

# Femtosecond solar energy harvesting and storage



**must**

Molecular Ultrafast  
Science and Technology

National Center of Competence in Research



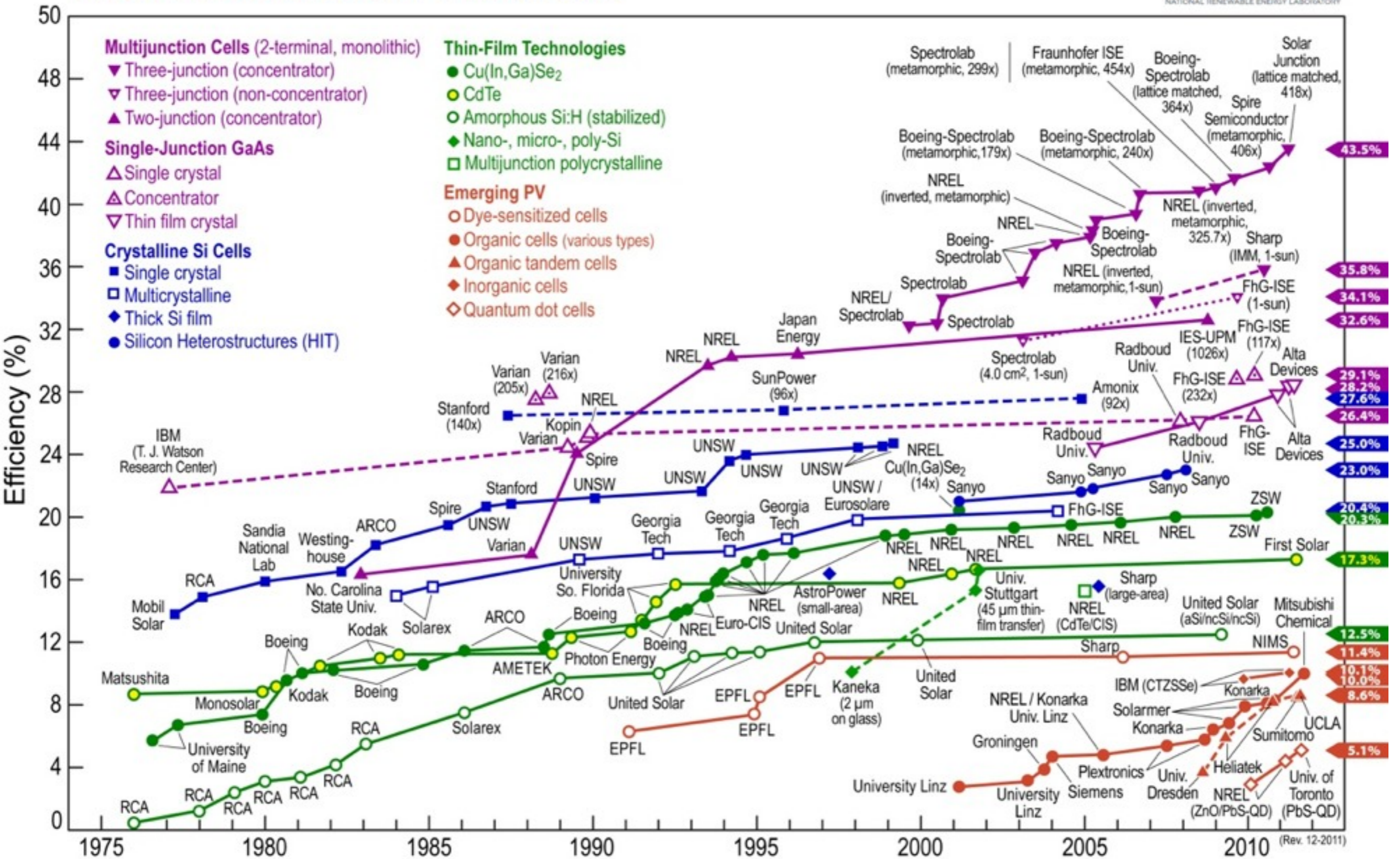
## Hubert H. Girault



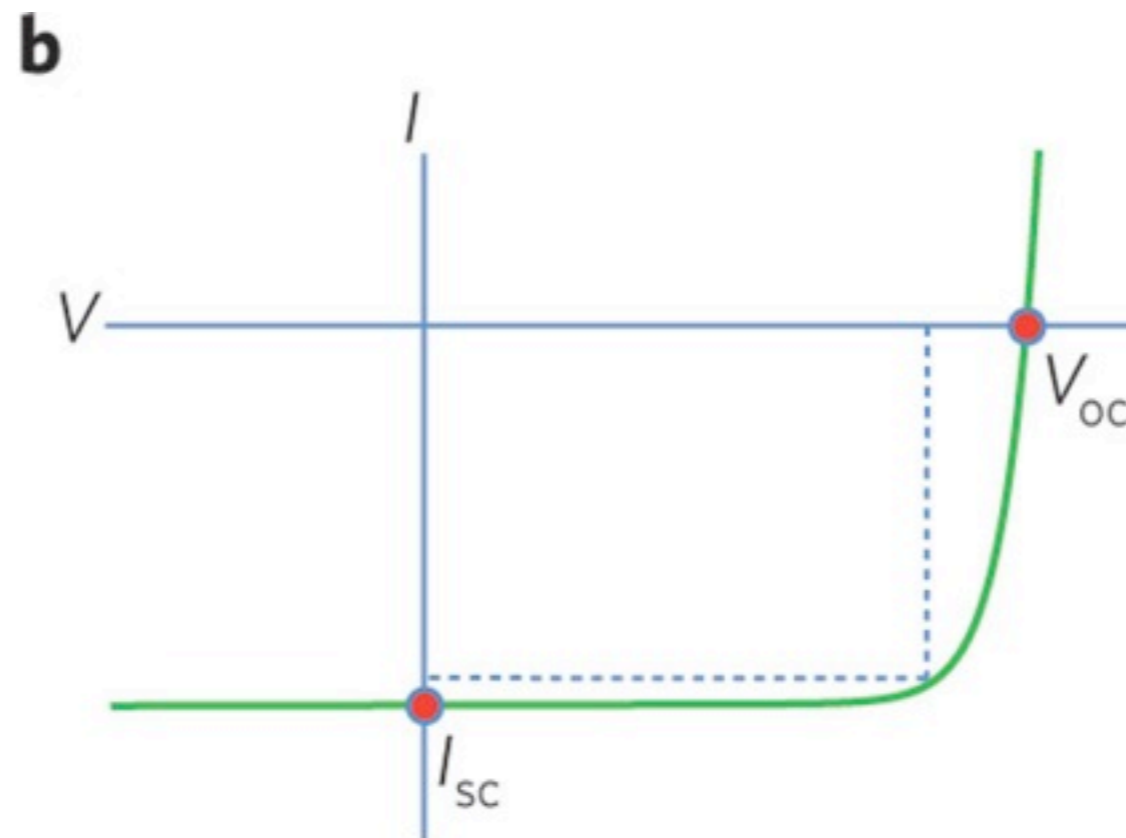
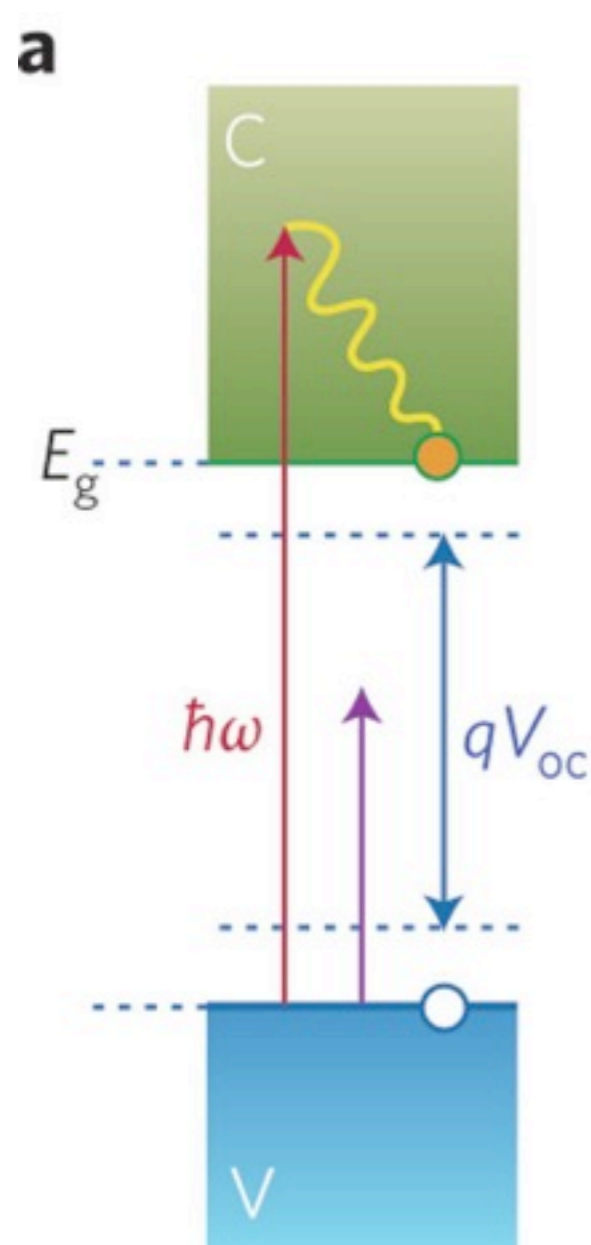
ÉCOLE POLYTECHNIQUE  
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June 13, 2012 - Lausanne

# Best Research-Cell Efficiencies

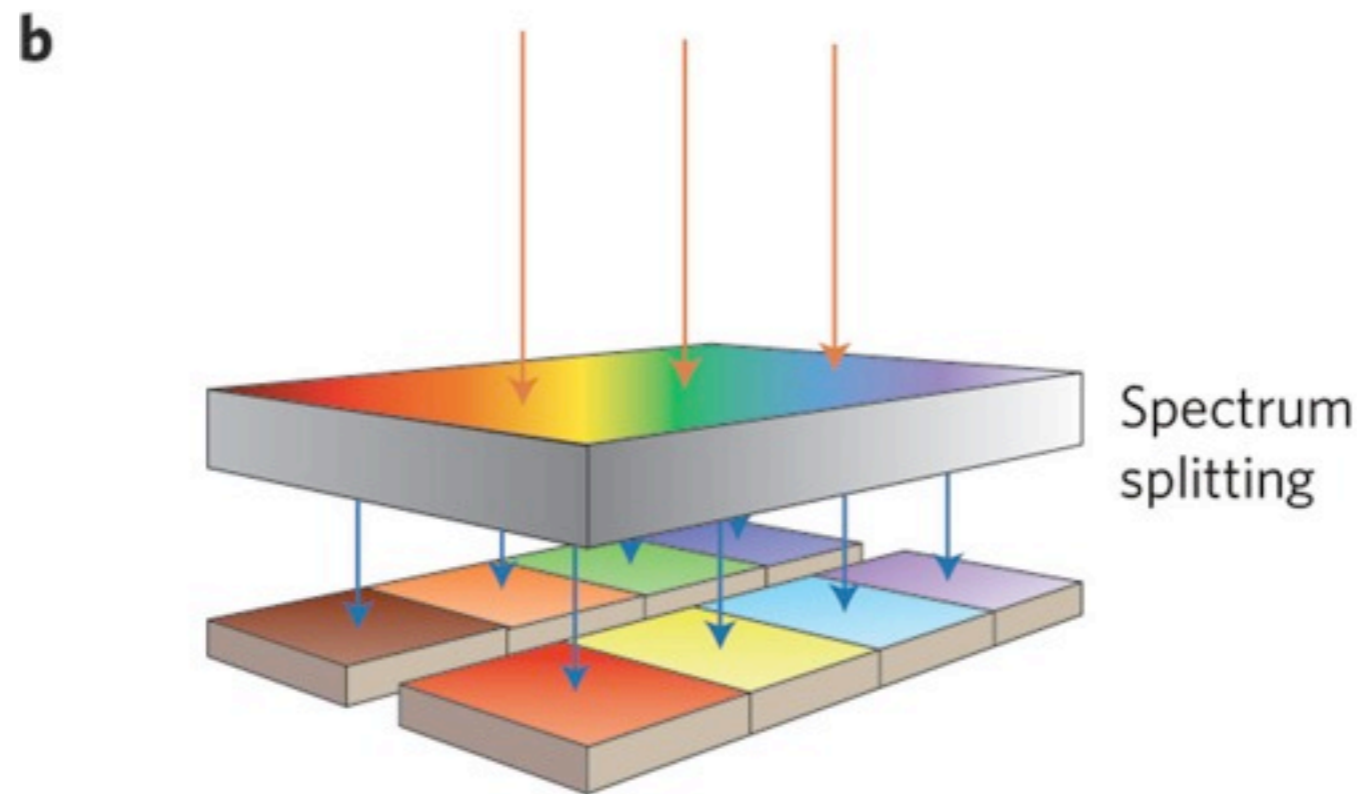
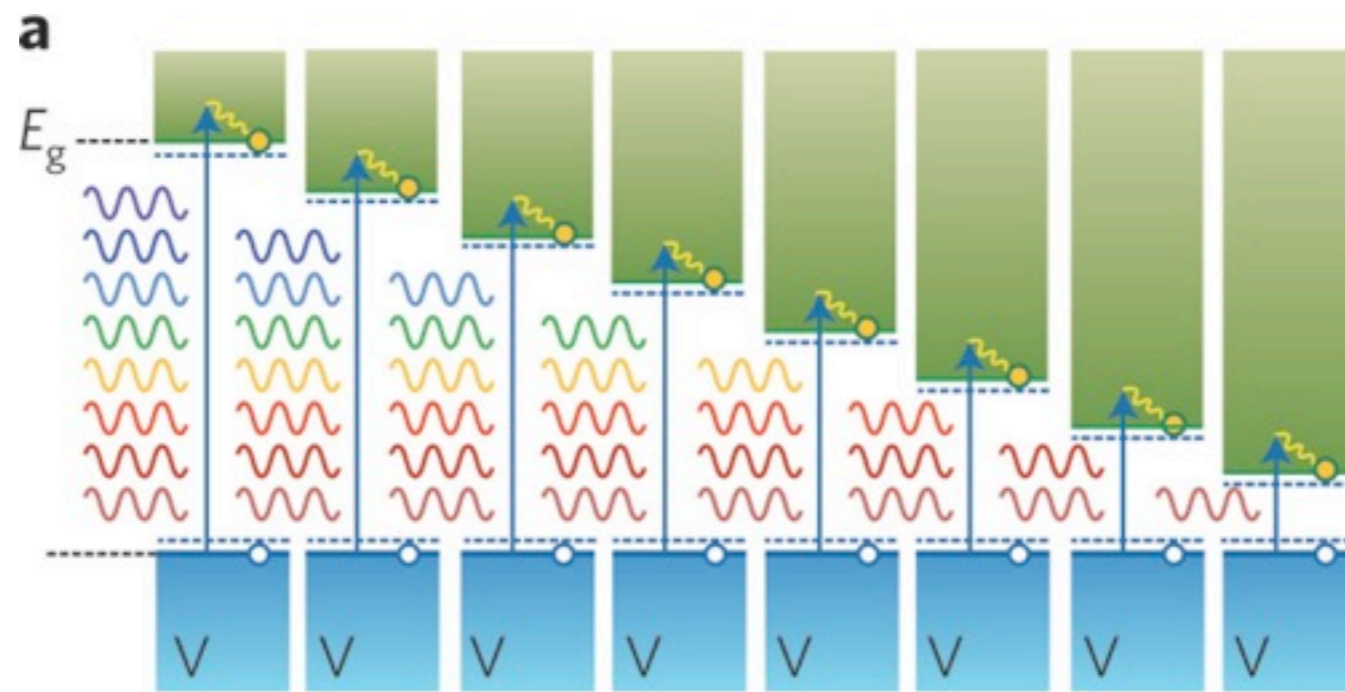


# Single Junction cell



Two basic elements arise in a thermodynamic analysis of high-efficiency photovoltaics within the **Shockley–Queisser** model: (1) reducing the deficit between the bandgap energy and the electron–hole quasi-Fermi-level splitting, and (2) minimization of carrier thermalization losses and absorption- loss of sub-bandgap light

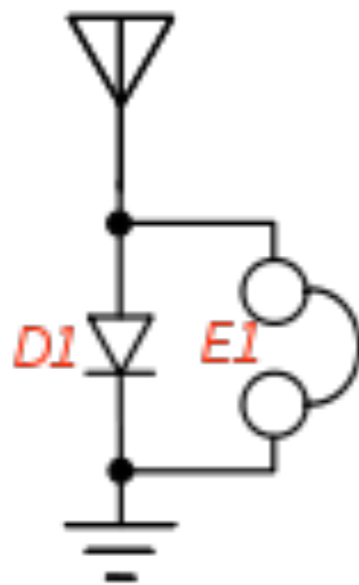
**a**, Energy diagram of a single-junction solar cell. Light at an energy  $\hbar\omega$  (red arrow) creates an excitation from the valence (V) to the conduction (C) band of a semiconductor. After thermalization in the conduction band an electron–hole pair is formed across the bandgap with energy  $E_g$ . Light with an energy below the bandgap (purple arrow) is not absorbed. **b**, Typical current–voltage ( $I$ – $V$ ) characteristics of a solar cell. The short-circuit current  $I_{sc}$  is a direct measure of the conversion efficiency from incident photons to electrical current. The open-circuit voltage  $V_{oc}$  is significantly lower than  $E_g$  due to entropic reasons. The maximum-power operating point of the solar cell is indicated by the dashed lines.



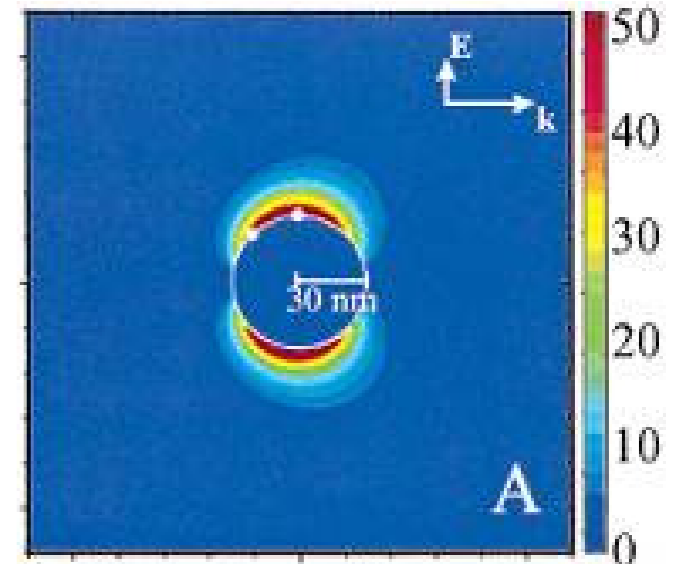
**a**, Multi-junction energy diagram. Semiconductors with different bandgaps convert different portions of the solar spectrum to reduce thermalization losses. The quasi-Fermi levels defining the open-circuit voltage are indicated by the horizontal blue dashed lines. The yellow dots represent the electrons. **b**, Parallel-connected architecture that can be realized using epitaxial liftoff and printing techniques of the semiconductor layers, followed by printing of a micro- or nanophotonic spectrum splitting layer.

# Rectification

## Galena Radio

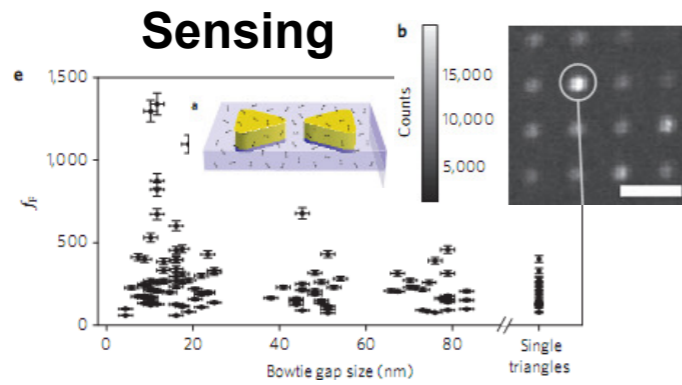


From radio waves to optical waves...

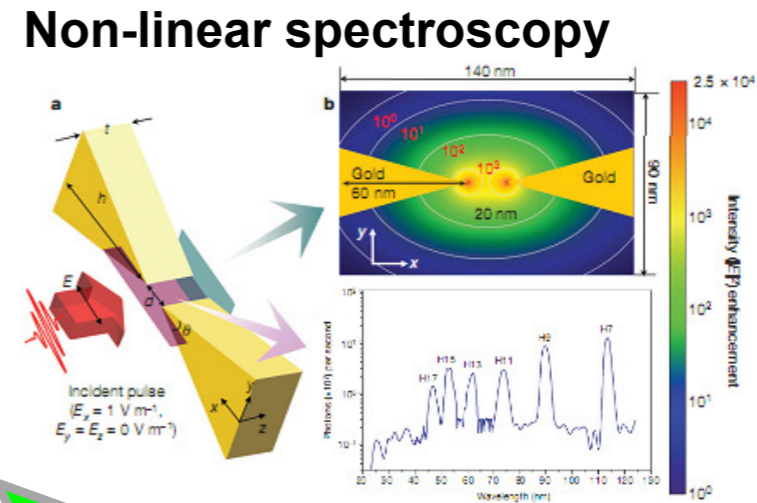


Anil Kumar, Dissertation, 2011, University of Illinois

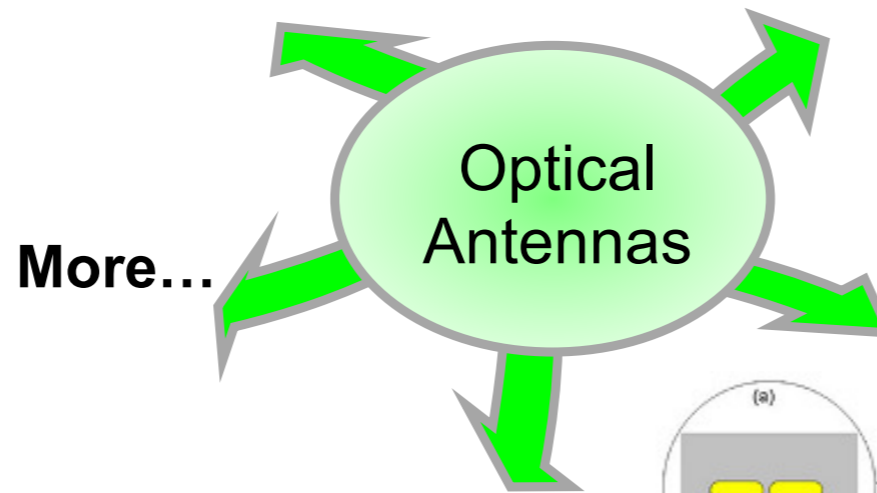
# Optical Antennas



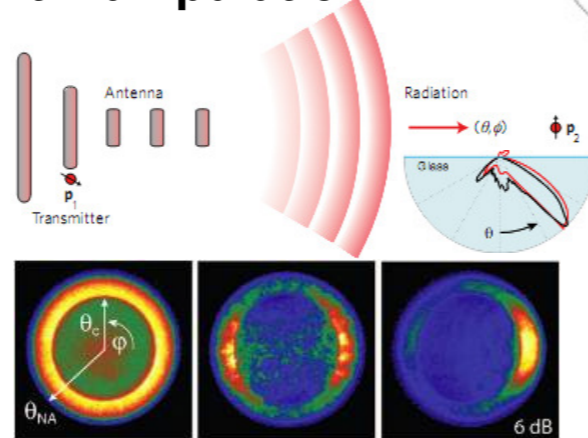
Kinkhabwala, *Nature Photon.*, 2009 [23]



Kim, *Nature*, 2008 [20]

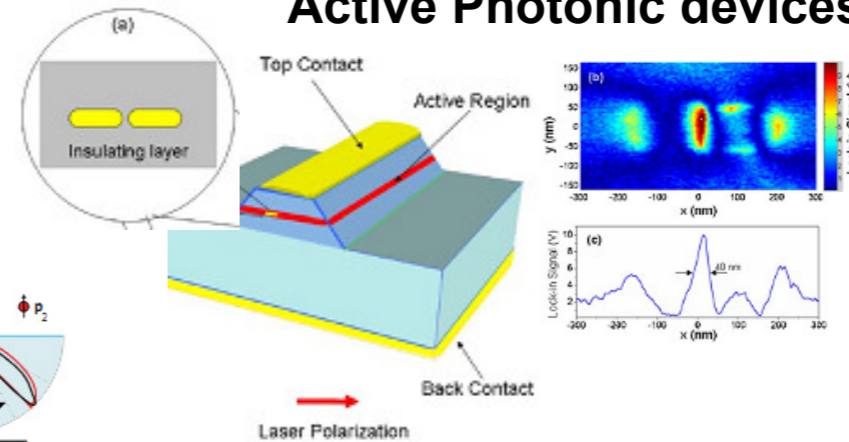


## Near-field light manipulation



Curto, *Science*, 2010 [29]

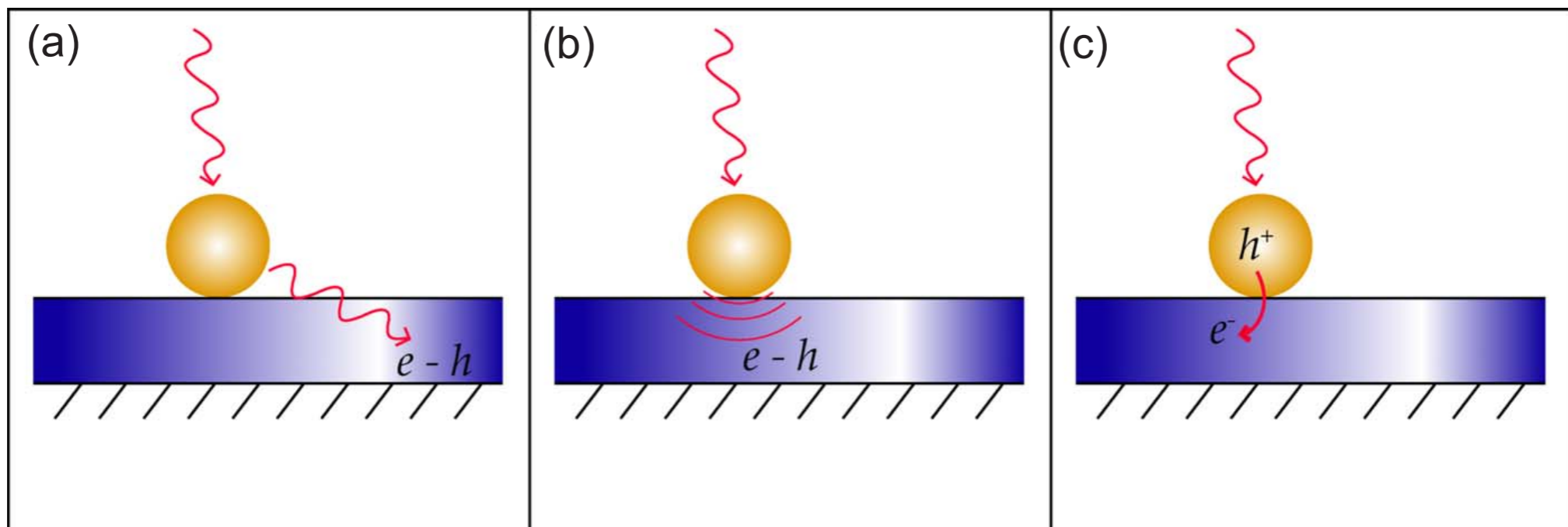
## Active Photonic devices



Cubukcu, *APL*, 2006 [112]

# Antennas for Photovoltaics

Cover a large spectrum by varying materials and shapes



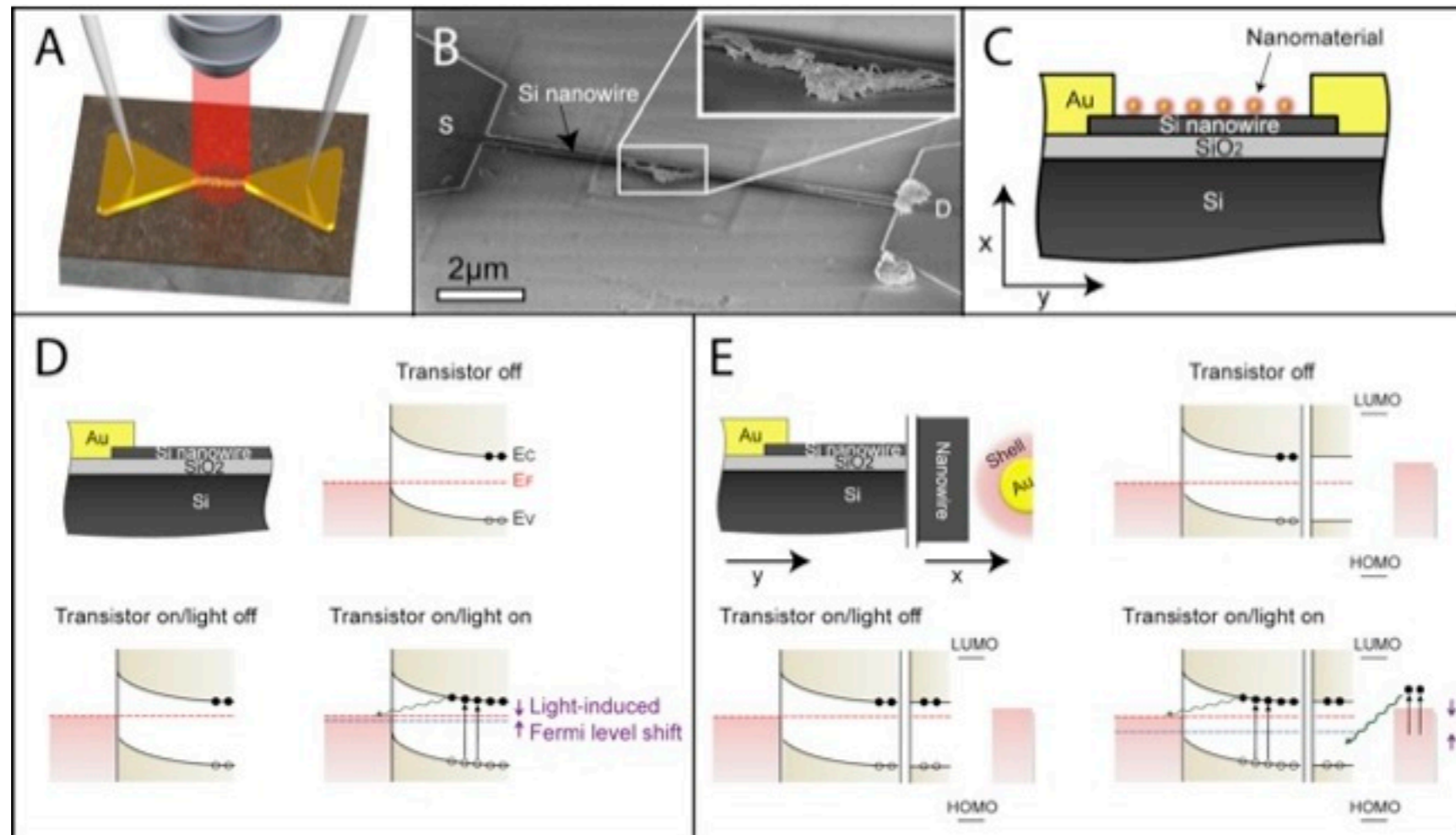
Schematic of different types of antenna effects in photovoltaics.

(a) Far-field scattering, leading to a prolonged optical path.

(b) Near-field scattering, causing locally increased absorption, and

(c) direct injection of photoexcited carriers into the semiconductor.

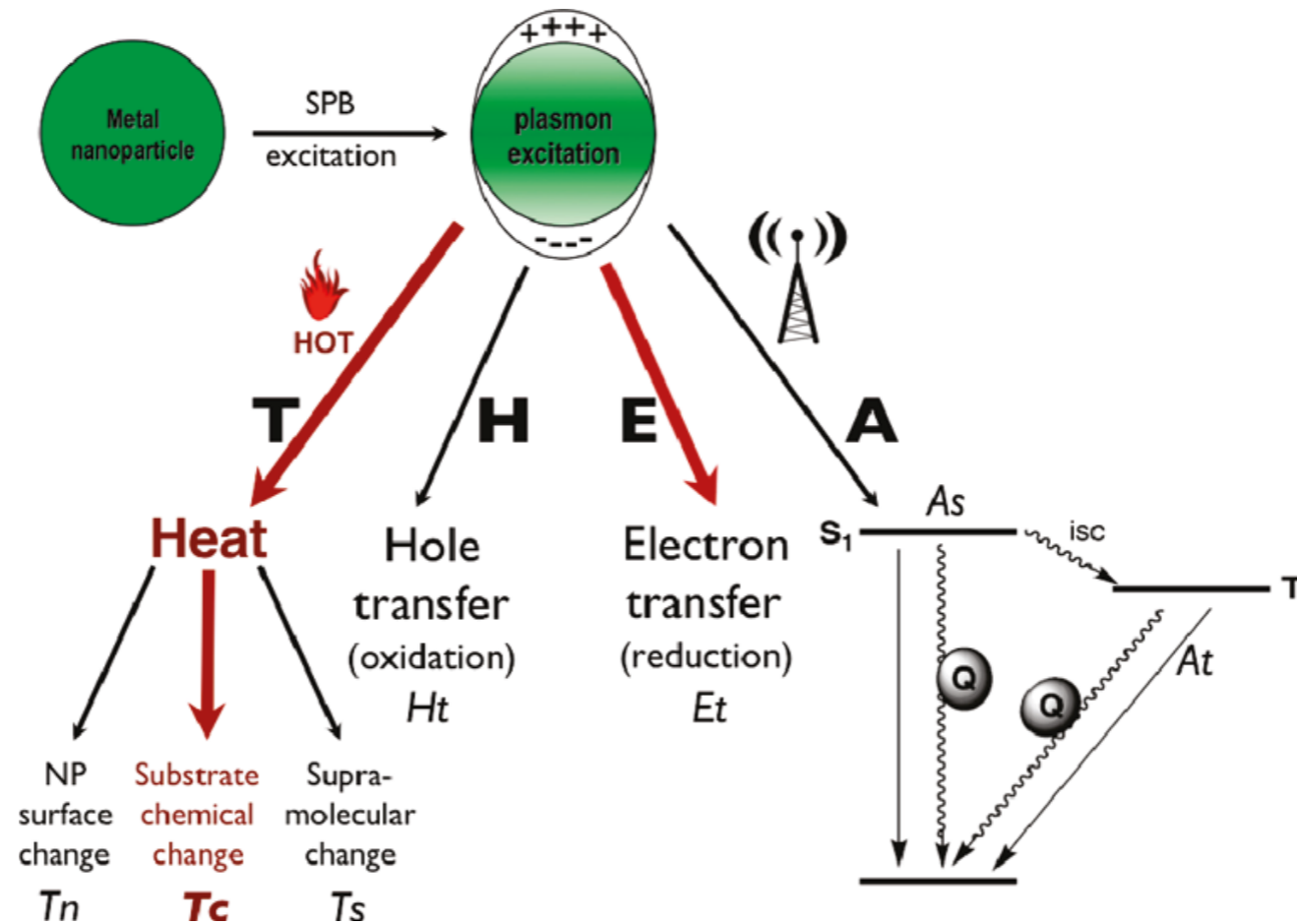
# Rectennas



(A) Scheme of the experimental set-up. (B) Scanning electron microscopy (SEM) image of a representative device, imaged at a  $52^\circ$  tilt angle. Inset: enlargement of the silicon nanowire coated with gold nanomaterials. (C) Cross-sectional schematic view of device. One of the gold electrodes acts as drain (D) and the other is source (S) electrode. Energy-band profile and photodetection mechanism in (D) uncoated- and (E) device coated with nanomaterials. In both (D) and (E), the red rectangular boxes denote the gold band and the light tan colored regions represent a silicon nanowire band structure together denoted with  $E_c$  and  $E_v$ , energy level in conduction and valence band, respectively: in (E), additional energy-band diagrams for the silicon and gold nanomaterial are shown too, together with the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the organic coating of the nanoparticles. The black filled and open circles represent the electron and hole, respectively, the dashed red line shows the Fermi level,  $E_F$ , the black solid arrow represents the process of CCG and the green curved arrows represent the process of CT, the dashed blue line is a fiducial line to show the Fermi level variation across the channel upon light illumination. **Francesco Stellacci, EPFL.**

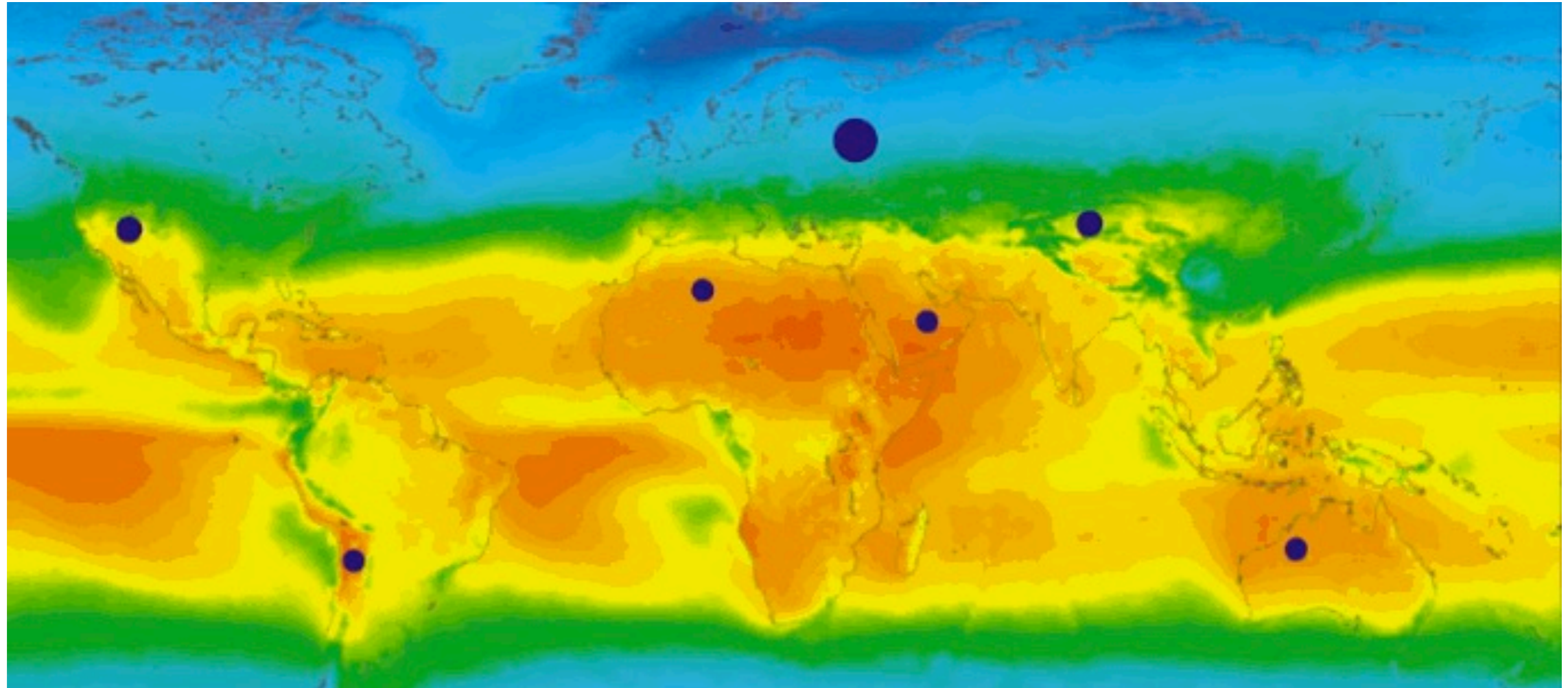


# Plasmonic energy transfer



Possible reaction pathways following plasmon excitation of metal nanoparticles in the presence of chemical molecules. In the presence of a suitable receiver, antenna effects (A) can result in excited state processes (As and At). Plasmon relaxation can lead to thermal effects (T) that can themselves induce supramolecular changes in guest molecules (Ts), chemical change (Tc) sometimes referred as photocatalysis, or changes in the nanoparticle itself (Tn) of either a physical or chemical nature (e.g., oxidation). Under plasmon excitation the nanoparticle can act as an electron donor (Et) or as an electron acceptor (Ht). (J. Phys. Chem., C, 2011, 115, 10784).

# Solar irradiation at the Earth's surface



0.3% of Saharan solar energy could power Europe.

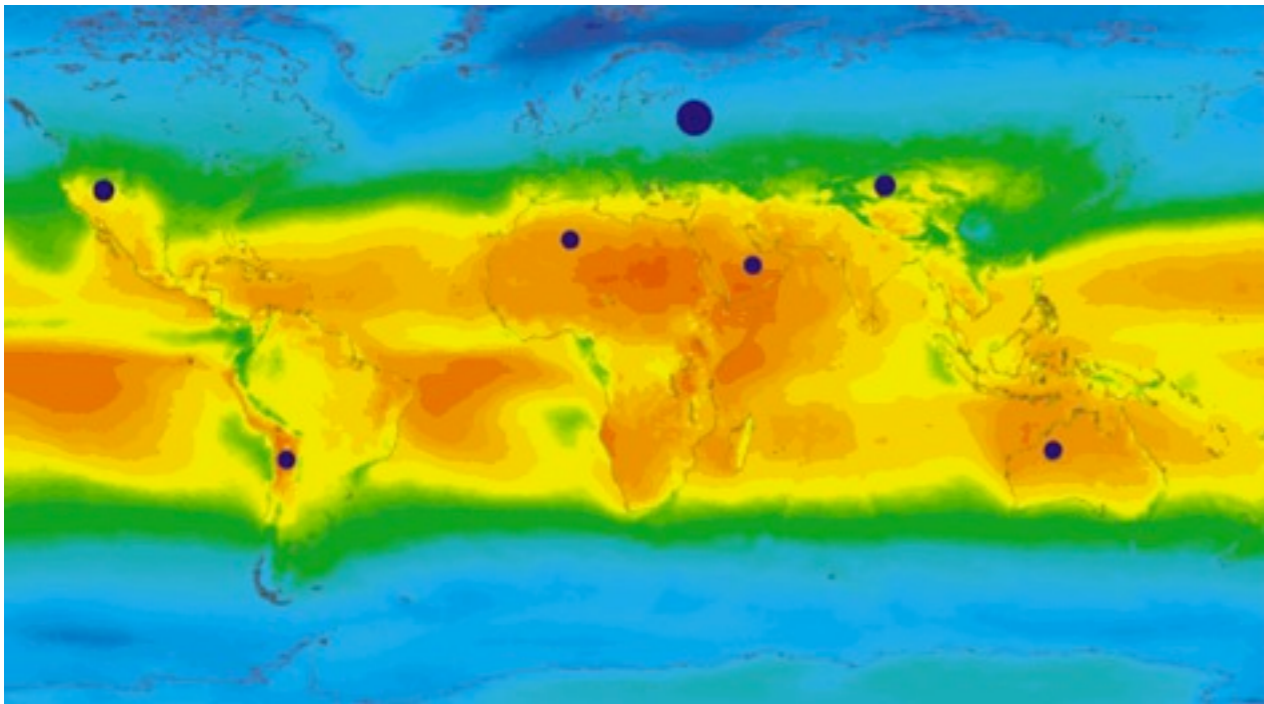
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Do you see a world of potential? We do.

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# Solar irradiation at the Earth's surface



The Sheffield Solar Farm

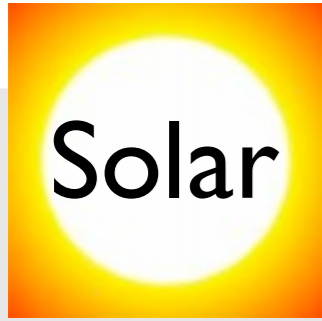
Solar radiation is higher at the equator, and lower further north and south. If covered in solar panels, each blue spot would provide more than the world's current energy demand.



NASA

Single night on planet earth....

# Energy conversion Storage



Solar

Chemical

Mechanical

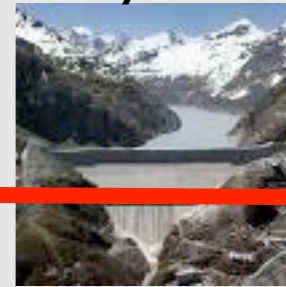
Electrical

Coal  
Gas  
Oil



CO<sub>2</sub>

Hydro



Grid



Electrolysis

Oil



Wind



Tide

Solar plant



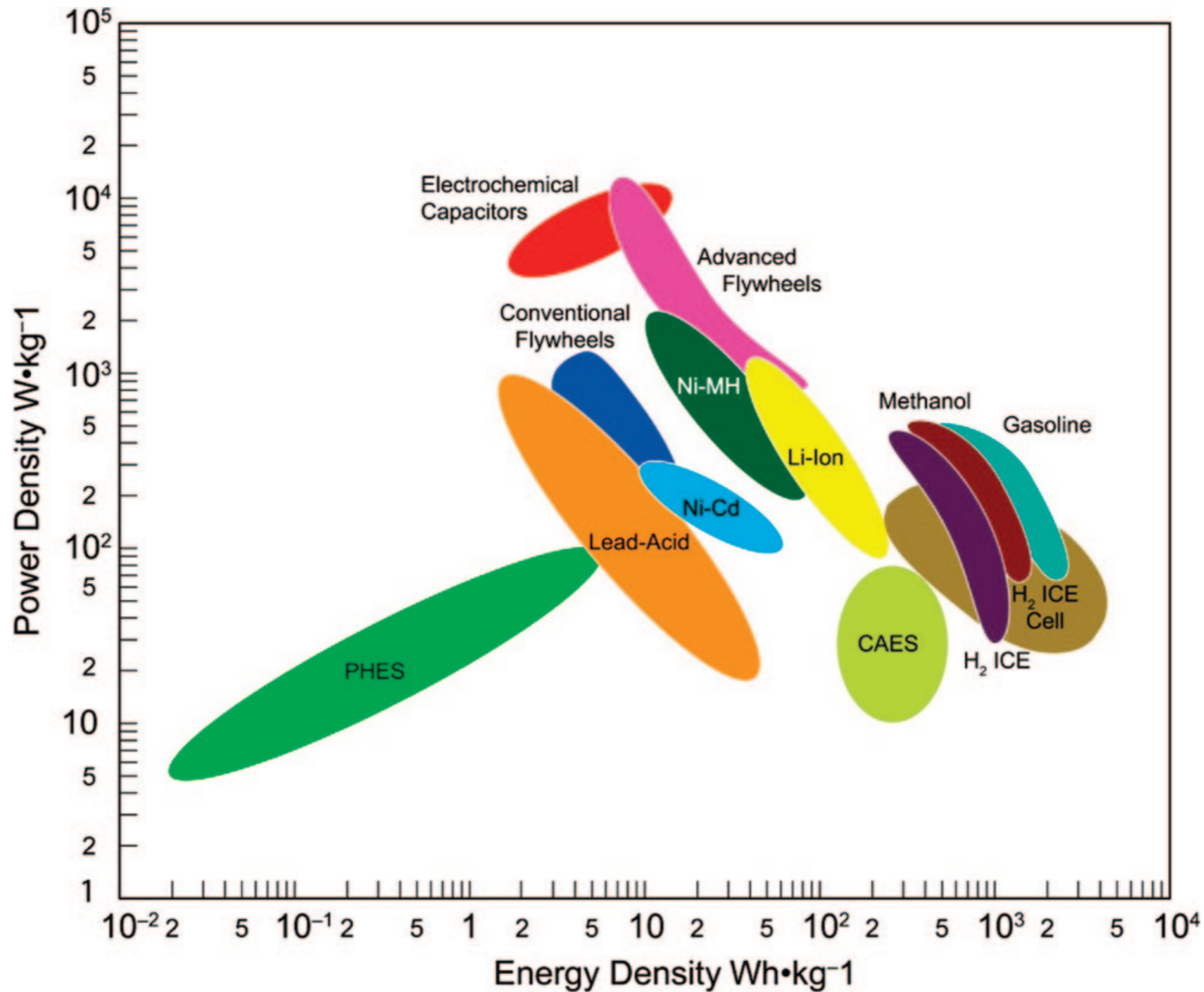
Photovoltaics



Batteries

Fuel cells

# Ragone Plot



PHES: Pumped hydroelectric energy storage, CAES : Compressed air energy storage,  
ICE : Internal combustion engine

Chem. Rev. 2010, 110, 6474–6502

# Alkaline water electrolysis

## Cell:

Electrolyte : 20-30% KOH

Diaphragm cell

Cell Voltage = 1.65 - 2 V

Energy consumption : 4-5 kW · h · m<sup>-3</sup>

Current yield: >98%

H<sub>2</sub> purity : >99.8%



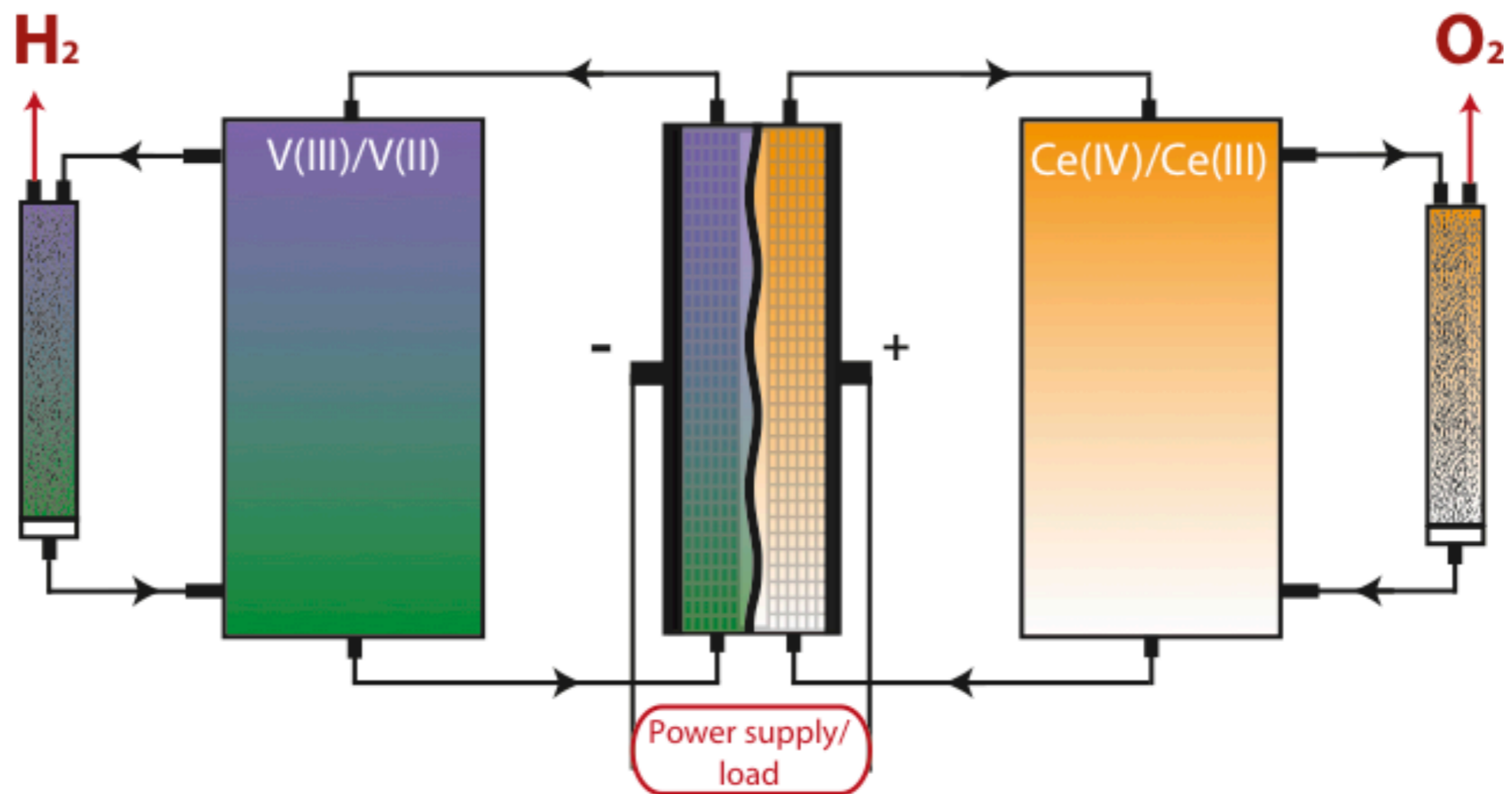
## Nickel electrodes :

Cathode: Pt coating - **Ni can dissolved in intermittent use**

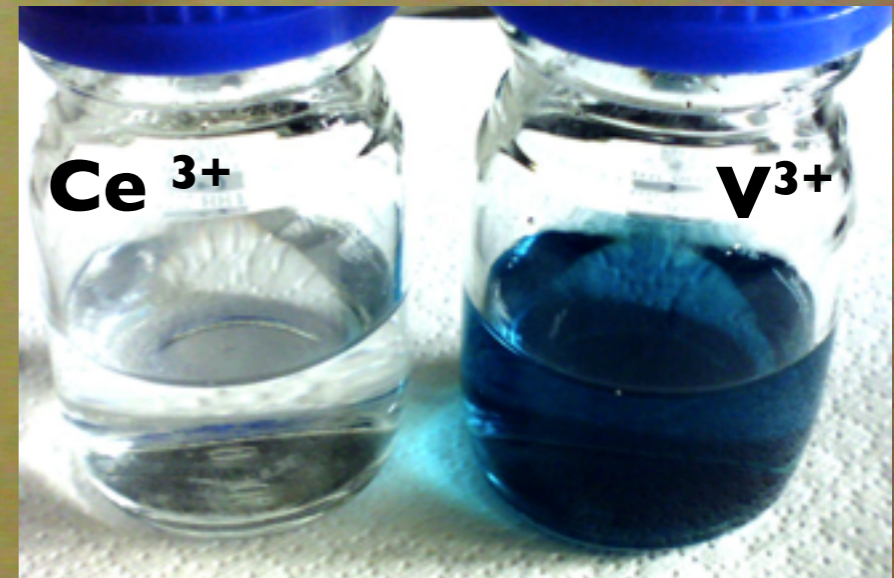
Anode : Oxide coating e.g. MnO<sub>2</sub>

# Redox flow batteries

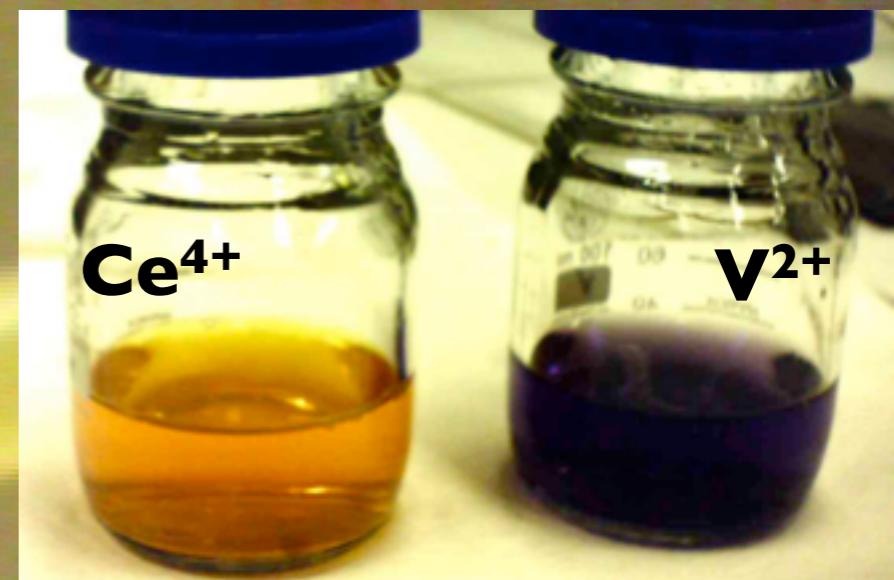
- A sustainable system coupling energy storage (redox flow battery) and energy conversion (catalytic beds to regenerate redox mediators)
- Allows the production of hydrogen, and oxygen or other oxidized products



# A cerium /vanadium redox flow battery for hydrogen generation



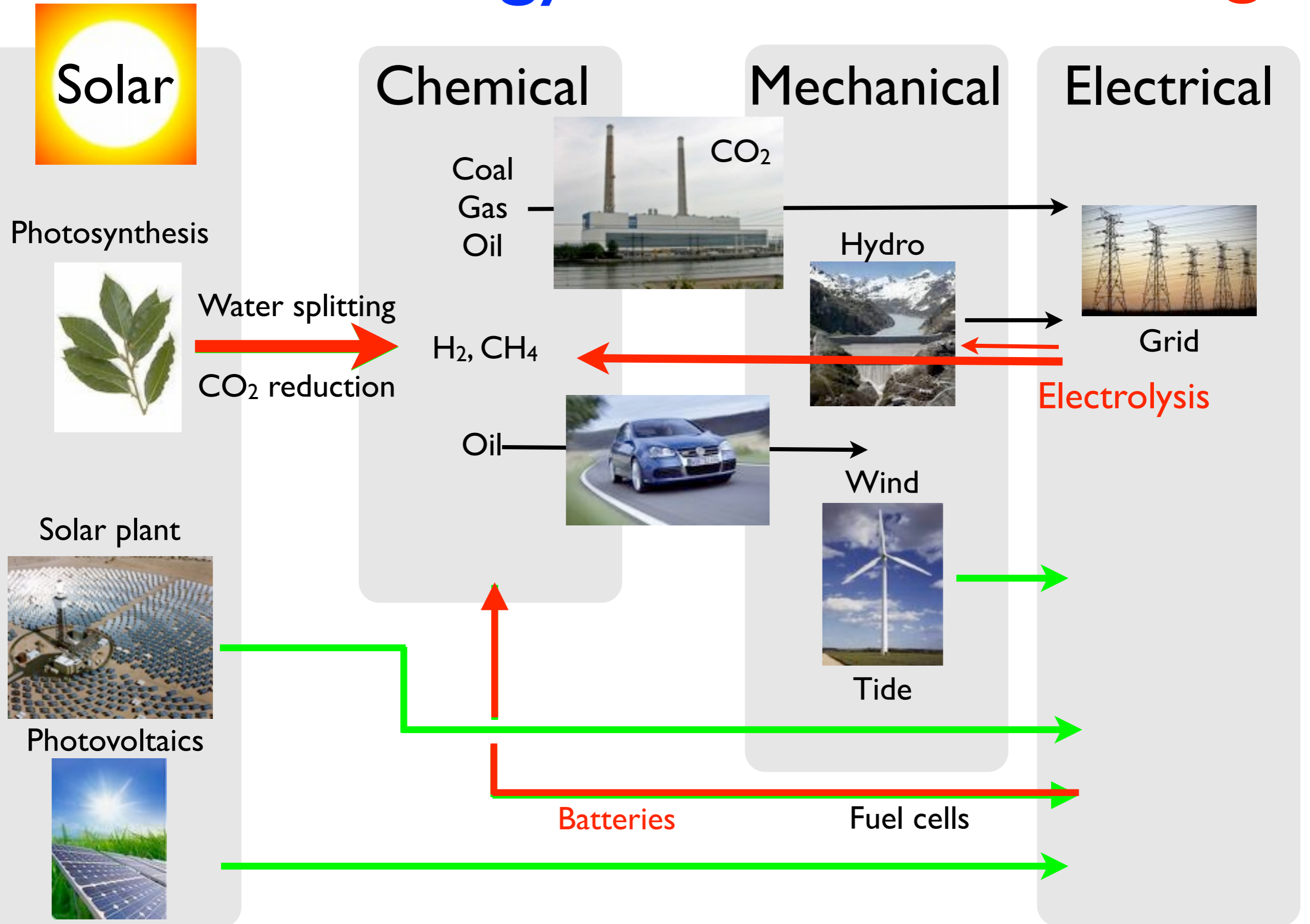
Discharged state



Charged state



# Energy conversion Storage



# Honda

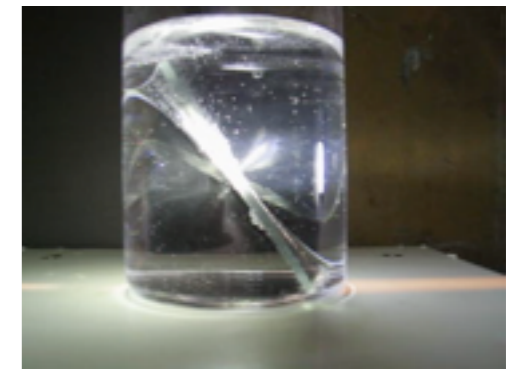


Belenos



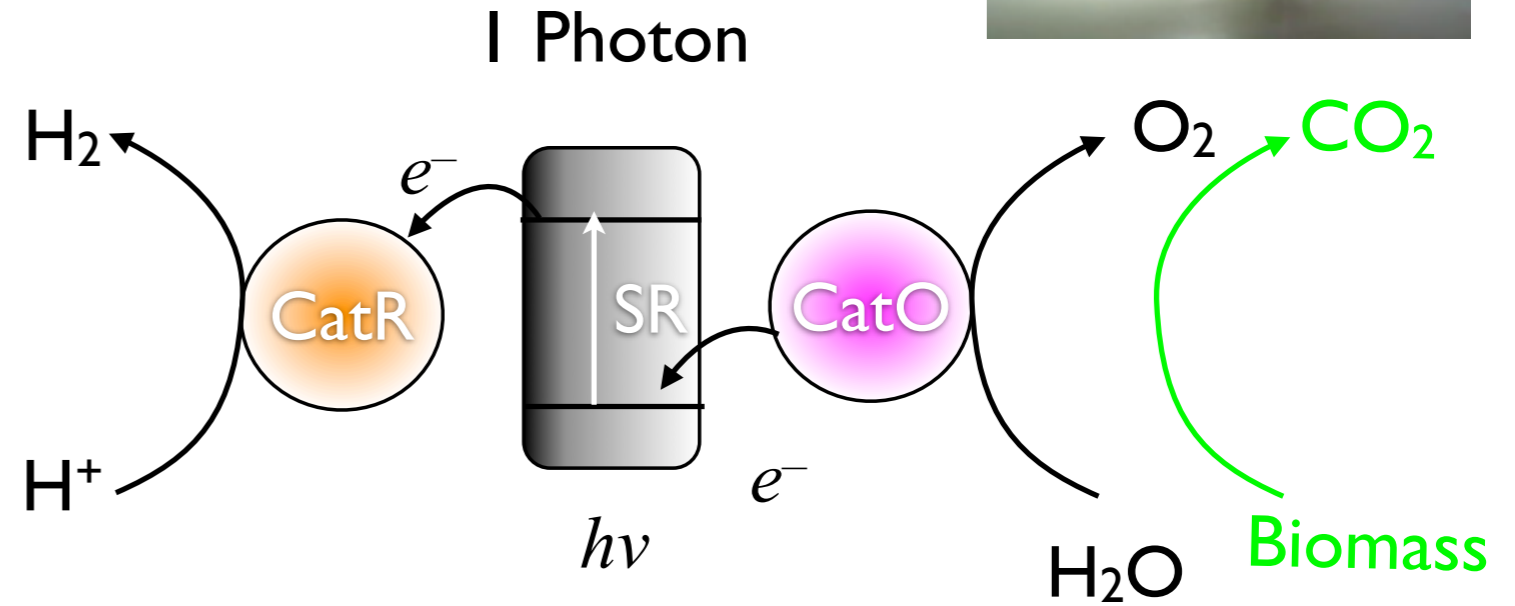
Honda's Next Generation Solar Hydrogen Station Prototype





# Technologies

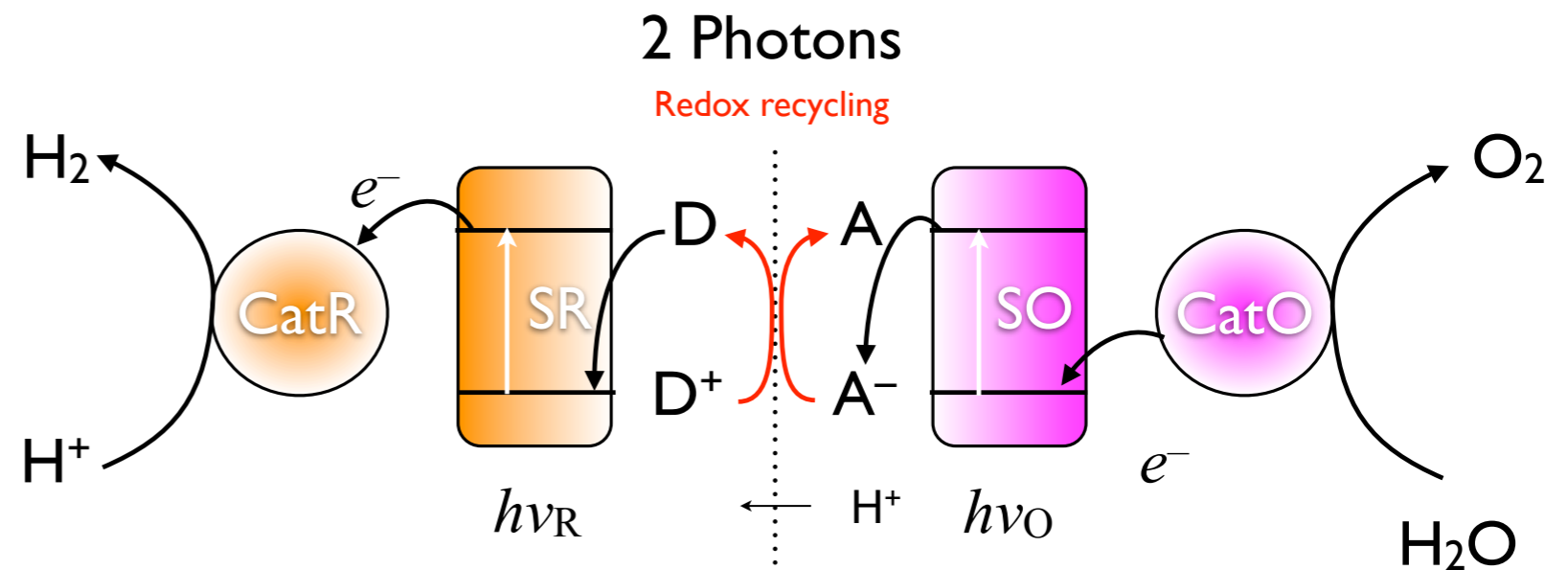
Photocatalysis Type 1



Solid semiconducting or molecular photosensitizers

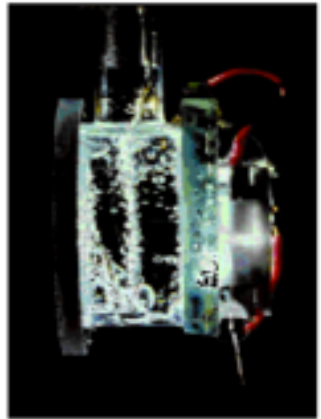
Semiconducting or molecular catalysts for reduction (CatR) and oxidation (CatO)

Photocatalysis Type 2

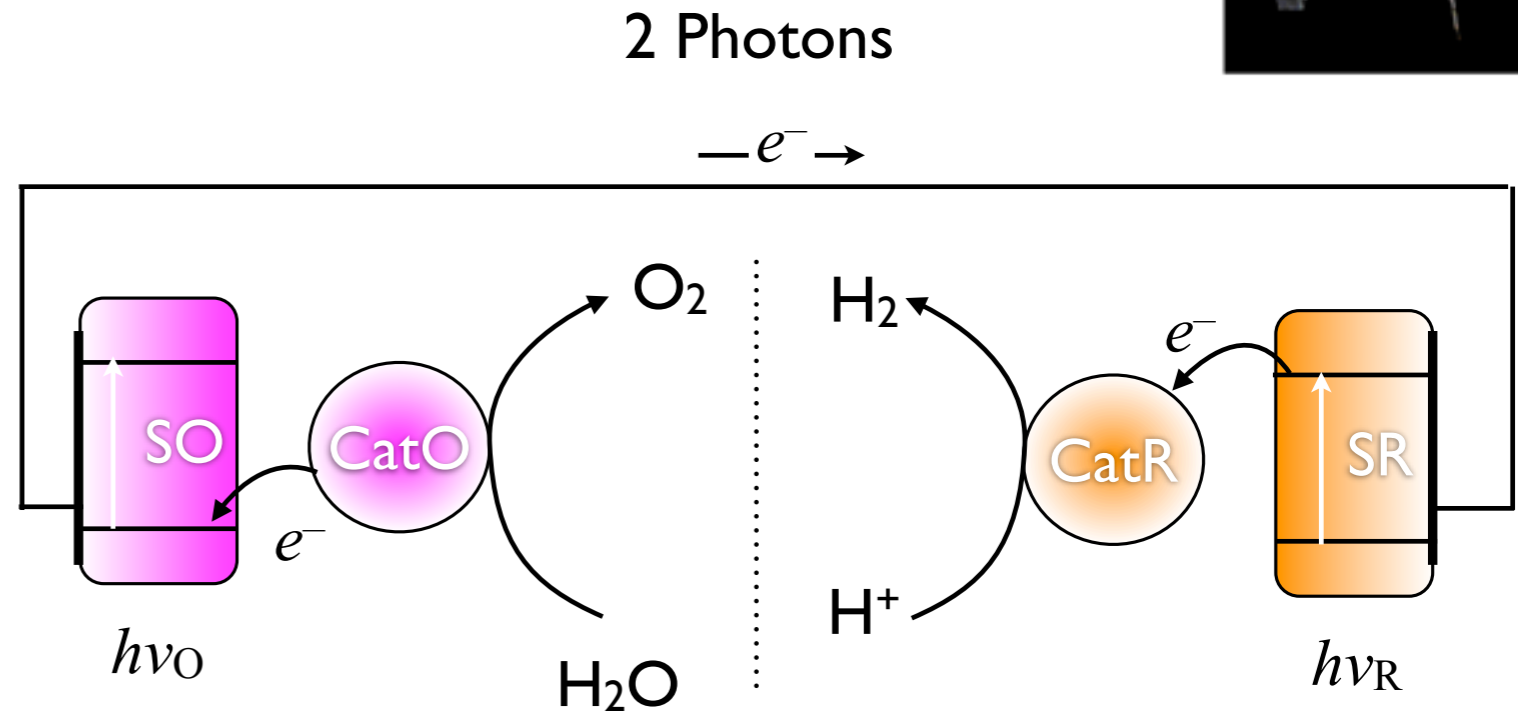


The two photosystems can be physical separated to collect the gases

# Technologies



Photocatalysis Type 3



# Hydrogen producing solar panels

M. Grätzel, EPFL

# Batch water splitting

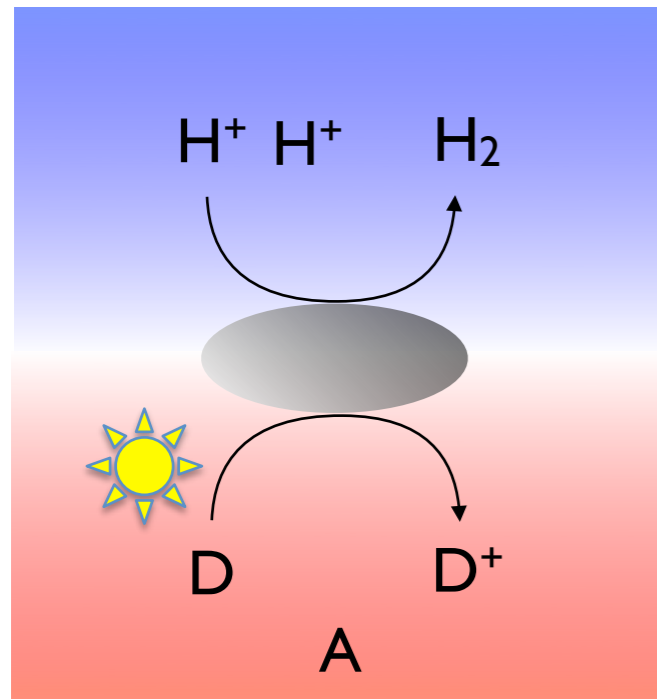


Photo-reduction  
Hydrogen Production

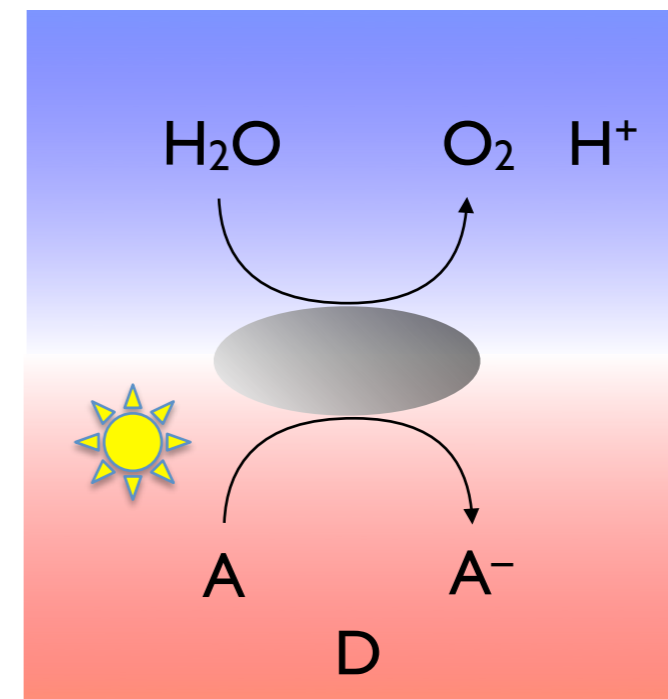
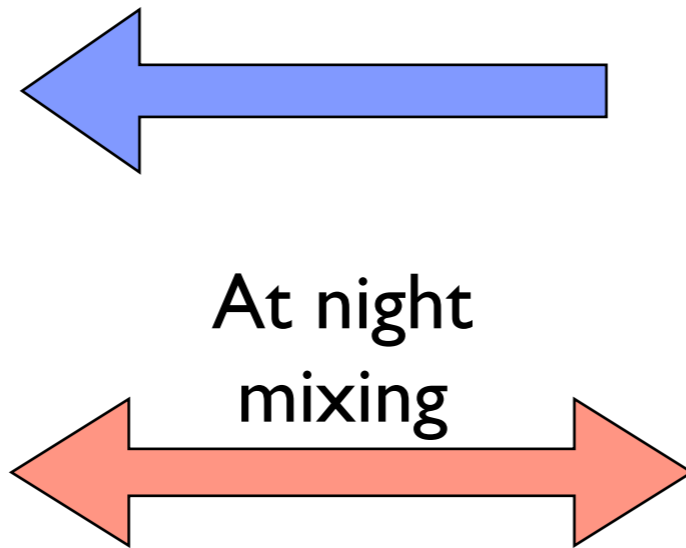
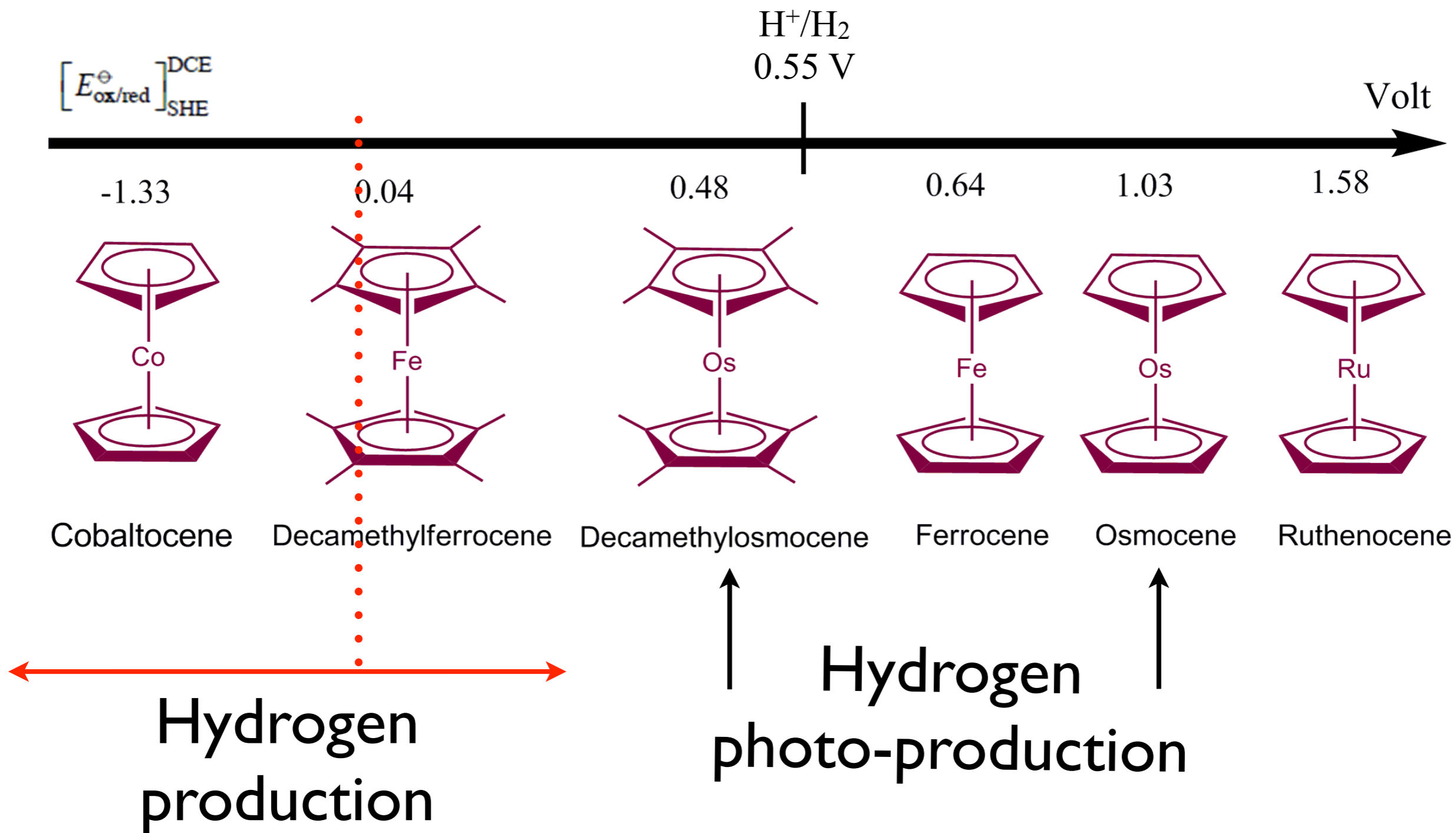


Photo-oxidation  
Oxygen Production

D: Sacrificial electron donor  
A : Sacrificial electron acceptor



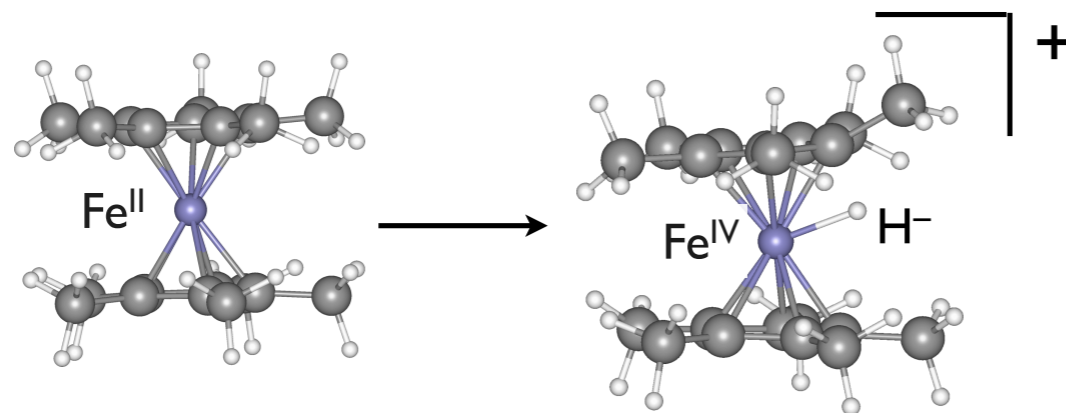
# Metallocenes



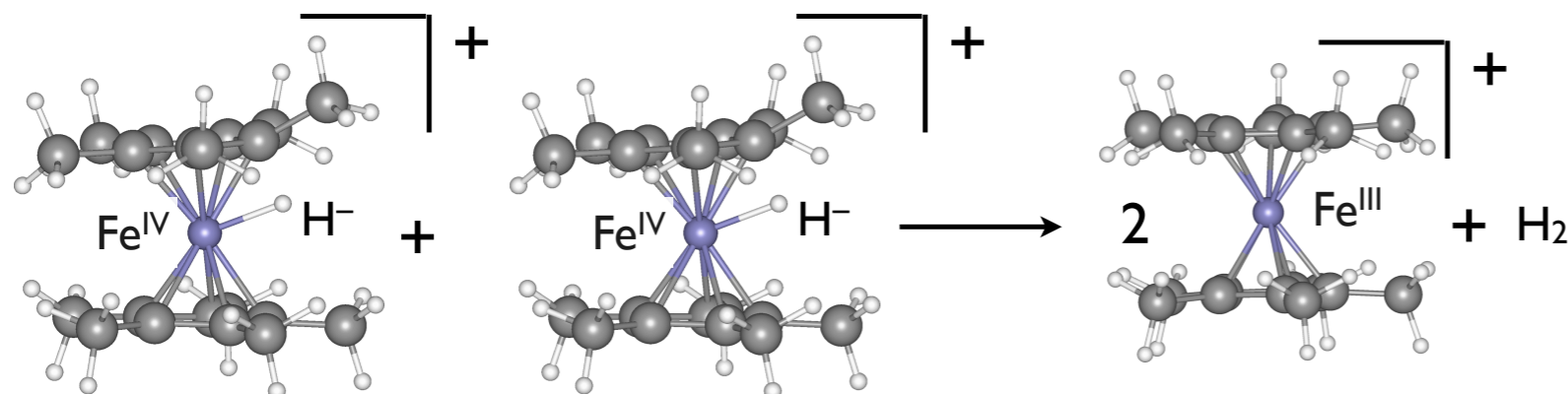
# Hydrogen production

## Interfacial Proton reduction by decamethylferrocene

### I. DMFc protonation - Volmer reaction



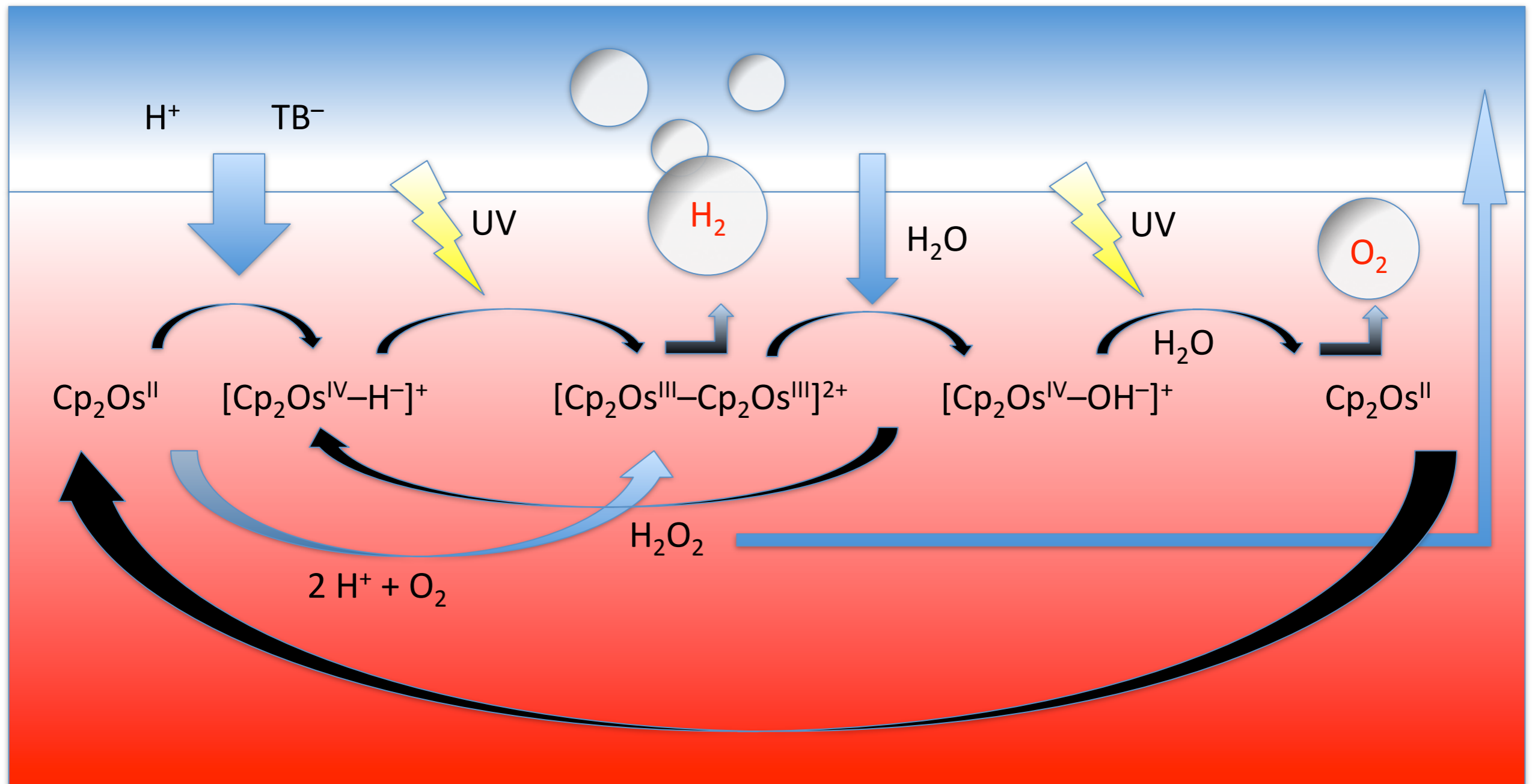
### 2. Bimolecular homolytic pathway - Tafel reaction



x 25

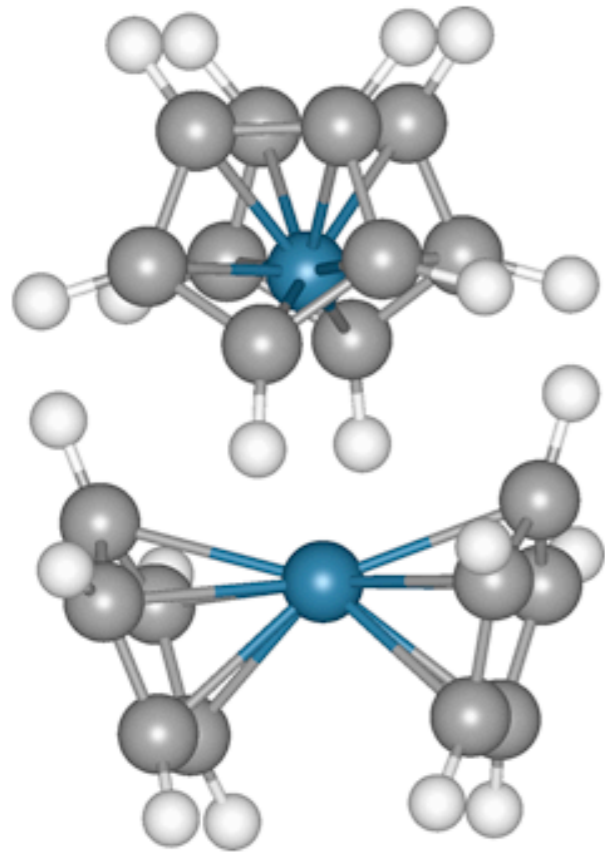


# Osmocene Water Splitting

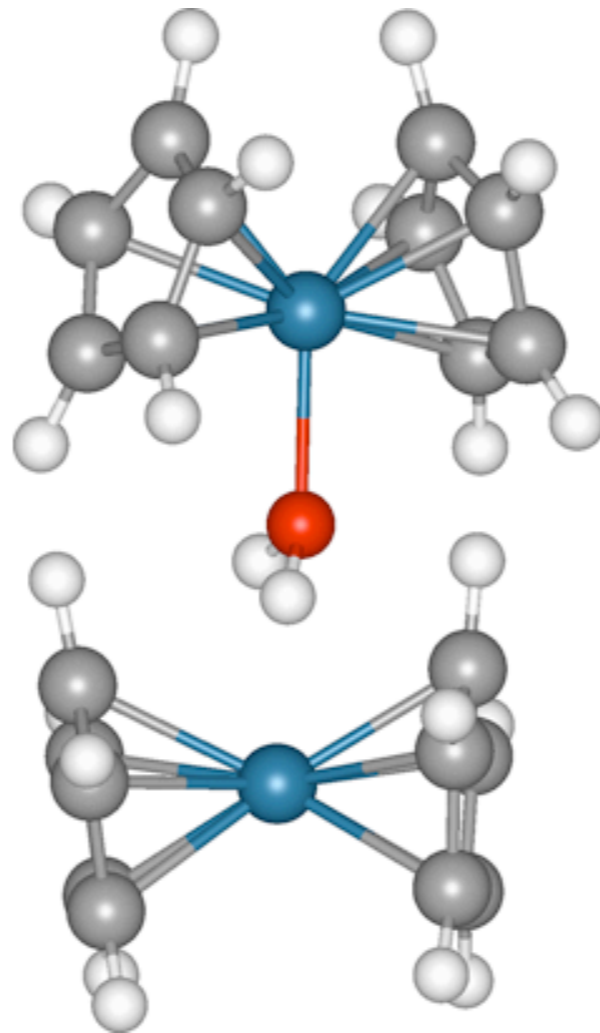




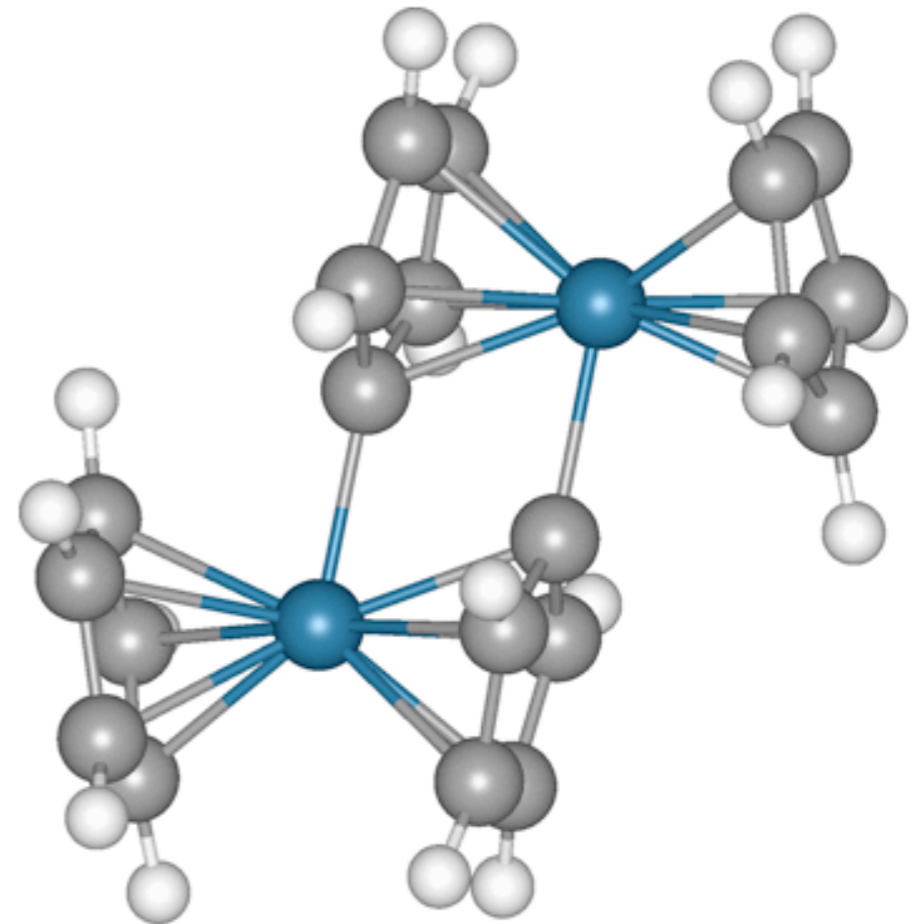
# Osmocenium dimer



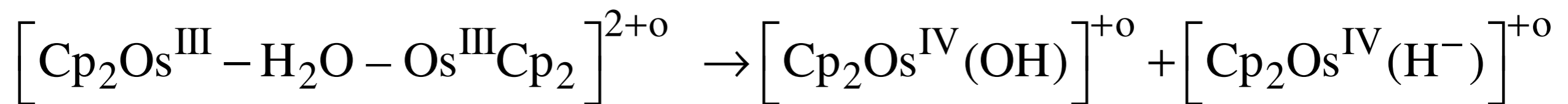
Metal-metal dimer



Water sandwich  
dimer

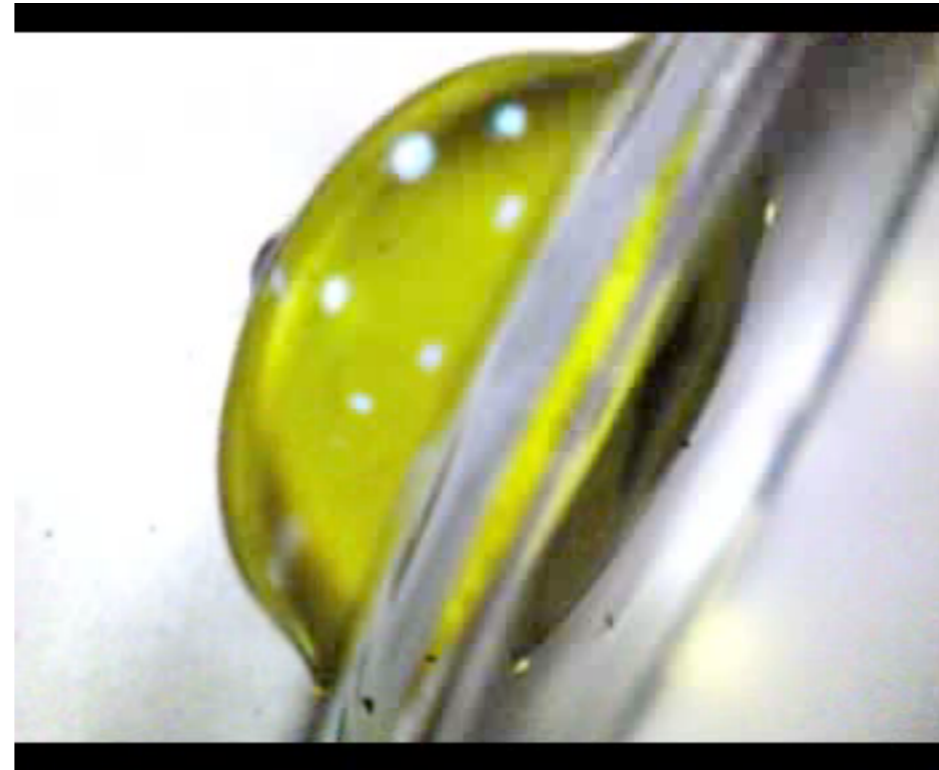
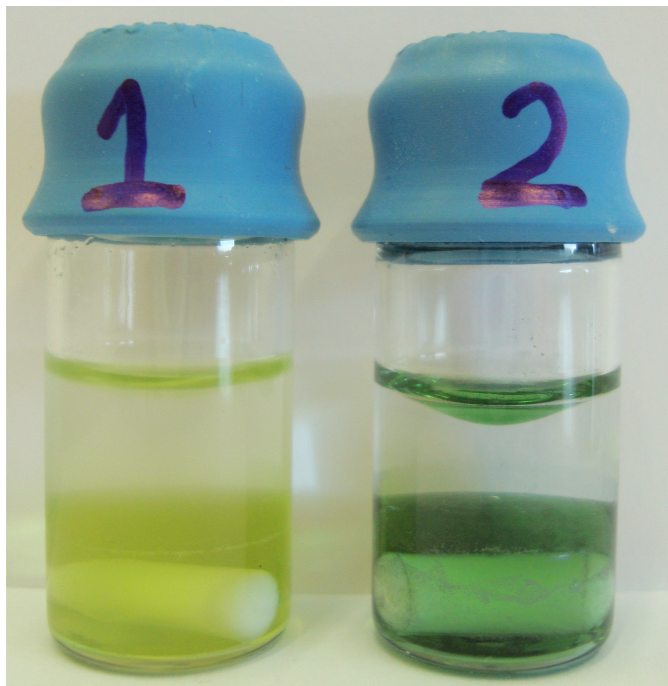


Ring-Ring dimer



# MoS<sub>2</sub>-catalysed Hydrogen Production

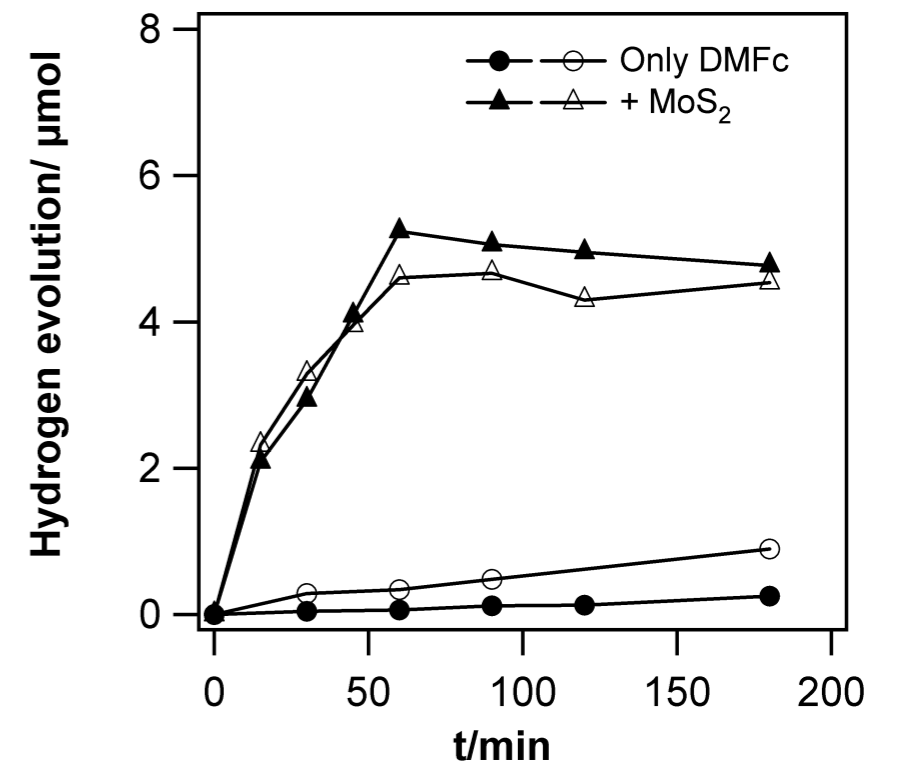
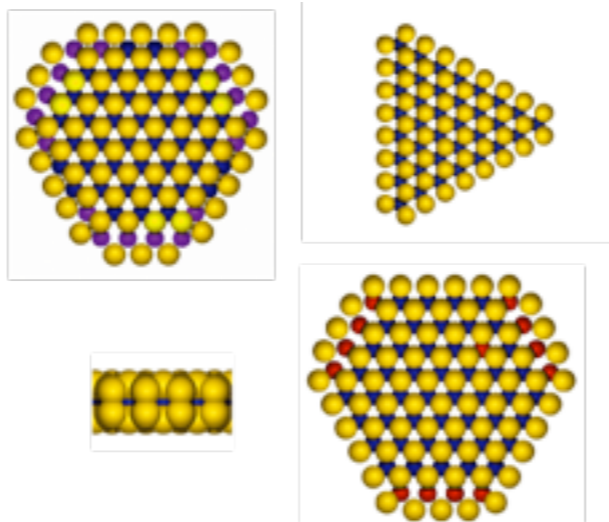
10 mM LiTB / 0.1M HCl



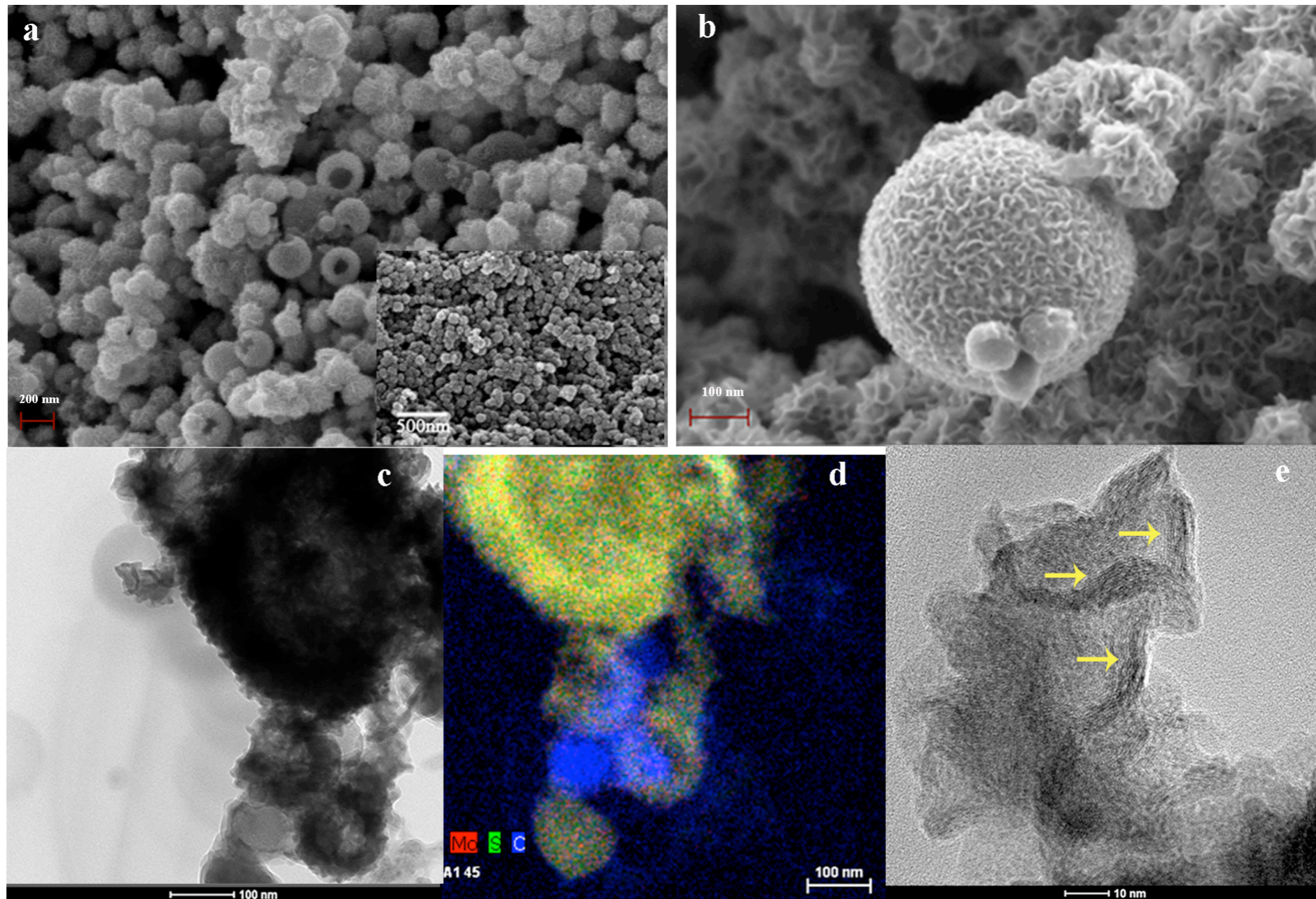
5 mM DMFc

5 mM DMFc  
0.6  $\mu$ M MoS<sub>2</sub>

After 1 hour

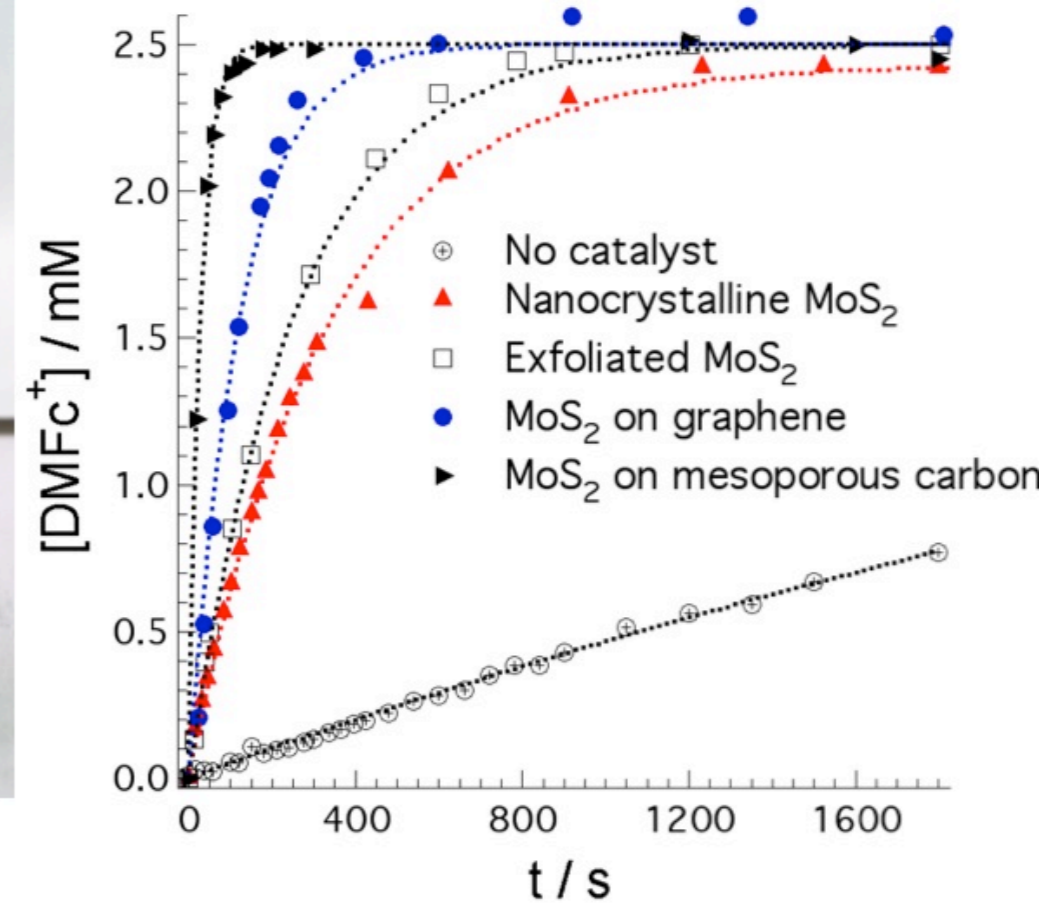
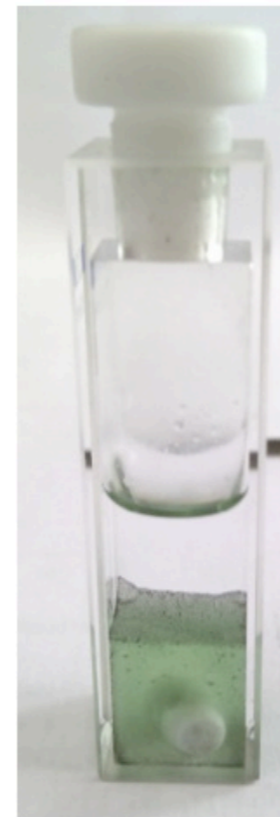
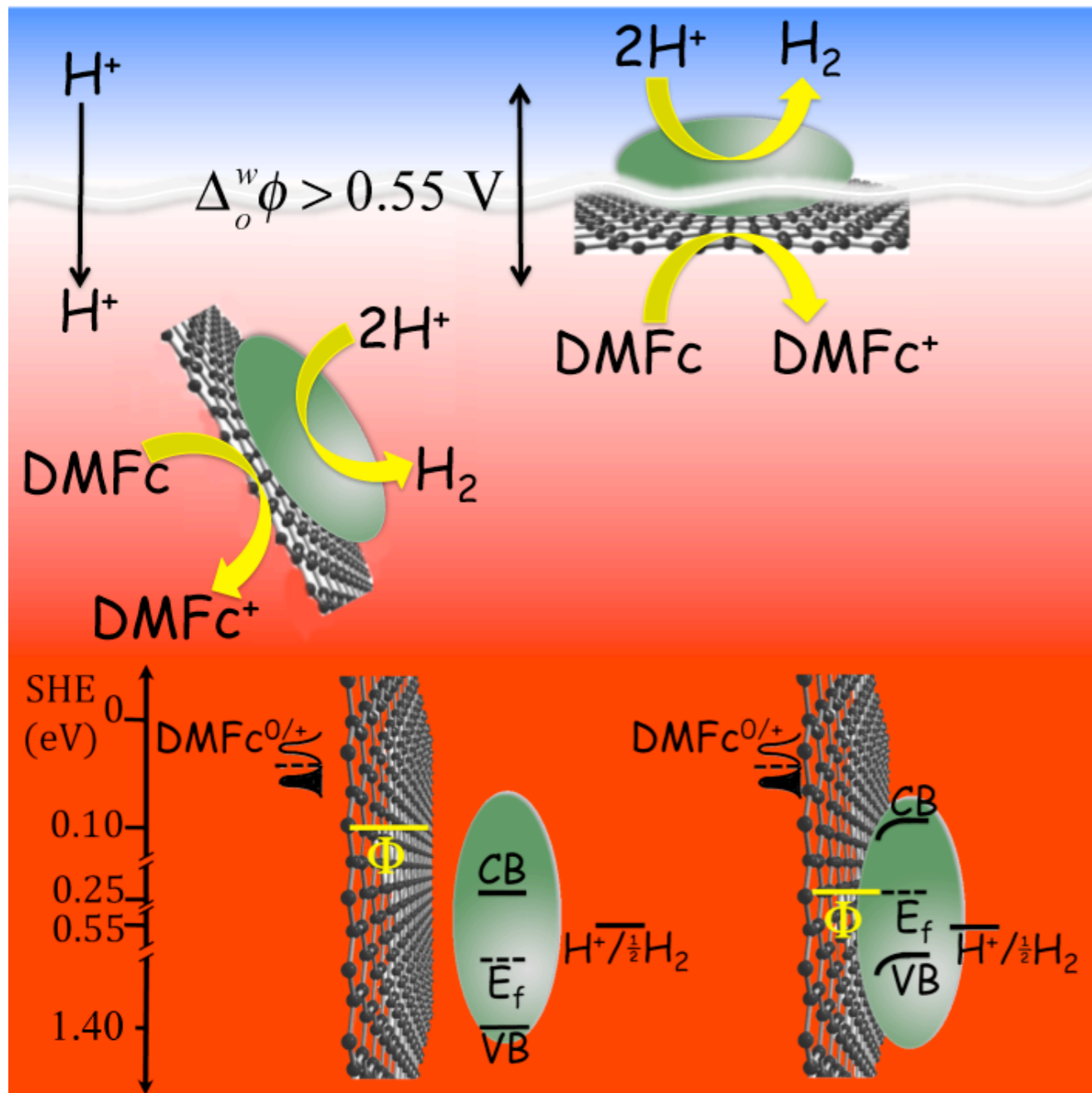


# Carbon supported MoS<sub>2</sub> catalyst



- (a) SEM image of MoS<sub>2</sub> on mesoporous carbon nanoparticles, magnification 28.6 k  
(b) SEM image of MoS<sub>2</sub> on mesoporous carbon nanoparticles, magnification 101.5 k.  
(c +d) TEM + EDX analysis images of MoS<sub>2</sub> on mesoporous carbon showing uniform coating of Mo and S on the carbon.  
(e) High resolution TEM of MoS<sub>2</sub> on mesoporous carbon (arrows indicate the location of MoS<sub>2</sub>).

# MoS<sub>2</sub>-catalysed Hydrogen Production



# Solar energy is also a chemical challenge...



Merci pour votre attention

Text

