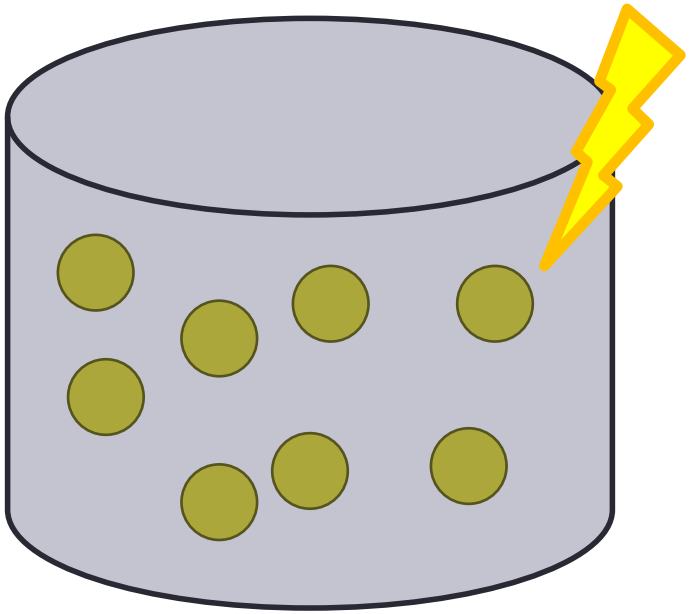
Electronic Supplementary Material (ESI) for Chemical Society Reviews.

Monolithic Cells for Solar Fuels

Jan Rongé, Tom Bosserez, David Martel,
Carlo Nervi, Luca Boarino, Francis Taulelle,
Gero Decher, Silvia Bordiga, Johan Martens

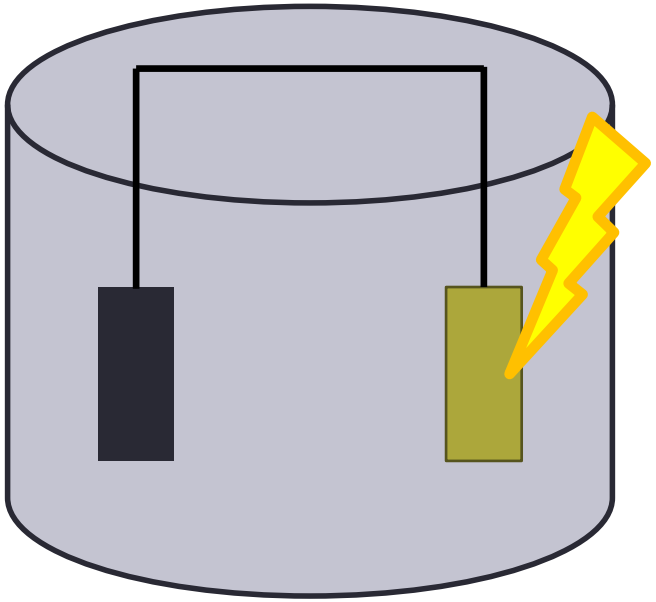
Solar fuel approaches

- *Photocatalytic*: suspended semiconductor nanoparticles



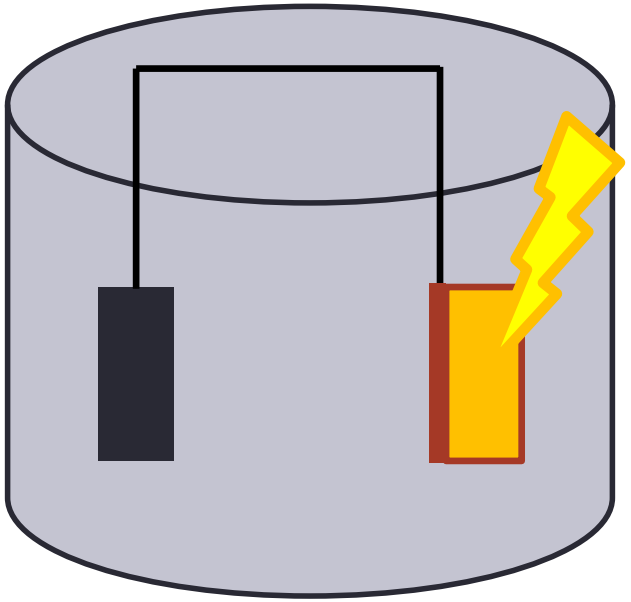
Solar fuel approaches

- *Photocatalytic*: suspended semiconductor nanoparticles
- *Photoelectrochemical*: semiconductor electrodes



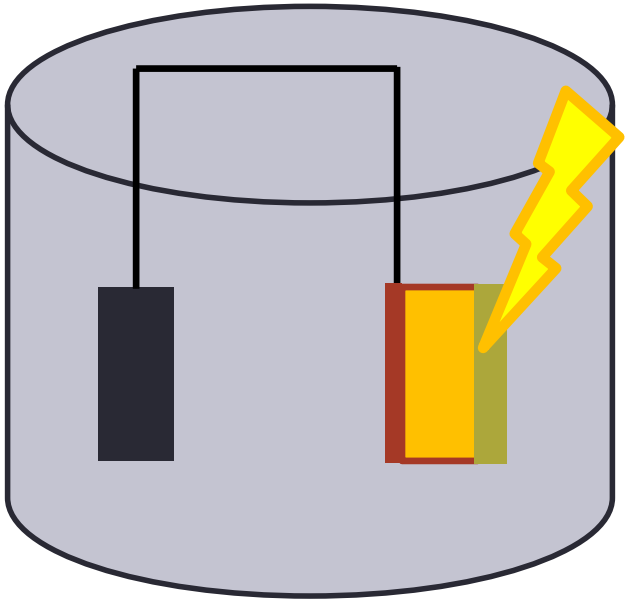
Solar fuel approaches

- *Photocatalytic*: suspended semiconductor nanoparticles
- *Photoelectrochemical*: semiconductor electrodes
- Internally biased by photovoltaics (PV)
  - *Buried PV*



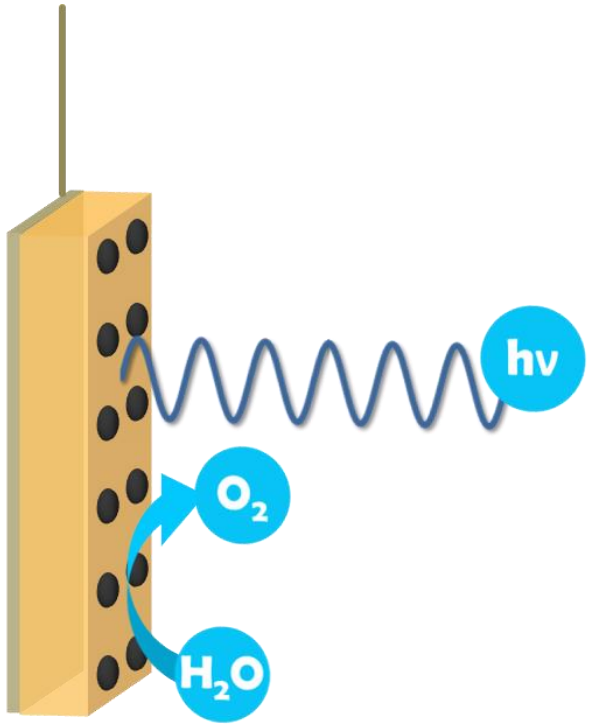
Solar fuel approaches

- *Photocatalytic*: suspended semiconductor nanoparticles
- *Photoelectrochemical*: semiconductor electrodes
- Internally biased by photovoltaics (PV)
  - *Buried PV*
  - *PV-PEC* (hybrid)



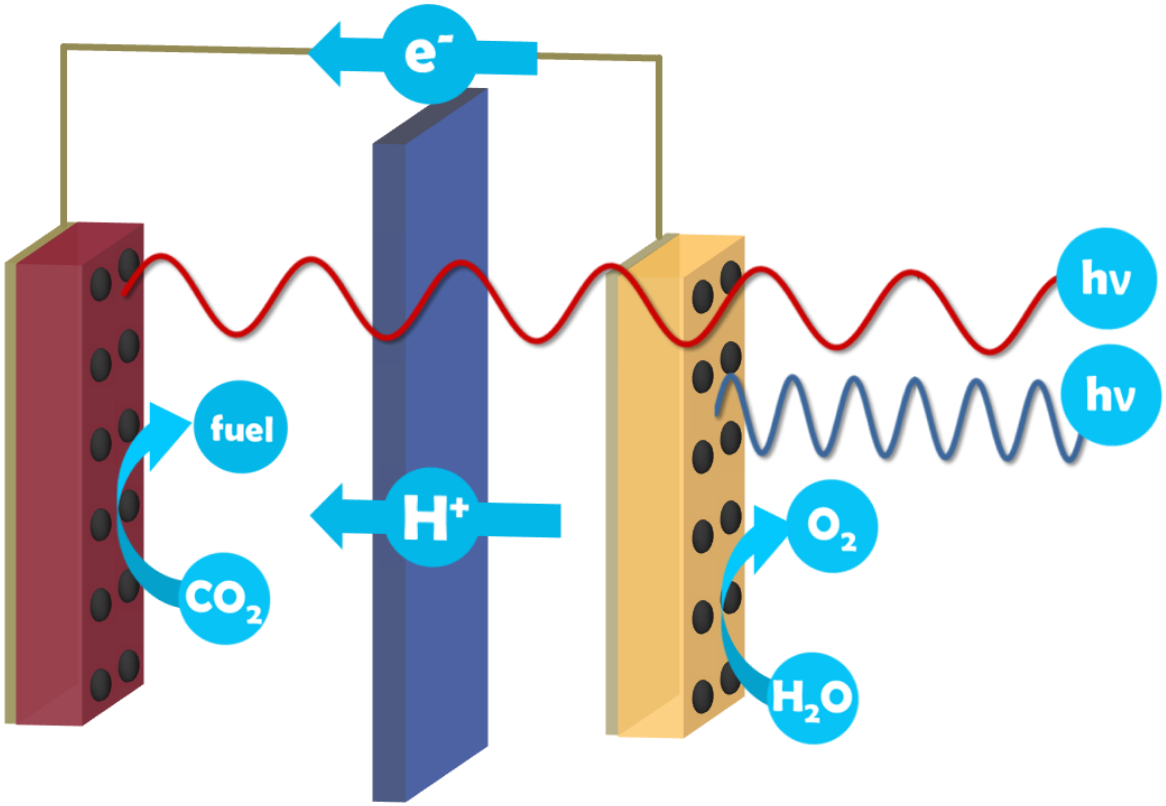
A photoelectrochemical cell

- *Photoelectrode*: a light-driven electrode that interacts with the electrolyte
  - Can be connected to a metal counter electrode or to a second photoelectrode
  - (Photo)anode: water oxidation electrode
  - (Photo)cathode: CO_2 reduction electrode



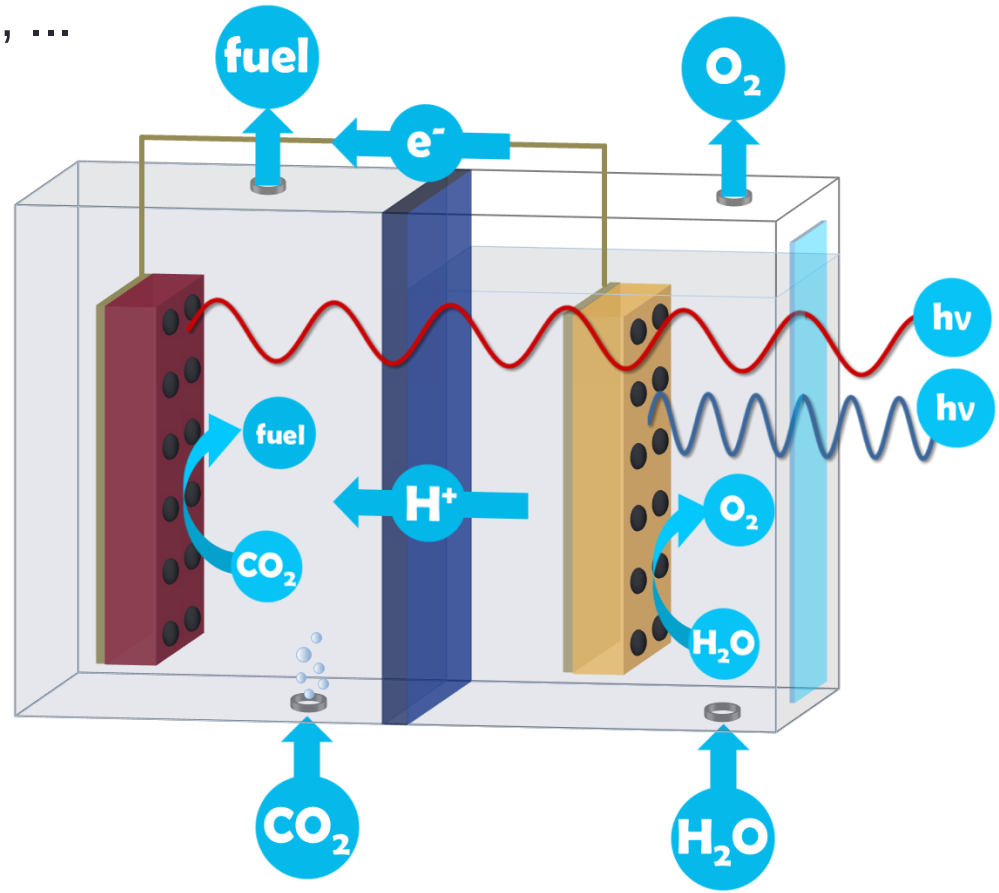
A photoelectrochemical cell

- Electrode assembly may contain:
  - (Photo)electrodes
  - Co-catalysts
  - Internal PV junctions
  - Membrane



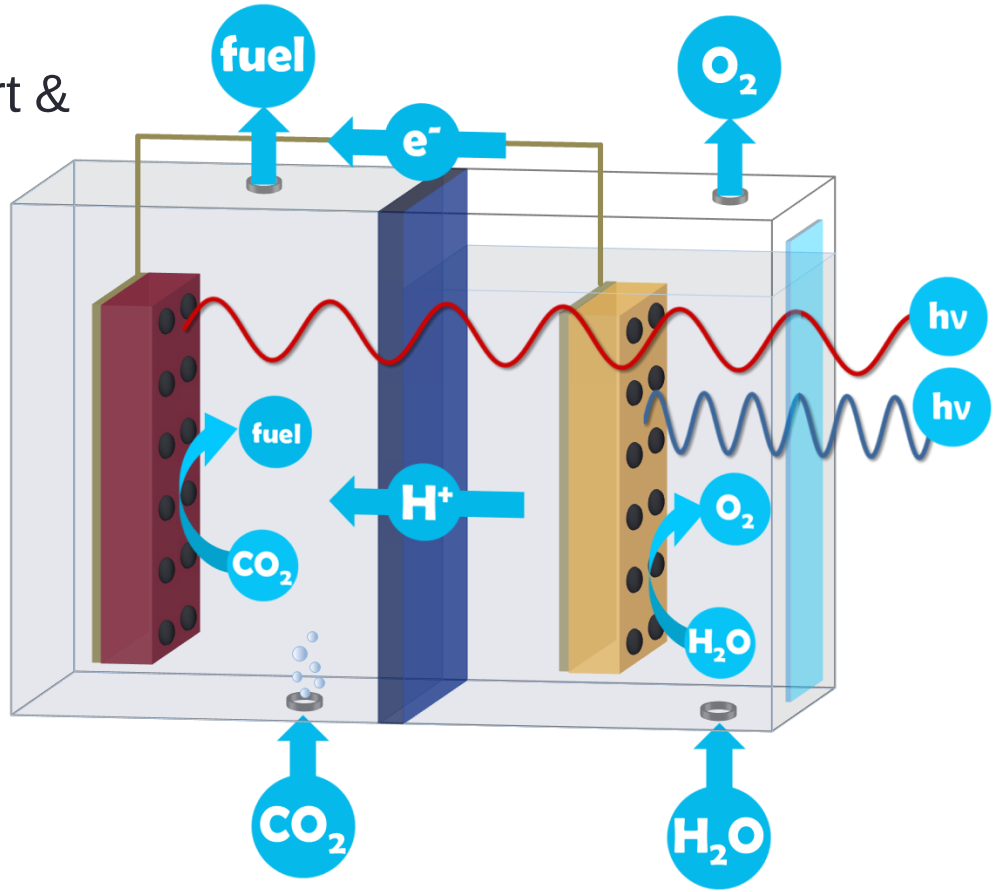
A photoelectrochemical cell

- PEC cell:
  - Electrode assembly
  - In- and outlets, reactor casing, ...
  - Electrolyte



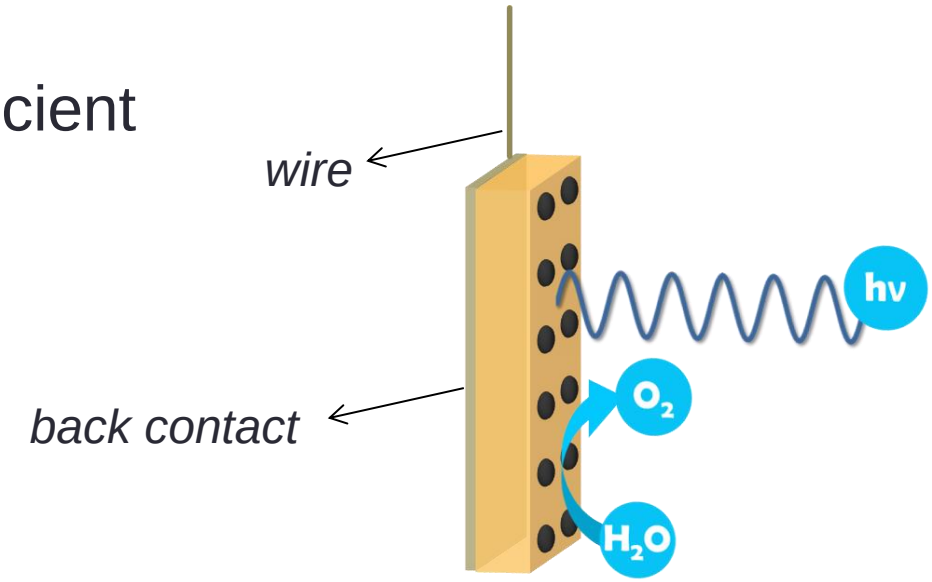
A photoelectrochemical cell

- Management of multiple species:
  - Electrons: electronic transport
  - Protons: ionic transport
  - Molecules: molecular transport & molecular barrier function
  - Photons: optical transparency



Electronic transport

- Every single active component of the PEC cell should be electrically connected!
  - Conducting substrates
  - Sufficiently high crystal quality of the semiconductor
  - Link semiconductor-catalyst
- Electrodes can be connected externally (through a wire) or internally (direct contact)
- Back contacts allow more efficient current collection



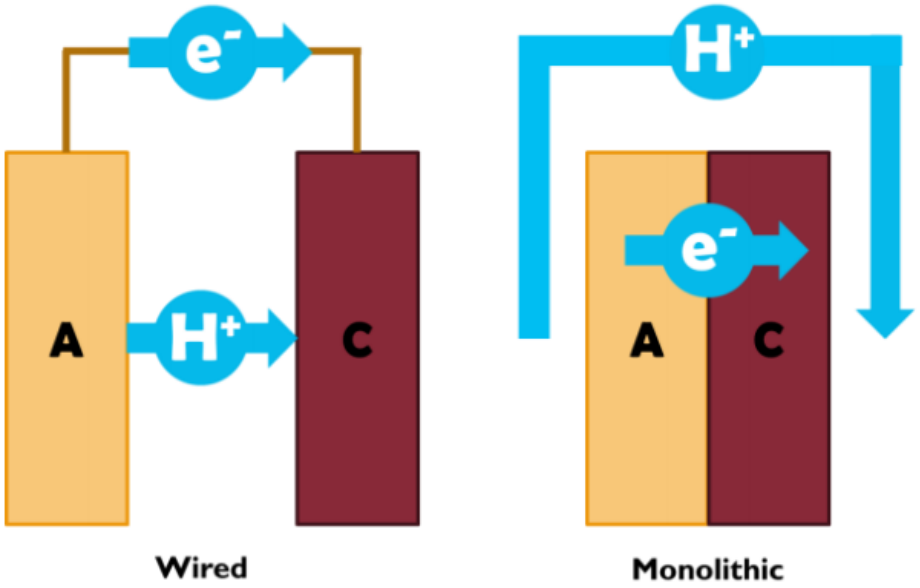
Ionic transport

- Negative or positive charges can be conveyed by hydroxide ions or protons, respectively
- Liquid electrolytes
  - High $[H^+]$ or $[OH^-]$ ➔ high conductivity
    ➔ high corrosivity!
- Redox mediator: e.g. IO_3^-/I^- as an electron shuttle
- Solid electrolytes: fixed counter-ions, no liquid electrolyte needed
  - No concentration gradients
  - No danger of leaks
  - Gas phase reactions possible

Ionic transport

- The ionic conductivity of the electrolyte is often lower than the electronic conductivity of back contacts, wires etc.

➔The ionic pathway should be kept as short as possible



$HCOO^-$	η = 0.14 %	η = 0.08 %	*Energy Environ. Sci.* **6,** 1274 (2013)
H_2	η = 4.7 %	η = 2.5 %	*Science* **334,** 645 (2011)

Molecular transport

- CO_2 supply can be limiting, depending on the reaction medium
  - Liquid water: low CO_2 solubility
  - Organic solvents: up to 8 times higher CO_2 solubility
  - Gas phase: pure CO_2 stream possible
    - Water supply may become limiting
    - Proton conductivity can be an issue
  - Supercritical CO_2 phase: very high CO_2 concentrations
    - The best results have been obtained in biphasic media (liquid / supercritical)
- Product evacuation can be problematic
  - Gaseous products in liquid medium: bubble formation
  - Liquid products in gaseous medium: electrode flooding

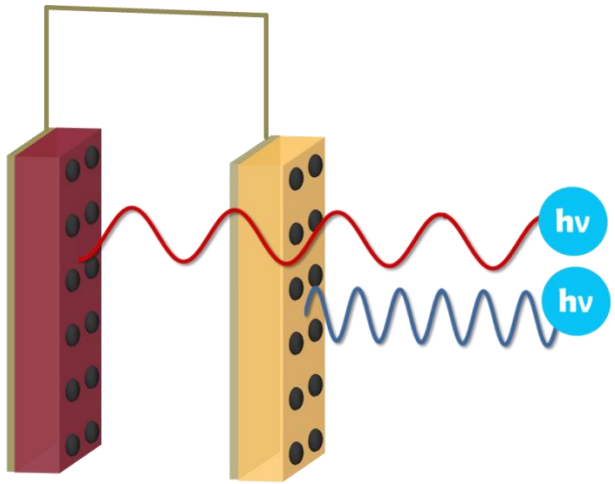
Molecular transport

- Product cross-over reduces yields in absence of a molecular barrier
  - Liquid products in liquid media will readily cross-over
  - Gaseous products with low solubility in the reaction medium reduce cross-over
- A molecular barrier impedes product cross-over
  - However, cross-over is never completely avoided
  - A molecular barrier also introduces additional ionic resistance

  ➔ trade-off between molecular barrier function / ionic conductivity

Transparency

- All materials located in the light path should be transparent
  - Window should transmit UV and visible light
  - Minimal light absorption by *e.g.* co-catalysts on the surface
- Nanostructures increase internal scattering ➔ less specular reflection and more light absorption
- When two semiconductors are used, the one absorbing long wavelengths should be at the bottom



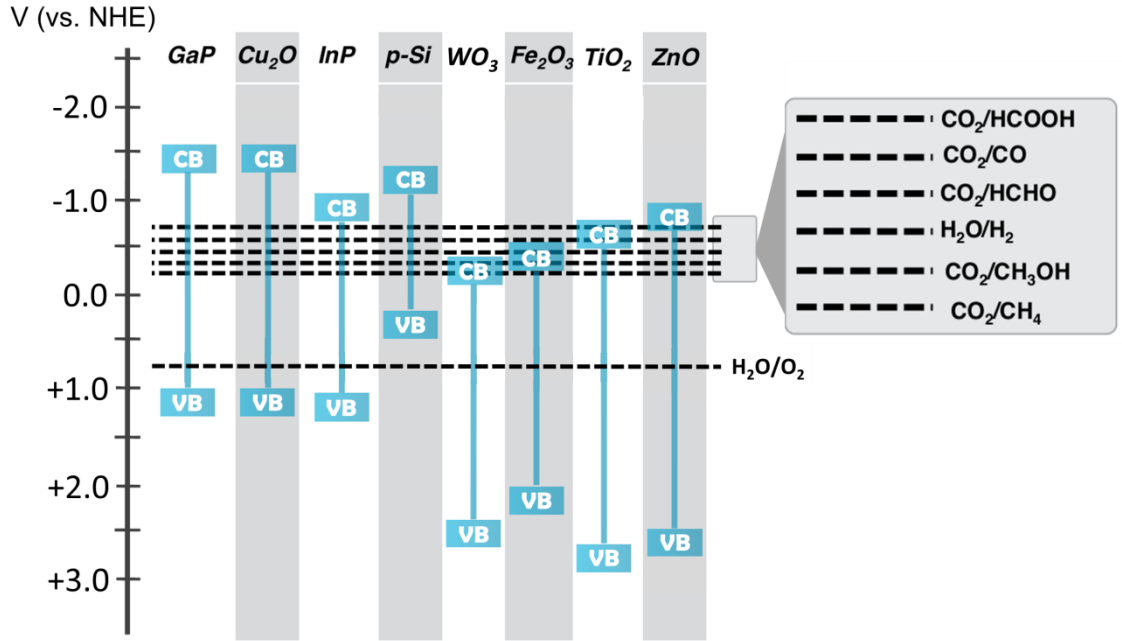
Oxidation and reduction reactions

- Electrons require a certain electrochemical potential for transfer to other species in reduction-oxidation reactions
- In addition, an *overpotential* is needed to compensate for kinetic and transport losses

$2\ H_2O \rightarrow O_2 + 4\ e^- + 4\ H^+$	$E^0 = +0.82$ V	(1)
$CO_2 + 2\ H^+ + 2\ e^- \rightarrow CO + H_2O$	$E^0 = -0.53$ V	(2)
$CO_2 + 2\ H^+ + 2\ e^- \rightarrow HCOOH$	$E^0 = -0.61$ V	(3)
$CO_2 + 4\ H^+ + 4\ e^- \rightarrow H_2CO + H_2O$	$E^0 = -0.48$ V	(4)
$CO_2 + 6\ H^+ + 6\ e^- \rightarrow CH_3OH + H_2O$	$E^0 = -0.38$ V	(5)
$CO_2 + 8\ H^+ + 8\ e^- \rightarrow CH_4 + 2\ H_2O$	$E^0 = -0.24$ V	(6)
$CO_2 + e^- \rightarrow CO_2^{\bullet -}$	$E^0 = -1.90$ V	(7)
$2\ H^+ + 2\ e^- \rightarrow H_2$	$E^0 = -0.41$ V	(8)

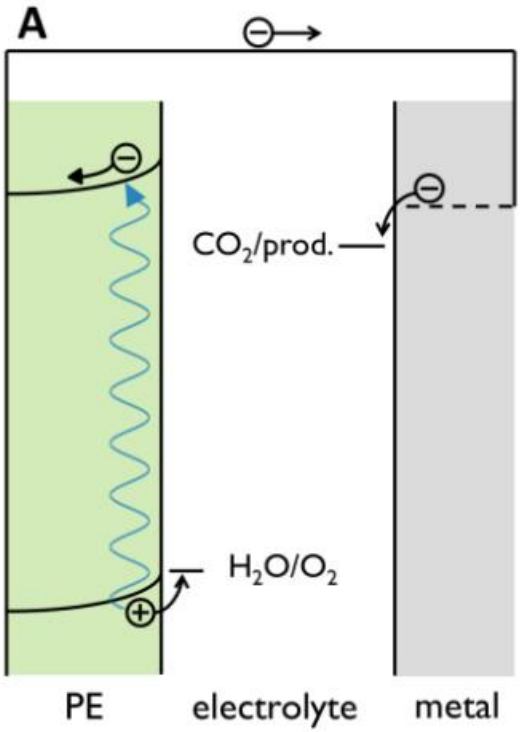
Oxidizing and reducing potential of a semiconductor

- The electrochemical potential is delivered by the semiconductor
- Conduction band electrons should be sufficiently negative, valence band holes should be sufficiently positive
- Large band gap = shorter wavelengths!



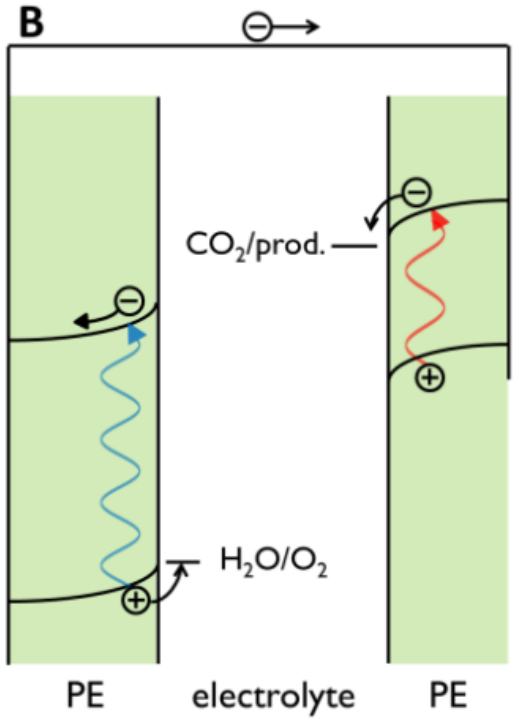
Photosystems

- Single photosystem
  - Only one photon provides the driving force for both half-reactions
  - Wide band gap materials are required
  - The solar spectrum is not optimally utilized



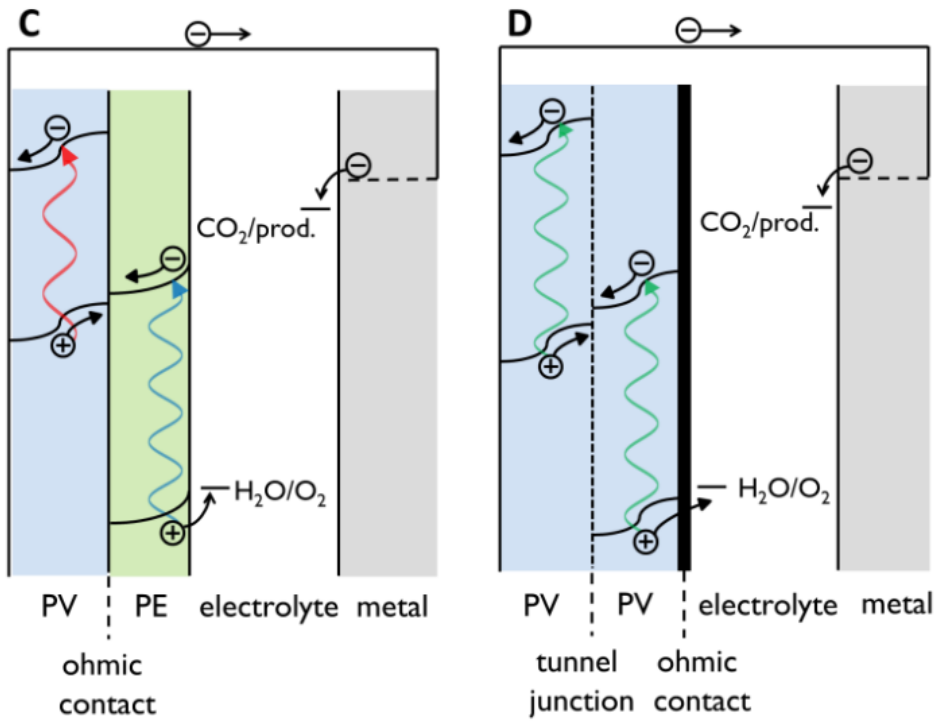
Photosystems

- Tandem photosystems
  - Two, longer wavelength photons provide the driving force
  - Smaller band gap materials can be used
  - Mimic of natural photosynthesis (‘Z-scheme’)



Photosystems

- Integrated PV photosystem
  - An internal PV junction provides (additional) bias
  - The PV junction is shielded (‘buried’) from its environment
  - The PV can be combined with a semiconductor photoelectrode: *PV-PEC*
  - The PV can be used as the sole photoactive element: *Buried PV*
  - Higher efficiency, but higher material cost



Semiconductor – co-catalyst assemblies

- Co-catalysts are often added to the semiconductor surface to enhance reaction rates by lowering the overall overpotential
- Semiconductors and co-catalysts are the workhorses that transform solar energy into chemical products, in three steps:
  1. Light absorption
  2. Charge separation and charge carrier transport
  3. Electrocatalysis

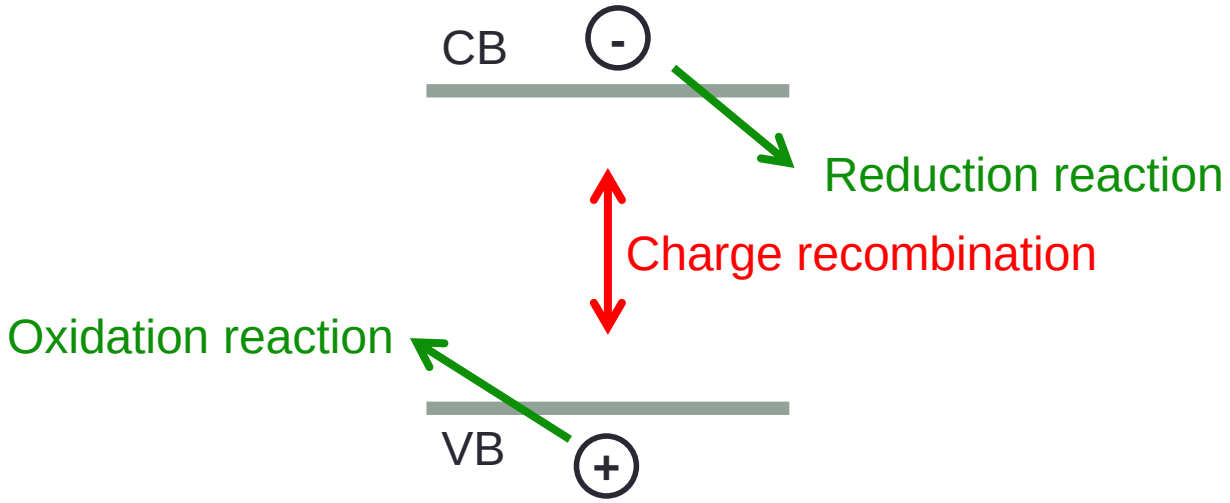
Light absorption

- Determined by thermodynamics
  - Band gap energy of the semiconductor
  - Wavelength of the photon
- Determined by the semiconductor absorption coefficient α
- Influenced by optical effects
  - (Internal) scattering
  - Specular reflection

➔See previous slides

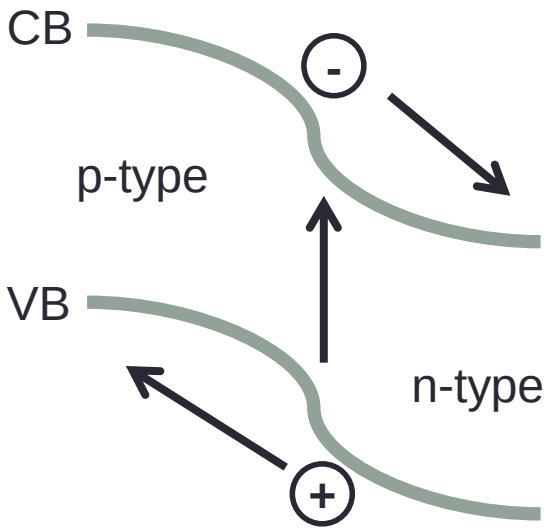
Charge separation and transport

- Charge carrier recombination (~ps-µs) is faster than interfacial reactions (~ms)
  - Recombination is avoided by increasing charge carrier lifetime
  - Charge carrier lifetime is increased by efficient charge separation
  - This can be achieved by an electric field in the semiconductor and nanostructuring of materials

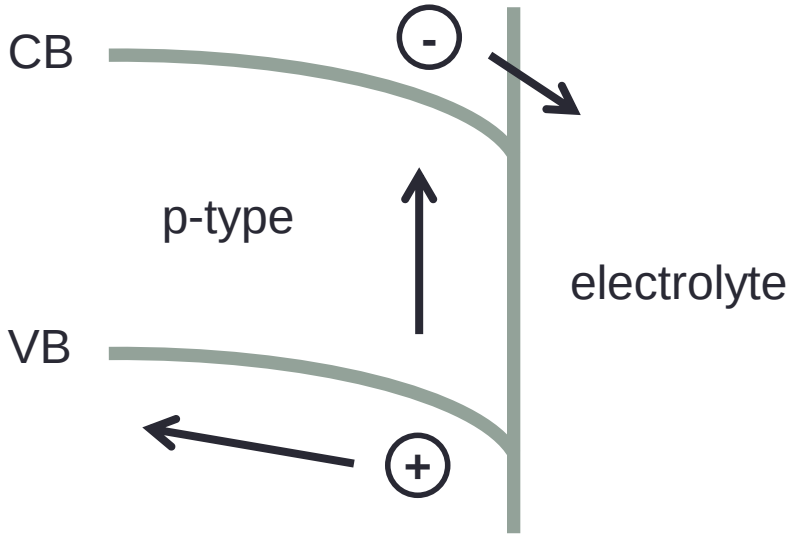


Charge separation and transport

- Electric fields in semiconductors are created by junctions
  - Solid state junction: typical for PV devices
  - Semiconductor-liquid junction: in PEC cells
  - Electric fields have also been induced by surface adsorbates



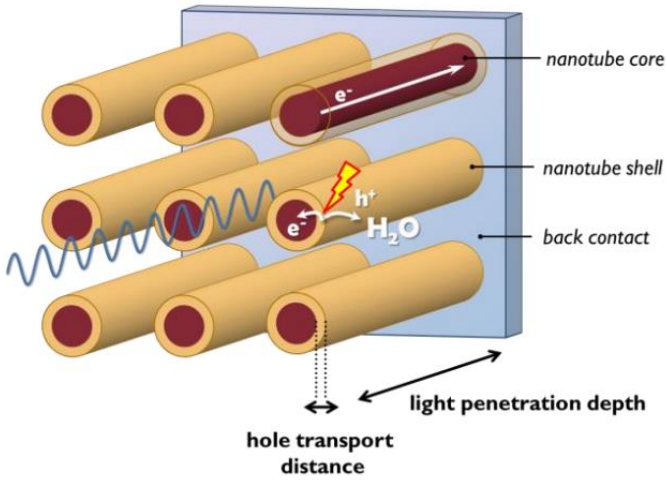
PV junction



Semiconductor-liquid junction

Charge separation and transport

- Charge carrier diffusion length: distance a carrier can travel before it recombines
  - Nanostructuring increases surface area but decreases the distance carriers have to travel to reach the semiconductor surface
  - 1D-nanostructures allow sufficient light absorption without long carrier travel distances
  - Semiconductor doping may increase carrier diffusion length
  - Host-guest structures combine a light absorber (guest) with a host material for charge carrier collection



Electrocatalysis

- Co-catalysts are required to activate the CO_2 molecule
  - Activation generally is achieved by breaking the linear symmetry of the molecule and forming C-H bonds
- 4 parameters are often used to quantify performance:

$$\text{Catalyst Selectivity (CS)} = \frac{\text{moles of carbon atoms in intended reaction products}}{\text{moles of carbon in all reaction products formed}}$$

$$\text{Turnover Number (TON)} = \frac{\text{moles of intended reaction product formed}}{\text{moles of catalytic sites}}$$

$$\text{Turnover Frequency (TOF)} = \frac{\text{TON}}{\text{reaction time}}$$

$$\text{Faradaic Efficiency (FE)} = \frac{\text{moles of electrons consumed in reaction product formation}}{\text{total moles of electrons transferred from anode to cathode}}$$

Electrocatalysis

- Metals: *e.g.* Cu, Au, Ag, Pd, Rh, Ru, Fe, Pb, Ni
  - Long-chain products
  - Mostly low selectrivity
  - Pt is less suitable: it favours H_2 formation
- Organic: *e.g.* pyridine, tetraalkylammonium salts
  - Abundant, low-cost
  - High selectivity
- Metal-organic: *e.g.* Ni(cyclam), $Re(bpy)(CO)_3X$
  - High selectivity
  - Mostly only 2-electron reductions possible
  - Often low stability, low TOF

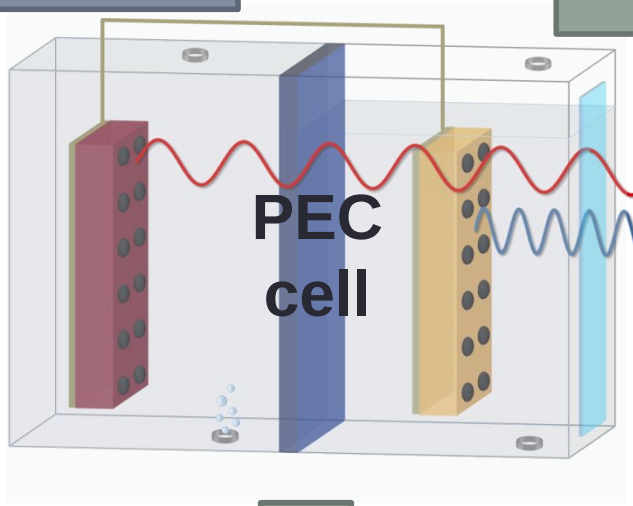
Stability

- PEC cells may suffer from illumination, high or low pH, highly oxidative and reductive electric potentials
- Semiconductor photocorrosion
  - Silicon, sulphides, phosphides: oxidized by valence band holes
  - Oxides: reduced by conduction band electrons
  - Can be prevented by protective coatings or rapid charge carrier extraction
- Co-catalyst corrosion
  - Catalysts change between multiple oxidation states, which alters their ligand environment
  - Some catalysts self-assemble and self-heal, to cope with this intrinsic difficulty

Overview

MATERIALS
- Reactor
- Semiconductors
- Co-catalysts
- Solid electrolyte
- Coatings, interconnects, ...

OPERATING PARAMETERS
- Temperature, pressure
- Electrolyte: composition, pH, physical state
- Flow rates
- Irradiation: intensity, wavelengths



OUTPUT

INPUT

CHARACTERISATION
- Products

IN-SITU CHARACTERISATION
- Photocurrent / -potential
- Intermediates
- Holes, electrons