Renewable Energy

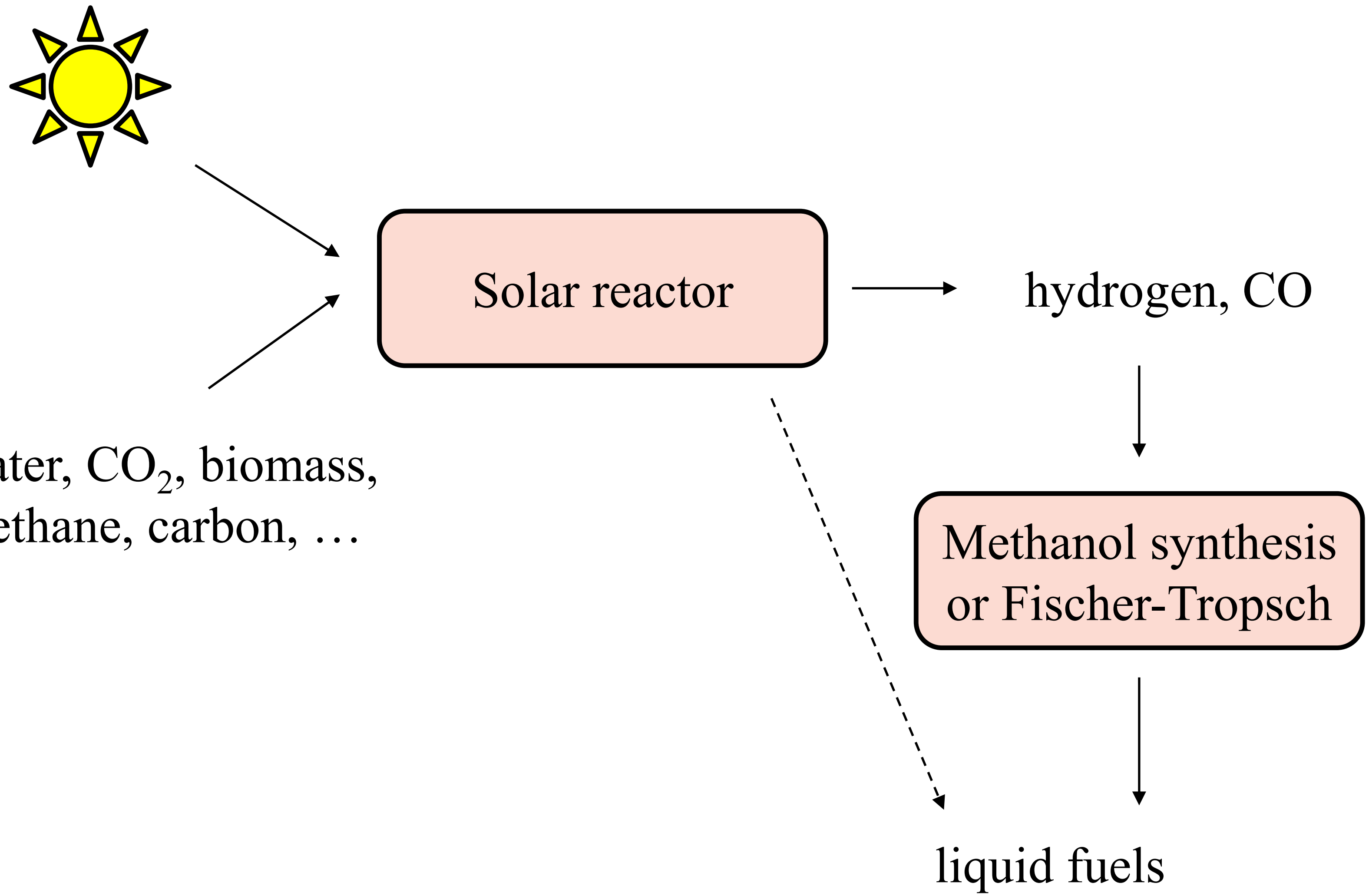
- Outline:
  - Conversion pathways solar-to-fuel
  - Hybrid pathways
  - Solar thermochemistry
  - Photochemistry

Learning outcomes of todays lecture

- Solar fuels:
  - How can solar energy be converted into fuels?
  - What is a hybrid pathway?
  - Why using fossil fuels together with solar energy?
  - What is solar thermochemistry and how can it be used for solar fuel processing?
  - Why is solar water-splitting via multi-step water splitting cycles preferred compared to direct thermolysis?
  - What is photoelectrochemistry and how can it be used for solar fuel processing?
  - What other chemical commodities or materials can be processed using solar energy?

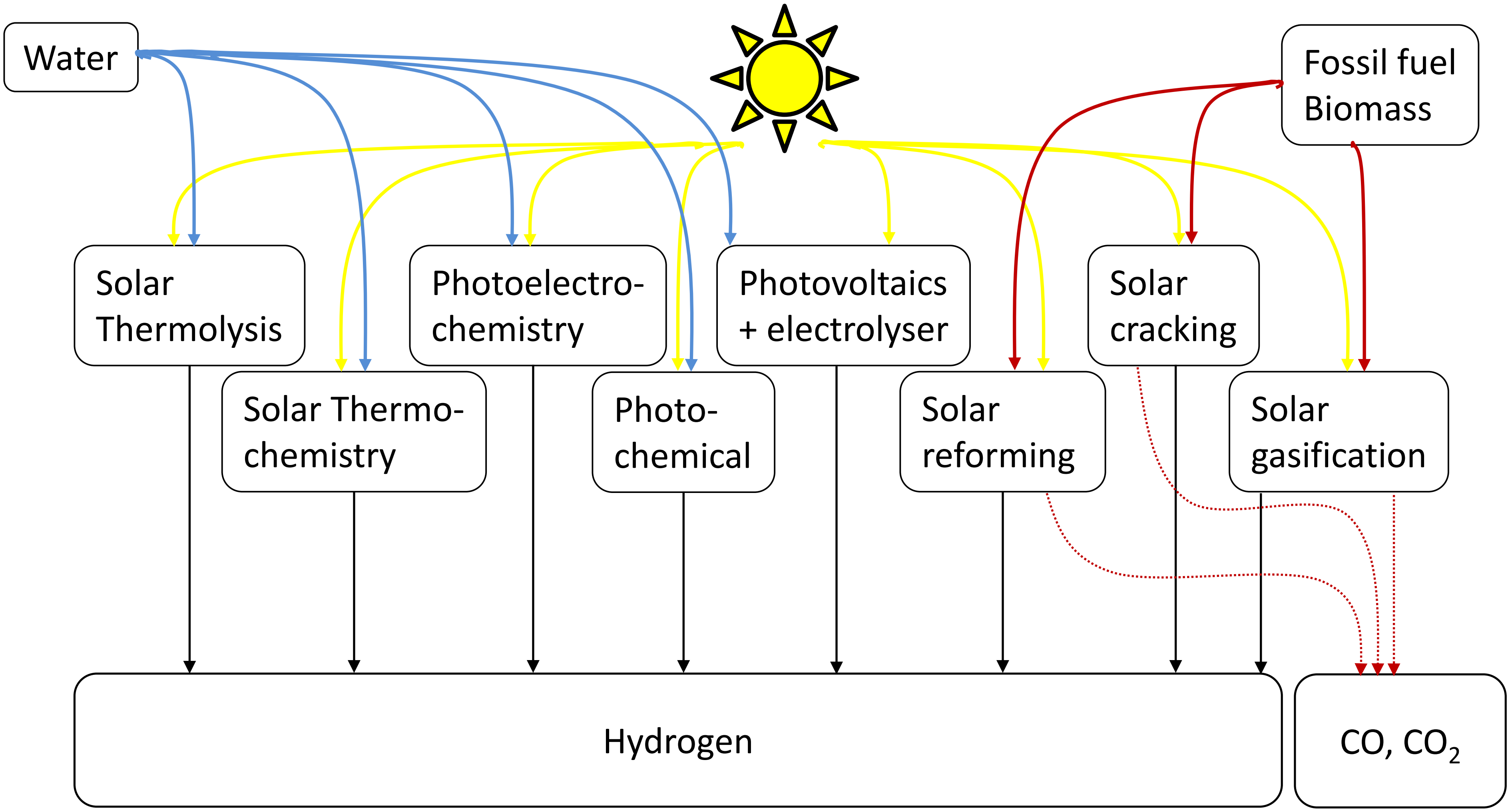
Conversion pathways

- Solar to fuels:



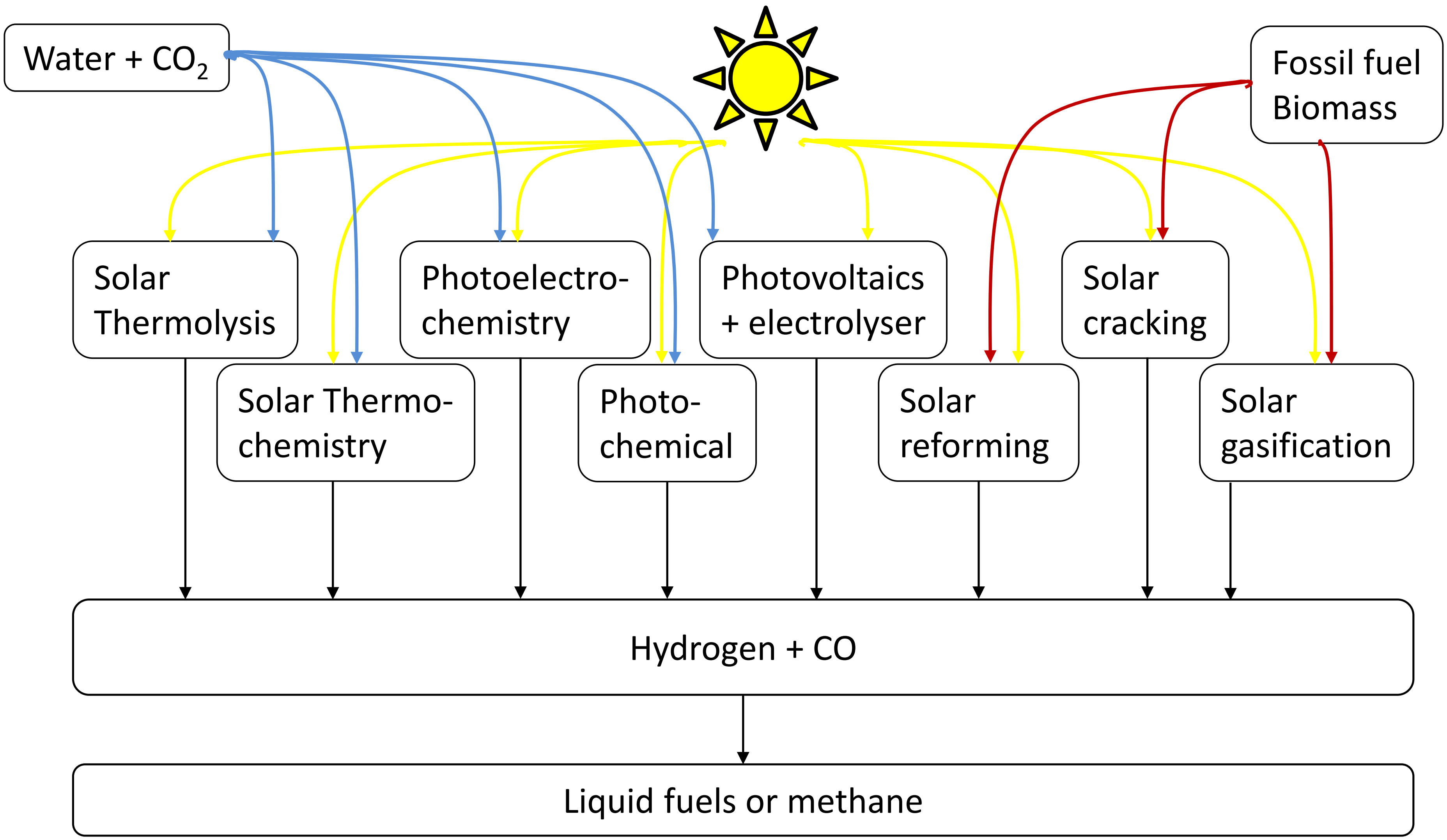
Conversion pathways

- Solar to hydrogen:



Conversion pathways

- Solar to synthesis gas (H_2+CO):

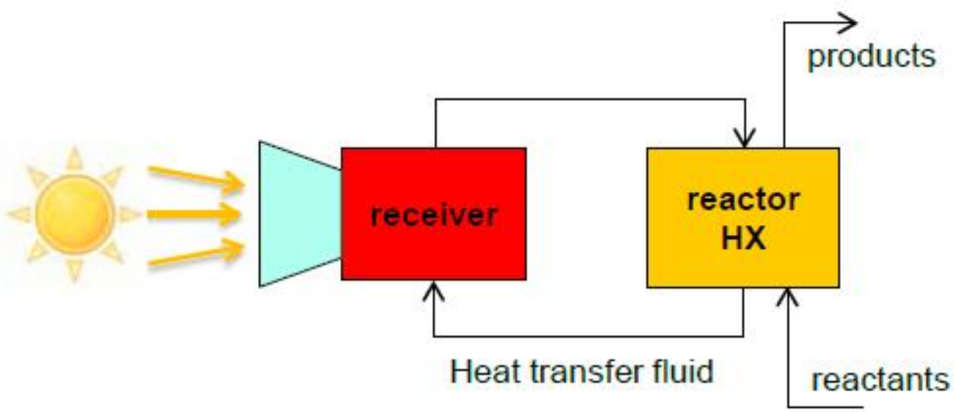


Conversion pathways

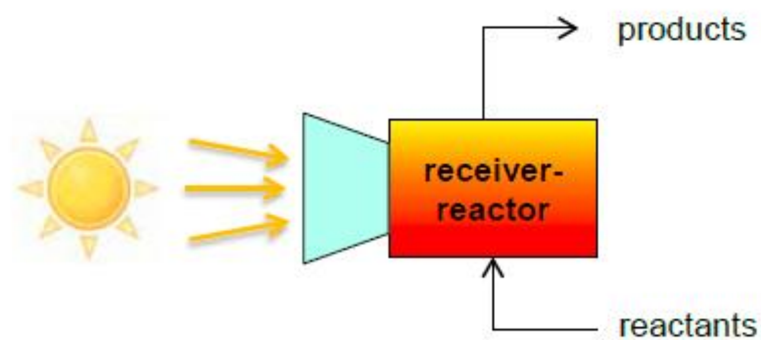
- General considerations:
  - What solar radiation concentration technology can be used (if needed)?
  - What solar reactor can be used and what are the requirements?
  - How can the sun be coupled into the process?
  - What can the reactor look like?

- Reactor concepts:

Decoupled receiver+reactor
Possibly with high-temperature storage



Coupled receiver-reactor



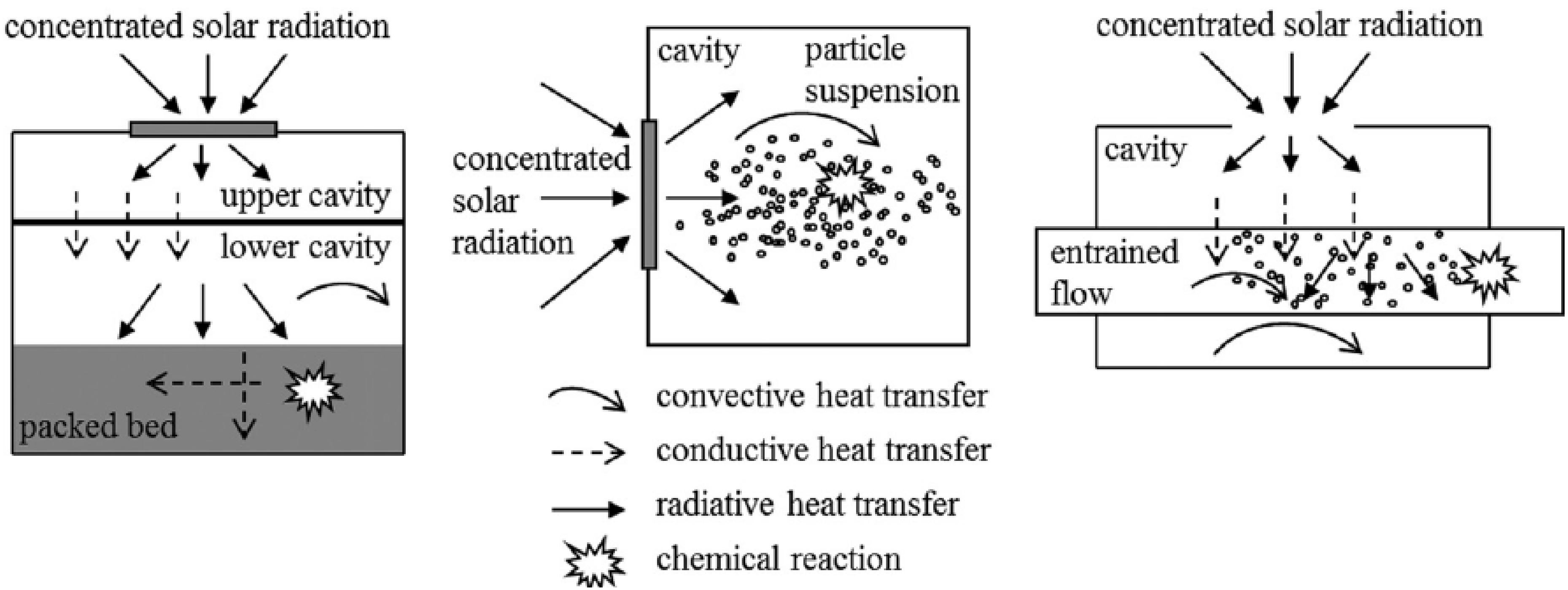
Conversion pathways

- Reactor concepts:

indirectly irradiated packed-bed

directly irradiated vortex-flow

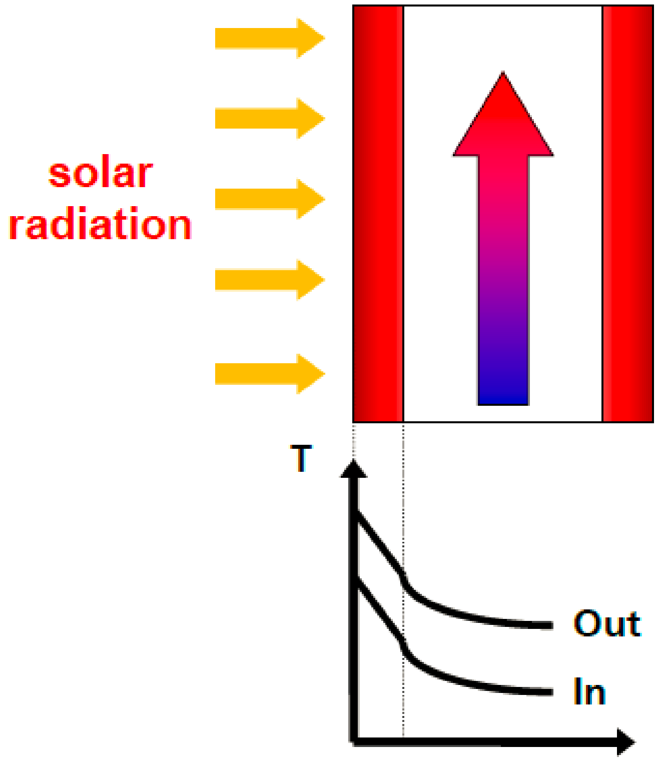
indirectly irradiated entrained flow



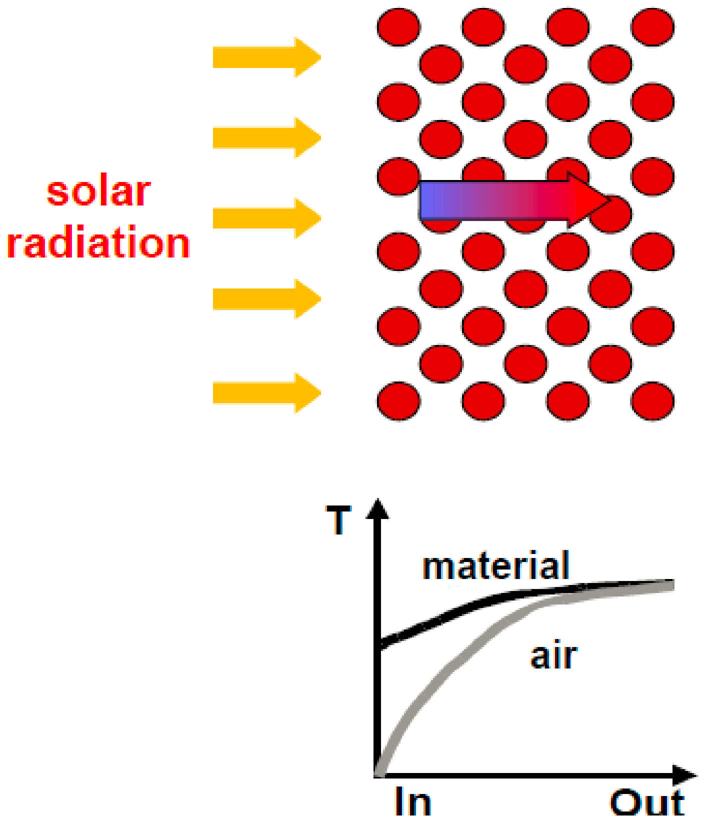
Conversion pathways

- Reactor concepts:

Tube receiver



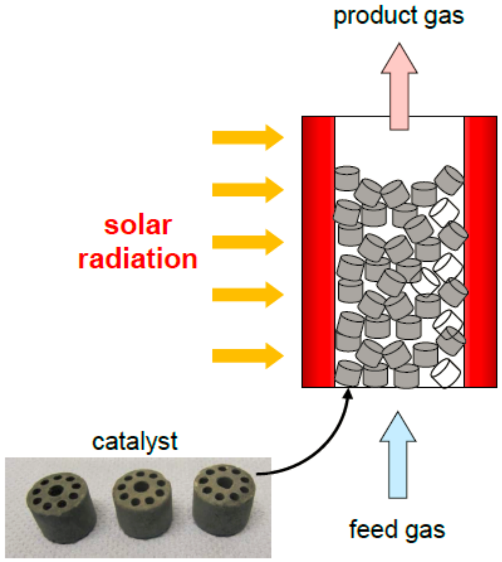
Volumetric receiver

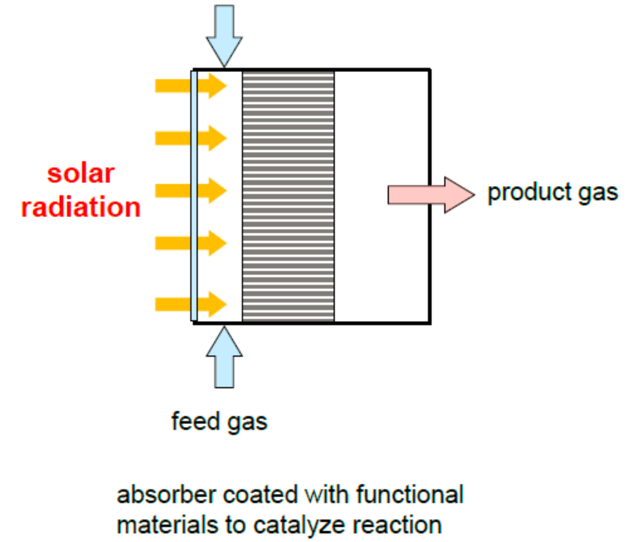


- Also: open versus closed systems

Conversion pathways

- Reactor concepts:
  - Stationary

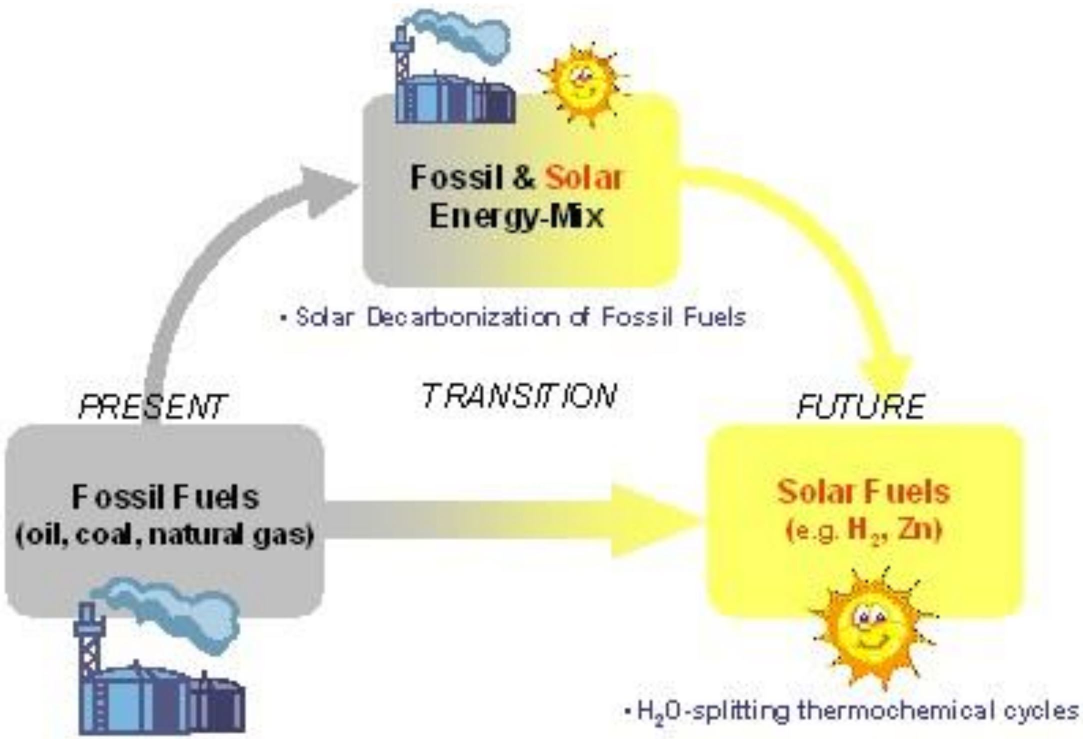




  - Moving:
    - Fluidized particle bed
    - Falling particle film
    - Rotating kiln
    - Moving particle bed

Hybrid solar conversion

- In the transition to a renewable future, hybrid pathways using fossil fuels exclusively as chemical source for the fuel production and solar energy as the process heat



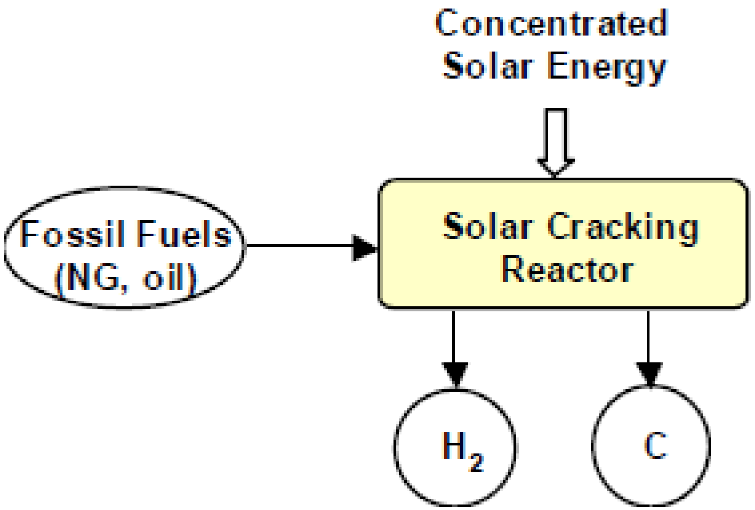
Hybrid solar conversion

- **Thermal cracking**: complex organic molecules such as heavy hydrocarbons are broken down into simpler molecules such as light hydrocarbons, by the breaking of carbon-carbon bonds in the precursors at high temperatures and by using catalysts

$$CH_4 \rightarrow C + 2H_2 \ (\Delta H = 74.85 \text{ kJ/mol})$$

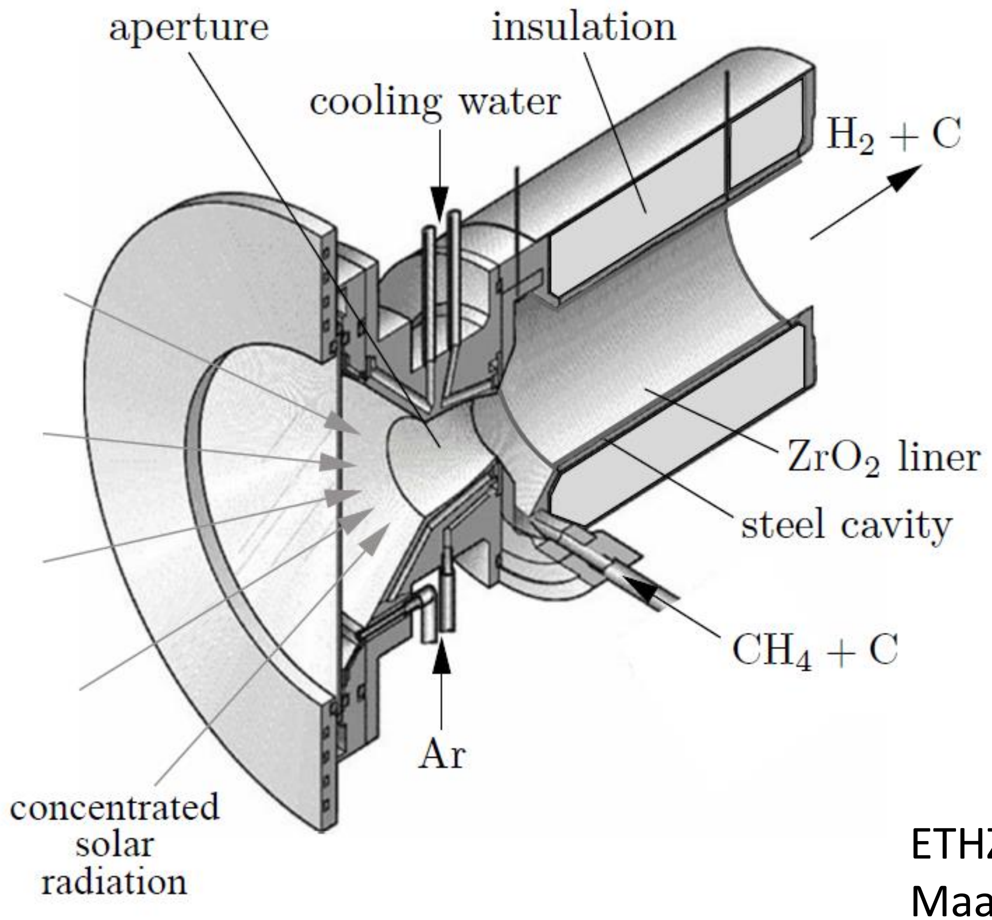
- General:

$$C_nH_m \rightarrow nC + (m/2)H_2$$



Hybrid solar conversion

- Solar reactors developed for thermal cracking:

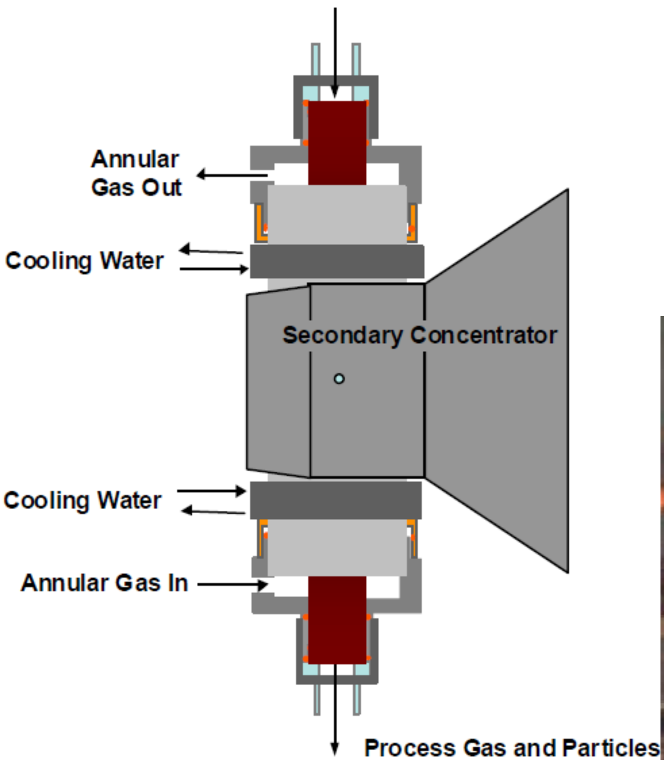


ETHZ and PSI
Maag et al., 2010.

Hybrid solar conversion

- Solar reactors developed for thermal cracking:

CU Boulder
Dahl and Weimer et al., 2004.



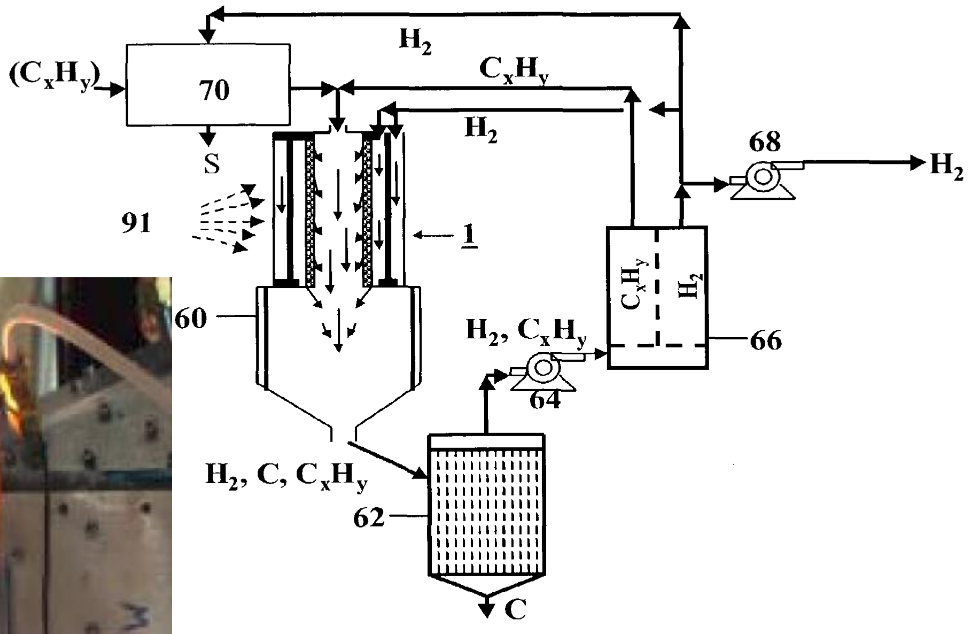


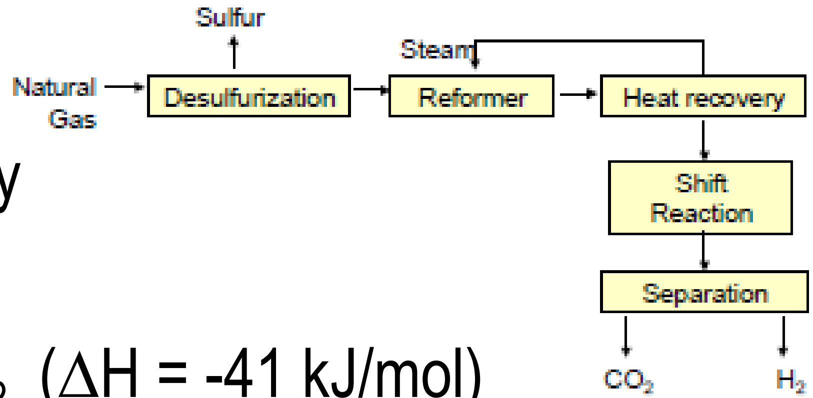
Figure 4

Hybrid solar conversion

- **Steam reforming**: uses light hydrocarbon feedstock, usually methane, reacts it at elevated temperatures with steam and catalytically converts the feed into hydrogen

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \ \ (\Delta H = 206 \text{ kJ/mol})$$

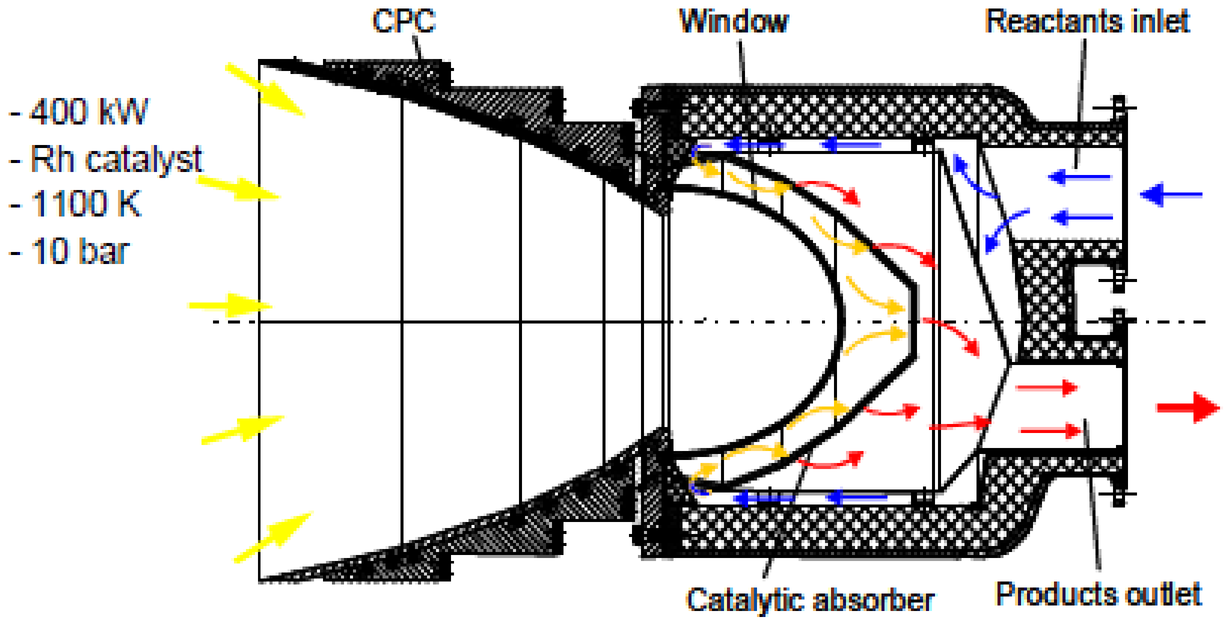
  - Operates around 700 – 925°C
  - Can achieve 65 – 75% efficiency

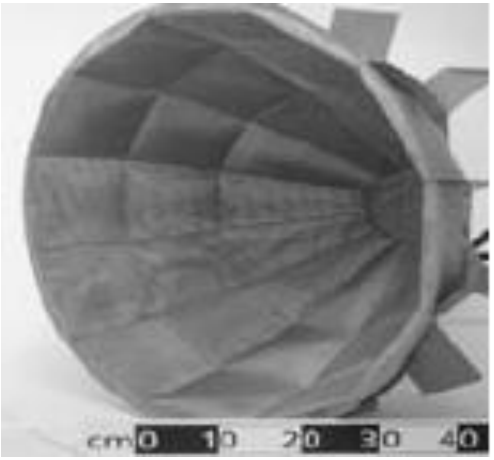


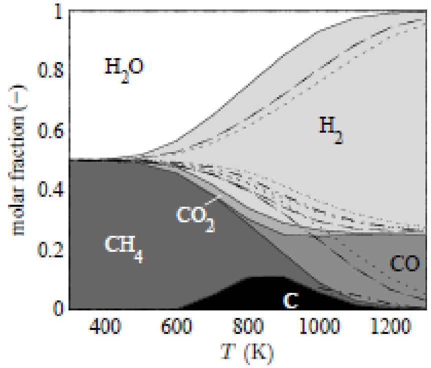
water gas shift: $CO + H_2O \rightarrow CO_2 + H_2 \ \ (\Delta H = -41 \text{ kJ/mol})$

Hybrid solar conversion

- Solar reactors developed for steam reforming
  Solar gasification of methane ($CH_4 + H_2O \rightarrow CO + 3H_2$), DLR
  SOLREF project







Hybrid solar conversion

- **Gasification**: uses carbonaceous materials, reacts it at high temperatures (>700 °C), without combustion, with a controlled amount of steam, oxygen, and/or CO_2. Results in CO, H_2, and CO_2.

- E.g. for coal, or C-sources

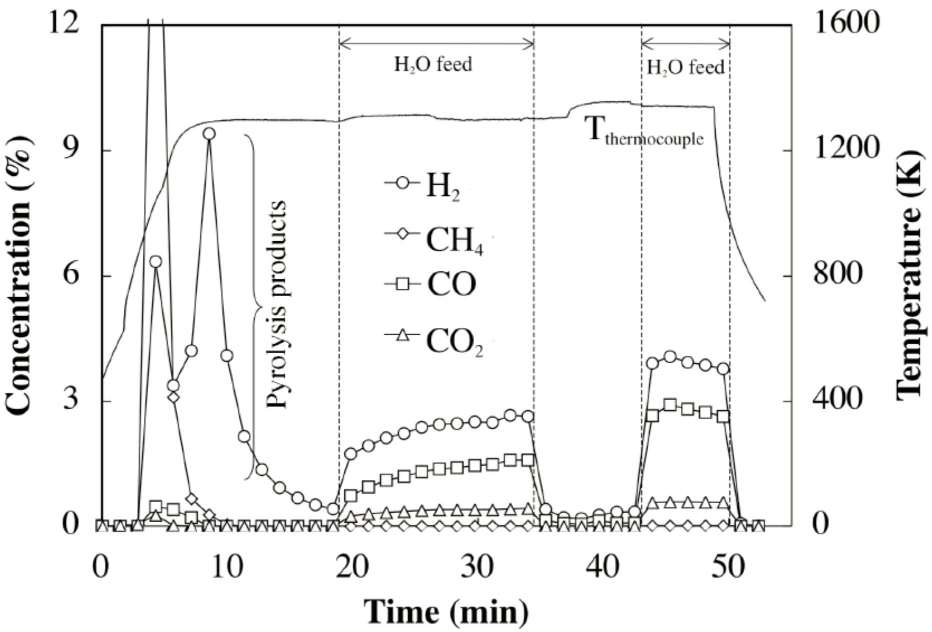
$$C + H_2O \rightarrow CO + H_2$$

- More realistic (especially for biomass, or C-waste):

$$\mathrm{CH}_x\mathrm{O}_y\mathrm{S}_z\mathrm{N}_u + (1-y)\mathrm{H_2O} = \frac{1}{2}(x+2(1-y)-2z)\mathrm{H_2} + \mathrm{CO} + z\mathrm{H_2S} + \frac{1}{2}u\mathrm{N_2}$$

Hybrid solar conversion

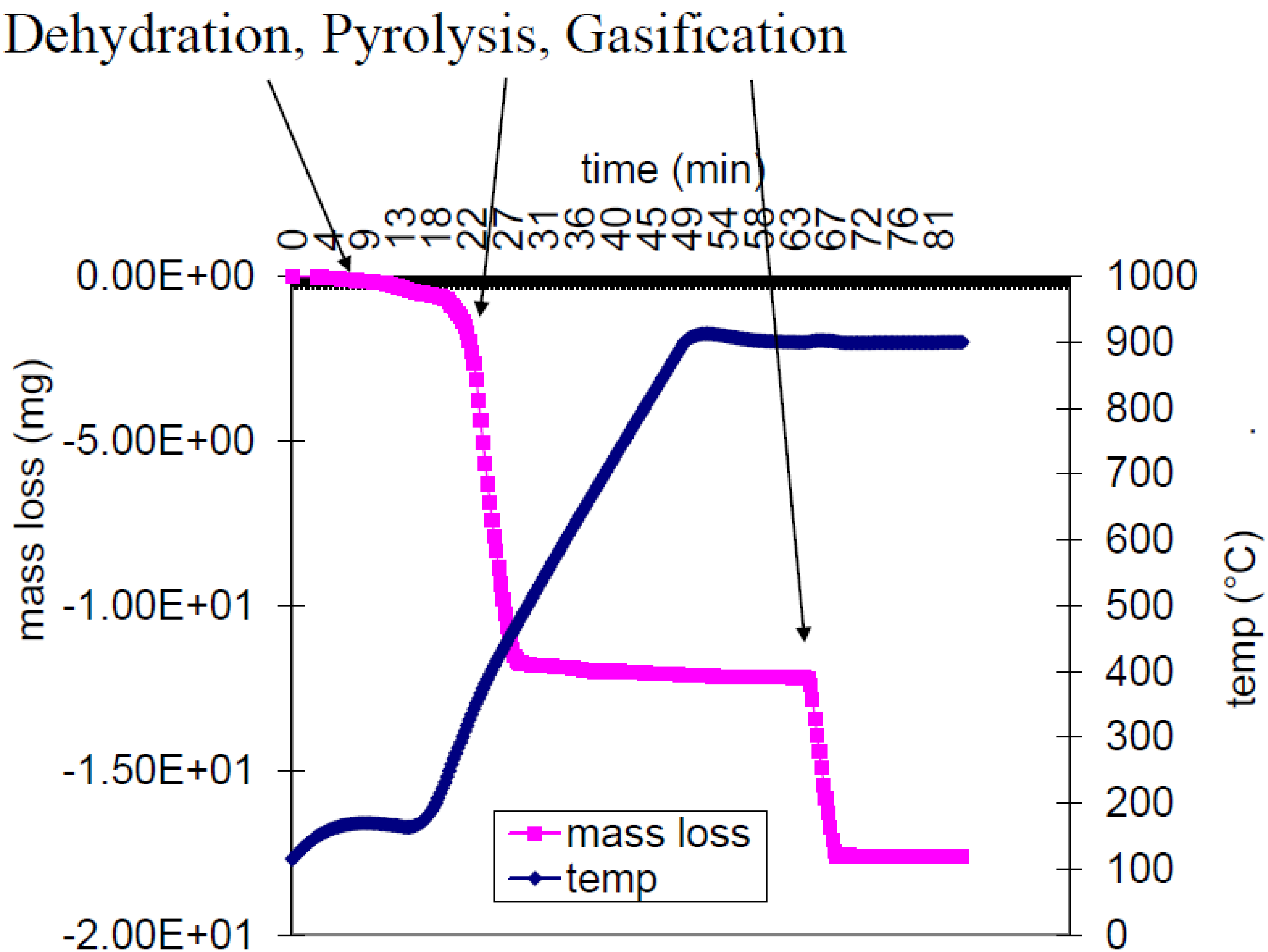
- Consists of (sequential or simultaneous):
  - Dehydration
  - Pyrolysis (thermal decomposition in the absence of O_2, devolatilization)
  - Gasification (heterogeneous gas-soild reaction of pyrolysis residue with reactive gas)
  - Combustion
  - Water-gas-shift



Trommer, Diss ETH, 2006.

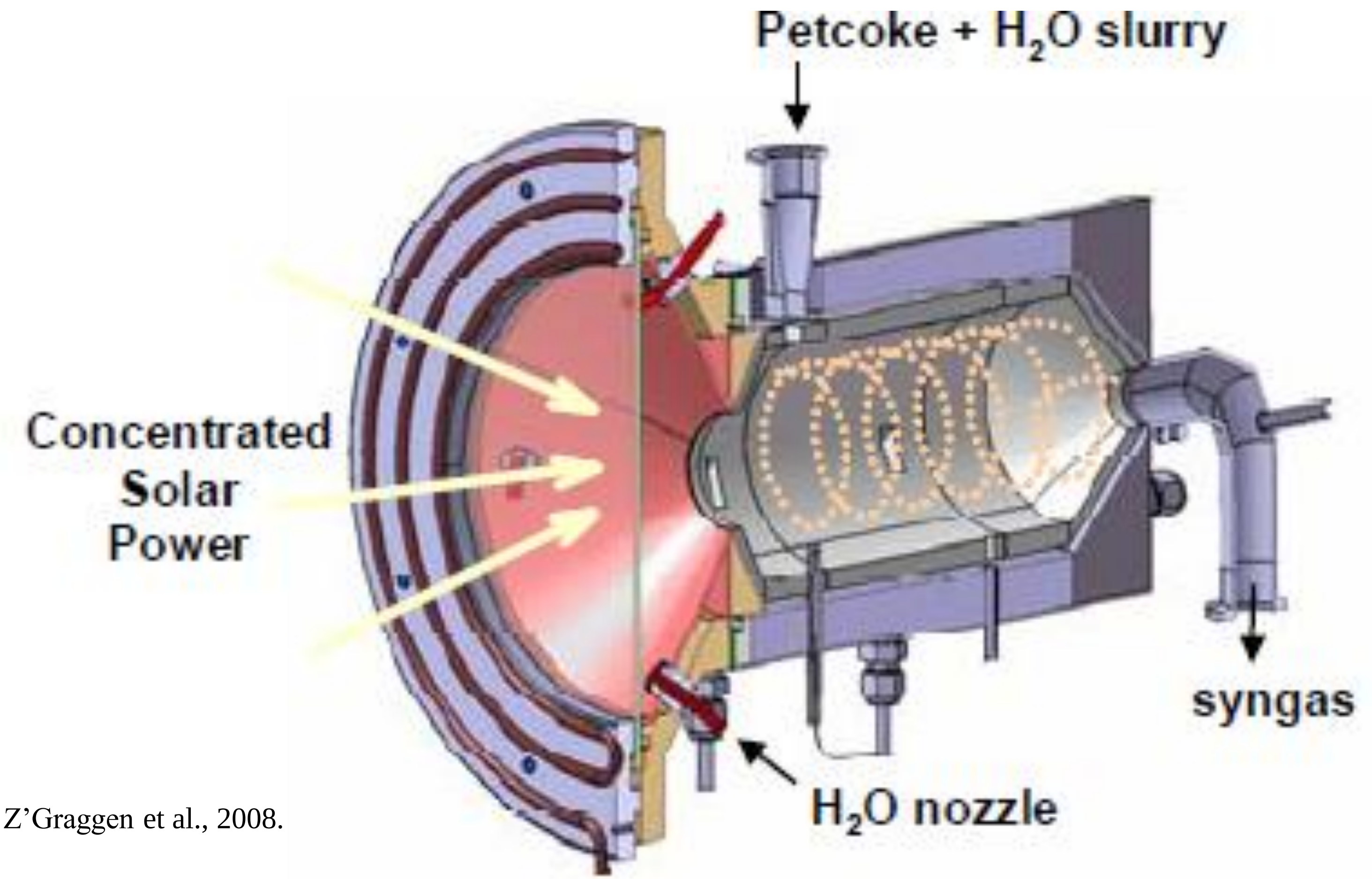
Hybrid solar conversion

- Gasification (thermographimetric experiment):



Hybrid solar conversion

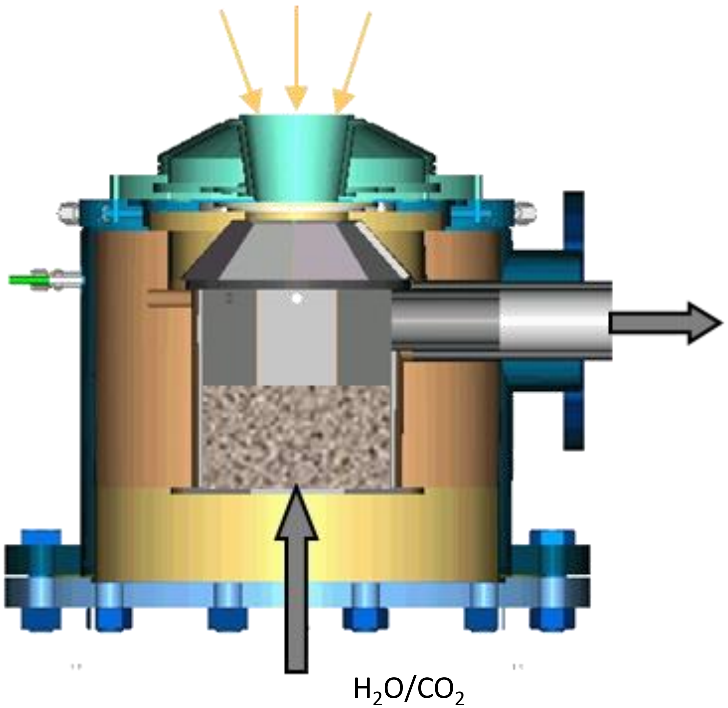
- Solar reactors developed for gasification:
  - Steam gasification of petcoke, ETH

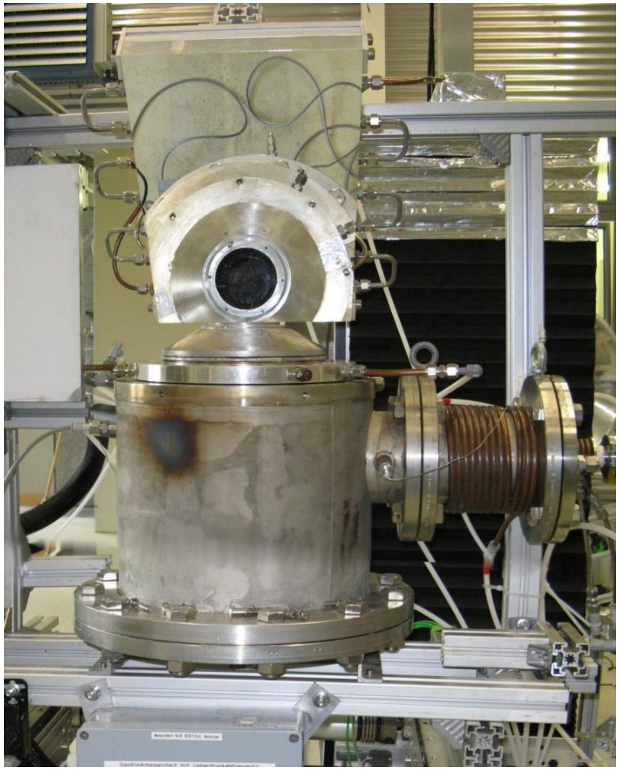


Z'Graggen et al., 2008.

Hybrid solar conversion

- Solar reactors developed for gasification:
  - Steam gasification of carbonaceous waste material (ETH, PSI)





Piatkowski et al., 2010.

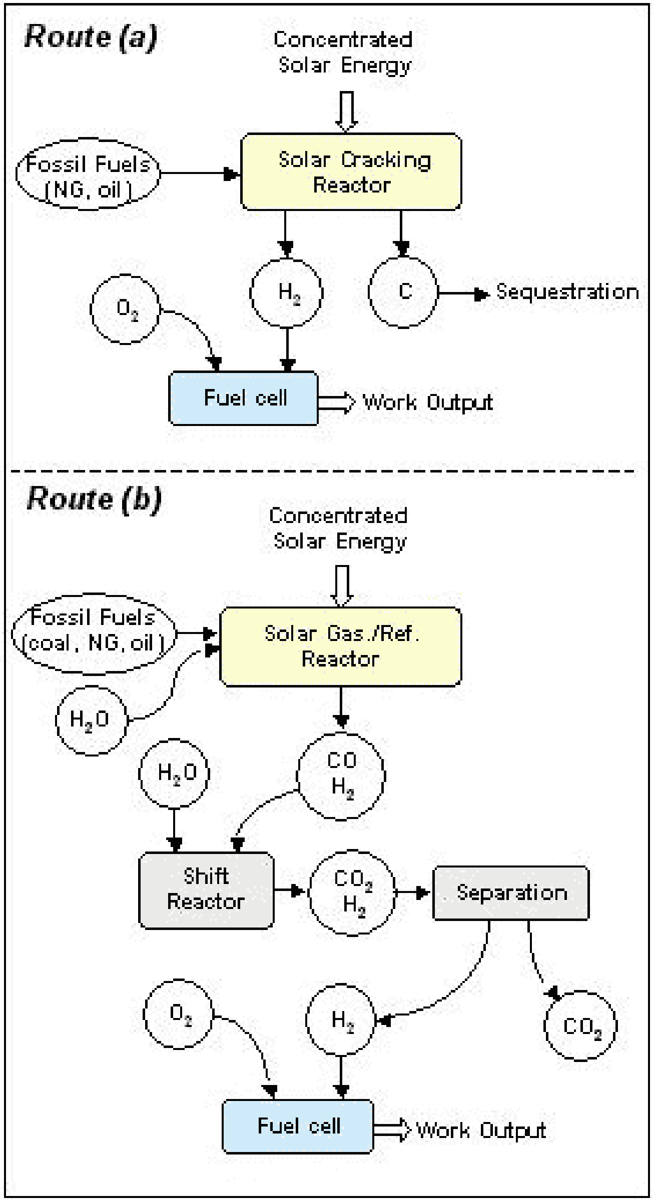
Hybrid solar conversion

- Hydrogen derived from fossil fuels has many impurities:
  - From combustion: CO_2, CO, N_2
  - From the feedstock: sulfur

- Purification:
  - Desulfurization for gaseous feedstock: calcium-based slurries (SO_2 to sulfites and sulfates)
  - Desulfurization from solid/liquid feedstock: via catalysts into H_2S
  - CO_2 removal:
    - temperature swing adsorption (solubility variation of CO_2 with temperature)
    - pressure swing adsorption (pressure dependent absorption of e.g. zeolites)
    - special membranes (cellulose)
  - CO removal from H_2 mixture: Hydrogen-permeable membranes made of metals (palladium)

Hybrid solar conversion

- Hybrid solar conversion
  - Advantage of hybrid process vs. conventional autothermal processes:
    - the gaseous products are not contaminated by combustion's by-products
    - the discharge of pollutants to the environment is reduced
    - the calorific value of the feedstock is upgraded
    - the fuel is decarbonized
    - there is no need for energy-intensive processing of pure oxygen



Renewable Energy

- Outline:
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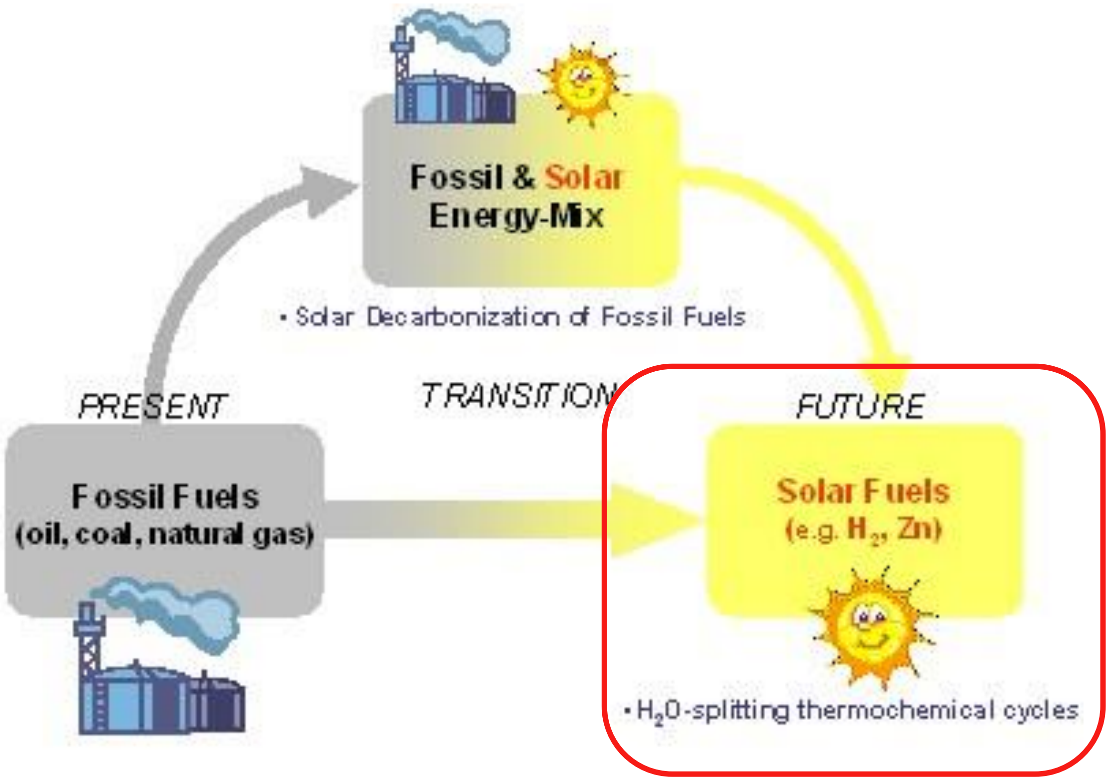
  - Solar thermochemistry
  - Photochemistry

EPFL

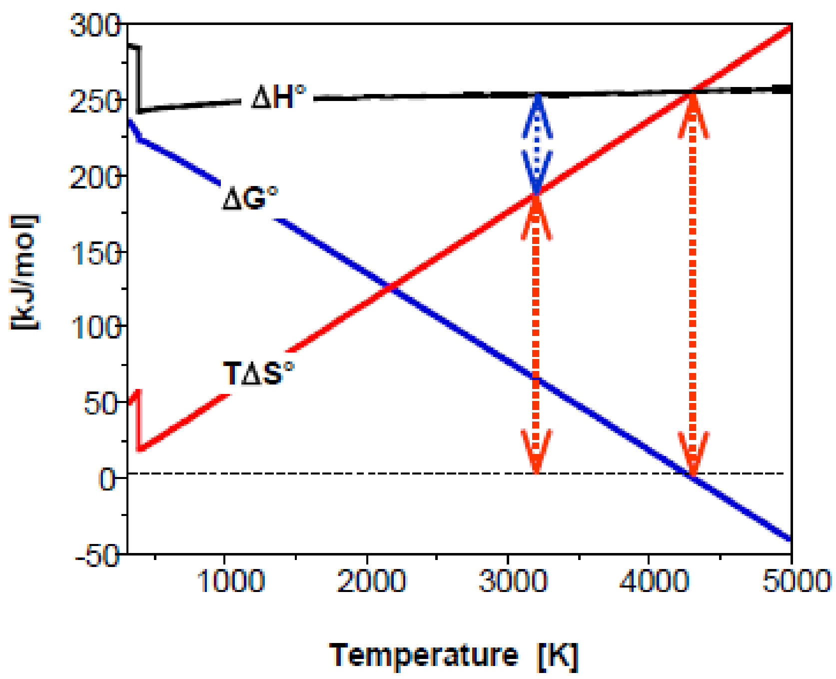
Solar thermolysis and thermochemistry

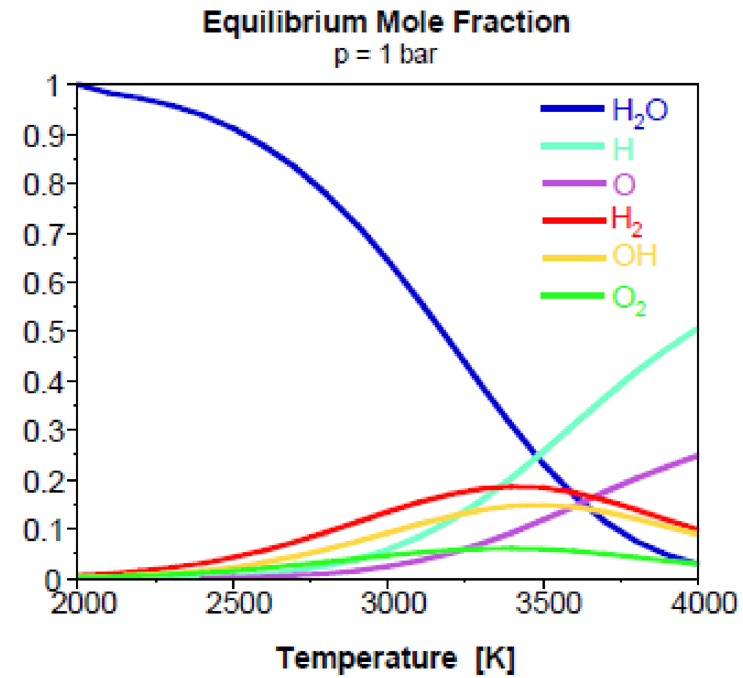
- In the transition to a renewable future, hybrid pathways using fossil fuels exclusively as chemical source for the fuel production and solar energy as the process heat



Solar thermolysis

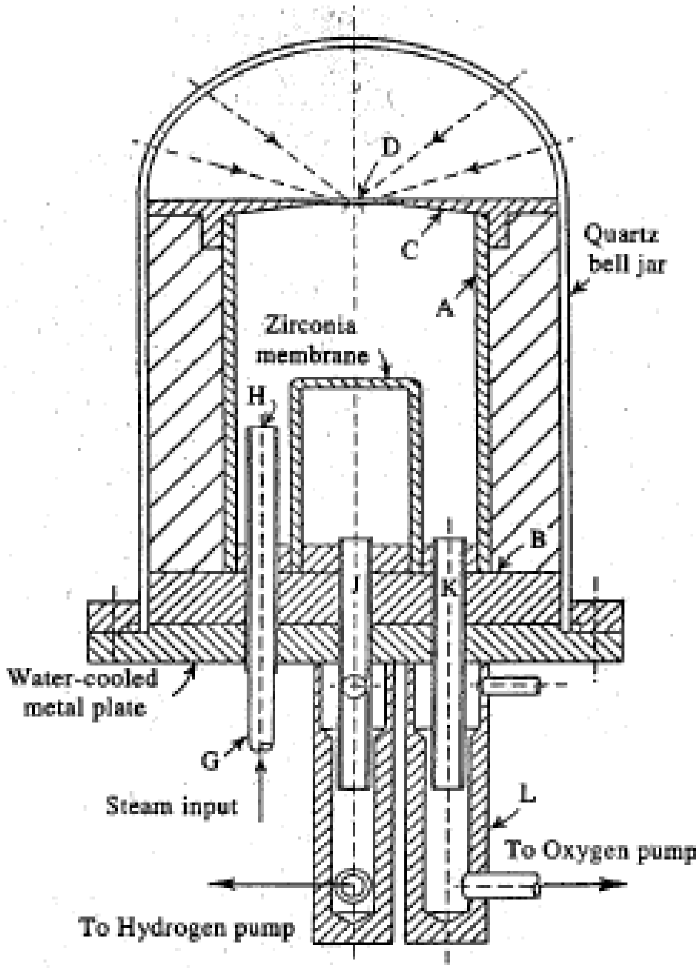
- Solar **thermolysis**
  - Solar energy is used as process heat of chemical reaction
  - Direct thermolysis of water: $H_2O \rightarrow 1/2O_2 + H_2$





Solar thermolysis

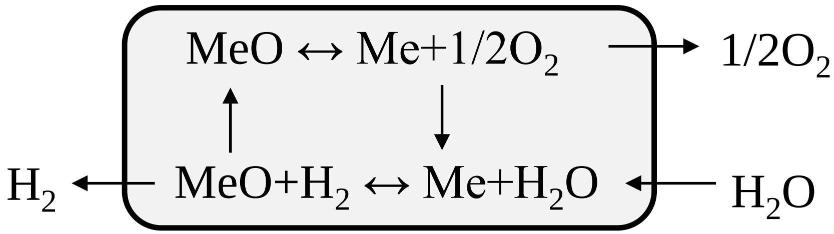
- Reactor concept for solar thermolysis
  - Product separation by:
    - High temperature membranes
    - Rapid quenching of products



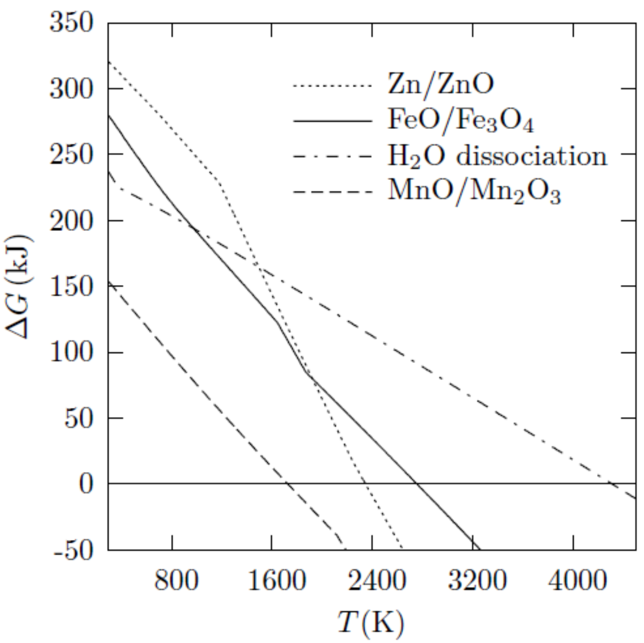
Kogan et al., 1998.

Solar thermochemistry

- Solar **thermochemical** cycles
  - Solar energy is used as process heat of chemical reaction
  - Multi-step water-splitting reactions:



  - Omit explosive hydrogen and oxygen mixture since produced in separate steps
  - Requires lower temperatures
  - Possible redox pairs (Me/MeO):
    - Fe_2O_4/FeO
    - Ce_2O_3/CeO_2,
    - ZnO/Zn
    - SnO/SnO_2 …



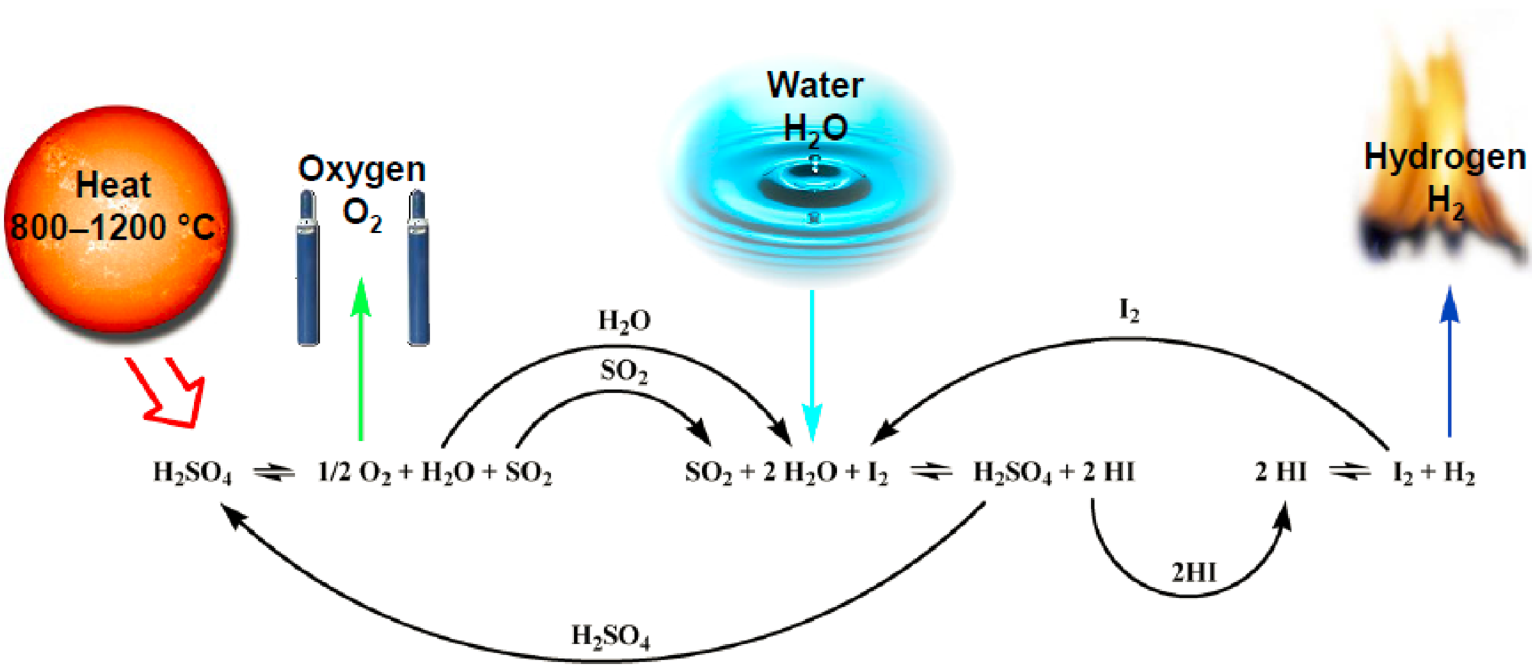
Solar thermochemistry

- Possible redox pairs for two-step cycles:

Cycle	Reactions	Cycle	Reactions
Zn/ZnO	$ZnO \rightarrow Zn + O_2$	SoO$_2$/SiO	$SiO_2 \rightarrow SiO + 1/2\ O_2$
	$Zn + H_2O \rightarrow ZnO + H_2$		$SiO + H_2O \rightarrow SiO_2 + H_2$
Fe_3O_4/FeO	$Fe_3O_4 \rightarrow 3\ FeO + ½\ O_2$	W/WO_3	$WO_3 \rightarrow W + 3/2\ O_2$
	$3\ FeO + H_2O \rightarrow Fe_3O_4 + H_2$		$W + 3H_2O \rightarrow WO_3 + 3H_2$
In_2O_3/In_2O	$In_2O_3 \rightarrow In_2O + 1/2\ O_2$	Hg/HgO	$Hg + H_2O \rightarrow HgO + H_2$
	$In_2O + 2H_2O \rightarrow In_2O_3 + 2H_2$		$HgO \rightarrow Hg + 1/2O_2$
SnO_2/Sn	$SnO_2 \rightarrow Sn + O_2$	Cd/CdO	$Cd + H_2O \rightarrow CdO + H_2$
	$Sn + 2H_2O \rightarrow SnO2 + 2H_2$		$CdO \rightarrow Cd + 1/2O_2$
MnO/$MnSO_4$	$MnSO_4 \rightarrow MnO + SO_2 + 1/2O_2$	CO/CO_2	$CO + H_2O \rightarrow CO_2 + H_2$
	$MnO + H_2O + SO_2 \rightarrow MnSO_4 + H_2$		$CO_2 \rightarrow CO + 1/2O_2$
FeO/$FeSo_4$	$FeSO_4 \rightarrow FeO + SO_2 + 1/2O_2$	Ce_2O_3/CeO_2	$CeO_2 \rightarrow Ce_2O_3$
	$FeO + H_2O + SO_2 \rightarrow FeSO_4 + H_2$		$Ce_2O_3 + H_2O \rightarrow 2CeO_2 + H_2$
CoO/$CoSO_4$	$CoSO_4 \rightarrow CoO + SO_2 + 1/2O_2$	Mg/MgO	$MgO \rightarrow Mg + 1/2O_2$
	$CoO + H_2O + SO_2 \rightarrow CoSO_4 + H_2$		$Mg + H_2O \rightarrow MgO + H_2$
Fe_3O_4/$FeCl_2$	$Fe_3O_4 + 6HCl \rightarrow 3FeCl_2 + 3H_2O + 1/2O_2$	SnO/SnO2	$SnO_2 \rightarrow SnO + 1/2O_2$
	$3FeCl_2 + 4H_2O \rightarrow Fe_3O_4 + 6HCl + H_2$		$SnO + H_2O \rightarrow SnO_2 + H_2$
Mo/Mo_2	$MoO_2 \rightarrow Mo + O_2$		
	$Mo + 2H_2O \rightarrow MoO_2 + 2H_2$		

Solar thermochemistry

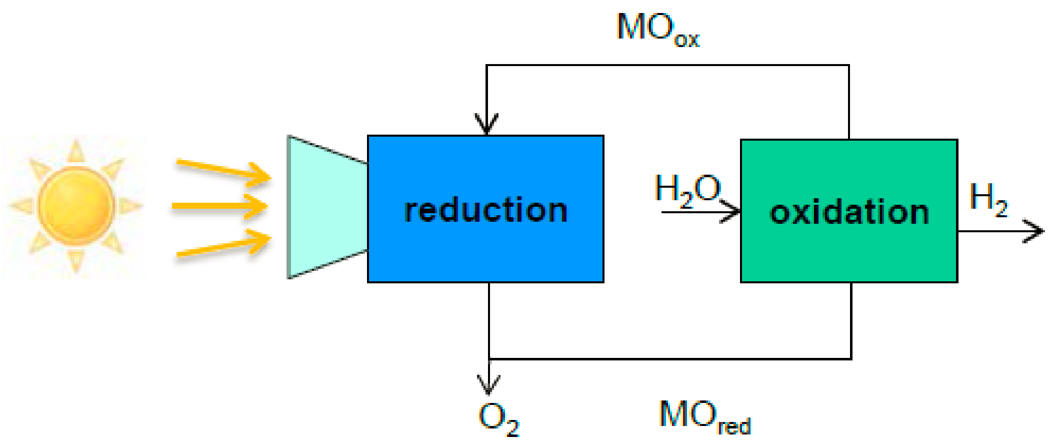
- Three-step water-splitting cycles, e.g. sulfur-iodine:
    - further lower temperatures
    - but run in corrosive environment



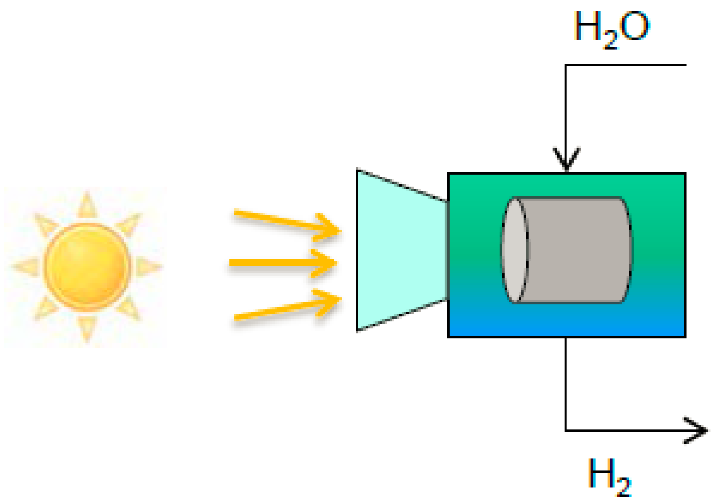
Solar thermochemistry

- Reactor concepts: two-step cycles

Moving material

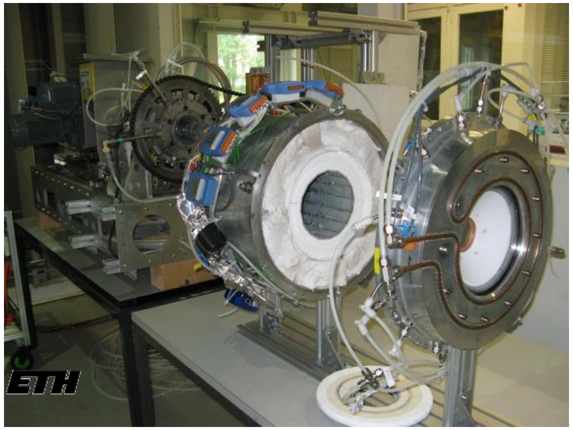


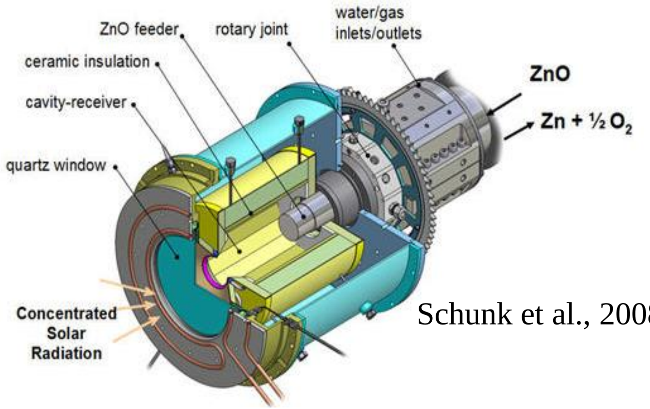
Stationary material



Solar thermochemistry

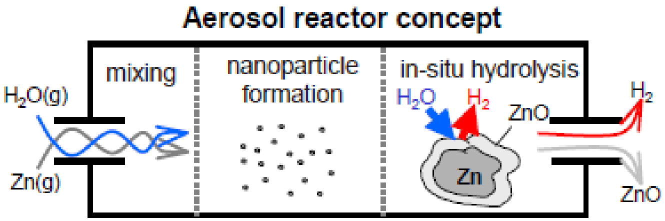
- Zn/ZnO-based proposed reactors, e.g. at ETH Zürich and PSI:
  - High-temperature reactor
    - 10 kW reactor
    - Reactor temperature: 2000 K
    - Peak concentration: 5800 suns





Schunk et al., 2008.

  - Hydrolysis reactor:
    - Reactor temperature: 1263 K

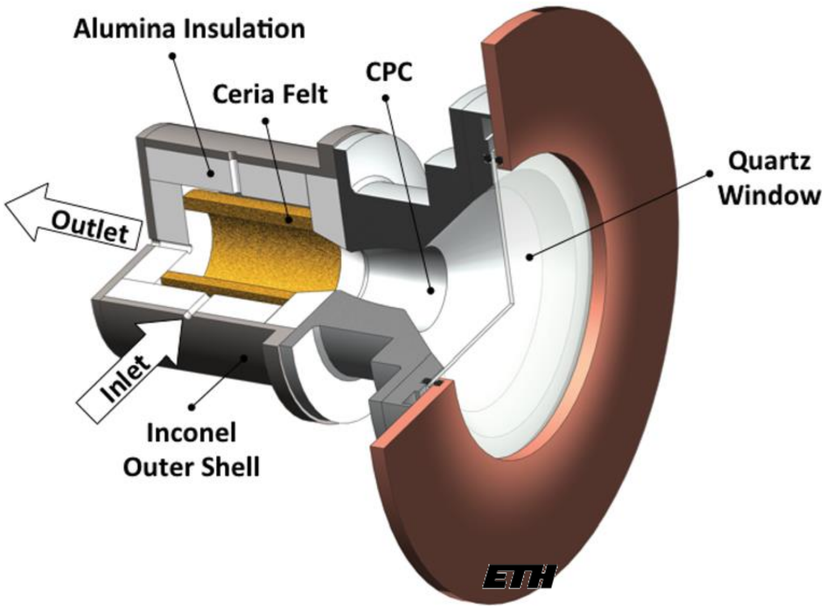


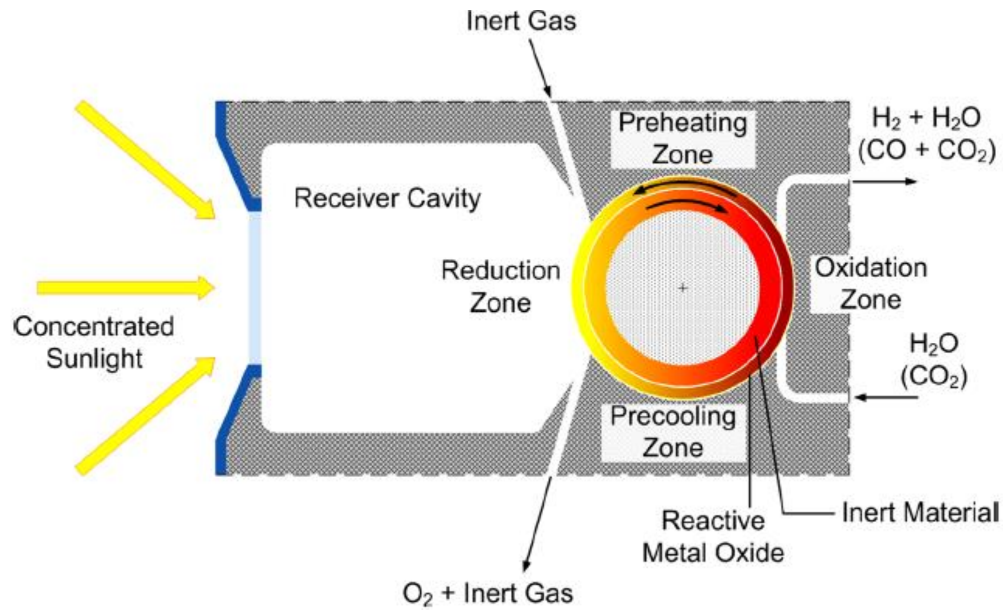
Melchior et al., 2009.

Solar thermochemistry

- Ceria-based proposed reactors, e.g.:

ETH Zürich — University of Minnesota



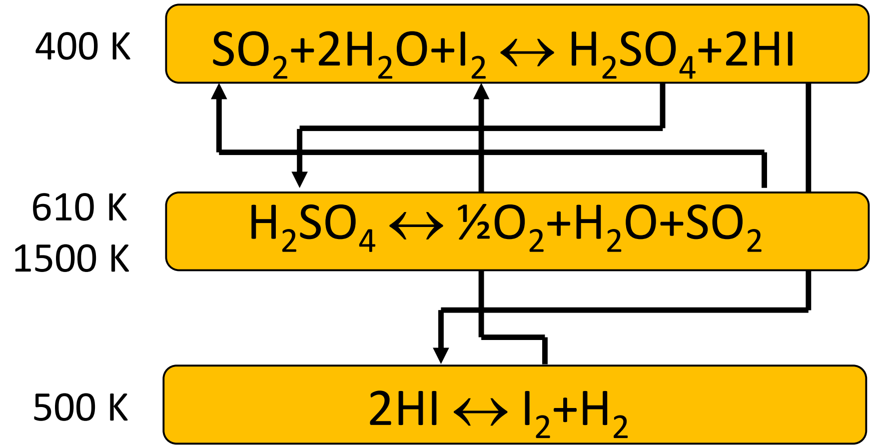


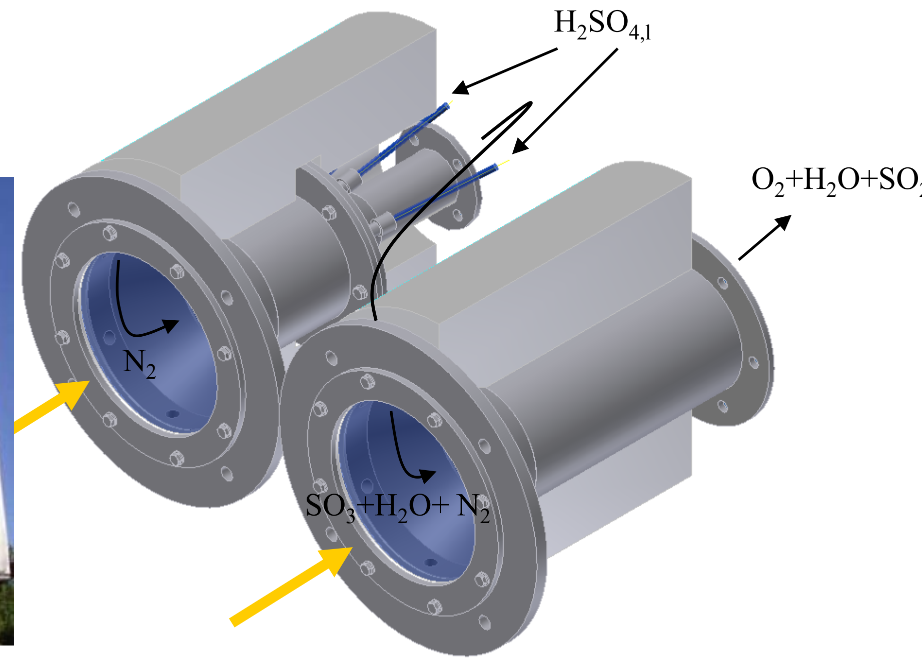
Temperature in reduction reaction: ~ 1800 K

Temperature in oxidation reaction: ~ 1200 K

Solar thermochemistry

- SI-cycle, DLR Germany





Renewable Energy

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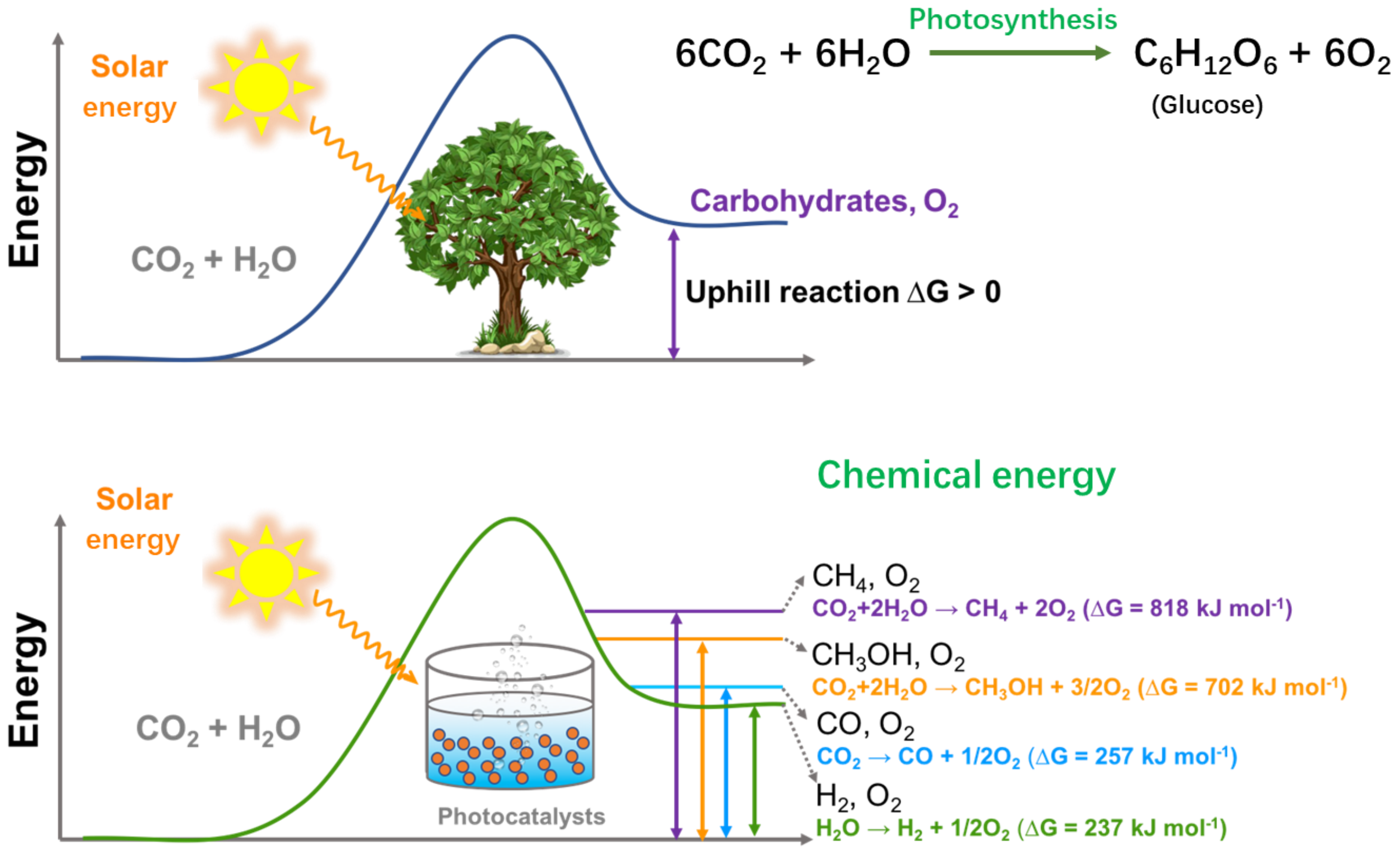
Photochemistry

Natural Photosynthesis

Artificial photosynthesis

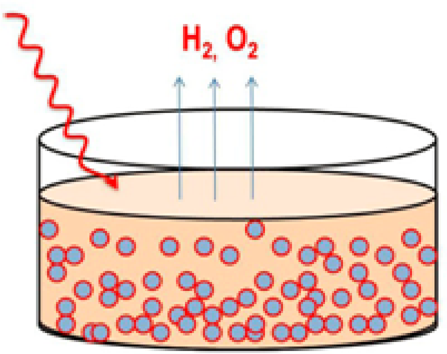


Water splitting

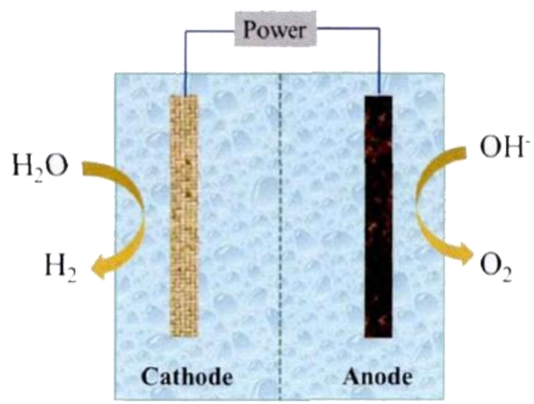
$$2H_2O \longrightarrow 2H_2 + O_2 \qquad \Delta G = 237.18 \text{ kJ/mol}$$

Driving force

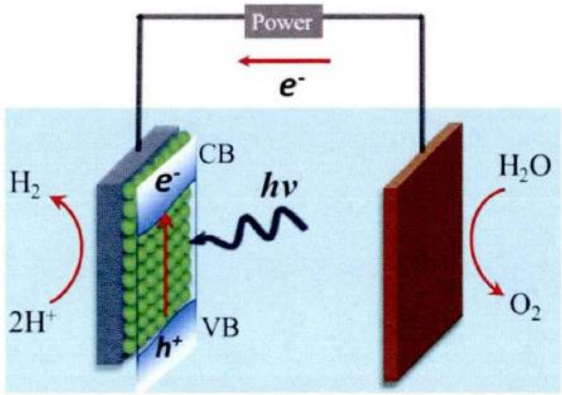
Photocatalysis



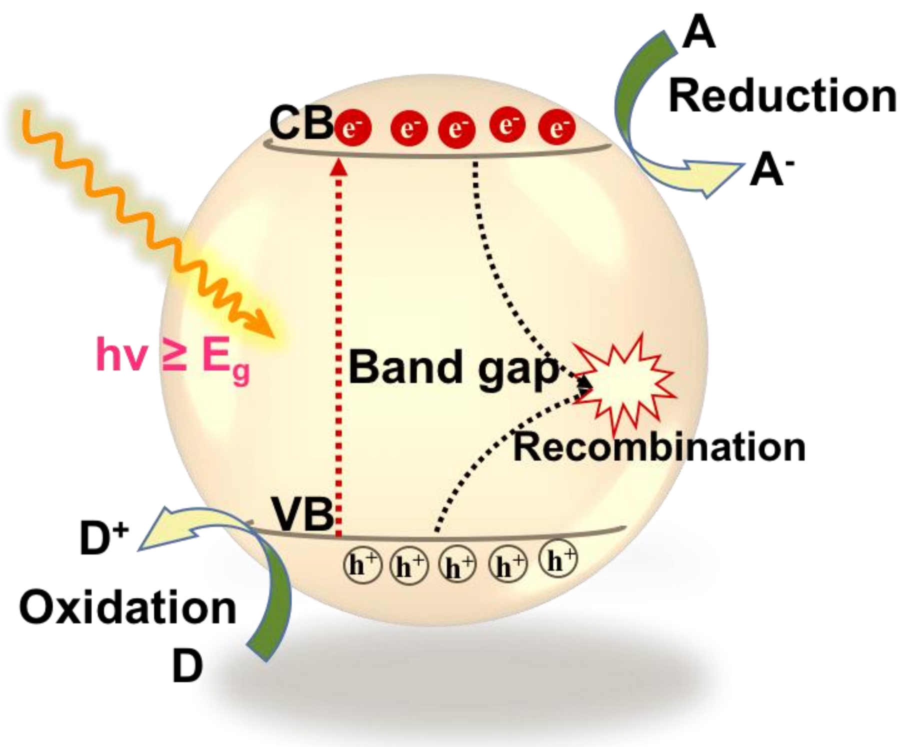
Electrocatalysis

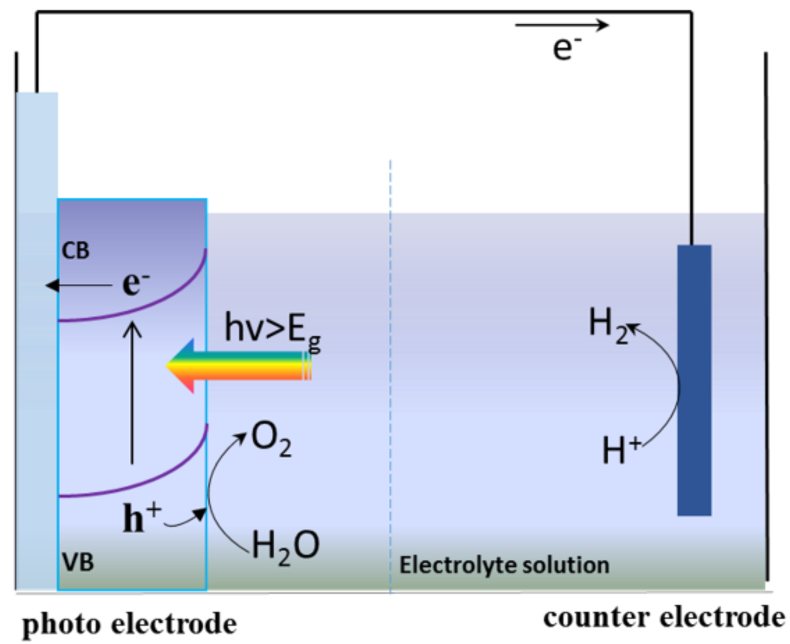


Photoelectrocatalysis



Key steps in photo(electro)catalysis





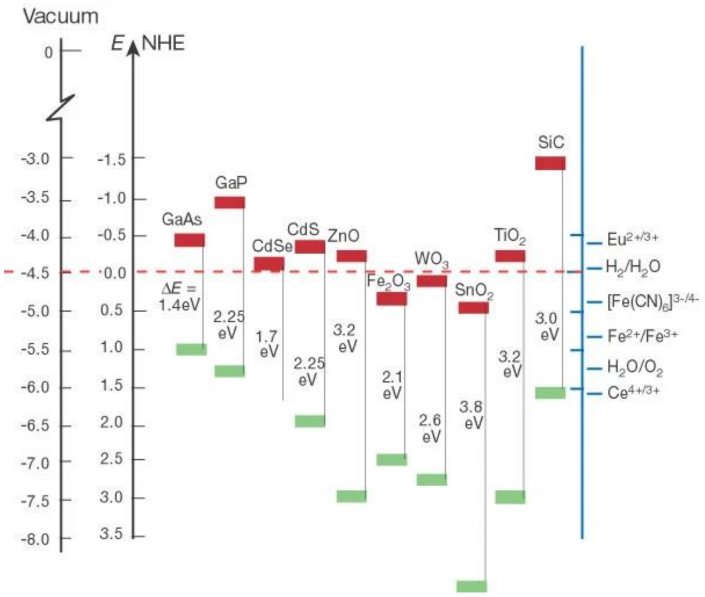
1) Capture of light energy 2) Separation of photogenerated charge carriers

3) Surface catalysis

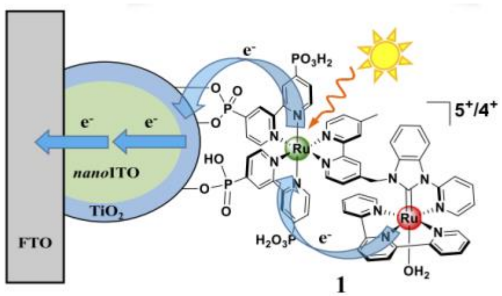
$$\Phi_{H_2} = \phi_{Abs.} \times \phi_{Sep.} \times \phi_{Cat.}$$

Semiconductors

- Stringent material requirements:
  - band gap size
  - suitable band edge position
  - high chemical stability in the dark and under illumination, as well as under highly acidic or base conditions
  - efficient charge transport in the semiconductor
  - selective and efficient electrochemical reactions
  - earth-abundance and low costs

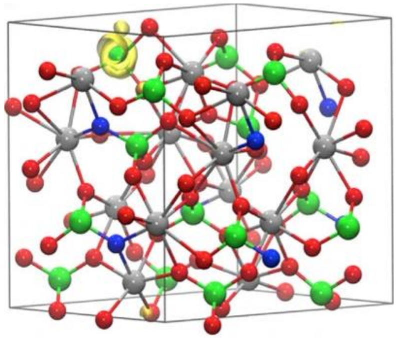


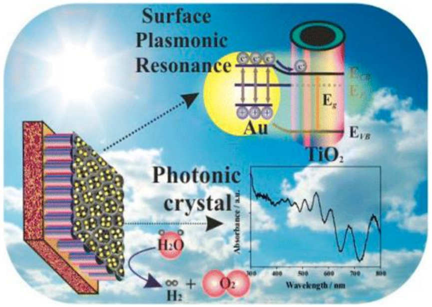
Strategies to improve activity



Sensitized

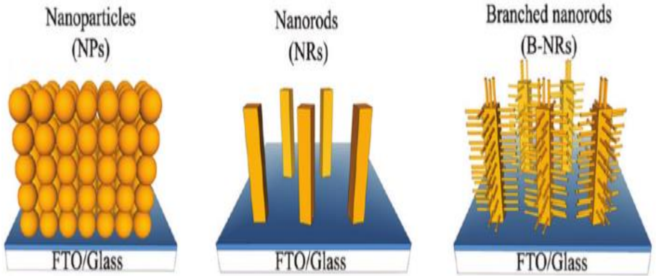
Doping



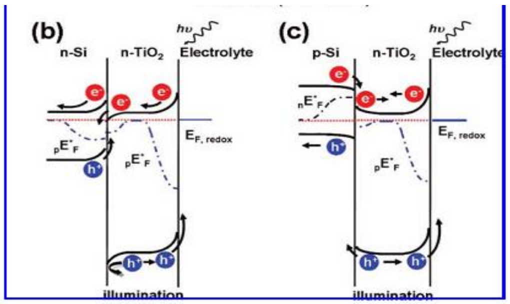


Plasmonic

Nanostructure



Heterojunction

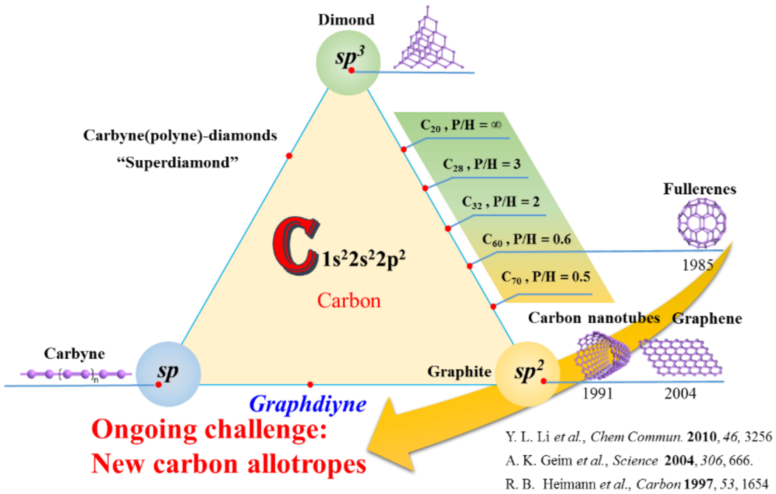


Kongkanand, A.; Kamat, P. V. et. al. *J. Am. Chem. Soc.* ***2008****, 130, 4007*
Wright, J. C.; Jin, S., et al. *Chem. Soc. Rev.* ***2013****, 42 , 2963-2985*

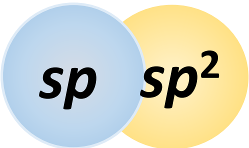
Smith, A. M.; Nie, S. *Acc. Chem. Res.* ***2009****, 43, 190.*
Yang, Y.; Lian, T. *et. al. Nano Lett.* ***2012****, 12, 4235*

Graphyne : Novel 2D Carbon Allotrope

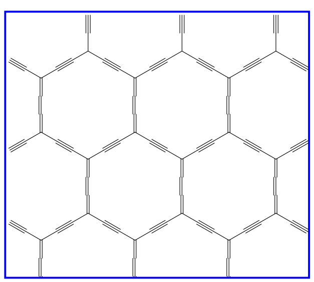
A new member of 2D carbon allotropes composed of *sp-sp*^{2} carbon atoms.



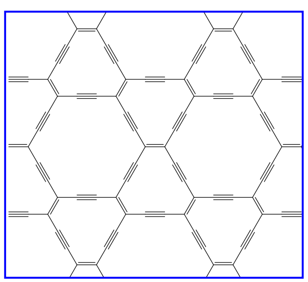
- ✓ Linear structure ("-C≡C-"),
- ✓ Free of Cis-trans isomers,
- ✓ Planar polymeric networks,
- ✓ Uniform pores,
- ✓ Highly Conjugated structure.



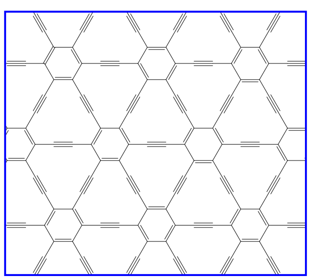
Graphyne Family:



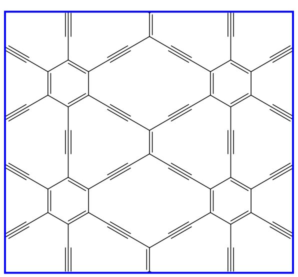
α-graphyne



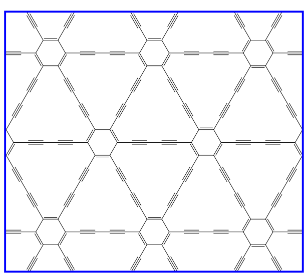
β-graphyne



γ-graphyne

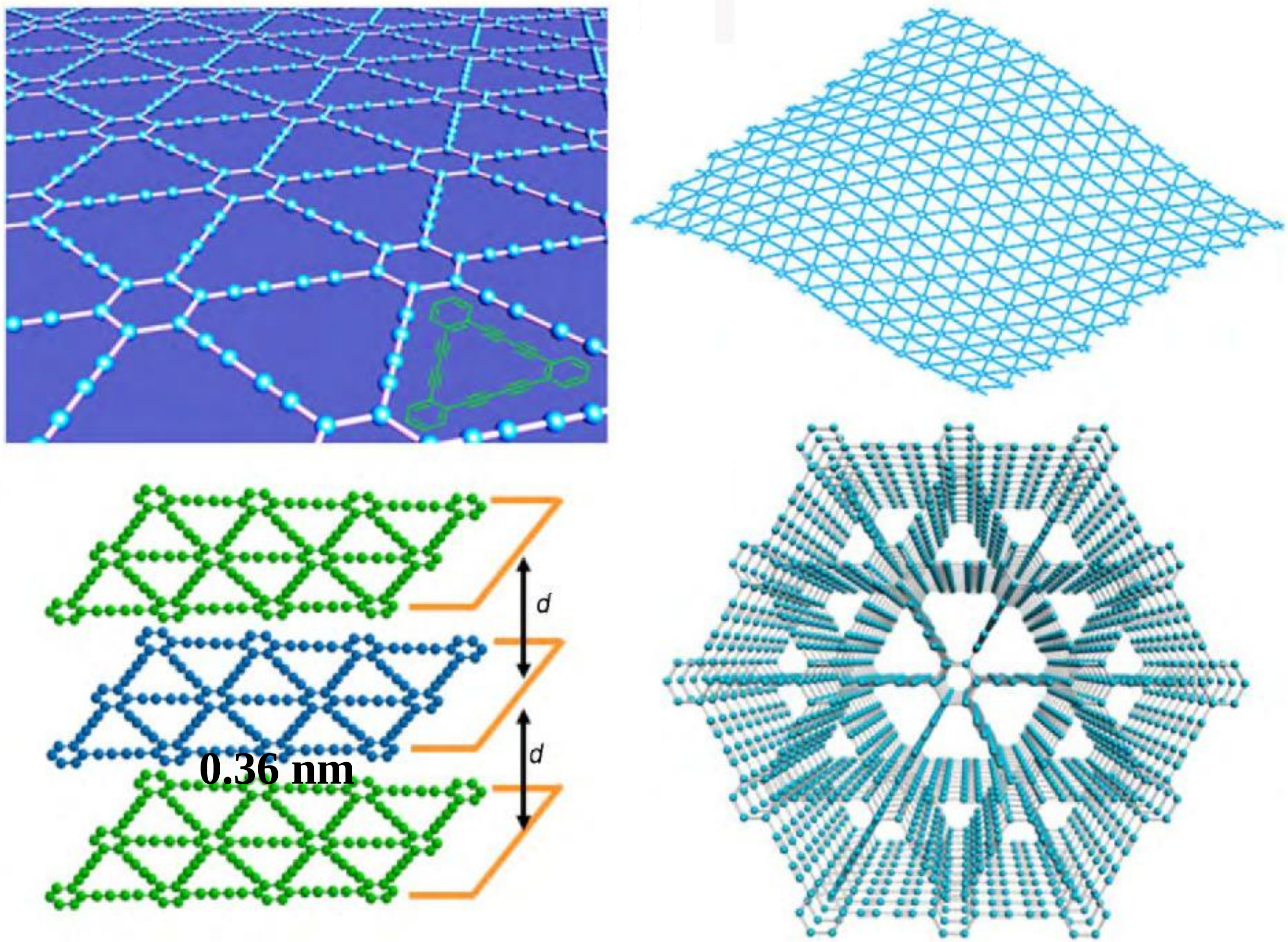


6, 6, 12 - graphyne



graphdiyne

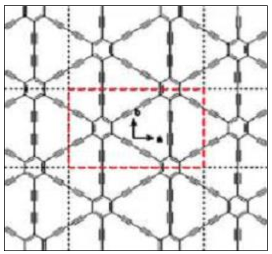
Graphdiyne : Molecular Structure

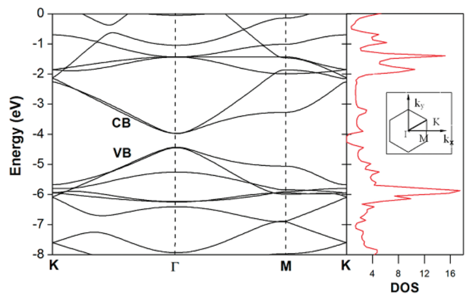


Li, Y. Li, Y. *et. al., Chem. Soc. Rev.* **2014**, *43*, 2572.

Huang, C. Li, Y. *et. al., Chin. Sci. Bull.* **2016**, *61*, 2901.

Graphdiyne : Electronic Structure

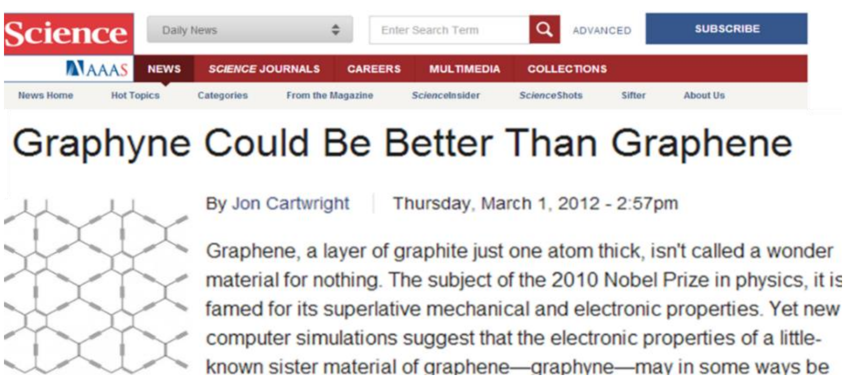




Graphdiyne

Semiconductor

High Carrier Mobility: $10^4 \sim 10^5$ cm^2/Vs
Band Gap: ~0.46 eV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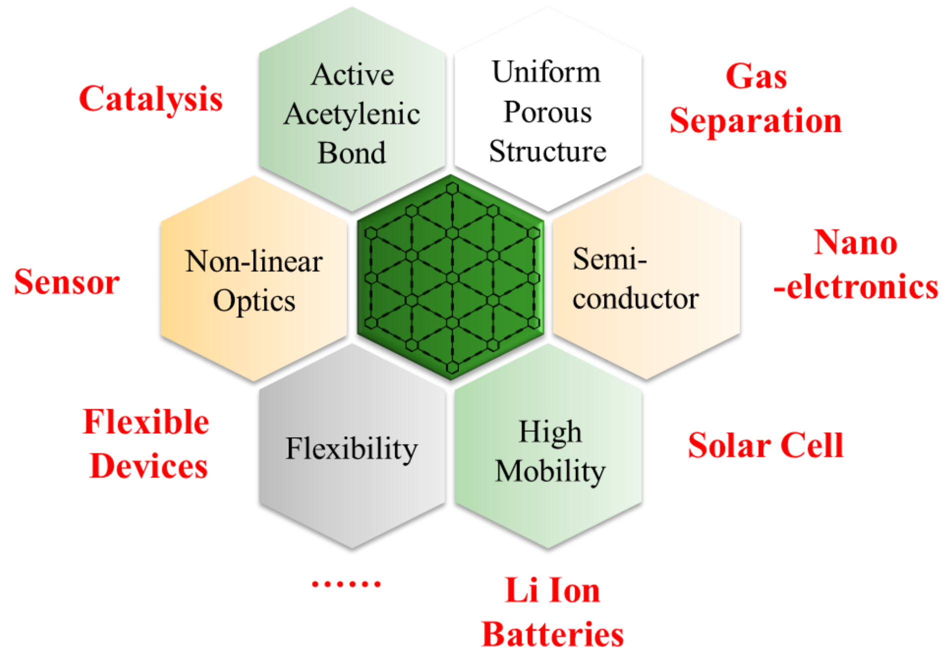
Graphyne Could Be Better Than Graphene

By Jon Cartwright | Thursday, March 1, 2012 - 2:57pm

Graphene, a layer of graphite just one atom thick, isn't called a wonder material for nothing. The subject of the 2010 Nobel Prize in physics, it is famed for its superlative mechanical and electronic properties. Yet new computer simulations suggest that the electronic properties of a little-known sister material of graphene—graphyne—may in some ways be



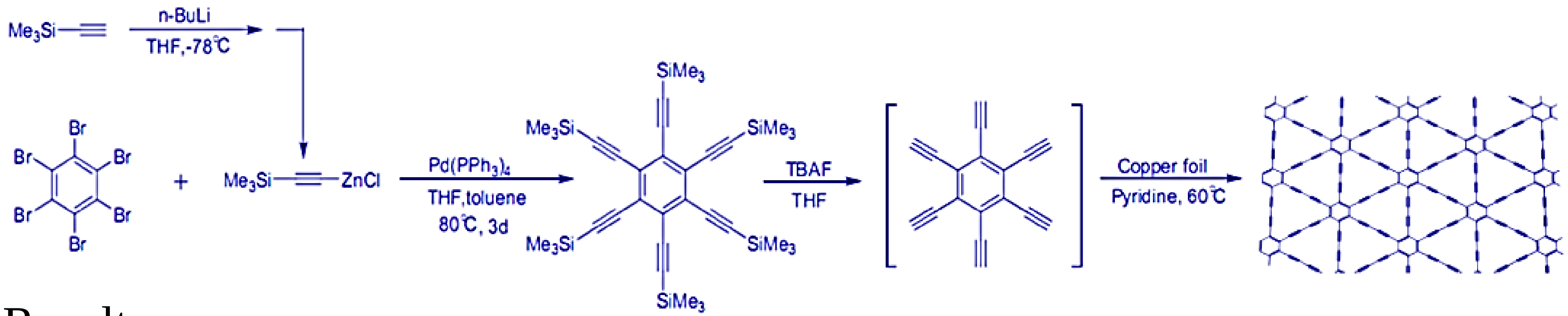
Promising in the diverse applications

D. Malko *et al.*, *Phys. Rev. Lett.* **2012**, *108*, 086804.

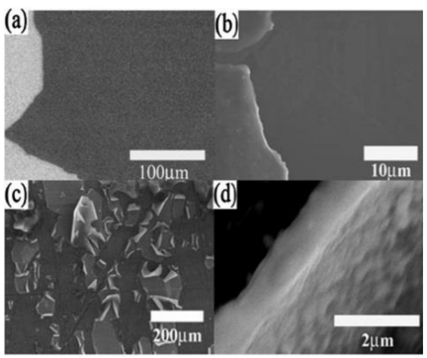
A. L. Ivanovskii, *Progress in Solid State Chemistry* **2013**, *41*, 1

Synthesis of graphdiyne

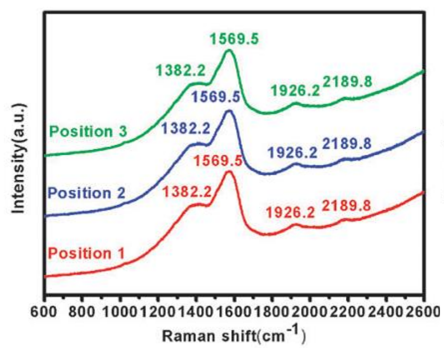
Synthetic Route:



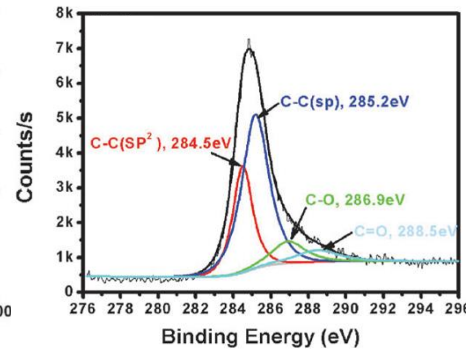
Results:



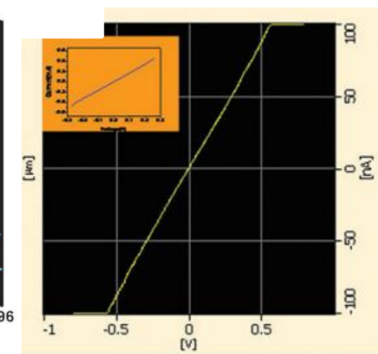
SEM images



Raman spectra



XPS spectra

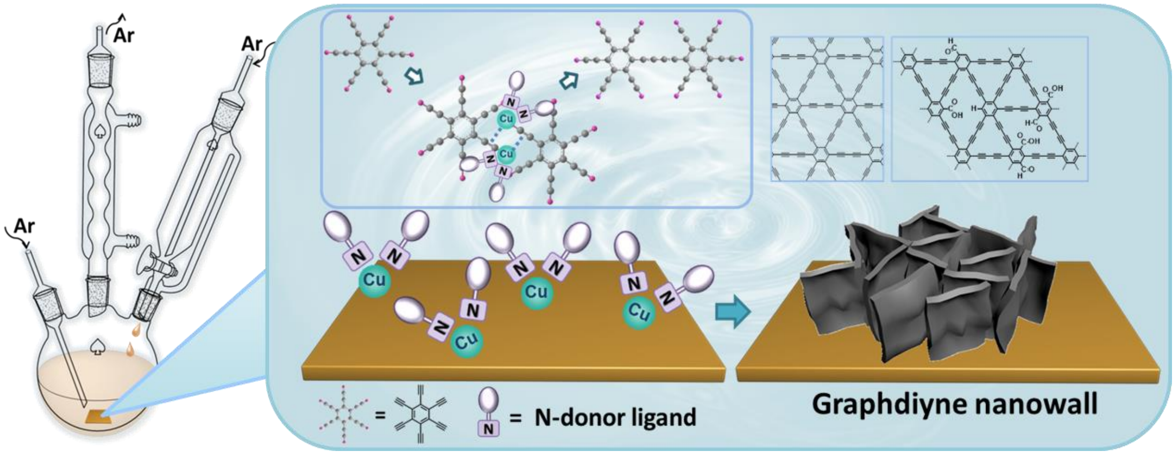


I-V curve

Uniform film (1μm), conductivity: 2.516×10^{-4} S/m

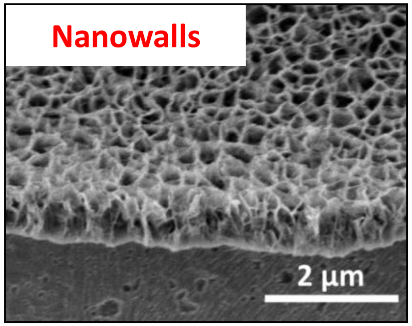
Y. L. Li *et al.*, *Chem Commun.* **2010**, *46*, 3256

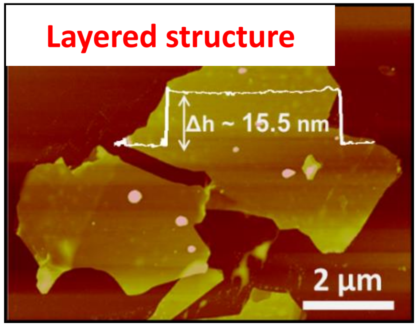
Graphdiyne nanowalls



- Cu foil (offering Cu^{+} catalyst)
- Ligand： TMEDA or Pyridine
- Hexaethynylbenzene
- 60 ℃

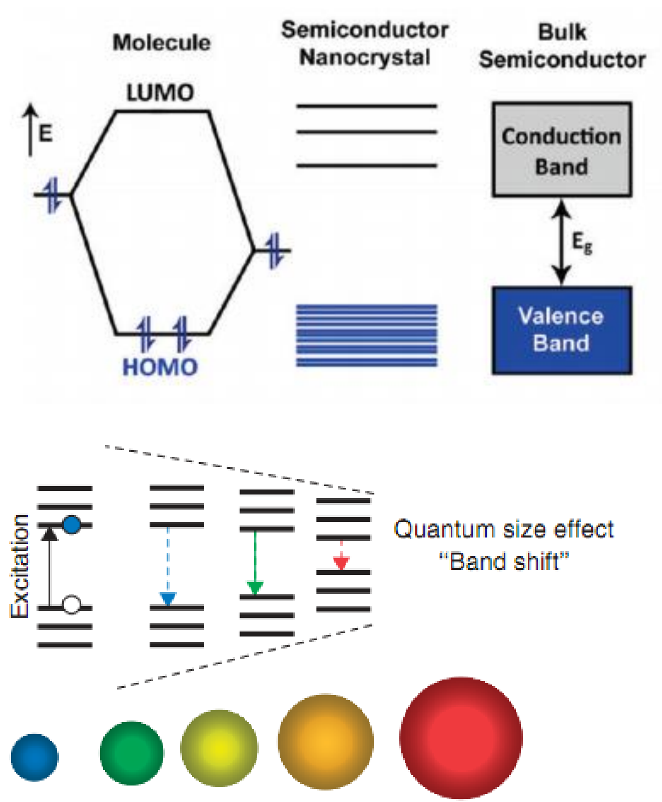
N, N, N’, N’ –tetramethylethylenediamine (TMEDA)

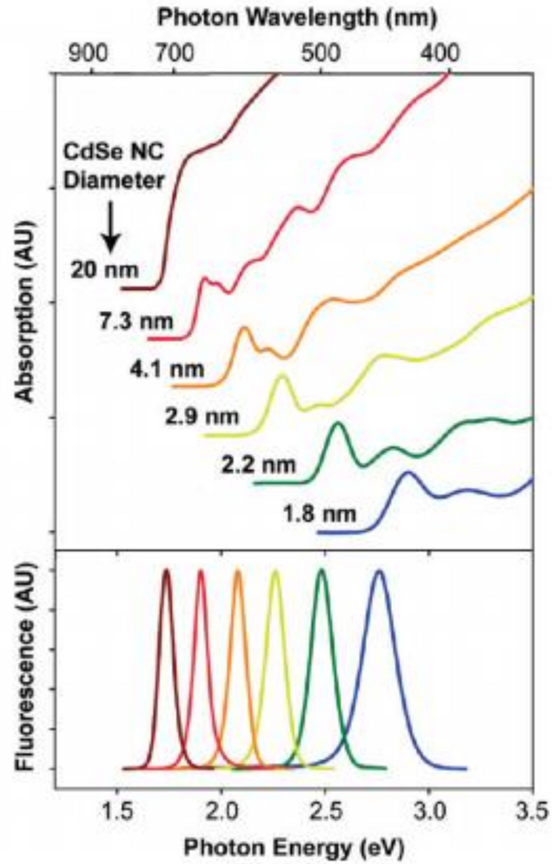




J. Zhou et.al, *J. Am. Chem. Soc.* **2015**, *137*, 7596.

QDs-Sensitized GDY Photocathode





hot electrons : 10^{10}-10^{12} s^{-1}

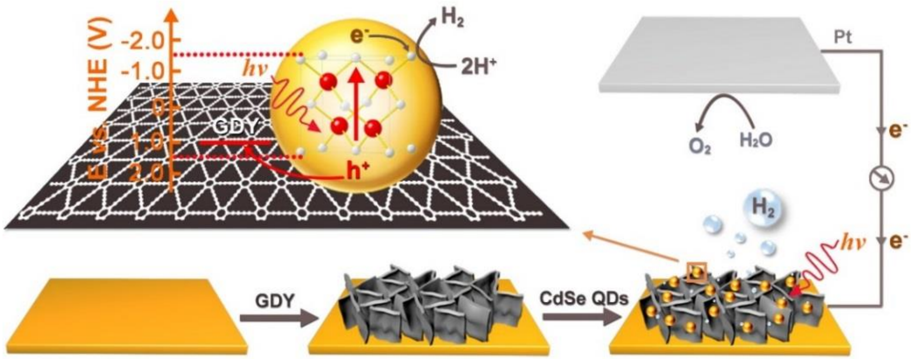
Hot holes: 10^{8}-10^{9} s^{-1}

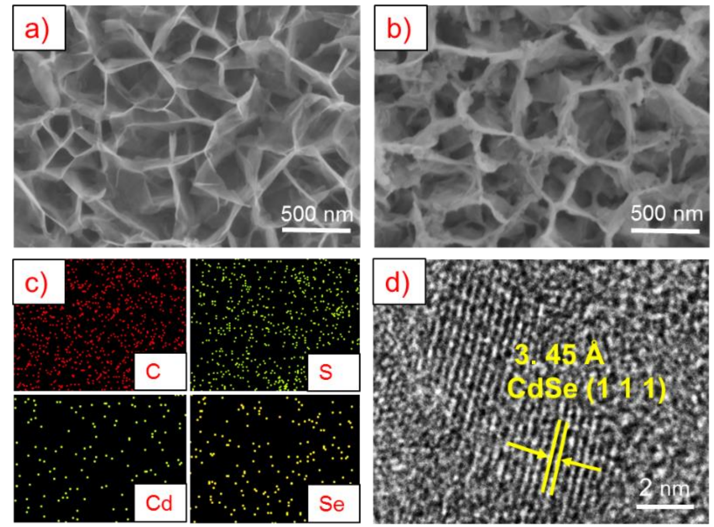
.

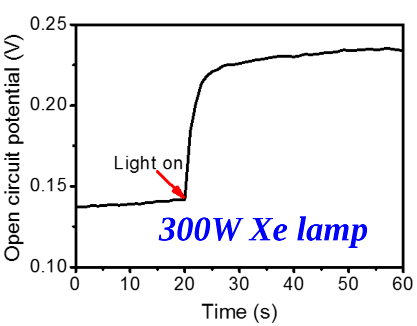
S. Kundu, A. Patra, *Chem. Rev.*, **2017**, *117*, 712-757.

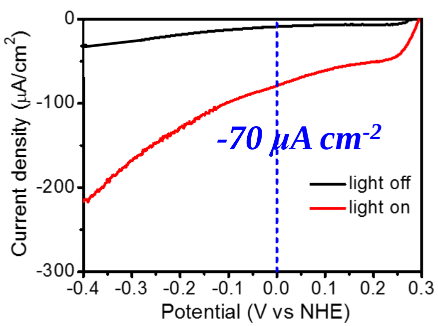
Kamat, P. V, *Langmuir* **2014**, *30*, 5716-5725.

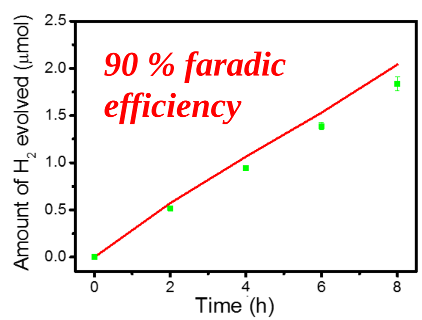
QDs-Sensitized GDY Photocathode

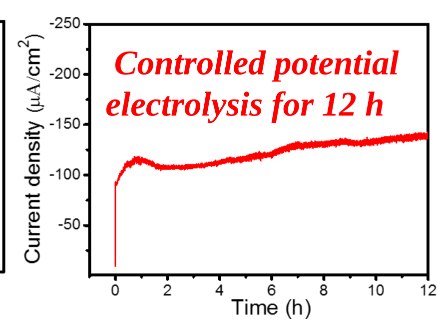








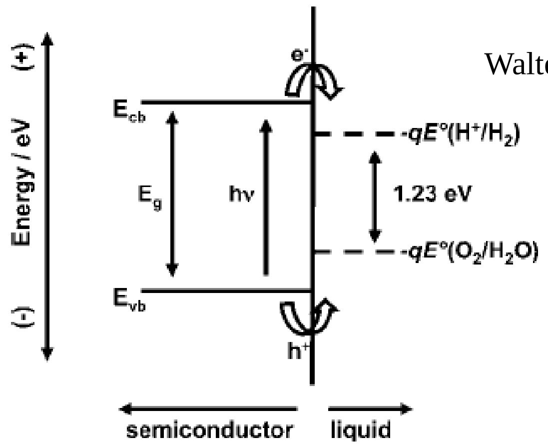




Li et.al *J. Am. Chem. Soc.* **2016**, *138*, 3954.

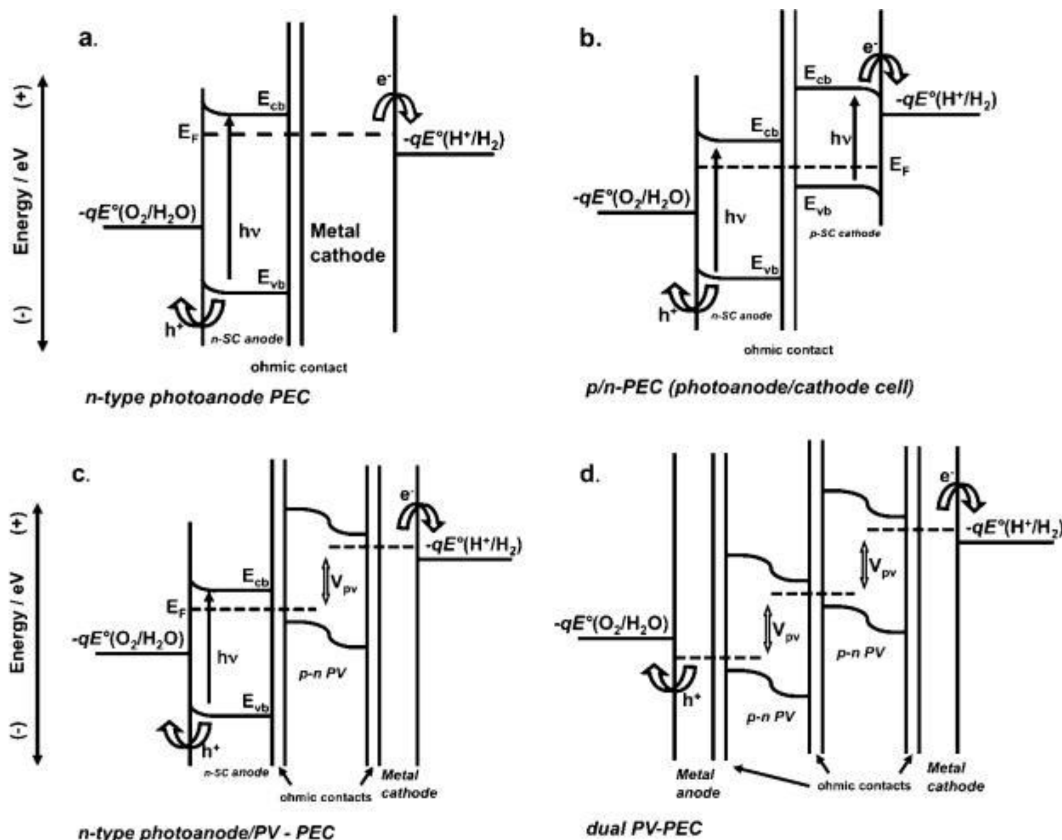
Photoelectrochemistry

- Band gap and band position of photoelectrode material must match reaction potentials:



Walter et al., 2006

- Various possible architectures:



Photoelectrochemistry

- Calculations:
  - Photoactive material(s) will show diode-like current-potential behavior:

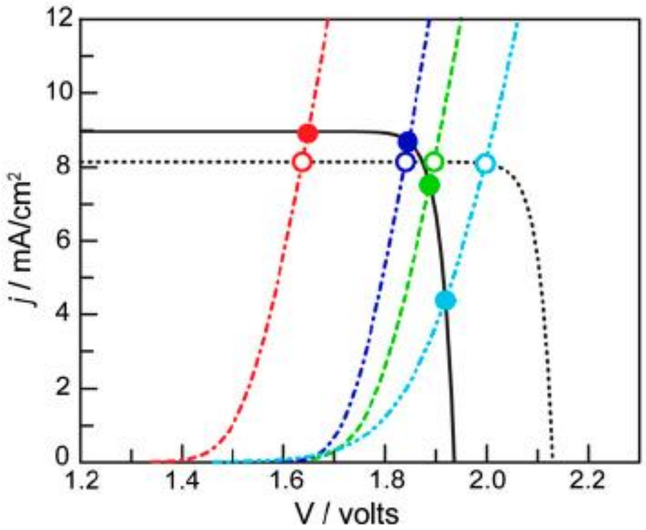
Elementary charge

$$i = i_L - i_0\left(\exp\left(\frac{qV}{kT}\right) - 1\right)$$

  - Electrochemical system shows losses:
    - Reaction overpotentials
    - Ohmic losses
    - Concentration losses

$$E = E_0 + \eta_a + \eta_c + iR_{sol} + E_{mem} + E_{conc} > E_0$$

  - Electrochemical load curve will show electrolyzer like load curve
  - Intersection between both is operating point



Surendranath et al., 2012

Photoelectrochemistry

- Calculations:
  - Electrochemical system shows losses:
    - Reaction overpotentials
      - E.g. via Tafel equations:

Tafel slope

$$\eta_{a} = a_1 \log\left(\frac{i}{i_{0a}}\right) \qquad \eta_{c} = a_2 \log\left(\frac{i}{i_{0c}}\right)$$

      - Or Buttler-Volmer:

Exchange current density

Transfer coefficient

$$i_{R} = i_{0a/c}\left[\exp\left(\frac{\alpha_{a} F \eta_{a/c}}{RT}\right) - \exp\left(\frac{\alpha_{c} F \eta_{a/c}}{RT}\right)\right]$$

    - Ohmic losses account for resistances in electrolyte, membrane, and solid conductor:

$$\Delta V_{ohm} = i \rho_{sol} l$$

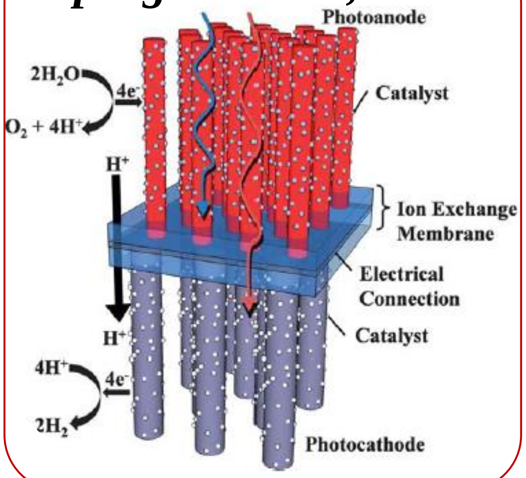
Characteristic ion and electron path length

resistivity

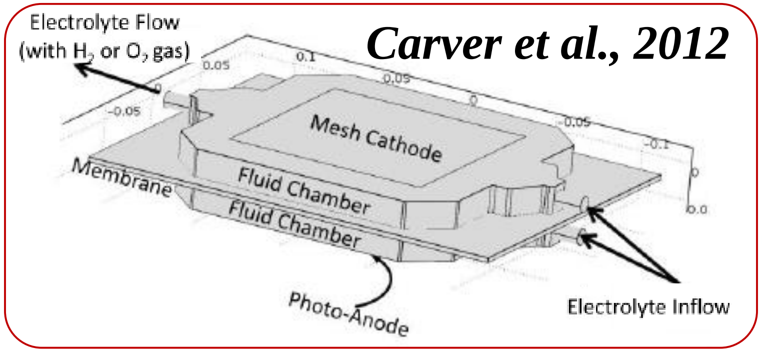
Photoelectrochemistry

- Proposed devices

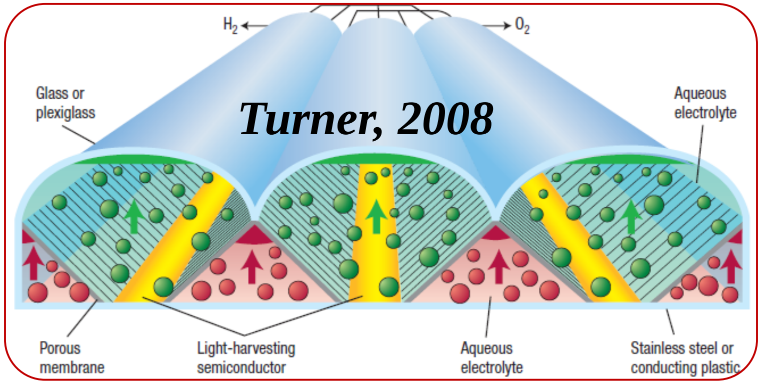
Spurgeon et al., 2011



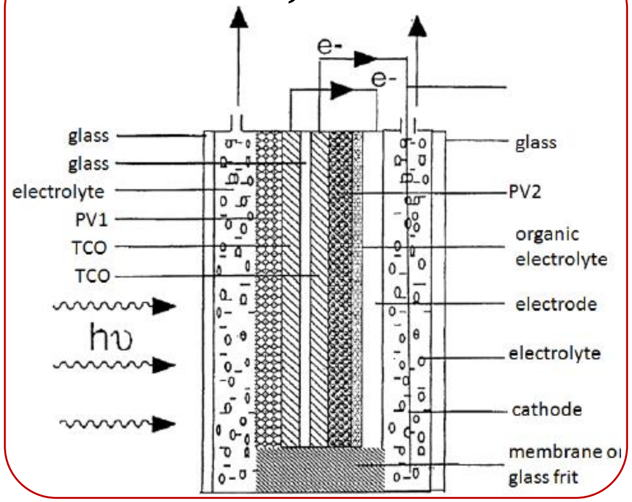
Carver et al., 2012



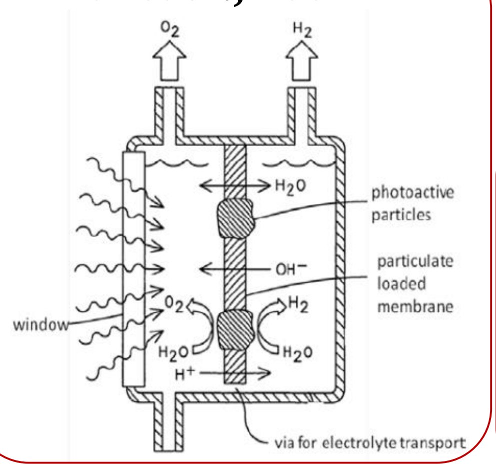
Turner, 2008



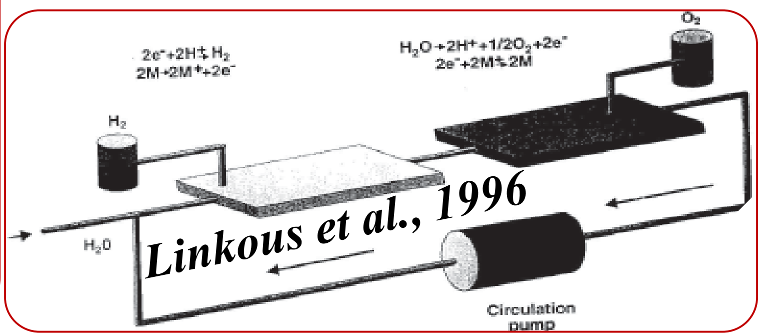
Grätzel et al., 2007



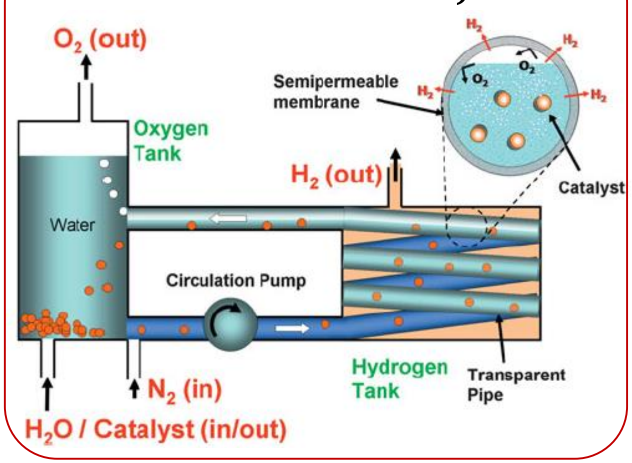
Miller et al., 2007



Linkous et al., 1996



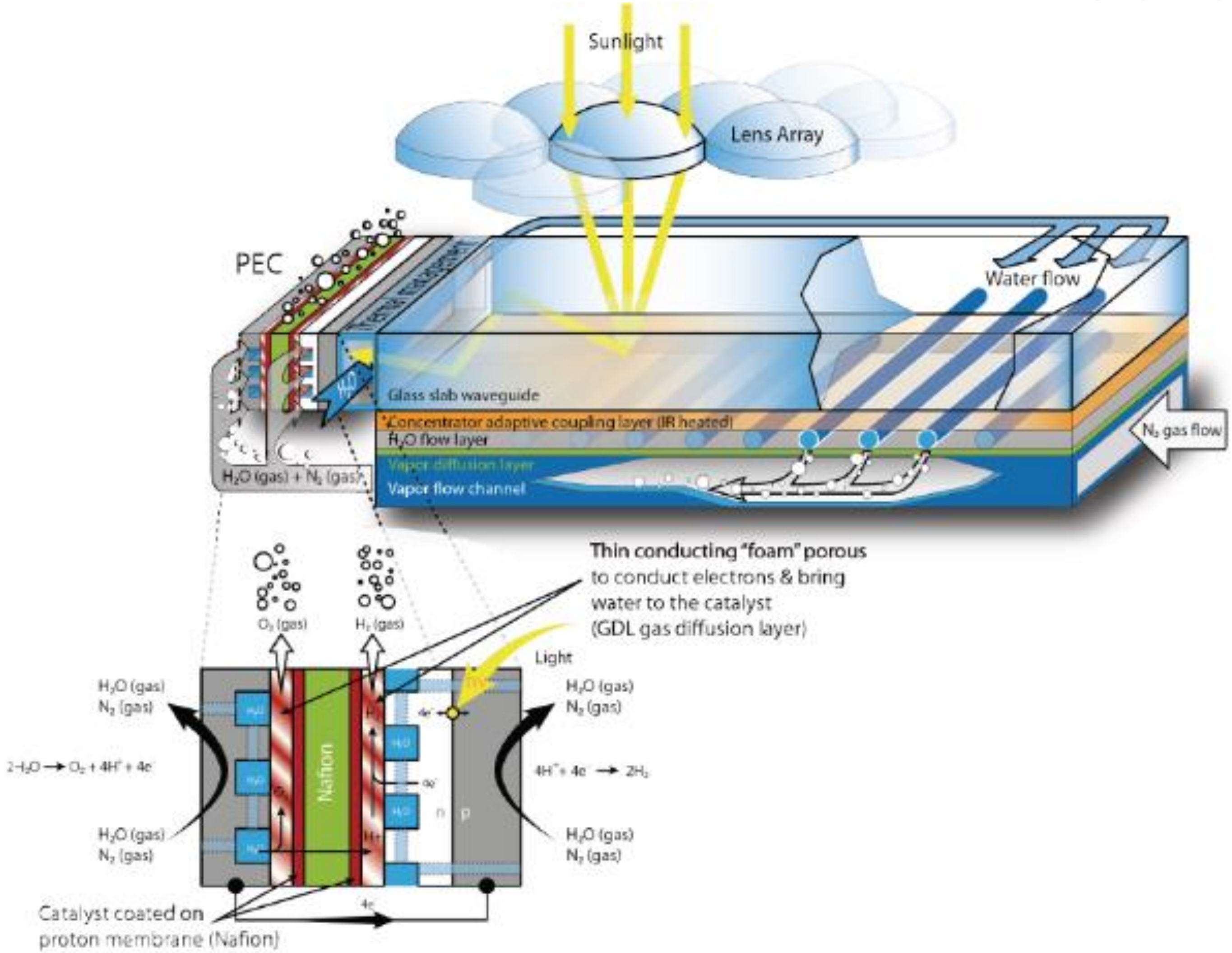
Parkinson et al., 2011



Photoelectrochemistry

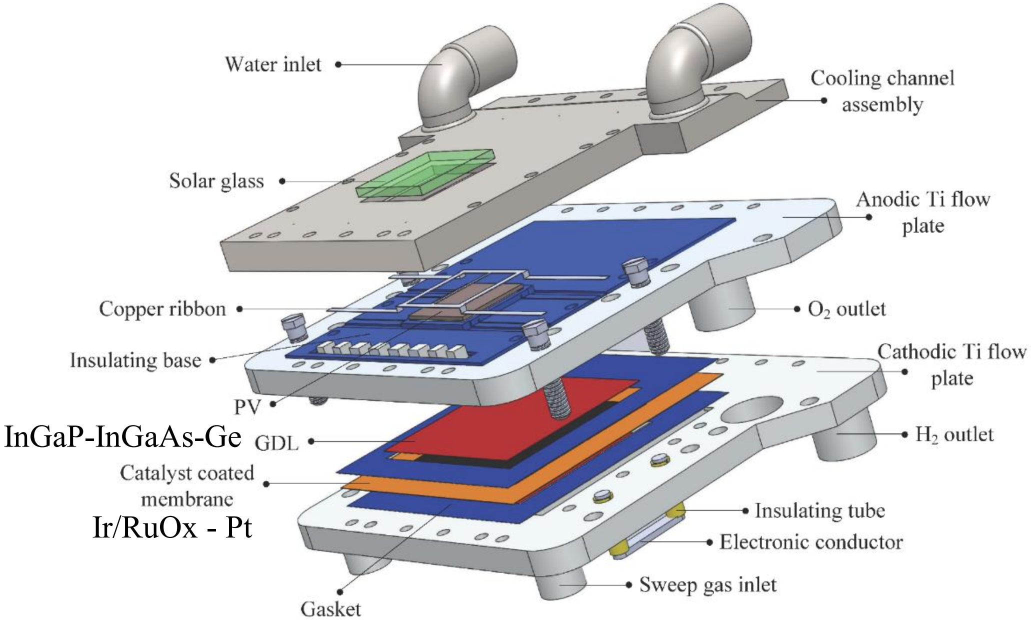
- Proposed devices

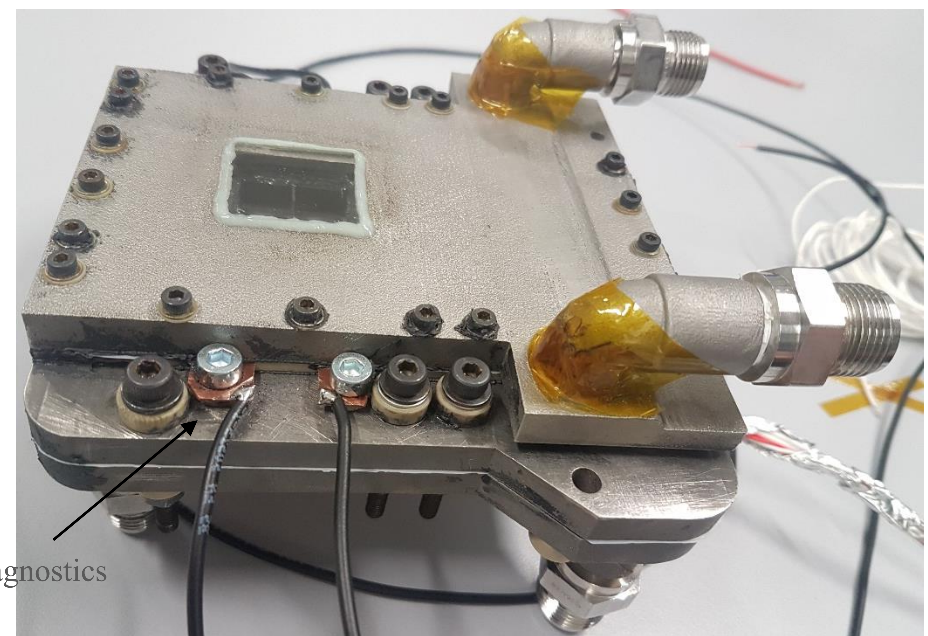
SHINE
Solar Hydrogen Integrated Nano Electrolysis

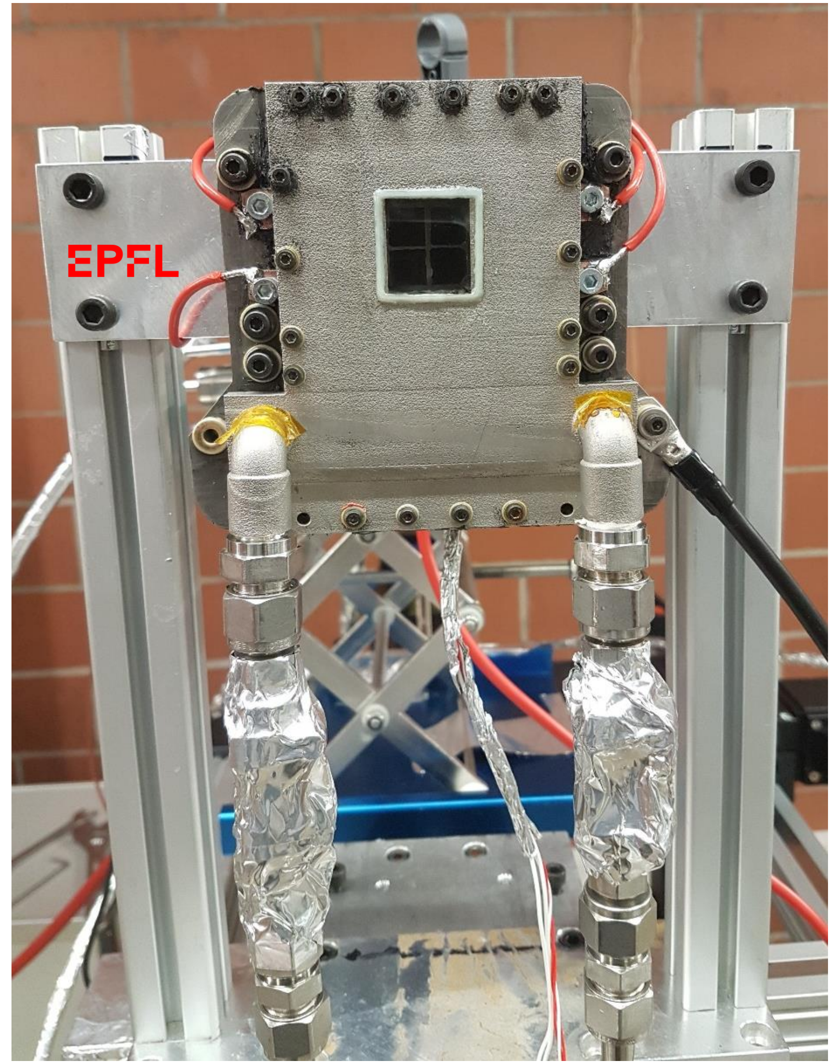


Photoelectrochemistry

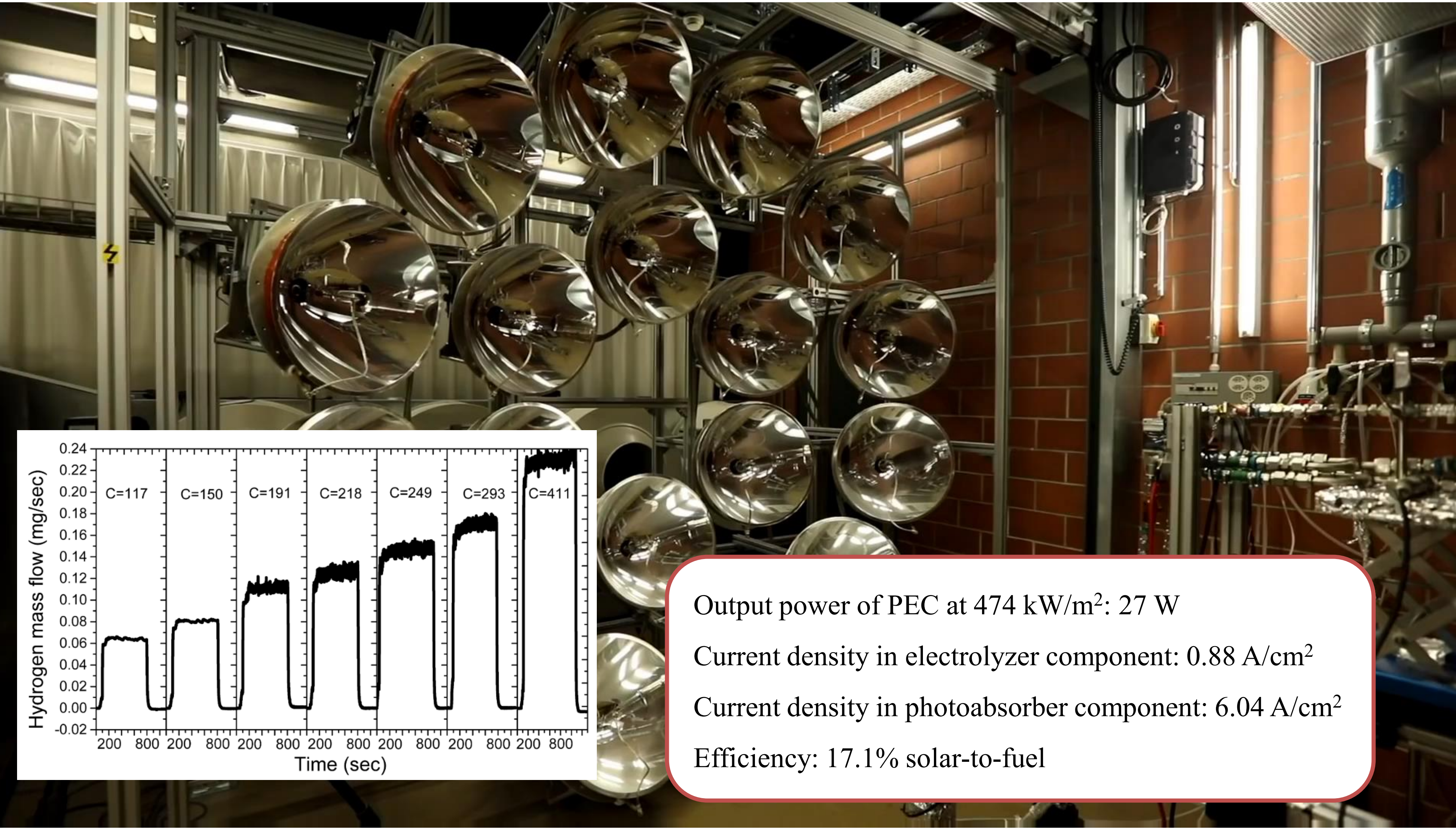
US Patent 62/376923
EP Patent 16020308.9







Experimental demonstration



Output power of PEC at 474 kW/m^2: 27 W

Current density in electrolyzer component: 0.88 A/cm^2

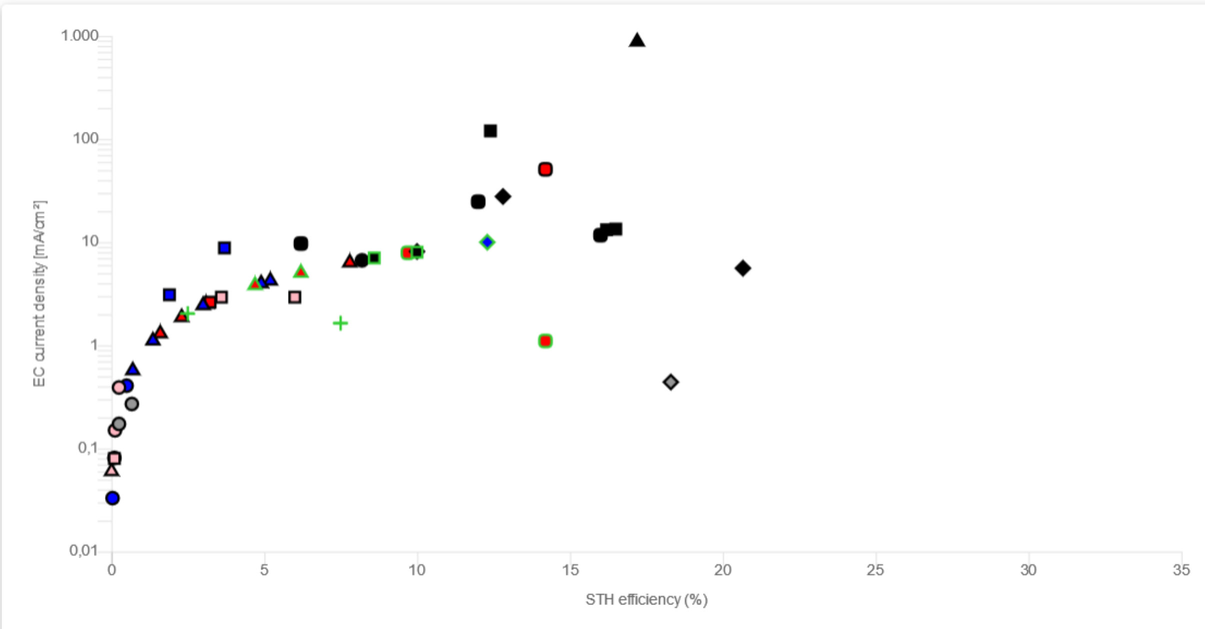
Current density in photoabsorber component: 6.04 A/cm^2

Efficiency: 17.1% solar-to-fuel

Tembhurne, Nandjou, Haussener, *Nature Energy*, doi: 10.1038/s41560-019-0373-7, 2019

Photoelectrochemistry - Comparison

- Community outreach: dynamic and online: – http://specdc.epfl.ch/



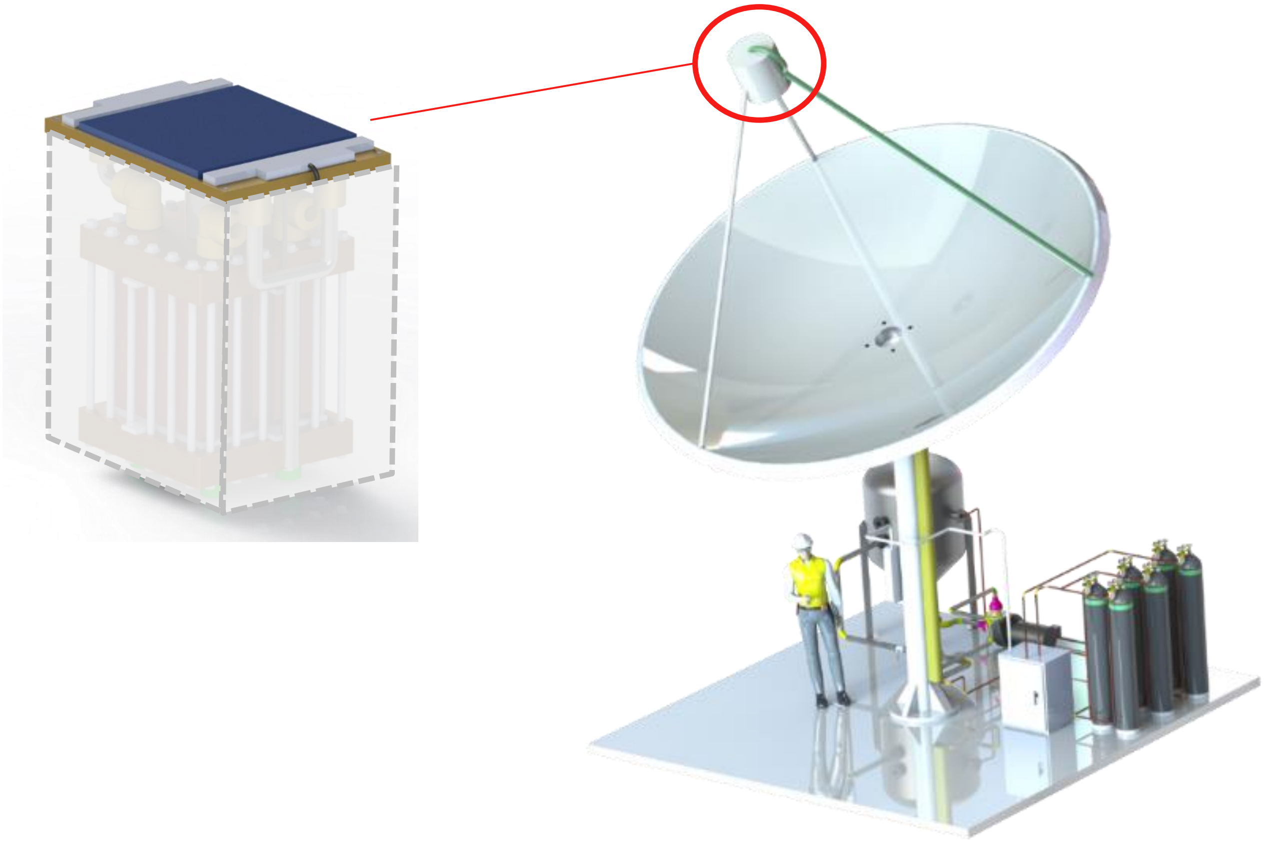
w/o multi-module demonstrations
w/o multiple electrolyzer demonstrations

LEGEND

Fill color - PV / photoabsorber material	Boundary color - EC material	Symbol shape - PV / photoabsorber and EC configuration	
All III-V	Rare metal-based (expensive)	○ 2J, integrated PVs and catalyst	+ 3J, integrated PVs and catalyst
Partial III-V	Abundant (cheap)	□ 2J, integrated PVs, wired catalyst	△ 3J, integrated PVs, wired catalyst
All Si		◇ 2J, non-integrated PVs or catalyst	O 3J, non-integrated PVs or catalyst
Partial Si			
Oxides and others			

Tembhurne, Nandjou, Haussener, *Nature Energy*, doi: 10.1038/s41560-019-0373-7, 2019

Scaling – ongoing @LRESE



kW-scale, long-term, on-sun demonstration, 0.5 kg of hydrogen per day

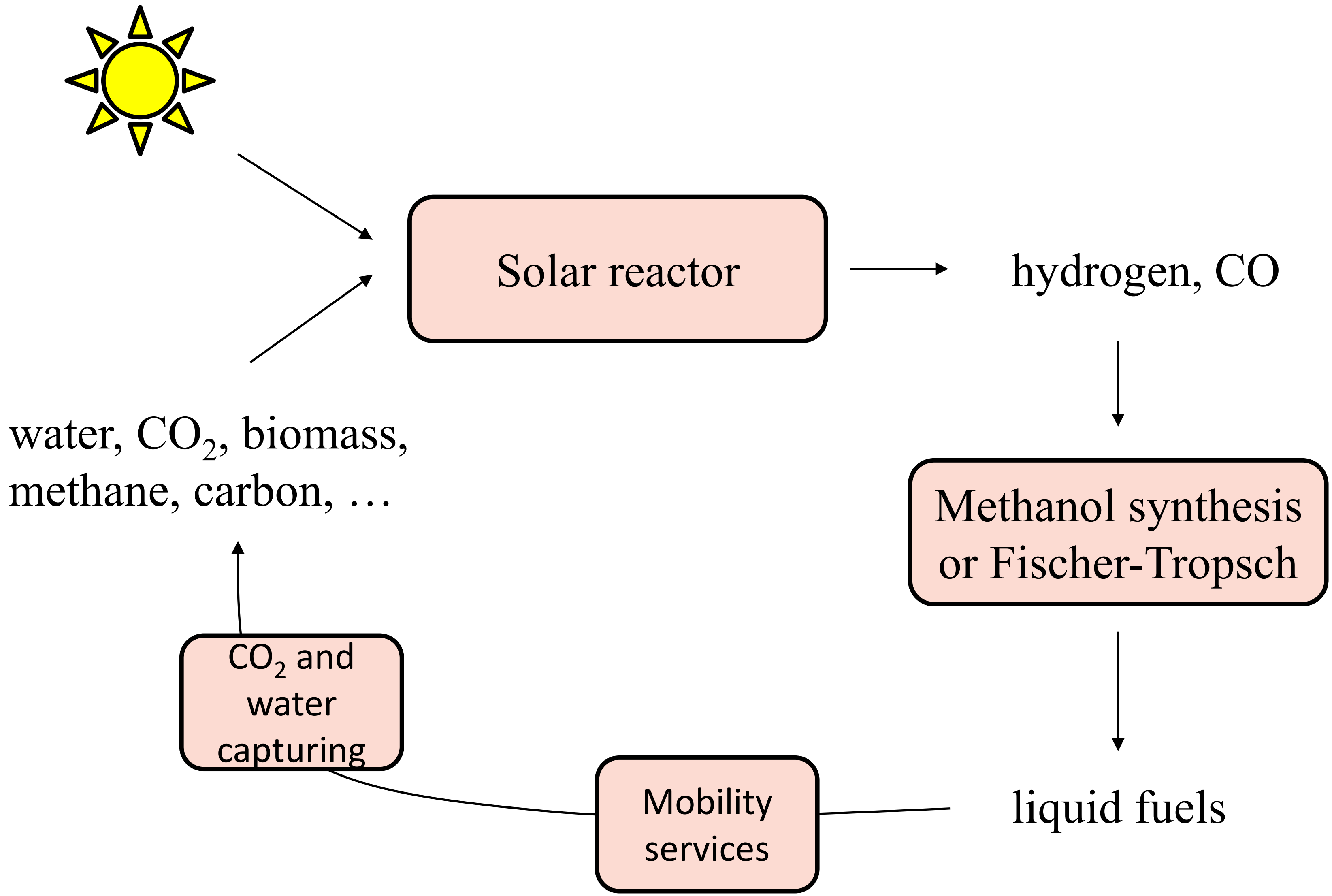
Scaling – ongoing @LRESE

Renewable Energy

- Outline:
  - Conversion pathways solar-to-fuel
  - Hybrid pathways
  - Solar thermochemistry
  - Photochemistry

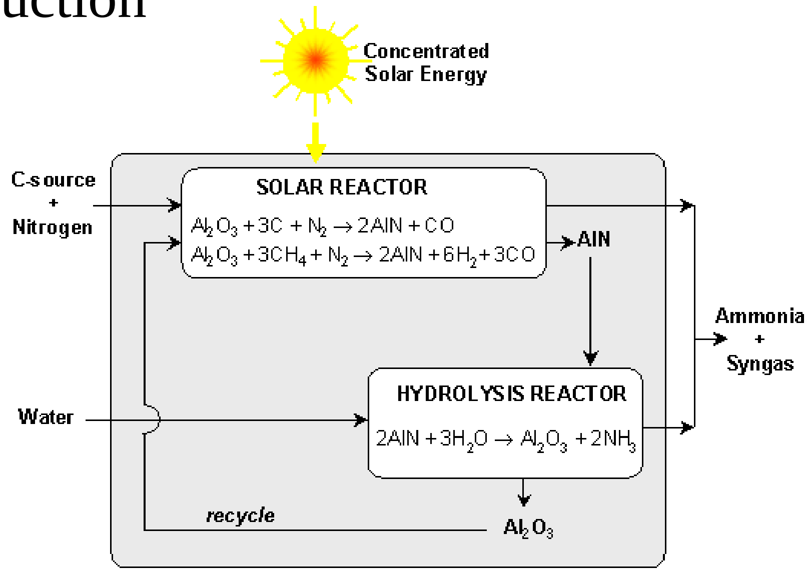
Sustainability issue

- Solar to fuels:



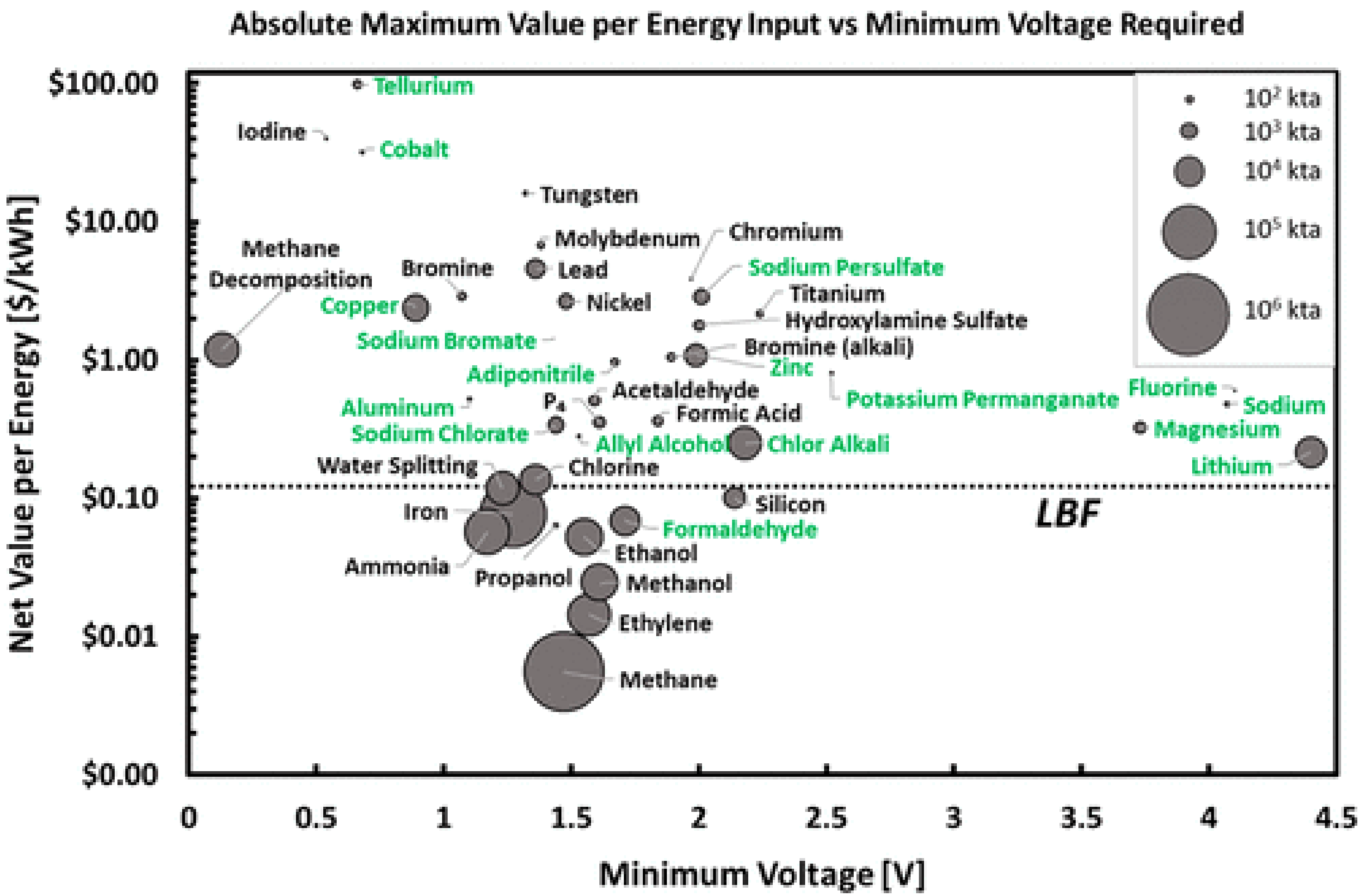
Solar materials

- Solar to materials:
  - In principle any other chemical reaction could be driven by solar thermochemistry or photoelectrochemistry if enthalpy of reaction matches solar irradiation, or equilibrium potential and band edge position matches solar irradiation and material combinations
  - E.g.:
    - Carbothermic reduction of alumina under near vacuum conditions
    - Ammonia production



Solar materials

- (Photo)electrochemical:



Maximum net value per energy input (log scale) plotted versus minimum voltage required for all electrochemical processes or electrochemical equivalents of thermochemical processes. For each point, the width of the circle corresponds to the relative market size. Processes highlighted in green are conducted electrochemically in industry, to any appreciable extent. The lower bound of feasibility (LBF) is plotted as the horizontal dashed line

Palmer et al., Technoeconomics of Commodity Chemical Production Using Sunlight, ACS Sustainable Chemistry & Engineering, 2018

Learning outcomes of todays lecture

- Solar fuels:
  - How can solar energy be converted into fuels?
  - What is a hybrid pathway?
  - Why using fossil fuels together with solar energy?
  - What is solar thermochemistry and how can it be used for solar fuel processing?
  - Why is solar water-splitting via multi-step water splitting cycles preferred compared to direct thermolysis?
  - What is photoelectrochemistry and how can it be used for solar fuel processing?
  - What other chemical commodities or materials can be processed using solar energy?

Solar energy conversion systems

- Literature
  - Review articles:
    - Meier et al., Solar thermochemical production of fuels, Advances in Science and Technology, vol. 74, pp. 303-312, 2010.
    - Lipinski et al., Review of heat transfer research for solar thermochemical applications, Journal of Thermal Science and Engineering Applications, 5: 021005, 2013.
    - Walter et al., Solar water splitting cells, Chemical Reviews, vol. 110, pp. 6446–6473, 2010.