ÉCOLE POLYTECHNIQUE
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Hydrogen Production by Solar Photolysis of Water

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Our planet - sunlight and water
=> hydrogen + oxygen => energy!

Ideal! - but to be realistic:

The "Solar Constant" is 1.37×10^{3} W/m^2

So Earth receives 1.2×10^{17} W insolation or 1.56×10^{18} kWh/year in total.

1 kg hydrogen = 39.4 kWh

So sunlight represents 3.9×10^{16} kg H_2

Typical solar cell efficiency is 10% so midday electric power is 100 W/m^2,

Annual energy harvest (N. Europe) 80kWh/m^2 , or 2 kg. H_2

But 0.13% of earth's surface covered with PV panels of 10% efficiency = present world total energy demand!

It's a matter of scale and economics!

Present-day PV is too costly - is there an alternative?

Hydrogen generation by solar photolysis of water

remains the prime target of research in photoelectrochemistry.

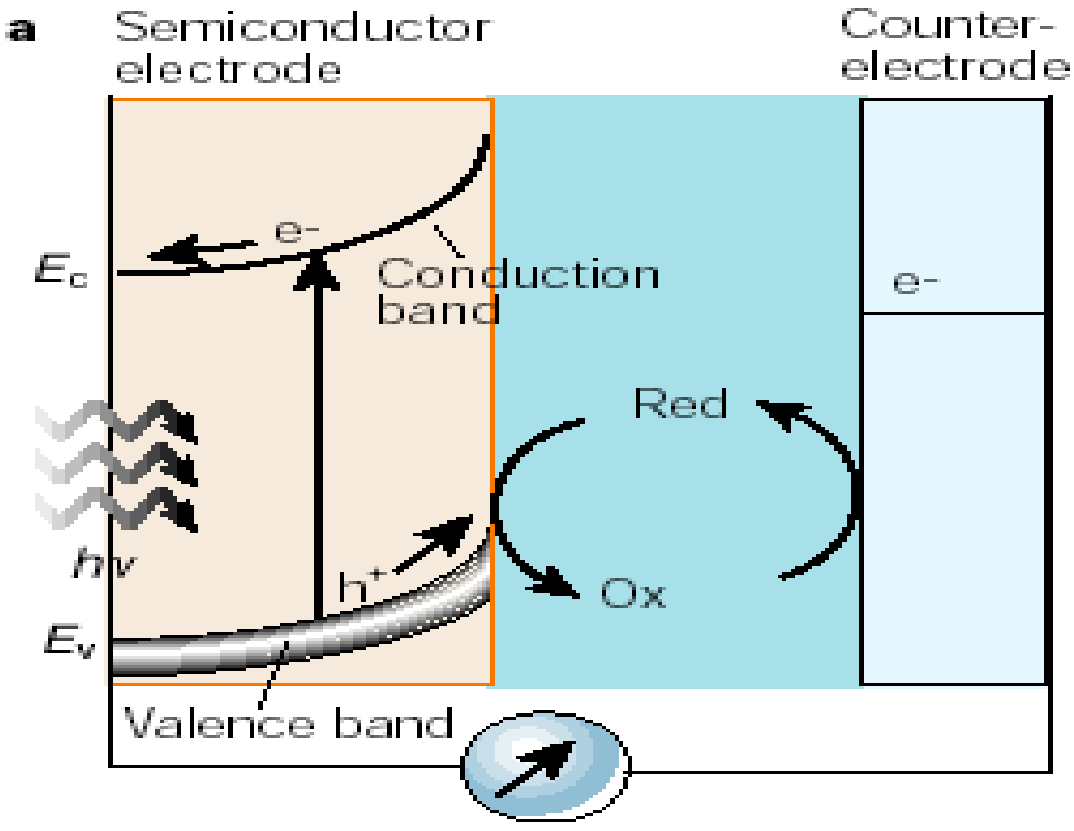
However electrolysis of water requires $\Delta V > 1.23$ V (1.45V adiabatic), i.e. three silicon PV cells in series

There are two options:

1. **The brute force approach: use solid state semiconductor PV arrays, electronic power management systems matched to a central electrolyser..**

2. **The direct water decomposition by photoelectrochemical cells - can it compete? Possible advantages, - cheap basic materials, low cost processing, simple system.**

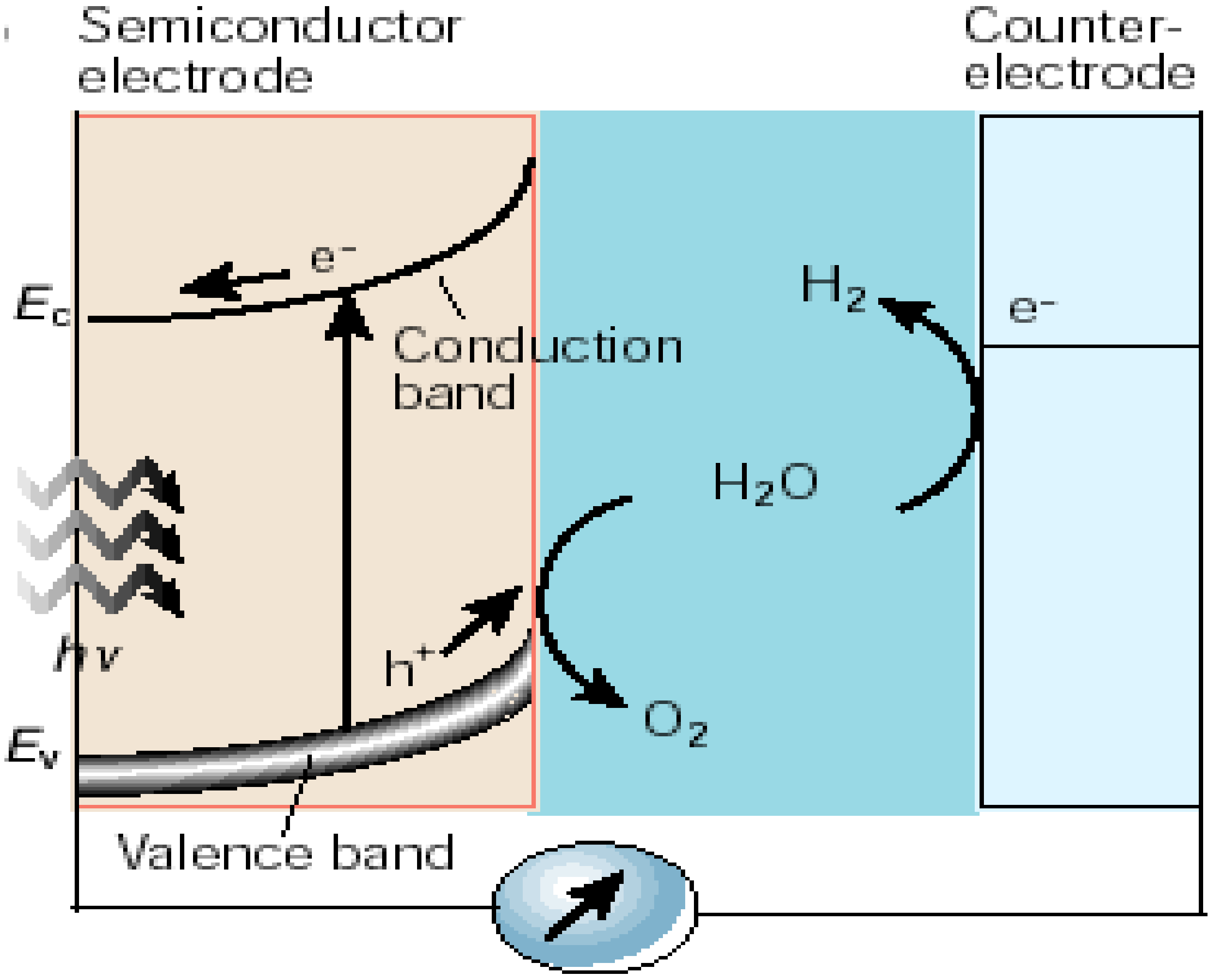
Regenerative photoelectrochemical cells



H. Gerischer J.Electrochem Soc. 1966 113, 1174

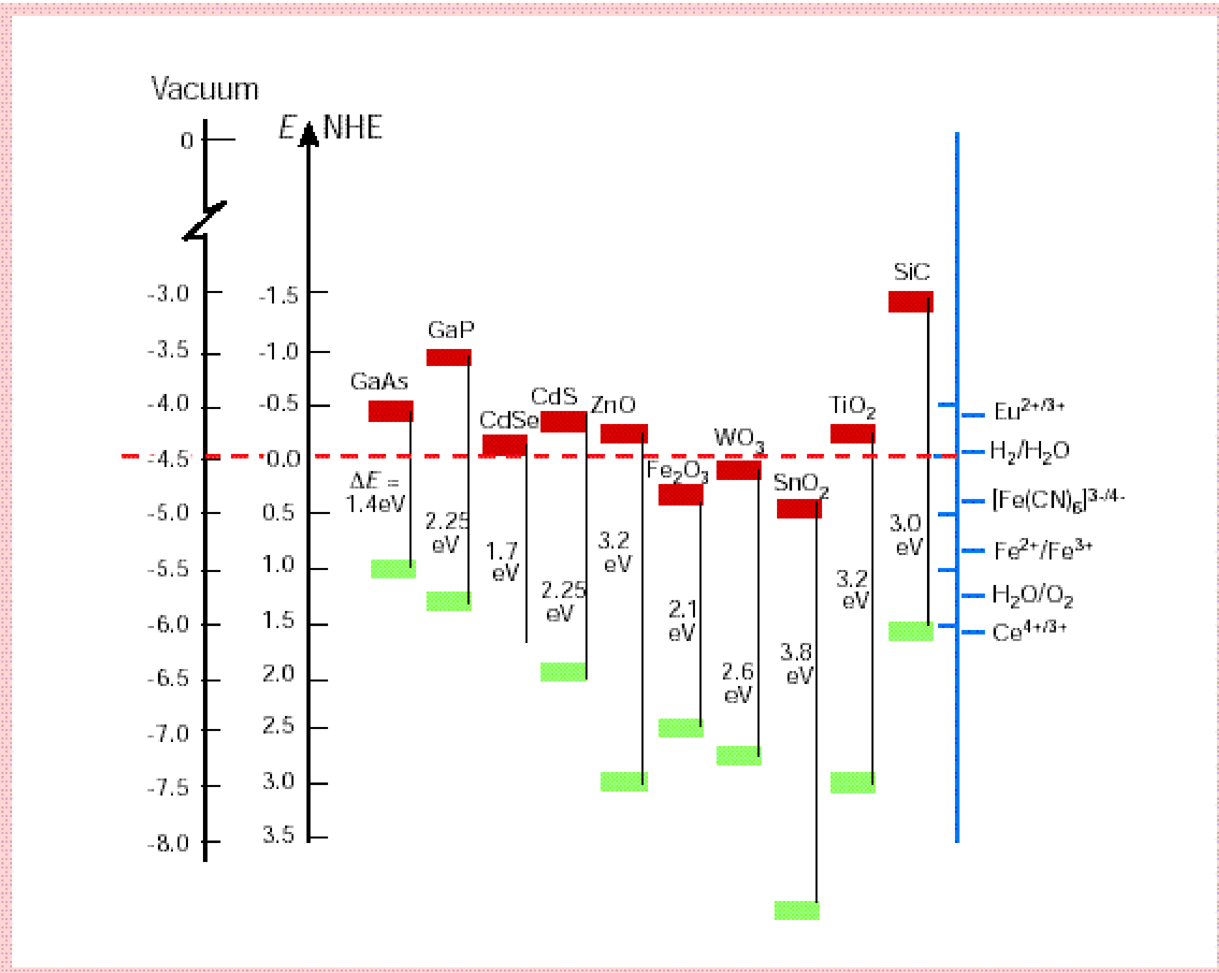
Generation of hydrogen by photoelectrolysis of water

(n-type semiconductor electrode)



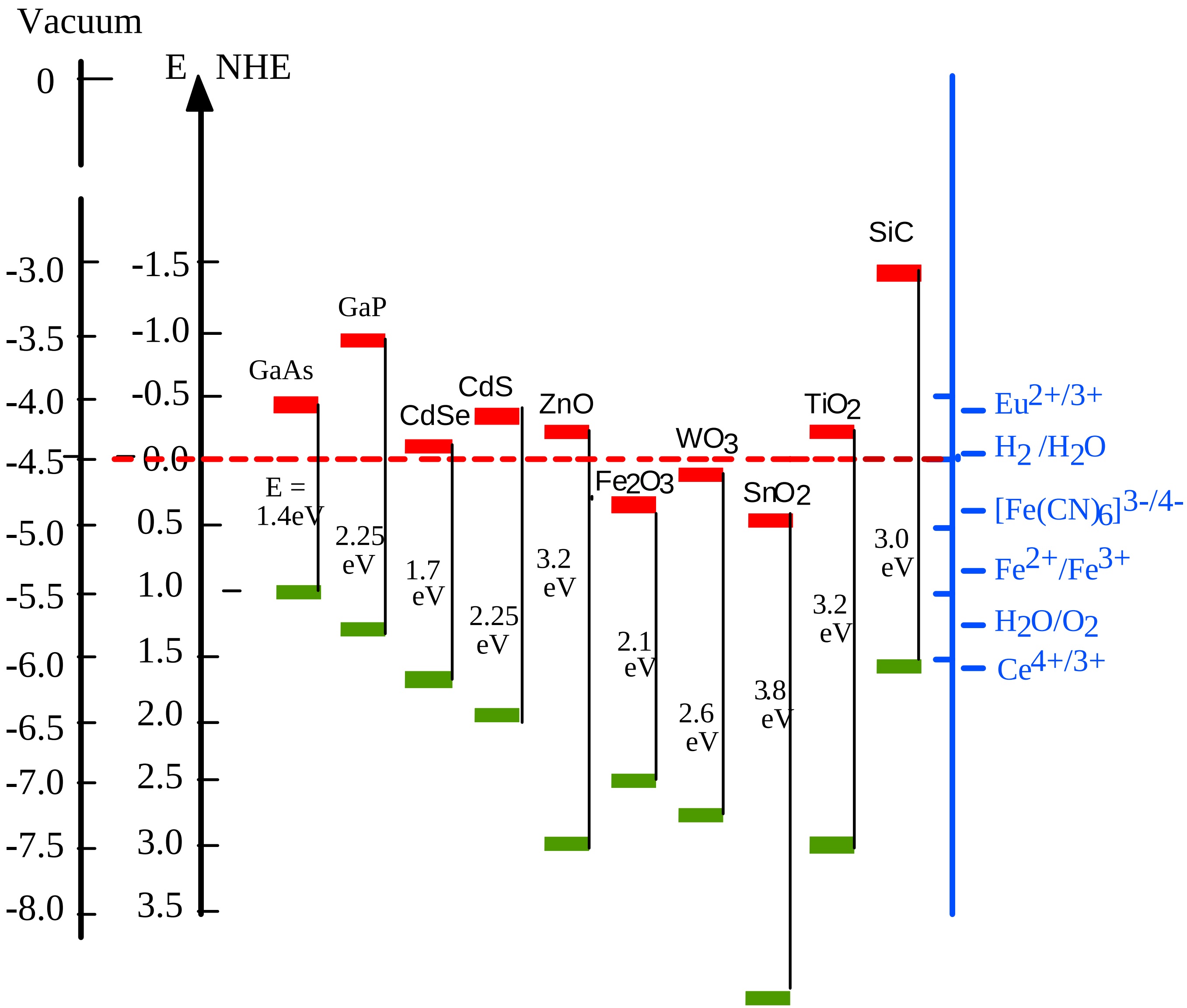
Semiconductor - electrolyte junctions -photoelectrochemistry

The photovoltaic effect requires a contact between two materials with different conduction mechanisms -two semiconductors, n- and p-type, a metal and a semiconductor (Schottky) or a semiconductor and an electrolyte in photoelectrochemistry (Becquerel, 1839)

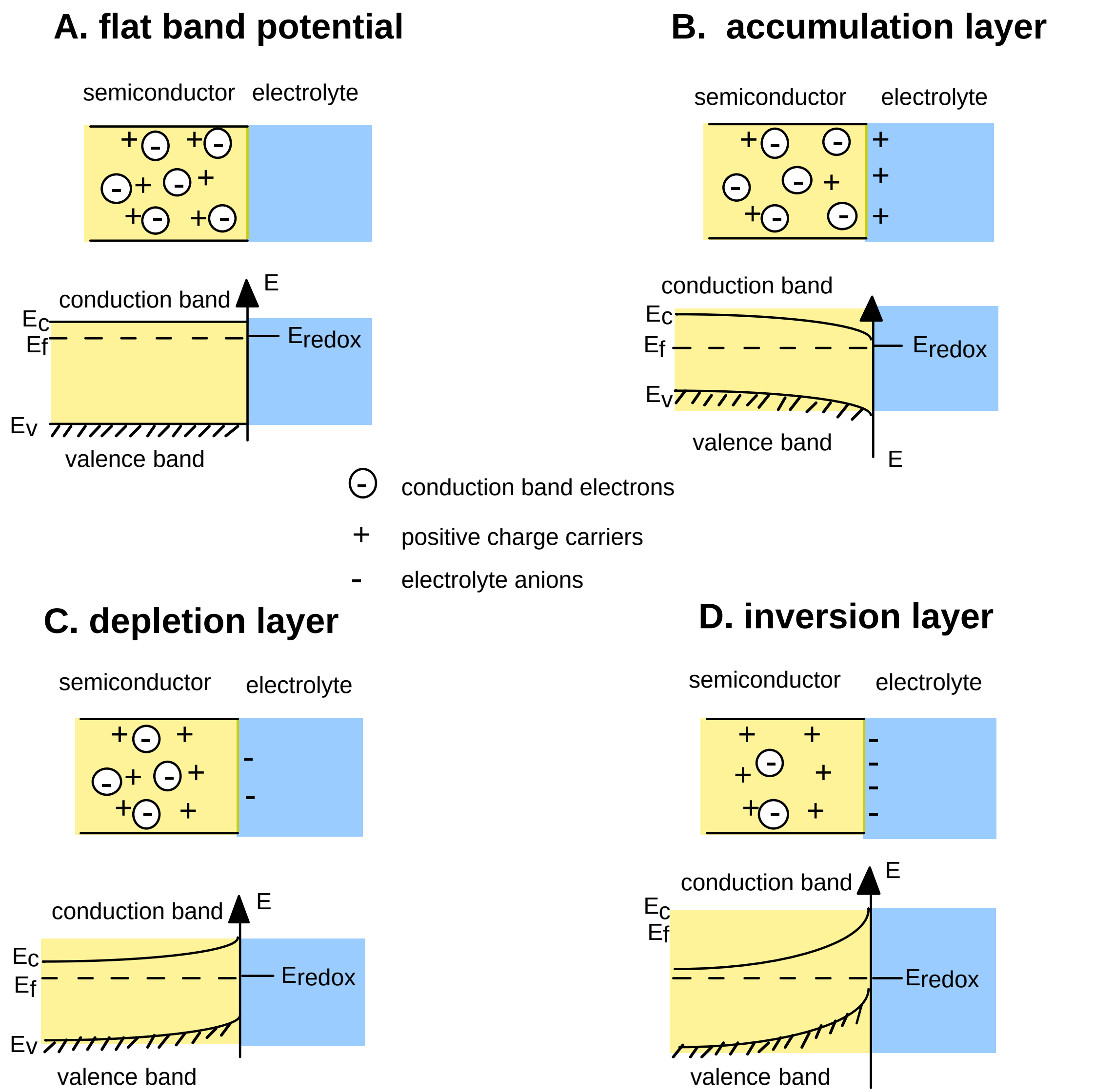


Narrow band-gap semi-conductors whose photo-response matches the solar spectrum are in general unstable in contact with electrolytes - so a sensitization method is required for wide band-gap, stable semiconductors.

Semiconductor energy levels



Bands and potentials



Efficiency of direct photolysis

$$I_{SC} = \int_0^\infty IPCE(\lambda)\, I_{sun}(\lambda)\, d\lambda$$

$I_{sun}(\lambda)$ = spectral intensity of solar emission

If it is assumed that all the photons emitted by the sun below 387.5 nm (band gap of anatase is 3.2 eV) are converted by the TiO_2 into electric current the photocurrent would be <u>0.5 mA/cm^2</u> and the solar to chemical conversion efficiency <u>0.7%</u> in the absence of any applied bias.

First report of a dye-sensitised photoeffect on an illuminated semiconductor - Moser, Vienna, 1887.

Notiz über Verstärkung photoelektrischer Ströme durch optische Sensibilisirung.[1]

Von Dr. James Moser.

(Aus dem physikalisch-chemischen Laboratorium der Wiener Universität).

(Vorgelegt in der Sitzung am 23. Juni 1887.)

Ich erlaube mir mitzutheilen, dass ich die von Herrn E. Becquerel entdeckten photoelektrischen Ströme erheblich dadurch verstärken konnte, dass ich die beiden chlorirten, jodirten oder bromirten Silberplatten in einer Farbstofflösung, z. B. Erythrosin, badete.

Beispielsweise war zwischen zwei chlorirten Silberplatten die elektromotorische Kraft im Sonnenlicht 0·02, zwischen zwei anderen in gleicher Weise behandelten, aber gebadeten Platten 0·04 Volt.

Bisher sind nur an jodirten Platten von Herrn Egoroff elektromotorische Kräfte beobachtet, und zwar bis $^1/_{15}$ Volt. Ich konnte bei jodirten und bromirten Platten durch Baden in Erythrosin $^1/_4$ Volt erreichen.

Ich halte es für meine Pflicht, schon an dieser Stelle Herrn Max Reiner, der mir bei diesen Versuchen assistirt, meinen verbindlichsten Dank auszusprechen.

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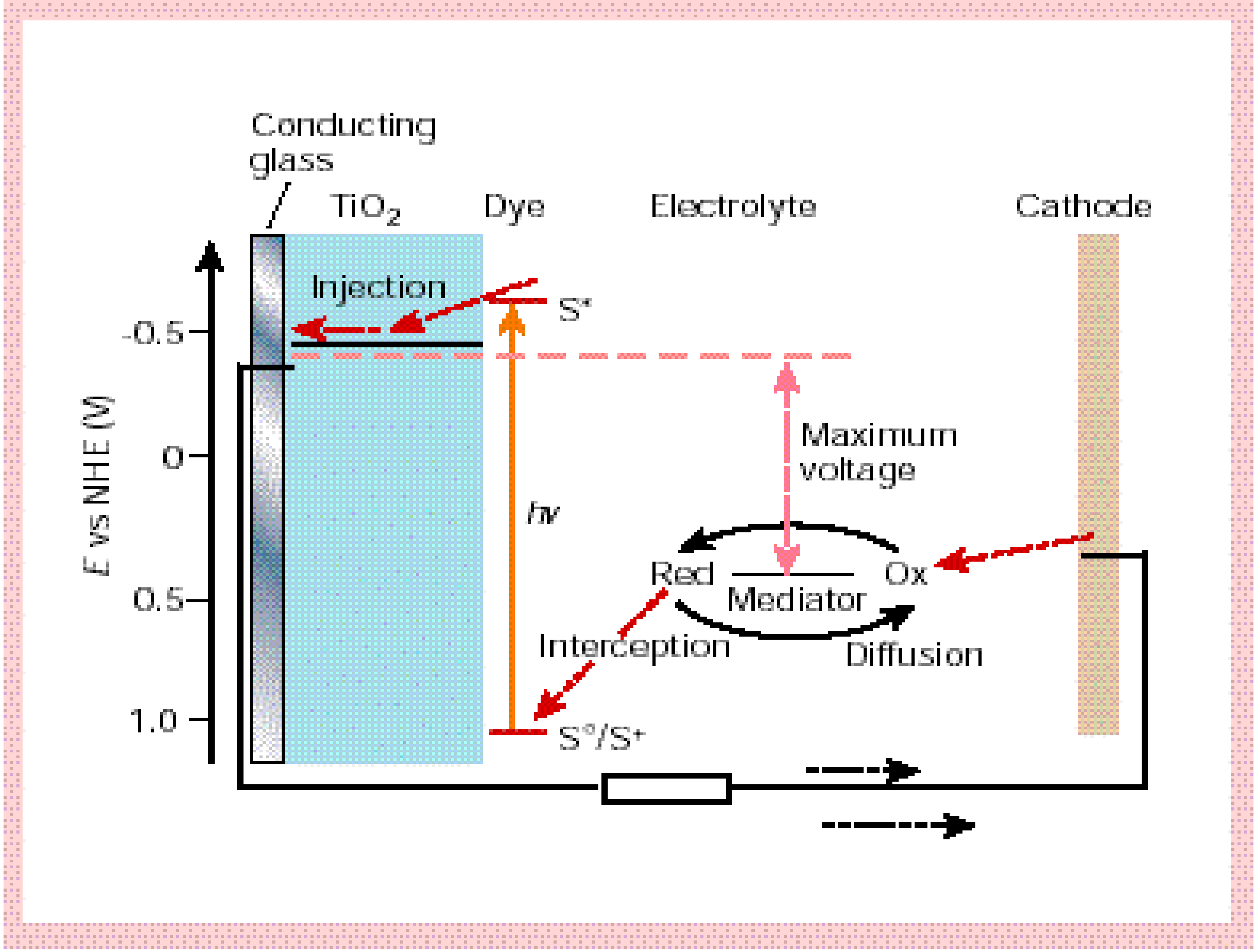
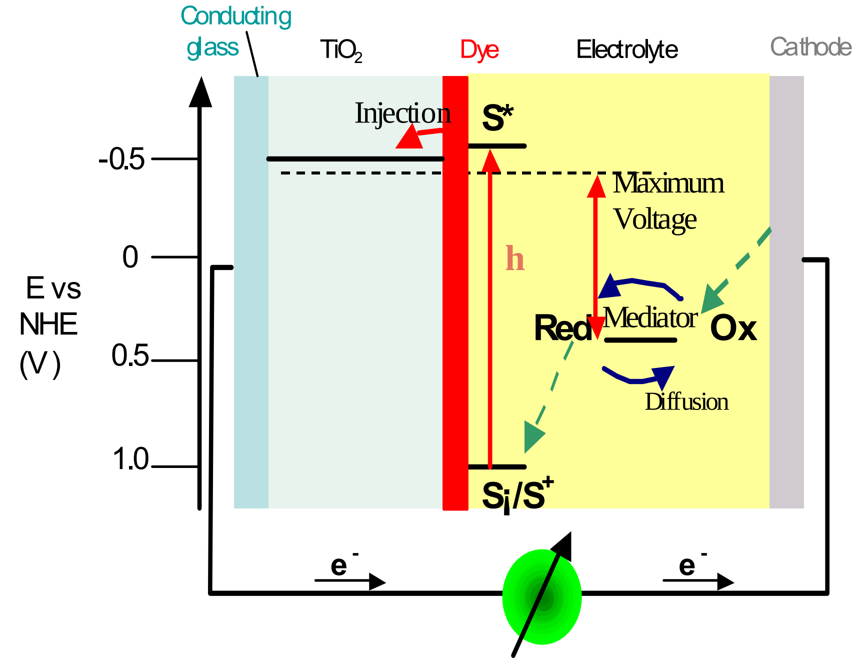
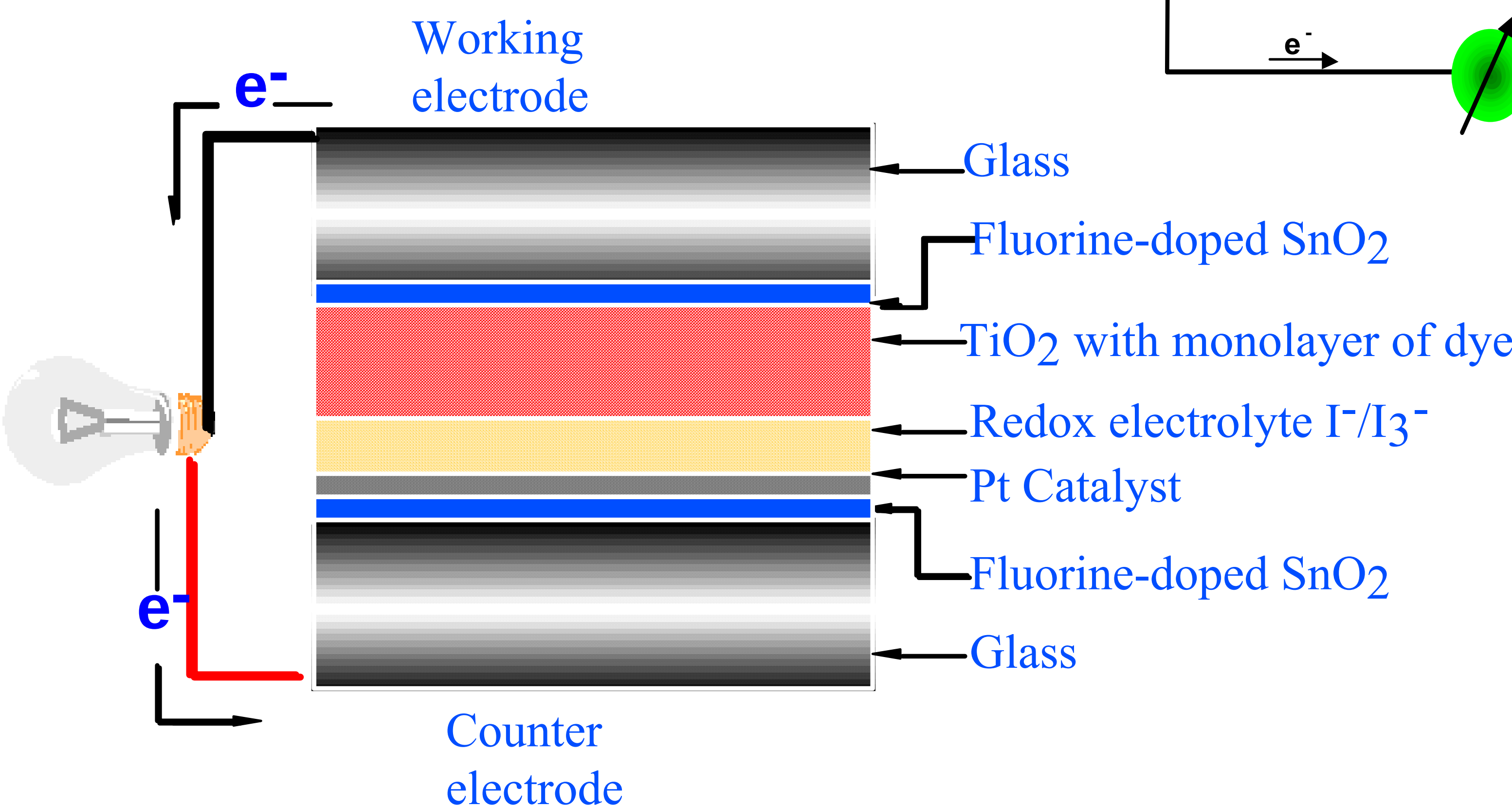
[1] Akadem. Anzeiger Nr. XVI.

Photoelectrochemical processes in a dye-sensitized solar cell.

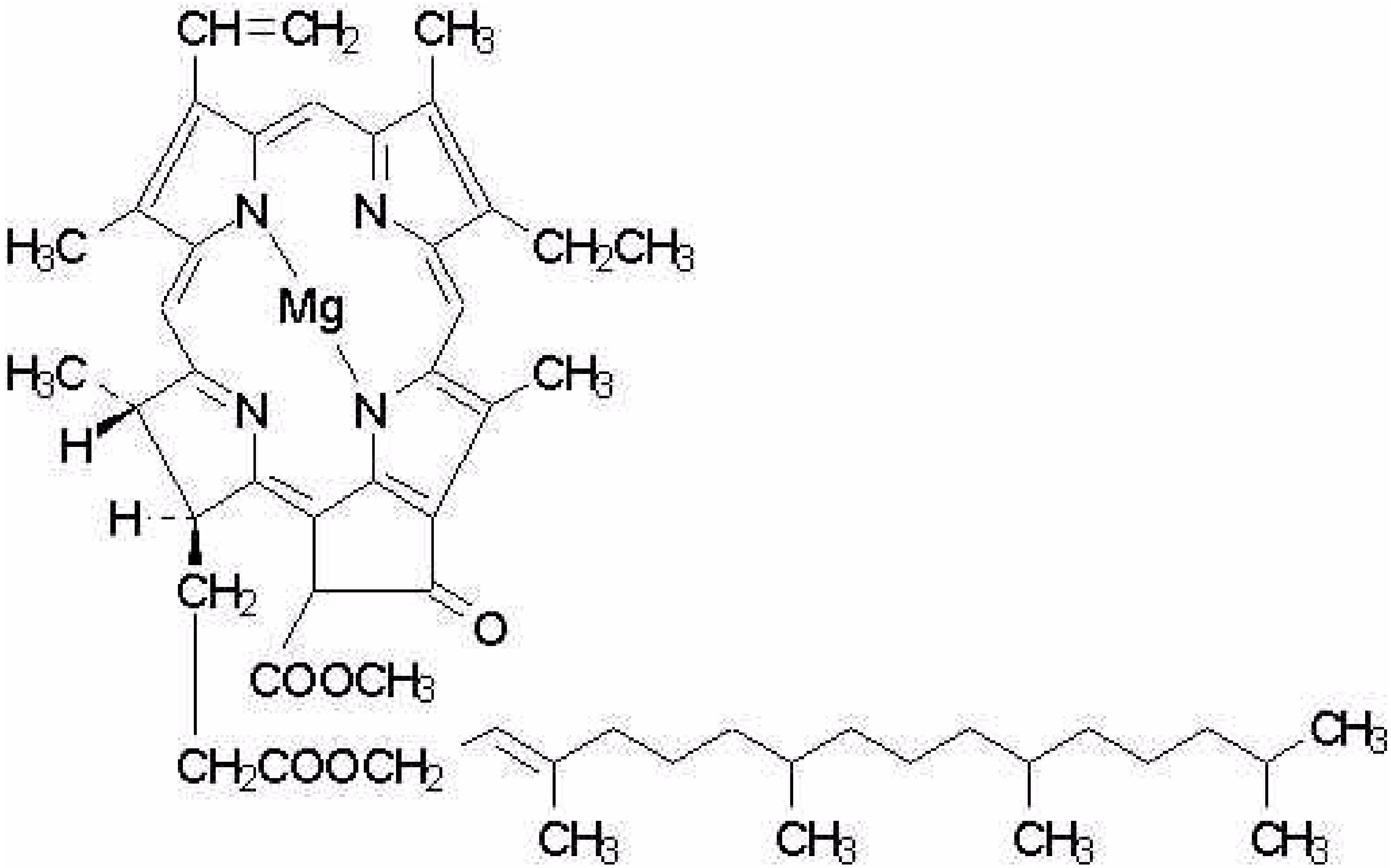


Photochemical energetics and structure of DSC

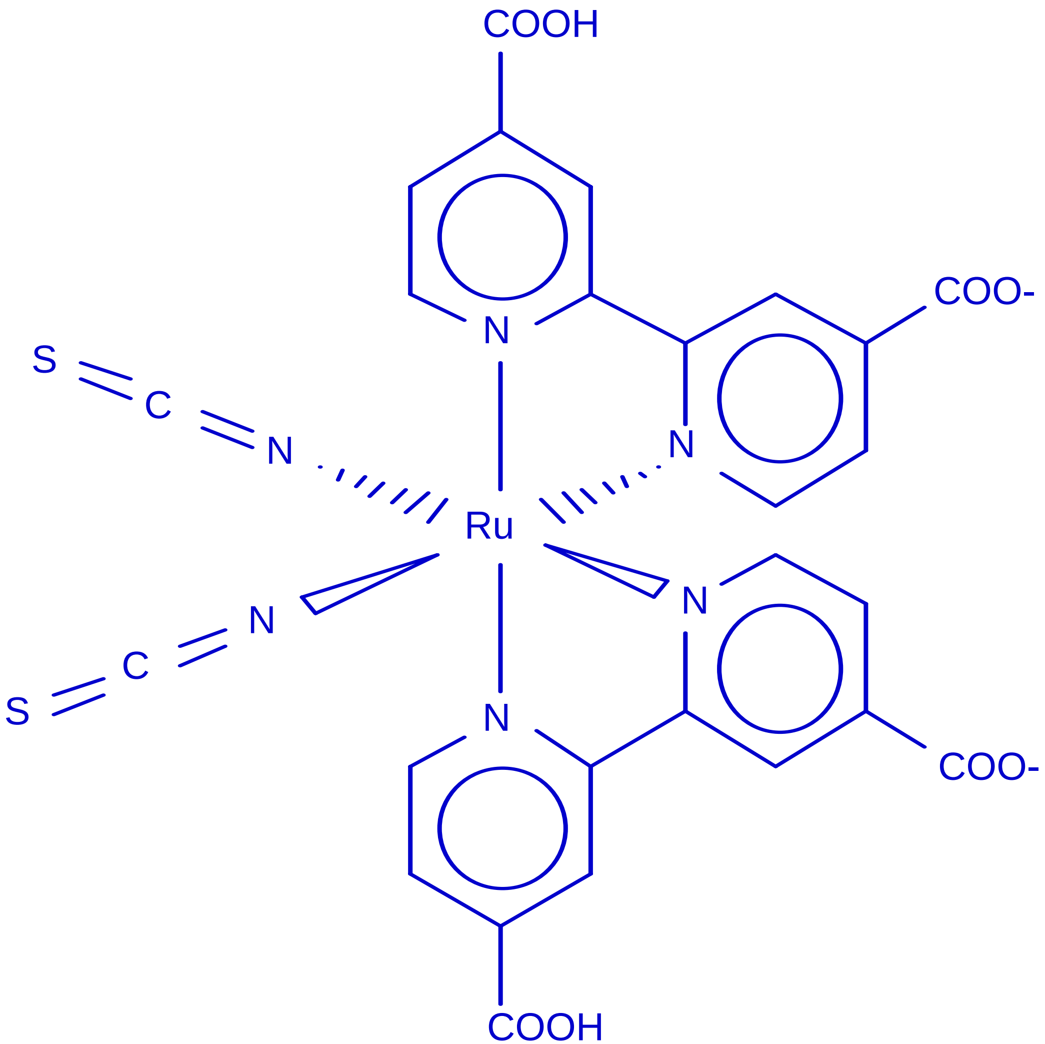




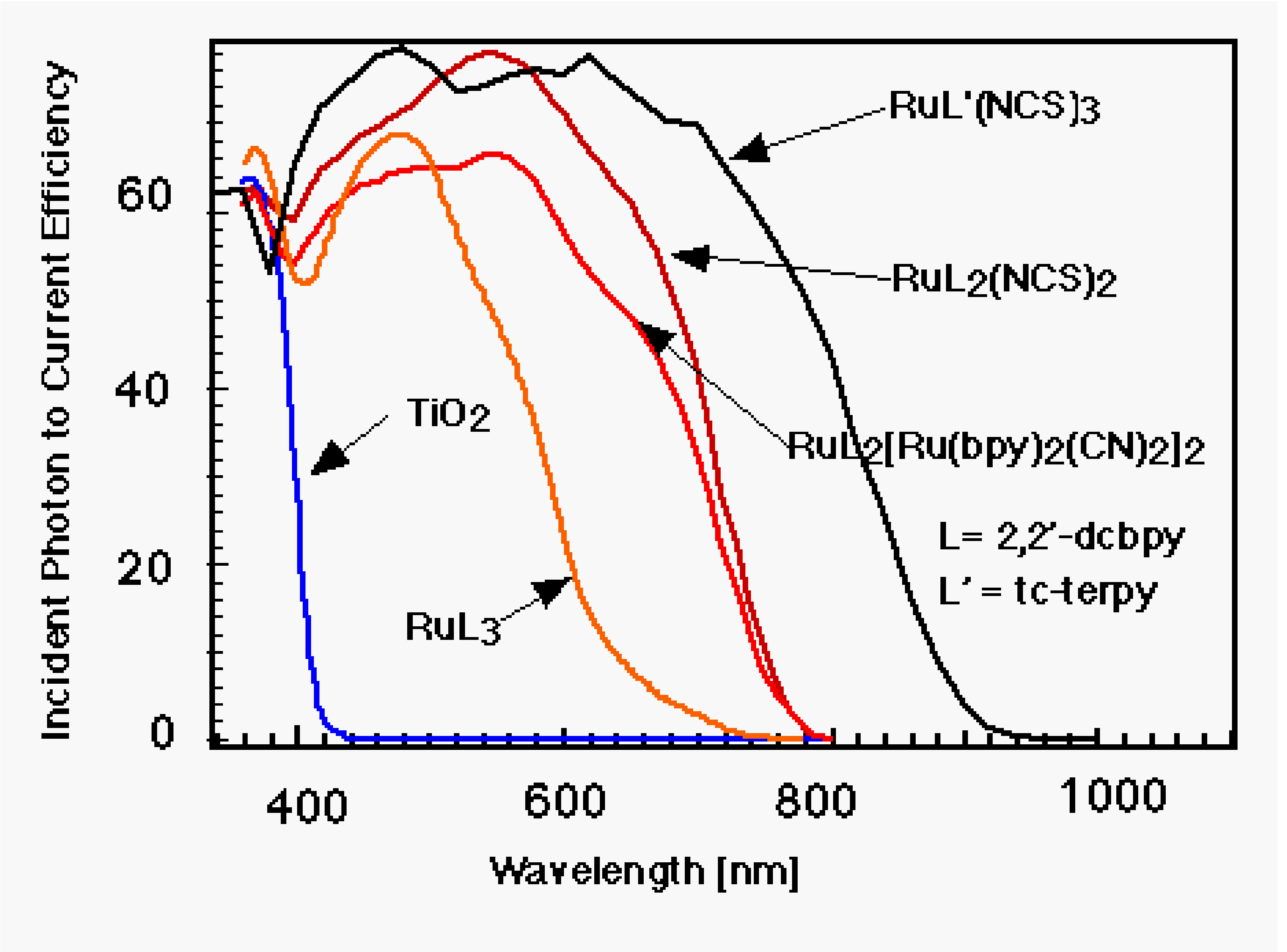
The natural prototype photochemical dye - chlorophyll



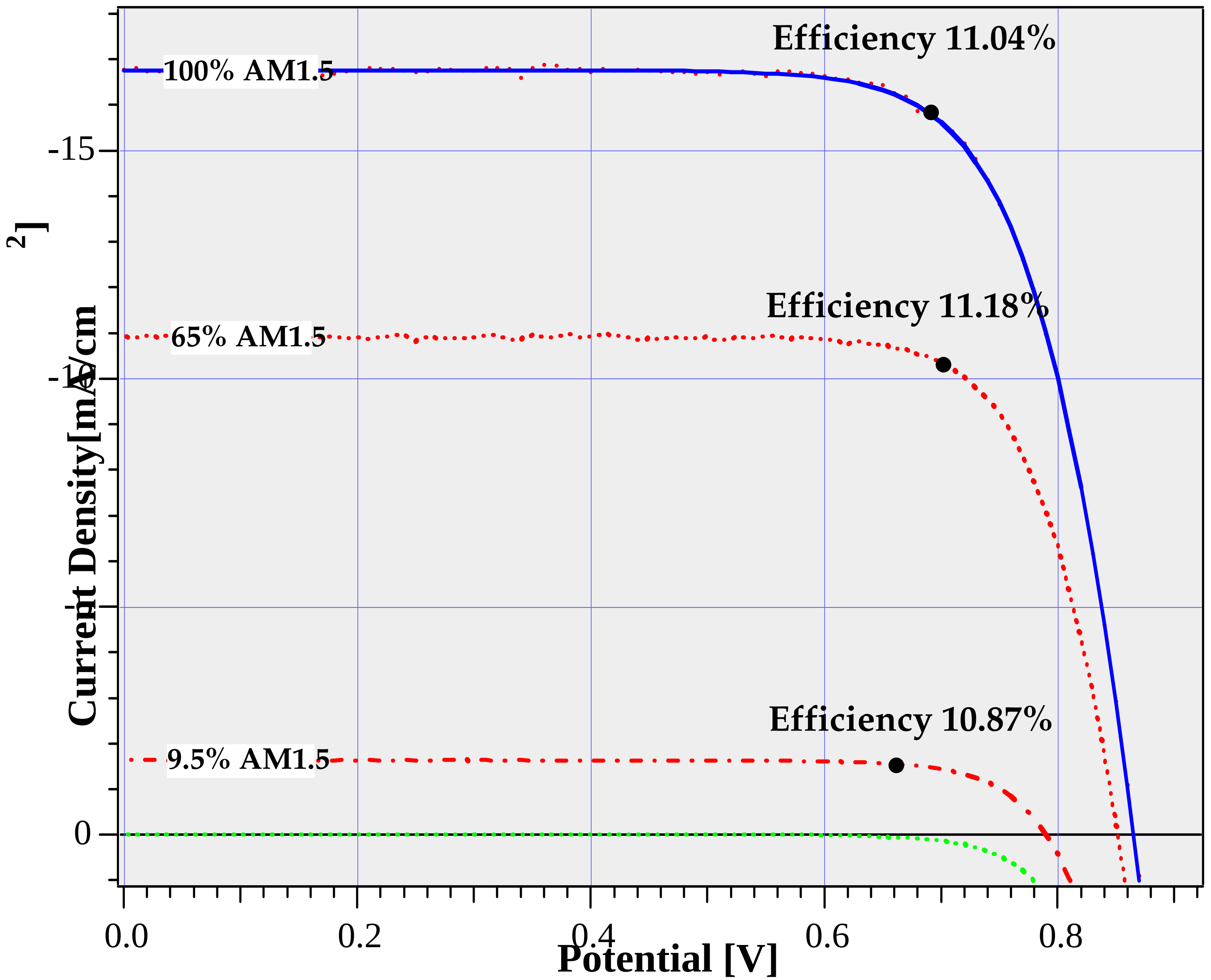
Standard dye for photoelectrochemical cell development - the EPFL « N3 » dye



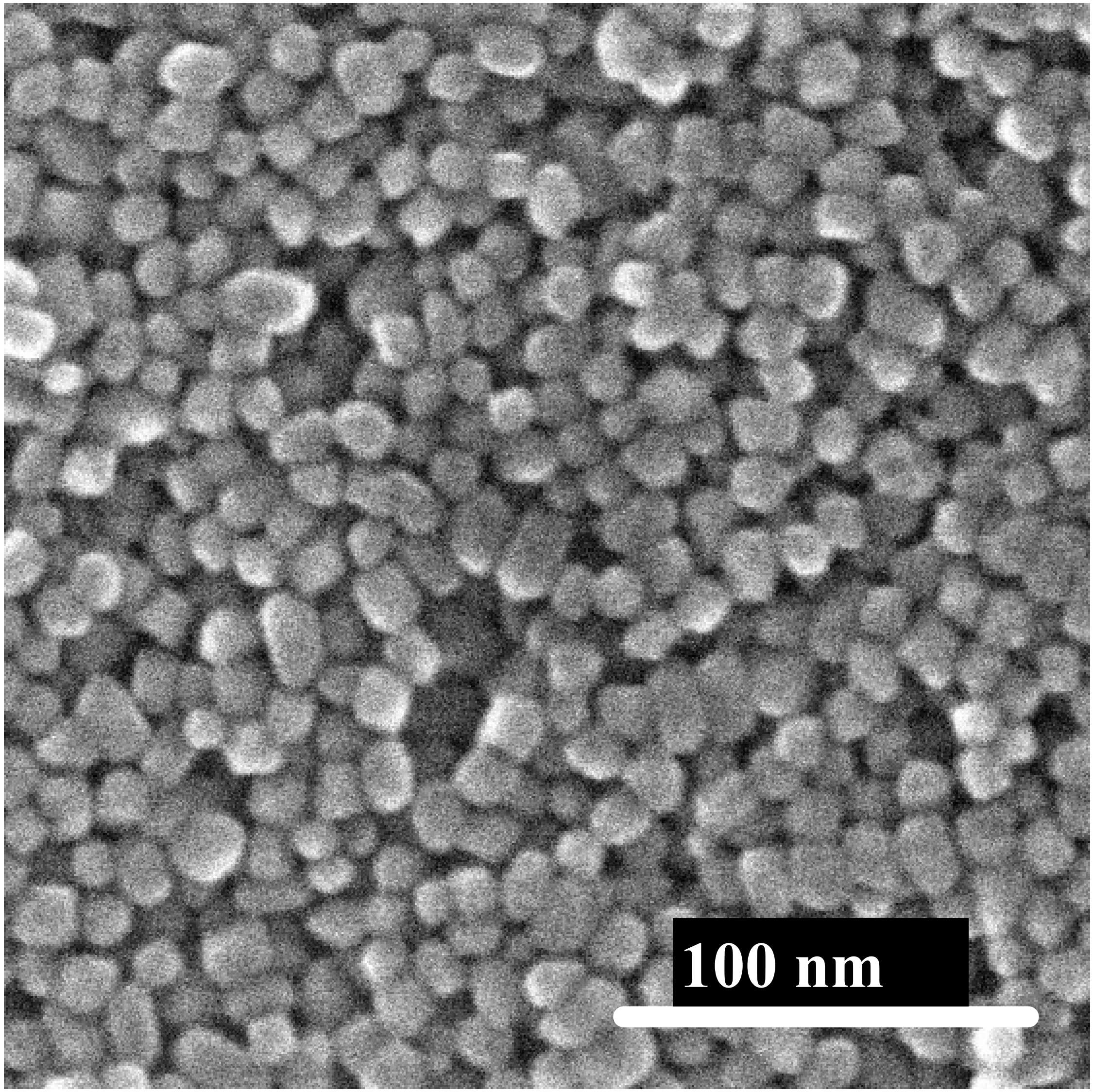
Optical absorption of titania - development of sensitizing dyes.



Characteristics of dye-sensitized solar cell

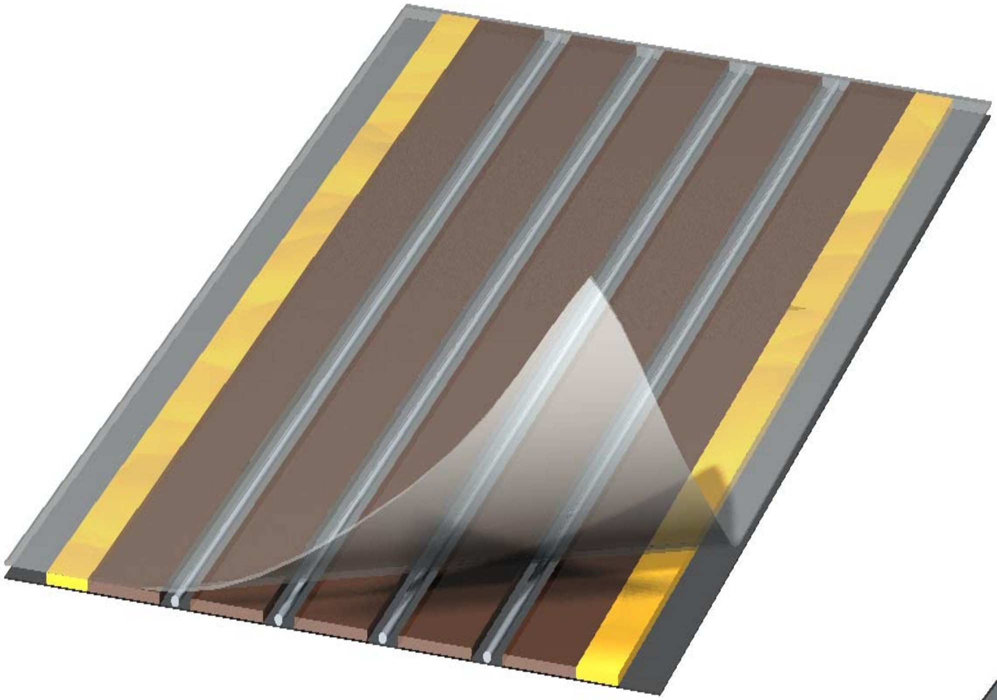


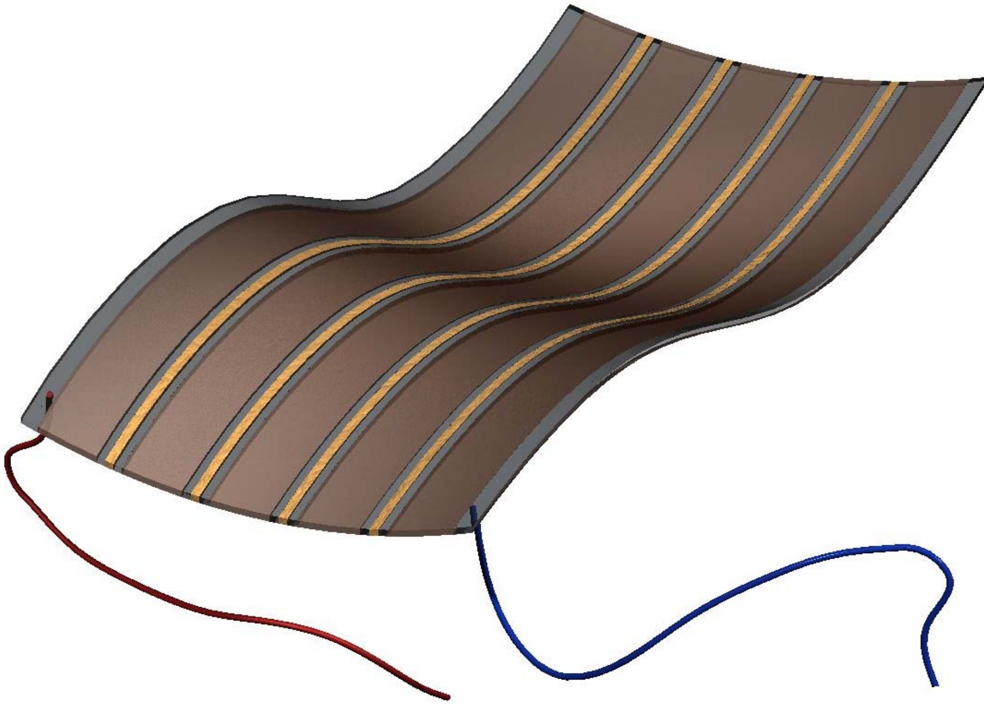
SEM image of a mesoporous titania film.



Product concept - flexible cells

(Konarka Inc., USA)





Product concept - flexible cells

(Hitachi-Maxell, Japan)

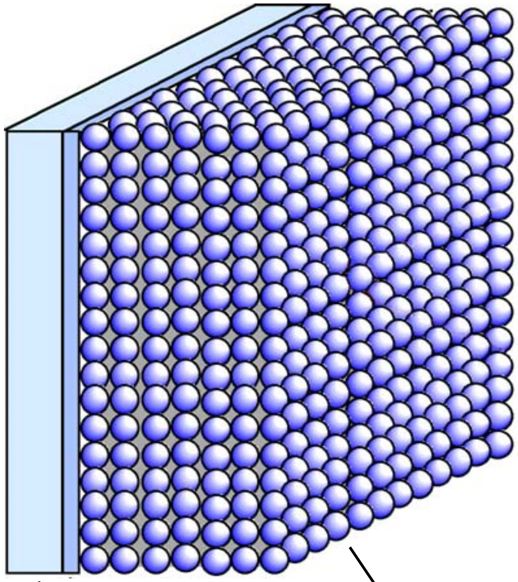
Outdoor installation -
CSIRO, Newcastle NSW, Australia

(Sustainable Technologies International, Australia)

Strategy for solar hydrogen

- **Water photolysis on oxide semiconductor electrodes**
- **Dye-sensitized tandem cell to provide voltage boost for water cleavage by visible light**
- **Relevance of hydrogen generation by solar photoelectrolysis of water to future hydrogen economy**

Nanocrystalline oxide photoanode



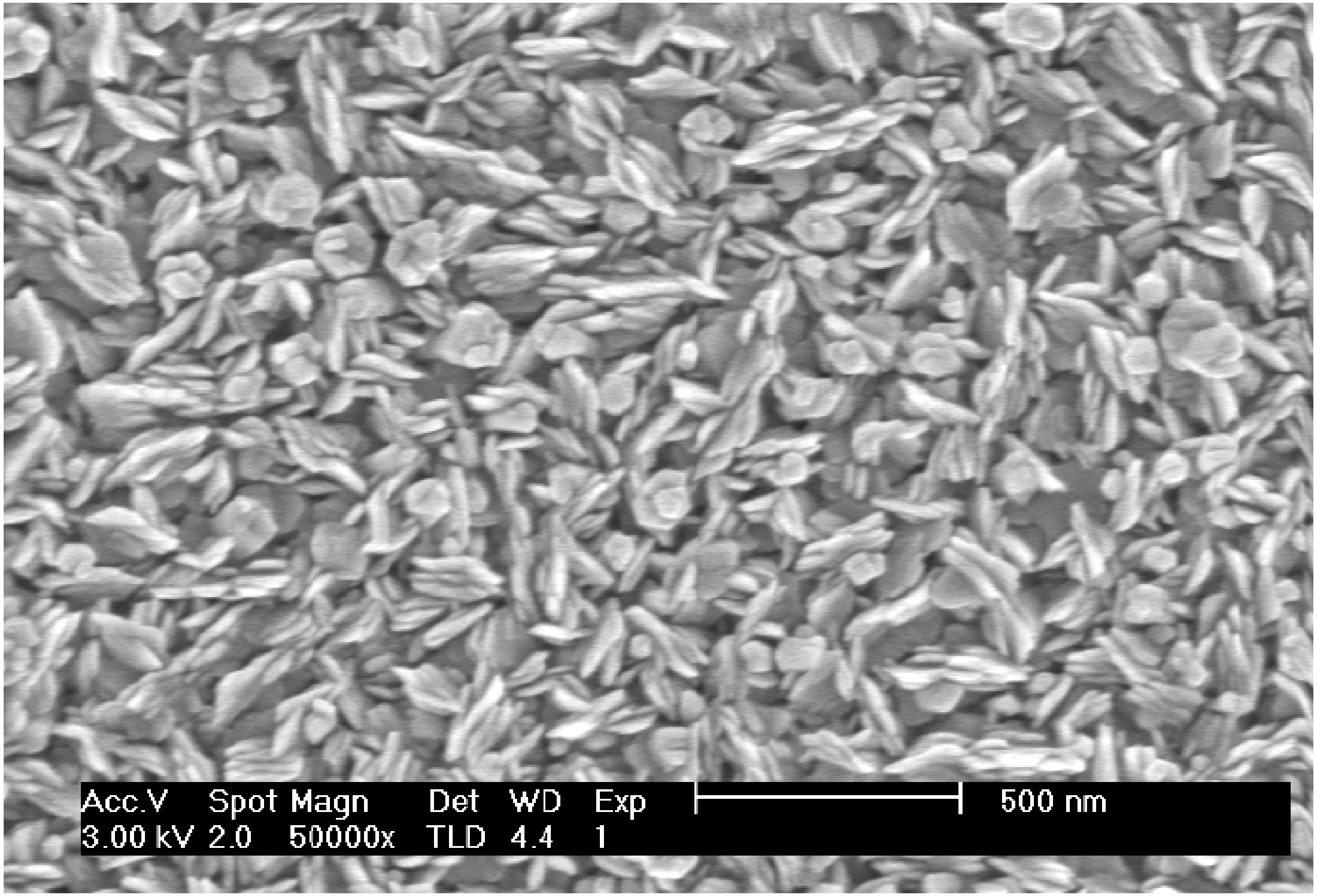
mesoscopic $\mathbf{WO_3}$ or $\mathbf{Fe_2O_3}$ film

Advantage of nanocrystalline oxide electrodes:

1) translucent electrode - avoids light scattering losses

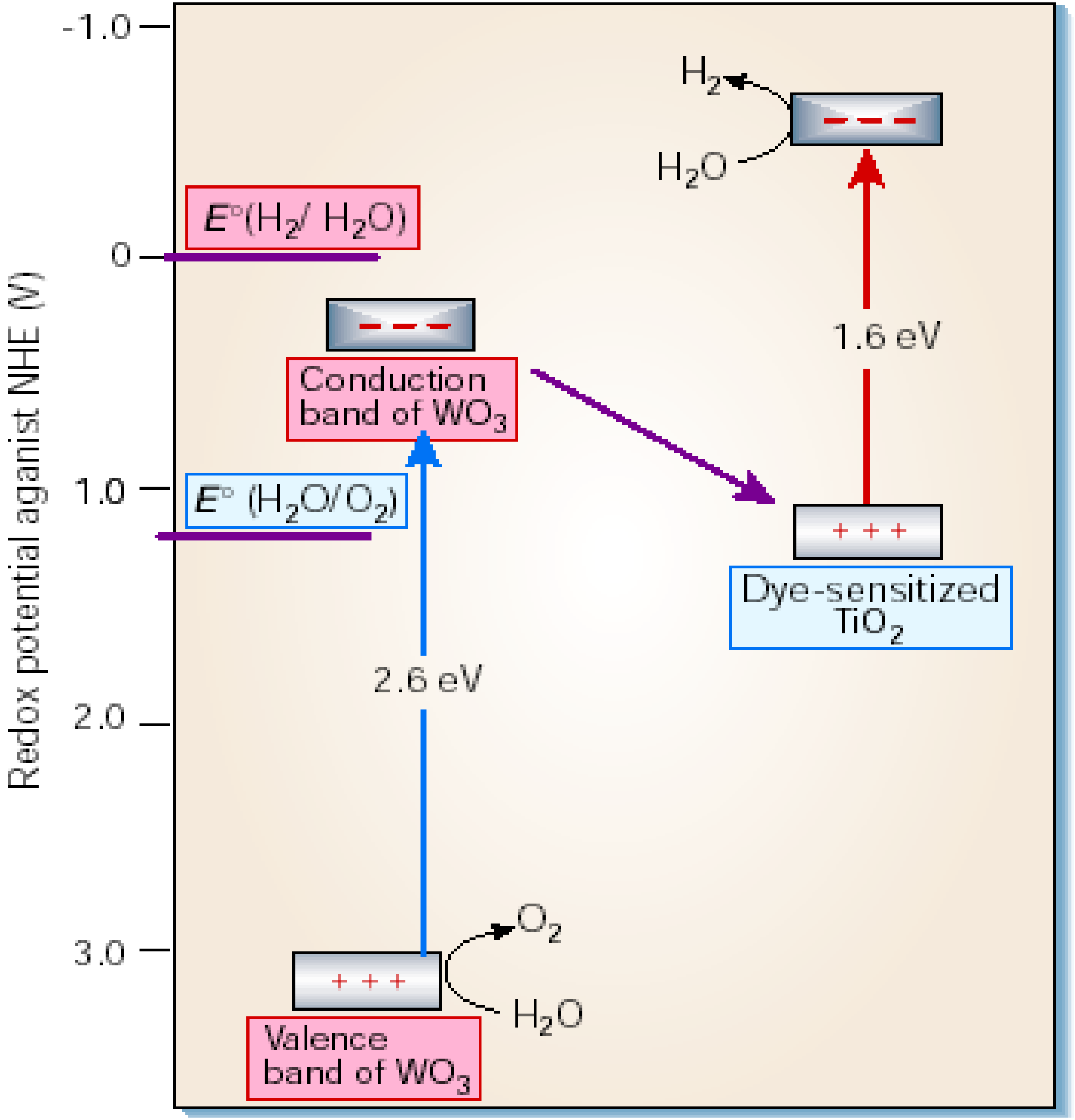
2) Small size is within minority carrier diffusion length, the valence band holes reach the surface before they recombine.

Ferric oxide (Fe_2O_3)- SEM image of spray-deposited electrode for water photolysis



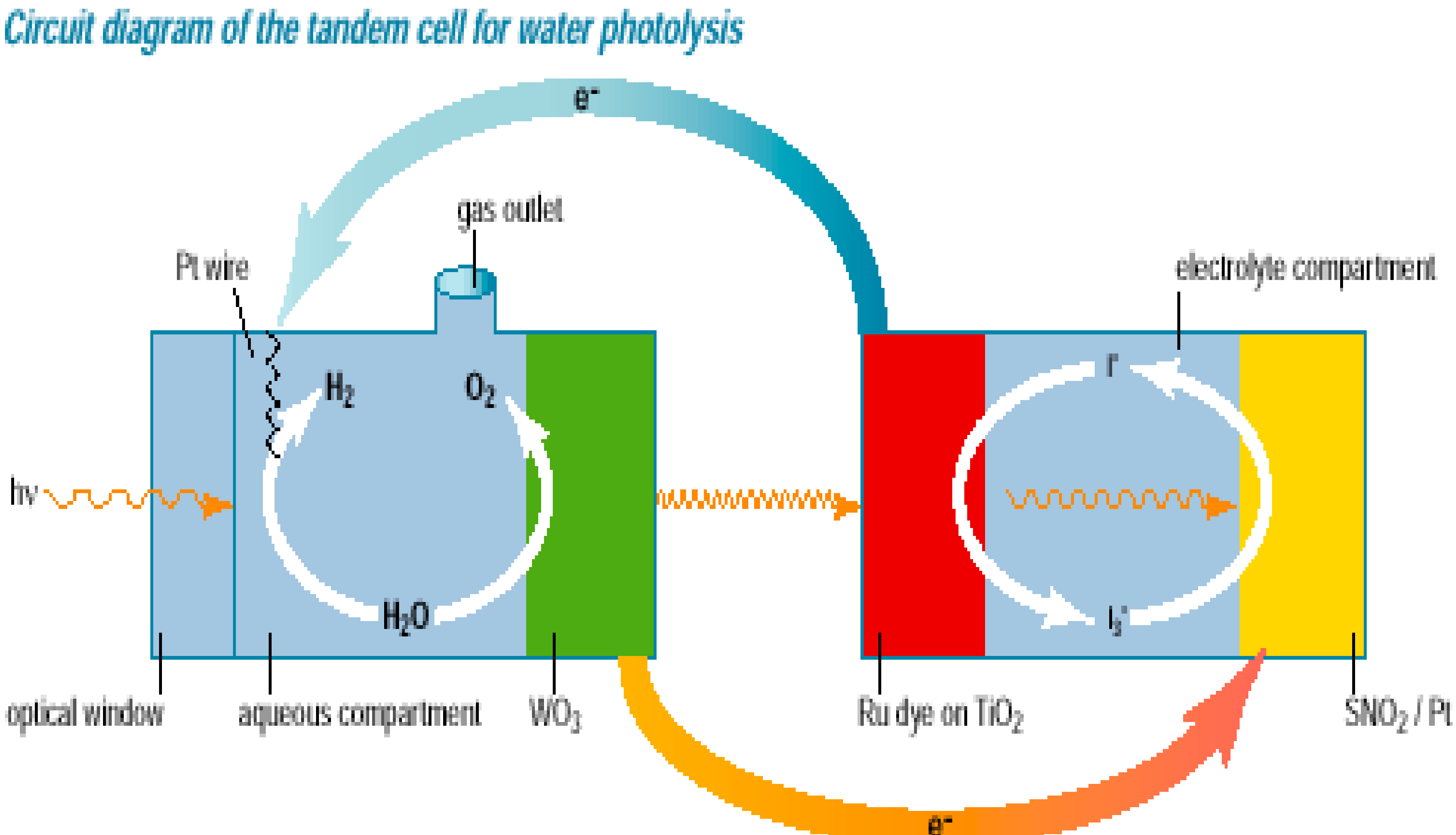
Tandem booster cell with spectral splitting

QuickTime™ and a Graphics decompressor are needed to see this picture.

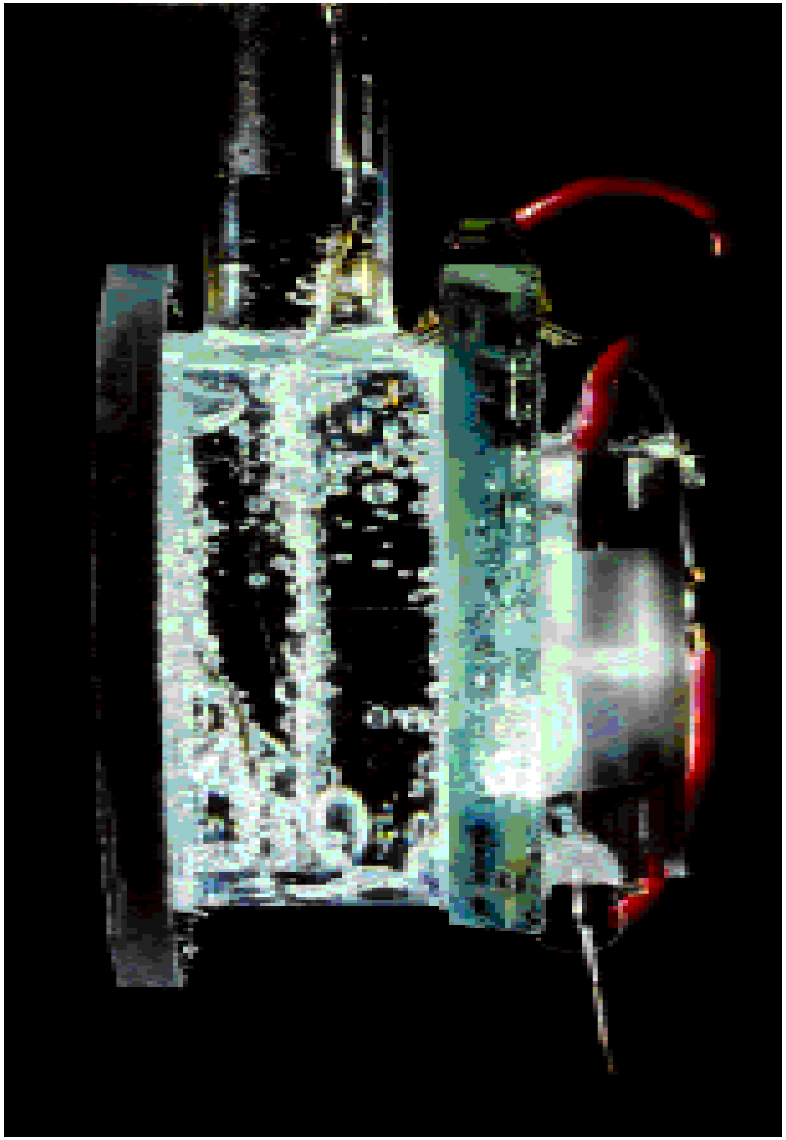


-1.0
0
1.0
2.0
3.0
Redox potential aganist NHE (V)
$E^o(H_2/H_2O)$
$E^o(H_2O/O_2)$
Conduction band of WO_3
Valence band of WO_3
2.6 eV
O_2
H_2O
H_2
H_2O
1.6 eV
Dye-sensitized TiO_2

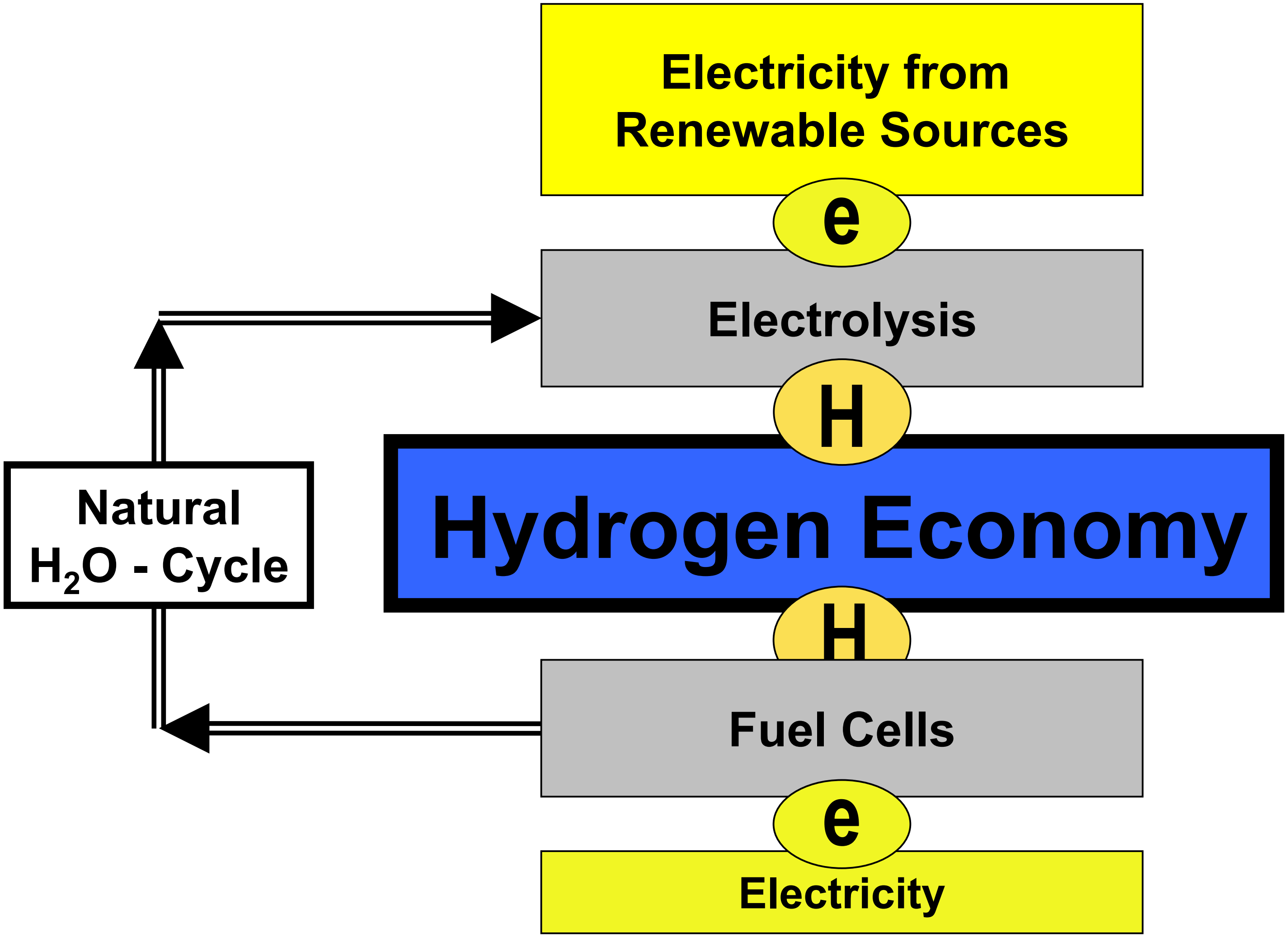
Schematic of tandem photolysis system



Laboratory test cell in operation

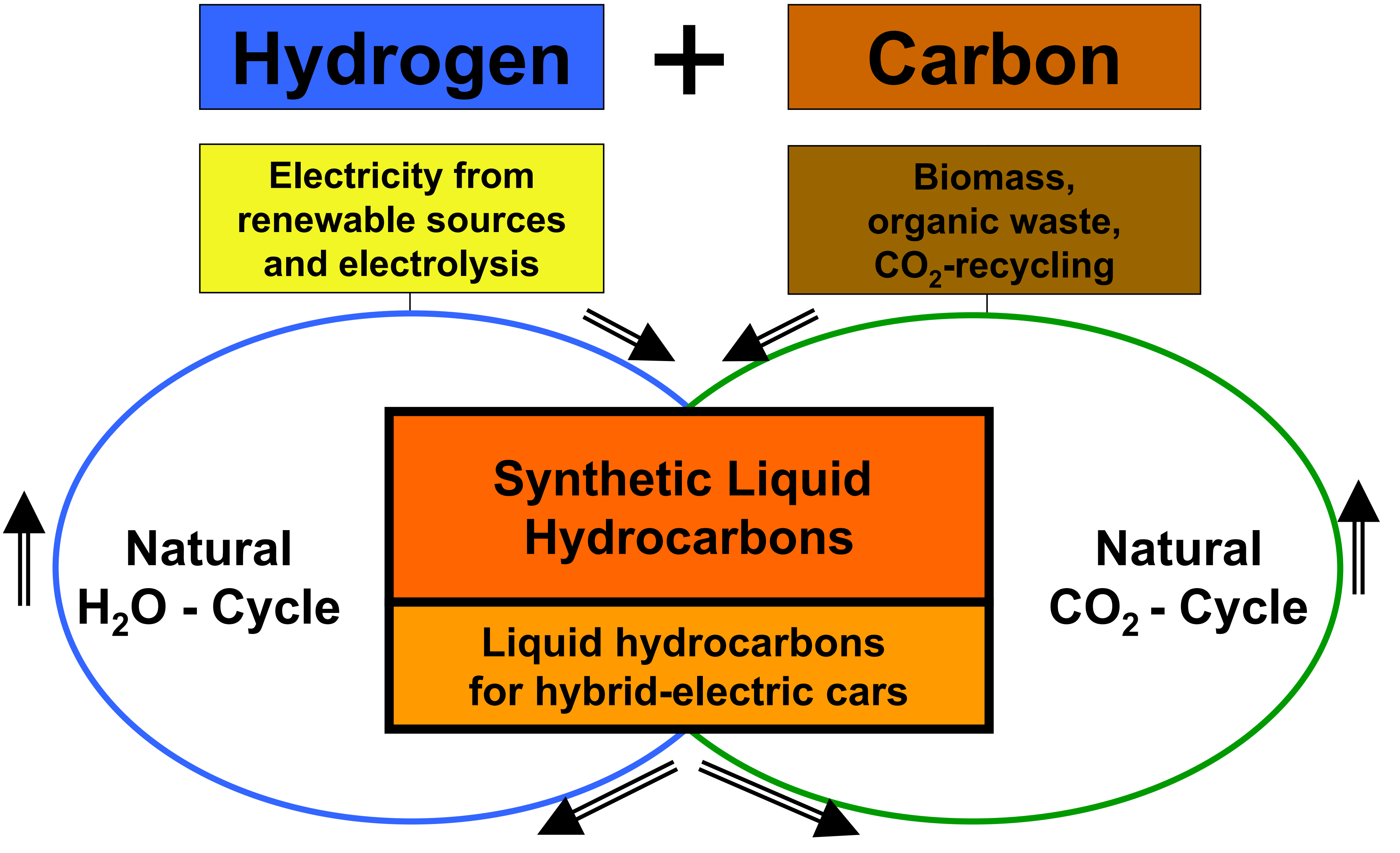


Energy Flow in a Hydrogen Economy



Synthetic Liquid Hydrocarbons

Is this the Future?



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