



Terra



Fuoco

**Conversione dell'energia solare con i semiconduttori**



Acqua



Aria



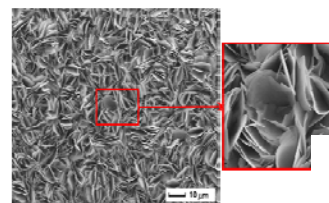
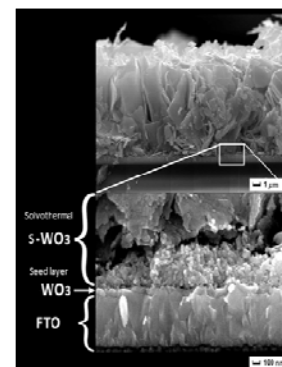
Stefano Caramori

Dipartimento di Scienze chimiche, farmaceutiche ed agrarie dell'Università di Ferrara

# Our Research:



## Transparent Photoelectrochemical Cells



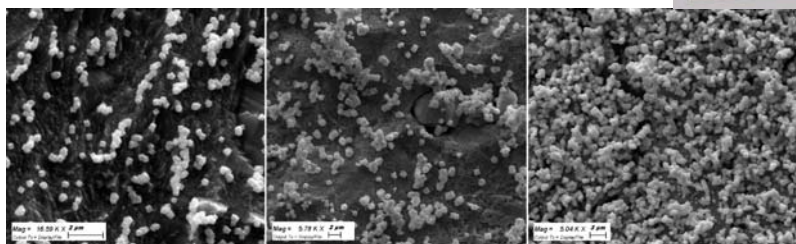
Photoelectrodes for water splitting, solar fuel production and environmental remediation



Combined suN-Driven Oxidation and CO<sub>2</sub> Reduction for renewable energy storage

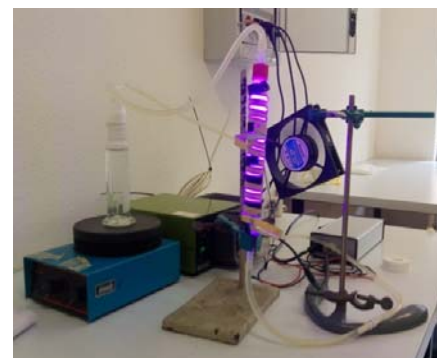


## Electrocatalysts for CO<sub>2</sub> reduction



*Marie Curie "Arcadia" (H2020-MSCA-IF 2015)*

## Photocatalysis for pollutant degradation



# An energy hungry society vs laws of thermodynamics

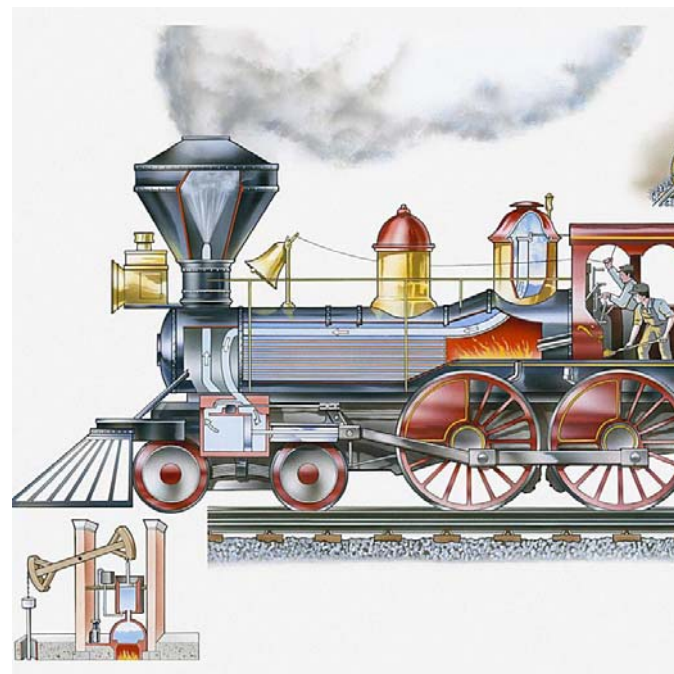
First Law: conservation of energy :  $\Delta U$  (Internal energy) =  $\Delta L$  (Work) +  $\Delta Q$  (Heat)

Second Law: entropy change in a spontaneous process:  $\Delta S_{universe} \geq 0$

**TABLE 8.3** Thermochemical Properties of Some Fuels

| Fuel                                      | Combustion Enthalpy |        |                    |
|---|---------------------|--------|--------------------|
|   | kJ/mol              | kJ/g   | kJ/mL              |
| Hydrogen, H <sub>2</sub>                  | -285.8              | -141.8 | -9.9 <sup>a</sup>  |
| Ethanol, C <sub>2</sub> H <sub>5</sub> OH | -1367               | -29.7  | -23.4              |
| Graphite, C                               | -393.5              | -32.8  | -73.8              |
| Methane, CH <sub>4</sub>                  | -890.3              | -55.5  | -30.8 <sup>a</sup> |
| Methanol, CH <sub>3</sub> OH              | -726.4              | -22.7  | -17.9              |
| Octane, C <sub>8</sub> H <sub>18</sub>    | -5470               | -47.9  | -33.6              |
| Toluene, C <sub>7</sub> H <sub>8</sub>    | -3910               | -42.8  | -36.7              |

<sup>a</sup>Calculated for the compressed liquid at 0°C



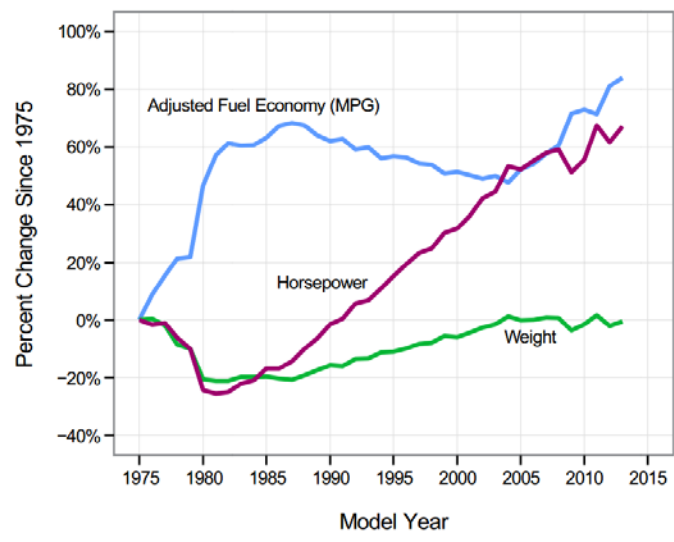
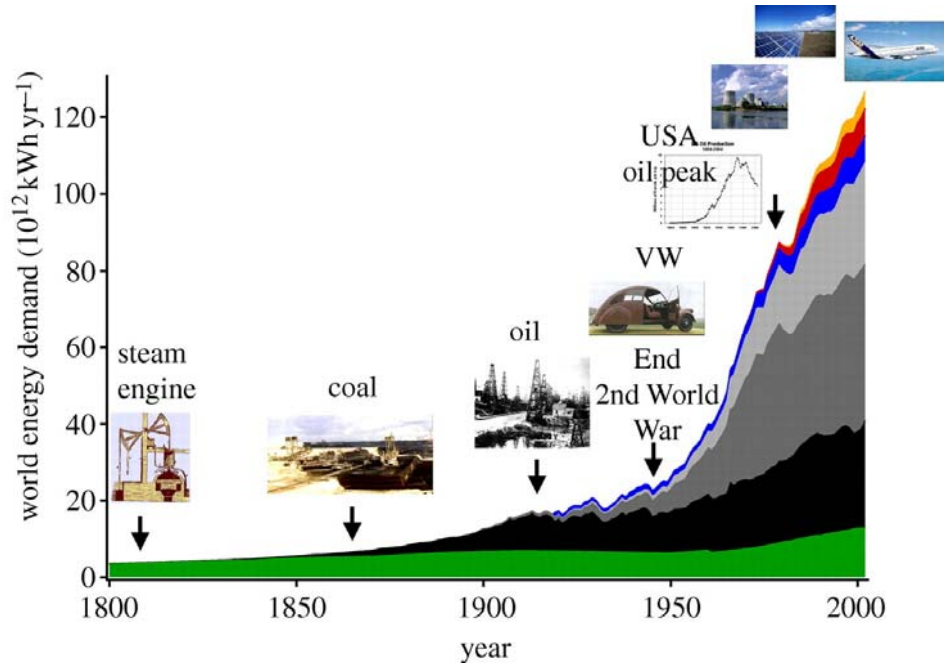
The opposite reaction does not **spontaneously** occur due to second law

Fuels are concentrated forms of internal energy (enthalpy) from which we can extract work and heat to power our society. We extract energy from breaking and forming chemical bonds.



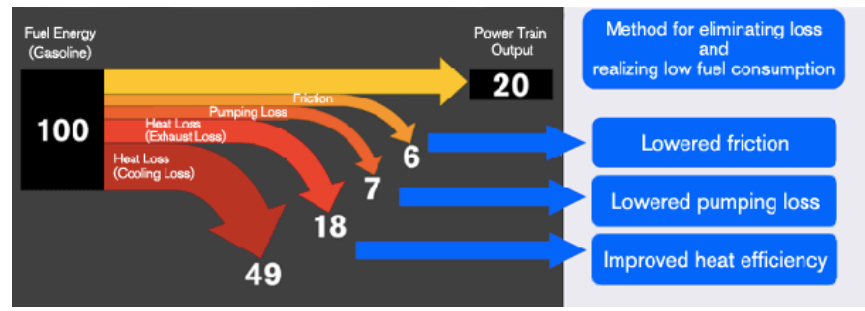


# « The energy Efficiency paradox »



PHILOSOPHICAL  
TRANSACTIONS  
OF  
THE ROYAL  
SOCIETY

*Phil. Trans. R. Soc. A* (2010) **368**, 3329–3342  
doi:10.1098/rsta.2010.0113



REVIEW

## Hydrogen: the future energy carrier

BY ANDREAS ZÜTTEL\*, ARNDT REMHOF, ANDREAS BORGSCHULTE  
AND OLIVER FRIEDRICHS

*Empa Materials Sciences and Technology, Department of Environment,  
Energy and Mobility, Division of Hydrogen & Energy,  
CH-8600 Dübendorf, Switzerland*



# Why Fossil fuels ?

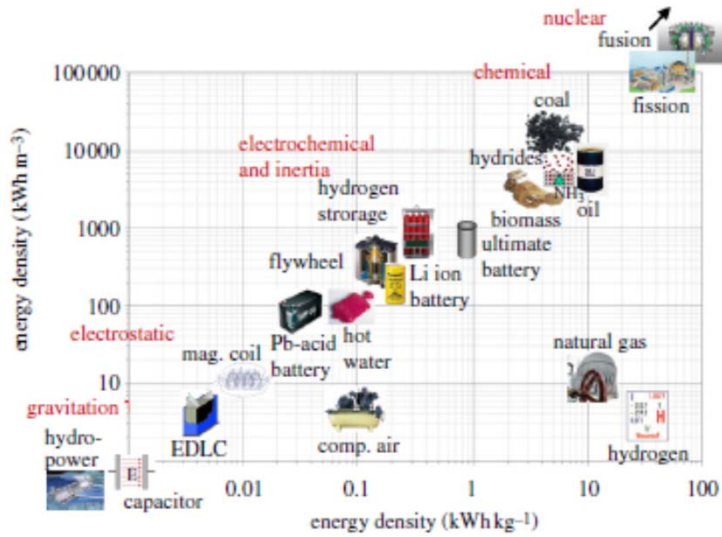
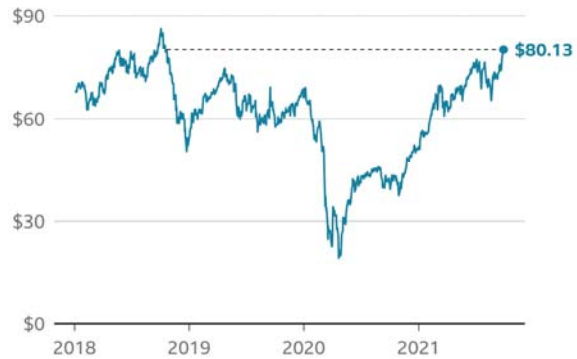


Figure 7. Volumetric versus gravimetric energy density of the most important energy carriers.

## Brent crude reaching \$80

US dollars per barrel

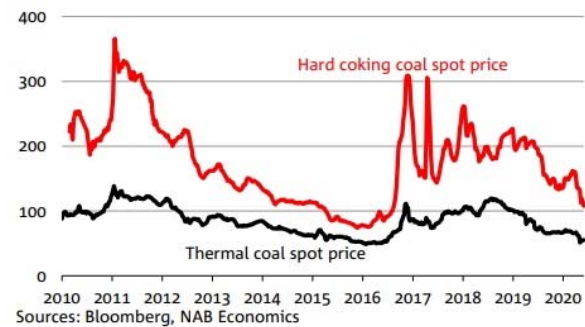


Source: Bloomberg, 28 September 2021, 12:35 GMT



## COKING COAL DOWN AS SUPPLY EASES

US\$/t (FOB)

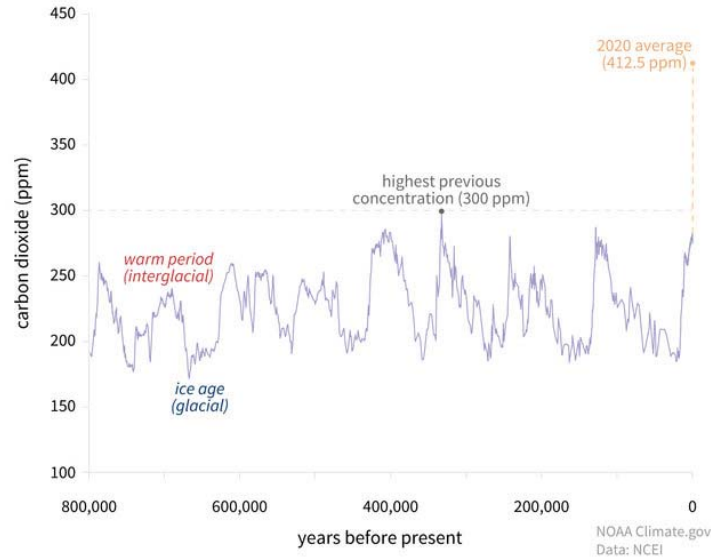
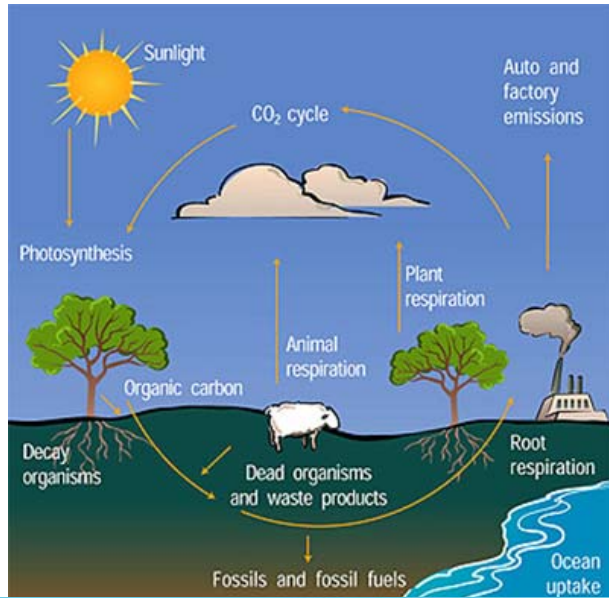


Sources: Bloomberg, NAB Economics

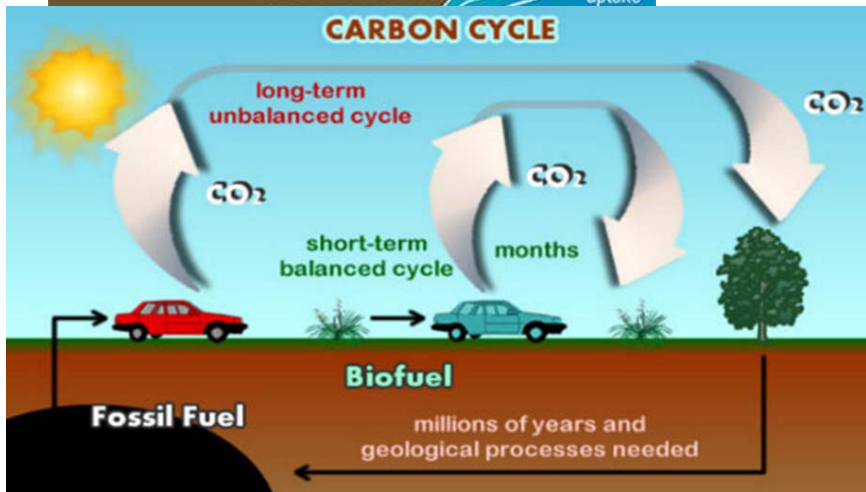


# Carbon Cycle

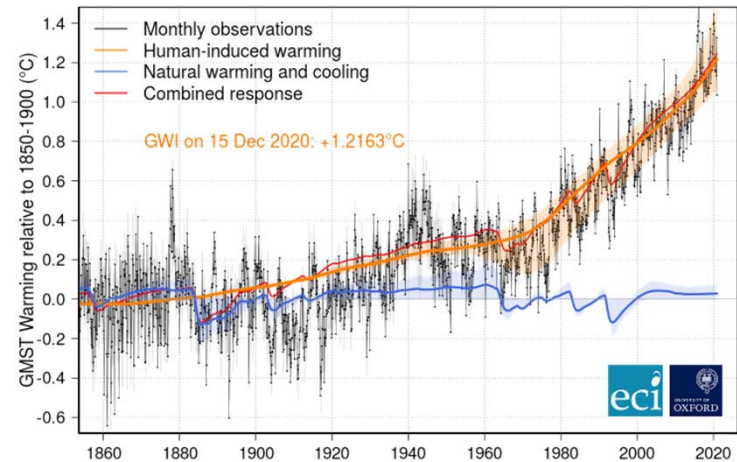
## CARBON DIOXIDE OVER 800,000 YEARS



<https://www.climate.gov/news-features/understanding-climate/climate-change-atmospheric-carbon-dioxide>



## Global Warming Index (aggregate observations) - updated to Dec 2020

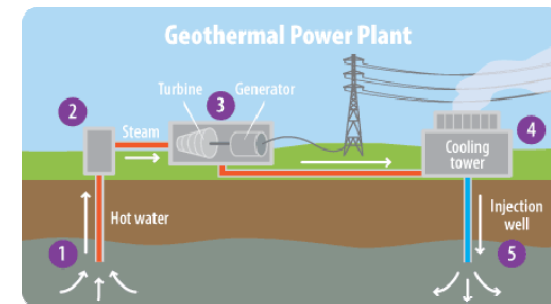
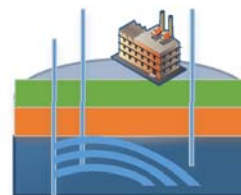
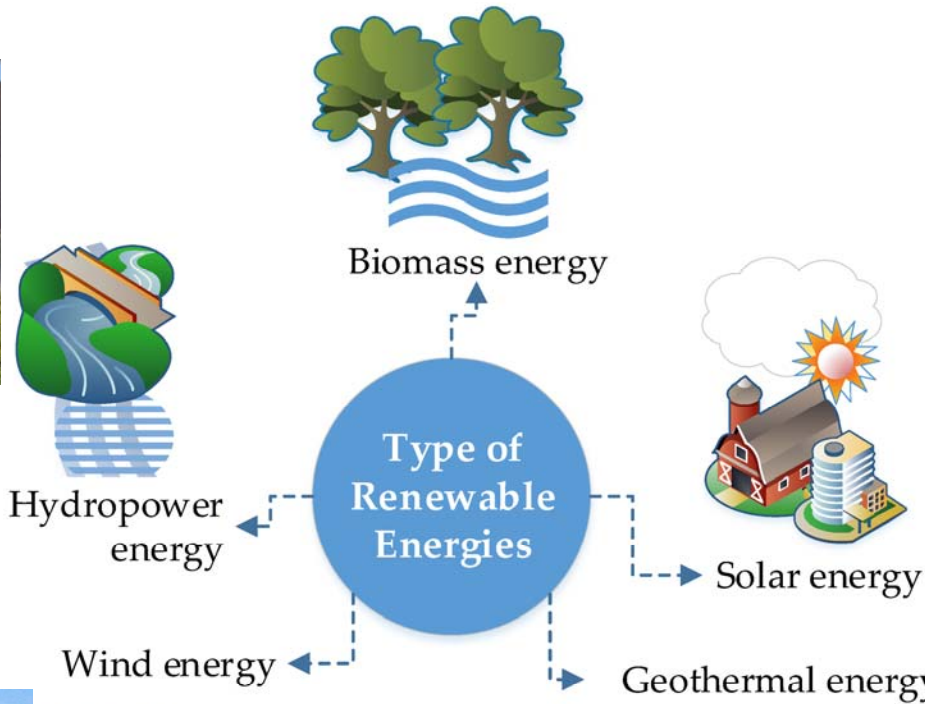


globalwarmingIndex.org



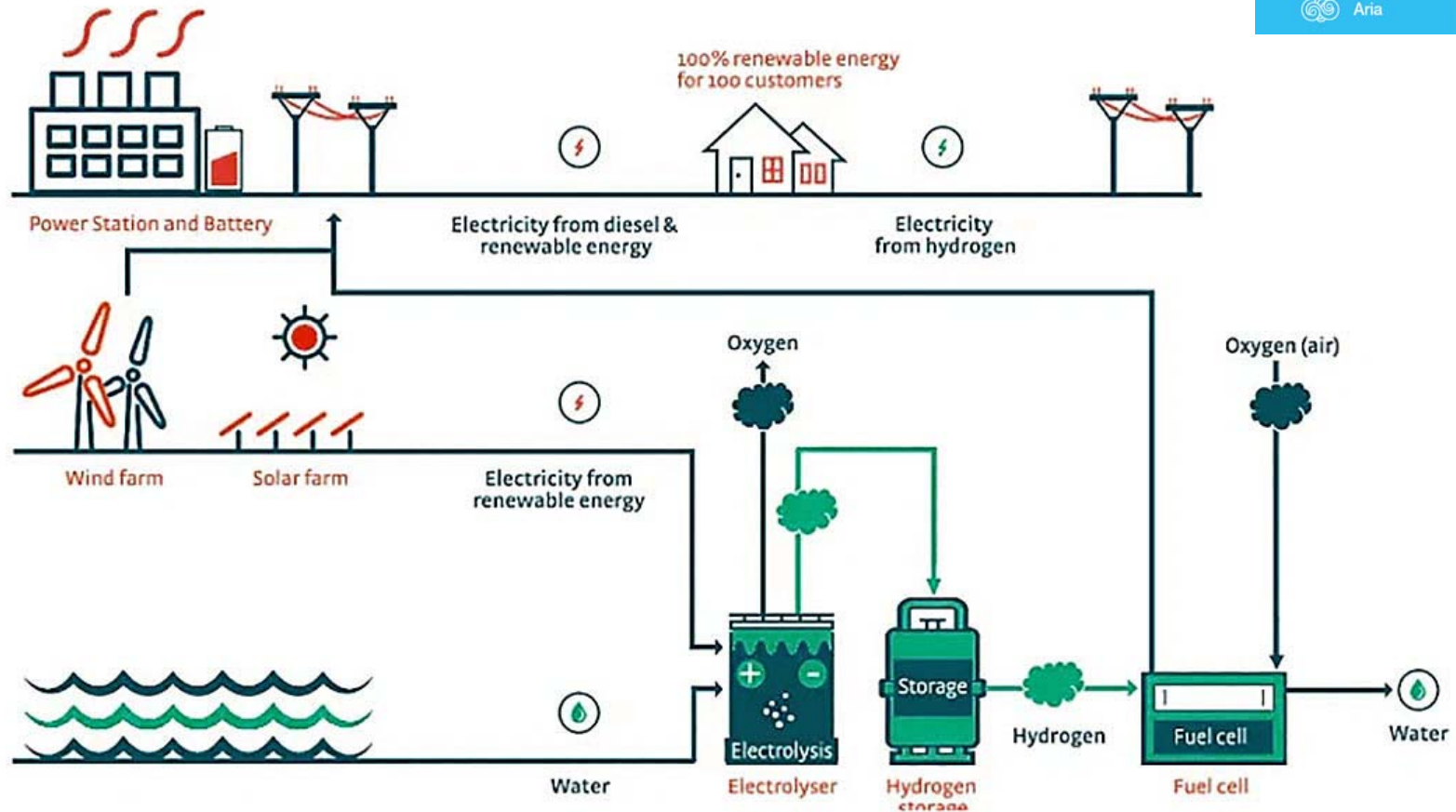


# Renewable energies: fast replenishing cycles or continuous supply



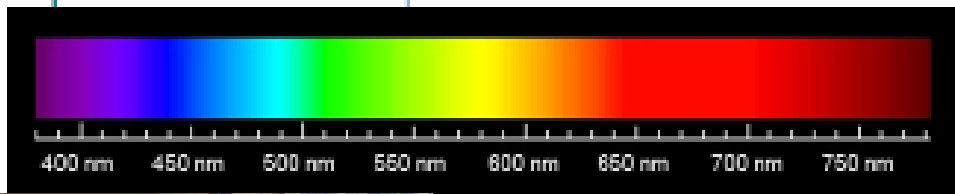
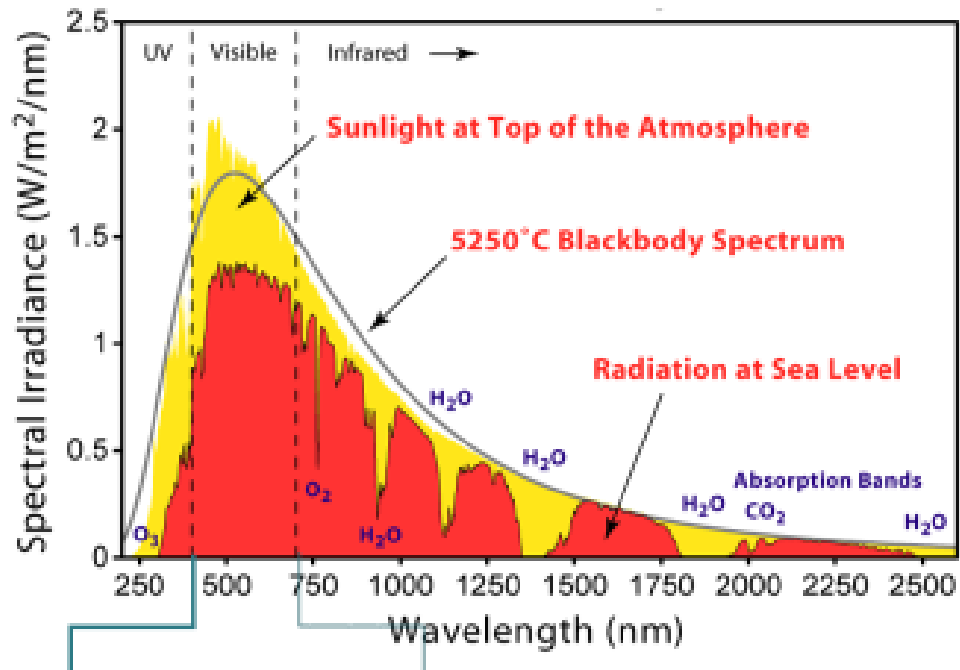


# A Sustainable Energy Cycle



<https://energyindustryreview.com/power/europe-at-the-top-of-hydrogen-electrolyser-projects/>

# Solar Energy: is it enough ?



# Sunlight exploitation



✓ Solar thermal:

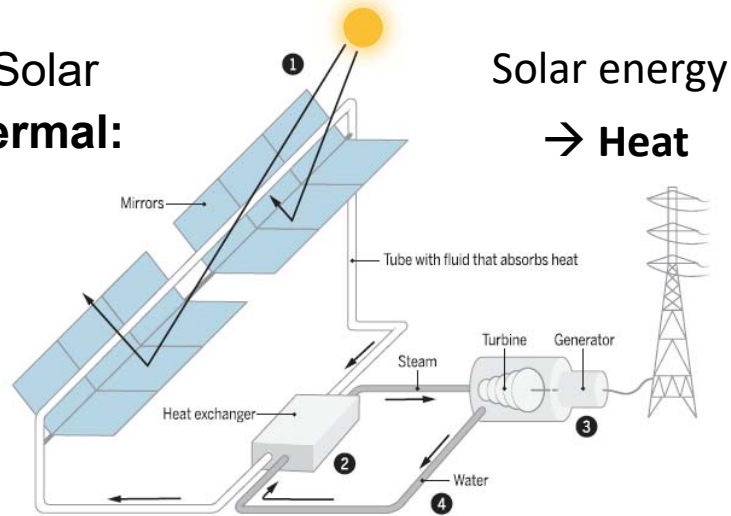


Fig. 4. Schematic of a typical 1D concentrating solar thermal system. The sunlight is focused along one dimension to heat up a thermal fluid—typically, either an oil or a molten salt—which is then passed through a heat exchanger to produce steam that is used in a turbine to produce electricity.

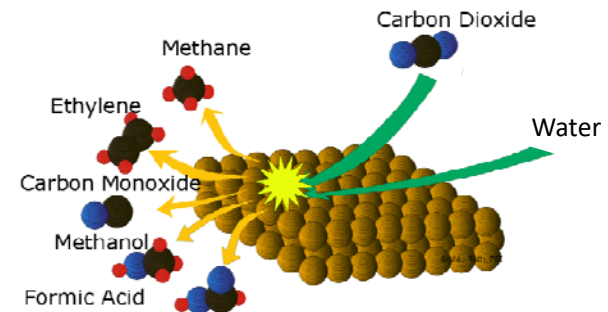
✓ Photovoltaics:  
Solar energy → Electricity



✓ Solar fuels  
(hydrogen,  
value-added  
products):

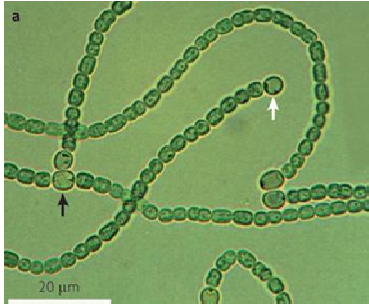


Solar energy → Chemical Energy

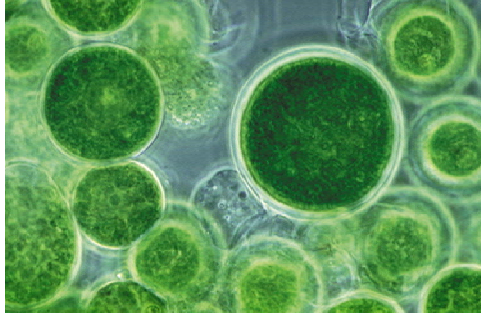




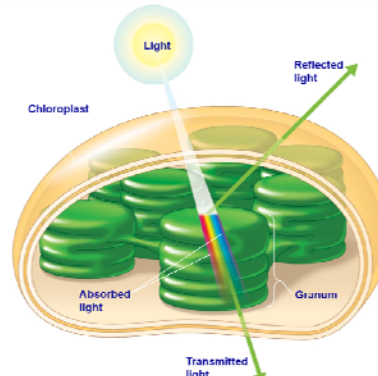
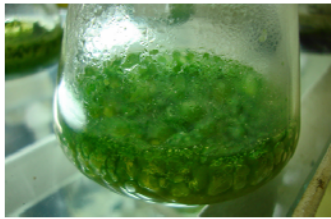
# Natural Photosynthesis: nature's way to solar harvesting



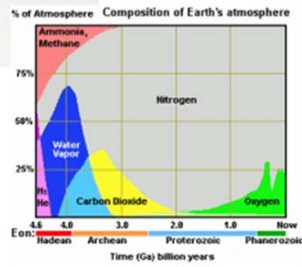
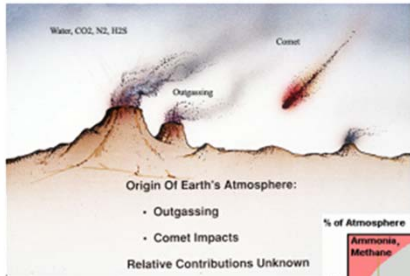
**Cyanobacteria**



**Chlorella sp.**

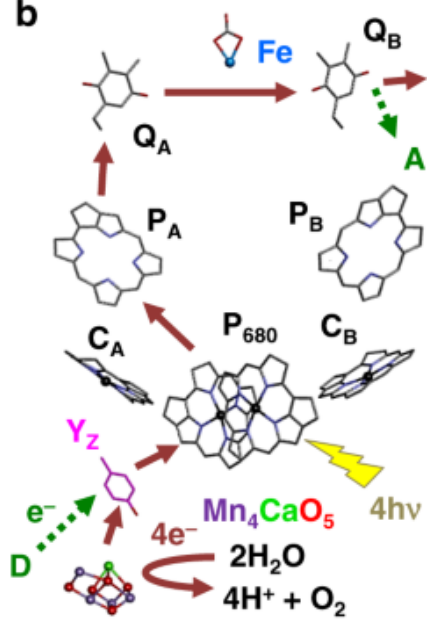
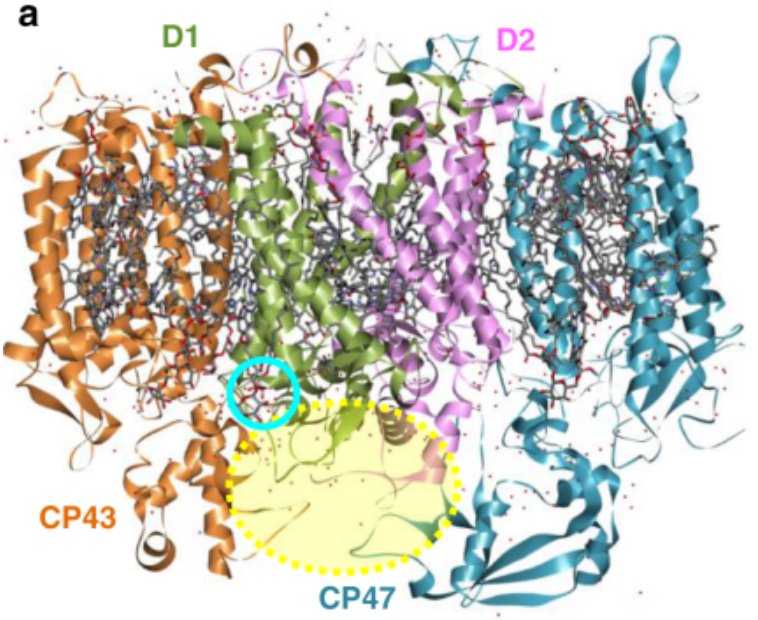
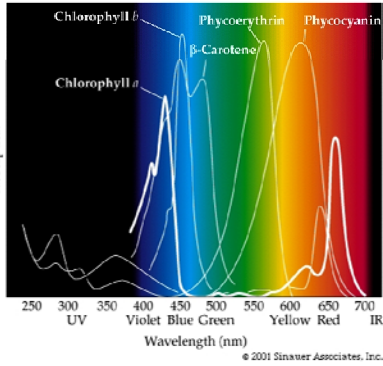
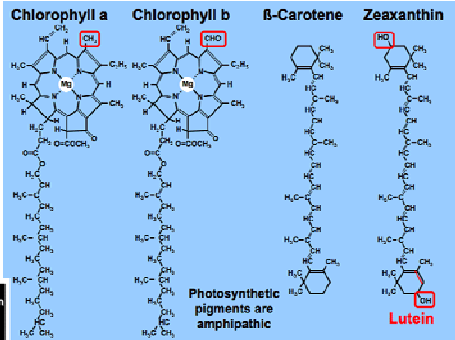
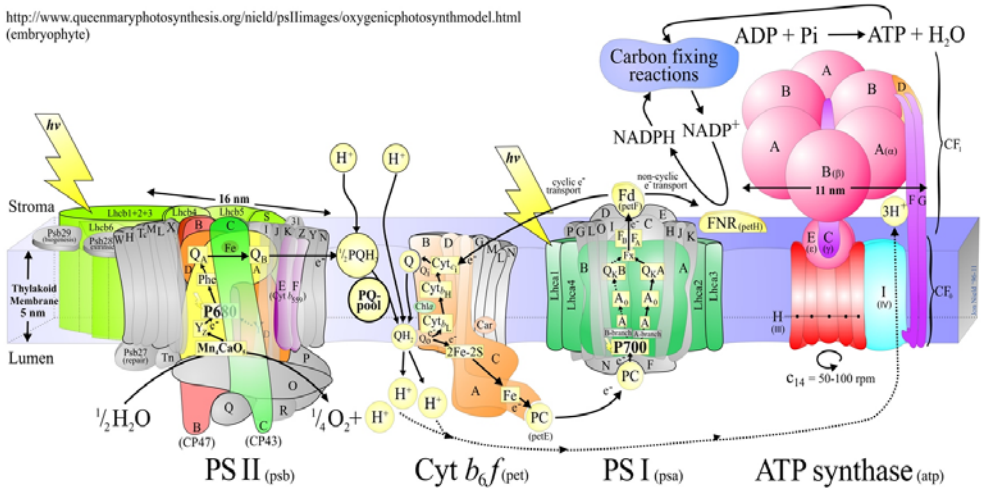


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# Natural Photosynthesis: molecular view

<http://www.queenmaryphotosynthesis.org/nield/psIIimages/oxygenicphotosynthmodel.html>  
(embryophyte)



ARTICLE <https://doi.org/10.1038/s41467-020-19852-0> OPEN [Check for updates](#)

Light-driven formation of manganese oxide by today's photosystem II supports evolutionarily ancient manganese-oxidizing photosynthesis

Petko Chernev<sup>1,3</sup>, Sophie Fischer<sup>1</sup>, Jutta Hoffmann<sup>1</sup>, Nicholas Oliver<sup>1</sup>, Ricardo Assunção<sup>1</sup>, Boram Yu<sup>1</sup>, Robert L. Burnap<sup>2</sup>, Ivelina Zaharieva<sup>1</sup>, Dennis J. Nürnberg<sup>1</sup>, Michael Haumann<sup>1</sup> & Holger Dau<sup>1,2</sup>

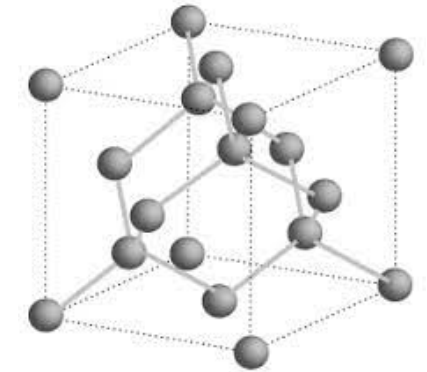
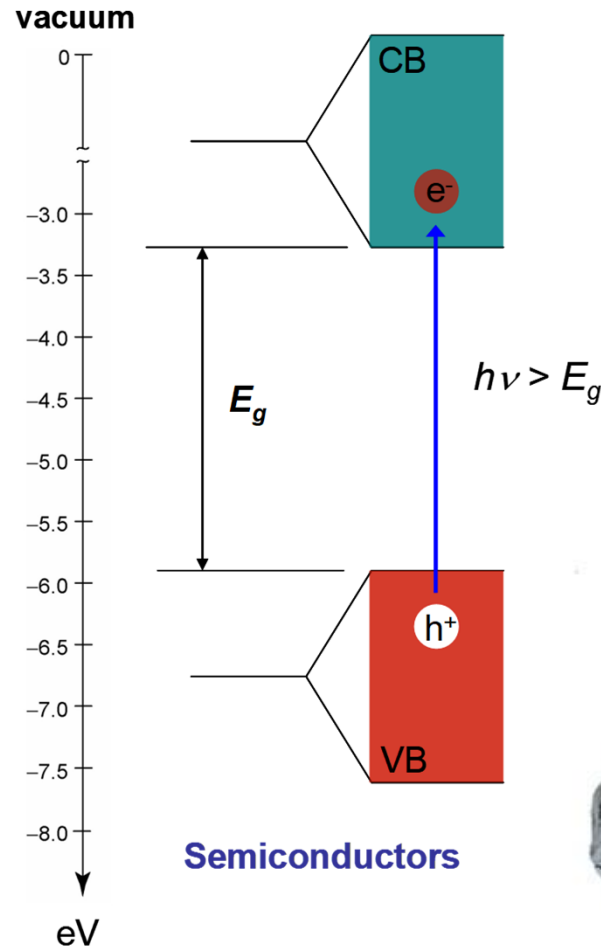
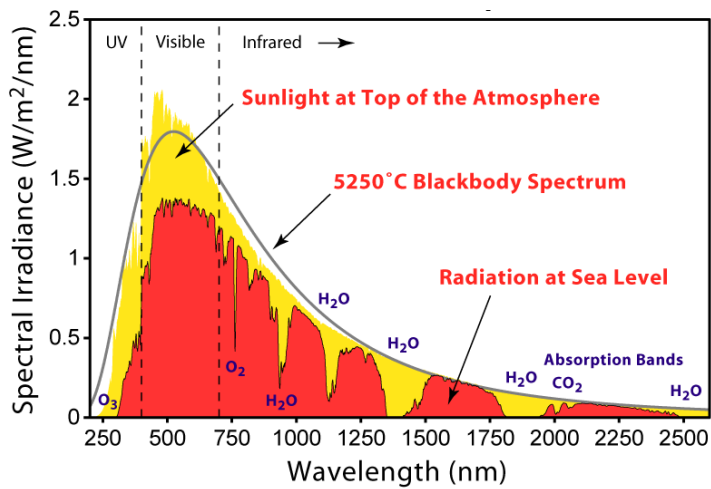




# «Artificial» harvesting of solar light with semiconductors

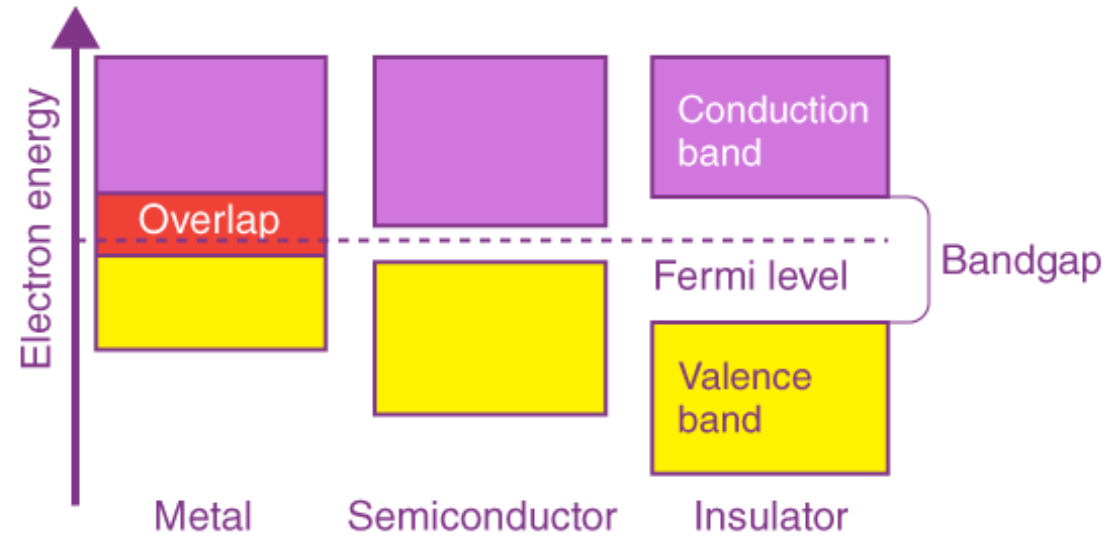
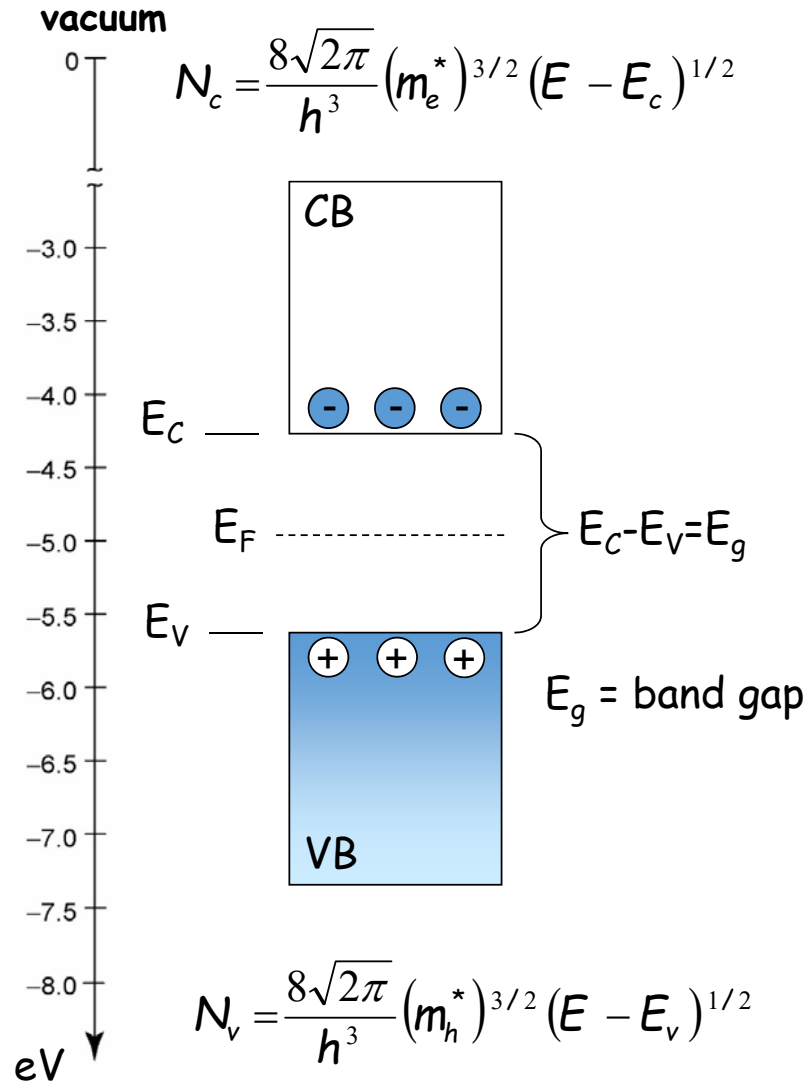


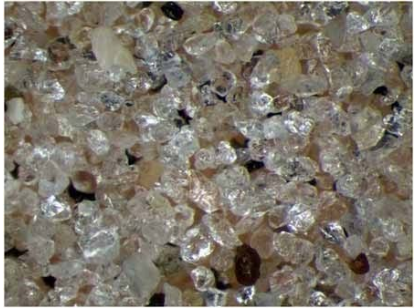
By using suitable catalyzers, it should be possible to transform the mixture of water and carbon dioxide into oxygen and methane, or to cause other endo-energetic processes.



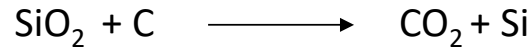


# Some details about the band structure of solids

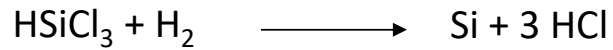
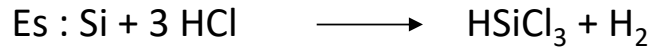




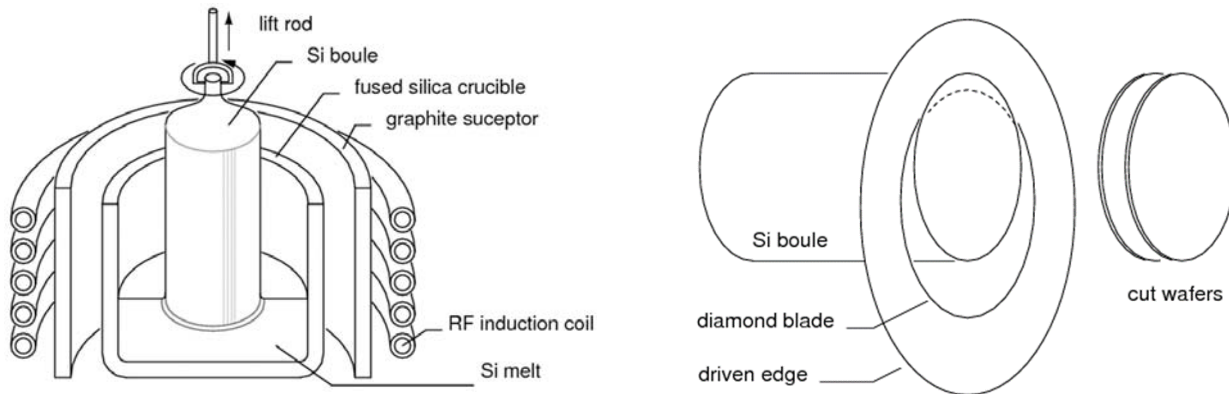
## How to produce Silicon



Purificazione tramite formazione di  $\text{SiCl}_4$  o  $\text{HSiCl}_3$  e successiva riduzione con idrogeno o metalli ultrapuri

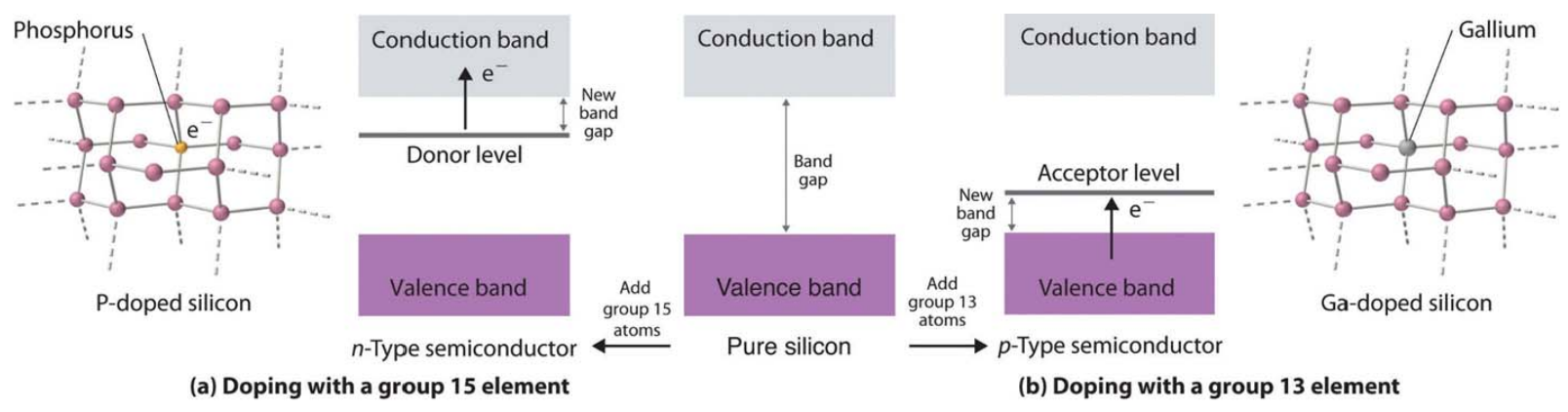
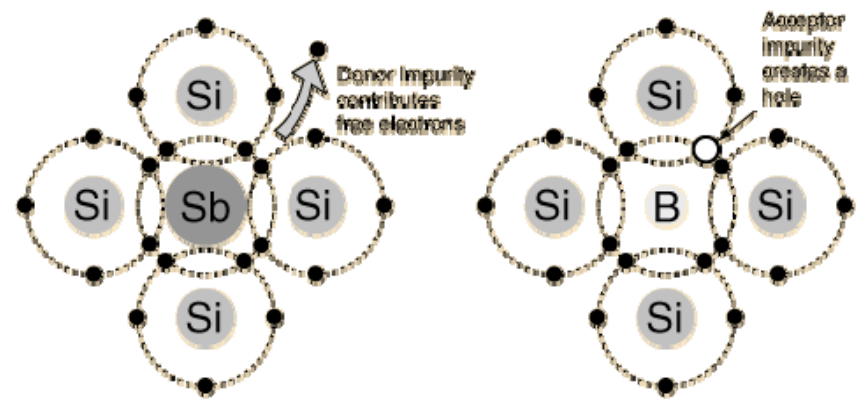


Successiva purificazione per ricristallizzazione da Si fuso i.e. Czochralsky





# Doping

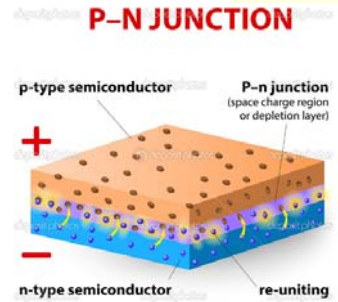
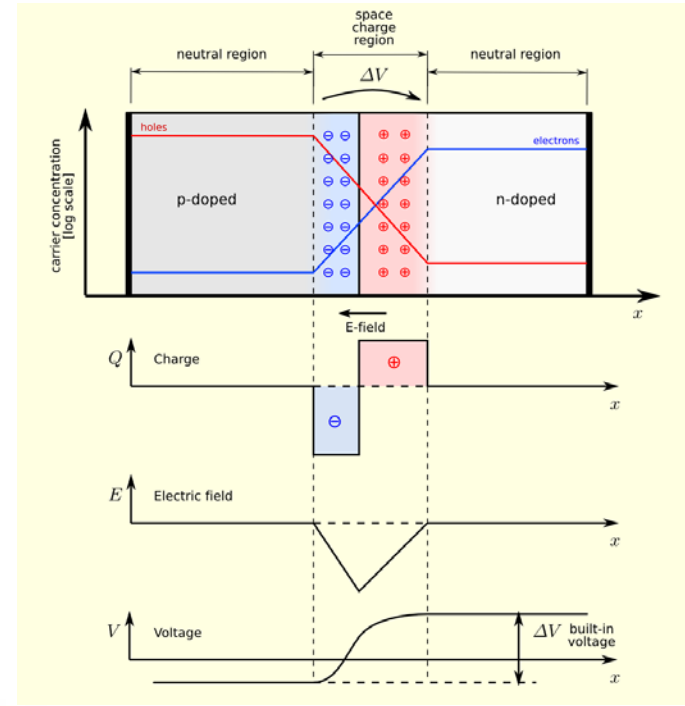
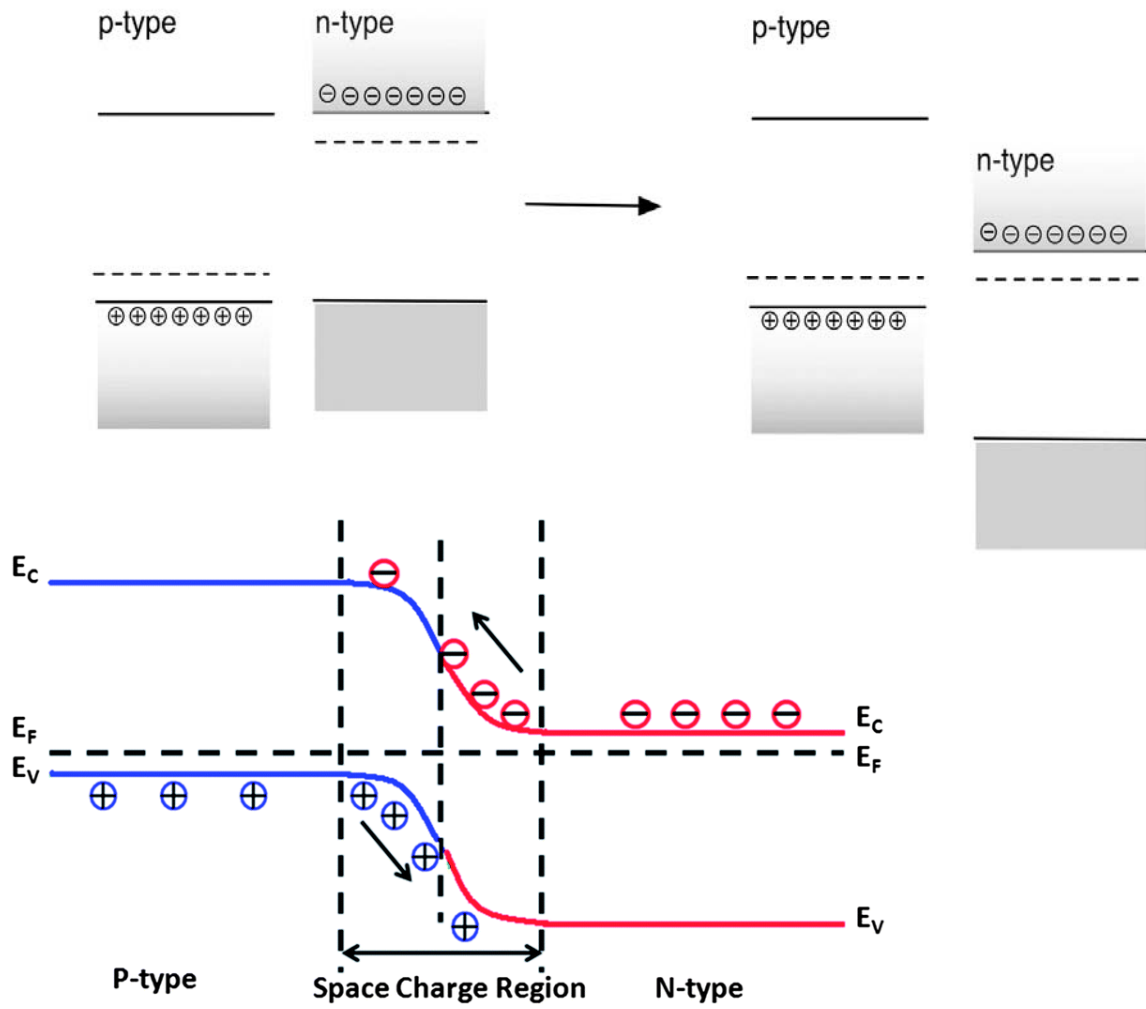


$$\epsilon_F^n = \frac{\epsilon_C + \epsilon_D}{2} + kT \ln \frac{N_D}{2N_C}$$

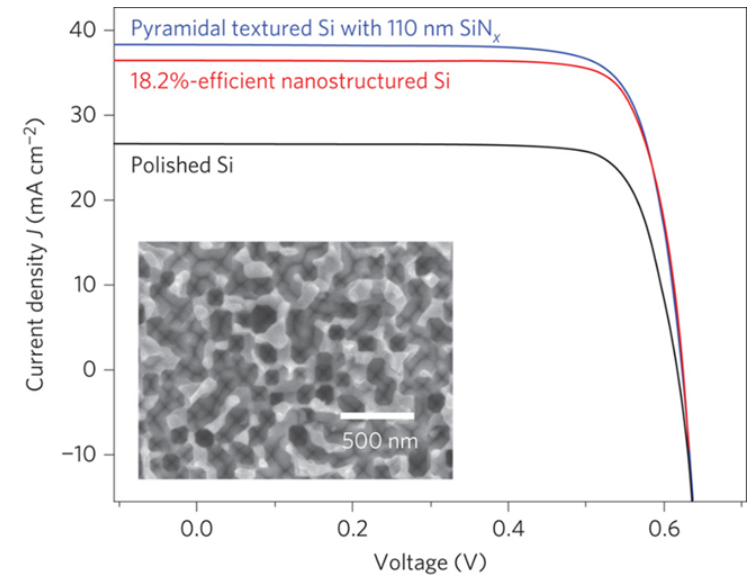
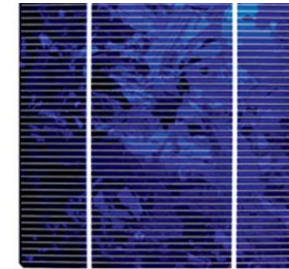
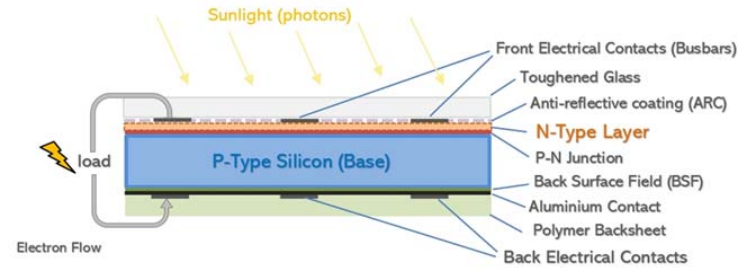
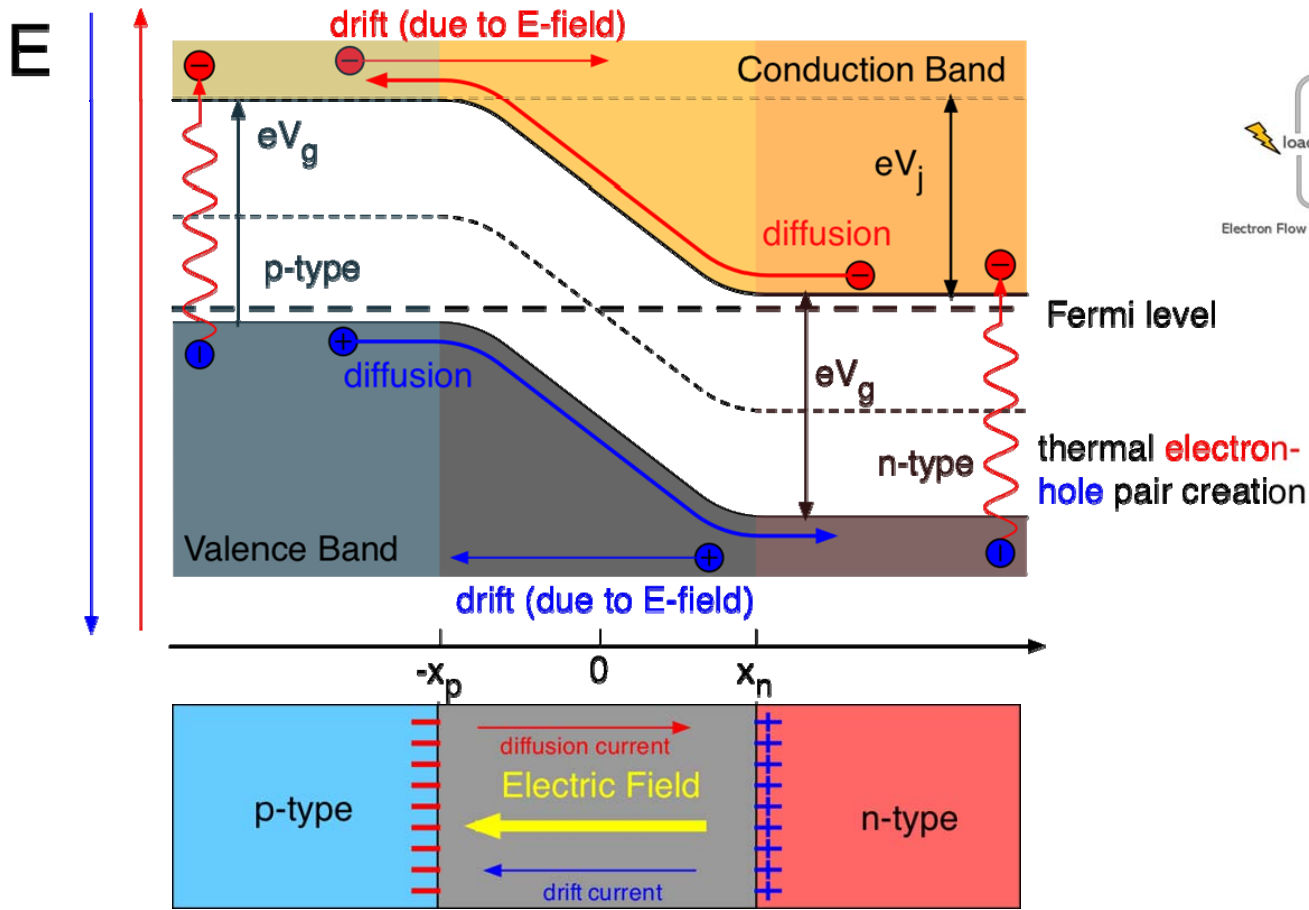
$$\epsilon_F^p = \frac{\epsilon_V + \epsilon_A}{2} - kT \ln \frac{N_A}{2N_V}$$



# Schottky Barrier at n-p junction: the «engine» of the solar cell



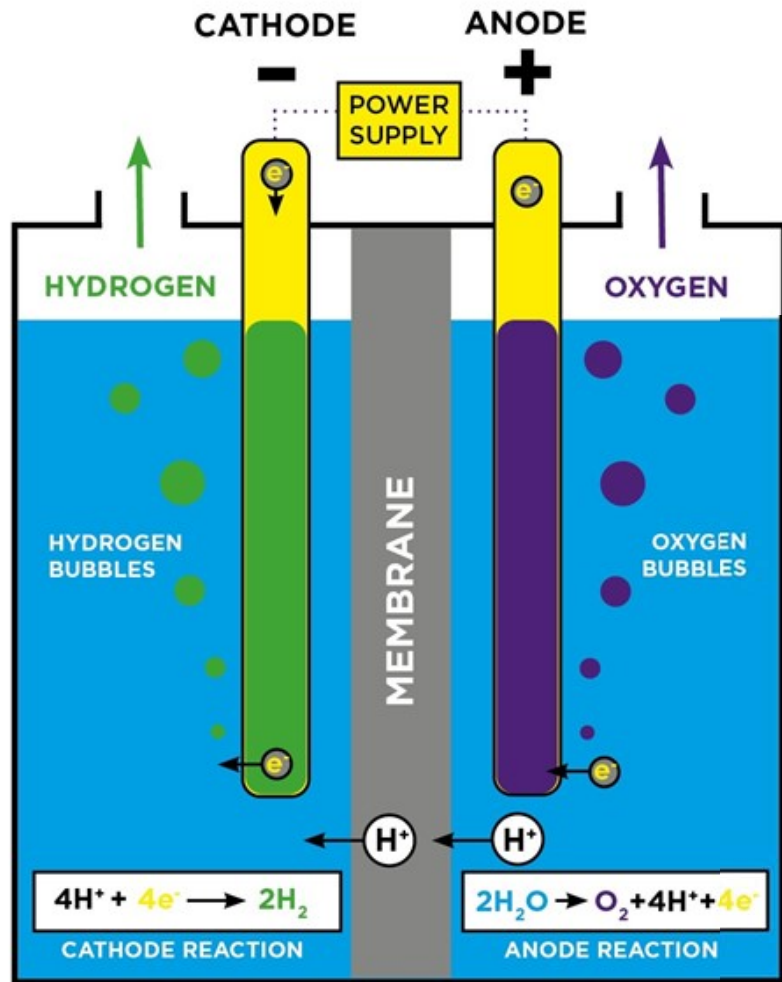
# n-p junction as a solar cell (photodiode)



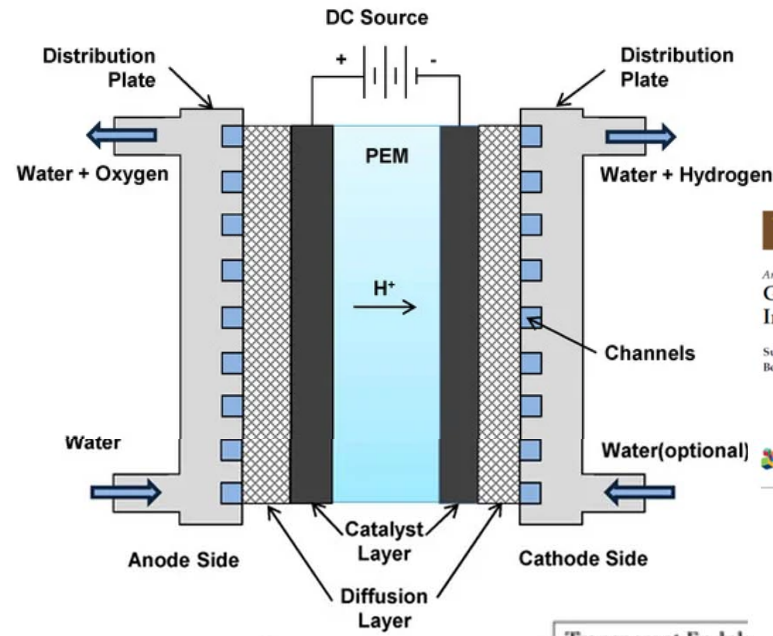
Schematic of pn-junction



# Water Electrolysis and Electrolysers



<https://www.tfphydrogen.com/markets/water-electrolysers>



**energies**

Article

**Generic Dynamical Model of PEM Electrolyser under Intermittent Sources**

Sumit Sood <sup>1,\*</sup>, Om Prakash <sup>1</sup>, Mahdi Boukerdja <sup>1</sup>, Jean-Yves Dieulot <sup>1</sup>, Belkacem Ould-Bouamama <sup>1</sup>, Mathieu Bressel <sup>2</sup> and Anne-Lise Gehin <sup>1</sup>

frontiers in Energy Research

ORIGINAL RESEARCH  
published: 10 April 2021  
doi: 10.3389/fenrg.2021.649367

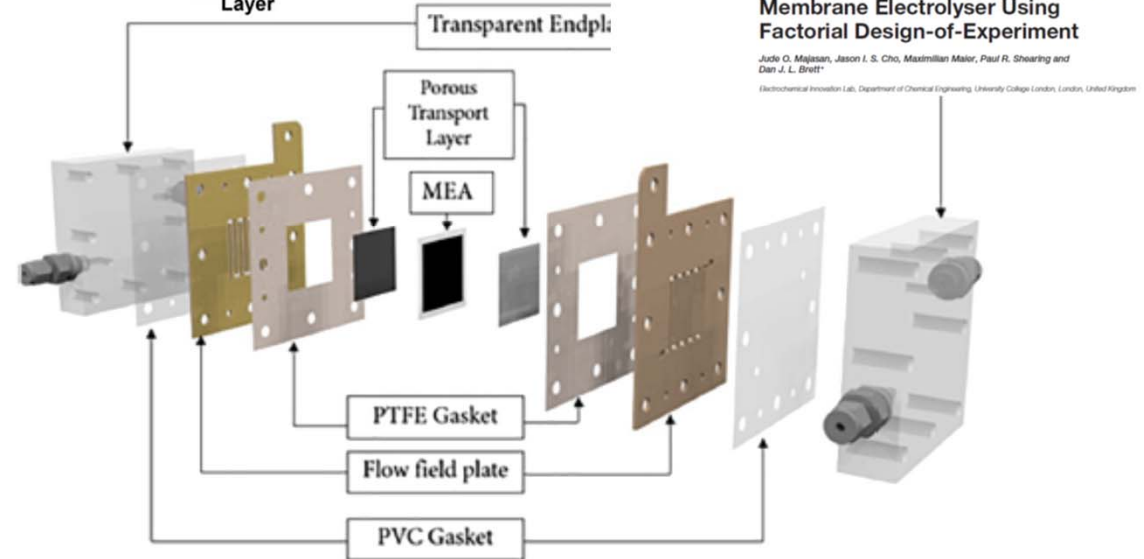
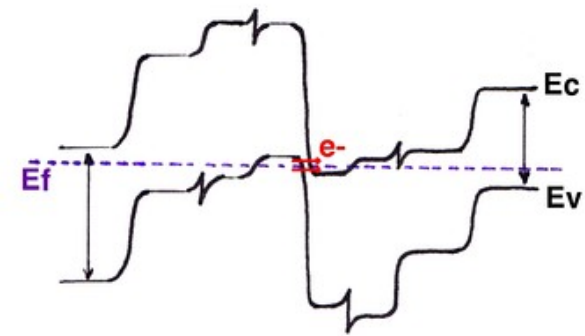
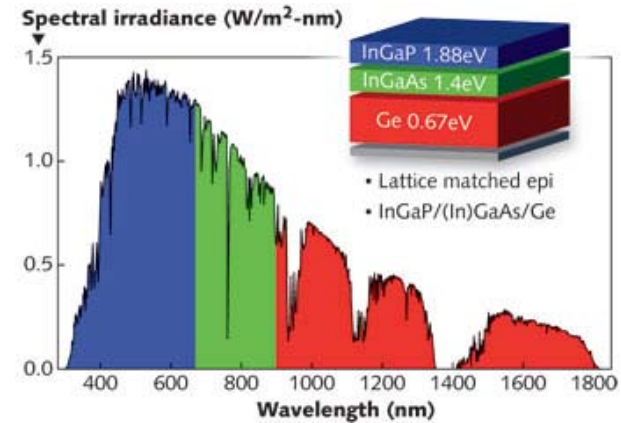
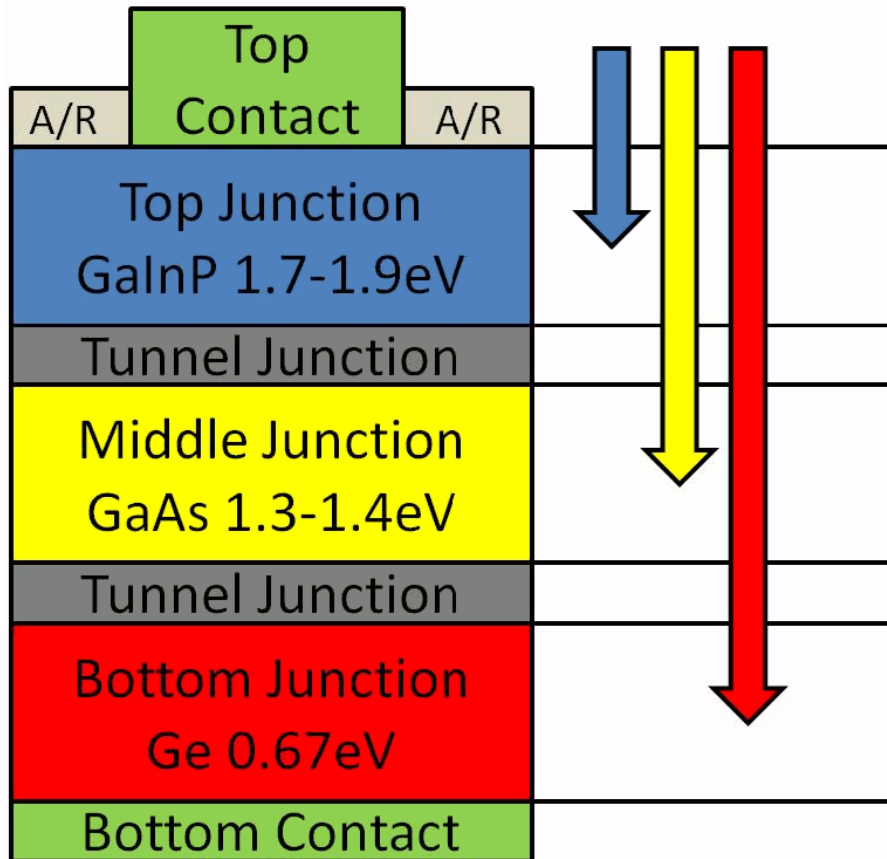


FIGURE 1 | Schematic of the PEMWE cell used for the study.



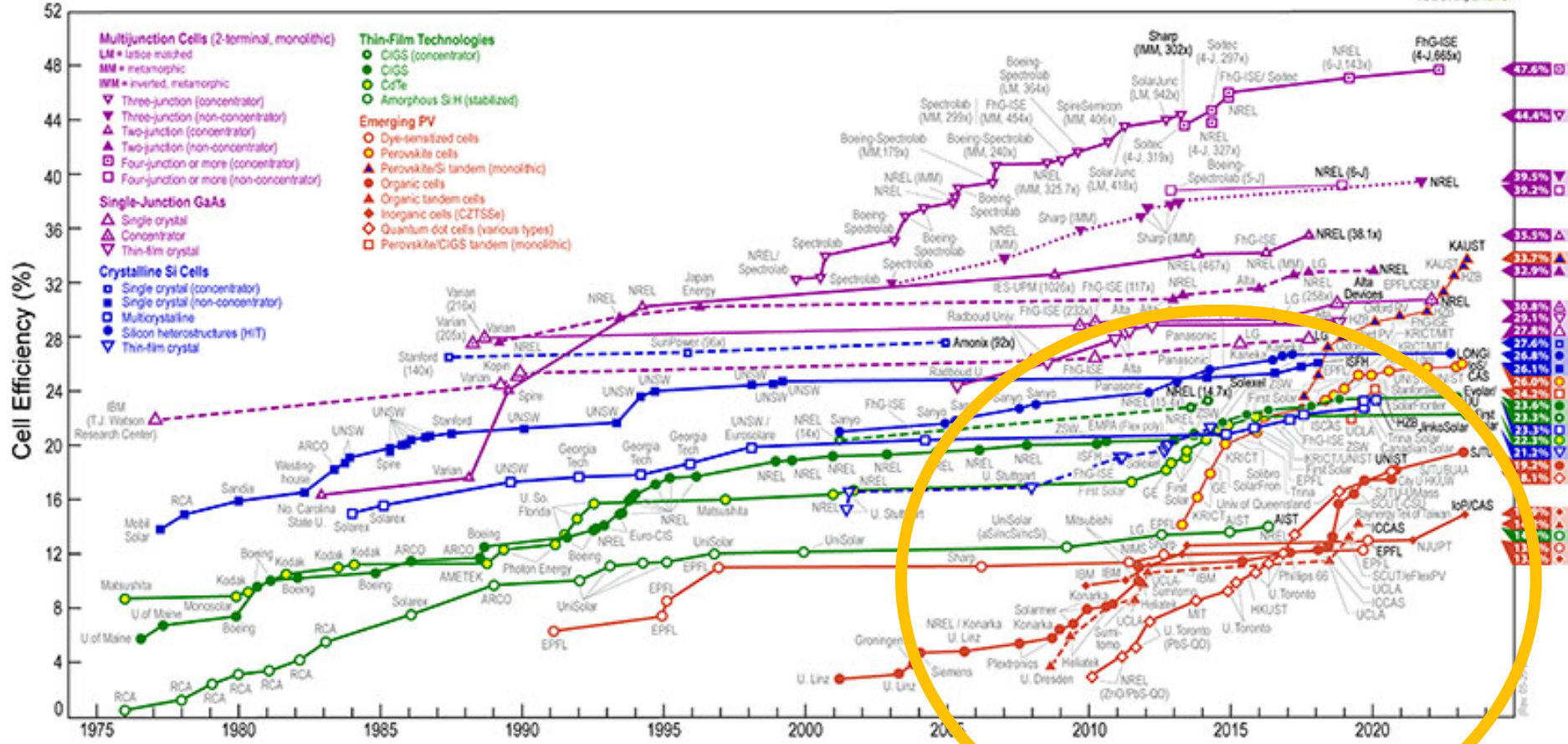
# Optimizing efficiency: Multijunction Solar Cells



|       |   |       |   |       |    |       |     |       |     |       |    |      |   |      |   |
|-------|---|-------|---|-------|----|-------|-----|-------|-----|-------|----|------|---|------|---|
| InGaP | n | InGaP | p | AlInP | p+ | InGaP | p++ | InGaP | n++ | AlInP | n+ | GaAs | n | GaAs | p |
|-------|---|-------|---|-------|----|-------|-----|-------|-----|-------|----|------|---|------|---|

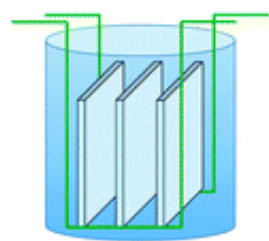


# Best Research-Cell Efficiencies



# Semiconductor preparation at Unife: search for scalable wet routes

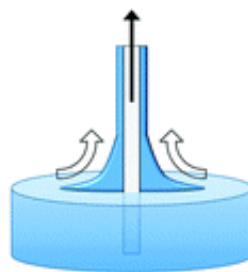
✓ Deposition of sol-gel colloidal suspensions or precursors' solutions



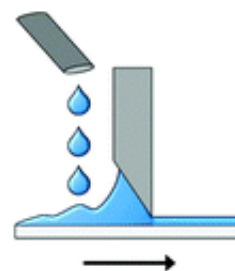
Chemical Bath



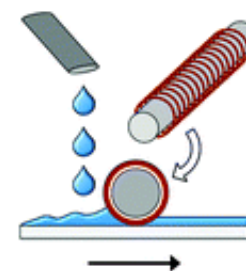
Spin-coating



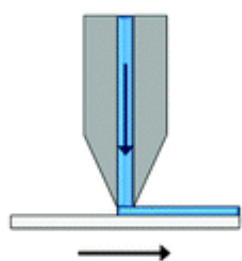
Dip-coating



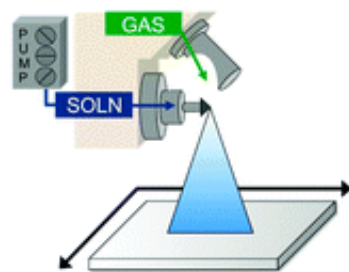
Doctor Blade



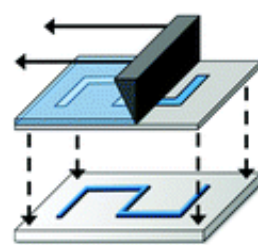
Metering Rod



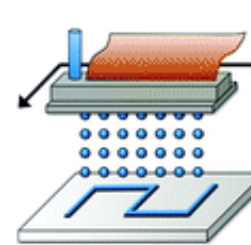
Slot-casting



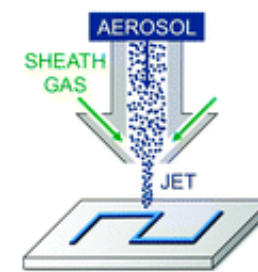
Spray-coating



Screen Printing



Inkjet Printing



Aerosol Jet





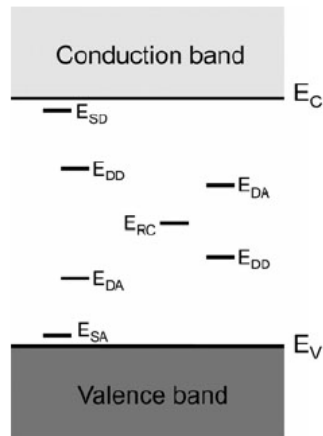
# Nanostructured Materials

## GOOD PROPERTIES

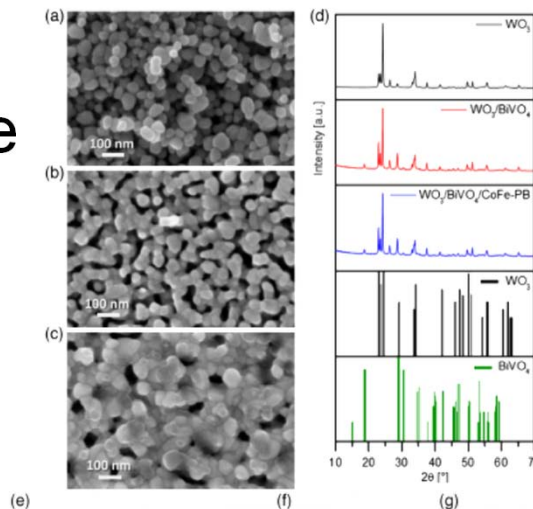
- Active Surface
- low T, wet routes available
- Diffusion Length

## Drawbacks

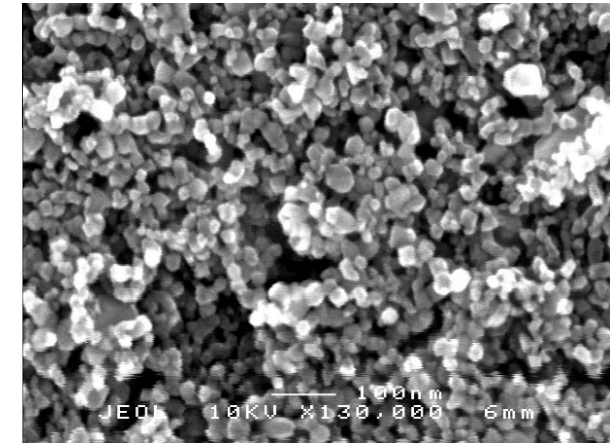
- Defects/SS
- Traps



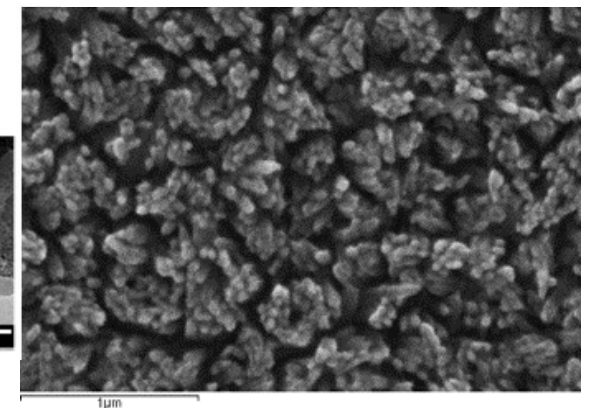
BiVO<sub>4</sub>/WO<sub>3</sub>



Sol-gel TiO<sub>2</sub>

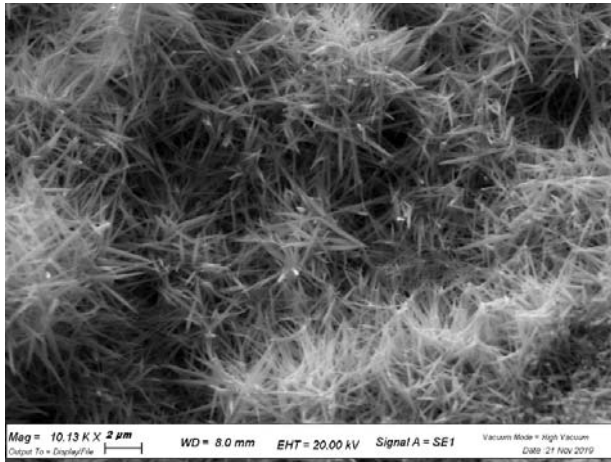


Fe<sub>2</sub>O<sub>3</sub> nanorods

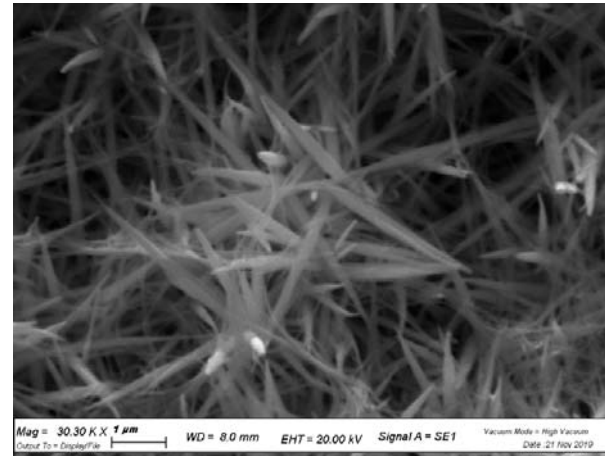




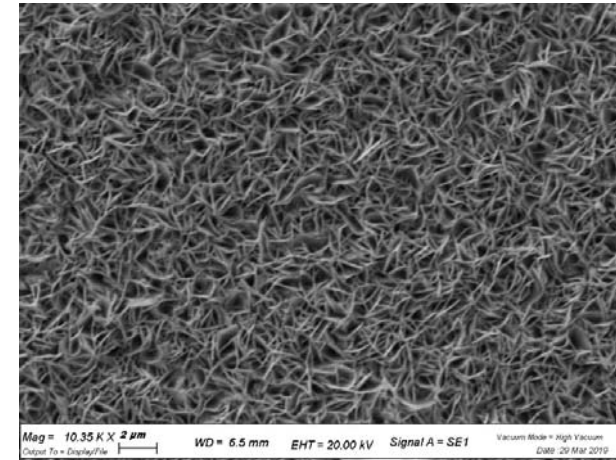
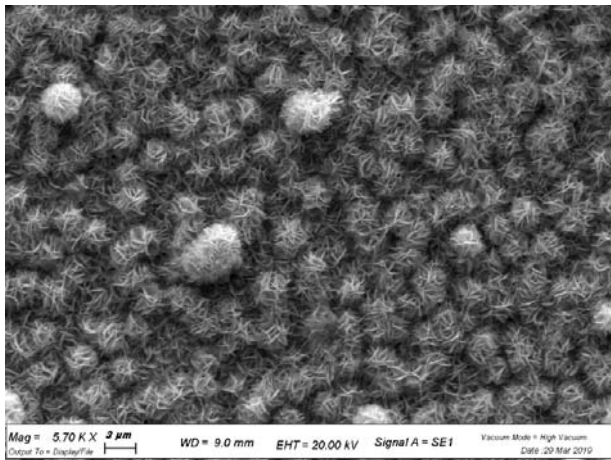
# WO<sub>3</sub> nano-morphologies from hydrothermal-Solvothermal Routes



Nano Flakes



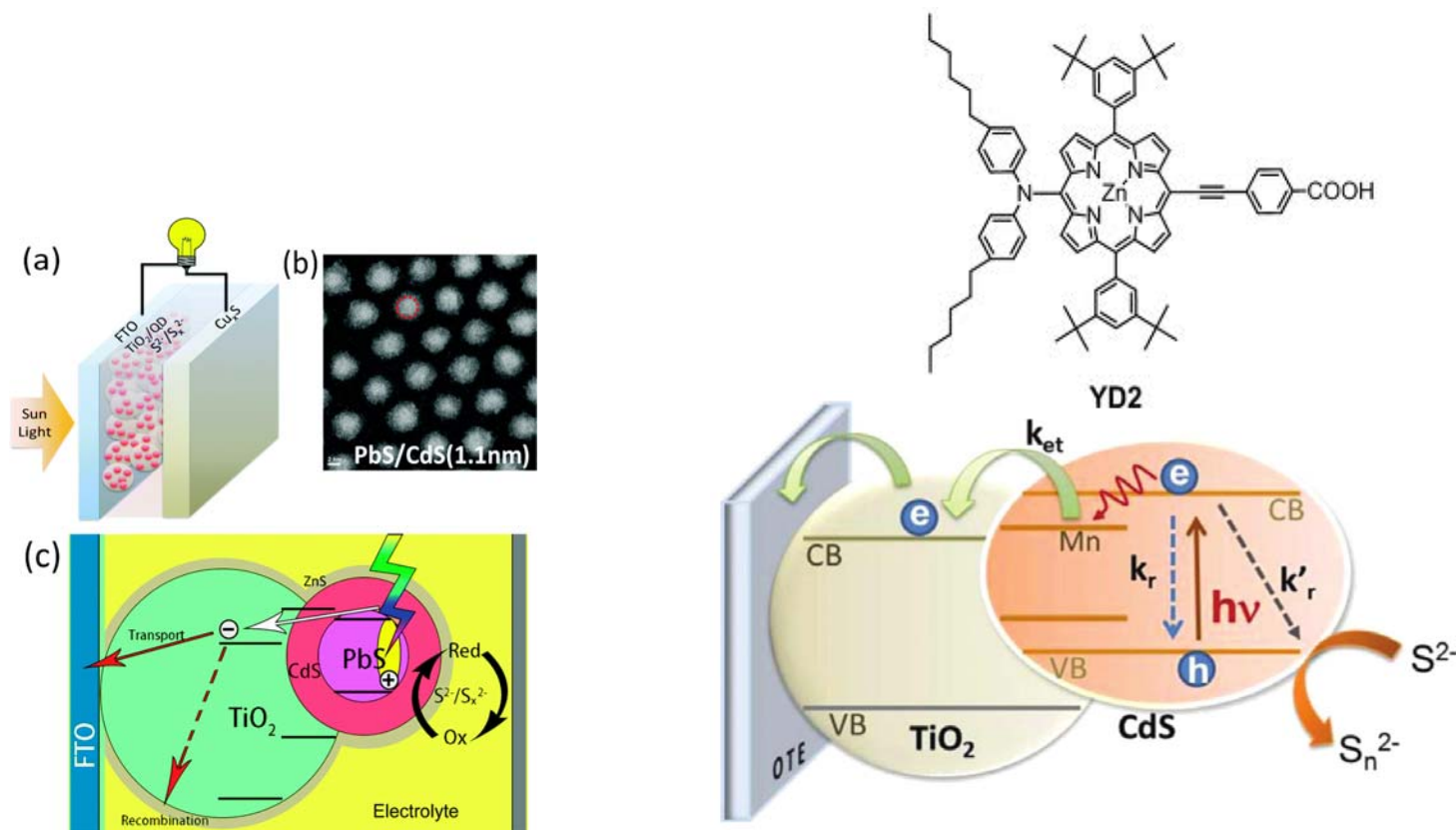
Nano Fiber Sheets



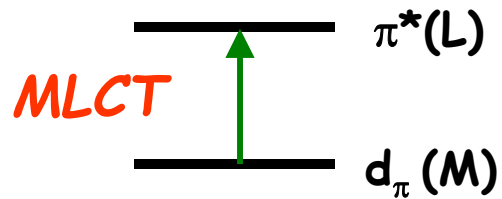
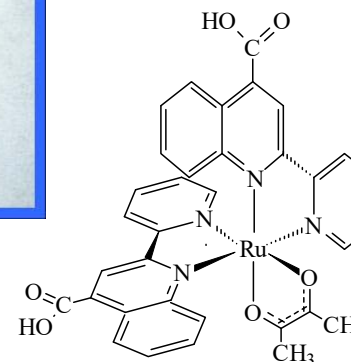
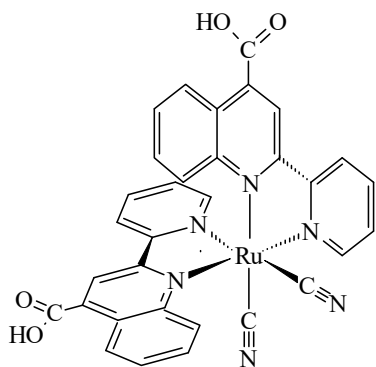
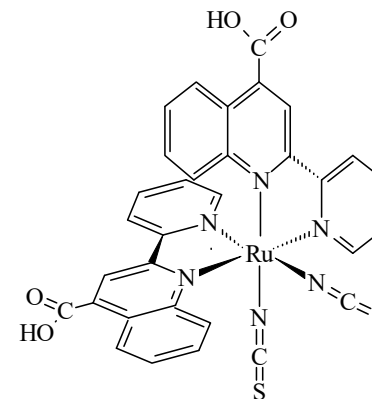
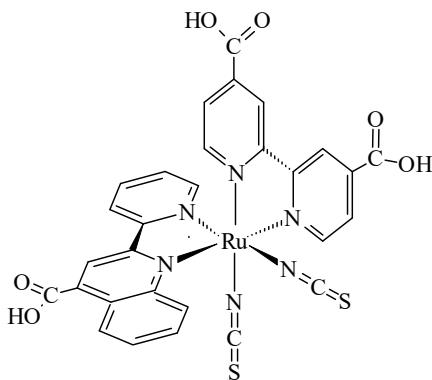


## Research at Unife: Spectral Sensitization

Light Absorption and Charge separation are originated by photoactive surface bound species. The wide band gap semiconductor acts as a physical support and as a conductor for majority carriers. Surface bound species can be either other semiconductors (e.g. Quantum dots) or molecular species.

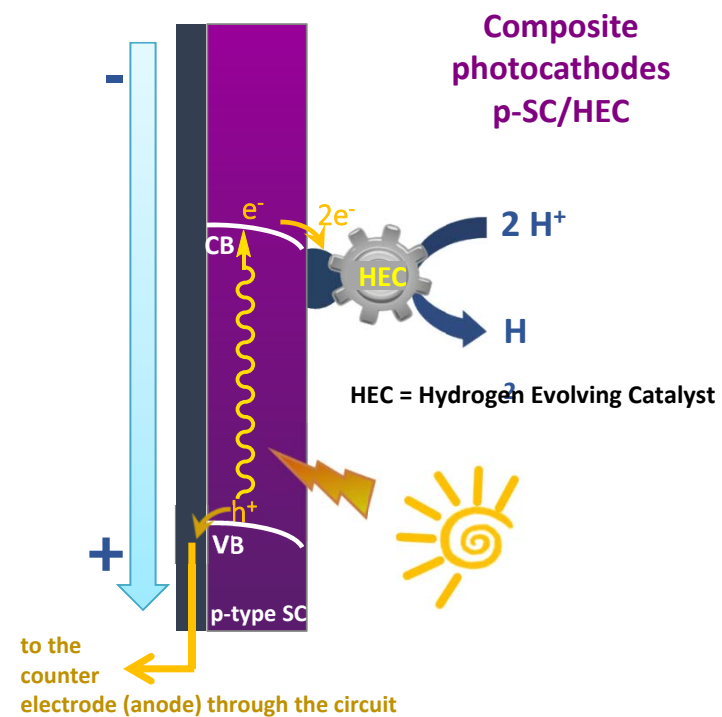
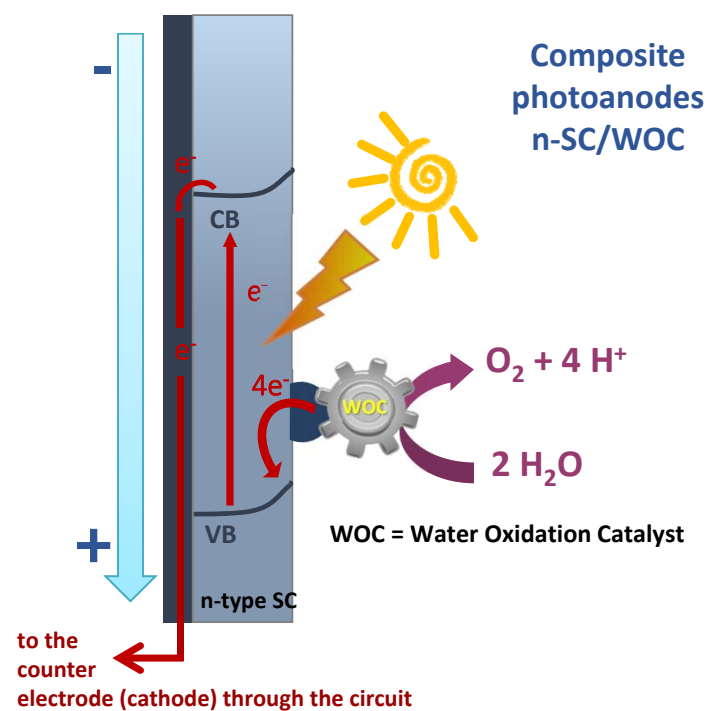


# Chromatic versatility of metal based dyes



## Tuning the surface properties with “catalytic” layers

### ➤ Catalytic layers as SCs overcoatings





# Some tandem PEC configurations

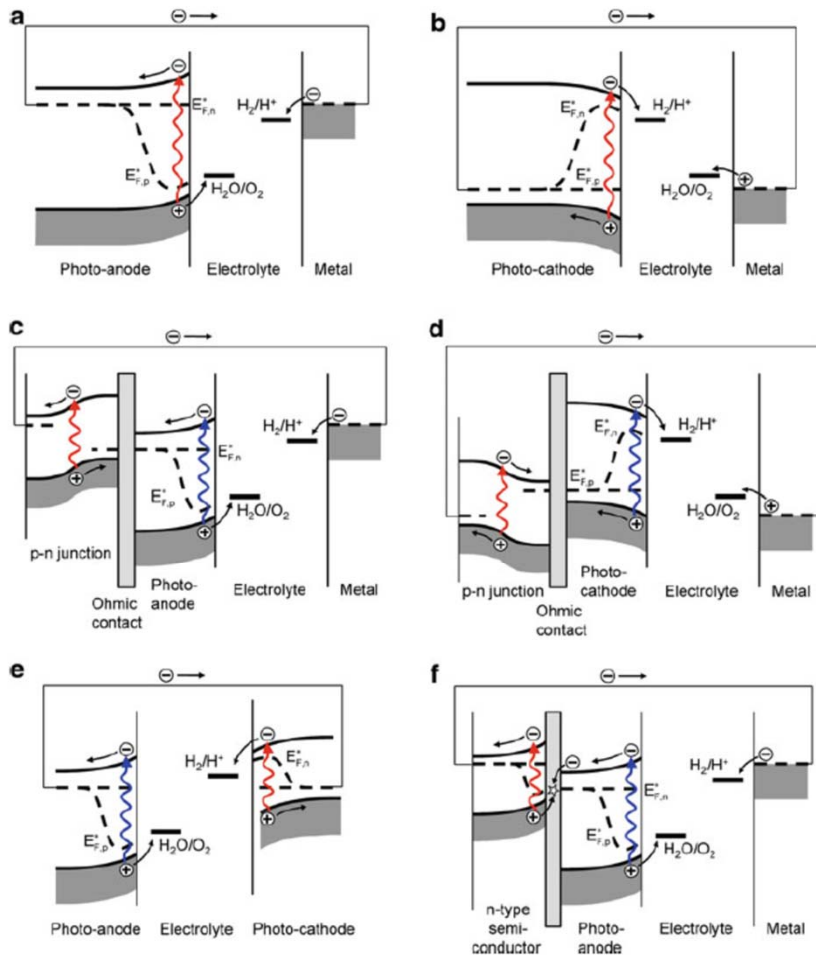


Fig. 2.25 Examples of possible PEC configurations under illumination. *Top row*: Standard single-semiconductor devices based on a photoanode (a) or photocathode (b) with a metal counter electrode. *Middle row*: Monolithic devices based on a photoanode (c) or photocathode (d) biased with an integrated p-n junction. *Bottom row*: p-n junction photoelectrochemical device (e), and an n-n heterojunction PEC device based on a photoanode deposited on top of a second n-type semiconductor that “boosts” the energy of the electrons (f)

## Highly efficient water splitting by a dual-absorber tandem cell

Jeremie Brillet<sup>1</sup>, Jun-Ho Yum<sup>1</sup>, Maurin Cornuz<sup>1</sup>, Takashi Hisatomi<sup>1</sup>, Renata Solaraska<sup>2</sup>, Jan Augustynski<sup>2</sup>, Michael Graetzel<sup>1</sup> and Kevin Sivula<sup>1\*</sup>

“Water splitters fabricated using triple-junction amorphous silicon<sup>1,2</sup> or III–V<sup>3</sup> semiconductors have demonstrated reasonable efficiencies, but at high cost and high device complexity”

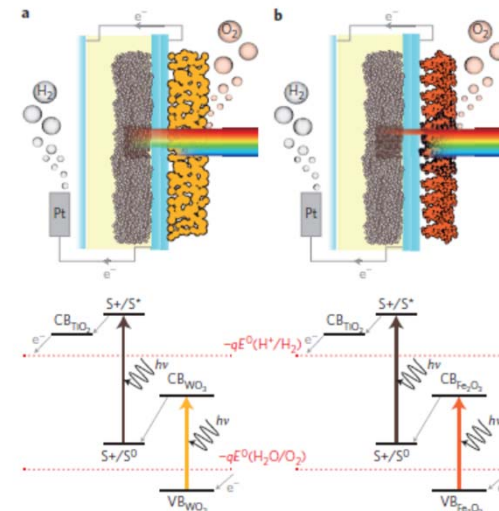
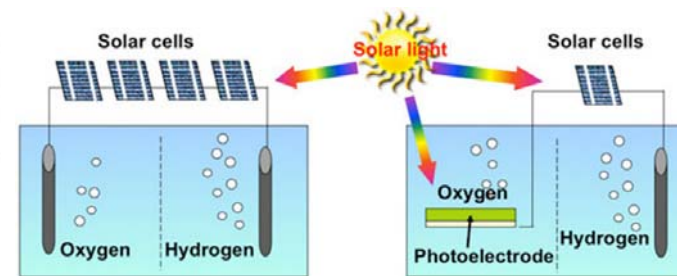
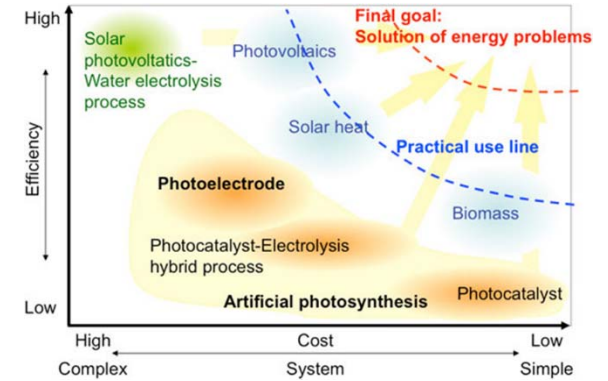
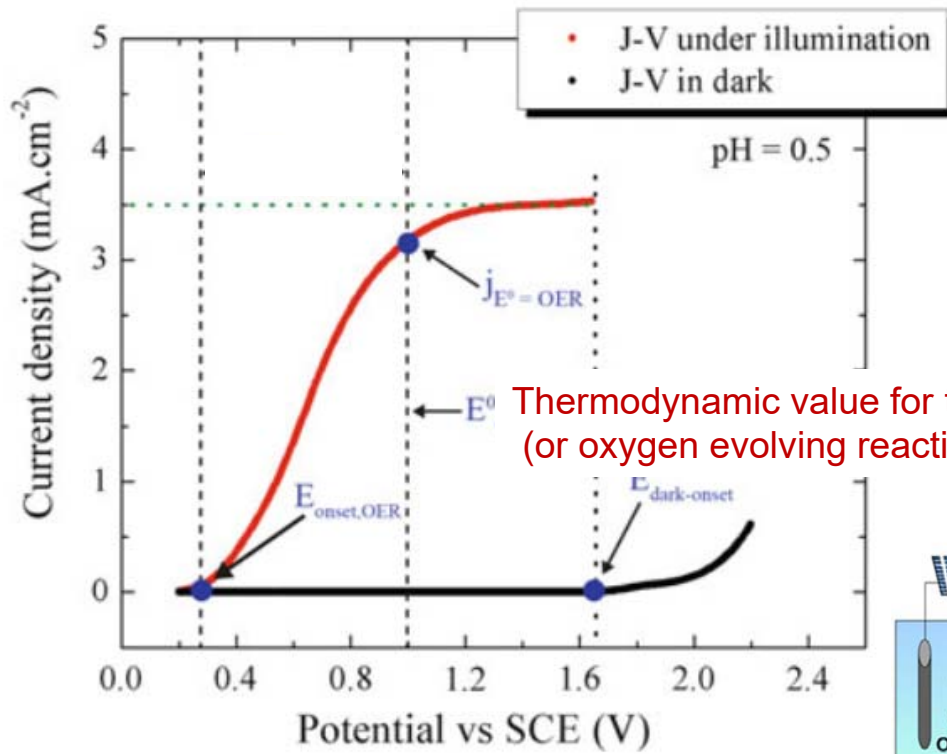


Figure 1 | General schemes and energy diagrams for a photoanode/DSC D4 tandem cell. a,  $\text{WO}_3$  tandem cell. b,  $\text{Fe}_2\text{O}_3$  tandem cell. Red dotted lines indicate the reduction and oxidation potentials of water.



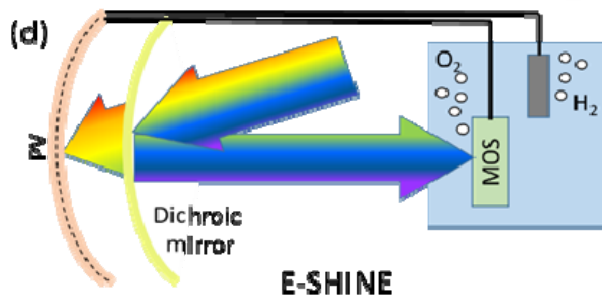
Typical n-type PEC Current/Voltage characteristic: **voltage saving with respect to conventional electrolysis**



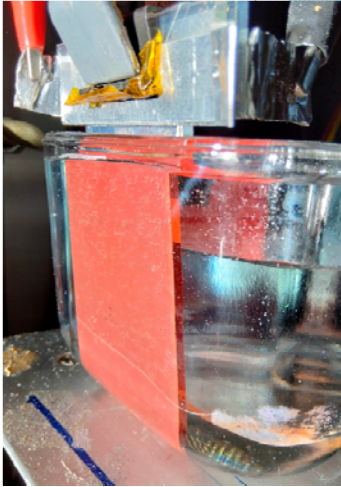
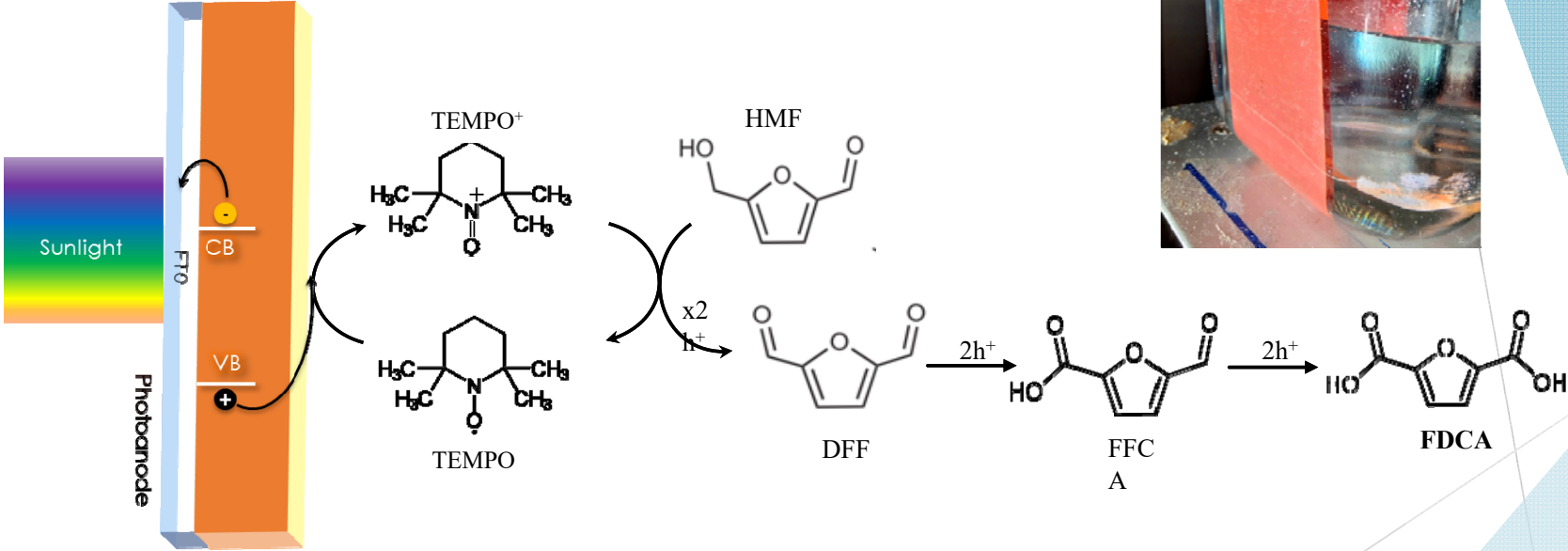
**Hydrogen production by normal water electrolysis using solar cells**  
 \*Including overvoltage more than 1.6 V of electrolysis voltage is needed.  
 (4 solar cells in series)

**Hydrogen production using photoelectrode**  
 \*Number of solar cells can be reduced because the voltage of auxiliary power supply can be reduced.

Total production cost can be reduced than the normal water electrolysis using solar cells.



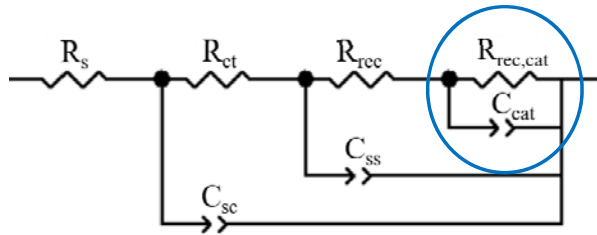
# CONDOR research: Hematite photoanodes for Biomass oxidation: from HMF to FDCA



Kawde, A. et al., *Catalysts* 2021, 11, 969

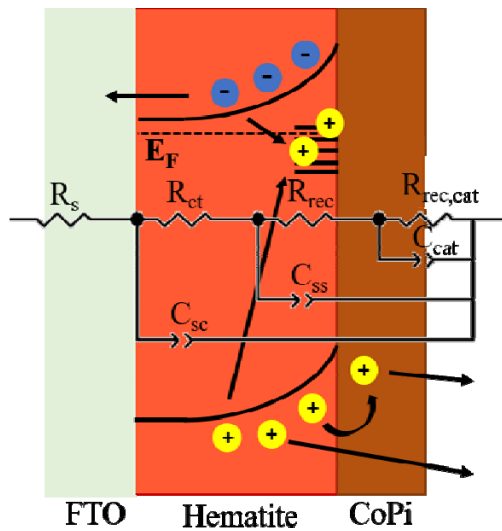


## Electrochemical Impedance Spectroscopy of Hematite with CoPi catalyst



Additional mesh to account for charge transfer through the CoPi layer.

Holes trapped in Hema's SS are transferred to the CoPi layer, which subsequently transfers them to the electrolyte



$R_{rec,cat}$  = recombination resistance through CoPi

$C_{cat}$  = capacitance associated to CoPi

$$R_{tot} = R_s + R_{ct} + R_{rec} + R_{rec,cat}$$

$$R_s = R_{series}$$

$$R_{ct} = R_{charge\ transfer}$$

$$R_{rec} = R_{recombination}$$

$$R_{rec,cat} = R_{recombination\ from\ cat}$$

$$C_{sc} = C_{space\ charge}$$

$$C_{ss} = C_{surface\ states}$$

$$C_{cat} = C_{catalyst}$$

Terra

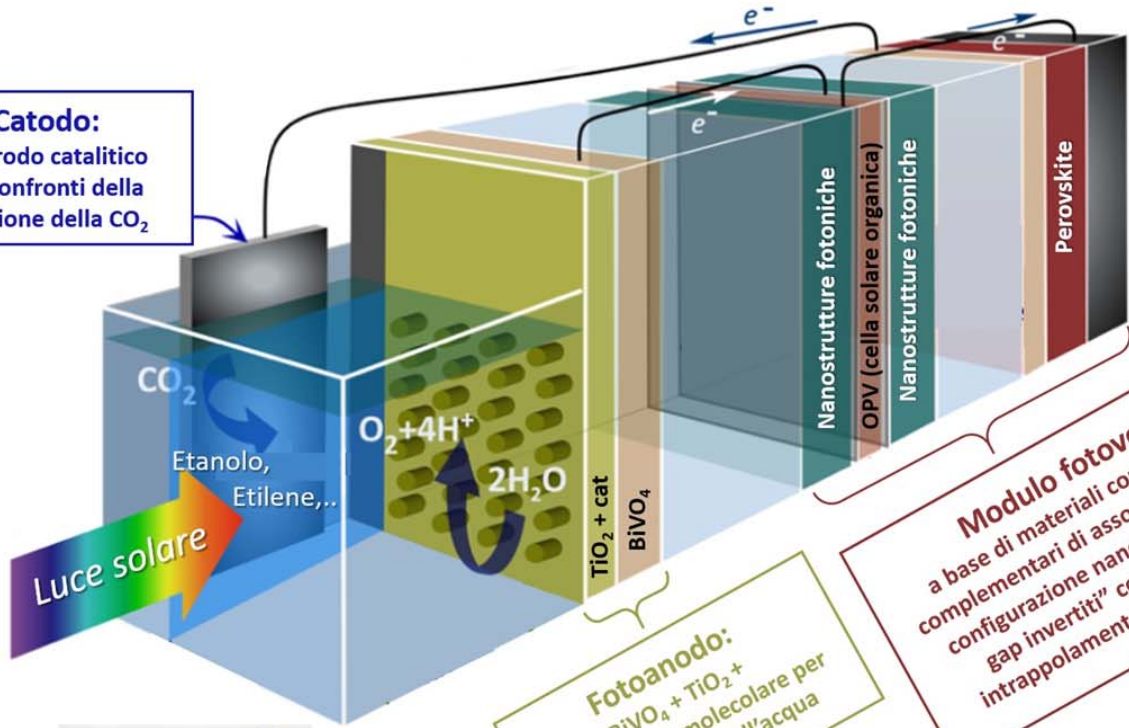
Fuoco

Acqua

Aria

# Integrated Cells for Solar Fuels

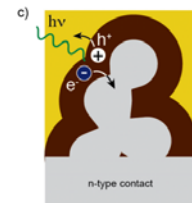
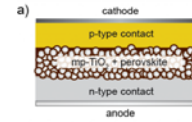
**Catodo:**  
Elettrodo catalitico  
nei confronti della  
riduzione della CO<sub>2</sub>



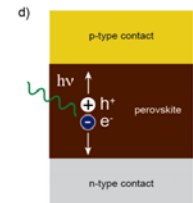
**Fotoanodo:**  
BiVO<sub>4</sub> + TiO<sub>2</sub> +  
catalizzatore molecolare per  
l'ossidazione dell'acqua

**Modulo fotovoltaico:**  
a base di materiali con caratteristiche  
complementari di assorbimento della luce;  
configurazione nanostrutturata a "band  
gap invertiti" con caratteristiche di  
intrappolamento della luce ottimizzate

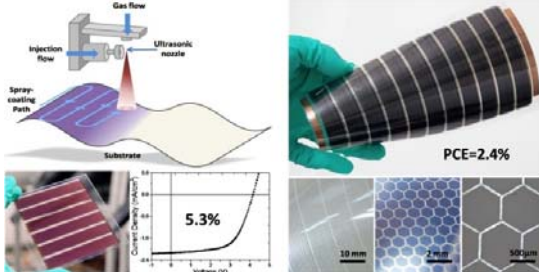
Sensitized perovskite solar cell



Thin-film perovskite solar cell



This project has received funding from the European Union's Horizon Europe research and innovation programme under the Grant Agreement n. 101084326



# General Remarks

Some emerging «low cost» technologies are becoming viable competitors of conventional PV junctions, and their efficiency are further rapidly growing.

PEC represent the most direct pathway to exploit low cost materials for storing solar energy into chemical energy, or to exploit solar power for environmental remediation processes.

Some materials, particularly metal oxides, are cheap, easy to produce and display stability under photoanodic conditions in water based electrolytes. They enjoy suitable energetics to drive demanding electrochemical reactions and to harvest a sizable portion of the solar spectrum.

The thermodynamic efficiency limit to the STH of many semiconductors is still far from being achieved. Fundamental research is still needed to understand the optimization of the interfaces, minimize recombinative losses, improve the light management, but results are being achieved and progresses being made made.





## Photo(electro)chemical People



 Terra

 Fuoco

 Acqua

 Aria