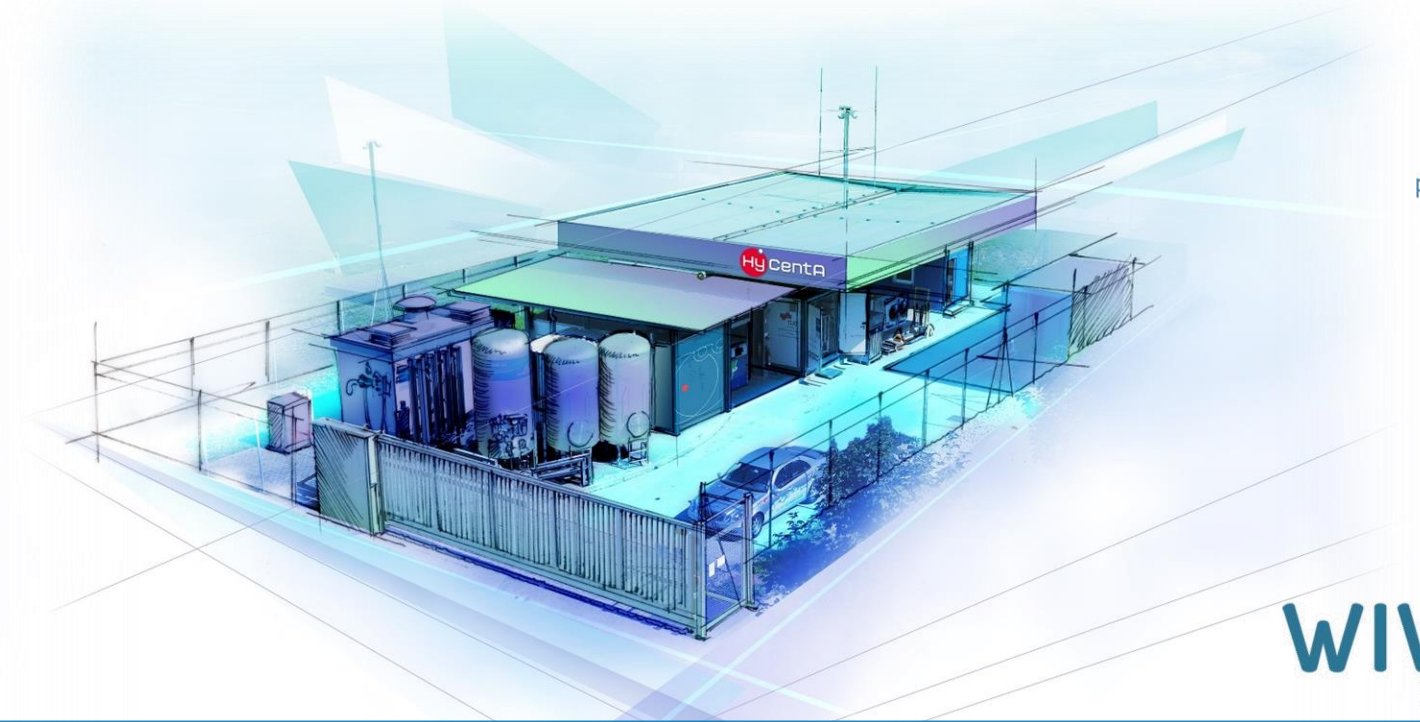

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FFG Promoting Innovation.

HYDROGEN AUSTRIA

WIVA P&G Energy Model Region

Elektrolyse und Photoelektrolyse

Stand der Technik und Potenziale

DI Dr. Marie-Gabrielle Macherhammer

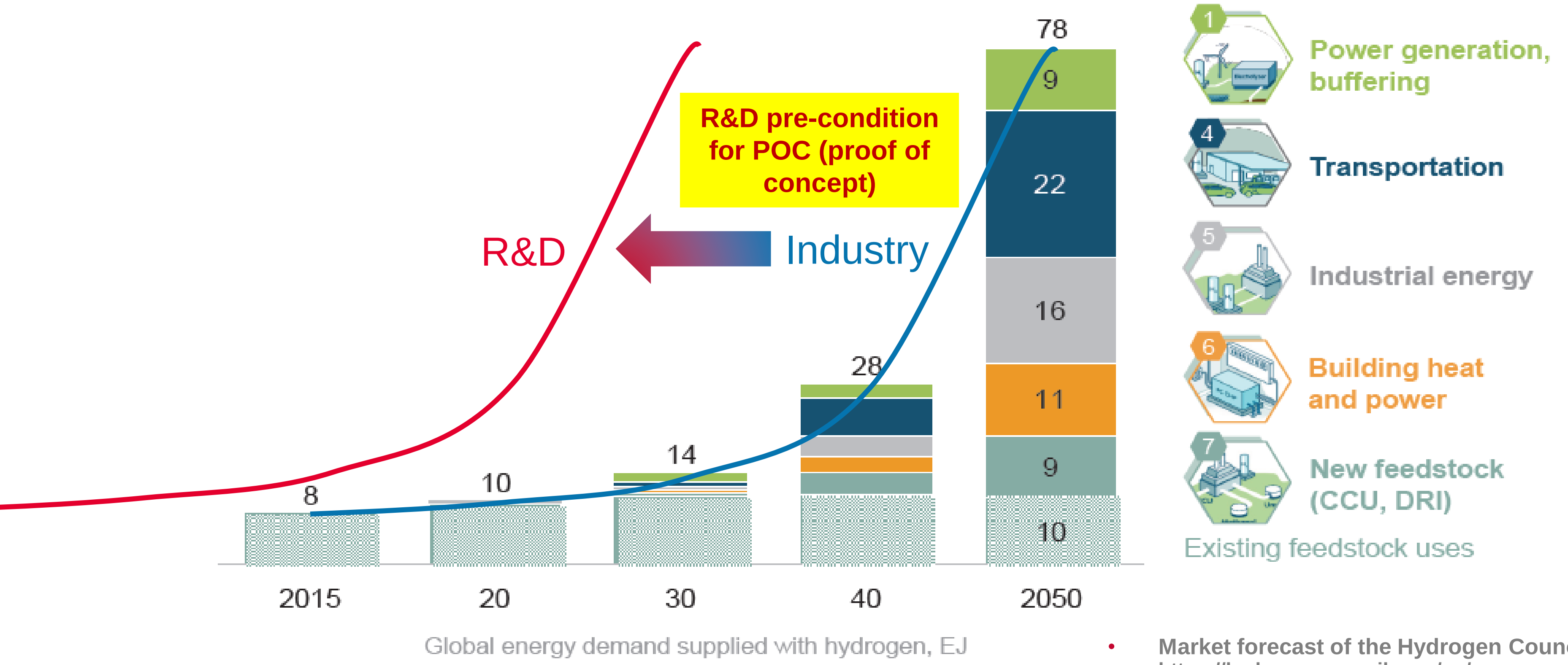
Graz, 06.09.2022

HyCentA HYDROGEN CENTER AUSTRIA

TU Graz

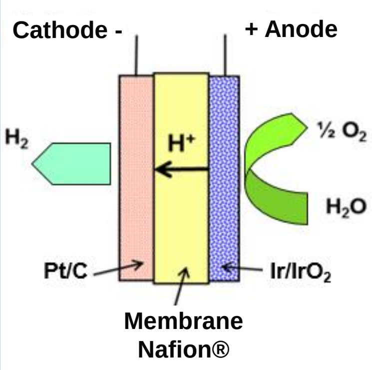
Hydrogen Economy

"H_2 has a long-term potential of 20-30 % of all energy sources"



- Market forecast of the Hydrogen Council https://hydrogencouncil.com/en/

Electrolysis – technology comparison

	PEM-EL Polymer Electrolyte Membrane Electrolysis
Electrolyte	acidic
	
Operating temperature	50 – 80 °C

PEMEL – state of the art & future targets

	2022	2050
Current density	1-3 A/cm^2	4-6 A/cm^2
Voltage range limit	1.4 – 2.3 V	< 1.7 V
Cell pressure	< 50 bar	> 70 bar
Load range	5 – 130 %	5 – 300 %
Electrical efficiency (stack)	47 – 66 kWh/kg$_{H2}$	< 42 kWh/kg$_{H2}$
Lifetime (stack)	50 000 – 80 000 h	100 000 – 200 000 h
Capital costs stack/system	400 / 700 – 1 400 $/kW	< 100 / 200 $/kW

Source: Cummins

Research focus:

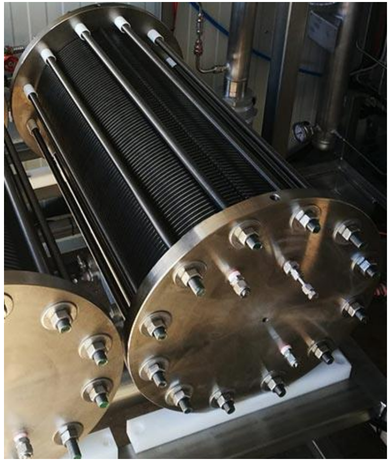
Mitigate membrane poisoning/deactivation by foreign elements from components and system

Increase catalyst utilisation of anode and cathode catalyst

Improve kinetics for oxygen evolution using iridium-free catalysts and maintain stability comparable to iridium SoA

AEMEL – state of the art & future targets

	2022	2050
Current density	0.2 – 2 A/cm^2	> 2 A/cm^2
Voltage range limit	1.4 – 2.0 V	< 2 V
Cell pressure	< 35 bar	> 70 bar
Load range	5 – 100 %	5 – 200 %
Electrical efficiency (stack)	51.5 – 66 kWh/kg$_{H2}$	< 42 kWh/kg$_{H2}$
Lifetime (stack)	> 5 000 h	100 000 h
Capital costs stack/system	? $/kW	< 100 / 200 $/kW



Source: Enerstack

Research focus:

- Development for cost effective PTLs for AEM electrolysis
- Improve kinetics for hydrogen and oxygen evolution and maintain long-term stability
- Increase anion exchange membrane durability

AEL – state of the art & future targets

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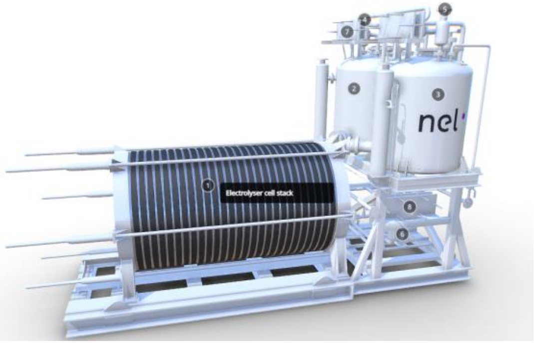
	2022	2050
Current density	0.2 – 0.8 A/cm^2	> 2 A/cm^2
Voltage range limit	1.4 – 3.0 V	< 1.7 V
Cell pressure	< 30 bar	> 70 bar
Load range	15 – 100 %	5 – 300 %
Electrical efficiency (stack)	47 – 66 kWh/kg$_{H2}$	< 42 kWh/kg$_{H2}$
Lifetime (stack)	60 000 h	100 000 h
Capital costs stack/system	270/500 – 1 000 $/kW	< 100 / 200 $/kW



Source: Nel Hydrogen

Research focus:

- High catalyst surface area > 50 m^2/g
- Improve kinetics for hydrogen and oxygen evolution with novel nickel-based alloys
- Eliminate mechanical degradation of catalyst layers (delamination, dissolution)

SOEC – state of the art & future targets

	2022	2050
Current density	0.1 – 1.0 A/cm^2	> 2 A/cm^2
Voltage range limit	1.0 – 1.5 V	< 1.48 V
Cell pressure	1 bar	> 20 bar
Load range	30 – 125 %	0 – 200 %
Electrical efficiency (stack)	35 – 50 kWh/kg$_{H2}$	< 35 kWh/kg$_{H2}$
Lifetime (stack)	< 20 000 h	80 000 h
Capital costs stack/system	> 2 000/? $/kW	< 200 / 300 $/kW

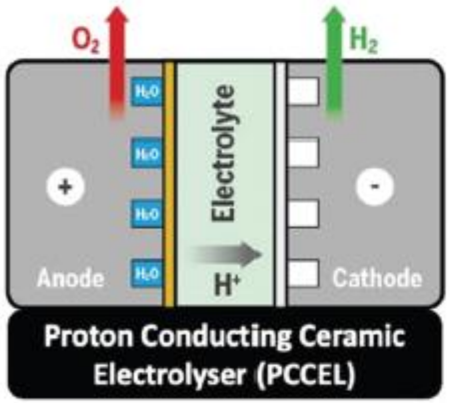
Source: Sunfire

Research focus:

- Reduce temperature to be able to use lower cost materials
- Understanding and controlling electrochemical degradation and thermo-mechanical stability
- Improve the electrolyte conductivity matching the thermal expansion coefficient of both electrodes

PCCEL – state of the art & future targets

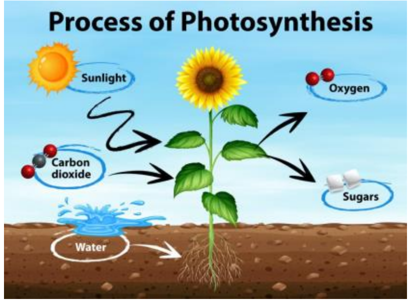
	2022
Current density	0.1 – 1.9 A/cm^2 (@1.3 V)
Temperature	300 – 600 °C
Electrolyte	(Y,Yb)-Doped-Ba(Ce,Zr)$O_{3-\delta}$
Catalyst (oxygen site)	Perovskite-type
Catalyst (hydrogen site)	Ni/YSZ, Ni-BZY/LSC, BCFYZ
Cell pressure	1 bar
Lifetime (stack)	?
Capital costs stack/system	?



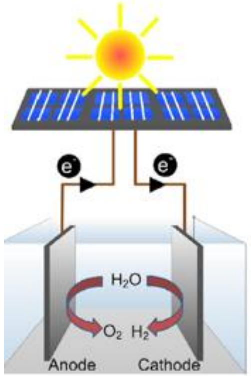
Source: DOI: 10.1039/d0cs01079k

Photoelectrolysis / Photolysis

- **Conventional design coupling of electrolysis and renewable energies**
- **Alternative: based on photosynthesis**
  - Direct water splitting with sun light
  - **Photocatalysis**: photocatalytical water splitting uses photons to split water directly into its components hydrogen and oxygen
  - **Photoelectrochemical water splitting**: based on the same principle but additional electrodes are introduced
  - **Direct PV/electrolysis coupling:** two different systems



Source: https://www.science-sparks.com/what-is-photosynthesis/

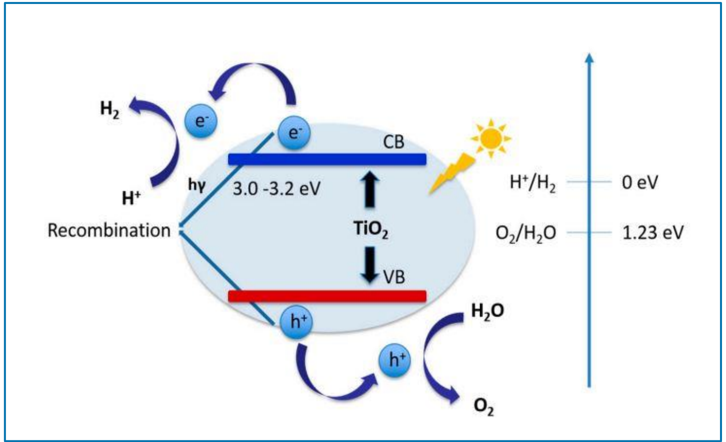


Source: 10.1016/j.enchem.2019.100014

Photocatalytical water splitting

- **Photons split water into H_2 and O_2:** $H_2O + 2h\nu \rightarrow H_2 + \frac{1}{2}O_2$
- **Photons with $E > E_G$ is absorbed, e^- jumps from VB to CB**
- **Absorption of light → electron-hole-pair is produced in photoactive semiconductor particle e.g., TiO_2**
- **Separation of charge, transport of e^-, h^+ important →**
- **Reduction and oxidation of water**
- **Solar-to-Hydrogen (StH) efficiency**
  - Rarely higher than 1% at PCWS

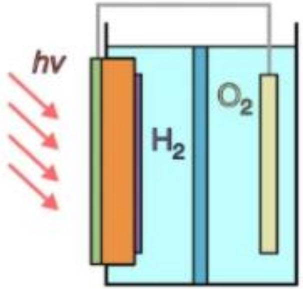
$$STH = \frac{\text{Total energy generated}}{\text{Total energy input}} = \frac{\Delta G r_{H_2}}{P_{sun}\ S},$$



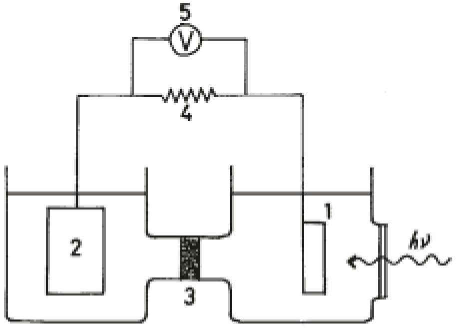
Source: https://doi.org/10.3390/molecules21070900

Photoelectrochemical cell

- **Again, photons are used for water splitting**
- **One cell consists of: 2 electrodes, photoanode + (photo)cathode, electrolyte and membrane**
- **Simple cell: TiO_2/Pt – cell of Honda & Fujishima (“S2”: single-absorber, 2 photons)**
- **Solar to Hydrogen efficiency**
  - 3-5 % (unassisted)
  - higher than 12 % (applied bias)



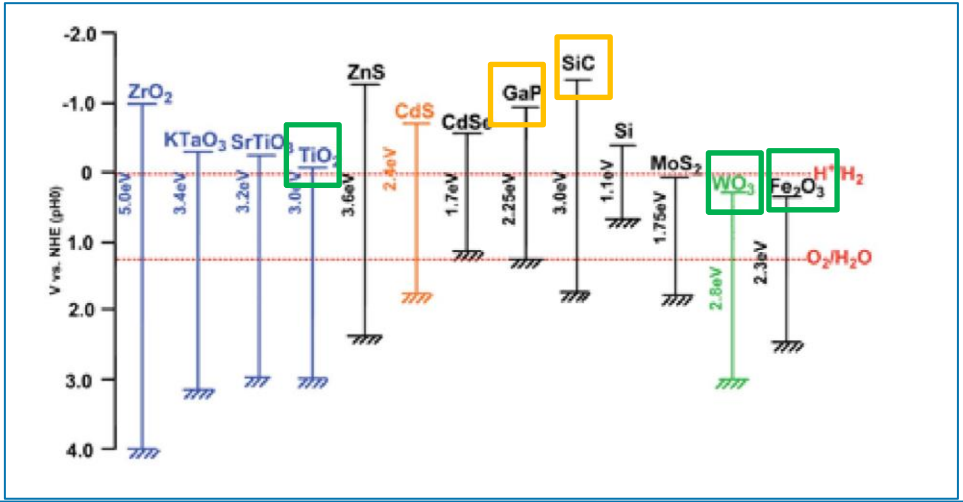
Source: 10.1038/ncomms12681



Source: https://doi.org/10.1038/238037a0

Materials for photoelectrodes

- **Photocathode**
  - Reduction of water – H^+/H_2
  - P-type semiconductor
  - Interesting materials: GaP, SiC



- **Photoanode**
  - Oxidation of water – O_2/H_2O
  - N-type semiconductor
  - Examples of promising photoanodes include monometallic oxides (TiO_2, ZnO, WO_3, and α-Fe_2O_3), bimetallic oxides ($BiVO_4$), and metal (oxy)nitrides (Ta_3N_5 and TaON).

Source: https://doi.org/10.3390/molecules21070900

Optimisation of PEC

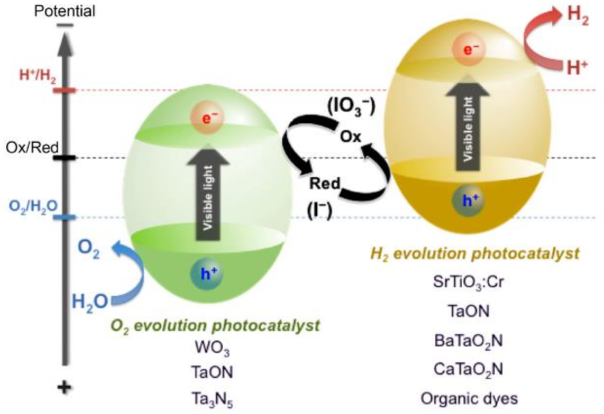
- **Z-scheme**
- **Surface modification**
- **Nanostructures / mesoporous surfaces**
- Heterojunction
- Solid solutions (mixed crystal)
- Dye-modified surfaces

Source:10.1117/1.JPE.7.012006

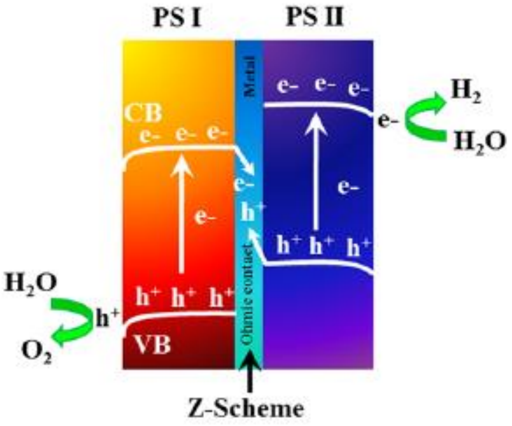
Biological photosynthesis – Z scheme

- **Nature leads the way – Photosynthesis**
- **It is difficult to find one semiconductor, which can provide the necessary bandwidth → combination of two materials**

- **Two reactions**
  - Reduction of H^+/H_2
  - Oxidation of H_2O/O_2



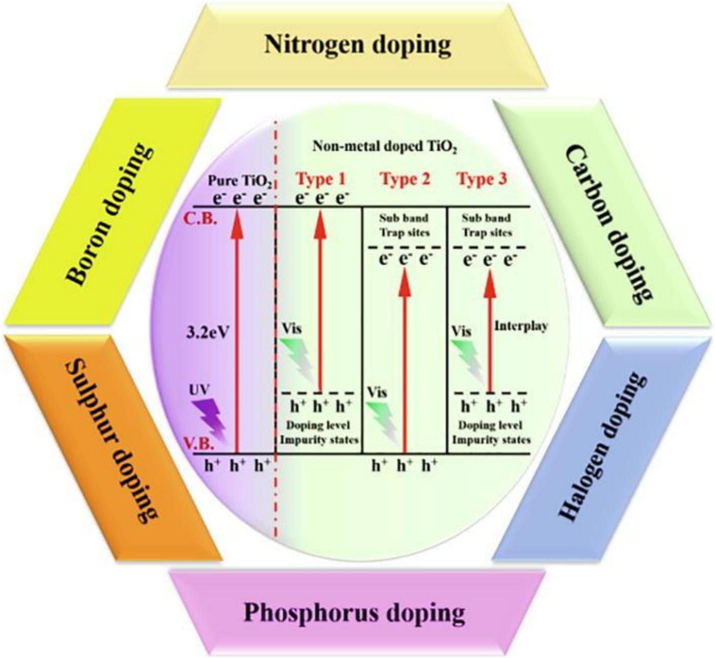
Source: https://doi.org/10.1016/j.jphotochemrev.2011.02.003



Source:10.1117/1.JPE.7.012006

Surface modification

- **Doping of PEC**
  - Narrowing of bandwidth
- **Addition of co-catalysts like Pt, IrO_2, …**
  - Alternative to PGM materials: Metal sulphides
- **Plasmonic metal nanostructures like**
  - Au/TiO_2 nanostructures

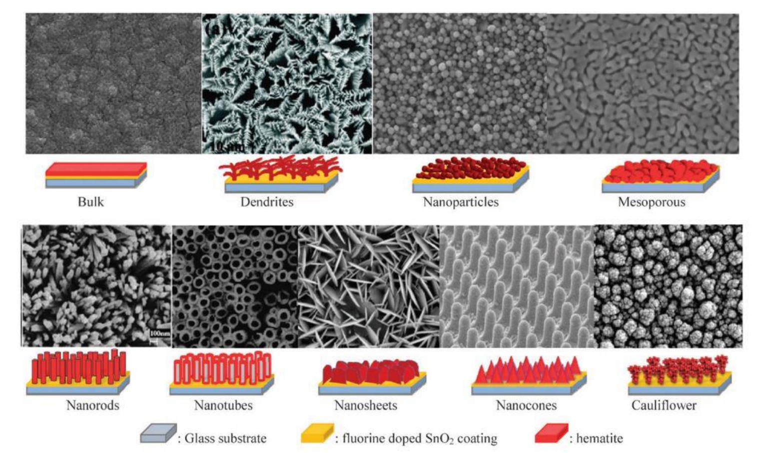


Doping for TiO_2
Source: https://doi.org/10.1016/j.jechem.2021.08.038

Nanostructures

- **Avoids high numbers of an charge recombination**
- **1D, 2D & 3D nanostructures help especially with n-type semiconductors**
  - 1D: Nanowires, nanorods and nanotubes
  - 2D: Nanosheets with high specific surface area and crystallinity
  - 3D: integrated different functional materials of 1D or 2D structures to construct 3-D hierarchical nanostructures

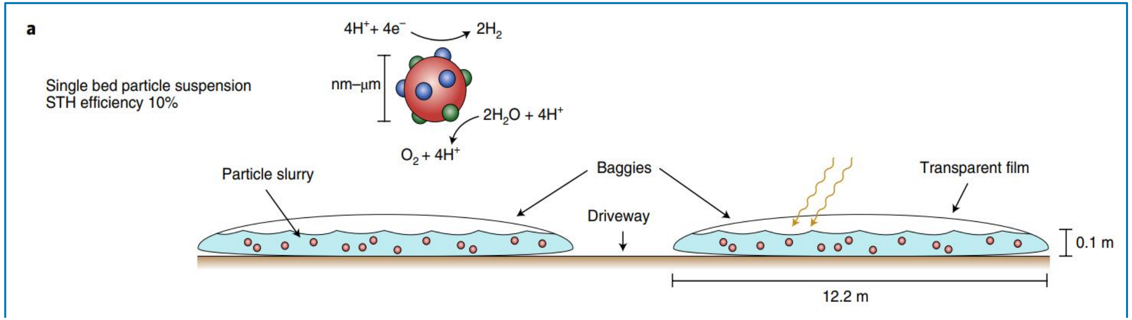
➢ increase large surface areas for light harvesting without inhibiting charge transfer and separation



Source: https://doi.org/10.1039/C5NH00098J

Reactor design photocatalysis

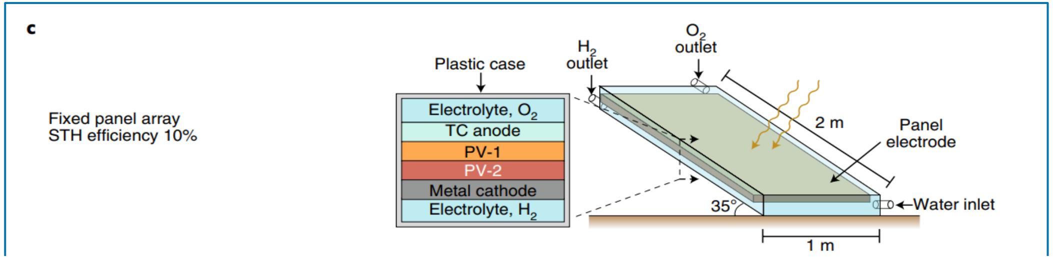
- **a) Type 1, reduction and oxidation of water happens on the same particle; gas is collected at the top, needs purification**
- **b) Type 2, two different bags for O_2 and H_2 production, needs membrane and redox mediator (e.g. Br, I, Fe complex)**



Source: https://doi.org/10.1039/C3EE40831K

Reactor design photoelectrochemical cell

- **c) PEC panel including planar electrodes and photoactive layers; separation of gas due to different outlets**
- **d) PEC panel with additional concentrator to increase light intensity**

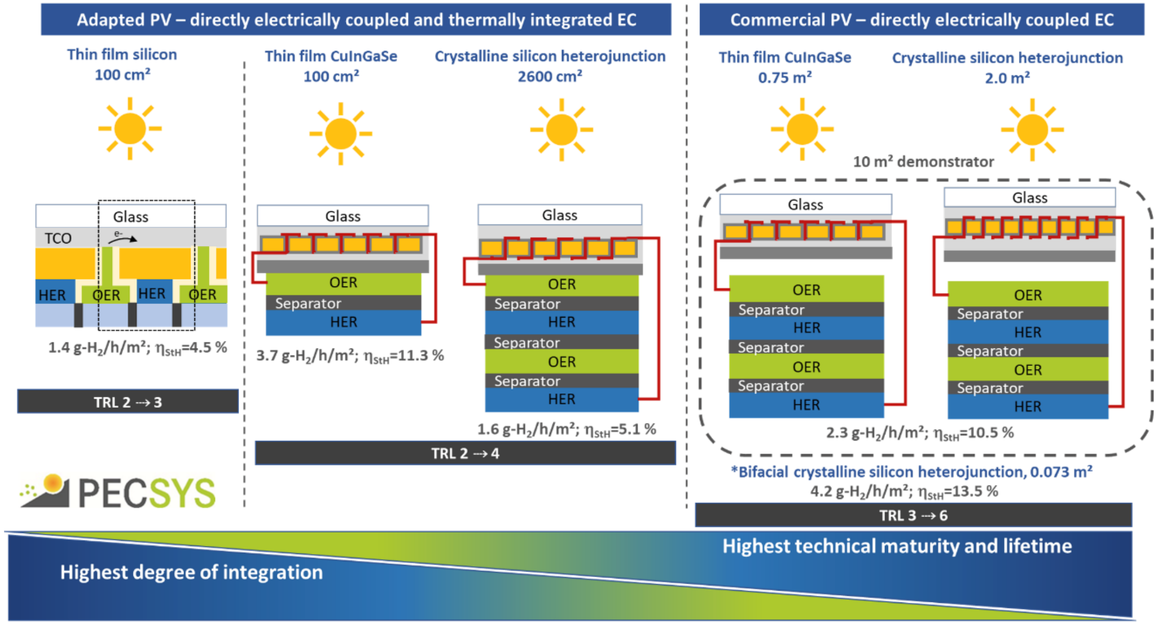


Source: https://doi.org/10.1039/C3EE40831K

EU PECSYS Project

The PECSYS consortium used predominantly low-cost, established photovoltaic (PV) technologies directly coupled to electrolyser units, instead of photoelectrochemical devices, for water splitting.

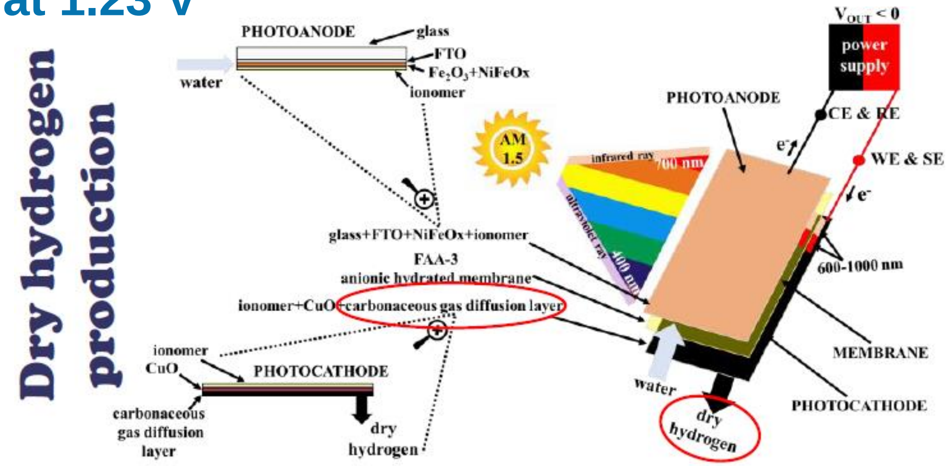
PECSYS
Technology demonstration of large scale photo-electrochemical system for solar hydrogen production



Source: https://www.helmholtz-berlin.de/projects/pecsys/

EU Project FotoH2

- **Non-noble photoelectrodes**
  - Hematite (anode) and cupric oxides (cathode)
  - Anion exchange membrane
- **Applied bias: 10 % throughput efficiency at 1.23 V**

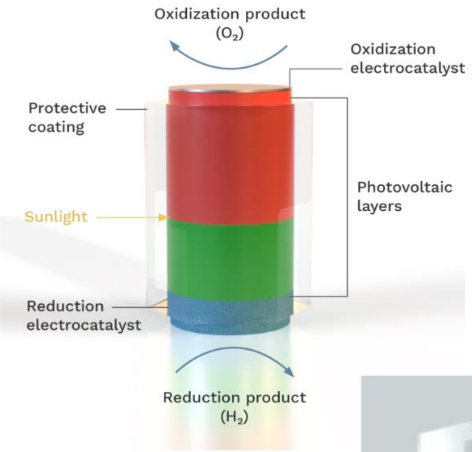


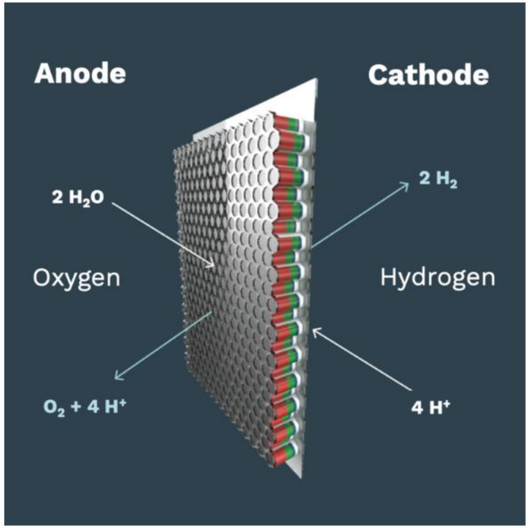
FotoH2 Panel
Glass **E**lectrode **M**embrane **A**ssembly (**GEMA**) concept

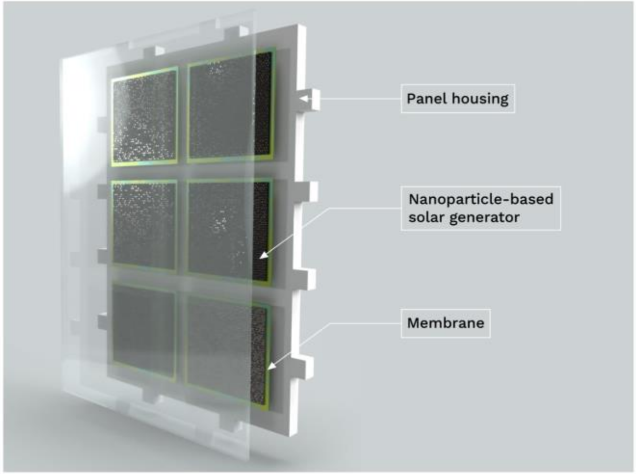
Source: https://fotoh2.eu/

SunHydrogen Inc.

- **Based on Z-scheme (p/n junction), added co-catalysts and membrane**
- **Materials unknown**







Source: https://www.sunhydrogen.com/

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