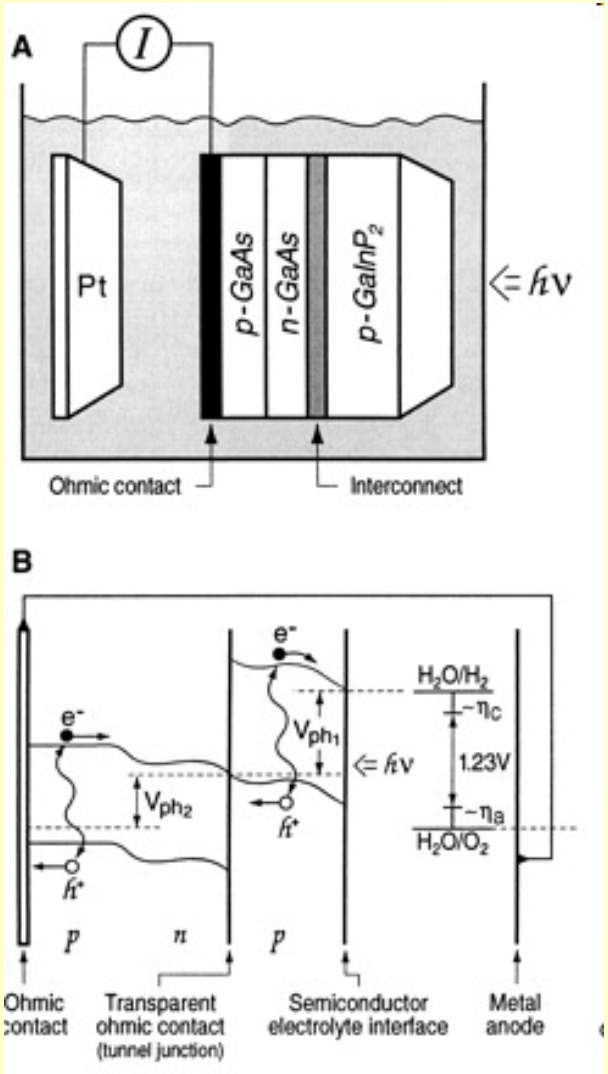
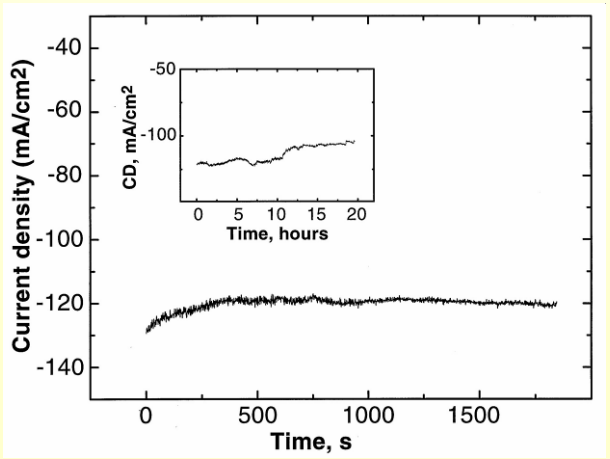
"Brute force" approach with a high voltage tandem solar cell



- The GaInP/GaAs tandem cell used has a V_{OC} of ca. 2.4 V
- The p-GaInP (with Pt catalyst layer) is in contact with the water, electrons go to the surface to drive the reduction reaction (protons to H_2)
- holes go to the Pt counter electrode to oxidize water
- current flow monitors redox chemistry (also checked gas products with mass spec)



11x ~AM1.5
12.4% efficient ☺

But photocathode degrades in time ☹

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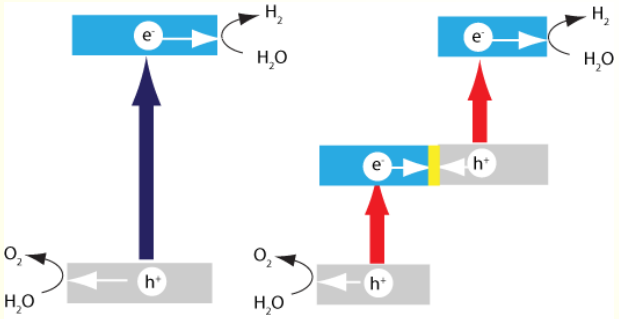
O. Khaselev, J. Turner, *Science* **280**, 425 (1998)

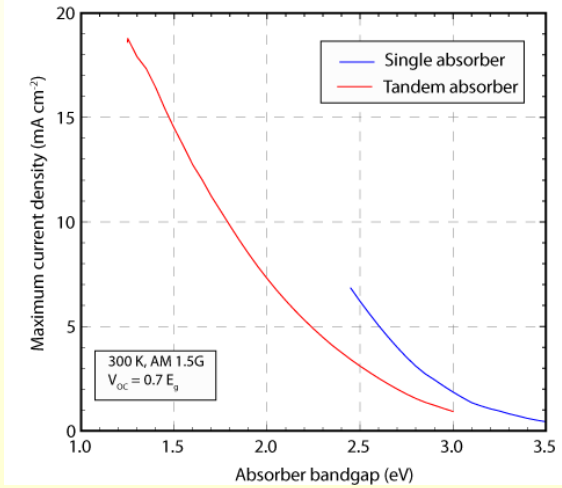
JCAP approach to the voltage

Two photons, stable and scalable materials

Arguments for a tandem or "Z-scheme" approach

- High conversion efficiencies for water splitting have been demonstrated with tandem solar cells + catalyst
  but with non-scalable approaches
- Can optimize properties (overpotentials, surfaces, etc.) of photoanode and photocathode separately
- Higher current possible
- It is what the natural system does





Maximum current densities (below) of 1 photon and 2 photon (tandem or Z-scheme) methods for photoelectrochemical fuel production. The maximum current density as a function of bandgap was calculated assuming an minimum operating voltage of 1.7 V and a V_{OC} of 70% of the bandgap; for the tandem cell, two cells with equal bandgaps were assumed (the maximum current is half that of a single cell at the same gap). Even higher currents are possible if the two absorbers have unequal gaps in a spectrally splitting approach

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- I will discuss photocathodes and photoanodes separately
  - *For spontaneous water splitting, the sum of their open circuit voltages vs. the H^+/H_2 and H_2O/O_2 potentials must be greater then 1.23 V*

- Then, we will put them together in series

p-Si is an attractive photocathode

Except it is short on voltage, < 0.5 E_g

Planar with Pt

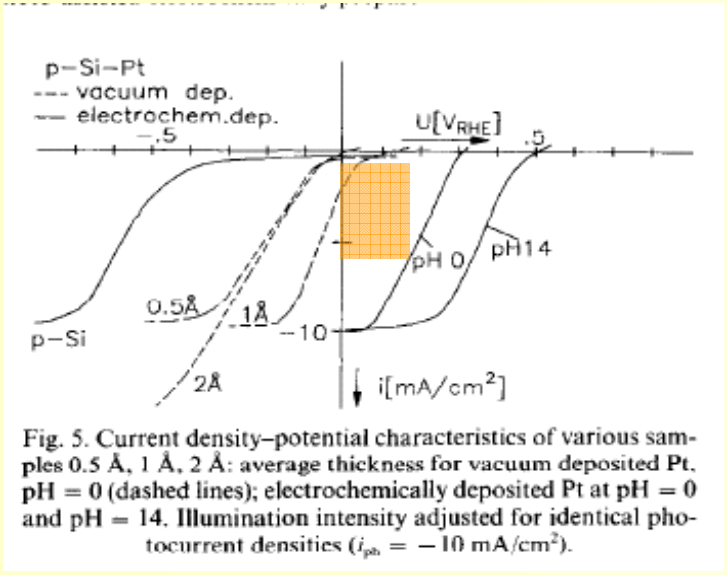
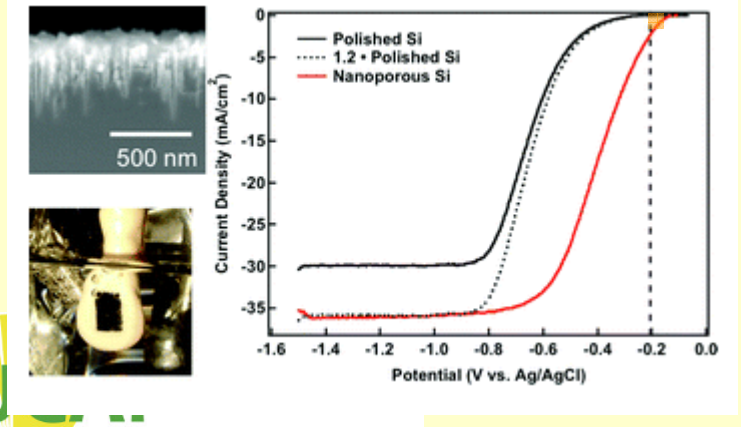


Fig. 5. Current density–potential characteristics of various samples 0.5 Å, 1 Å, 2 Å: average thickness for vacuum deposited Pt, pH = 0 (dashed lines); electrochemically deposited Pt at pH = 0 and pH = 14. Illumination intensity adjusted for identical photocurrent densities ($i_{ph} = -10$ mA/cm²).

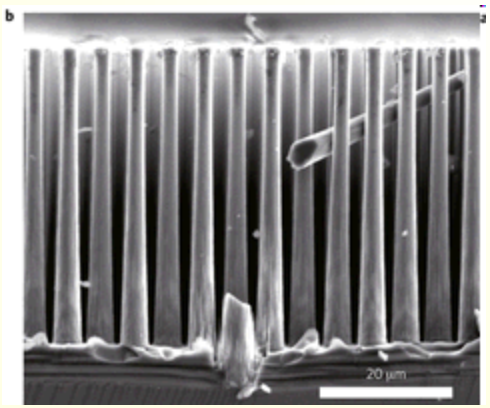
Maier *et al.*, 1996

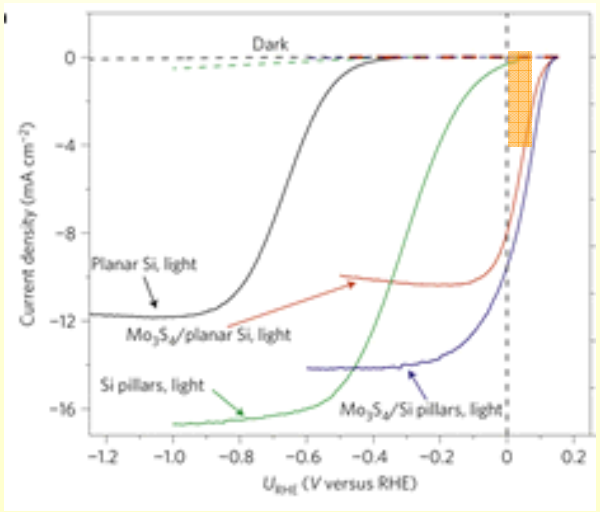
"black" Si



Oh, Deutsch, Yuan, Branz, 2011

Si nanowires with Mo-based reduction catalyst





Hou *et al.*, Nature Materials, 2011

So let's start with a very good photocathode…

InP contains a non-abundant element (In) but is otherwise very promising

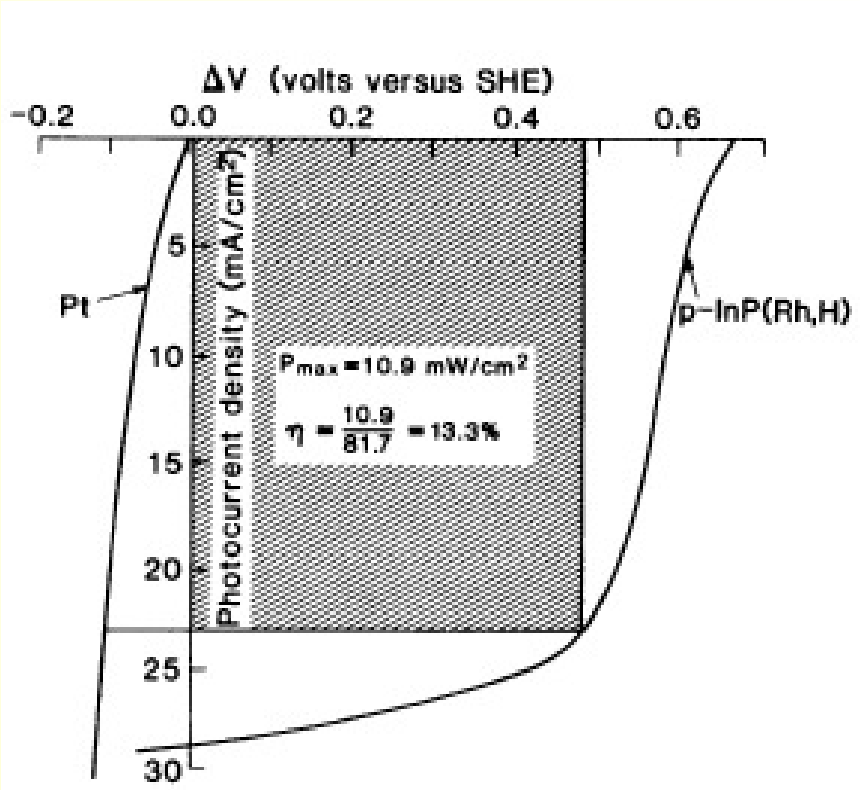


Fig. 6 (right). Photocurrent bias reduction characteristics of a *p*-InP/(hydrogen-saturated rhodium) photocathode in 1*M* $HClO_4$ under sunlight at 81.7 mW/cm². The solar-to-hydrogen conversion efficiency is 13.3 percent (*80*).

Heller, Science, 1984

very large reported photocathodic current densities for InP

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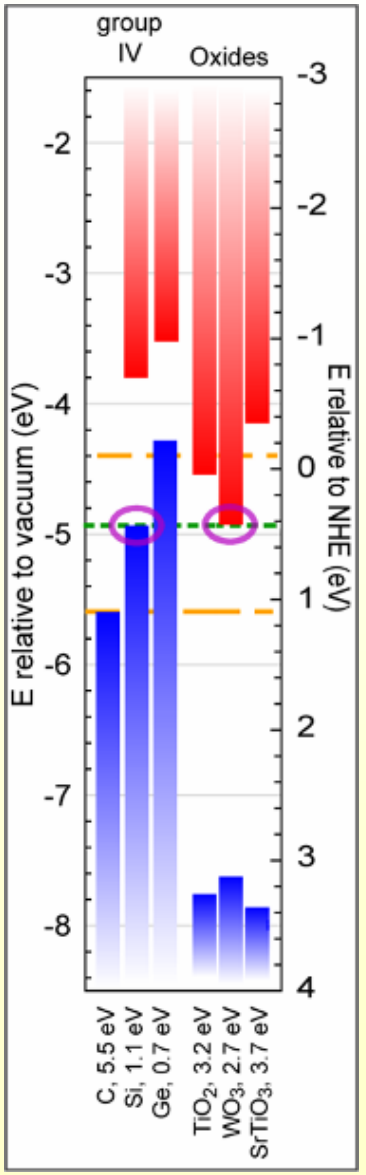
Why it is harder for the photoanodes

- Reaction is more difficult
  - 4 electron transfers vs. 2
    - But trying to reduce CO_2 may even the field
- Surface holes are (in general) more corrosive to the semiconductor than electrons
- Oxides bring stability but also a low CBM position (lowering V_{oc})



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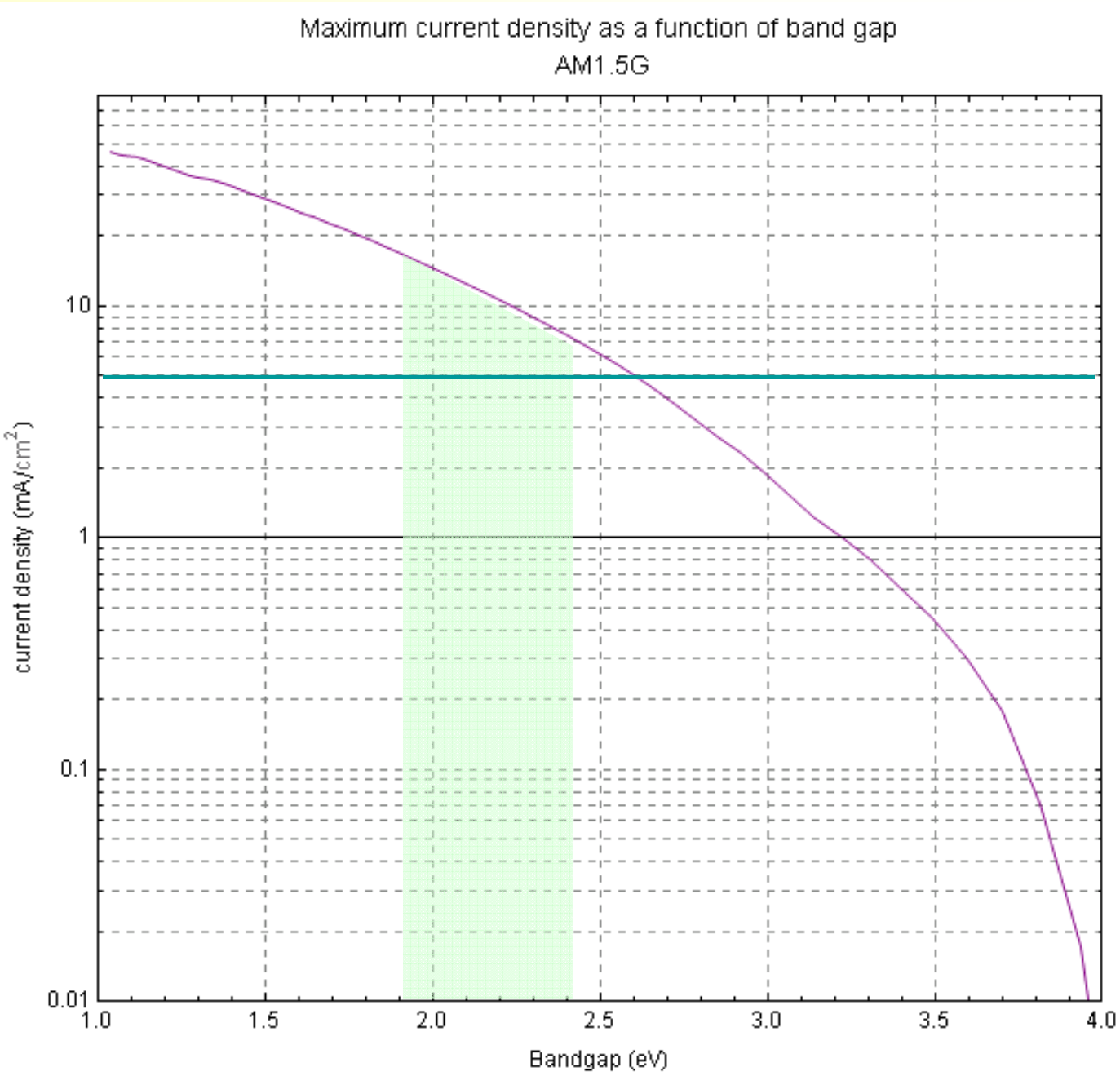
If we can get 75% EQE and half the band gap as V_{OC}

And the photocathode does half the work

Then photoanode target range is 1.9-2.4 eV



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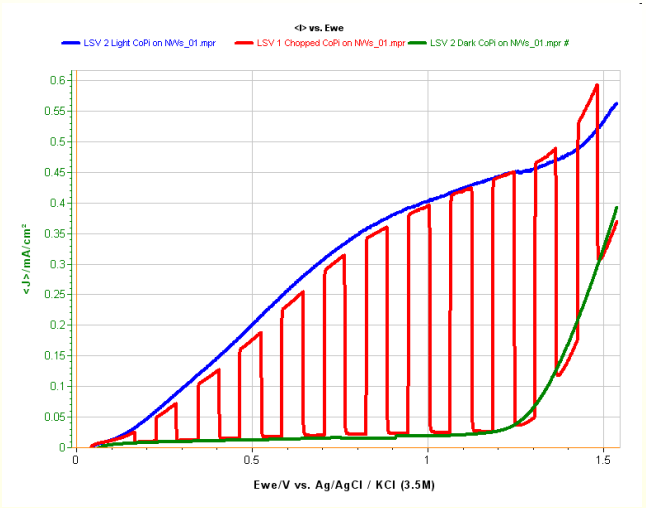
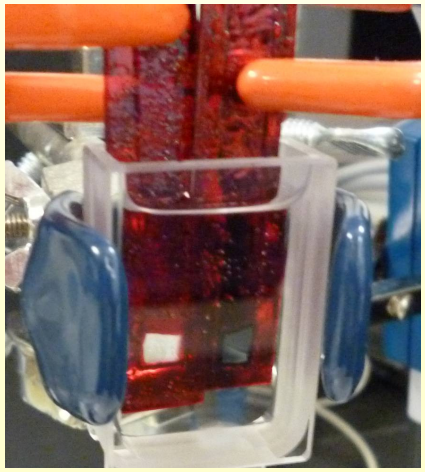
Technical summary

- Photocathode
  - H_2 production with efficiencies comparable to solar cells achieved with InP
  - TiO_2 protects absorber with little loss in photocurrent
- Photoanode
  - >0.5 V open circuit vs. O_2/H_2O with WO_3 and $CuWO_3$
  - Current density remains a challenge
- Tandem system
  - Spontaneous water splitting achieved with InP/WO_3, $InP/CuWO_4$, and InP/TiO_2
  - V_{oc} matters, a lot
    - We can always use more!
    - From the photocathode, potentially
    - From the tail of the photocurrent onset
    - From a better material or surface





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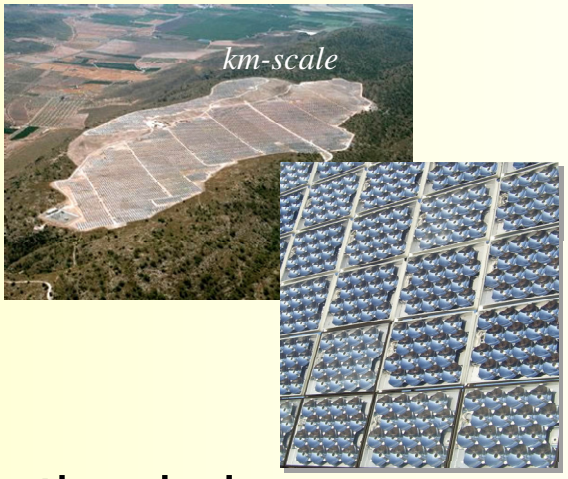
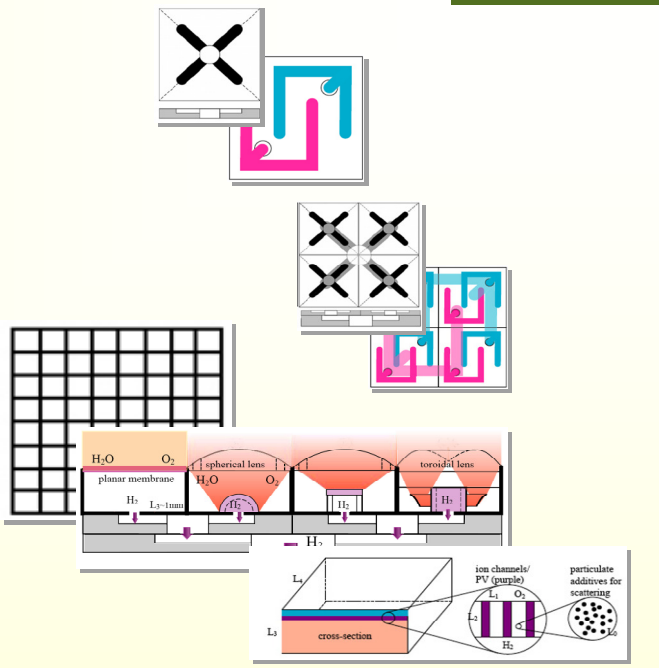
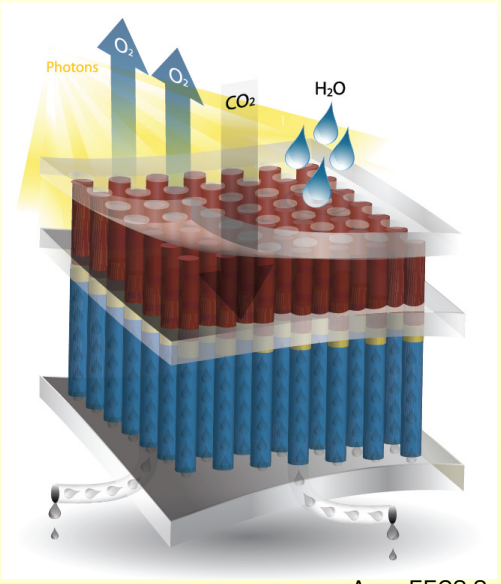
Looking forward





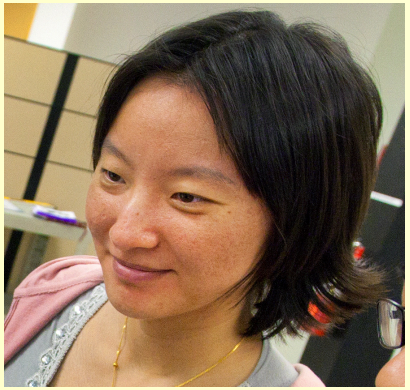
- Artificial photosynthesis is challenging…but not impossible
- LBNL research is addressing the fundamental challenges
- When/if it works, we will have a (large) carbon-neutral source of transportation fuels

http://www.solarfuelhub.org

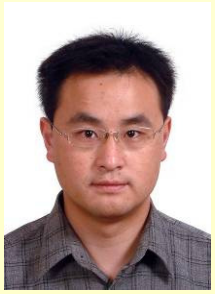


- JCAP North PIs: P. Yang, P. Alivisatos, L.-W. Wang, J. W. Ager
- Collaborating PIs, North: J. Neaton, A. Javey
- North Staff: Le Chen, Ty Matthews, Bala K. (now at IIT Bombay), Jianwei Sun, Min Hyung Lee, Shiyou Chen
- North Guests: Esther Alarcón, Junjun Zhang

- Many collaborations and interactions





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Thank you