Solar Photovoltaics & Energy Systems

Lecture 6 - Solar-to-fuel Conversion: motivation and approaches

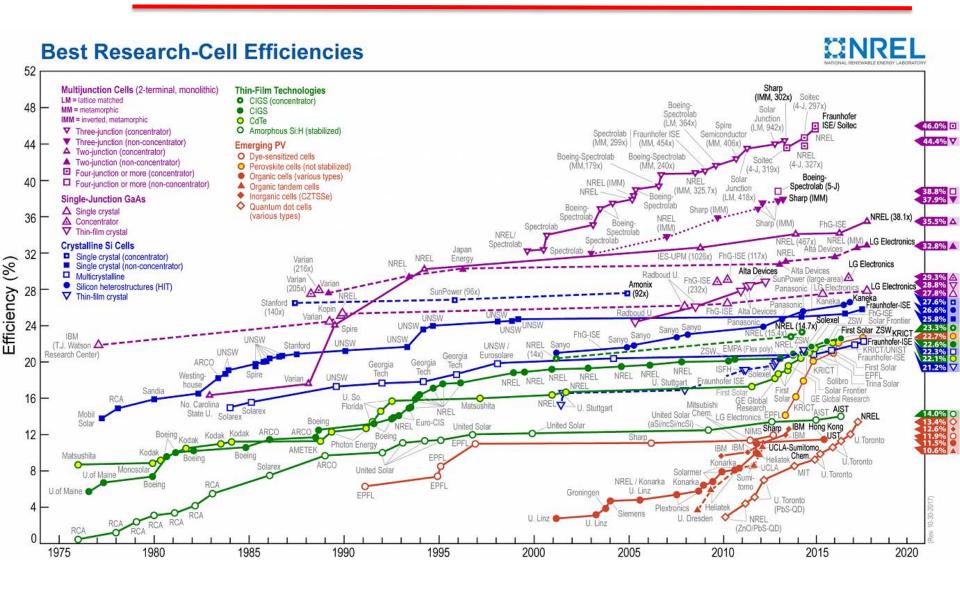
ChE-600

Néstor Guijarro Carratala, Spring 2018



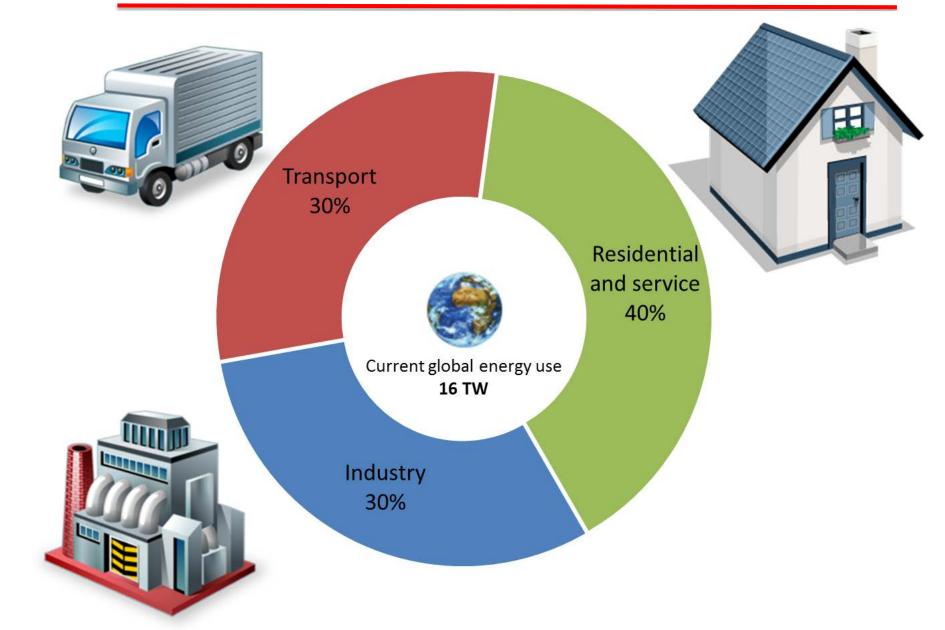


PV performance overview



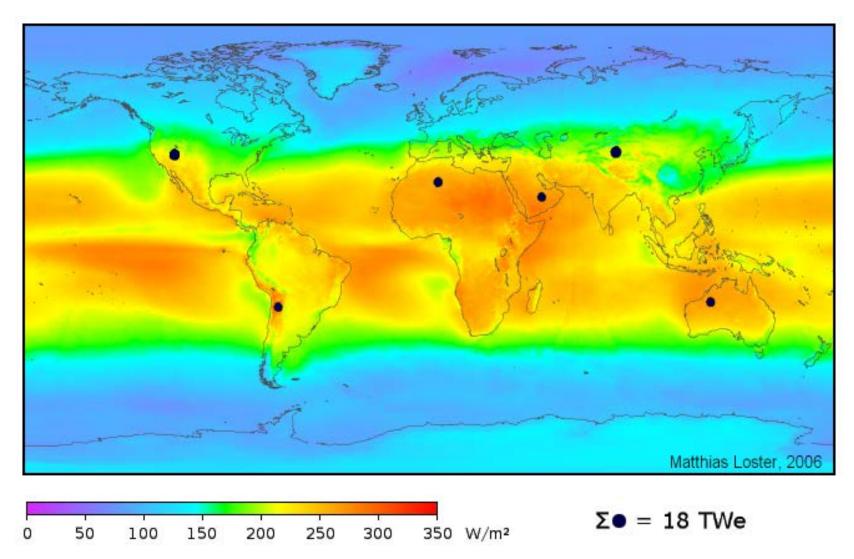


Energy use today and in the future



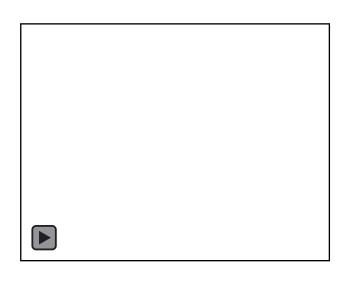


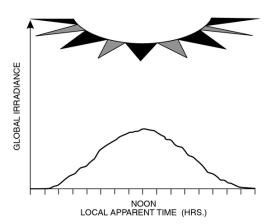
Averaged Solar Irradiance

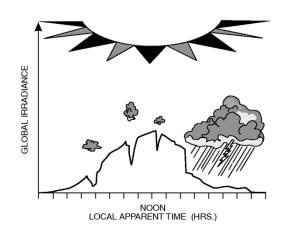




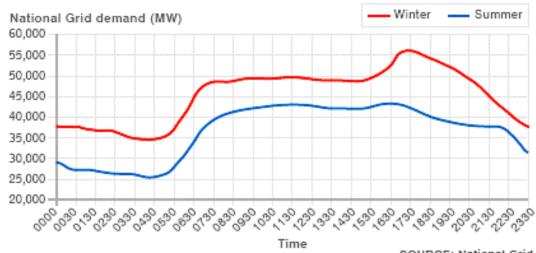
Supply and Demand Disaccord







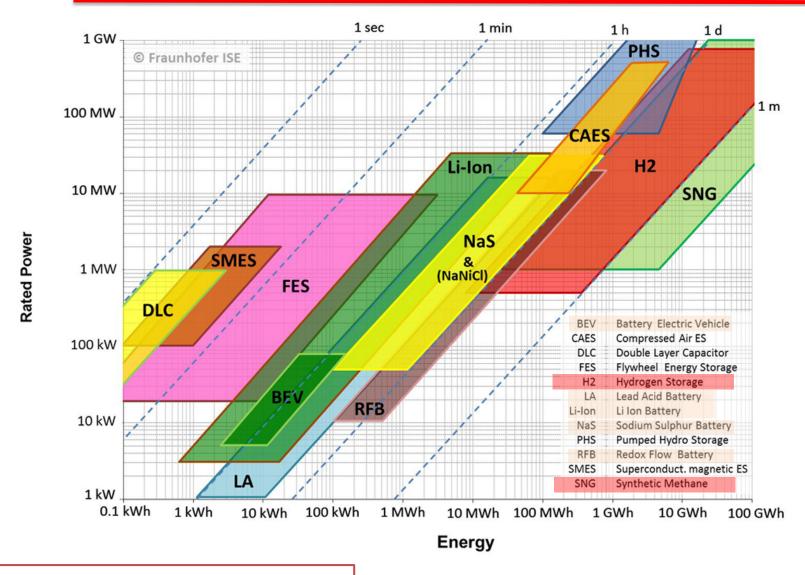
TYPICAL SUMMER AND WINTER DEMANDS



SOURCE: National Grid



Storing Solar Energy for Use on Demand

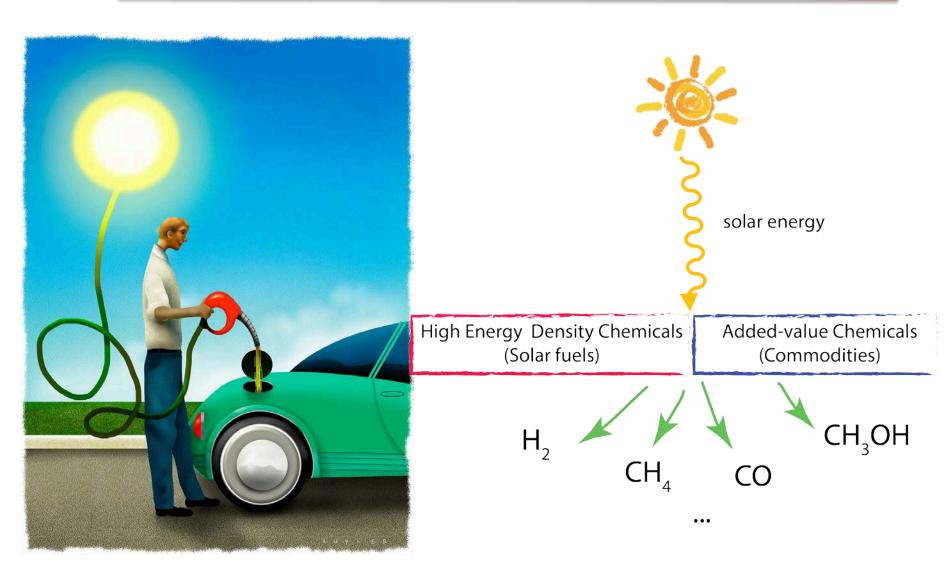


 $Power \times time = Energy$

APPLICATION determines the **STORAGE SYSTEM**



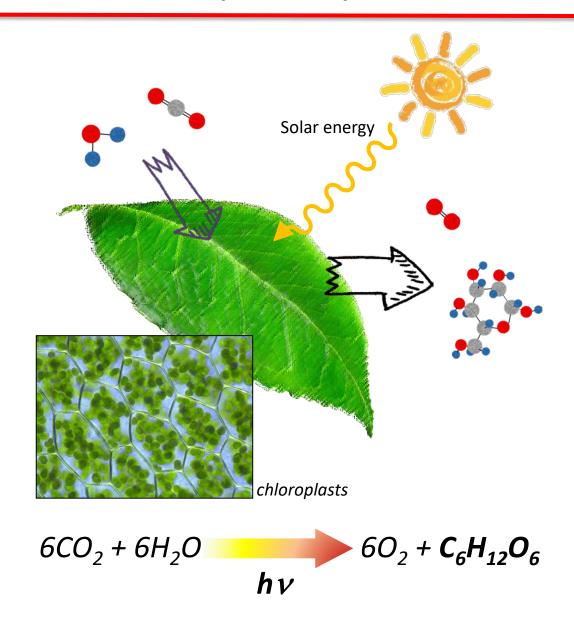
Storing Solar Energy for Use on Demand



Bourzac PNAS 2016, 113, 4545

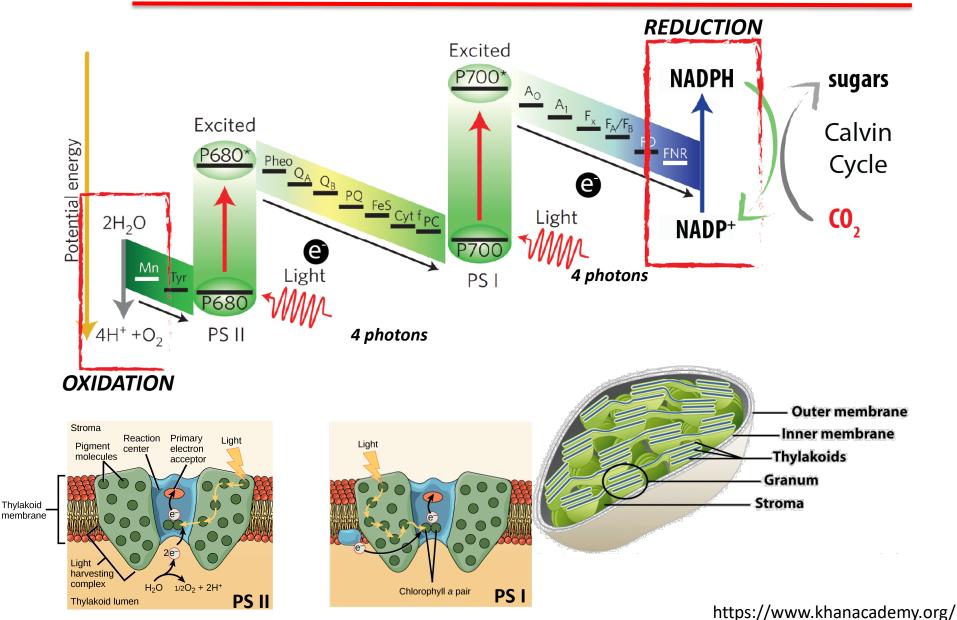


Natural photosynthesis





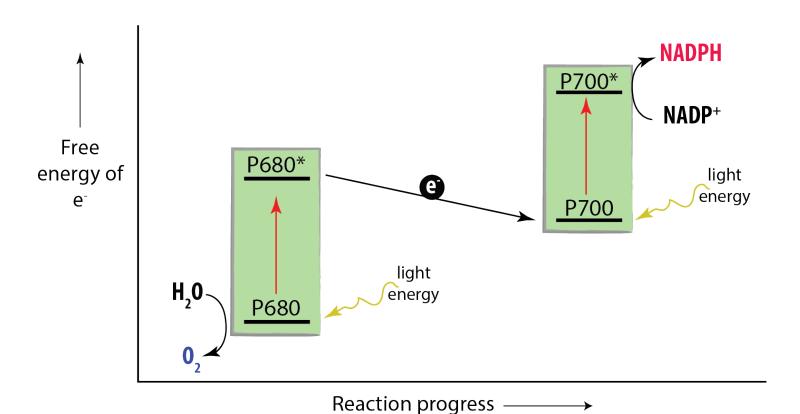
Natural photosynthesis





Natural photosynthesis

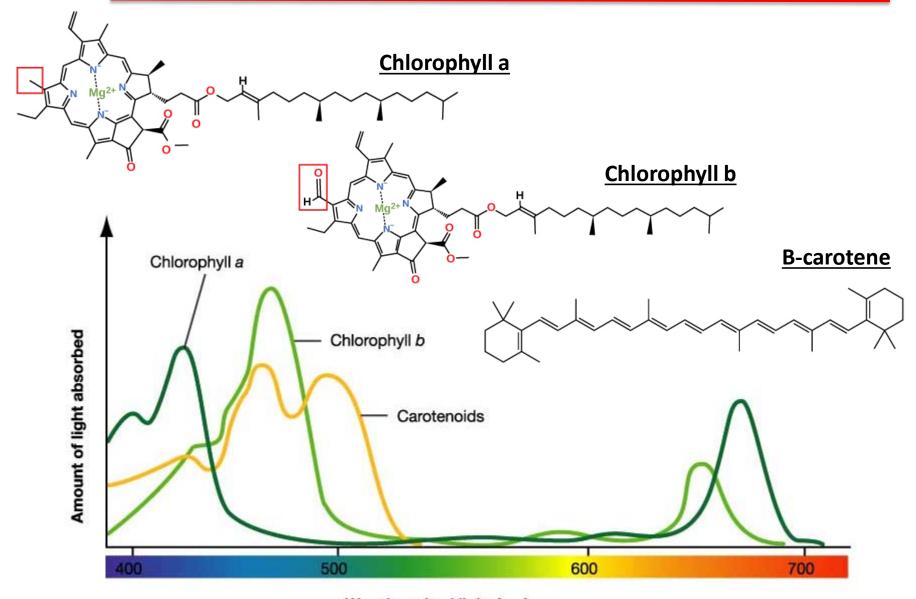
"Z-Scheme"



https://www.khanacademy.org/



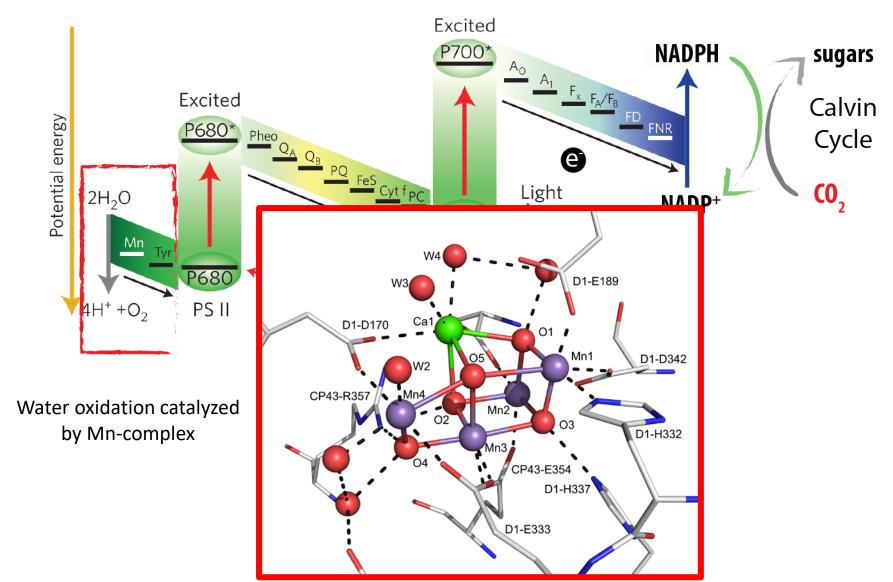
Light harvesting



Wavelength of light (nm)



Catalysis is also a key process





Taking advantage of natural photosynthesis

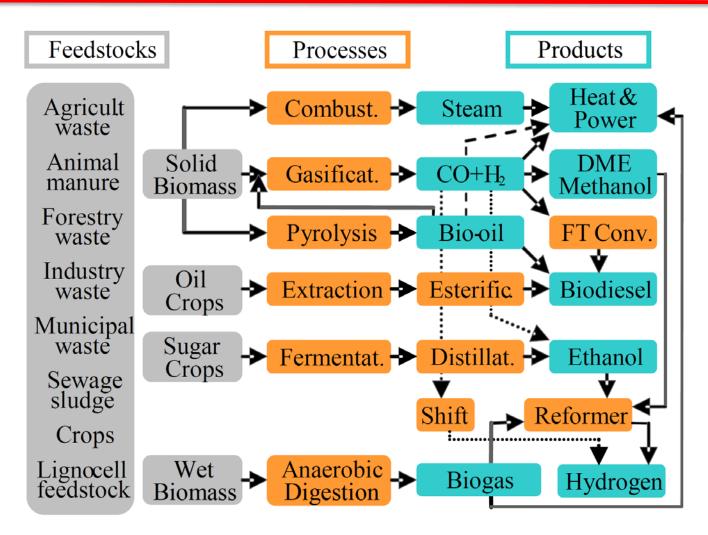
Biomass refers to the material originally produced as a result of photosynthesis that can be eventually harvested to be utilized as a fuel or platform chemical in industry.

Biomass is considered a *renewable* energy source





Biomass use today

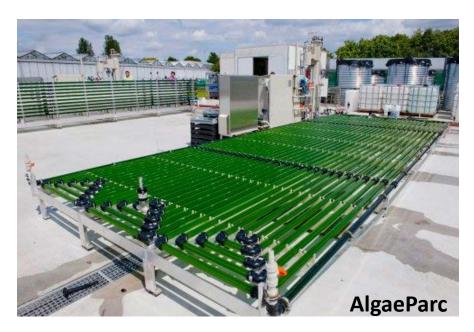


Biomass provides **10** % of global energy use

Biomass Conversion Paths



Biomass use today



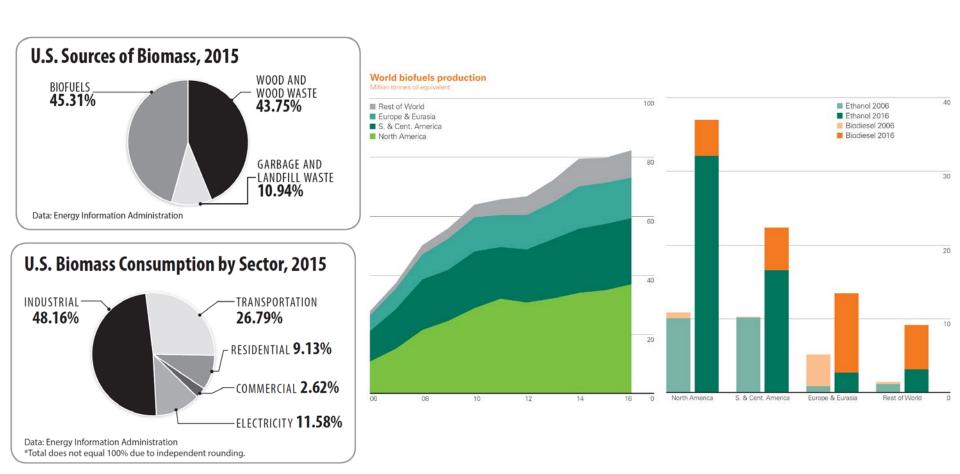
Biofuels from microalgae

- Processing raw biomass (transesterification, pyrolysis...)
- Direct photobiological production of biofuels (with genetically engineered cyanobateria): H₂, butanol, isoprene, etc.





Biomass use today



http://www.bp.com/ http://www.need.org/files/curriculum/infobook/BiomassS.pdf



Could Biomass be our primary energy source?



Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

A review of the ecological and socioeconomic effects of biofuel and energy policy recommendations

Xi Ji*, Xianling Long

Renewable and Sustainable Energy Reviews 61 (2016) 41–52

Energy & Environmental Science

Dynamic Article Links

Cite this: Energy Environ. Sci., 2012, 5, 5531

www.rsc.org/ees

REVIEW

Photosynthesis-to-fuels: from sunlight to hydrogen, isoprene, and botryococcene production

Energy Environ. Sci., **2012**, *5*, 5531

Anastasios Melis*



Available online at www.sciencedirect.com

ScienceDirect



Limitations and prospects of natural photosynthesis for bioenergy production

AWD Larkum

Current Opinion in Biotechnology 2010, 21, 271



Could Biomass be our primary energy source?





- Energy conversion can be as high as η_{solar} = 11% in the early stages of photosynthesis
- Best solar energy conversion (e.g. sugar cane, Napier grass) η_{solar} = 1.6%

Photosynthesis in air

• Land usage. Competition for resources with traditional agriculture for food supply.



Total arable land on Earth $19.8 \times 10^6 \text{ km}^2$ (3.9 % of total world's surface)

Arable land on Earth in Temperate zone $9.50 \times 10^6 \text{ km}^2$ (1.9 % of total world's surface)



Average global irradiation 170 W m⁻²

 $\eta_{solar} = 1.0\%$

Average Global irradiation in Temperate Zones = 350 W m⁻²



Global energy demand 500 EJ/year = 15.85 TW 50% Global energy demand 500 EJ/year = 7.61 TW

% of the world's surface needed = 4.4% % of the world's surface needed = 1.05%

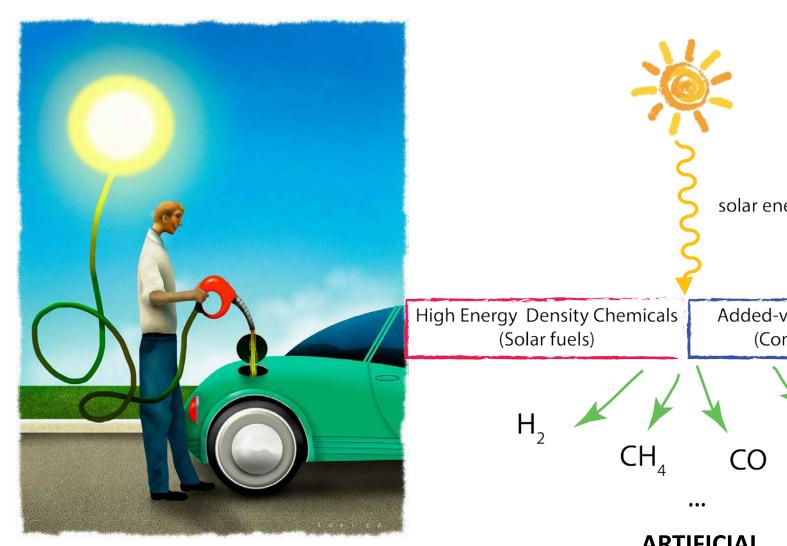


Brief outlook on biofuels

- η_{solar} needs to be drastically improved
 - Ultimate max conversion: 8% in plants like sugar cane
- Microalgae systems have slightly higher η_{solar} = 1 4%
 - Can be used on non-arable land
 - Higher η_{solar} needed to make economical biofuels
 - Efficiency is not a selection pressure
- "The 1–2% efficiency of plants, algae and cyanobacteria <u>cannot</u> <u>compete</u> with solar photovoltaic panels or solar thermal collectors. Nevertheless natural photosynthesis will become increasingly used for the production of <u>biofuels and organic products</u> in a world where these will increasingly come into short supply. <u>It seems unlikely that algae</u> <u>and cyanobacteria will be used as a source of bioenergy</u>."
- "Even though integrated microalgae production systems have some clear advantages and present a promising alternative to highly controversial first generation biofuel systems, the associated hype has often exceeded the boundaries of reality."



Storing Solar Energy for Use on Demand



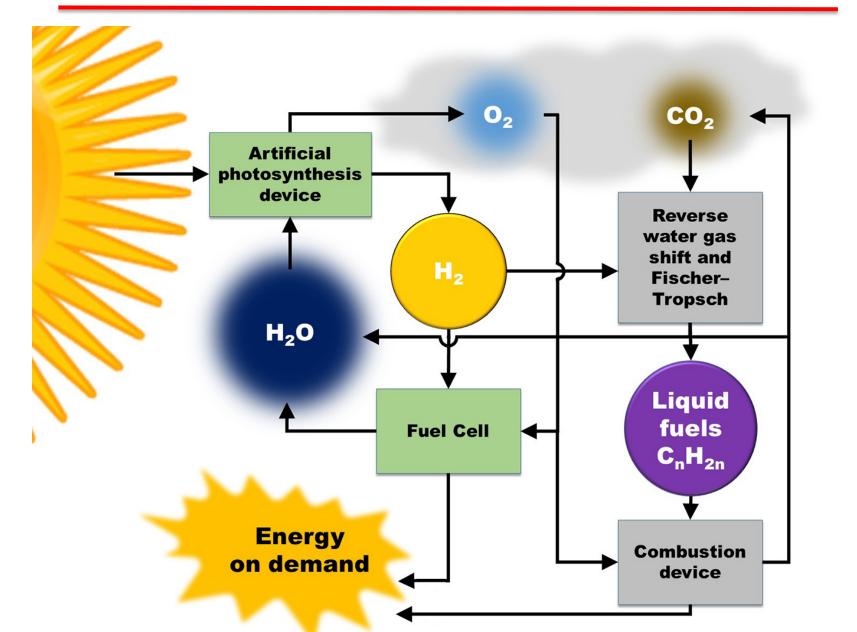
Bourzac PNAS 2016, 113, 4545

solar energy Added-value Chemicals (Commodities) **ARTIFICIAL**

PHOTOSYNTHESIS

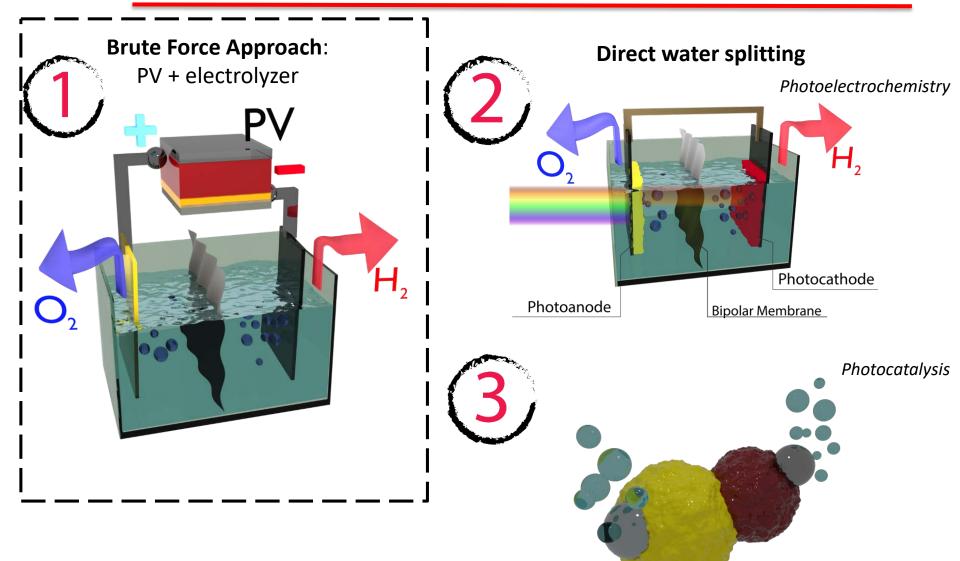


Artificial photosynthesis as storage route





Artificial photosynthesis as storage route





Artificial photosynthesis as storage route



Electrolyzer

- First demonstrated in early 1800s (Volta and Grotthus). Earlier demonstration of electrolysis of water by Deiman and Trootswijk using an electrostatic machine by discharge on Au electrodes.
- Abundant starting material (H₂O)
- Clean process to split water into H₂ and O₂

COST 5.20 \$ Kg H₂

Mostly due to cost of electricity

Today's Hydrogen (> 95%) is produced at large scale by **steam reforming of natural gas**

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

Cost approx. 1.50-2.50\$ Kg H₂

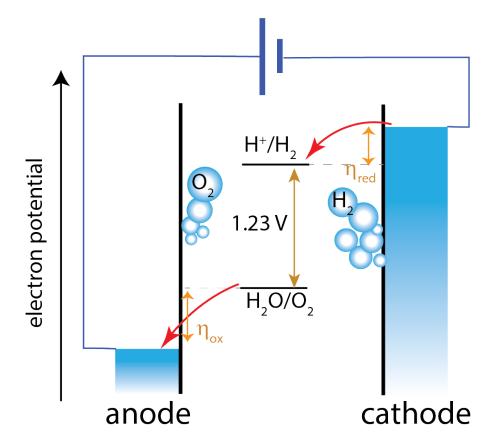


$$2H_2O(l) \to 2H_2(g) + O_2(g)$$

Anode (oxidation):

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- E_{ox}^0 = -1.23 V$$
 Cathode (reduction):

$$2H^{+}(aq) + 2e^{-} \rightarrow H_{2}(g)$$
 $E_{ox}^{0} = 0.00V$



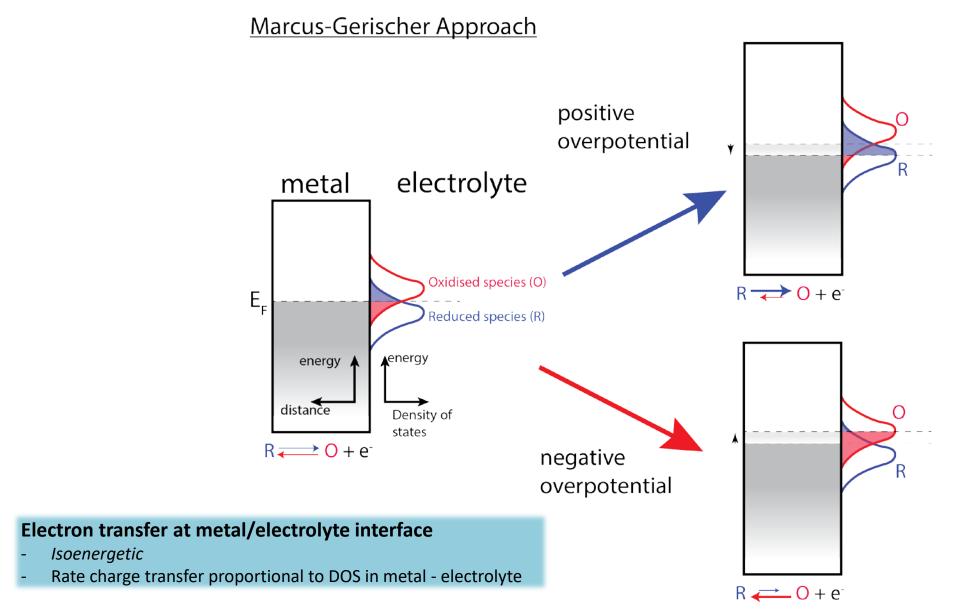
Thermodynamics

Minimum required 1.23 V for water splitting

Total potential required (> 1.23 V)

$$V = E_{red} - E_{ox} + \eta_{red} + \eta_{ox}$$







$$2H_2O(l) \to 2H_2(g) + O_2(g)$$

Anode (oxidation):

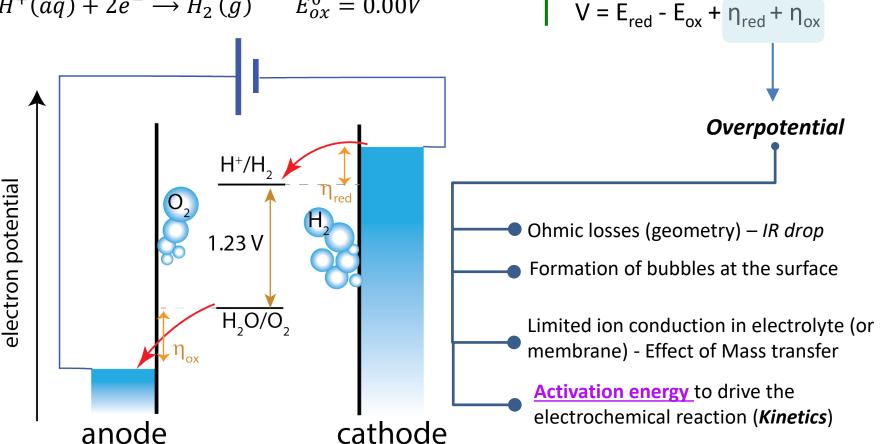
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Thermodynamics

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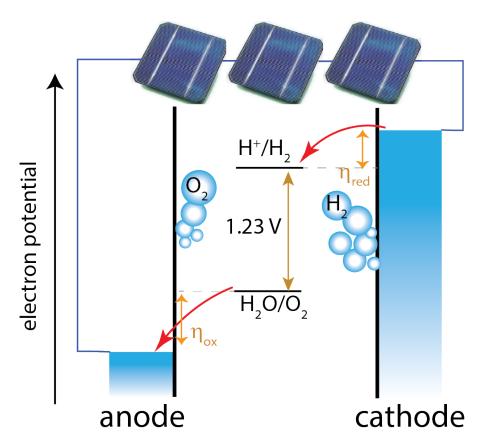
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 $E_{ox}^{0} = 0.00V$



Potentially reduce cost of H₂ from electrolysis

- Reducing voltage demand (reduce overpotentials of electrodes)
- Coupling PV cells to provide the energy input
- Limited by price, availability of traditional photovoltaics
- Voltage output of Si PV strongly dependent on irradiation intensity
- Up to 50% energy loss
- Current cost under ideal conditions: ~\$10/kg H₂ (Si PV costs ~\$200-300/m²)

COST 10 \$ Kg H₂

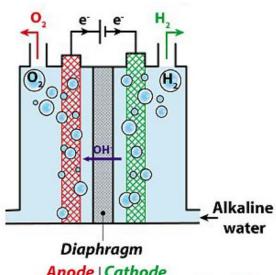
Hinkley et al. **2016** CSIRO Energy Sivula J. Phys. Chem. Lett. **2015**, **6**, **975**



Alkaline or PEM electrolysis?

Alkaline Electrolyzer

40-90 °C



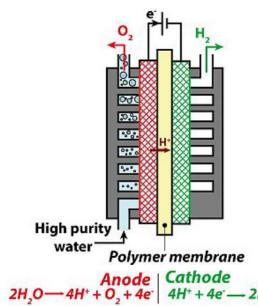
Anode | Cathode 4 OH - 0, + 2H, 0 + 4e 4H, 0 + 4e - 2H, + 40H

Advantages

- Well-established technology
- Long-term Stability
- Relative Low cost
- Stack in the MW range

PEM Electrolyzer

20-100 °C



 $2H_1O \longrightarrow 4H^+ + O_1 + 4e^- \longrightarrow 2H_1$

High current densities High voltage efficiency Good partial load range

Rapid system response High gas purity

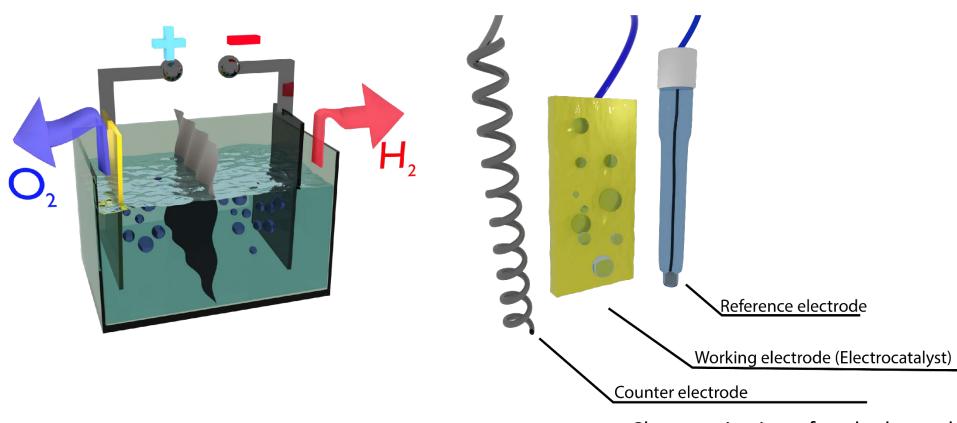
Disadvantages

Low current densities Crossover gases (degree of purity) Low operational pressures Corrosive liquid electrolyte

High cost of components Acidic corrosive environment Possible low durability Commercialization with stacks (below MW range)



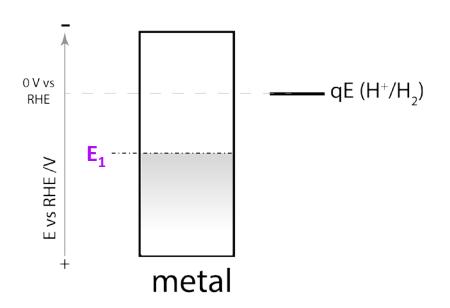
Catalysts – Basic metrics

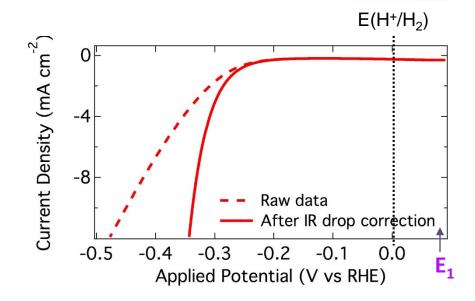


Characterization of each electrode in a "3-electrode configuration"



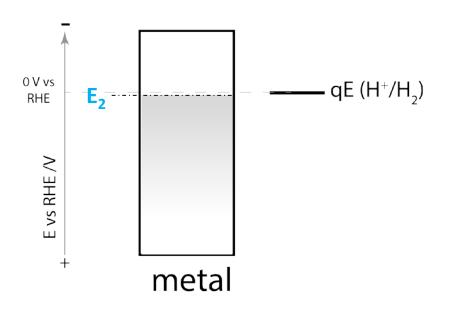
Catalysts – Basic metrics

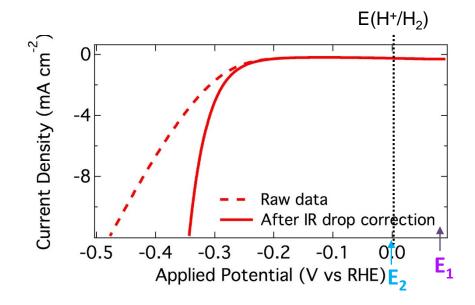






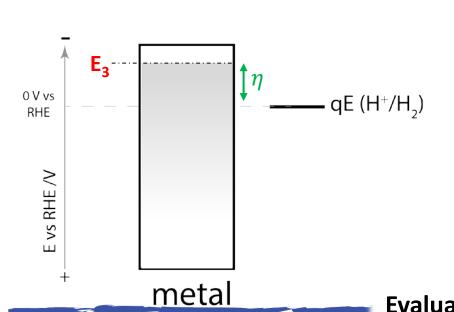
Catalysts – Basic metrics

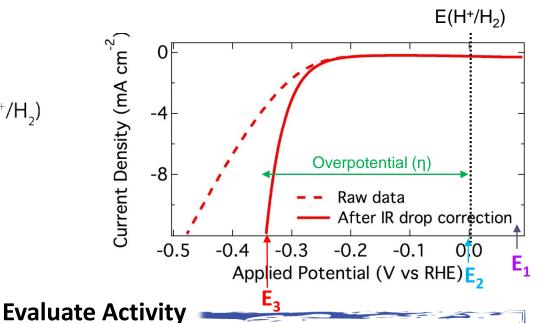






Basic metrics and Figures of Merit for electrocatalyst activity





Overpotential needed to reach a given current density η_{10mA/cm^2}

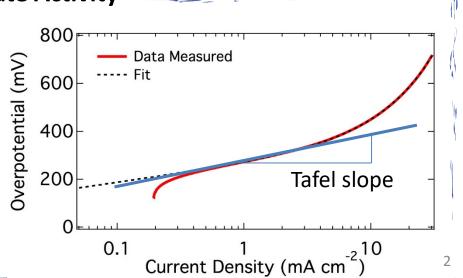
7 Tafel model:

$$\eta = A \cdot \ln \left(\frac{j}{j_0} \right) + R \cdot j$$

A: Tafel slope (mV decade-1)

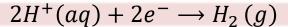
 j_0 : exchange current density (mA cm⁻²)

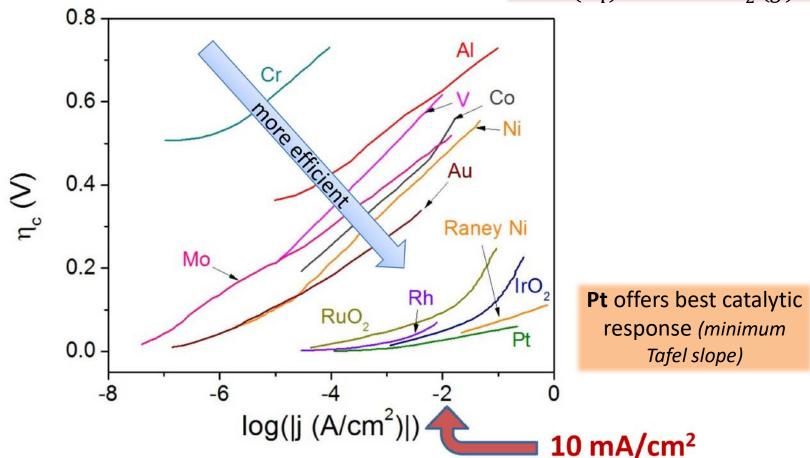
R: resistance (Ω)





HER catalysts current state-of-the-art





Tafel slope contains information on the *mechanism of* water reduction (the **rate determining step –RDS-**)



Basic metrics and Figures of Merit for electrocatalyst activity

Volmer-Tafel mechanism

$2H^+(aq) + 2e^- \rightarrow H_2(g)$ Volmer-Heyrovsky mechanism

Volmer

$$2 x \{H^+(aq) + e^- \longrightarrow H^*(ad)\}$$

Volmer

$$H^+(aq) + e^- \rightarrow H^*(ad)$$

Tafel

$$2H^*(ads) \rightarrow H_2(g)$$

Heyrovsky

$$H^+(aq) + H^*(ads) + e^- \rightarrow H_2(g)$$

Tafel slope: ~ 118 mV/decade (RDS Volmer)

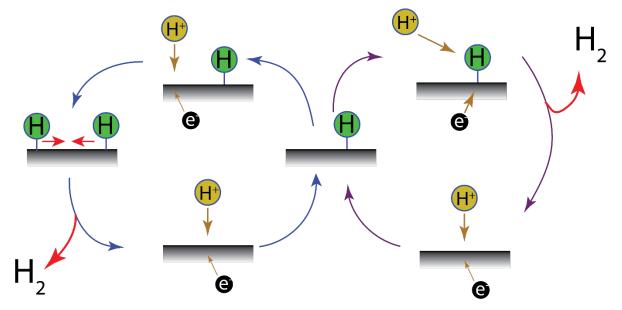
~ 29 mV/decade (RDS *Tafel*)

~ 44 mV/decade (RDS Heyrovsky)

From: Gimenez *et al.* Photoelectrochemical Solar Fuel Production. *Chapter 3*. (Springer, 2016)

chemical desorption

electrochemical desorption

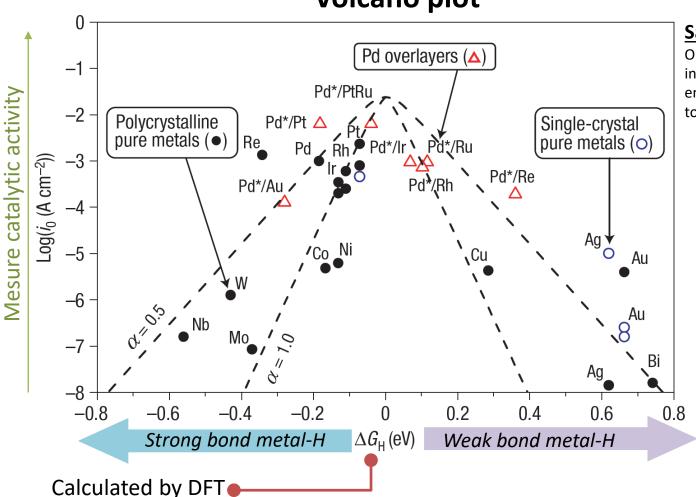




Why is the Pt so special?

 $2H^+(aq) + 2e^- \rightarrow H_2(g)$

Volcano plot



Sabatier Principle

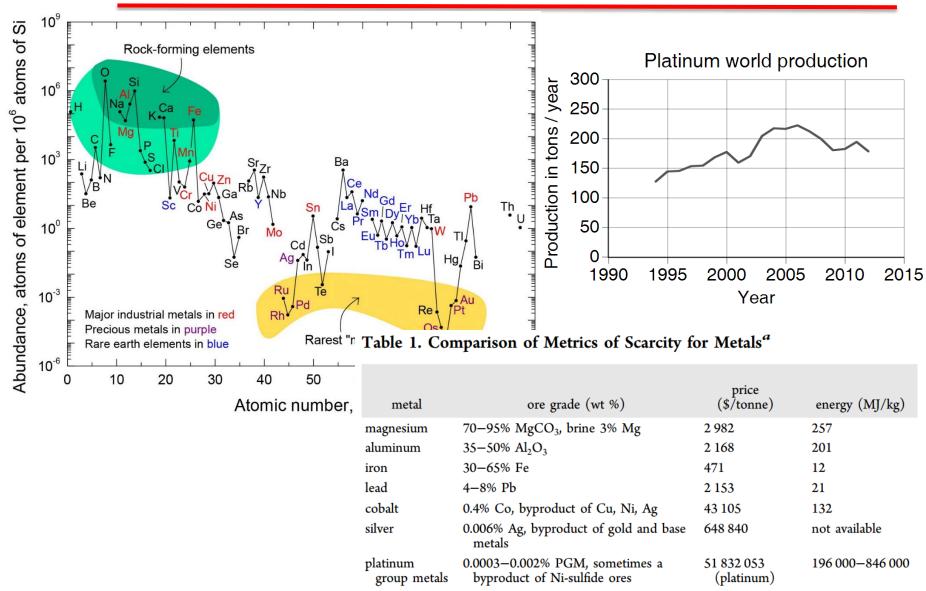
Optimum catalyst binds reaction intermediate with "moderate" binding energies (ΔG_{ads}) – not too weak not too strong.

Best HER catalyst should exhibit

 $\Delta G_H \approx 0$

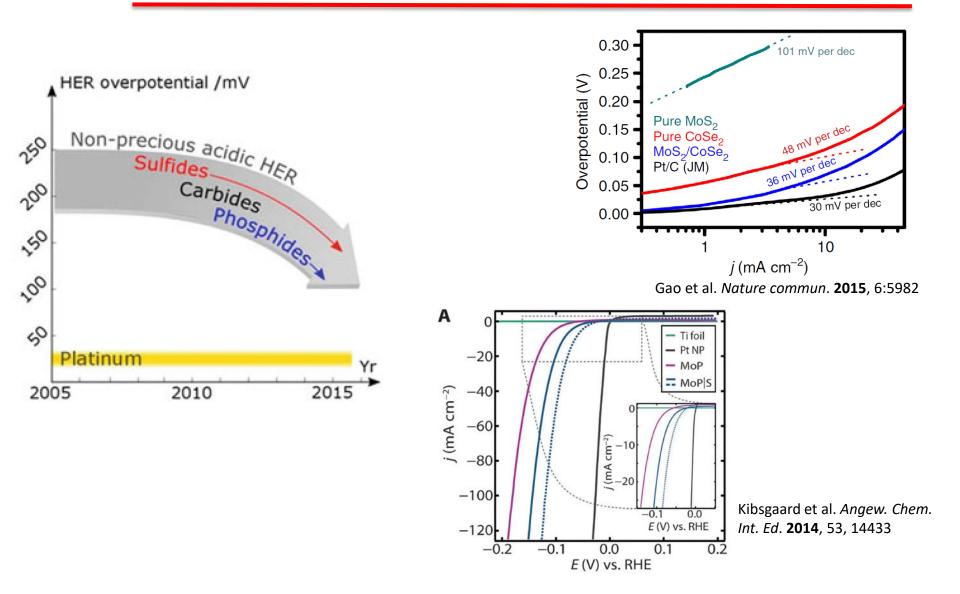


Platinum Availability for Future Technologies





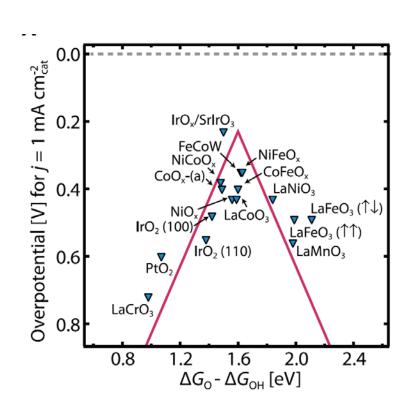
New generation of **HER** catalysts

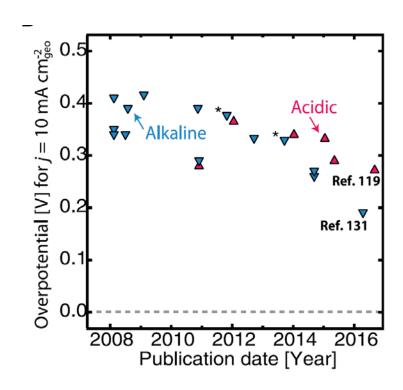




OER catalysis state-of-the art and prospects

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$

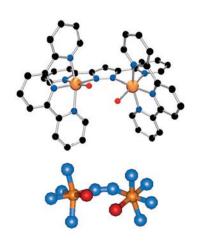




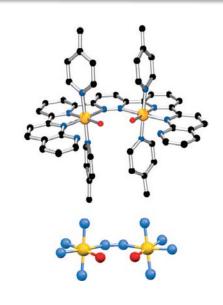
Good performance of "cheap" multinary metal oxides as electrocatalyst for OER



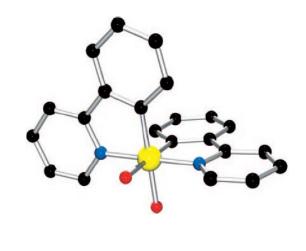
Other Molecular Water Oxidation Catalysts



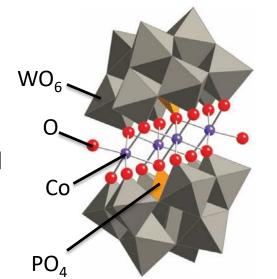
Llobet et al. [ruthenium]



Thummel et al. [ruthenium]



Bernhard et al. [*iridium*]



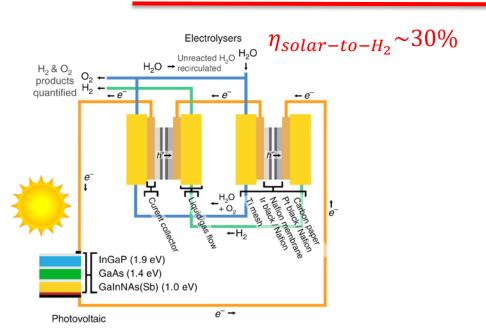
Hill et al. [cobalt]

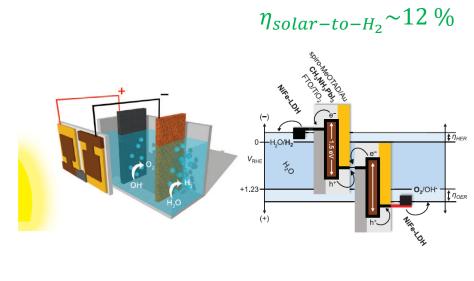
Yin et al. *Science* **2010**, *328*, 342. Tinker et al. . *J. Mater. Chem.* **2009**, *19*, 3328.

Sala et al. *Angew. Chem. Int. Ed.* **2009**, *48*, 2842.



PV + Electrolyzer technology (examples)





Photovoltaic cell

High efficiency (working under 42 suns)

Expensive PV cell

 $\eta_{solar-to-elec.}{\sim}39~\%$

Electrolyzer

Expensive electrocatalysts based on Ir and Pt

From: Jia et al., Nature commun., 2016, 7:13237

Photovoltaic cell

Cheap processing PV cell

$$\eta_{solar-to-elec.} \sim 15-20 \%$$

Electrolyzer

Low-cost electrocatalysts based on NiFe

From: Luo et al., Science, 2014, 345, 1593



Metrics for defining efficiency of conversion

Faradaic efficiency:

(for the electrochemical production of a certain product)

$$\eta_F = \frac{\textit{Current expected based on desired production rate}}{\textit{Current measured}}$$

Energy conversion efficiency (Solar-to-Hydrogen (STH) Conversion Efficiency)

Input: Solar irradiation AM1.5G (1000W/m²)

Output: H_2 $\Delta G^\circ = +238 \text{ kJ/mol} = +1.23 \text{ eV/electron}$ (thermodynamic minimum to split water)

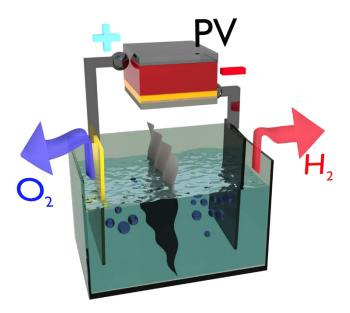
$$\eta_{STH} = \frac{\textit{Power output}}{\textit{Power input}} = \frac{(\textit{hydrogen production rate}) \times (\textit{hydrogen energy density})}{\textit{Solar flux integrated over illuminated area}} = \frac{(\textit{hydrogen production rate}) \times (\textit{hydrogen energy density})}{\textit{Solar flux integrated over illuminated area}} = \frac{(\textit{hydrogen production rate}) \times (\textit{hydrogen energy density})}{\textit{Solar flux integrated over illuminated area}} = \frac{(\textit{hydrogen production rate}) \times (\textit{hydrogen energy density})}{\textit{Solar flux integrated over illuminated area}} = \frac{(\textit{hydrogen production rate}) \times (\textit{hydrogen energy density})}{\textit{Solar flux integrated over illuminated area}} = \frac{(\textit{hydrogen production rate}) \times (\textit{hydrogen energy density})}{\textit{Solar flux integrated over illuminated area}} = \frac{(\textit{hydrogen production rate}) \times (\textit{hydrogen energy density})}{\textit{Solar flux integrated over illuminated area}} = \frac{(\textit{hydrogen production rate}) \times (\textit{hydrogen energy density})}{\textit{Solar flux integrated over illuminated area}} = \frac{(\textit{hydrogen production rate}) \times (\textit{hydrogen energy density})}{\textit{Solar flux integrated over illuminated area}} = \frac{(\textit{hydrogen production rate}) \times (\textit{hydrogen energy density})}{\textit{Solar flux integrated over illuminated area}} = \frac{(\textit{hydrogen production rate}) \times (\textit{hydrogen energy density})}{\textit{Solar flux integrated over illuminated area}} = \frac{(\textit{hydrogen production rate}) \times (\textit{hydrogen energy density})}{\textit{Solar flux integrated over illuminated area}} = \frac{(\textit{hydrogen production rate}) \times (\textit{hydrogen energy density})}{\textit{Solar flux integrated over illuminated area}} = \frac{(\textit{hydrogen production rate}) \times (\textit{hydrogen energy density})}{\textit{Solar flux integrated over illuminated area}} = \frac{(\textit{hydrogen production rate}) \times (\textit{hydrogen energy density})}{\textit{Solar flux integrated over illuminated area}} = \frac{(\textit{hydrogen production rate}) \times (\textit{hydrogen energy density})}{\textit{Solar flux integrated over illuminated area}} = \frac{(\textit{hydrogen production rate}) \times (\textit{hydrogen energy density})}{\textit{Solar flux integrated over illuminated area}} = \frac{(\textit{hydrogen hydrogen production rate)} \times (\textit{hydrogen hydr$$

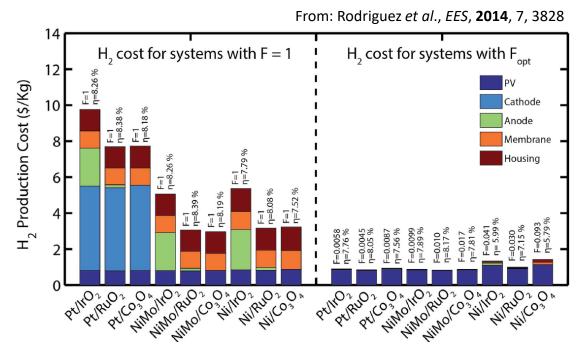
$$\eta_{STH} = \frac{J_{ph}(mA \ cm^{-2}) \times \eta_F \times 1.23 \ (eV)}{100 \ (mW \ cm^{-2})}$$



PV + Electrolyzer technology (examples)

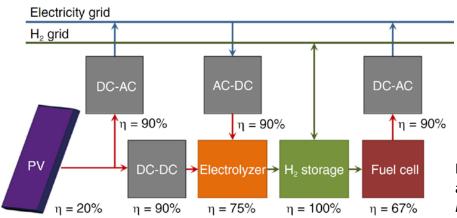
PV + electrolyzer





2 MODULE SYSTEM

Complexity increases price and potential losses

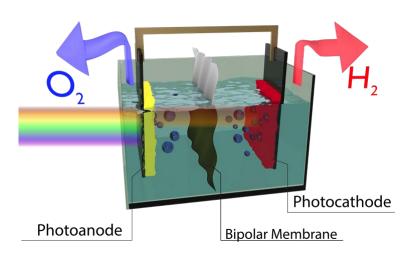


From: Ronge et al., Oil & Gas Science and Technology -Rev. IFP Energies Nouvelles, 2015, 70, 863



Emerging technology for solar water splitting

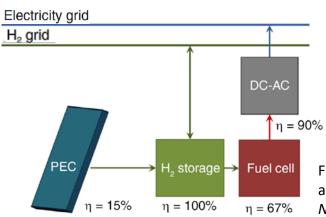
Direct water splitting using photoelectrochemistry



1 MODULE SYSTEM

Simpler device configuration

- Avoid encapsulation or metal evaporation of PV cells.
- Materials in direct contact with electrolyte
- Single material act as light-absorber and electrocatalyst.

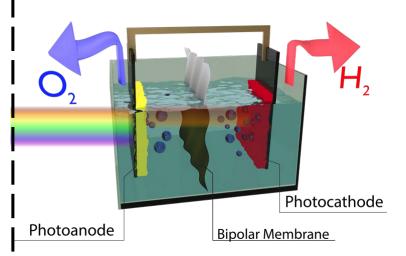


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Emerging technology for solar water splitting

<u>Direct water splitting using</u> <u>photoelectrochemistry</u>

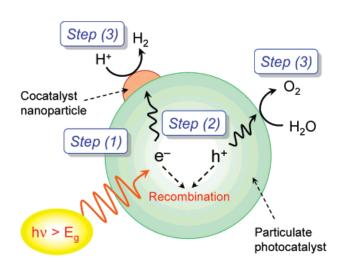


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Nanoparticle/molecules dispersed in electrolyte Simpler design

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- Drawback difficult gas separation



Photoelectrochemical water splitting: First demonstration

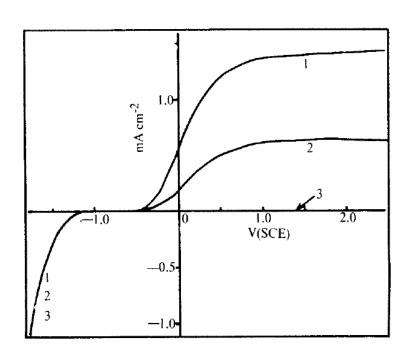
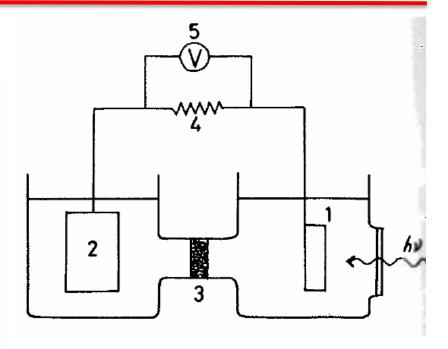
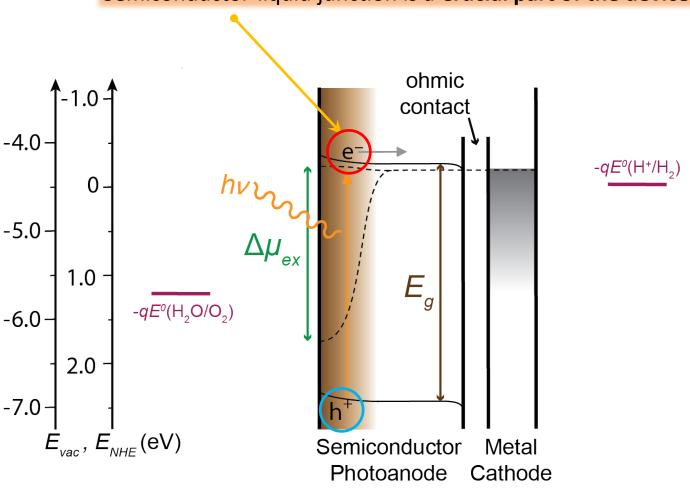


Fig. 1 Current-voltage curves for TiO_2 n-type semiconductor. A single crystal wafer of n-type TiO_2 (rutile) was used after treatment at 700° C at 10^{-4} $\sim 10^{-5}$ torr for roughly 4 h to increase the conductivity of the crystal. This wafer was approximately 1.5 mm thick and the exposed (001) surface area was approximately 1.0 cm². Indium was evaporated on to one side of the surface to ensure ohmic contact and a copper lead wire was connected on the indium layer with silver paste. All other surfaces were sealed by epoxy resin.

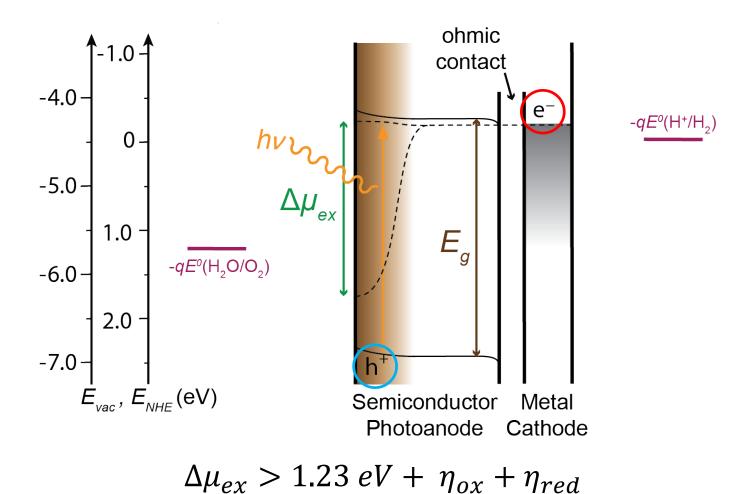


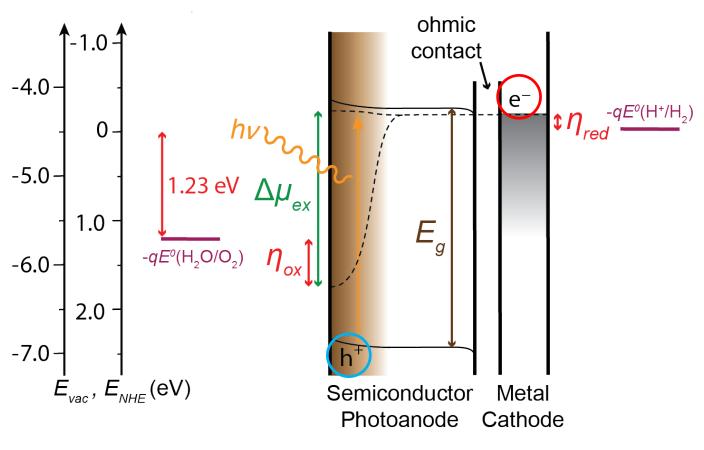
- N-type photoanode: TiO₂ (rutile structure)
- 3 electrode potentiostatic measurement of current in electronic circuit

Semiconductor-liquid junction is a Crucial part of the device



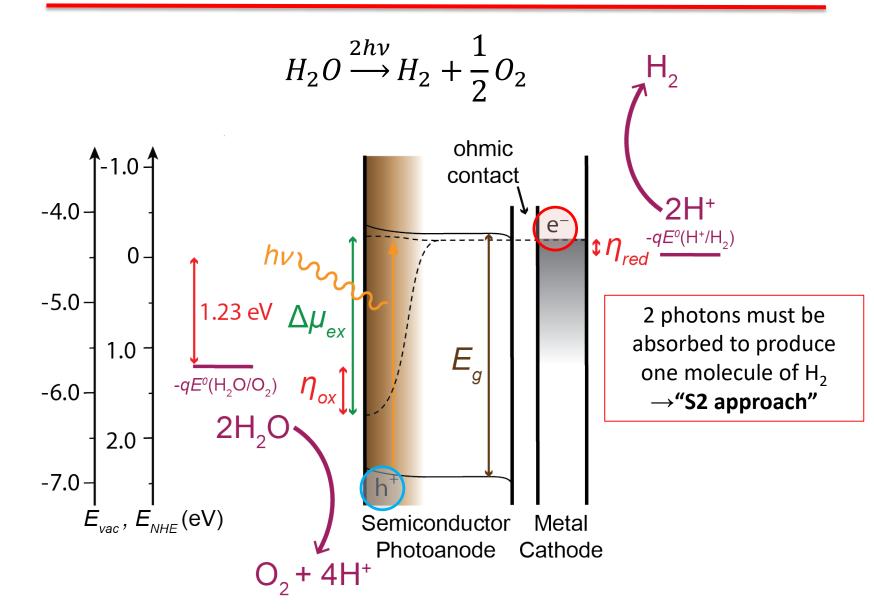
$$\Delta \mu_{ex} > 1.23 \ eV + \eta_{ox} + \eta_{red}$$





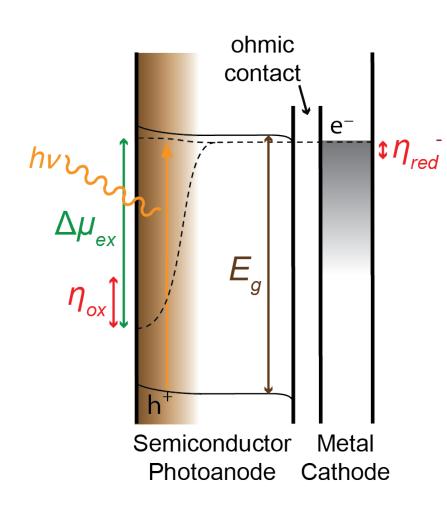
 $\Delta \mu_{ex} > 1.23 \ eV + \eta_{ox} + \eta_{red}$







Limitations of the S2 approach



Under 1 sun illumination: $\Delta\mu_{ex} \approx 0.75 E_a$.

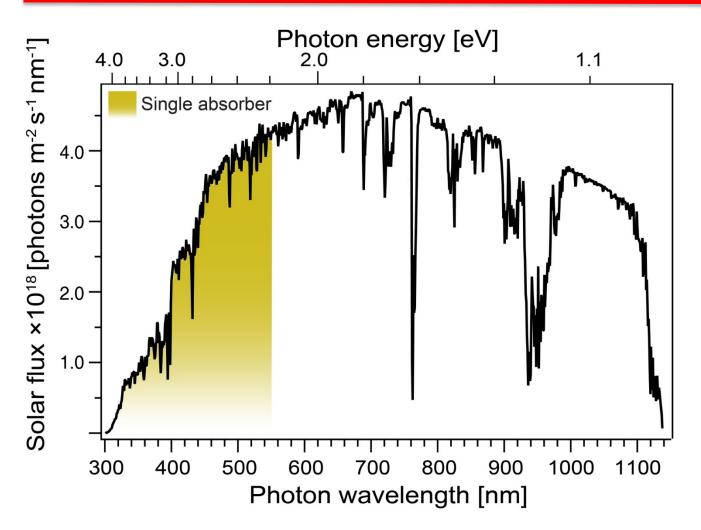
 η_{ox} is large (0.2 – 0.4 eV) for ca. 10 mA cm⁻²

 U_{loss} can be up to 1.0 eV per photon

Maximum Solar to hydrogen conversion efficiency (STH) is 12.7 % (with $E_g = 2.23 \text{ eV}$)



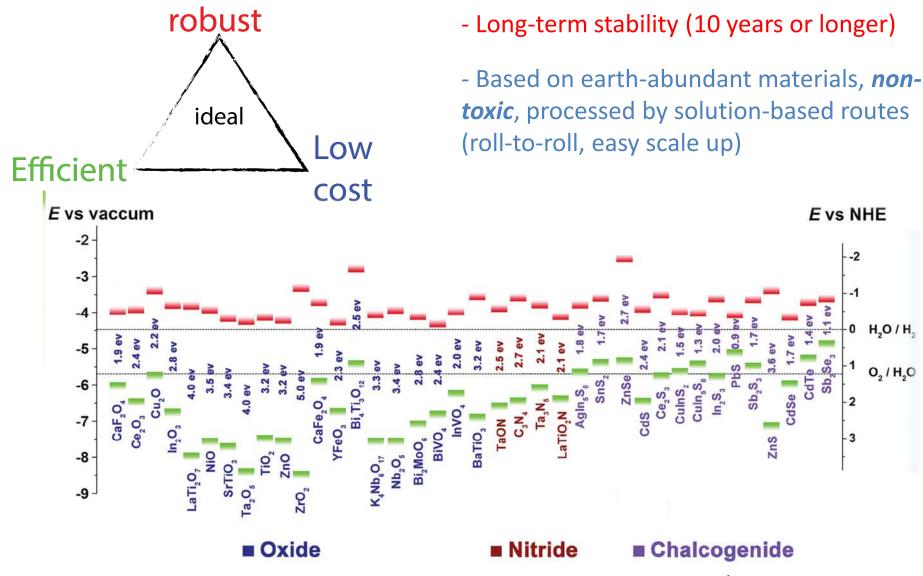
Limitations of the S2 approach (2)



A **single absorber** performing overall water splitting harvests an small portion of the solar spectrum Typically, due to large overpotentials and inefficient charge separation within the semiconductor only materials with large band gaps (> 3 eV) are able to carry out unassisted overall water splitting.



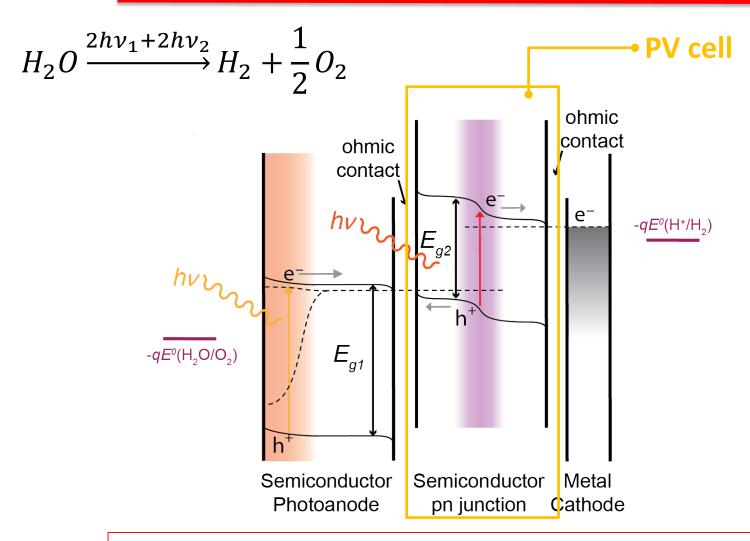
Ideal photoelectrode requirements



Lu et al. **2016**, 28, 1917-1933



Tandem cell Approach (1): PV Bias- PEC

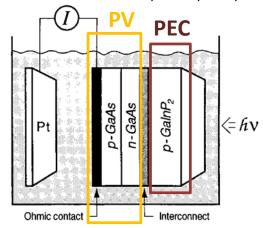


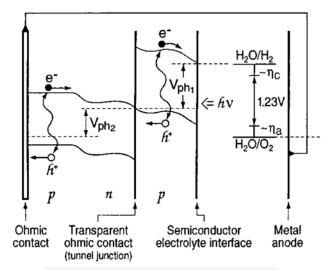
4 photons must be absorbed to produce one molecule of H_2 \rightarrow "D4 approach"



Tandem cell Approach (1): PV Bias- PEC

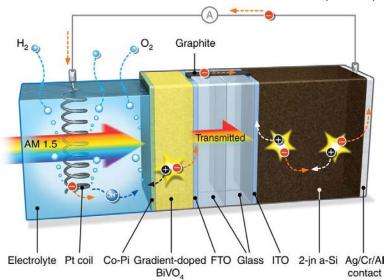
Khaselev et al. Science, 1998, 280, 425

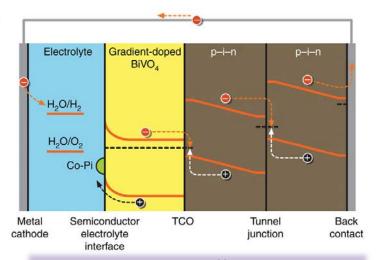




Solar-to-hydrogen efficiency = 12.4 %

Abdi et al. Nature Commun, 2013, 4, 2195

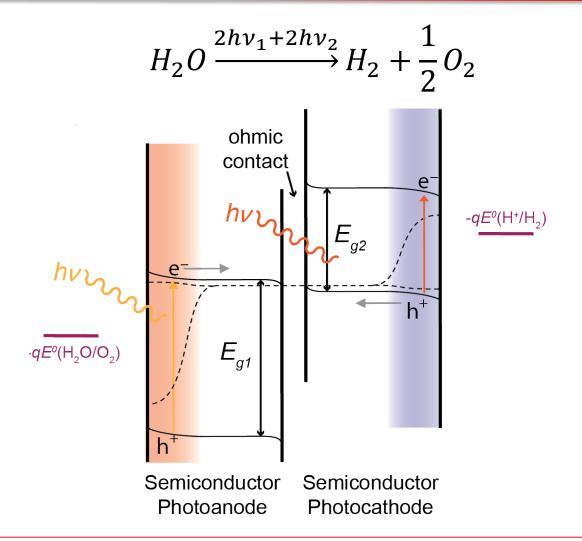




Solar-to-hydrogen efficiency = 4.9 %



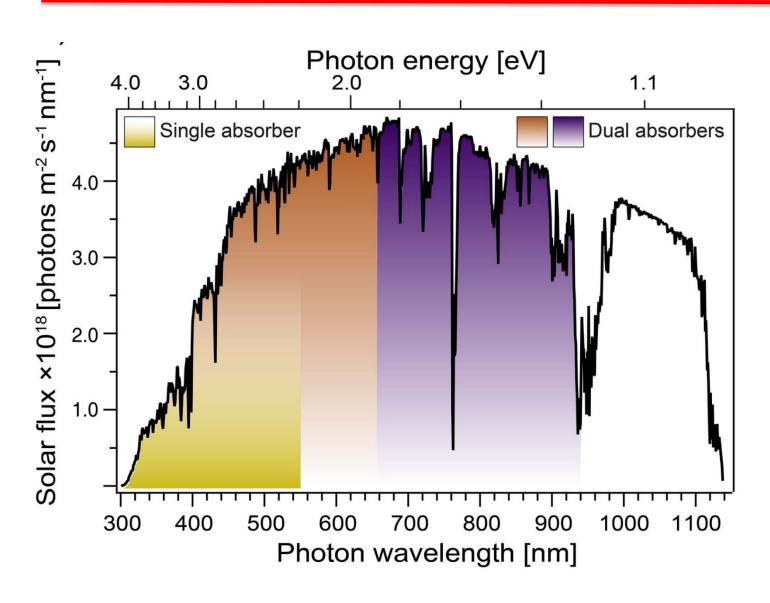
Tandem cell approach (2) – Dual PEC absorber



4 photons must be absorbed to produce one molecule of H_2 \rightarrow "D4 approach"



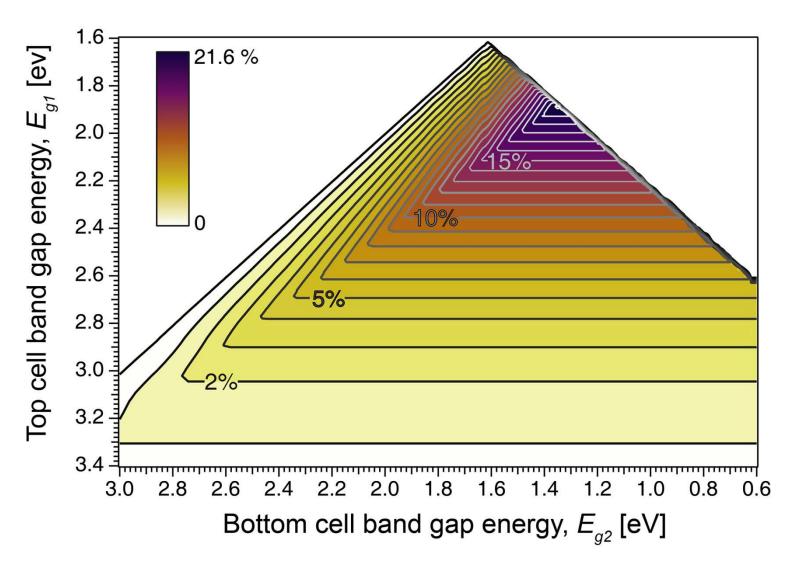
Tandem cell approach (2) – Dual PEC absorber





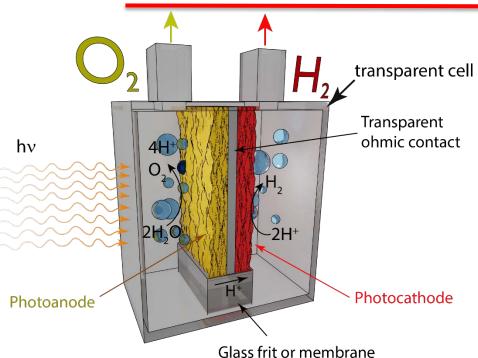
Tandem cell approach (2) – Dual PEC absorber

Using assumption of U_{loss} of 1.0 eV per photon





Techno-economical considerations



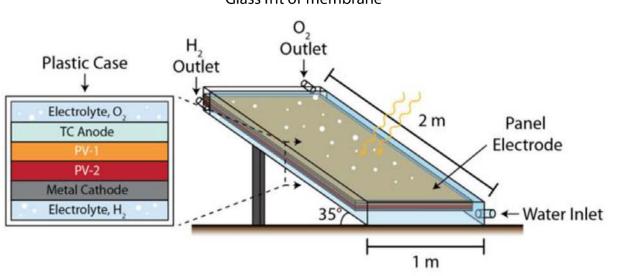
Net production (Kg H ₂ per day, yearly average)	1000
PEC cell efficiency (STH %)	10
Cost of PEC cell (per m²)	153 USD\$
PEC cell lifetime (years)	10
Cost of H ₂ produced	10.40 \$/Kg

Pinaud *et al. EES* **2013**, *6*, 1983



Lowering cost to close to \$1-2 Kg⁻¹

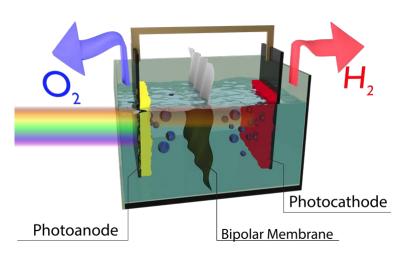
- Higher stability (20 years)
- Higher efficiency
- Solution processing





Emerging technology for solar water splitting

<u>Direct water splitting using</u> photoelectrochemistry

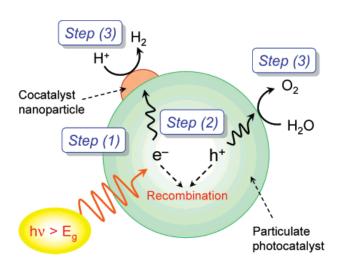


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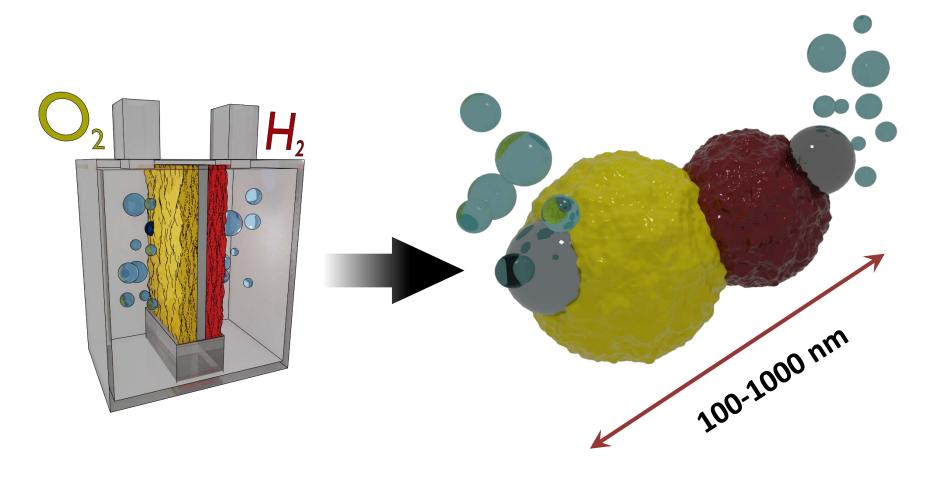


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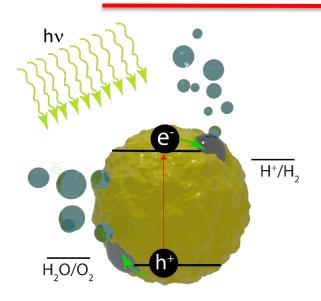


Photocatalysis approach





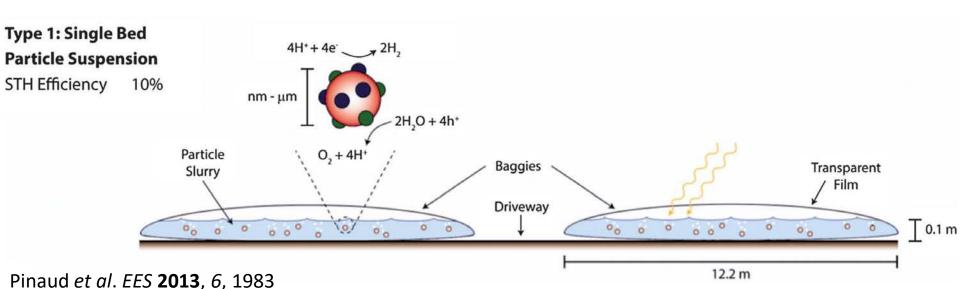
Photocatalyst – Single Absorber



Record STH:

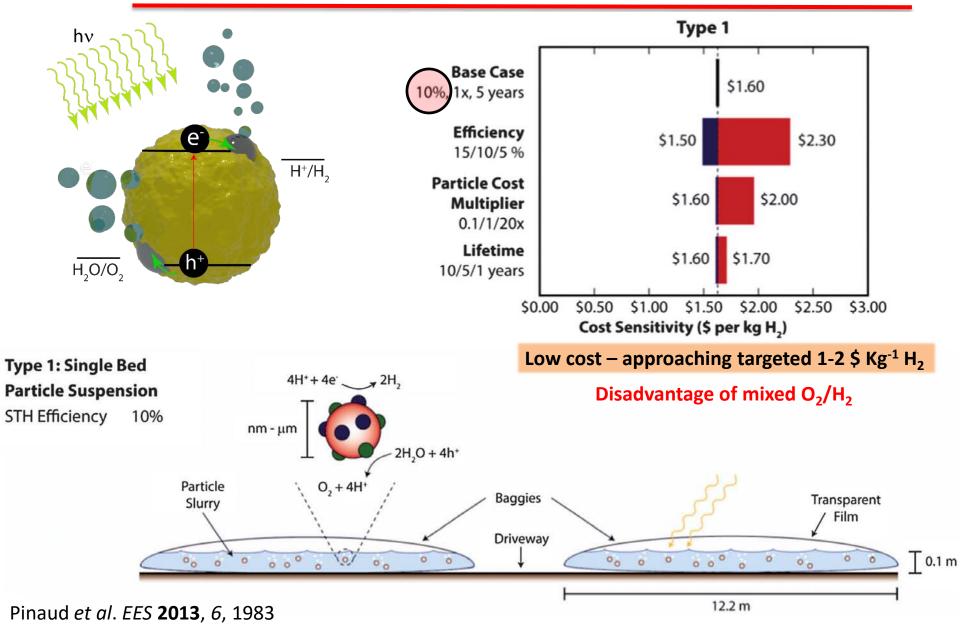
CoO (<515 nm) STH=5% GaN:Mg/InGaN:Mg (Rh/ Cr_2O_3) (<475 nm) STH=1.8 %

Chen et al. Nature Materials Reviews 2017, 2, 17050



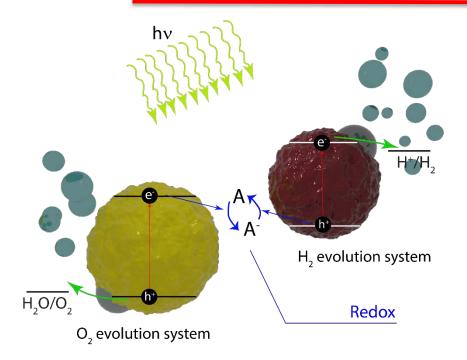


Photocatalyst – Single Absorber





Photocatalyst – Dual absorber



Record STH:

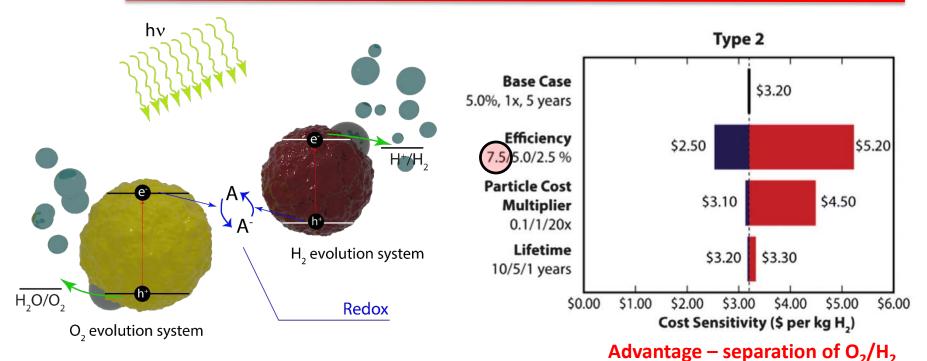
Ru/SrTiO₃:Rh (<520 nm) + BiVO₄ (<520 nm) Fe³⁺/Fe²⁺ (*mediator*) **STH=0.1** %

Chen et al. Nature Materials Reviews 2017, 2, 17050

Low STH - Redox mediator absorbs light
- Still large band gaps



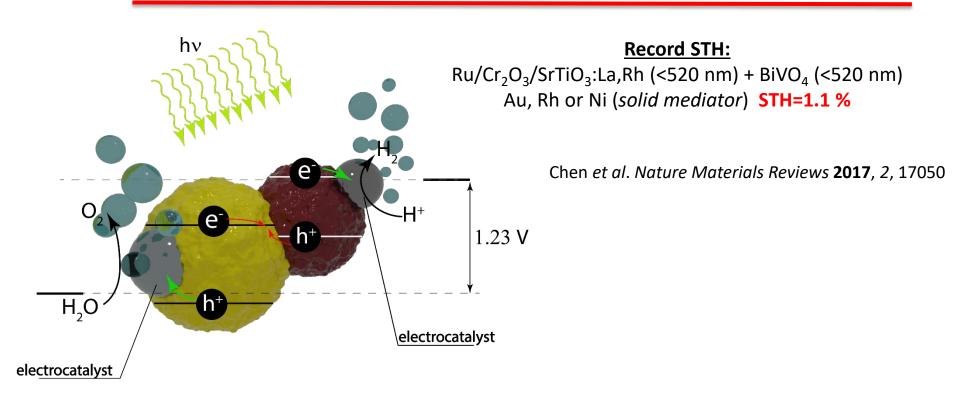
Photocatalyst – Dual absorber

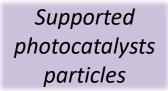


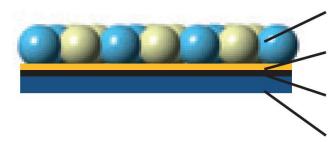
Type 2: Dual Bed 4hv + 2H,O + 4A _ ,O, + 4H++ 4A. 4hv + 4H+ + 4A 2H, + 4A **Particle Suspension** STH Efficiency Perforated **Porous Pipes Particle** Transparent Bridge Slurry Film Driveway 0 0 0.1 m 2 m 1 m O, Baggie H, Baggie



Photocatalyst – Dual absorber







Particle layer Gold layer Carbon tape Glass plate

Wang et al. Nature Materials 2016, 15, 611



Summary

Efficient and reliable methods to **STORE SOLAR ENERGY** chemically are highly desirable

Natural Photosynthesis – stores solar energy by oxidizing water and fixing CO₂
Biofuels are important to today's economy, but cannot meet all the energy demand

Artificial Photosynthesis – for HYDROGEN production is a potential route for large scale solar energy storage and replacement of H_2 production by steam reforming of natural gas.

PV + Electrolyzer are not **yet** economically competitive (cost of cells, durability)

Photoelectrochemical tandem cells (dual absorber) with stable (> 10 years), efficient (> 10 %) and solution-based could meet target 1-2 \$ Kg⁻¹ H₂

Photocatalyst (dual absorber) with stable (> 5 years), efficient (> 7 %) and low-cost could achieve the target 1-2 \$ Kg⁻¹ H₂