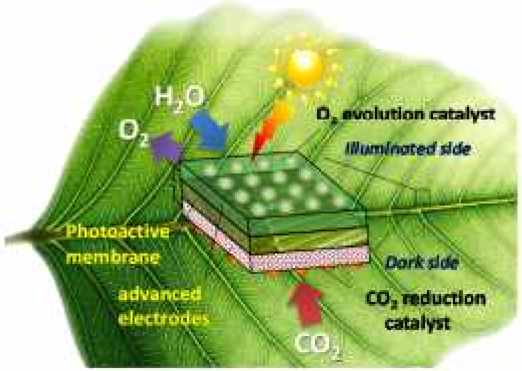
STOA EuCheMS Workshop
The energy storage challenge: which contribution from chemical sciences?
11 February 2014, 14:30-17:00 / European Parliament, Brussels, Room A1E-2

Artificial Photosynthetic Leaves



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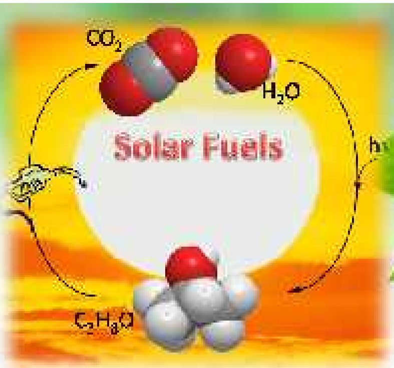
INSTM
European Research Institute of Catalysis

Solar fuels

which link between
CO_2 and energy storage



- **Concept of solar fuels**
  - energetic molecules obtained from the use of *renewable energy* sources and which *avoid the use of fossil fuels* for energy applications.
  - Simpler solar fuel is H_2 (⇨ *renewable* H_2)
  - BUT the actual trend is to **produce liquid fuels**
    - *can be easier stored and transported to long distance.*

- **Role of CO_2**
  - the fuels which can be produced from CO_2 and *ren.*H_2 (methanol, DME, hydrocarbons, etc.) are the *preferable energy vectors* which *integrate well* into the actual energy infrastructure (eg. low investments for transition)

G. Centi, S. Perathoner, *Greenhouse Gases: Science and Techn*. 2011, 1, 21–35.

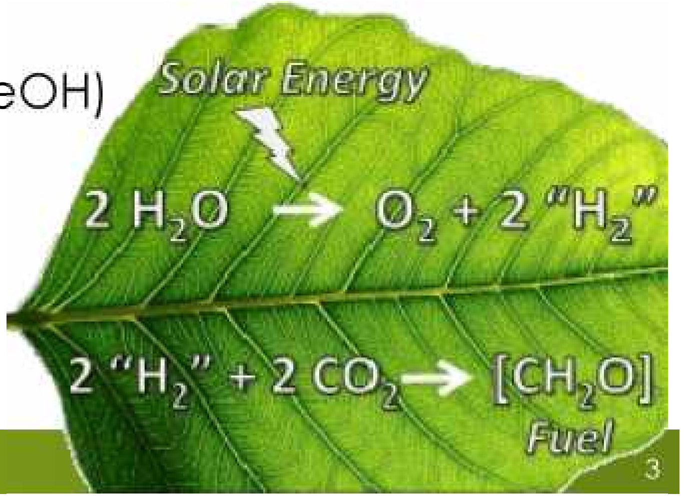
G. Centi, S. Perathoner, *ChemSusChem* 2010, 3, 195-208.

CO_2 utilization

- **Realize energy efficiency**
  - A resource & energy efficiency chemical production
    - reduce use fossil fuels as raw material AND energy vectors
    - introduce renewable energy in the chemical production chain
  - Import unexploited renewable energy (RE) resources
    - via renewable H_2 (water electrolysis) using remote RE sources and CO_2 conv. to methanol or other CO_2-derived energy vectors
    - produce solar fuels and chemicals

a 7 Gtons CO_2 eq. potential impact,
larger than CCS or biofuels

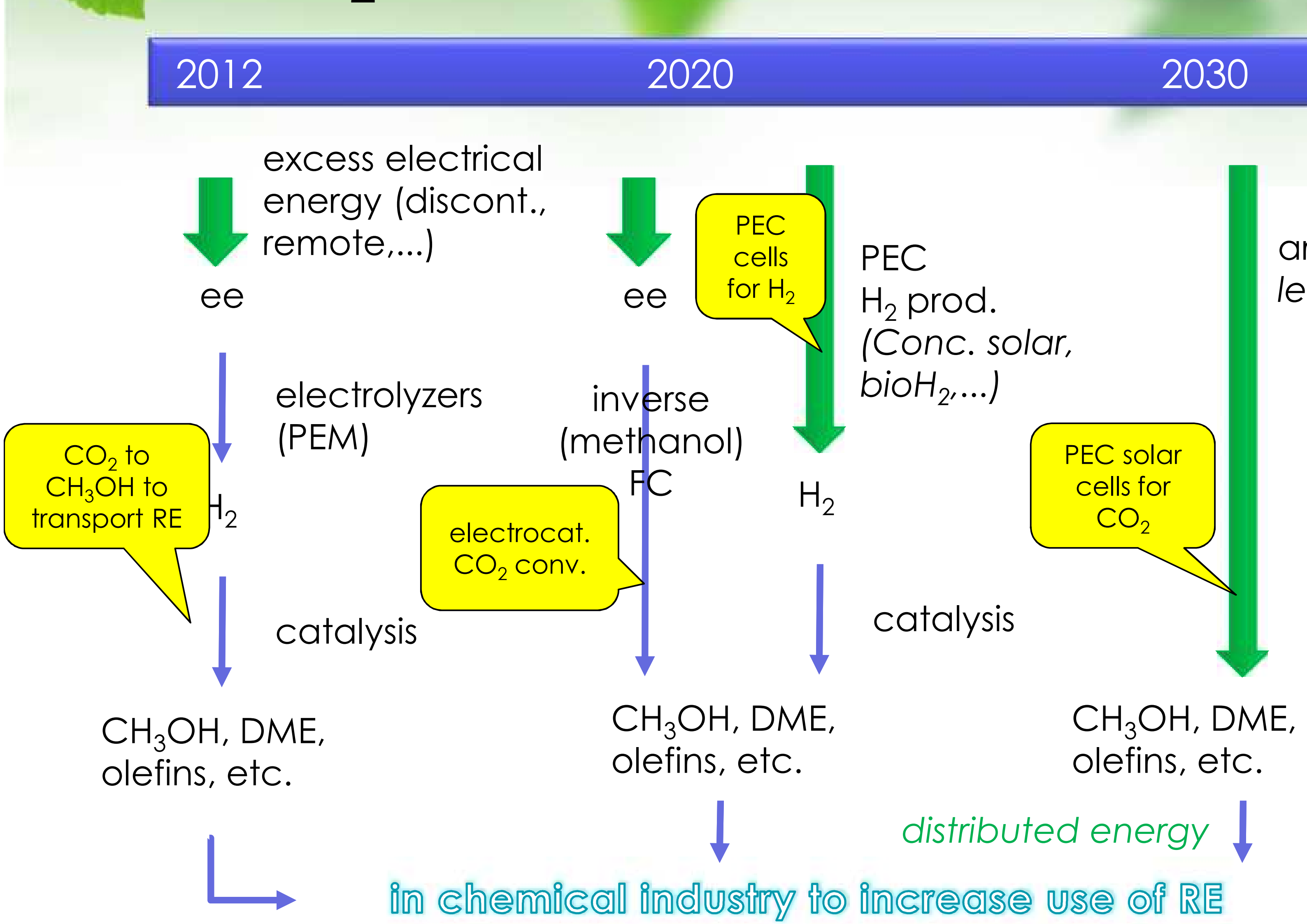
  - Local storage on RE in smart grids
    - Power-to-gas (CO_2 to CH_4) or to-liq. (FT, MeOH)
  - **Develop artificial leaves**
    - in a long-term, for distributed production



G Centi, EA Quadrelli, S Perathoner. Energy Environ. Sci. 2013, 6(6), 1711-1731

A CO_2 roadmap

A vision to sustainability



2012

2020

2030

excess electrical energy (discont., remote,...)

ee

electrolyzers (PEM)

H_2

catalysis

CH_3OH, DME, olefins, etc.

CO_2 to CH_3OH to transport RE

ee

inverse (methanol) FC

electrocat. CO_2 conv.

PEC cells for H_2

PEC H_2 prod. *(Conc. solar, bioH_2,...)*

H_2

catalysis

CH_3OH, DME, olefins, etc.

artificial *leaves*

G. Centi, S. Perathoner et al., *ChemSusChem*, 2012

PEC solar cells for CO_2

CH_3OH, DME, olefins, etc.

distributed energy

in chemical industry to increase use of RE

G. Centi, E. A. Quadrelli, S. Perathoner, *Energy Environ. Sci.*, 2013, 6, 1711

An impactful path for Europe

A great potential and economic opportunity

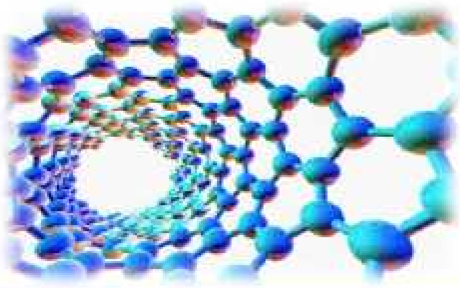
The European chemical industry has a unique opportunity to:

- Use as feedstock the only carbon resource we have in abundance (without land use, *decrease dependency on fossil resources)*
- Reduce GHG emissions
- Increase renewable energy potential
- Take leadership in sustainable technologies *(require European to combine efforts (industry+ academia) to win this race)*

Converting CO_2 is technically feasible and can be economically competitive

BUT a number of developments are necessary:

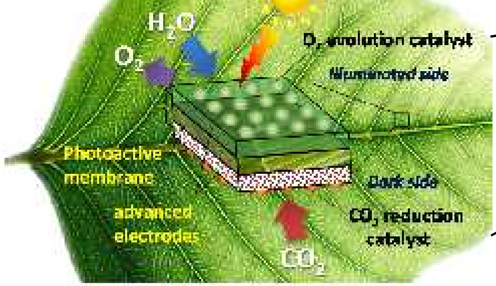
- improved materials for using RE sources (solar, wind, etc.)
- improve electrolyzers and related materials to produce H_2 from water using electrical energy
- improve technologies for capturing and transport CO_2
- improved catalysts and processes for converting CO_2
- ....



Nano-technologies are the enabling factors
to realize this sustainable scenario

Vision 2030: CO_2/artificial leaves

- **Provide a delocalized energy**
  - to smart cities and buildings
  - for mobility and industry



Light reaction

$2H_2O \Rightarrow O_2 + "2H_2"$

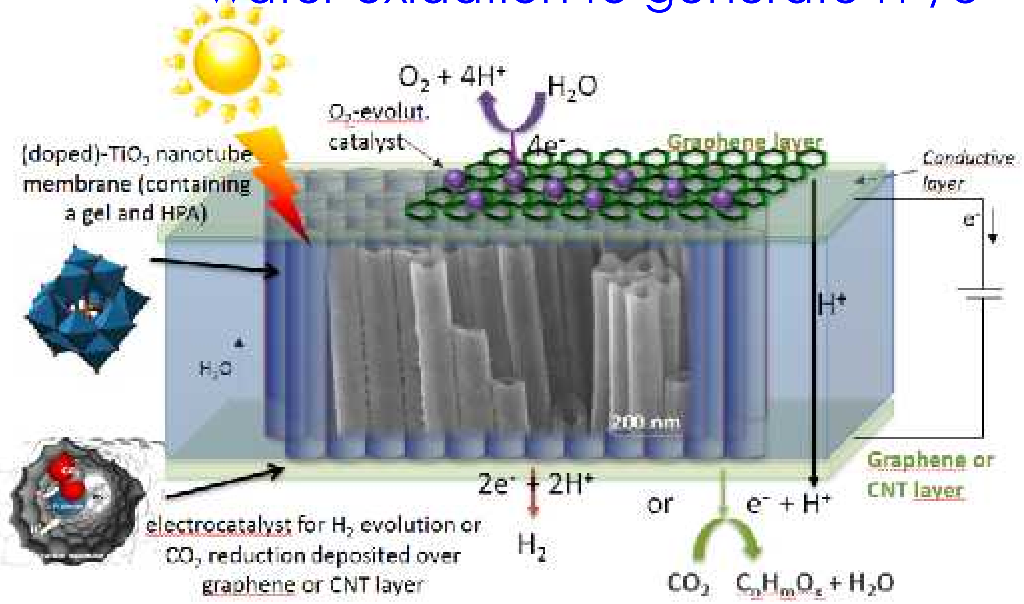
Dark reaction

$"2H_2" + CO_2 \Rightarrow (CH_2O)$ *(liq. HC, alcohols)*

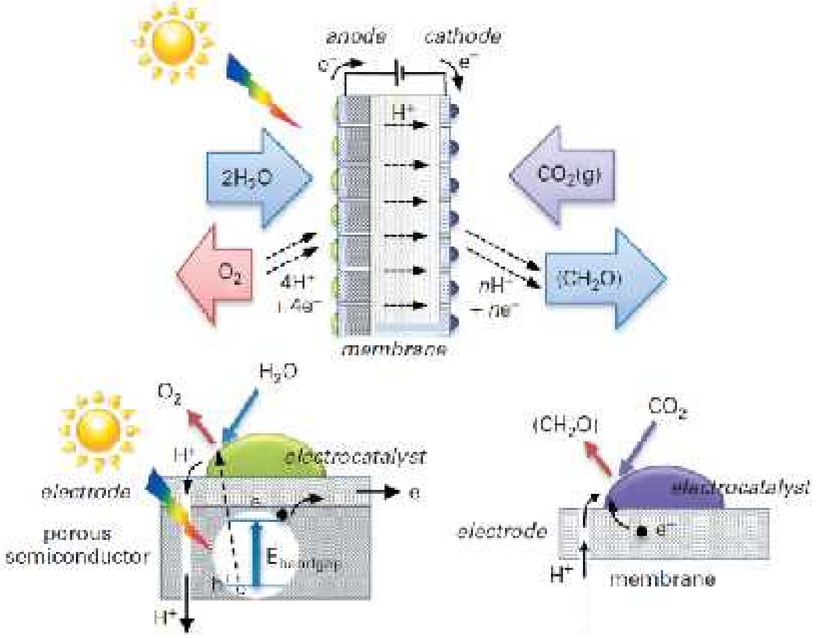
Nanotech to enable this future scenario

- *Going to artificial leaves*

water oxidation to generate H^+/e^-



CO_2 to hydrocarbons/alcohols



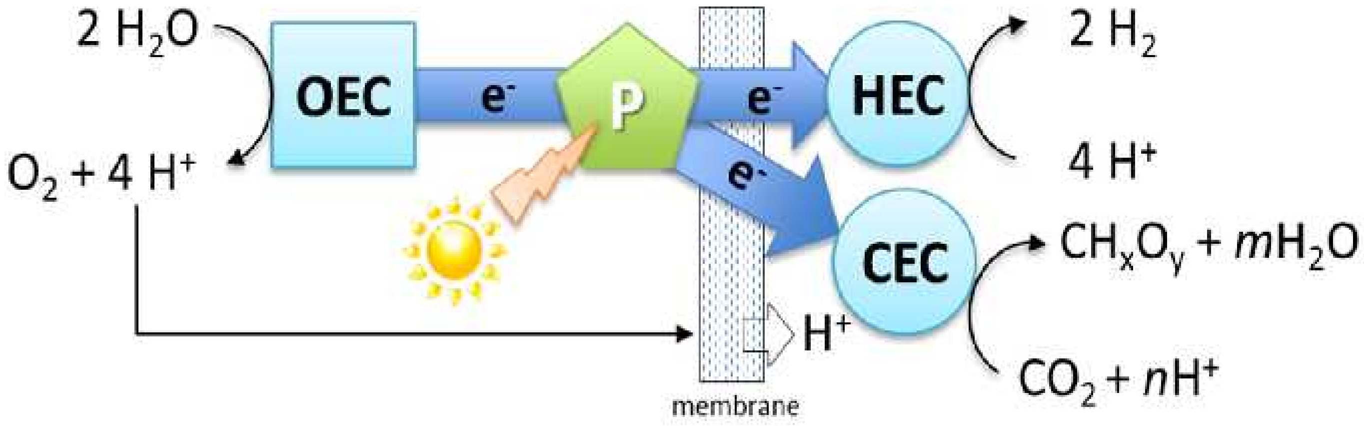
Many challenges, nanoscale control is the key to improve performances

G. Centi, S. Perathoner et al., *ChemSusChem*, 2012

PEC: photoelectrocatalytic

PEC solar cells: main elements

- light-harvesting centers to capture photons and transduce them into electrons which are injected into the photosynthetic chain;
- proton and electron transfer elements (along the photosynthetic chain), causing local, spatial charge separation;
- separation of the zones of evolution of O_2 and H_2 or the products of CO_2 reduction through a membrane;
- catalytic redox reactions to oxidize water to O_2 and protons (OEC) and to produce H_2 (HEC) or reduce CO_2 (CEC).



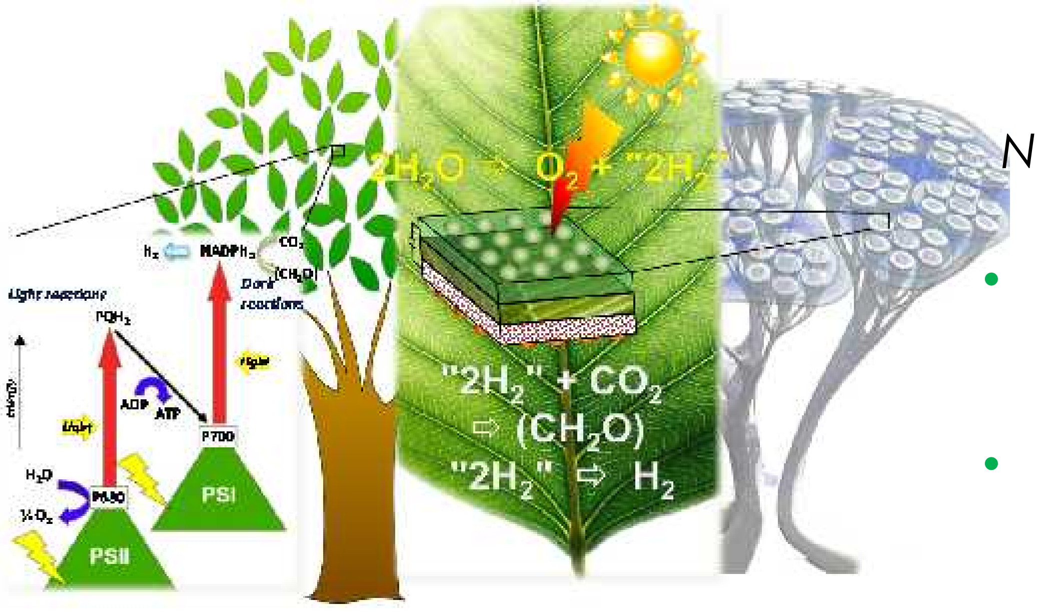
Electrons flow from OEC to HEC/CEC when catalysis occurs, due to the potential difference.
A membrane separates the photoanodic from the electrocatalytic cathodic zone.

G. Centi, S. Perathoner, Artificial Leaves, *Kirk-Othmer Encyclopedia*, 2013

BUT Artificial Photosynthetic Leaves should NOT mimicking the natural processes

by inspired, not reproduce

- *with respect to complex machinery present in natural systems* (key role by self-regulation and -reparation)
- necessary to intensify the processes, at least of one or more order of magnitude, to improve the cost-effectiveness.



New functional and robust design to realize two goals:

- i) intensify the process, thus allowing a higher productivity and efficiency in converting sunlight
- ii) use solid components which keep functionalities, but are more robust, scalable and cost-effective.

move from H_2 production to CO_2 reduction

Requirements for practical implementation of PEC solar cells

- productivity intensification (to improve cost-effectiveness),
- robustness even with temperatures higher than room temperature and eventually under pressure (necessary to achieve the first goal),
- chemical inertness (nascent O_2 or H_2O_2 on one side and electrons on the other side of PEC device are very reactive species),
- low cost of construction and use of non-rare materials,
- selectivity in the nature and distribution of the products obtained by CO_2 reduction, and in avoiding side reactions such as H^+/e^- recombination to give H_2 (rather than hydrogenate CO_2).
    - overcome the limits of natural systems by designing conceptually different devices,
    - several of the current research activities do not meet these requirements

need to approach the topic from different perspectives of those investigated up to now (for example, artificial photosynthesis).

Target objective for PEC solar cells: cost-effectiveness

1/2

- most common way to assess a photocatalyst's efficiency → external QY

$$QY\ (\%) = \frac{\text{Photochemical reaction rate}}{\text{Photon absorption rate}} \cdot 100\% = \frac{r}{I_o \cdot F}$$

I_o is the incident photon flux and F is the integrated absorption fraction in the system over the useful wavelength range

- **target (for implementation):** 10% (15%) (?)

- from a practical perspective ⇨ sunlight is not a raw material, being virtually zero its cost. It is thus necessary to introduce a cost-effectiveness parameter ⇨ **productivity of the device per cost unit.**

- *reference*: cost of H_2 production using the PV-electrolyser combination
- current conventional electrolysers have a conversion performance of about 50 kWh/kg H_2 (4,5 kWh/m^3 H_2) ⇨ specific productivity (PV ~ hourly power of 200 W per m^2): H_2 production is $0{,}4\ g\ H_2 \cdot m^{-2} \cdot h^{-1}$ (if RE cost < 5 cents/kW (actual 10-15 at the best, but possible in some remote areas) ⇨ H_2 cost < 3 $/kg)

Target objective for PEC solar cells: *cost-effectiveness*

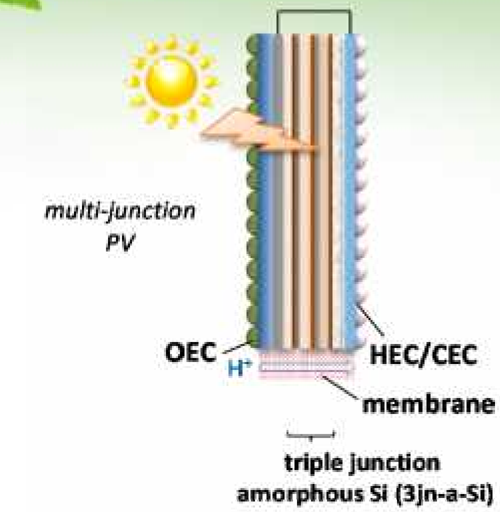
2/2

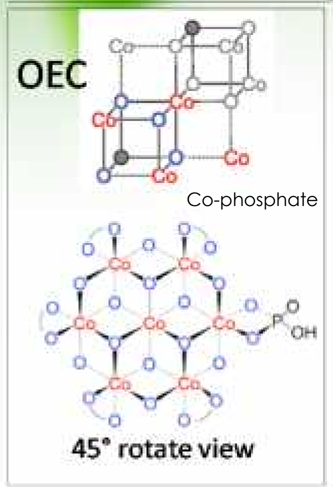
- ***PV-electrolyser*** *(current)*: H_2 production is 0,4 g $H_2 \cdot m^{-2} \cdot h^{-1}$

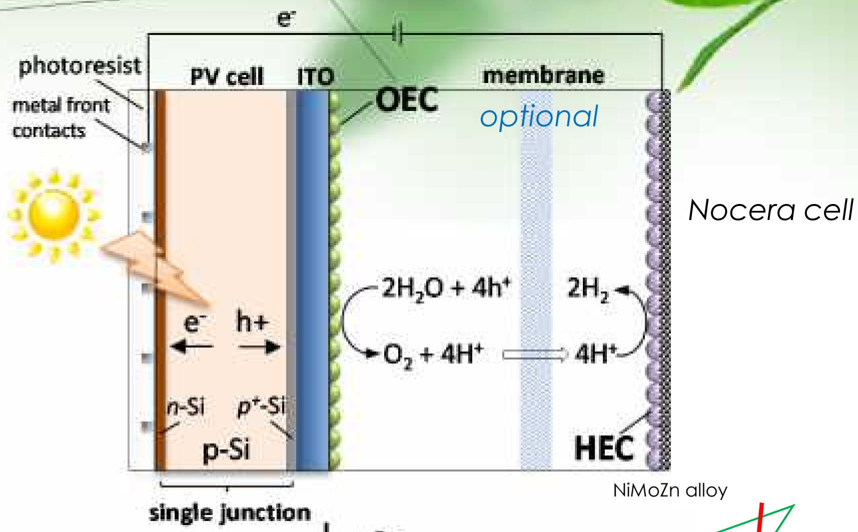
- **PEC device:**
  - cost of manufacture of the module can be estimated (when industrialized) at least 5 times higher than those for PV unit, but the electrolyser cost is absent as well as those for the additional devices necessary for PV-electrolyser connections (DC-DC converter, controllers, etc.)
  - due to the higher panel cost per m^2, it is necessary to reduce their size by having a higher specific productivity. Maintenance and running cost are also slightly higher.

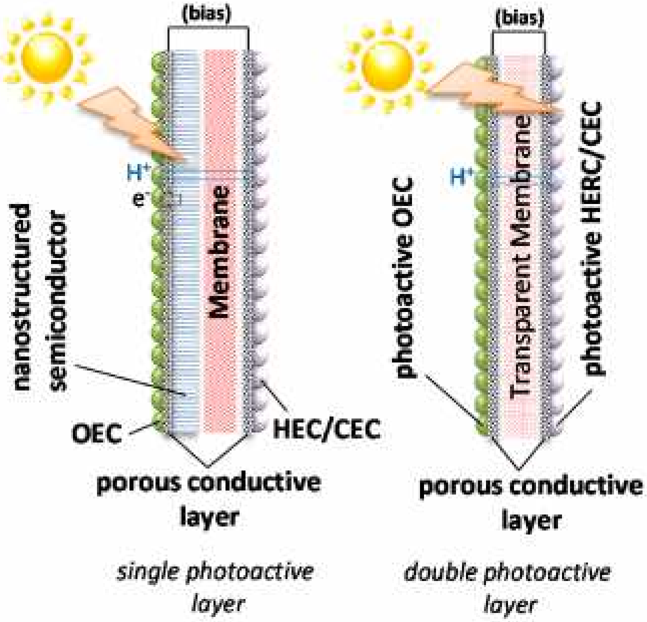
  - reasonable indicate that a minimum target H_2 production (using sunlight) should be about **3-5 g $H_2 \cdot m^{-2} \cdot h^{-1}$** for PEC cells having a *target cost* around 2000 $/$m^2$ (for industrial production).
  - These parameters should be a reference to estimate techno-economic feasibility of PEC solar cells for water photoelectrolysis
  - Current data indicate a productivity at the best of about 0,2 g $H_2 \cdot m^{-2} \cdot$h-1, but often much lower.
  - Productivity is clearly related to QY, but which should be increased at constant PEC device cost and meeting also cell design constrains.

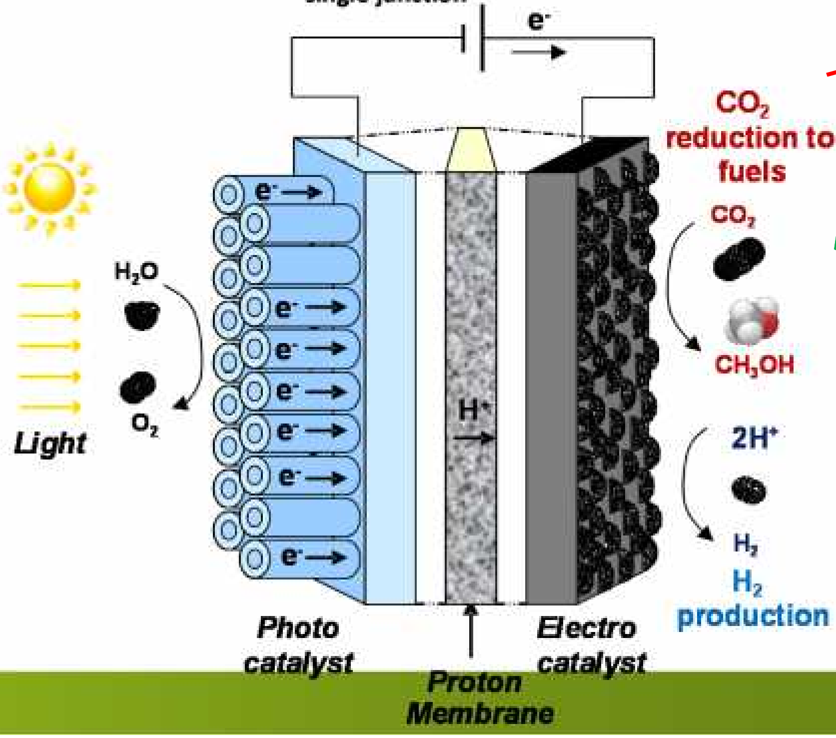
PEC solar cells

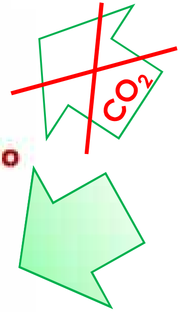












Conclusions

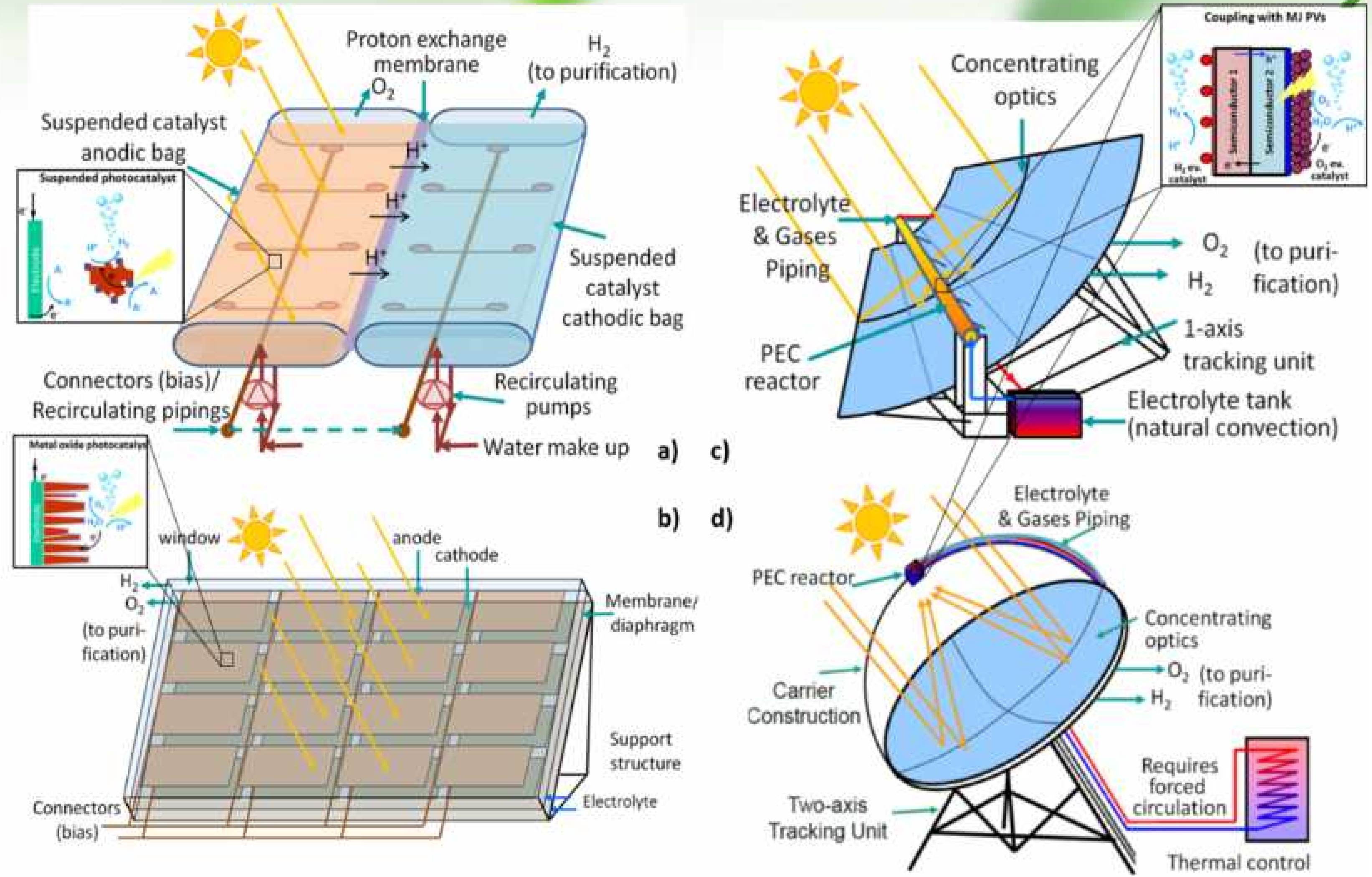
- Although bio-mimicking approach provides inspiration, *a radically different strategy*, particularly in terms of system design, is necessary.
- Smart, cheap and robust devices are necessary. The use of inorganic materials would be necessary, because most of the investigated molecular complexes are too costly, not robust enough and/or require special reaction conditions.
- At least at a conceptual level and in the definition of the artificial leaf elements (catalysts, electrodes, membranes, sensitizers), a *system design approach* is necessary because the cell engineering (mass/charge transport, fluid-dynamics, sealing, etc.) are critical elements to consider already at the initial stage.

CO$_2$/Artificial Leave

Creating tomorrow's solar fuels today

Creating tomorrow's solar fuels today

Alternative plant design for PEC reactors and water splitting processes



a) ambient pressure, suspended photocatalysts in bags; b) Flat, low-pressure (4 bar) PEC reactor; c) Tubular, high-pressure (30 bars) PEC reactor at the receiver of an axial sun concentration system (low concentration ratios 10:1 – 30:1); d) Tubular, high-pressure (30 bars) PEC reactor at the receiver of an parabolic sun concentration system (high concentration ratios: up to 500:1).