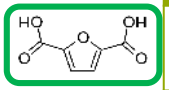
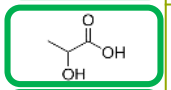
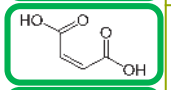
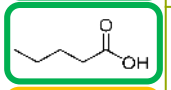
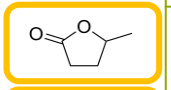
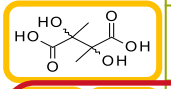
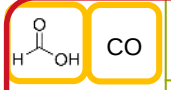
Electrocatalysis: Development of electrocatalysts for solar fuels

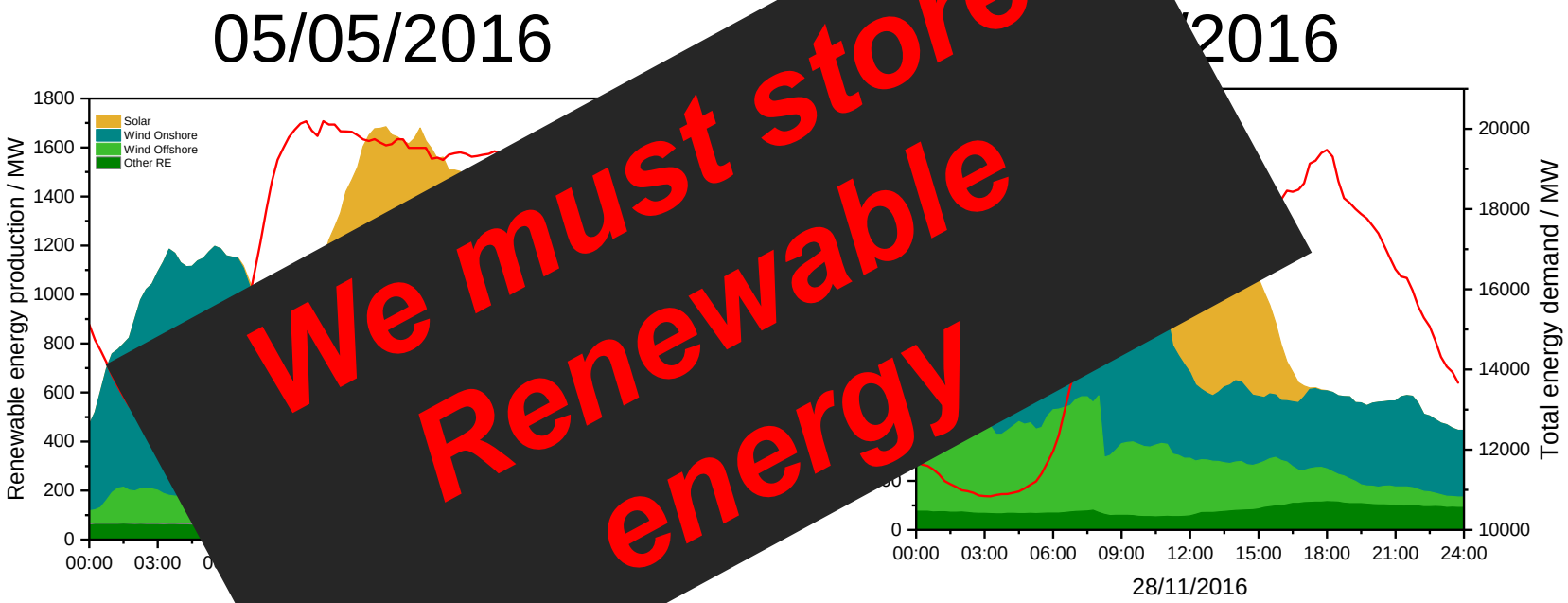
Applications of interest

1. Fuel cells
2. Electro organic synthesis
3. Other industrial electrochemical application
4. CO_2 Valorization
5. Green H_2 production

Interesting reactions

	Reaction	Yield	Reaction conditions		TRL	Application
	**$HMF + 2H_2O \rightarrow FDCA + 3H_2$**	**90%**	Ni	**20 - 30 ^{0}C, atm, water pH 12-13**	**5**	**Plastics**
	**$PDO + H_2O \rightarrow$ Lactic acid $+ 2H_2$**	**80%**	C	**30 - 40 ^{0}C, atm, water pH 9-10**	**3**	**Plastics, food, pharma**
	**Furfural $+ 4H_2O \rightarrow$ Maleic acid + $CO_2 + 4H_2$**	**80%**	Pb (V_2O_5)	**20 - 35 ^{0}C, atm, water pH 0**	**3**	**Plastics, building block**
	**Levunilic acid + H2O → Valeric acid + O_2**	**>95%**	Pb	**20 - 50 ^{0}C, atm, water pH 0**	**3**	**Biofuel, cosmetics**
	Levunilic acid + H2O → γ-Valerolactone + O_2	**>90%**	Pb	**20 - 50 ^{0}C, atm, water pH 7-8**	**2**	**Green solvent**
	**Pyruvic acid + H2O** → DMTA + O_2	60%	Pb		**2**	**NA**
 CO	**$CO_2 + H_2O \rightarrow$ FA or CO + O_2**	**>80%**	Sn/Au	**RT, 0 – 80 bar, water, pH 6-9**	**2**	**Building block/fuel**
H_2	**$2H_2O \rightarrow 2H_2 + O_2$**	**>90%**	Pt TiO_2	**RT, 0 – 80 bar, water, pH 6-9**	**2**	**Fuel**

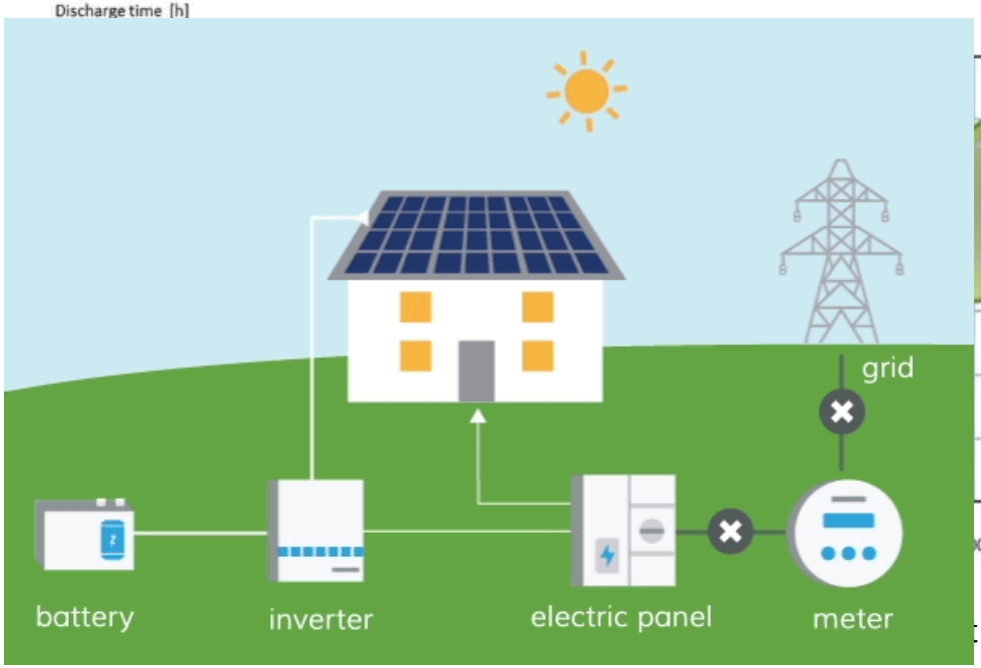
Renewable energy production in the Netherlands



We must store Renewable energy

Data source: https://transparency.entsoe.eu.
Own graphic

Energy storage technologies

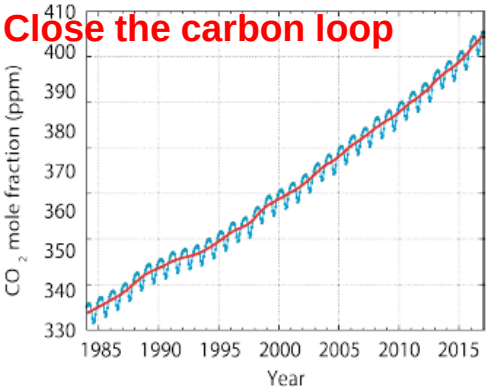


et al., 2010

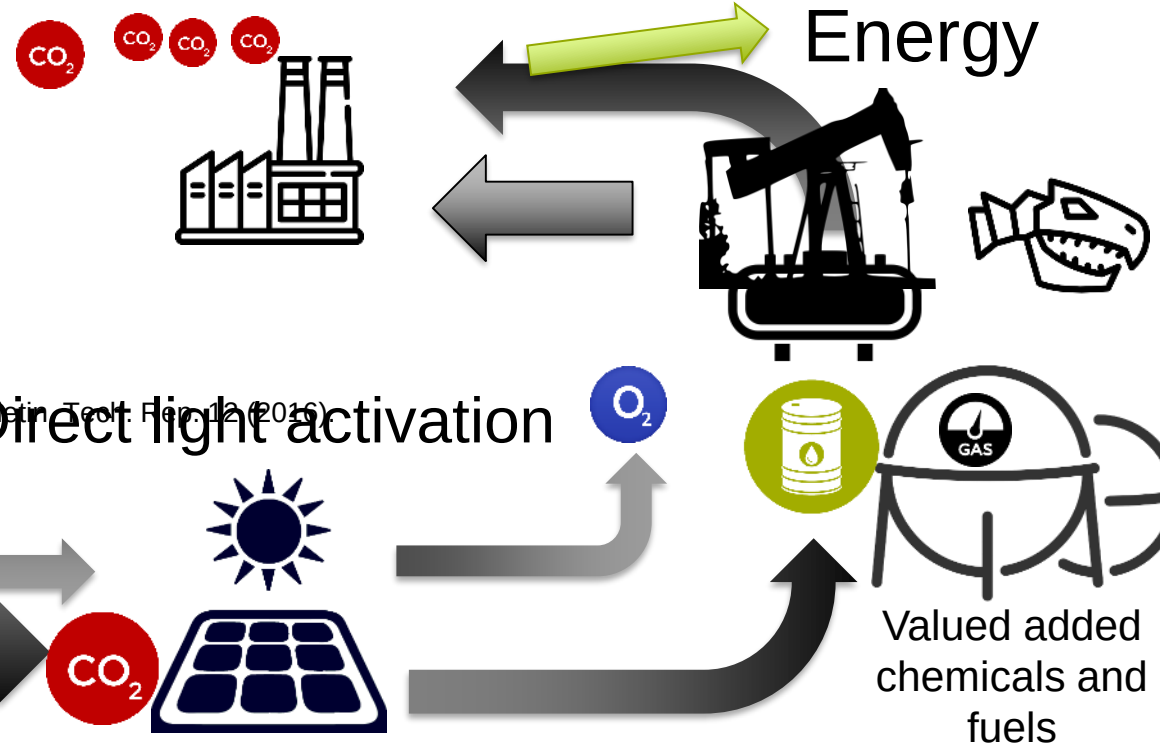
https://www.energysage.com/

Solar fuels. The idea

Close the carbon loop



World Meteorological Organization, WMO Bulletin, Tech. Rep. 12 (2016).

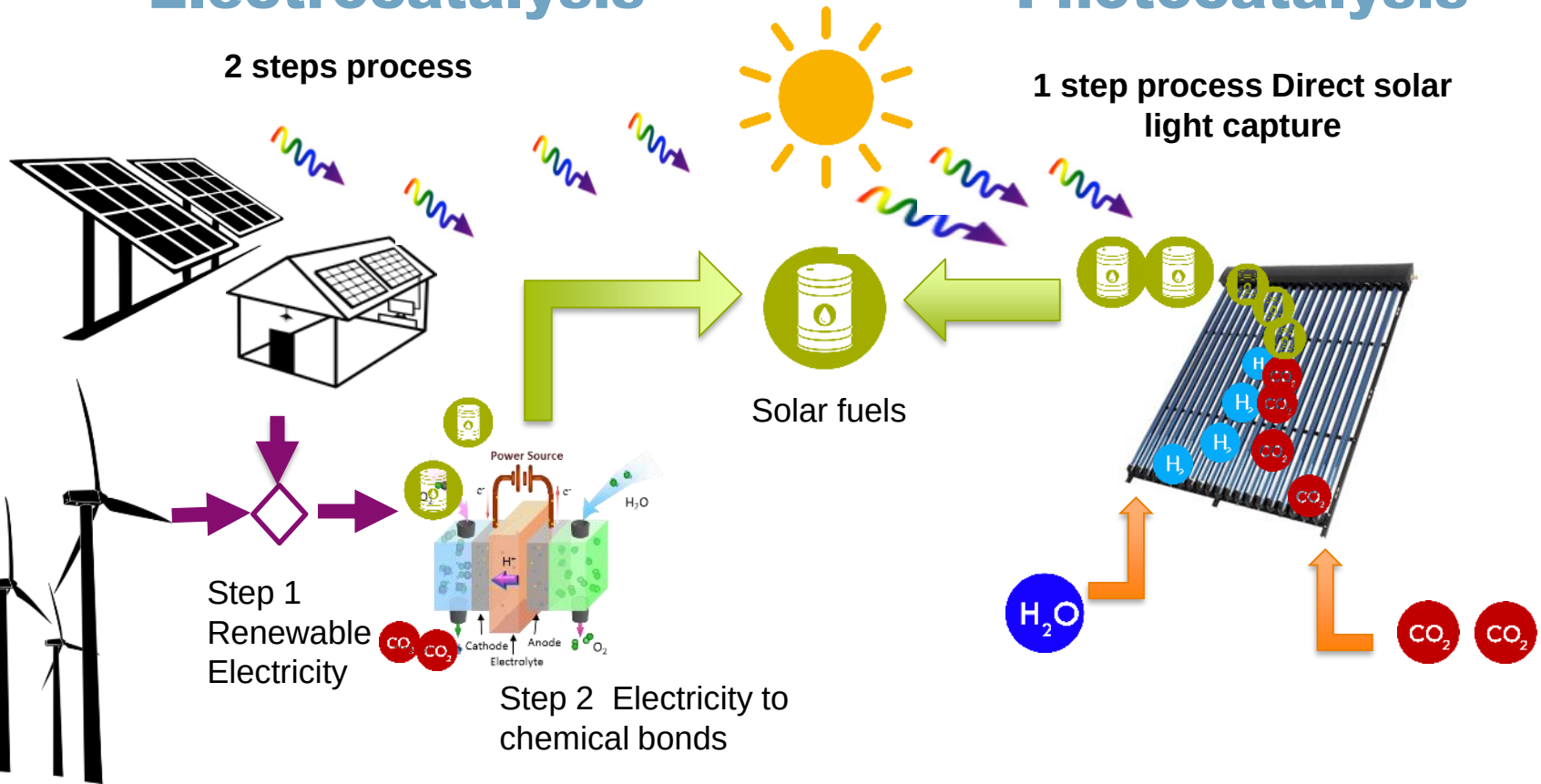


Electrocatalysis

2 steps process

Photocatalysis

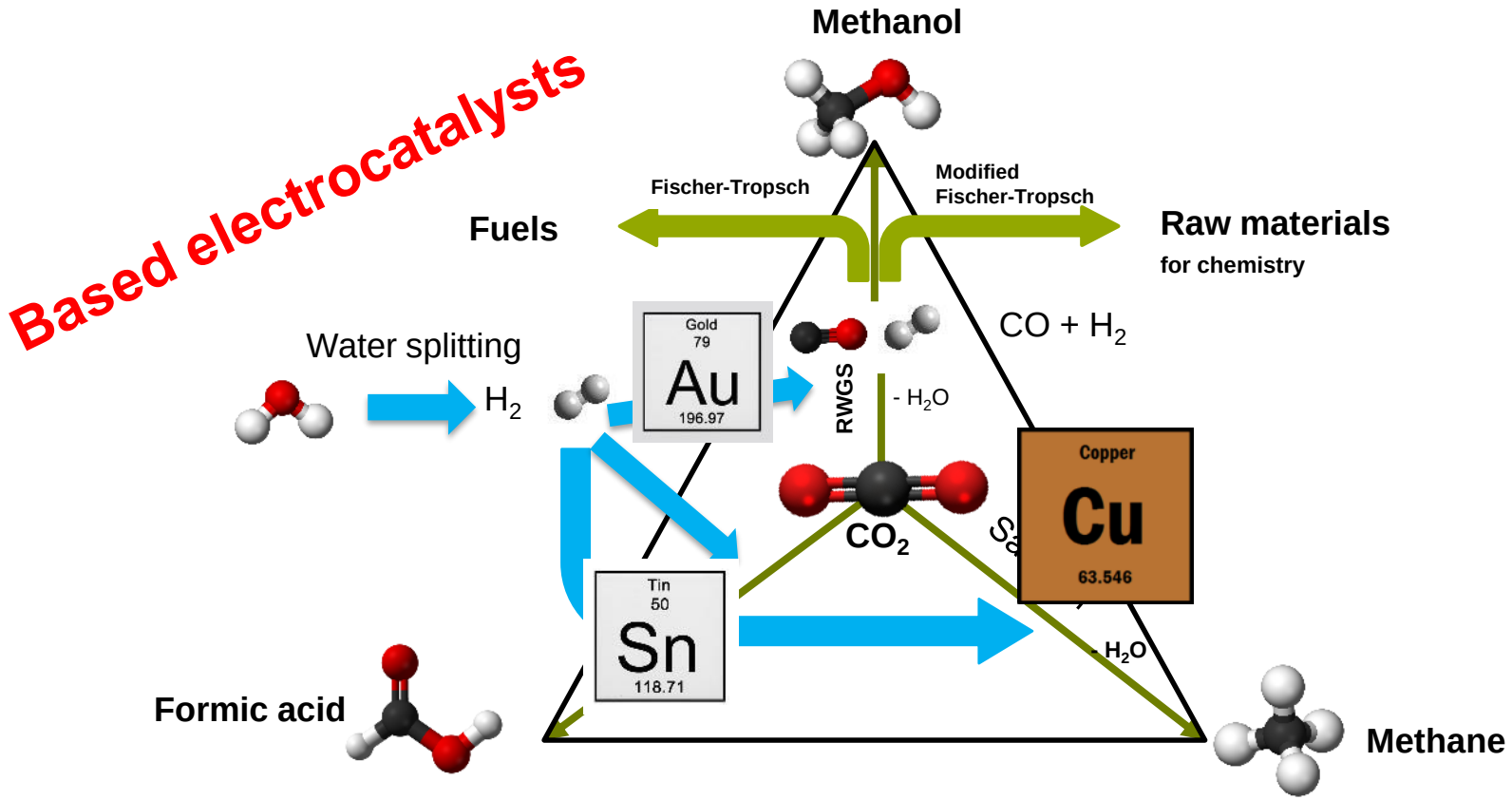
1 step process Direct solar light capture



Step 1
Renewable Electricity

Step 2 Electricity to chemical bonds

Routes CO_2 into fuels. Electrocatalysis

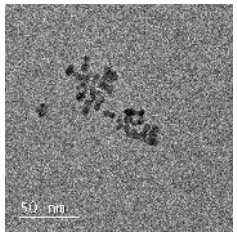


Nanopaticles

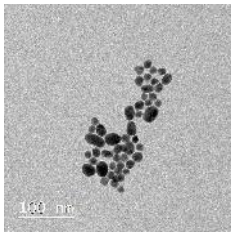
Control size & shape

Spheres

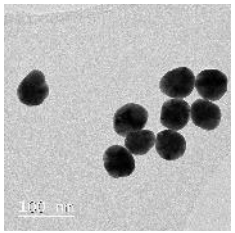
5 nm



15 nm

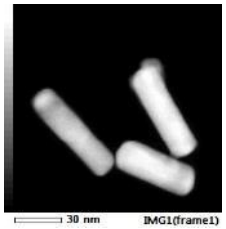


100 nm

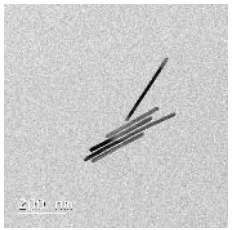


Rods

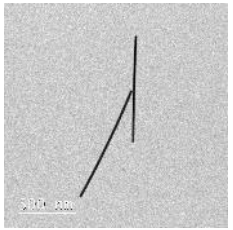
50 nm



500 nm



1000 nm



Synthesis scale-up

- Synthesis scale-up from 1 ml to 10 L

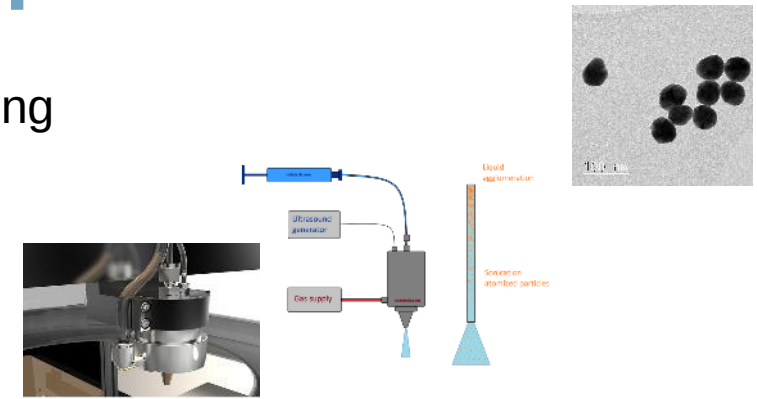
0.001 L

2L

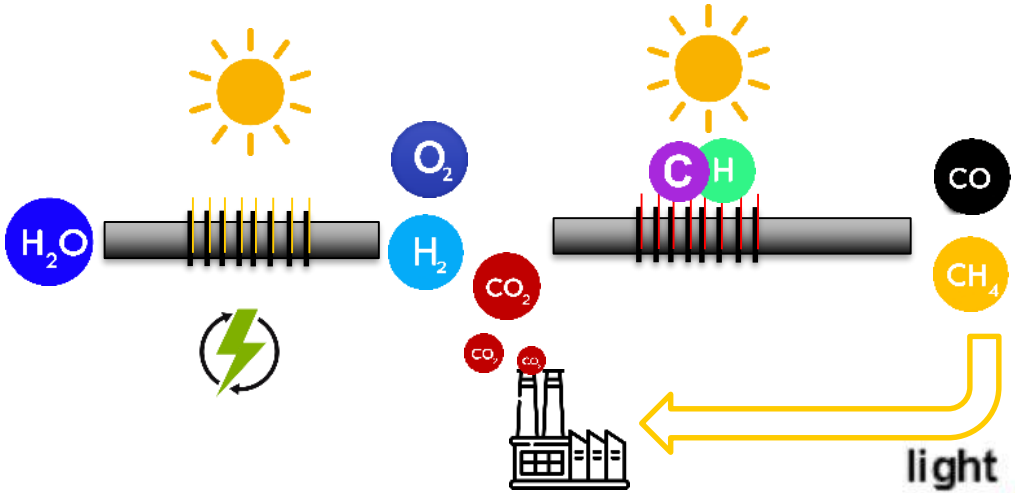
10L

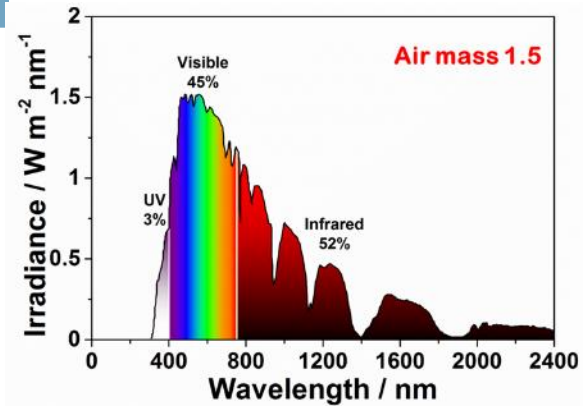
Electrodes preparation

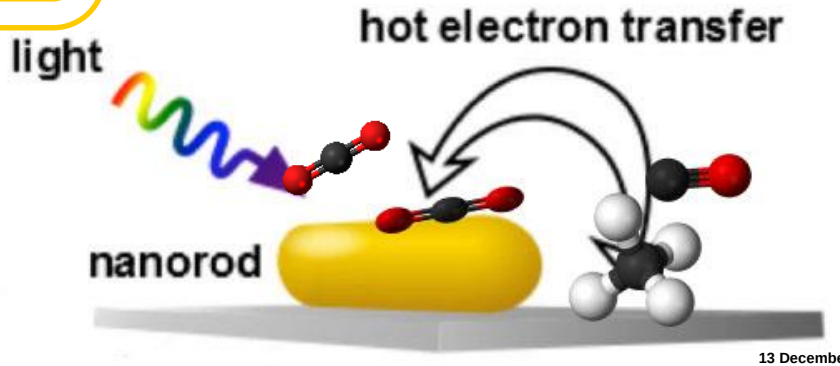
Ultrasonic spray Coating



Photocatalysis- Plasmon activated







Why hydrogen?

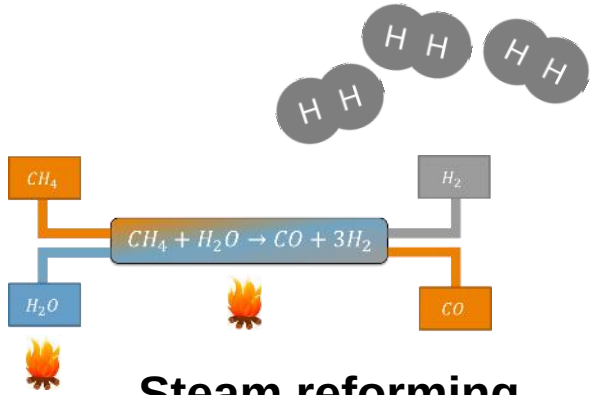
- **Key role for sustainable future**
  - Energy carrier
    - Electricity
    - Mobility
    - Heating
  - Chemical reactant
    - Fertilizer production
    - Oil refining

Solar fuel:
harvesting the sun

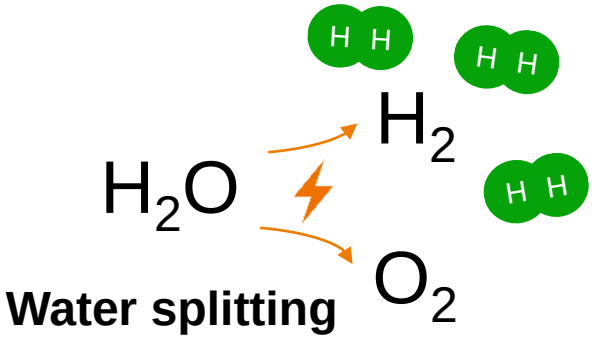
(e.g. $H_2 + CO_2 \rightarrow CH_4 + H_2O$)

Why water splitting?

- **'Grey' versus 'Green' Hydrogen**
  - Steam reforming
    - Fossil fuel based
    - Additional heat required
    - Very low price (1$·kg^{-1})
  - Water splitting
    - Possibly based on renewable energy sources
    - Electricity required
    - Expensive (6 $·kg^{-1})



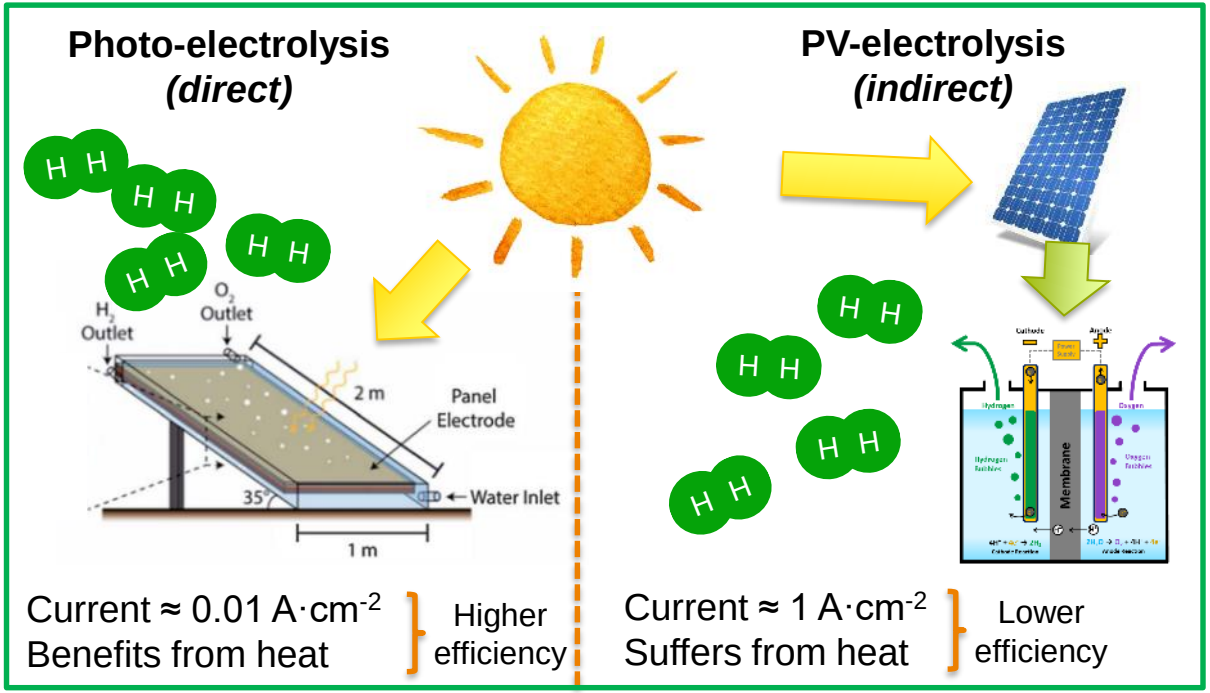
Steam reforming



Water splitting

Why photo-water splitting?

- **Two different ways of producing green H_2**
  - ‘Direct’ is the integrated approach with highest efficiency, and benefits from heat
  - ‘Indirect’ depends on electricity price, suffers from large current, but is more mature



How do we split water directly?

- **Different approaches**

Photo-chemical

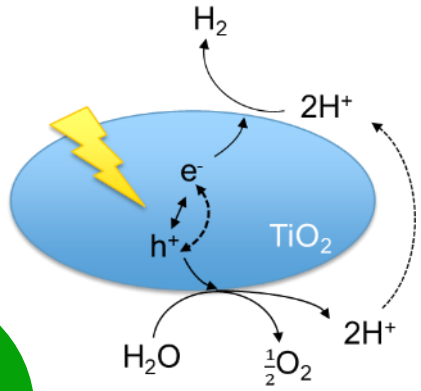
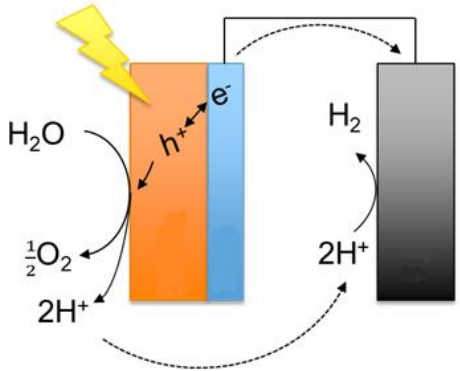
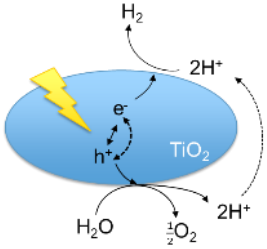


Photo-*electro*-chemical

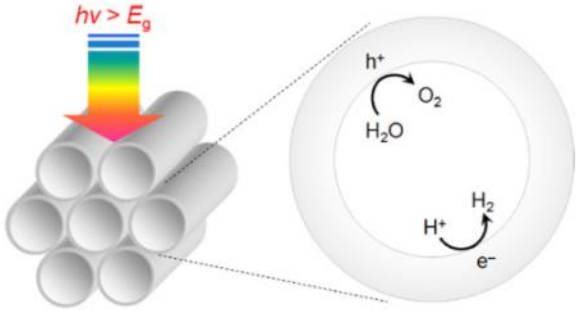


How do we split water directly?



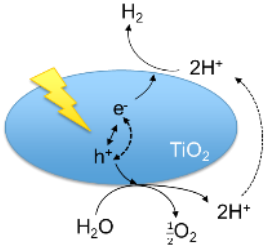
- **Photo-chemical water splitting: oppertinities**
  - Particle based system (slurries)
  - Low efficiency system
  - (very) Low cost
  - Safety to be addressed by processing

} Low cost of green hydrogen



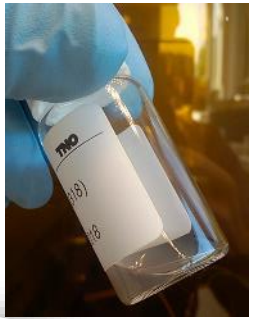
Maeda et al., J. Photochemistry and Photobiology C: Photochemistry Reviews 12 (2011) 237– 268

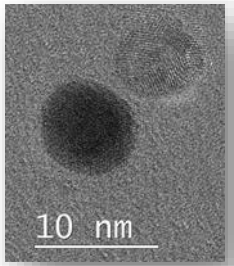
How do we split water directly?

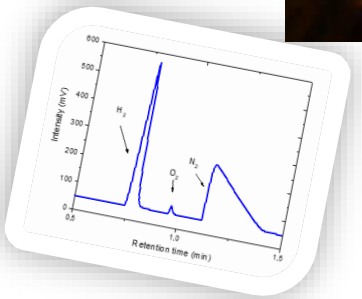


- **Photo-chemical: development**
  - Typical materials: TiO_2 combined with co-catalyst (e.g. Pt)
  - Tuning light harvesting, suitable bandgap and (photo)corrosion

  - Research on commercial and non-commercial catalysts
  - Durable catalysts
  - Aiming at cost efficient water splitting



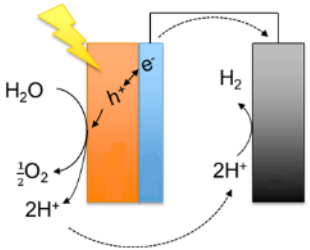


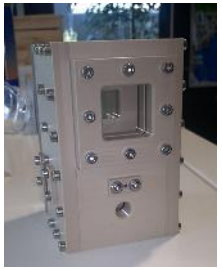


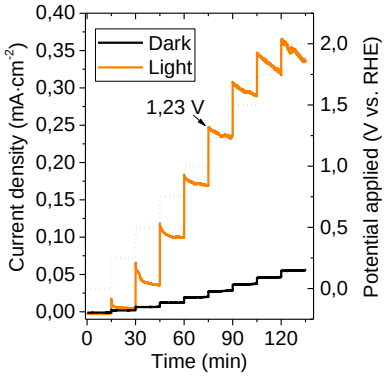
How do we split water directly?

- **Photo-electro-chemical: opportunities**
  - Device based – resembles a PV panel
  - High cost
  - Potentially very high efficiency
  - No safety issues
  - Yielding pressurized hydrogen

Low cost of green hydrogen

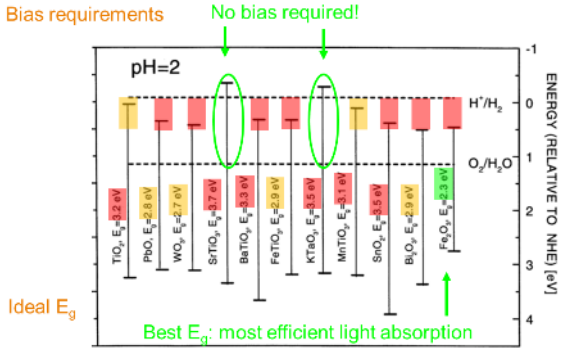


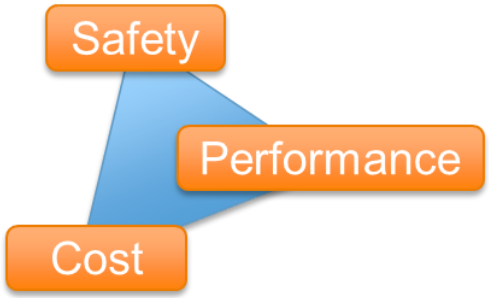


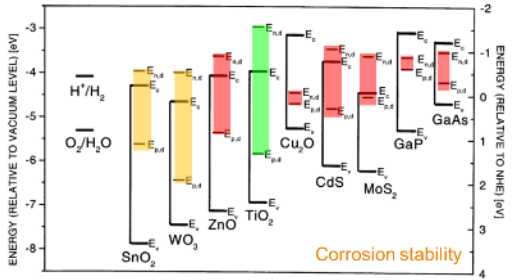


How do we split water directly?

- **Photo-electro-chemical: material development**
  - Typical materials: CIGS with Si-solar cell
  - Tuning suitable bandgap, required voltage bias and (photo)corrosion
  - Scale up of photoelectrode manufacturing by ultrasonic spray deposition







Van de Krol et al., in Photoelectrochemical Hydrogen Production (2012) 14-69

When is al this realized?

- **Price vs. Performance: difficult to beat ‘grey hydrogen’**

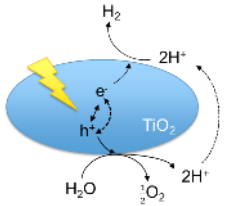


Photo-chemical

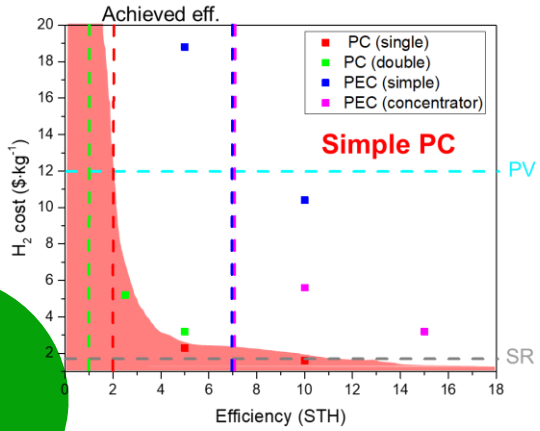
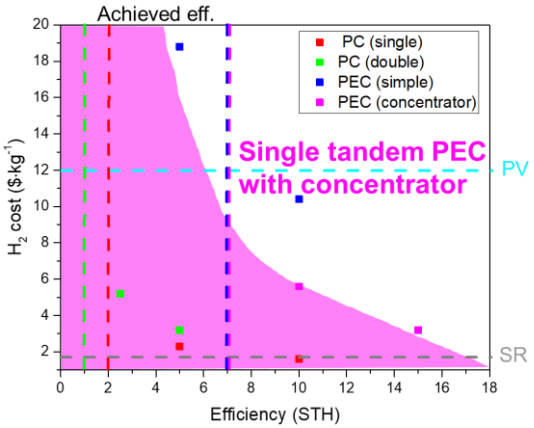
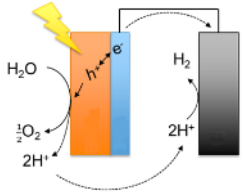


Photo-*electro*-chemical



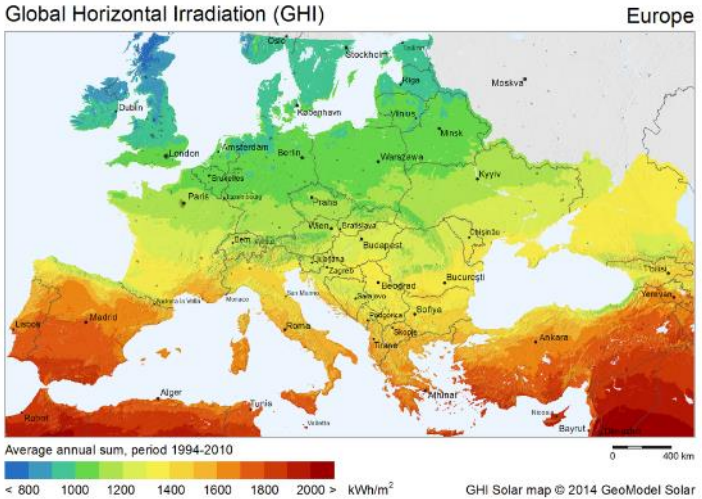


When is al this realized?

- **Price vs. Performance: development**
  - Focus on stability of materials, rather than high efficiency
  - Tailoring specific chemistry for large centralized vs. local decentralized operation
    - Producing H_2 with purity and pressure for industrial scale directly
    - Device integration for local energy harvesting

Electrocatalysis vs. Photocatalysis ?

- Location.
- 24/7 vs. day time.
- Centralized vs. decentralized.
- Return on investment.



Carbon capture storage and/or utilization ?

- CO_2 concentration.
- Location.
- CO_2 taxes.

Green Hydrogen

- Subsidies and/or CO_2 taxes.
- Centralized vs. decentralized
- (Photo)catalyst durability.