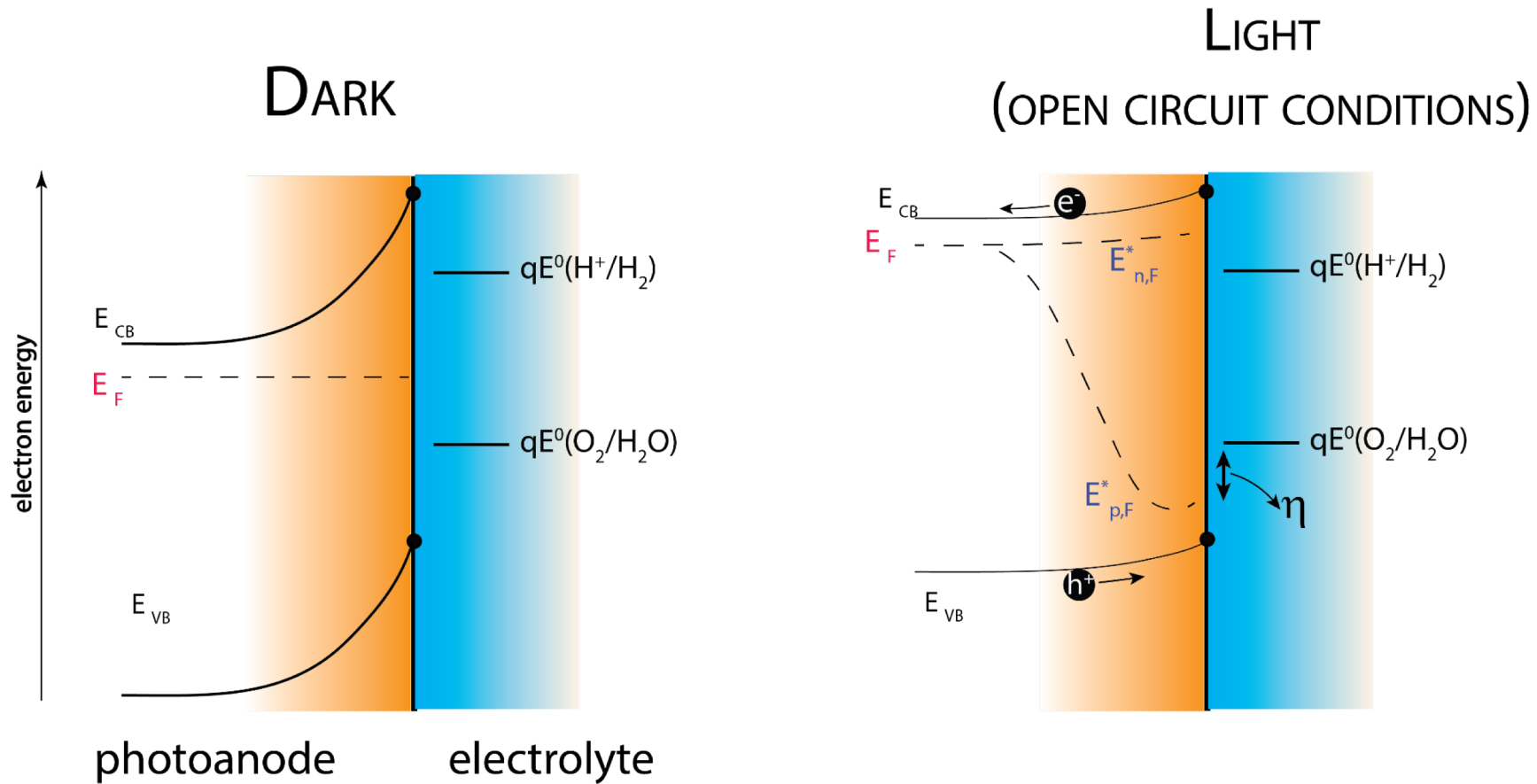


Energy Conversion by Semiconductor Devices

Jun-Ho YUM

junho.yum@epfl.ch



$$E_{n,F}^* = E_F + k_B T \ln \left(\frac{n + \Delta n^*}{n} \right)$$

$$E_{p,F}^* = E_F + k_B T \ln \left(\frac{p + \Delta p^*}{p} \right)$$

If n-type semiconductor

$$n \gg p$$

$$n \gg \Delta n^*$$

$$p = \Delta p^*$$

$$E_{n,F}^* \sim E_F$$

$$E_{p,F}^*$$

Photo-induced carrier concentration

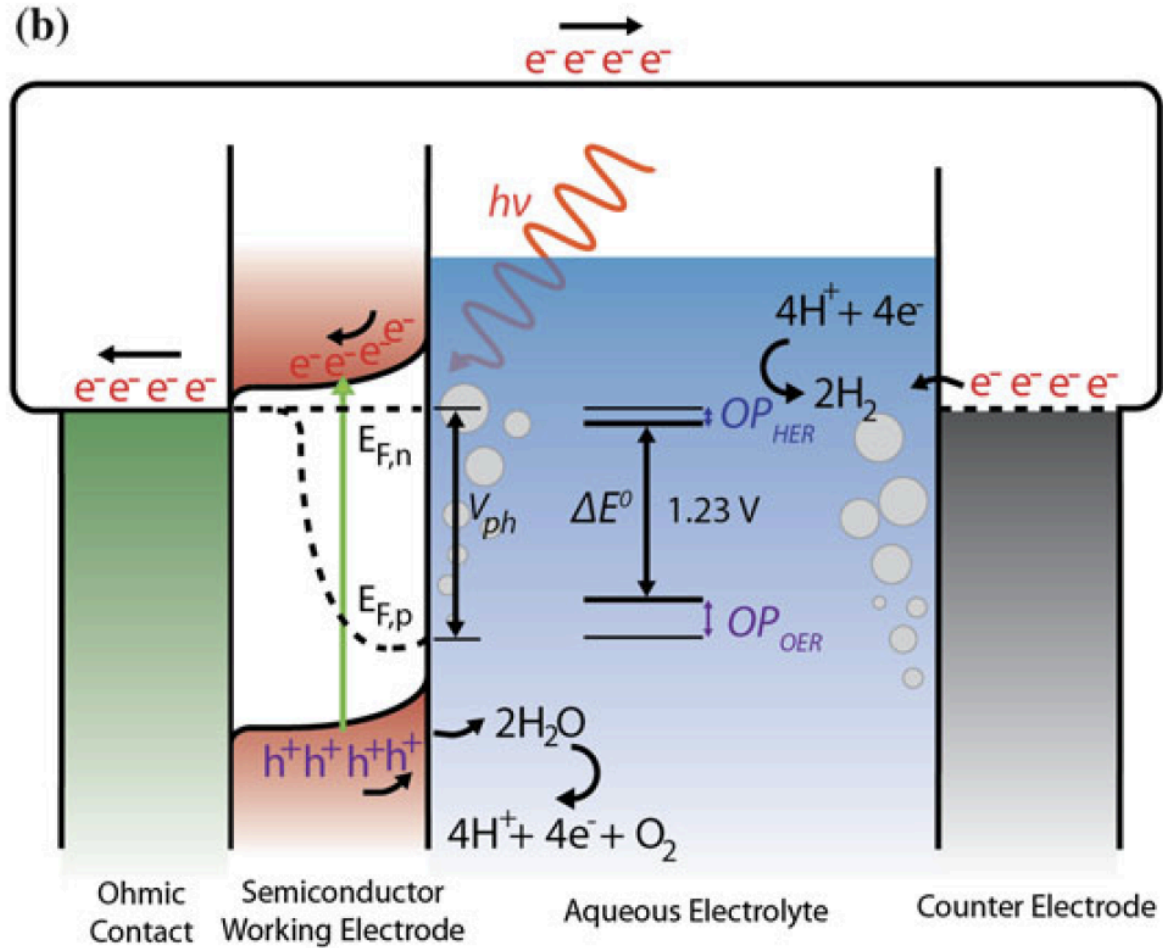
$$n^* = n + \Delta n^*$$

$$p^* = p + \Delta p^*$$

dark

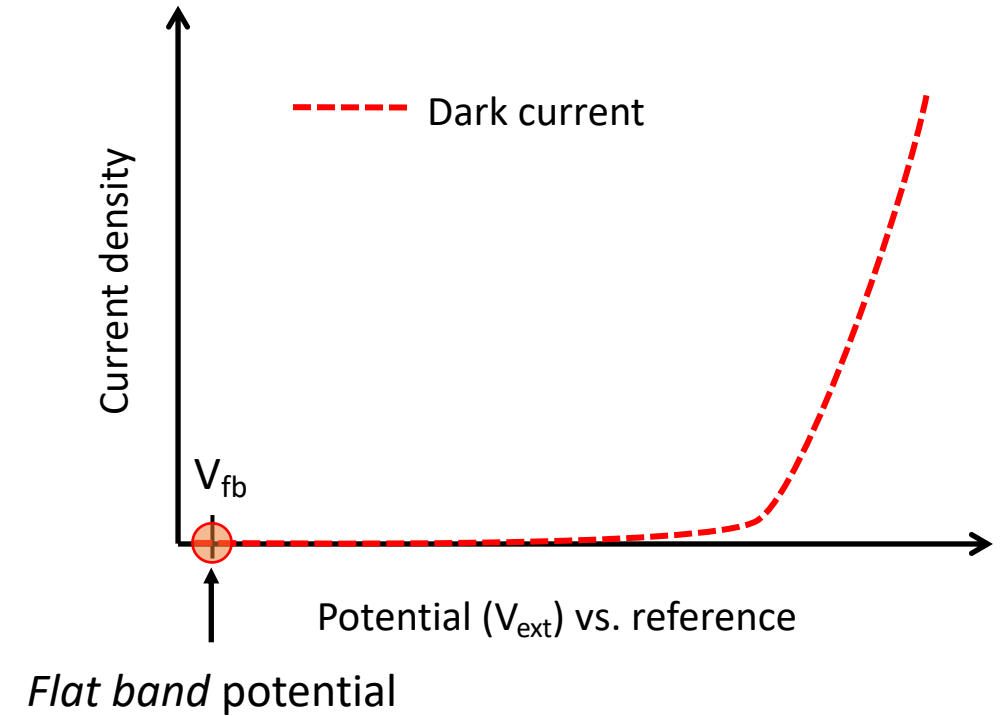
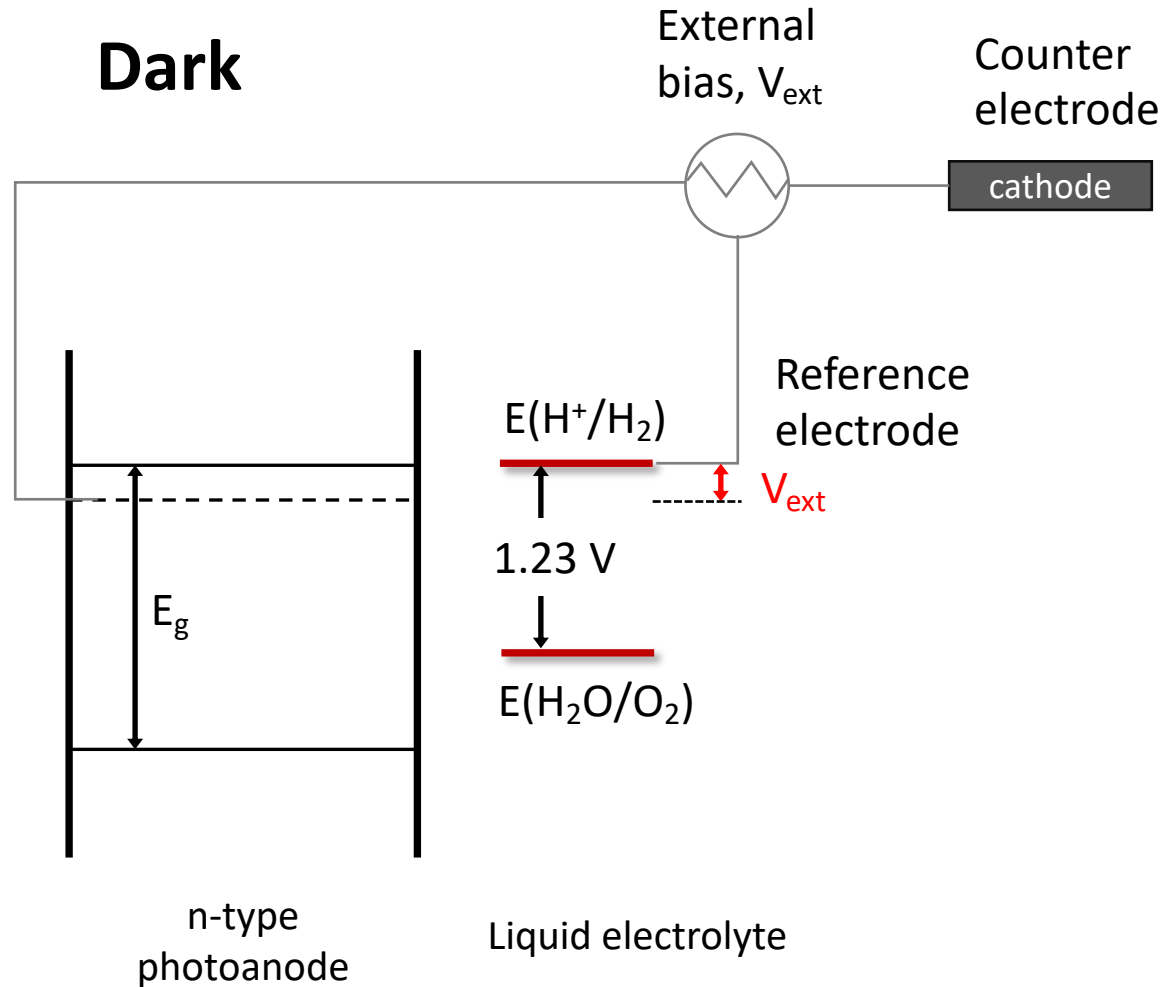
Increase by light

EPFL Thermodynamic Energy to Split Water



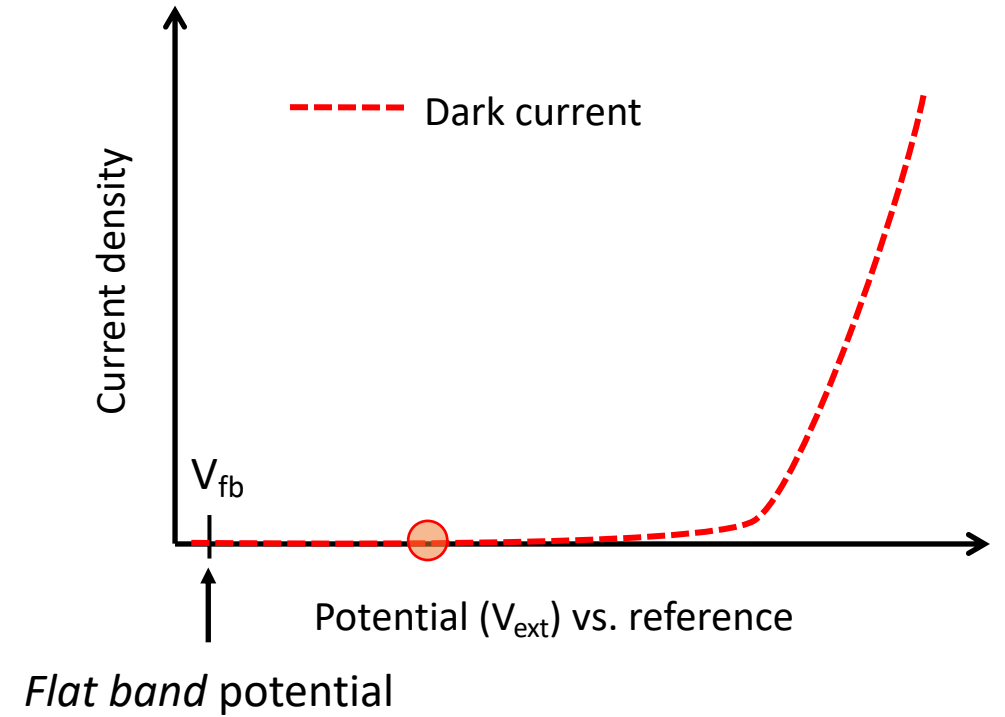
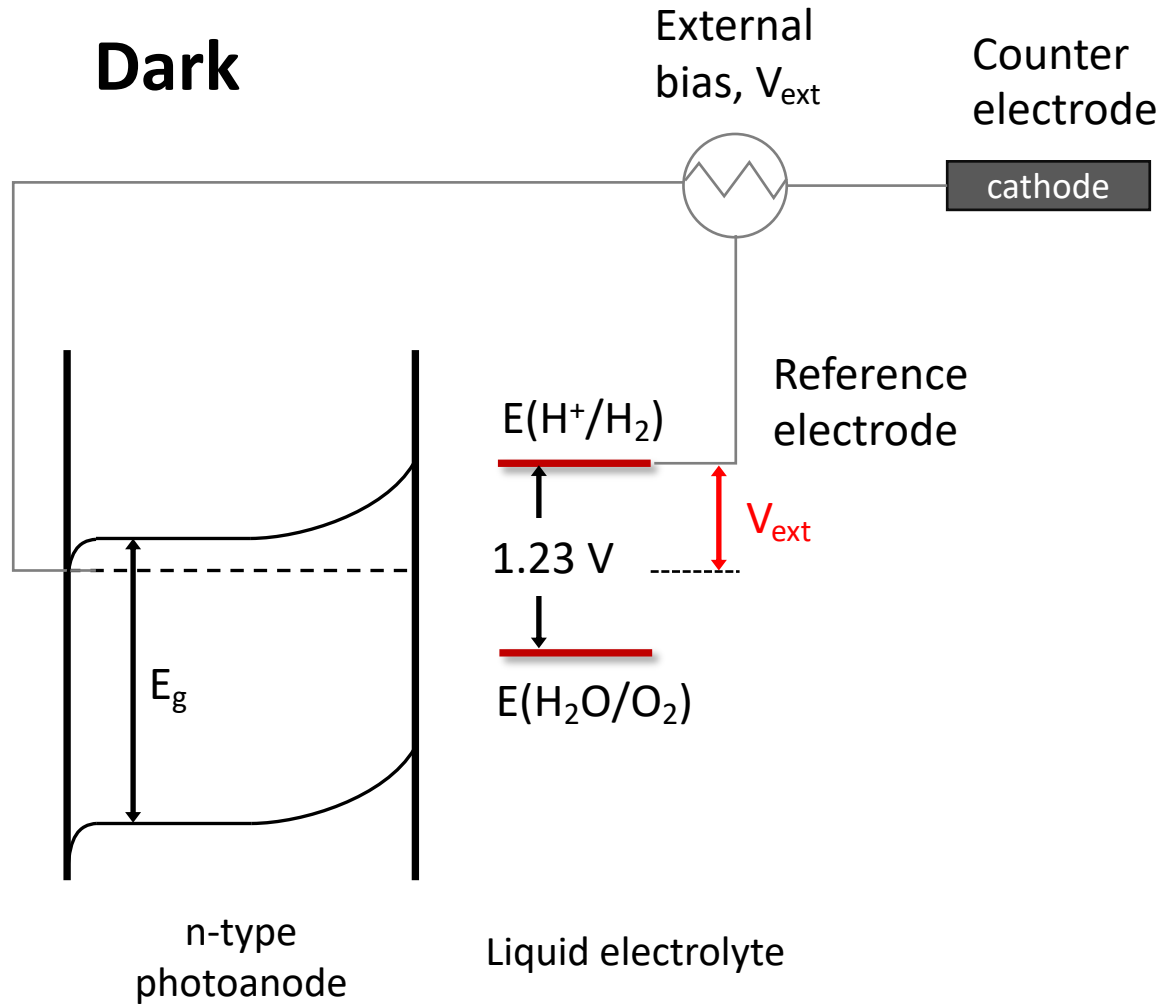
- The photovoltage in the semiconductor is **the potential difference between the quasi-Fermi levels of electrons ($E_{F,n}$) and holes ($E_{F,p}$) under illumination.**
- $V_{ph} < E_g$ of the SC due to losses (arising from factors such as radiative recombination, incomplete light trapping, and non-radiative recombination).
- In addition to the thermodynamic requirement, there are **overpotentials associated with driving the kinetics of the HER and OER** at the solid–liquid interface.

EPFL Metrics in Photoelectrode Development



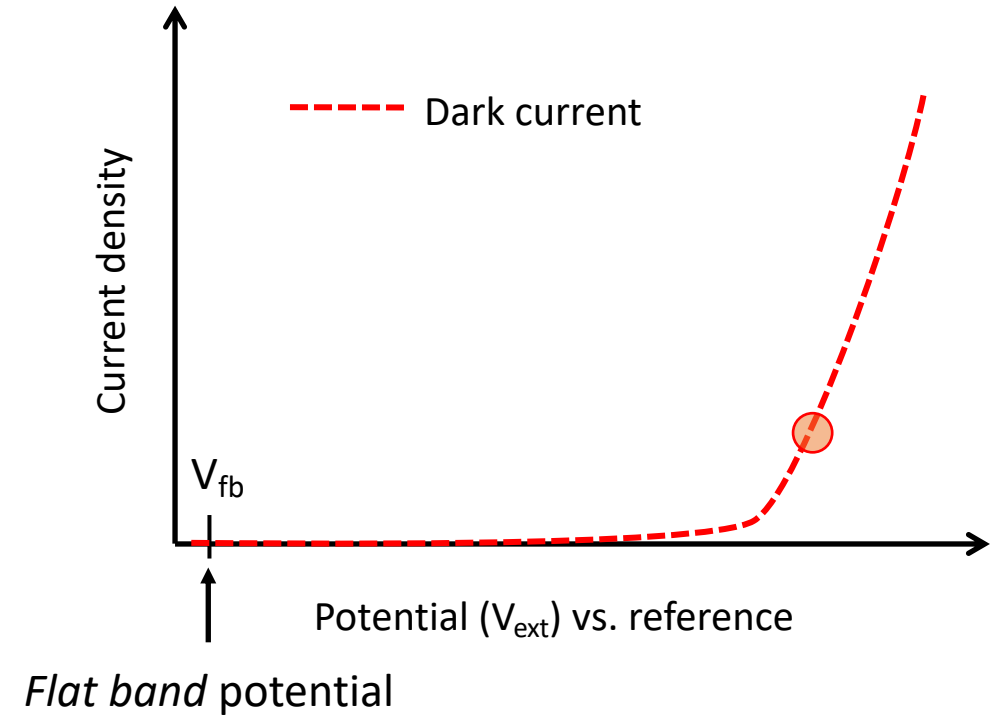
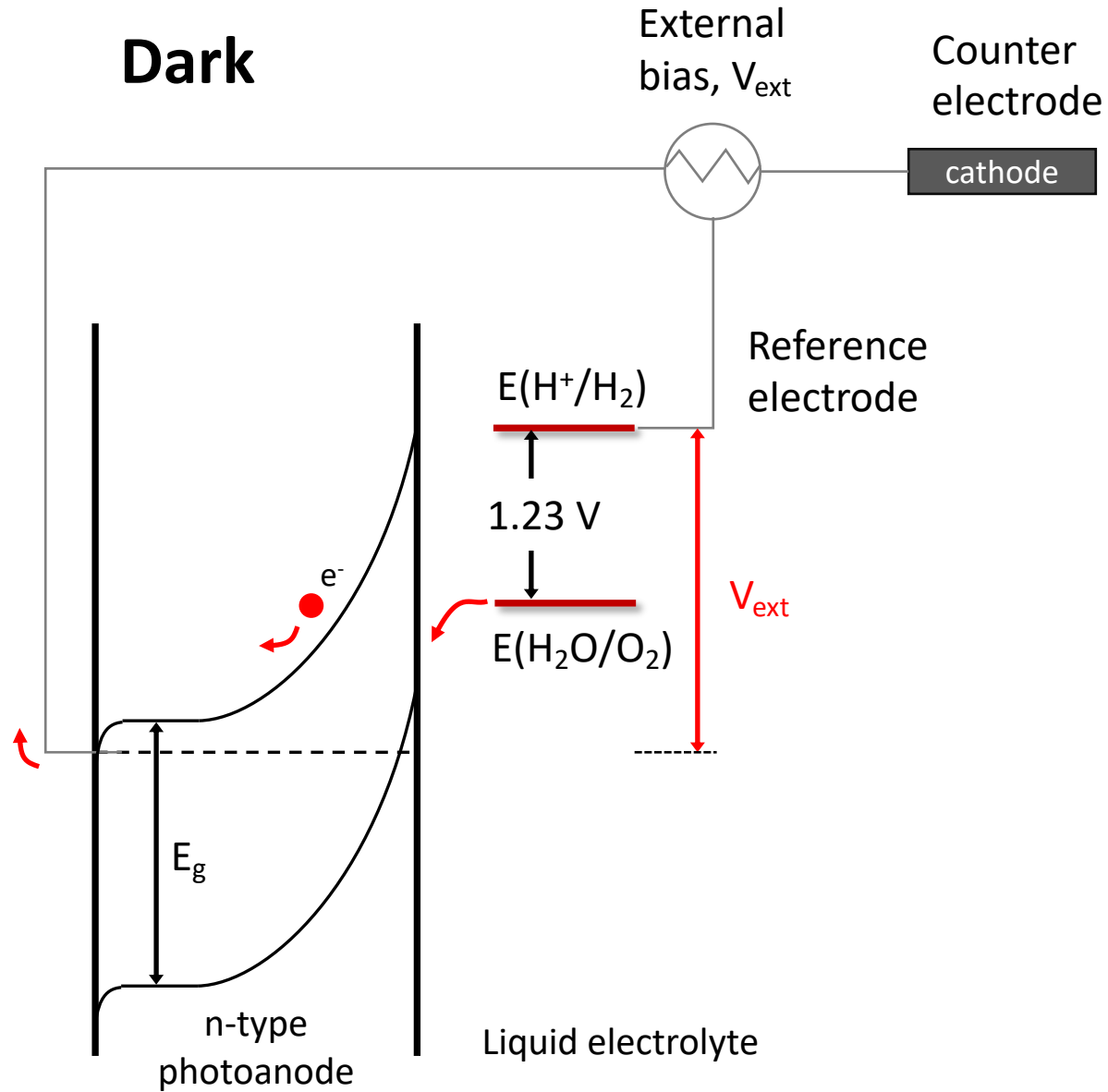
Dark current before onset should be small, indicating no irreversible processes

EPFL Metrics in Photoelectrode Development



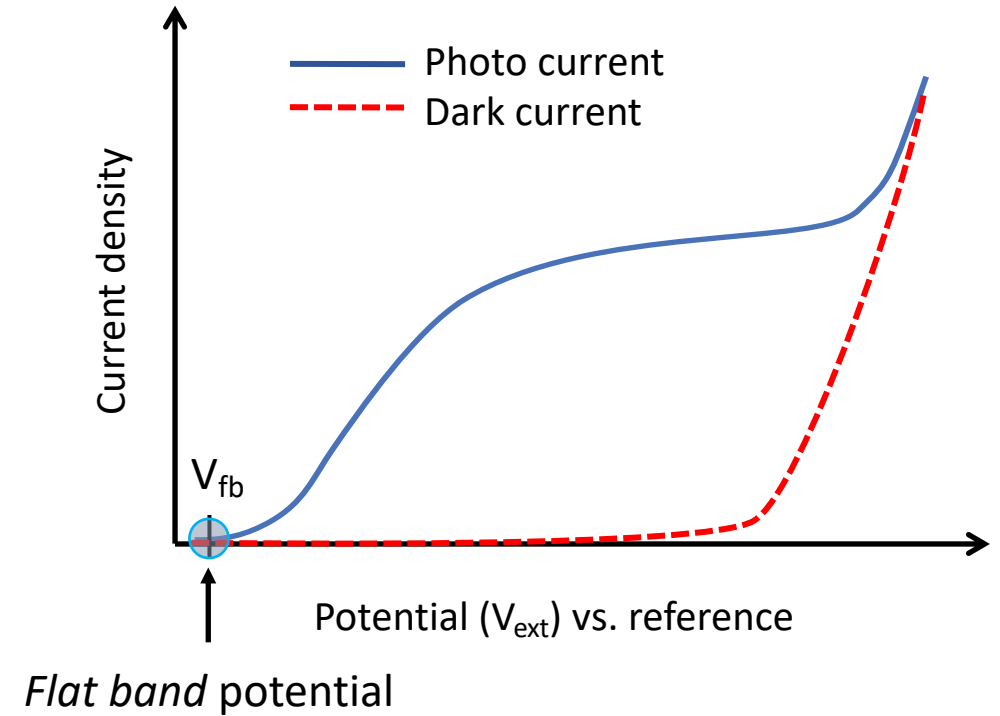
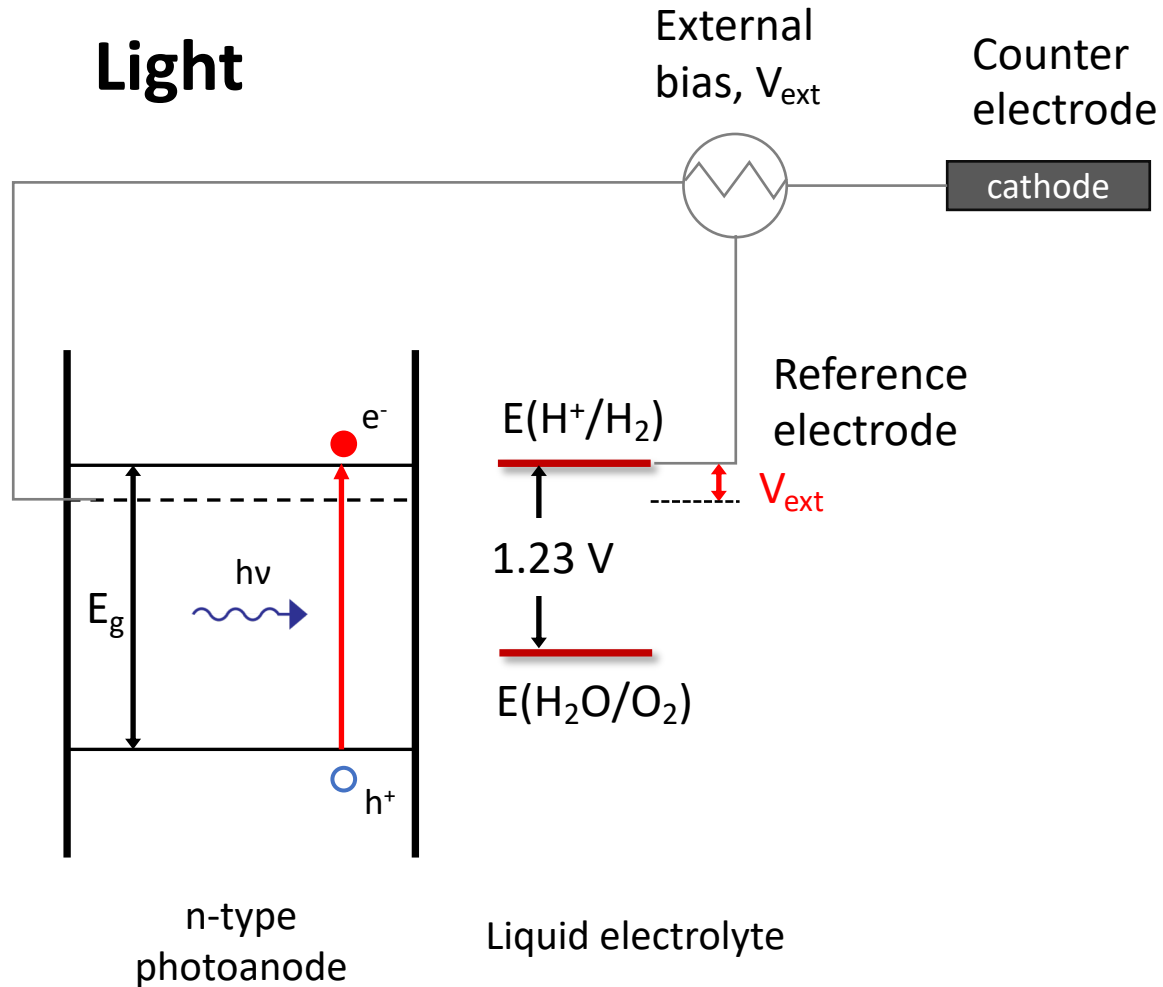
Dark current before onset should be small, indicating no irreversible processes

EPFL Metrics in Photoelectrode Development



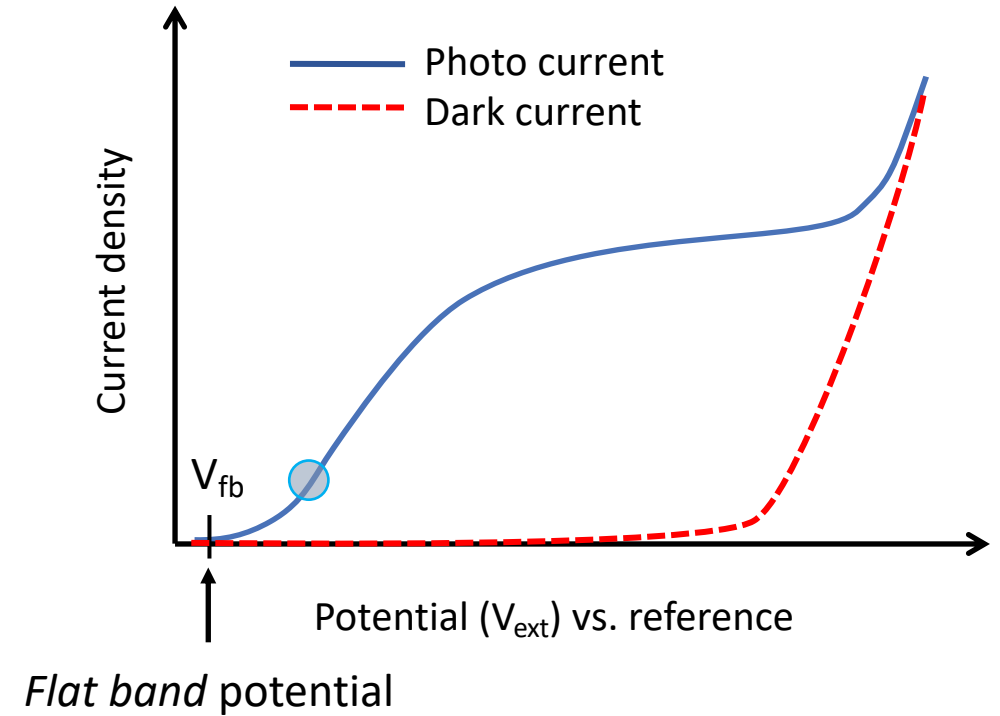
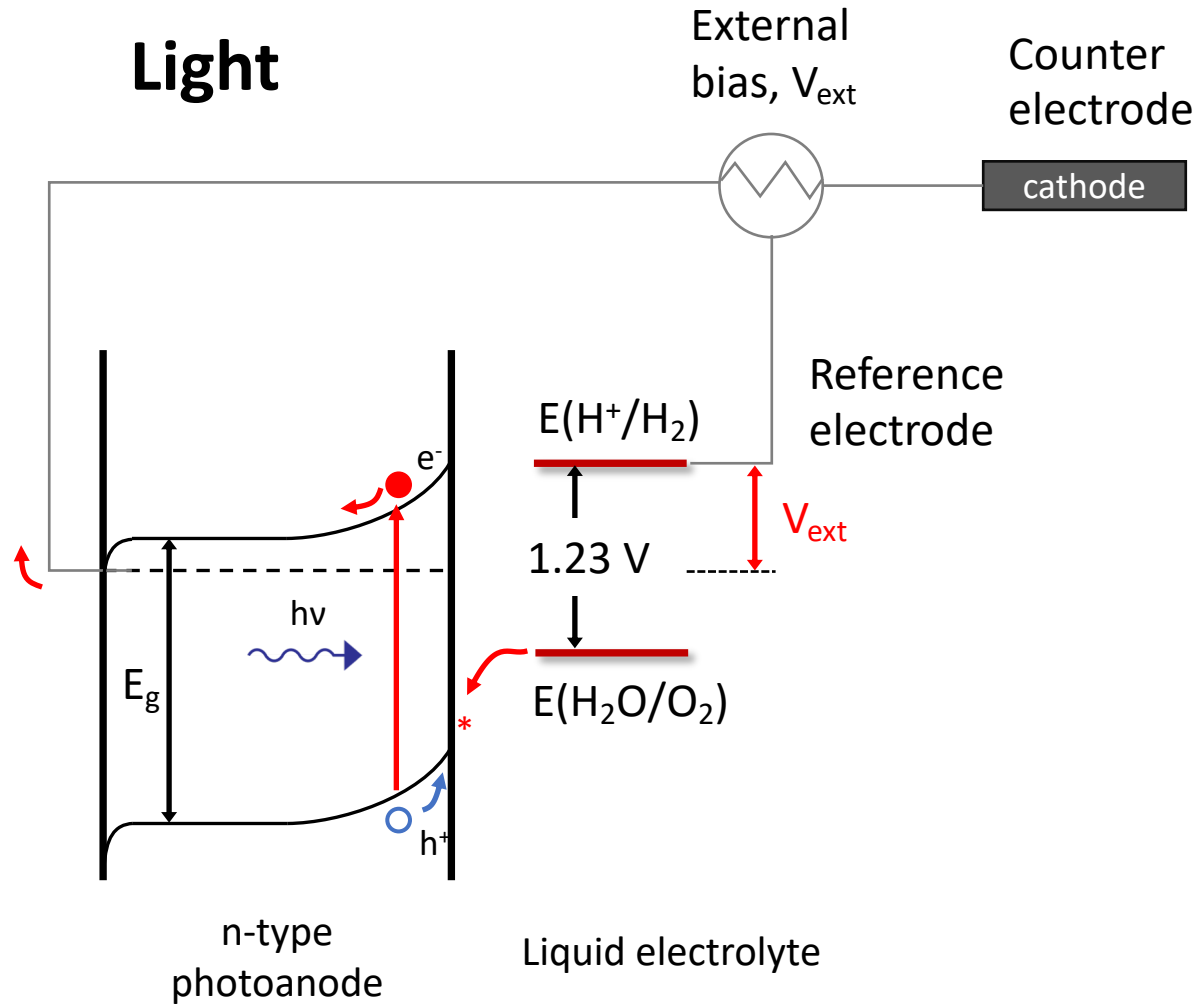
Dark current increases when energy states become available in conduction band.

EPFL Metrics in Photoelectrode Development



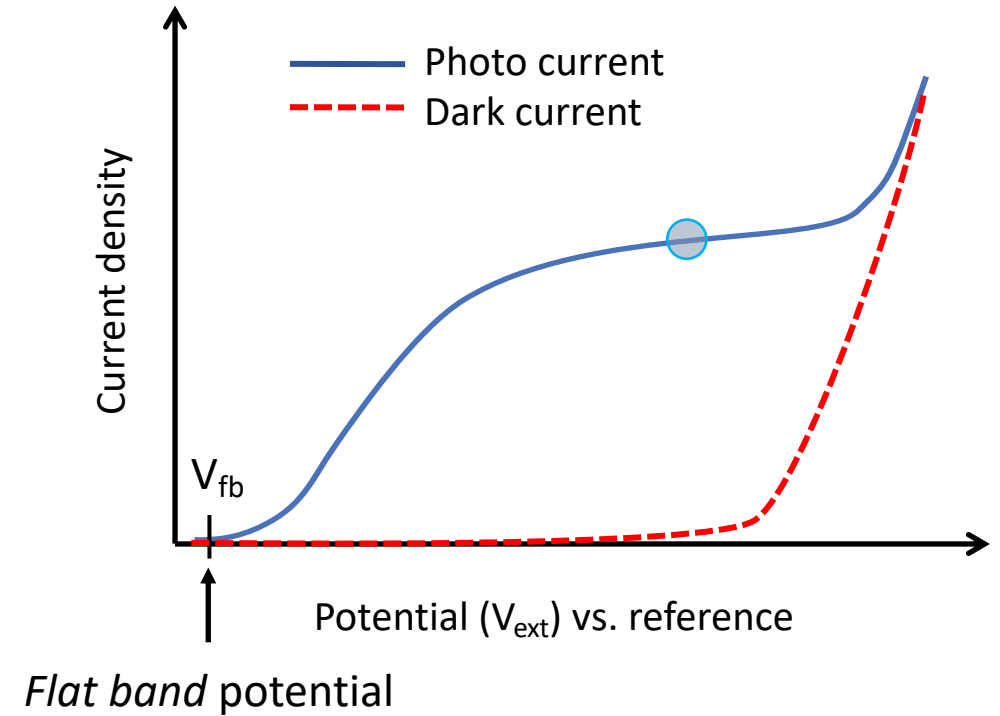
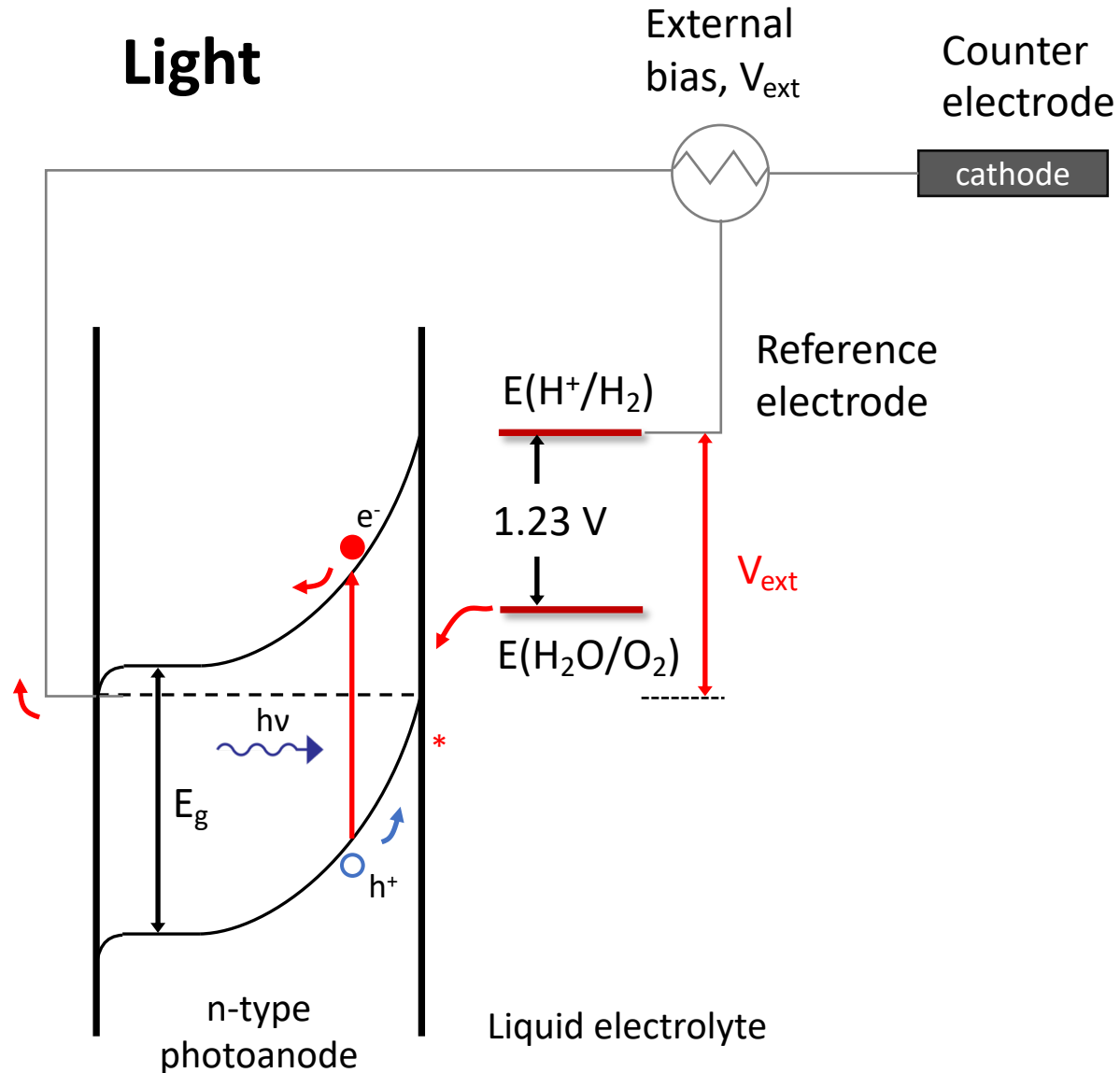
At the V_{fb} , there is no electric field to separate the photoexcited electron-hole pairs.

EPFL Metrics in Photoelectrode Development



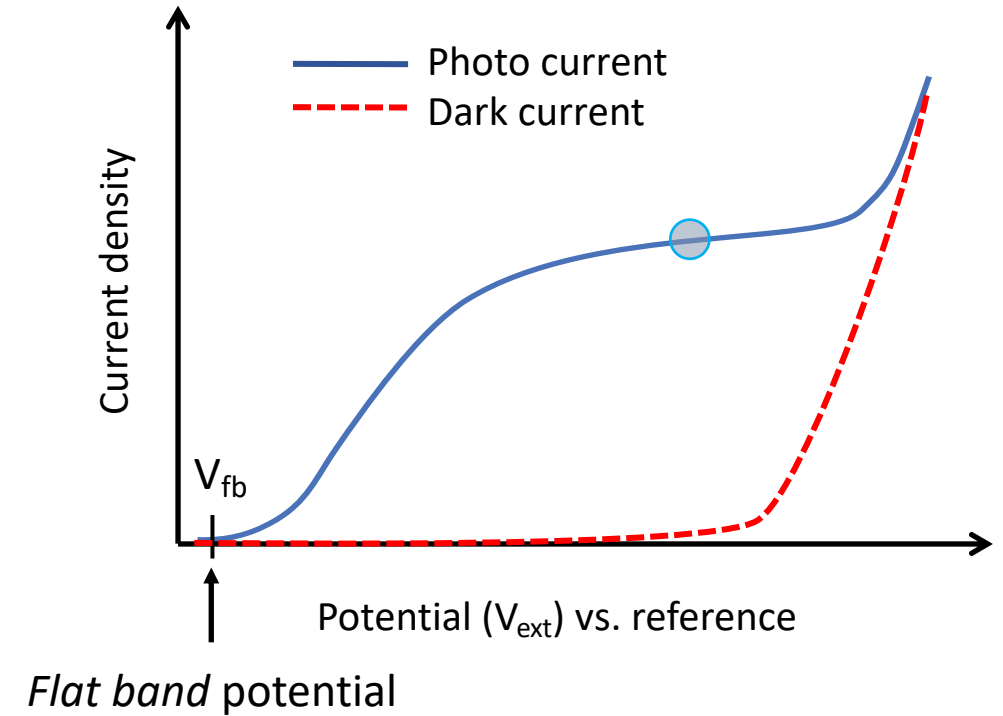
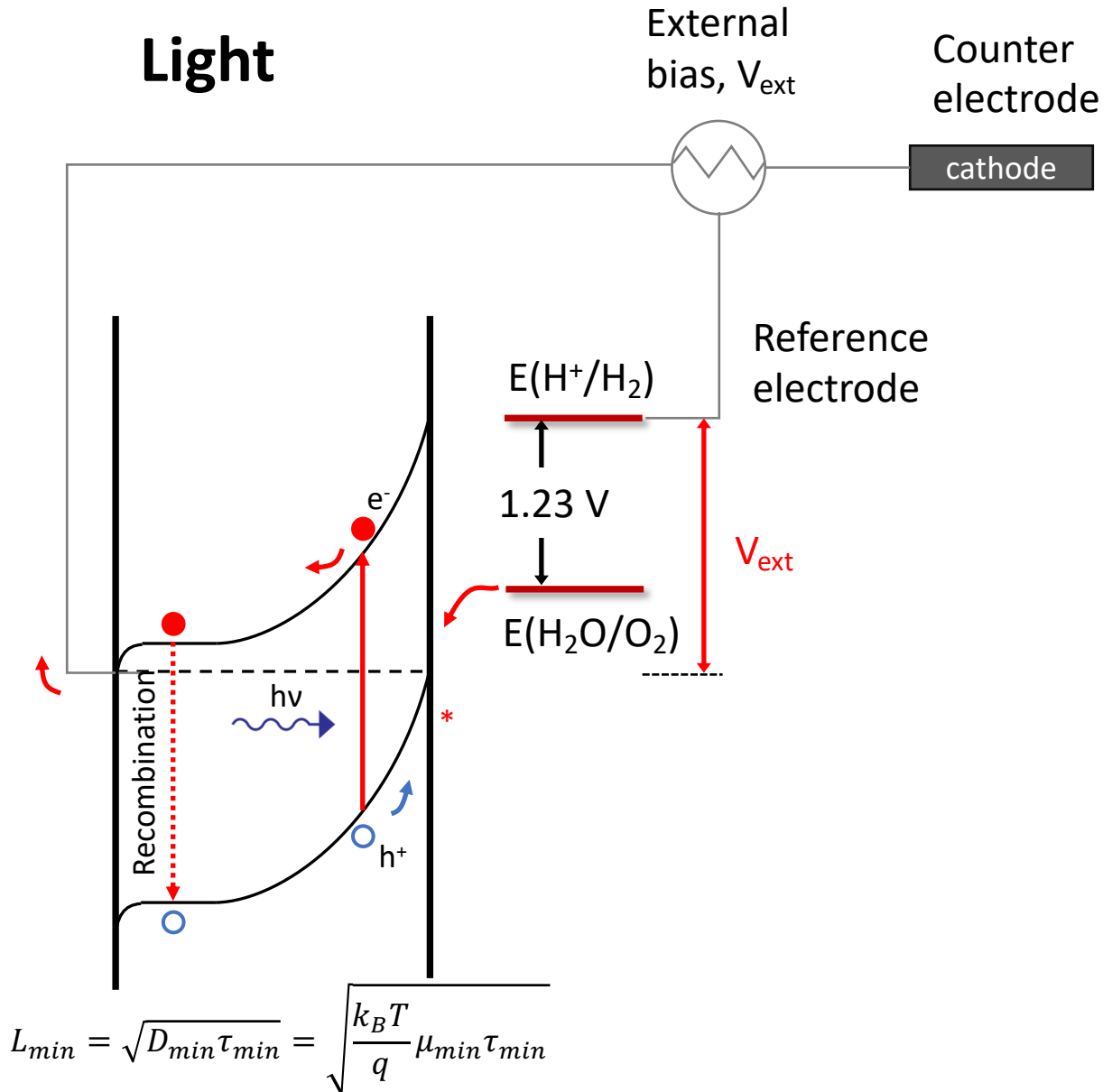
Under illumination ($h\nu > E_g$) a photocurrent is observed due to the presence of holes at the interface between the semiconductor and the electrolyte

EPFL Metrics in Photoelectrode Development



The photocurrent increases and eventually plateaus due to limitations of light absorption, surface kinetics, carrier transport, etc. Eventually, the dark current sets in.

EPFL Metrics in Photoelectrode Development



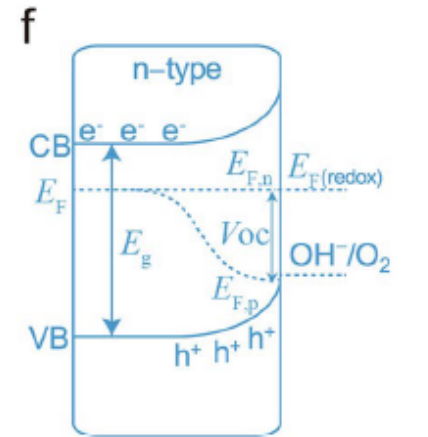
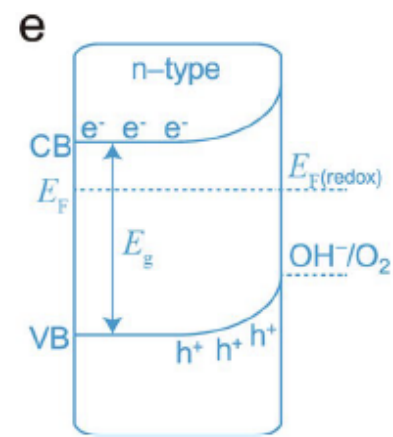
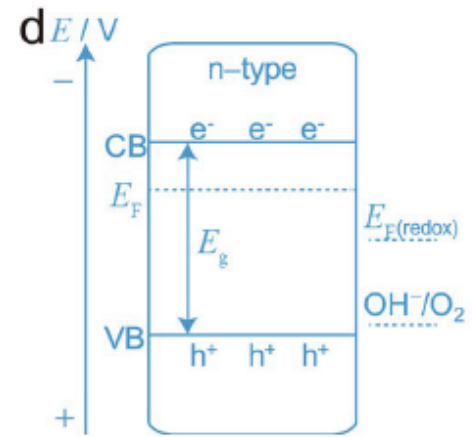
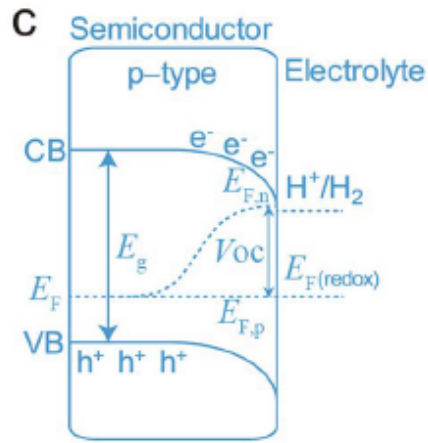
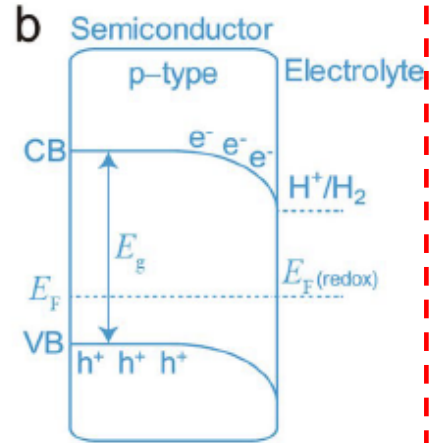
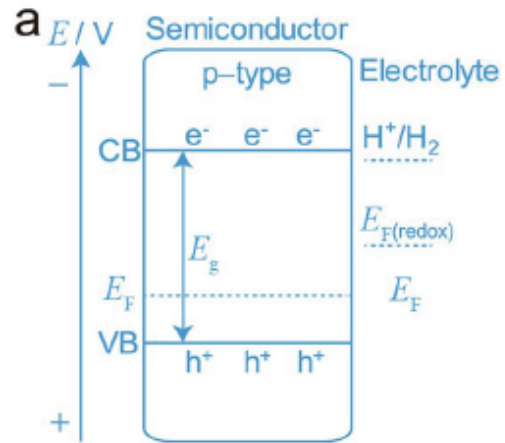
The photocurrent increases and eventually plateaus due to limitations of light absorption, surface kinetics, carrier transport, etc. Eventually, the dark current sets in.

EPFL Photoanode and Photocathode

At equilibrium

With light

Photocathode



Photoanode

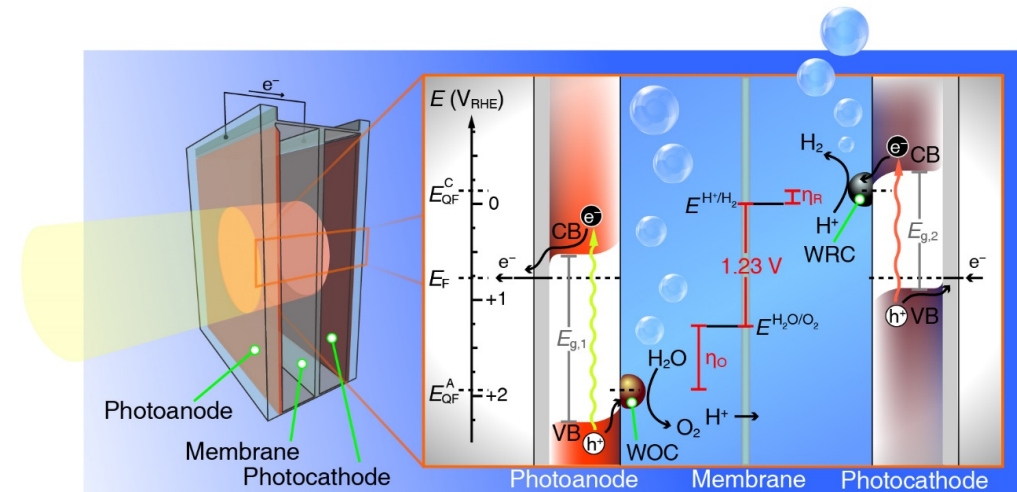
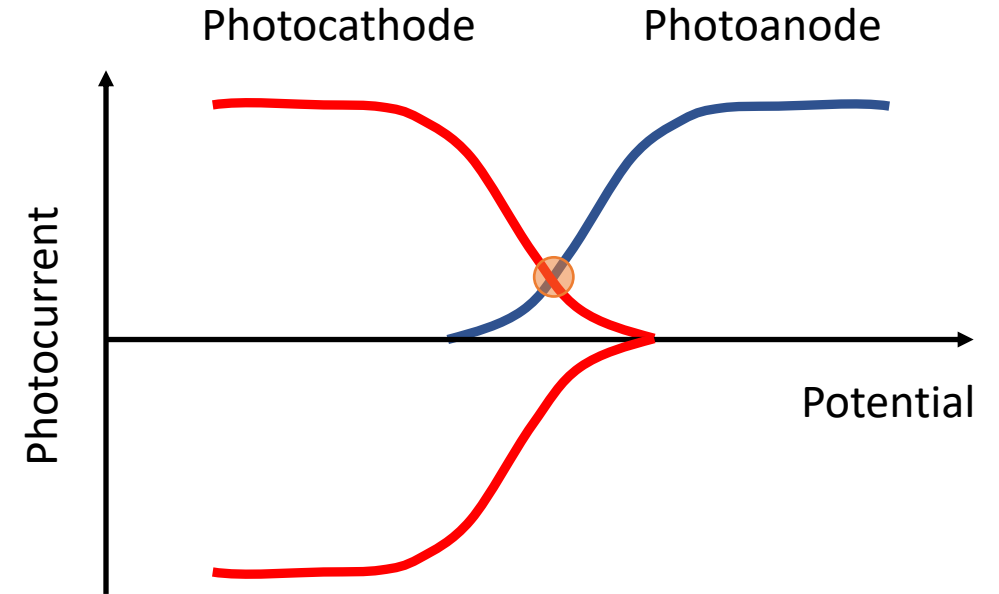
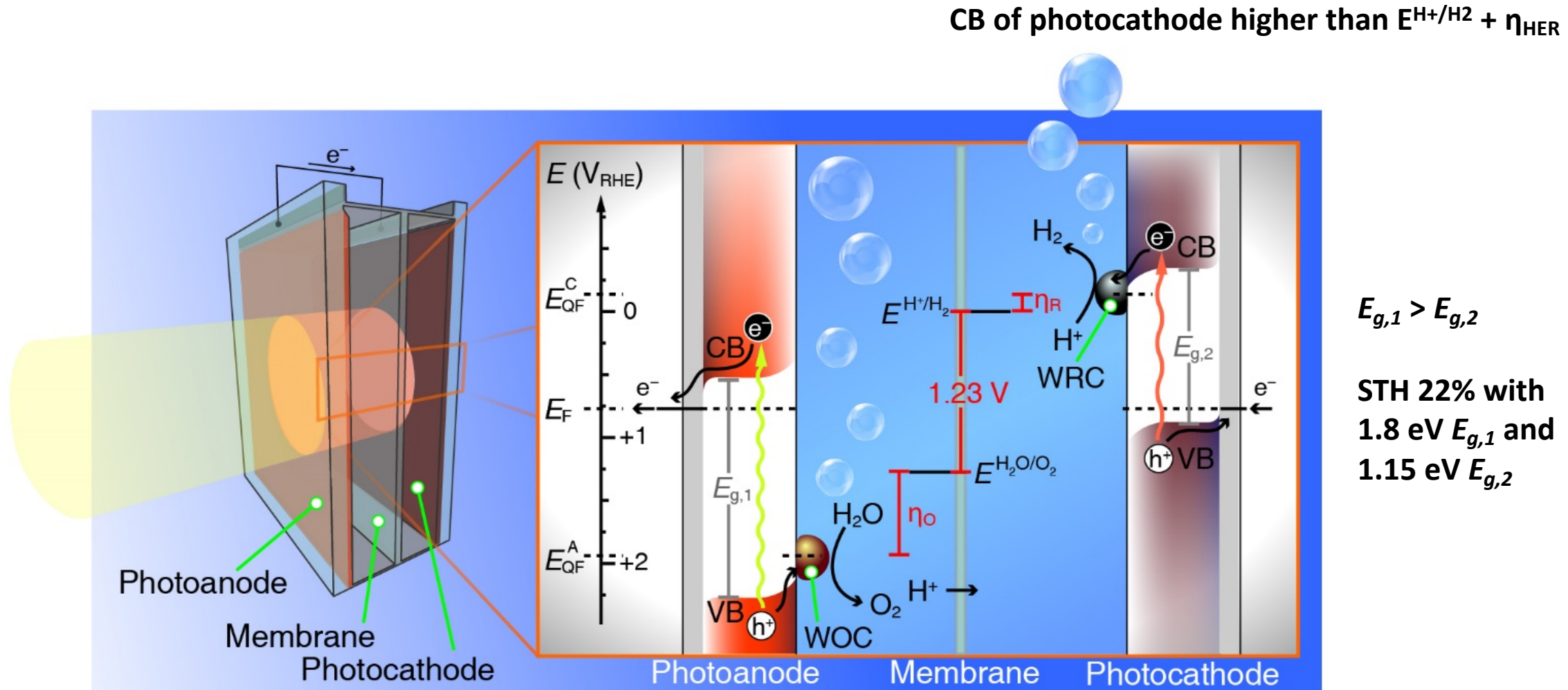


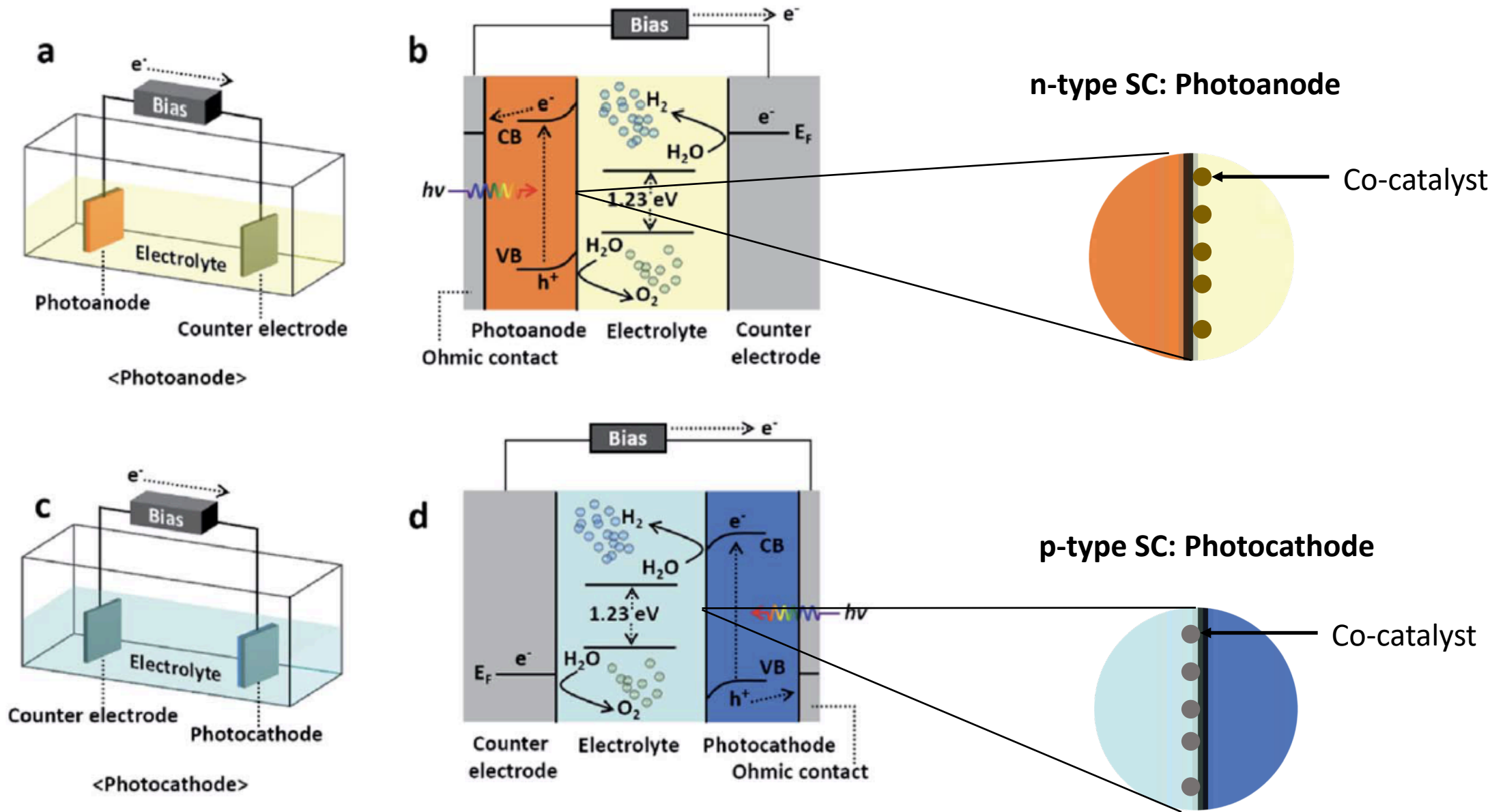
Image taken from Y- Zhao et al., Electrochem. Energy Rev., 6:14 (2023)



VB of photoanode lower than $E^{H_2O/O_2} + \eta_{OER}$

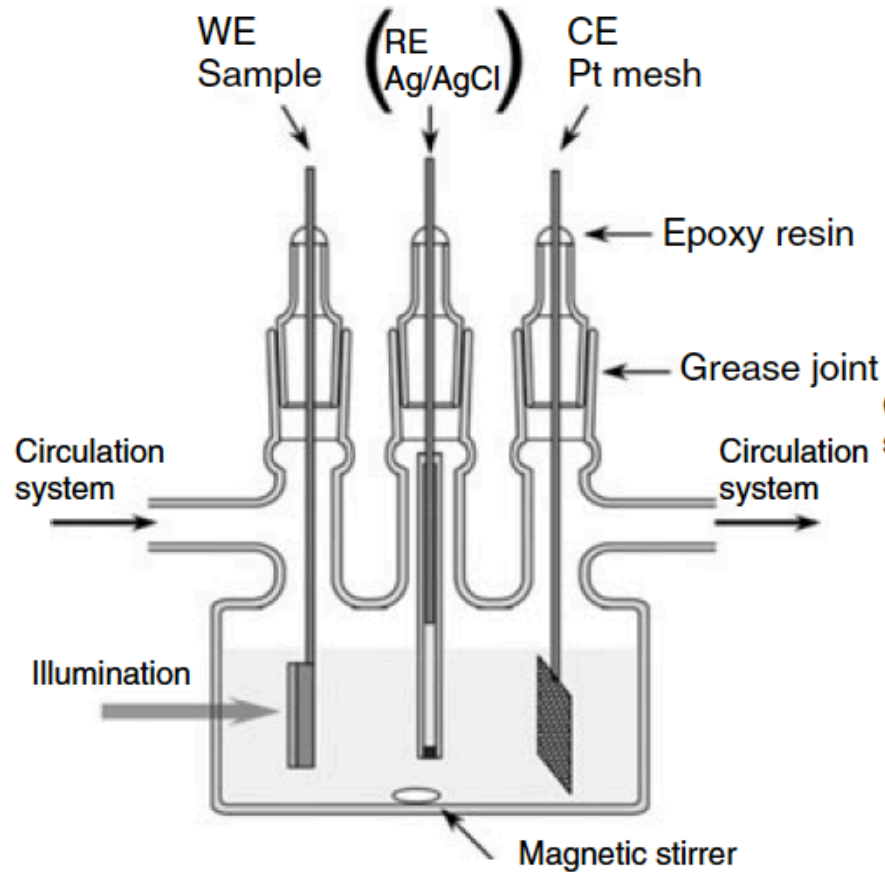
WRC: water reduction catalyst
WOC: water oxidation catalyst

EPFL Photoanode and Photocathode

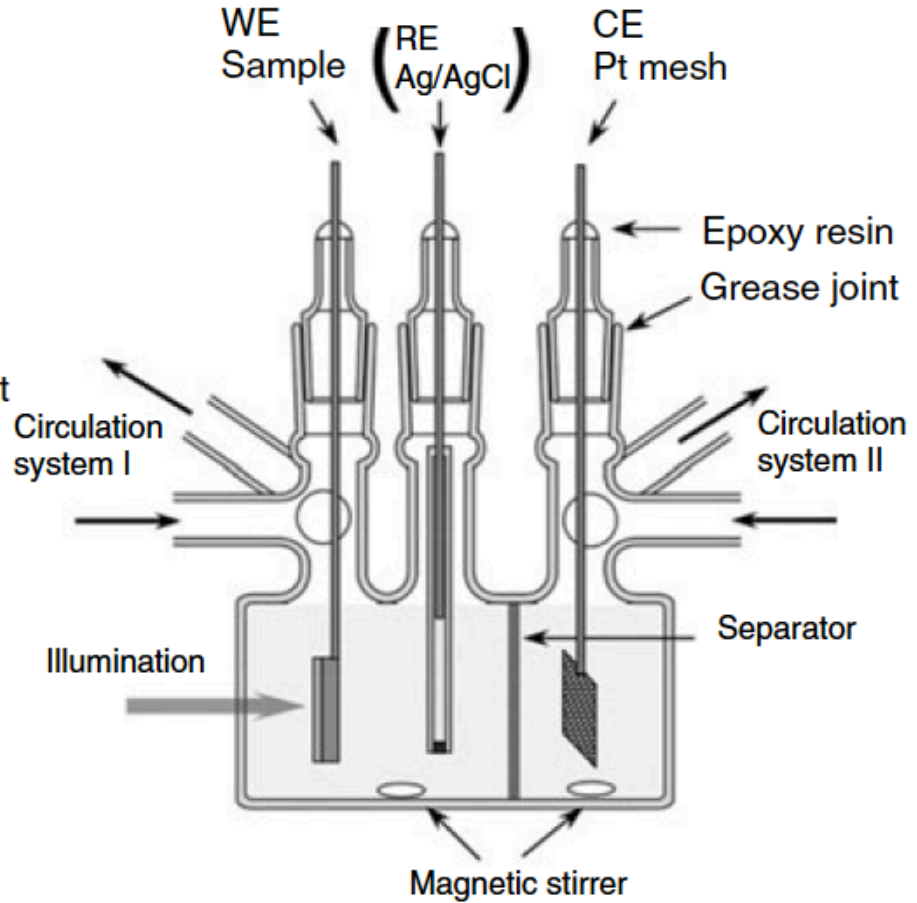


Park et al., *RSC Adv.*, **9**, 30112 (2019)

a Single Vessel Cell

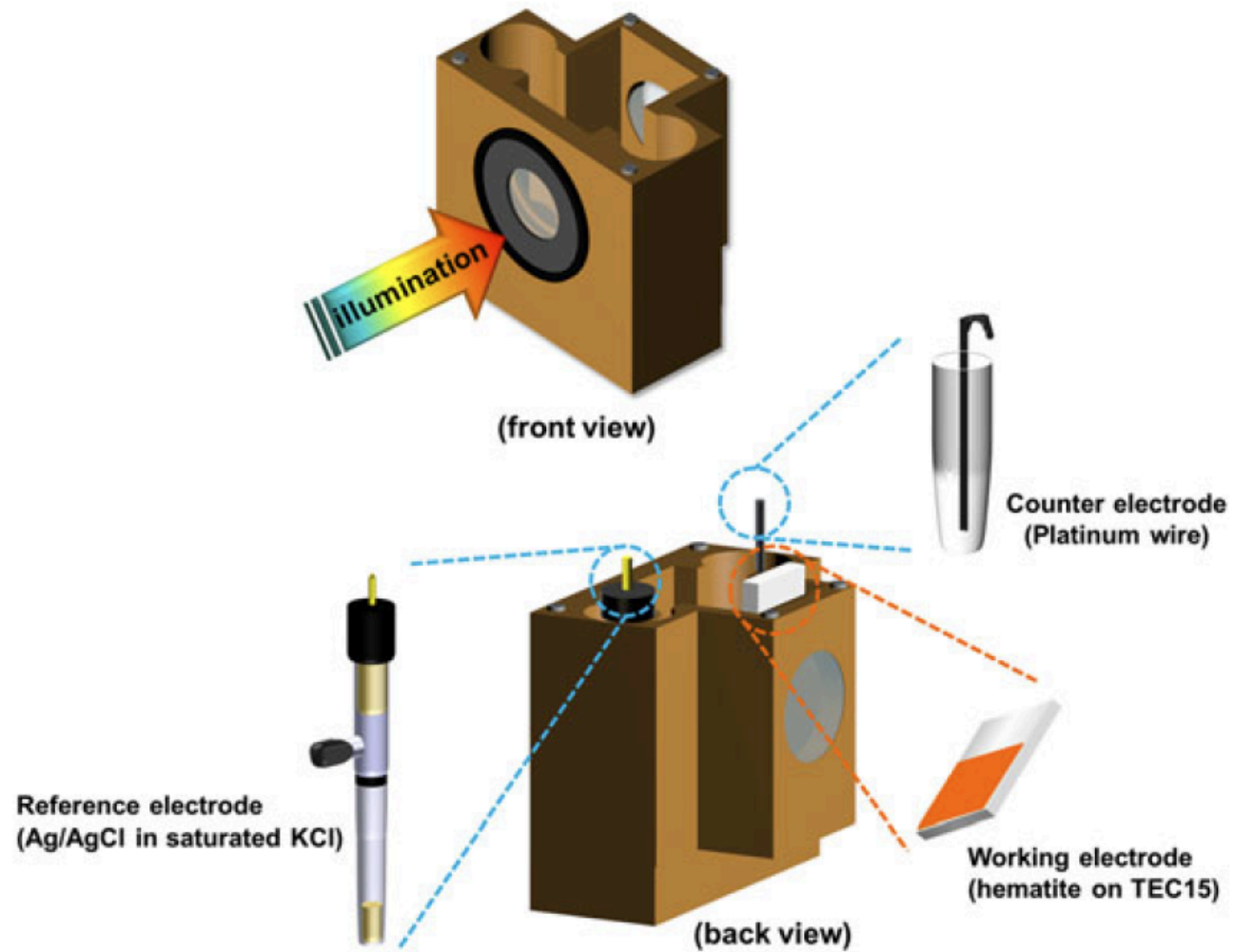


b Double Vessel Cell

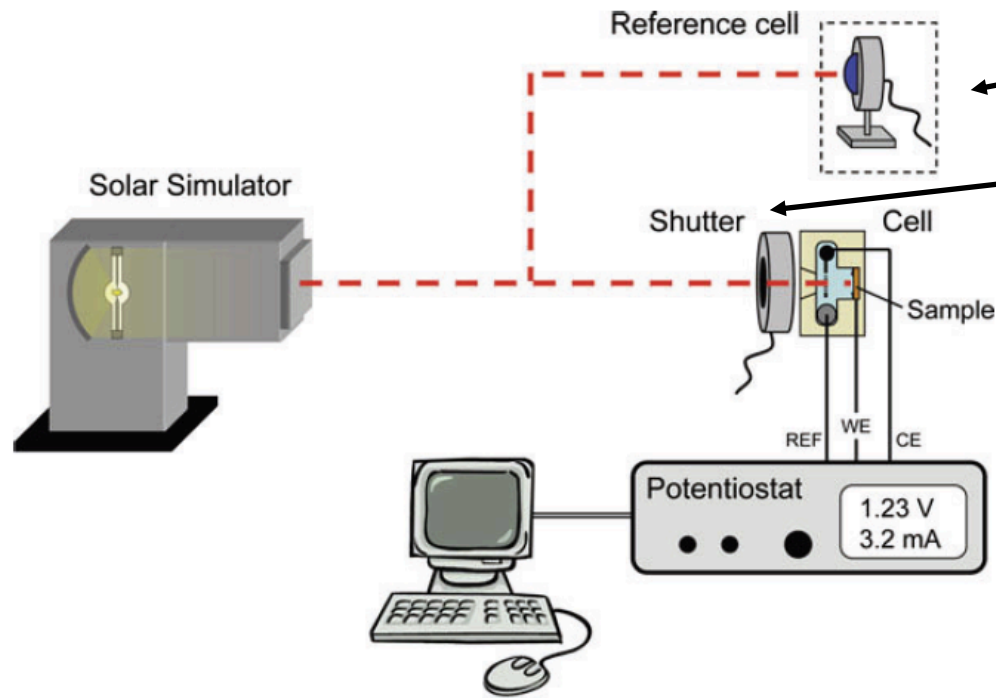


Z. B. Chen et al., *J. Mater. Res.*, **25**, 3–16 (2010)

EPFL Photoelectrochemical Test Setup



EPFL Photoelectrochemical Test Setup



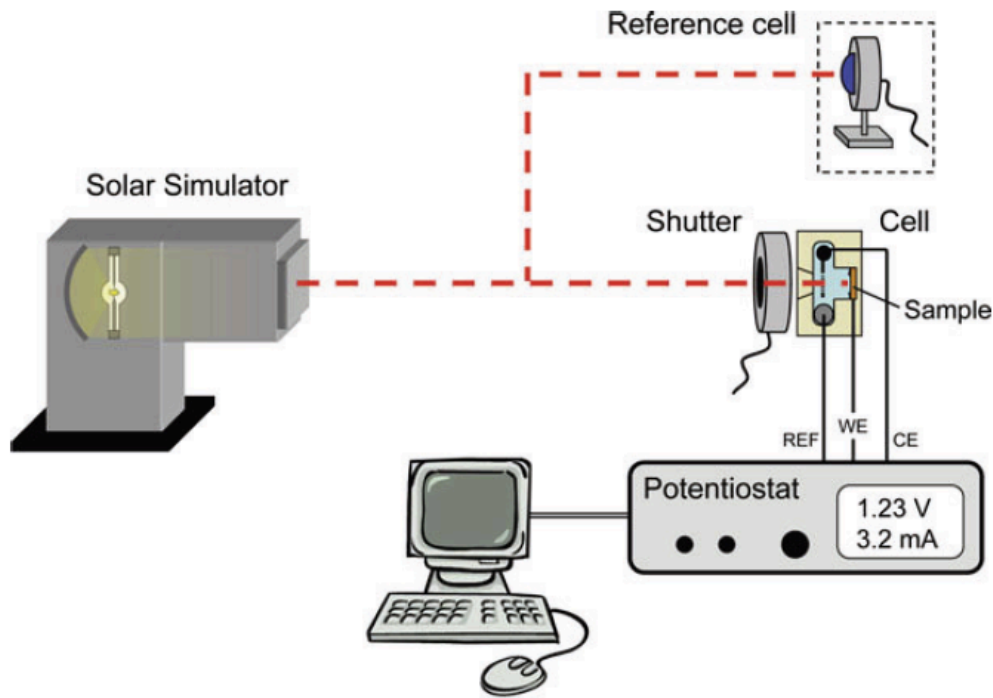
Verify the intensity of the solar simulator

Block the light, e.g. chopped light experiments

Control the sample's potential
Measure the current

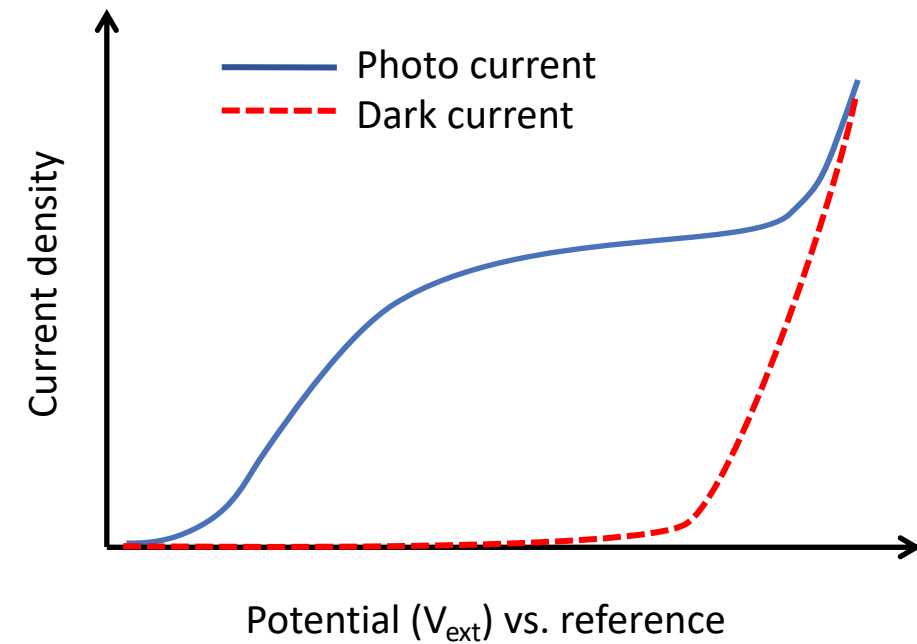
Experimental setup for measuring the performance of a photoelectrode under irradiation with simulated sunlight.

EPFL Photoelectrochemical Test Setup

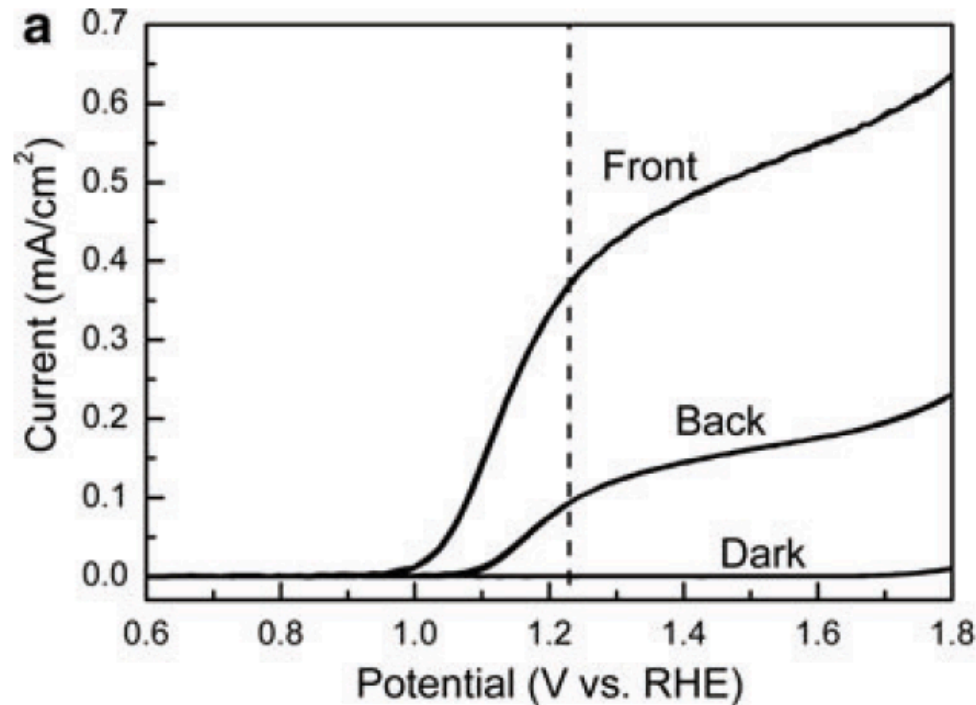


Experimental setup for measuring the performance of a photoelectrode under irradiation with simulated sunlight.

Current-Voltage Curve

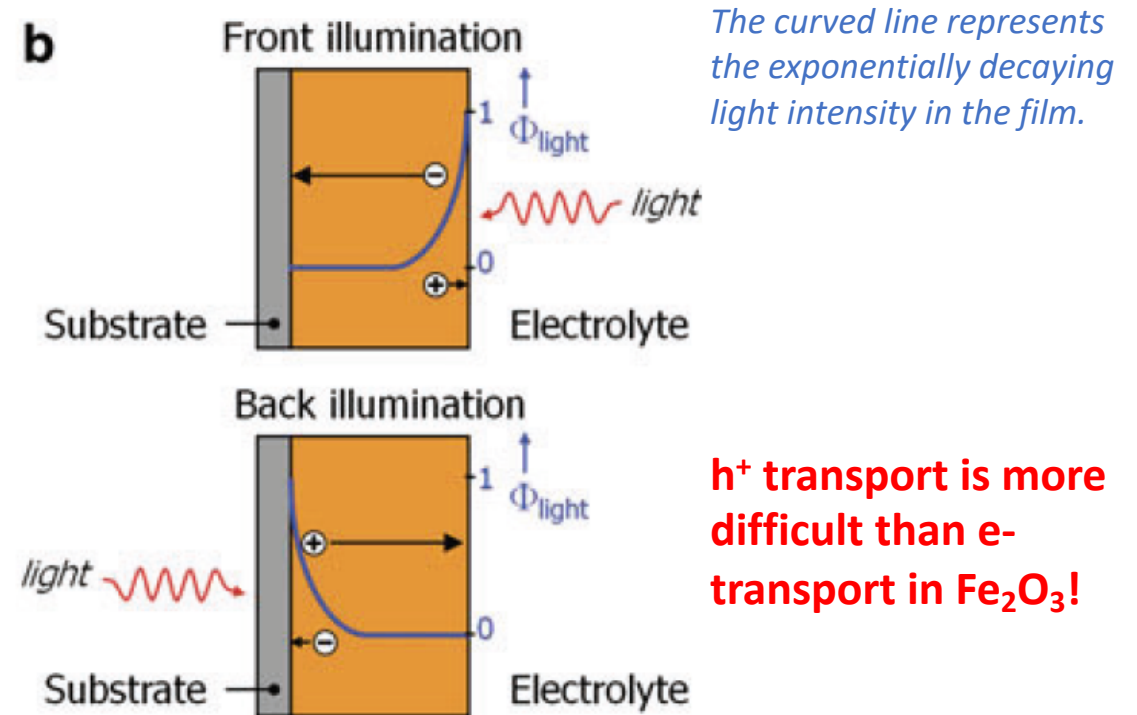


Front- and Back-side Illumination



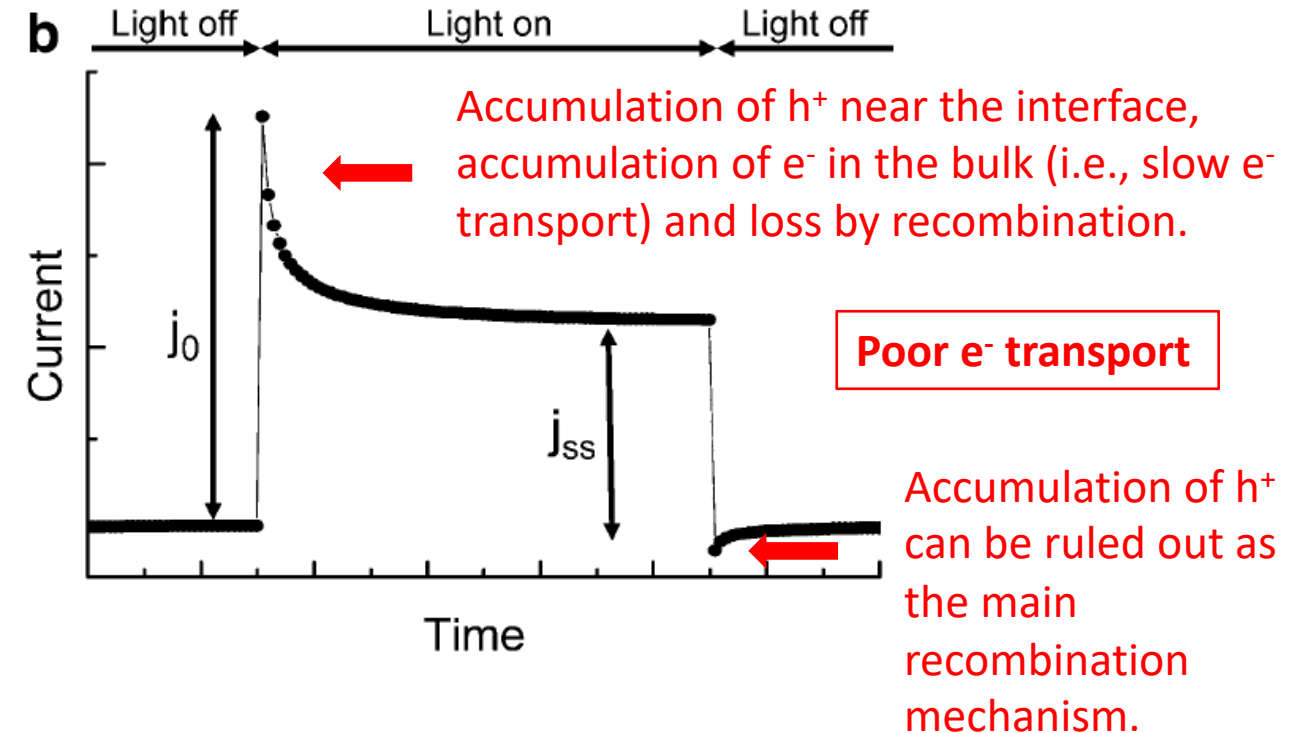
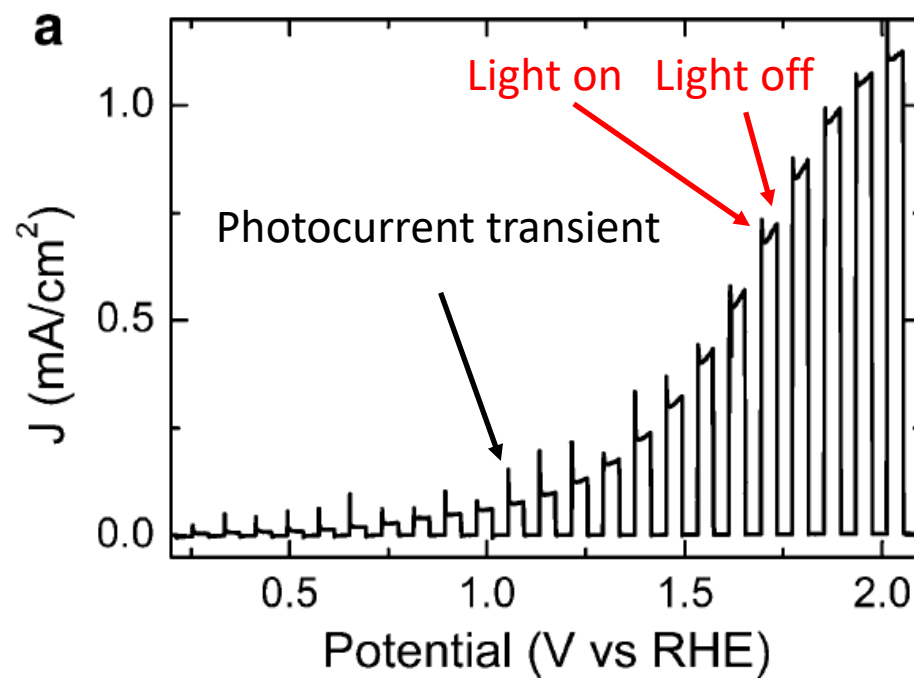
Current–voltage curve of a spray-deposited film of 0.2% Si-doped $\alpha\text{-Fe}_2\text{O}_3$ in the dark and under continuous front- or back-side illumination with 80 mW/cm^2 simulated sunlight.

Y. Liang et al., Int. J. Photoenergy, Article ID 739864 (2008).



Under front-side illumination, most light is absorbed near the semiconductor/electrolyte interface. This means that the photogenerated electrons have to travel a larger distance before reaching the interface than the photogenerated holes. For backside illumination, the situation is reversed.

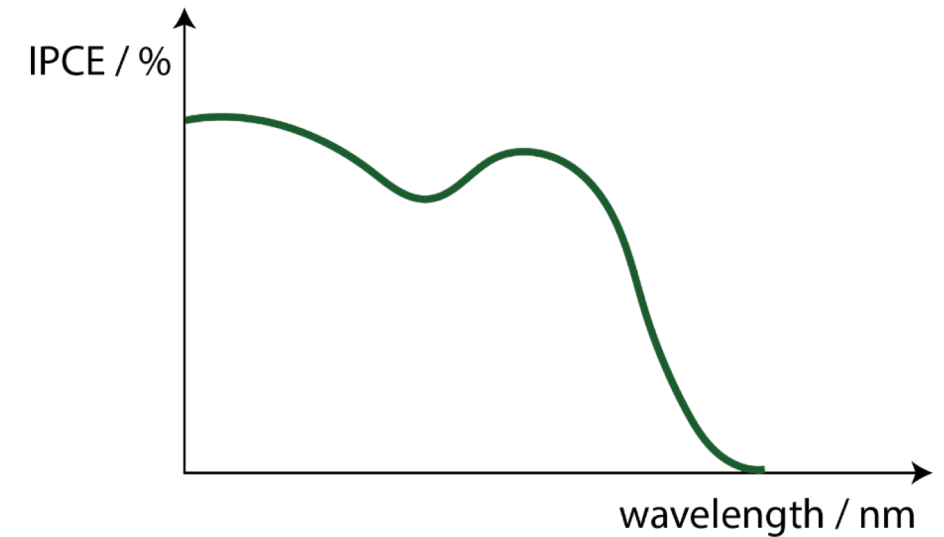
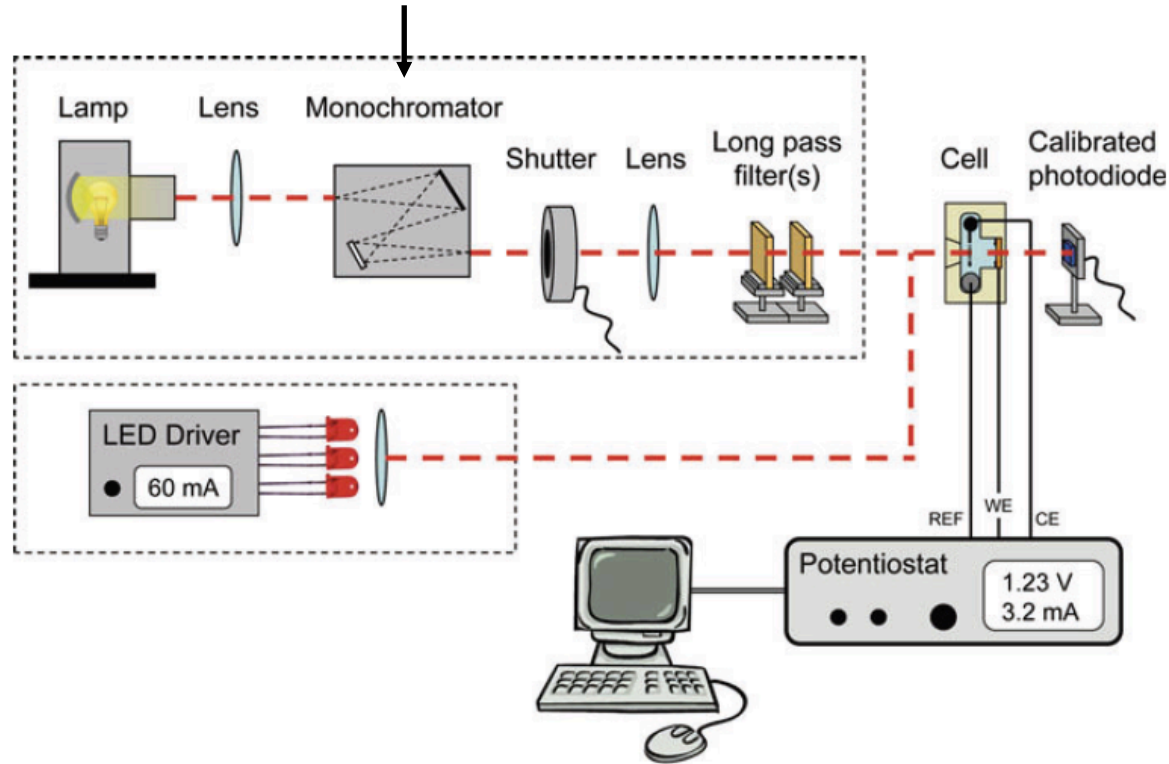
Chopped Voltammogram



- (a) Voltammogram for a spray-deposited BiVO₄ **photoanode** on FTO glass under chopped AM1.5 illumination.
- (b) Current vs. time curve for BiVO₄ under high-intensity illumination with 364 nm light from a continuous-wave Ar⁺ laser at a potential of 1.23 V_{RHE}. In both cases, a 0.15 M K₂SO₄ aqueous electrolyte solution was used.

EPFL Photoelectrochemical Test Setup: EQE

A monochromator is used to filter out a narrow part of the spectrum centered around the wavelength of interest.



Experimental setup for measuring the photocurrent and/or quantum efficiency as a function of wavelength.

Incident Photon-to-Current (Conversion) Efficiency (IPCE) or External Quantum Efficiency (EQE) =

$$\frac{\text{Collected electrons at a given wavelength}}{\text{Photons in at a given wavelength}} = \frac{J_{sc}/q}{P_{in}/h\nu} = \frac{J_{sc}(A/cm^2)}{P_{in}(W/cm^2)} \times \frac{1240}{\lambda(nm)} \times 100$$

Absorbed Photon-to-Current (Conversion) Efficiency (APCE) or Internal Quantum Efficiency (IQE) =

$$\frac{\text{electrons/sec}}{\text{absorbed photons/sec}} = \frac{EQE}{1 - R - T} = \frac{EQE}{LHE}$$

Applied Bias Photon-to-Current (Conversion) Efficiency (ABPE or ABPC) =

$$\frac{(\text{Total power output} - \text{Electrical input power})}{\text{Light power input}} = \frac{J_{sc} \times (1.23 - |V_a|) \times \eta_F}{P_{in}}$$

Faraday efficiency (also called faradaic efficiency, faradaic yield, coulombic efficiency or current efficiency) **describes the efficiency with which charge (electrons) is transferred in a system facilitating a desired electrochemical reaction.** In other words, the faraday efficiency is the ratio of experimentally measured moles of gas divided by the theoretical number of moles of product gas.

$$\eta_F = \frac{n_{prod}}{Q/nF}$$

n_{prod} is the gas measured experimentally in mole.

Q is the charge in coulombs corresponding to the photocurrent at time (s) ($C = A \times s$)

F is faraday's constant (96485.33 C/mol)

n is the number of charges needed to drive the reaction

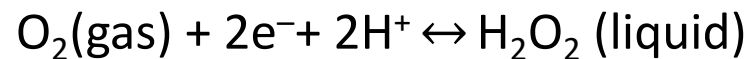
For H_2 production: $\eta_F = \frac{n_{H_2}}{Q/2F}$

For O_2 production: $\eta_F = \frac{n_{O_2}}{Q/4F}$

Faradaic losses are experienced when electrons or ions participate in unwanted side reactions.

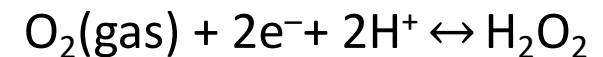
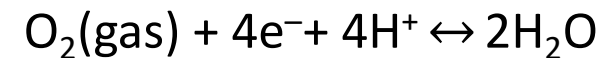
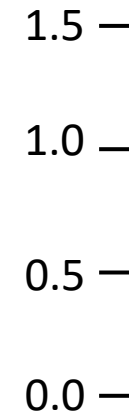
These losses appear as chemical byproducts and/or heat.

Example 1) In the oxidation of water to oxygen at the positive electrode in electrolysis, some electrons are diverted to the production of hydrogen peroxide. The fraction of electrons so diverted represent a faradaic loss.



$$E_{\text{H}_2\text{O}_2/\text{O}_2}^0 = 0.682 \text{ V } vs. SHE$$

E^0 (V) vs SHE



- Solar-To-Hydrogen (STH) efficiency is defined as ***chemical energy of the hydrogen produced*** divided by ***solar energy input from sunlight incident on the process***.
- The ***chemical energy of the hydrogen produced*** = The rate of hydrogen production (mmol H₂/s) multiplied by the change in Gibbs free energy per mole of H₂ ($\Delta G^0 = 237.2$ kJ/mol at 25 °C).

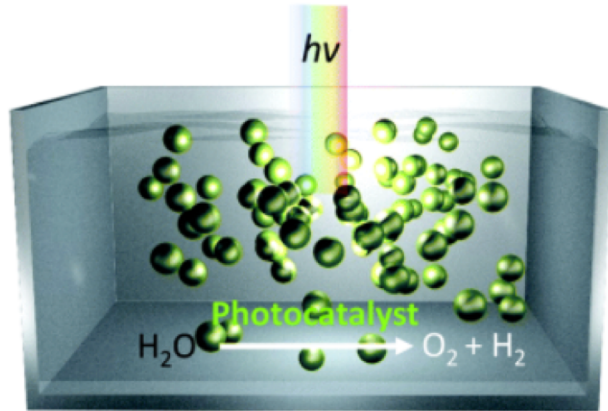
$$STH = \left[\frac{(\text{mmol } H_2/\text{s}) \times (237,200 \text{ J/mol})}{P_{total} \left(\frac{\text{mW}}{\text{cm}^2} \right) \times \text{Area} (\text{cm}^2)} \right]_{AM1.5G}$$

← This equation calculates the power output (numerator) based on the direct measurement of the true H₂ production rate by an analytical method such as gas chromatography or mass spectrometry.

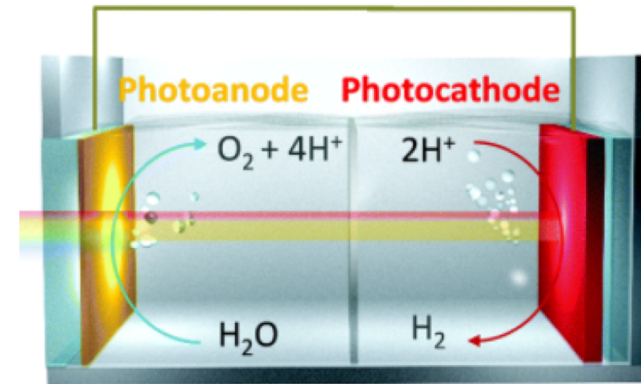
$$STH = \left[\frac{(J_{sc} (\text{mA}/\text{cm}^2) \times (1.23 \text{ V}) \times \eta_F)}{P_{total} \left(\frac{\text{mW}}{\text{cm}^2} \right)} \right]_{AM1.5G}$$

← Alternatively, this equation uses the relation that power is the product of the minimum energy to split water, current, and the Faradaic efficiency for hydrogen evolution

PC



PEC

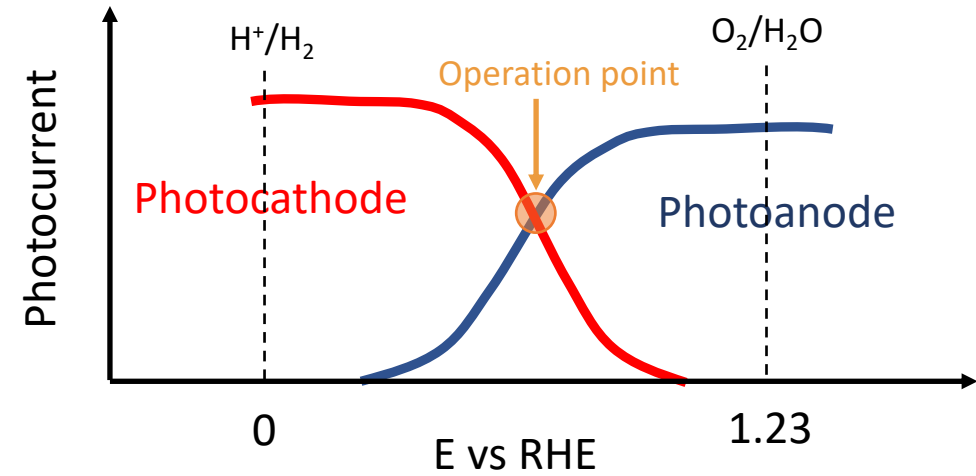
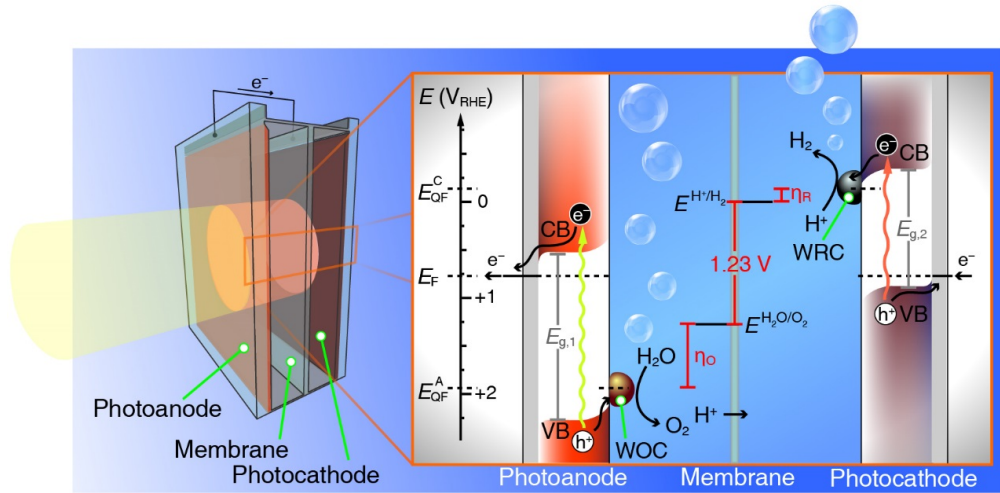


$$STH = \left[\frac{(\text{mmol H}_2/\text{s}) \times (237,200 \text{ J/mol})}{P_{\text{total}} \left(\frac{\text{mW}}{\text{cm}^2} \right) \times \text{Area} (\text{cm}^2)} \right]_{AM1.5G}$$

$$STH = \left[\frac{(J_{sc} (\text{mA}/\text{cm}^2) \times (1.23 \text{ V}) \times \eta_F)}{P_{\text{total}} \left(\frac{\text{mW}}{\text{cm}^2} \right)} \right]_{AM1.5G}$$

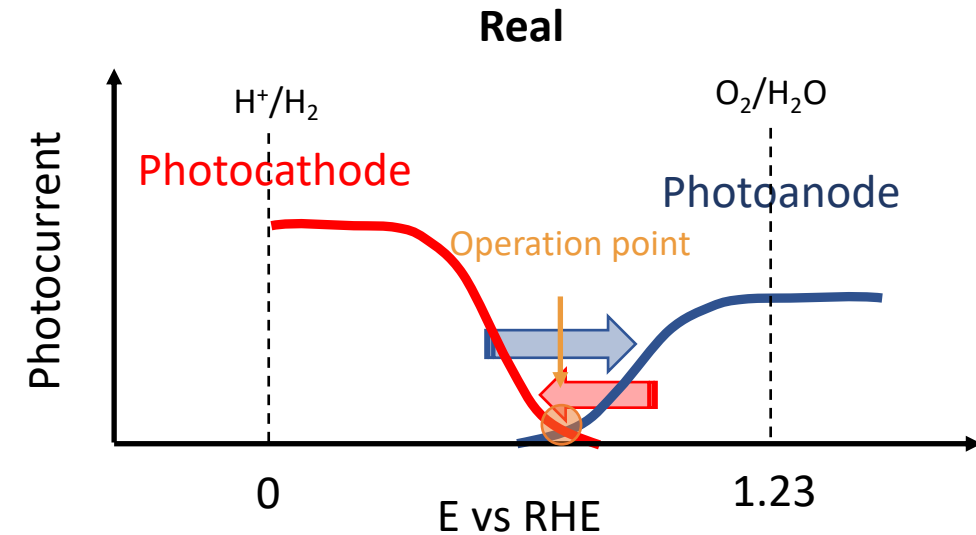
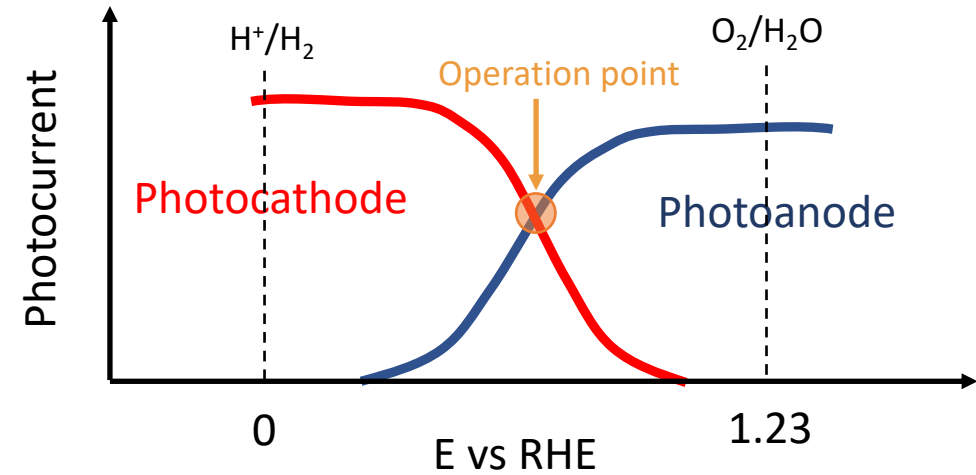
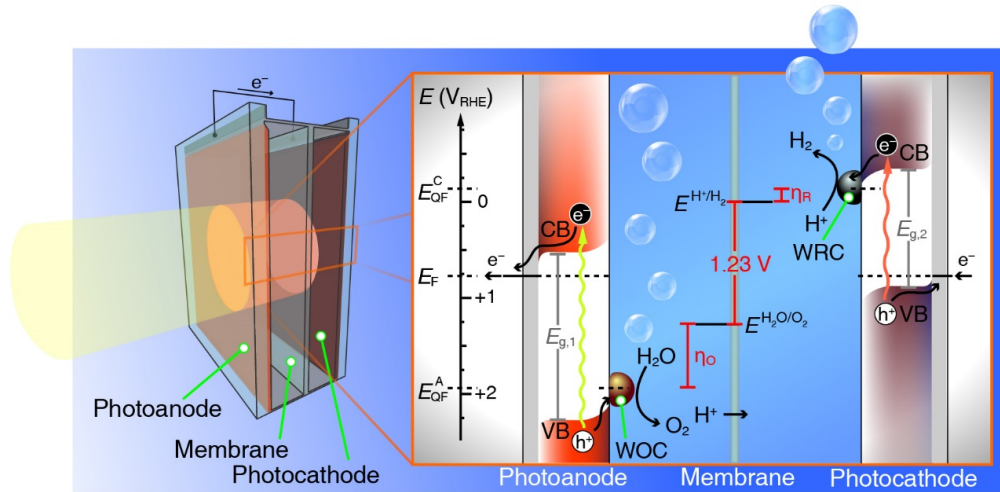
- Benchmark efficiency (suitable for mainstream reporting of stand-alone water splitting capability)
 - solar-to-hydrogen conversion efficiency (STH)
- Diagnostic efficiencies (to characterize and understand materials system/interface performance)
 - external quantum efficiency (EQE) = incident photon-to-current efficiency (IPCE)
 - internal quantum efficiency (IQE) = absorbed photon-to-current efficiency (APCE)
 - applied bias photon-to-current efficiency (ABPE)

EPFL Assessment of a Dual Tandem PEC Cell



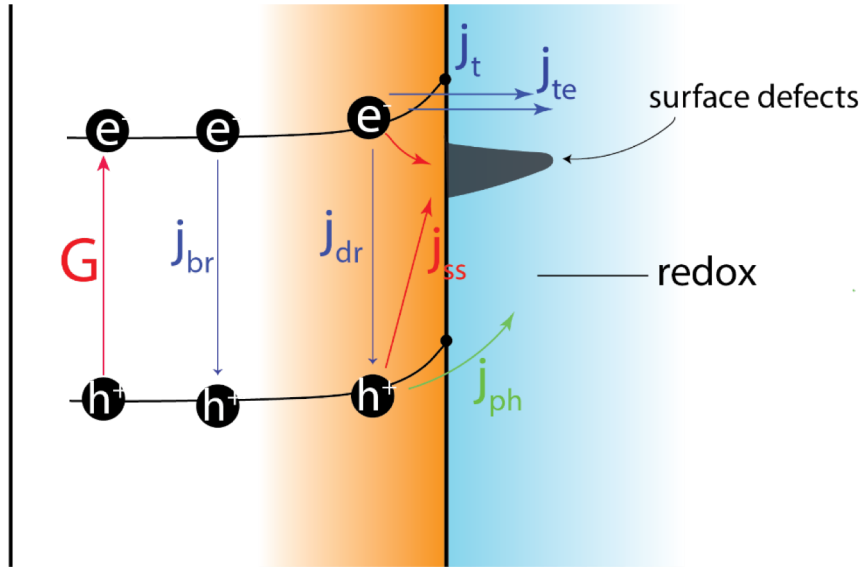
Examine separately photoelectrodes.
Predict 'best' performance (*overlapping of JV curves*)

EPFL Assessment of a Dual Tandem PEC Cell



Today's low-cost PEC cells suffer from poor STH

- Poor performance of photoelectrodes
- Non-optimized combination of photoelectrodes (band gaps)



$$J_{ph} = G - J_{br} - J_{dr} - J_{ss} - J_t - J_{te}$$

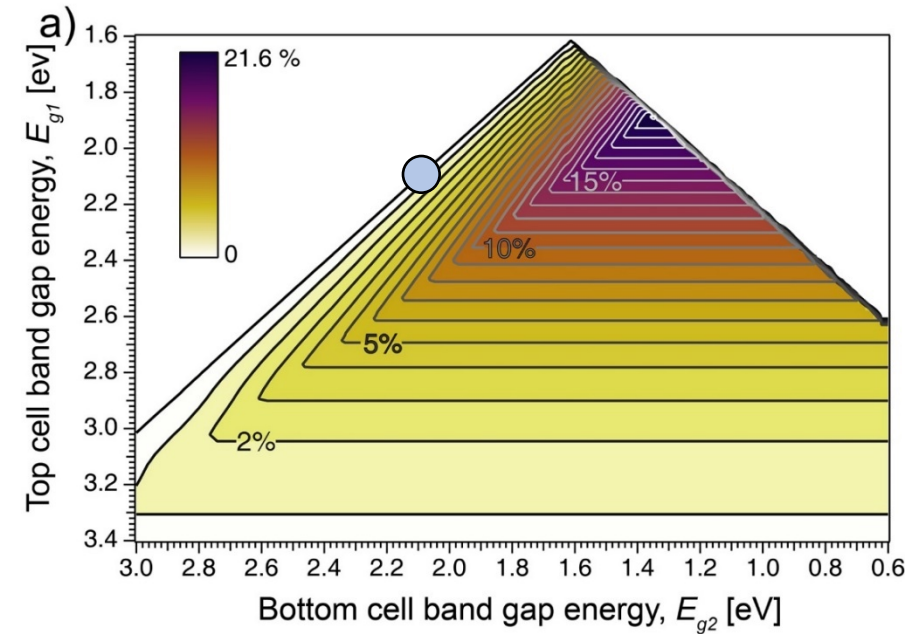
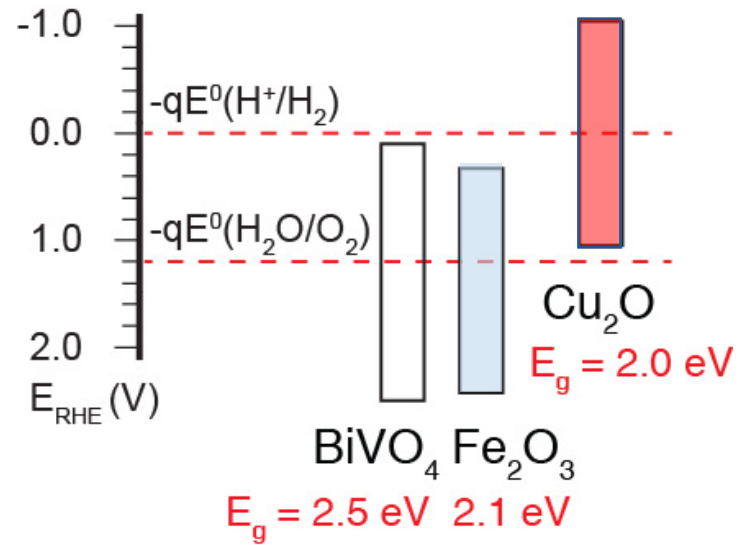
- Charge recombination in the bulk (br), in the depletion layer (dr) and via surface states (ss).
- Electron losses by reaction with redox through tunneling (t) across the potential barrier or at the surface (te)

BULK PROPERTIES

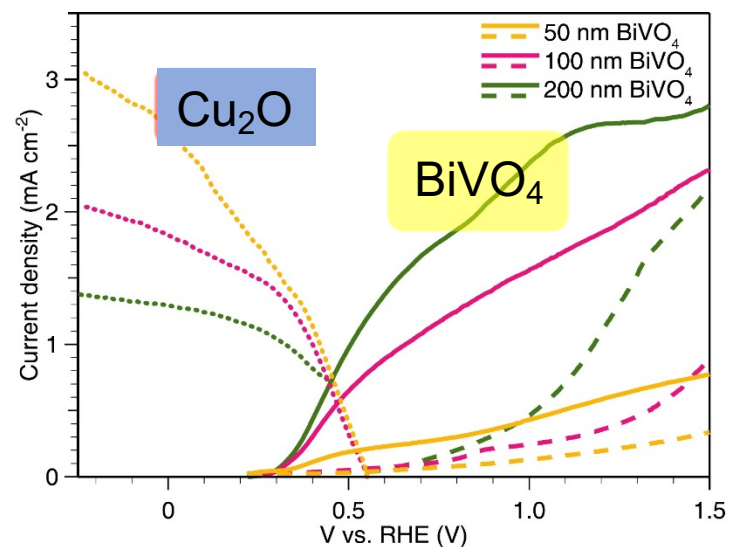
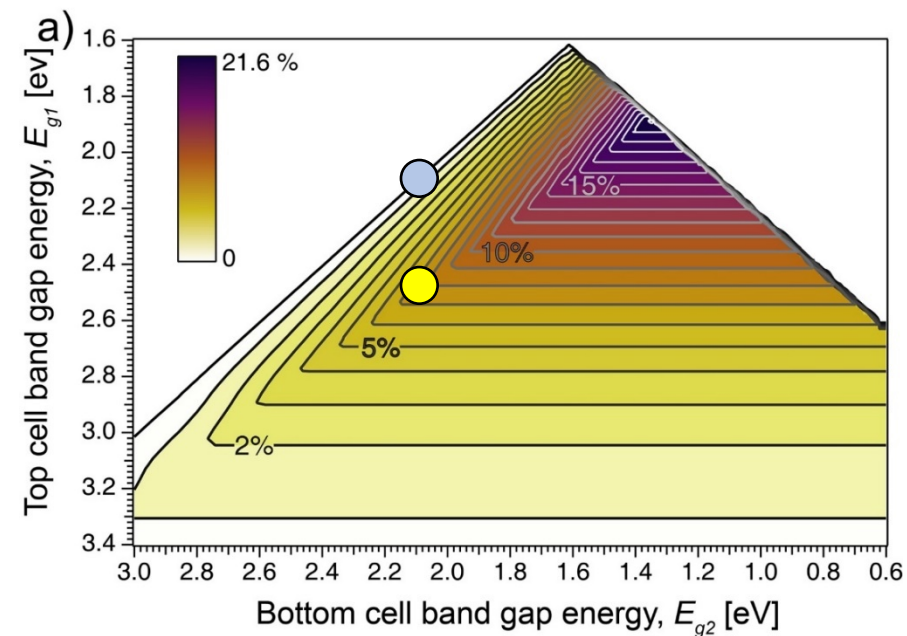
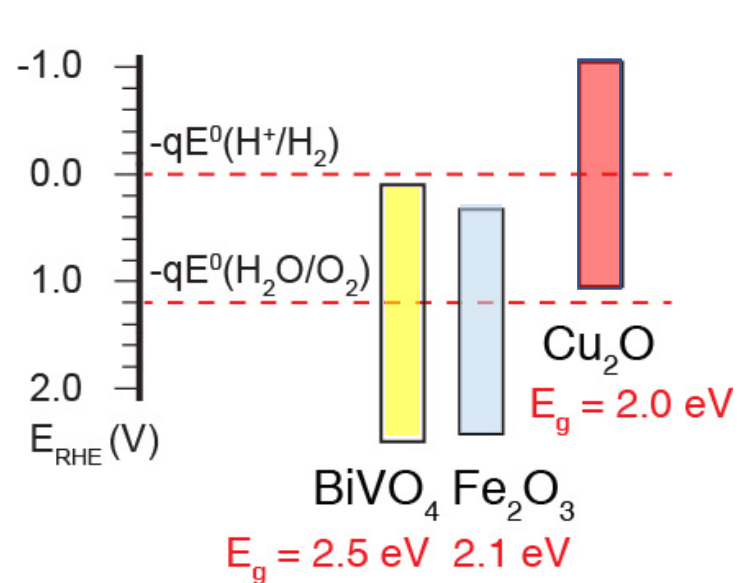
- Bulk defects (recombination)
- Carrier transport
- Doping density (conductivity, depletion depth)
- Morphology (charge collection)

SURFACE PROPERTIES (Semiconductor-liquid junction)

- Surface defects (recombination)
- Catalytic properties
- Stability



Low performance (non-complementary light absorption).
Hematite filters useful light for Cu_2O



Photoanode (n-type SC)



WO_3

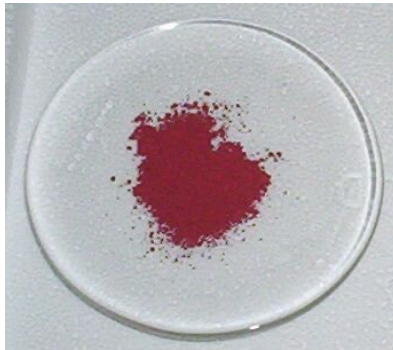


BiVO_4

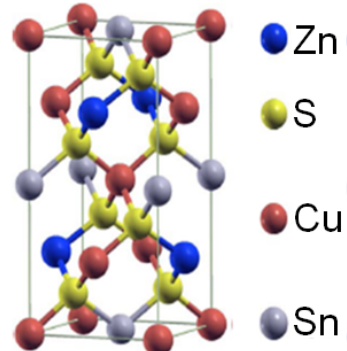


$\alpha\text{-Fe}_2\text{O}_3$

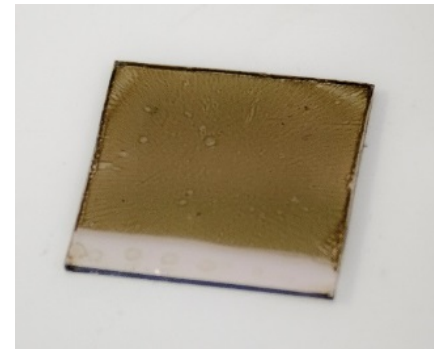
Photocathode (p-type SC)



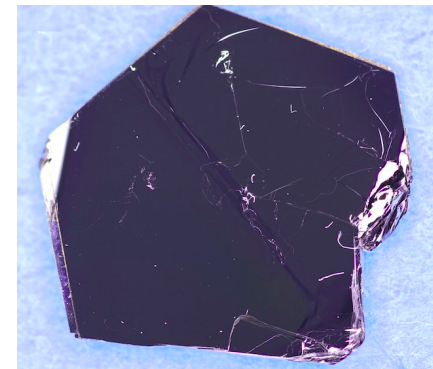
Copper(I) oxide



$\text{Cu}_2\text{ZnSnS}_4$



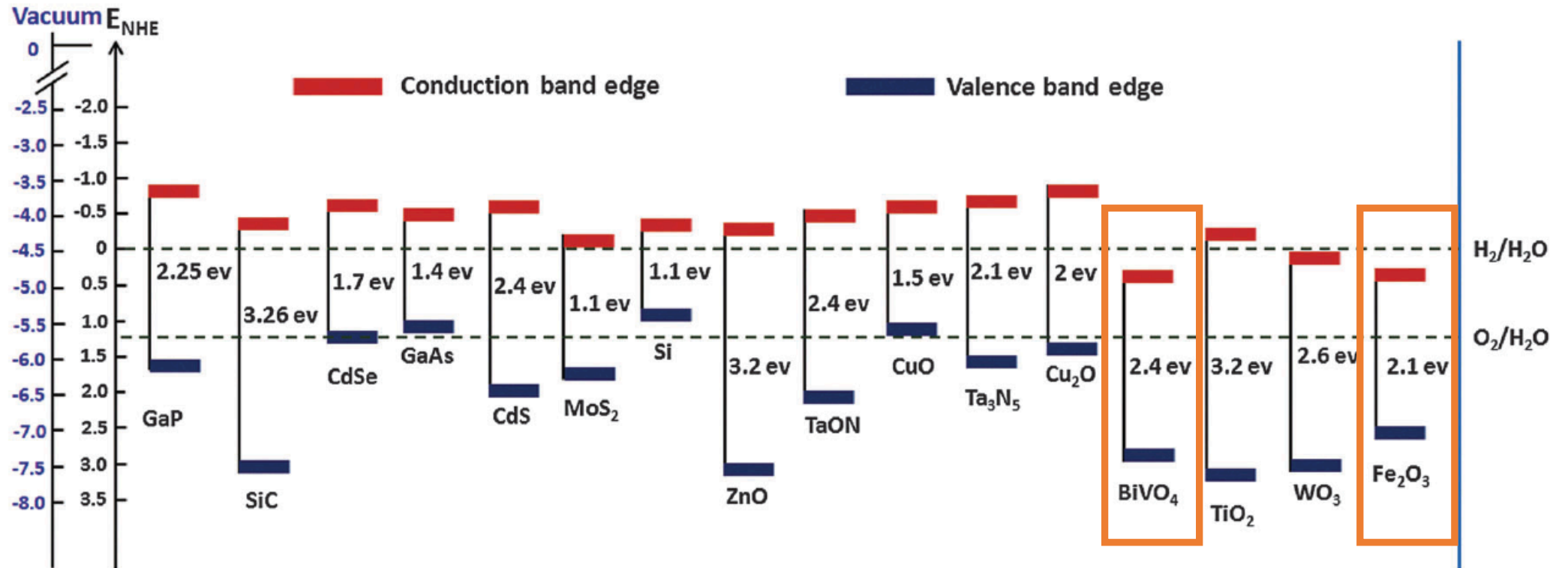
CuFeO_2



WSe_2

EPFL Examples of Photoelectrodes

Band edge positions of semiconductors in contact with the aqueous electrolyte at pH = 0 relative to NHE and the vacuum level.



Advantages

- Cheap and abundant (Fe in the earth crust, 6.3% by weight)
- Stable
- Environmentally benign
- Absorbs over 16 % (AM 1.5G, $E_g = 2.1$ eV)
- Theoretical max STH = 15%, $J_{max} = 12.5$ mA/cm²

Challenges

Bulk problems

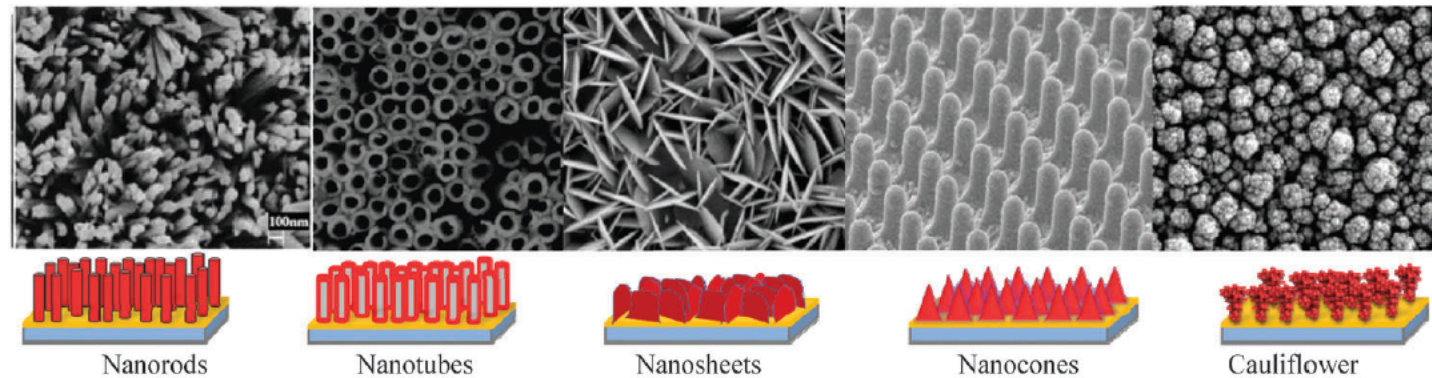
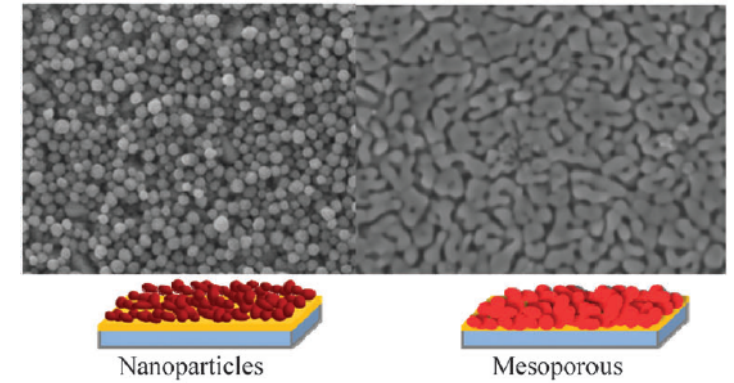
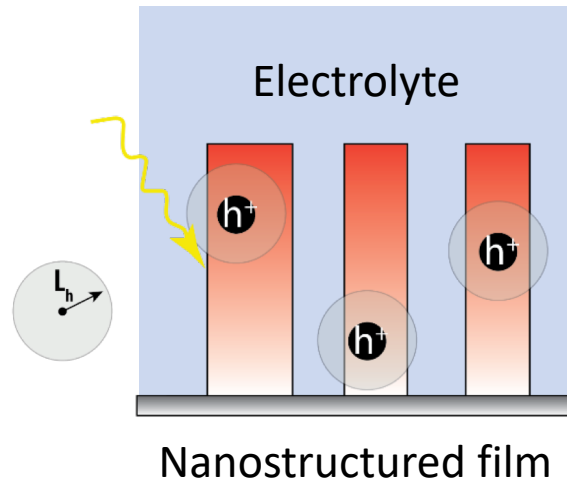
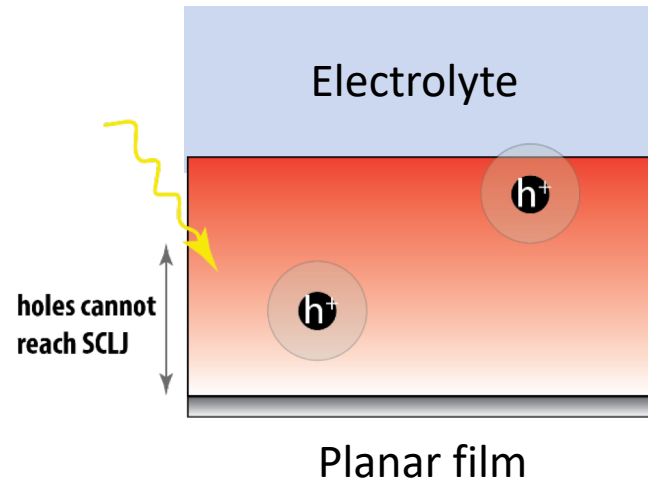
- Short hole diffusion length ($L_D = 5$ nm) (light penetration depth of 118 nm at 550 nm wavelength)
- Poor conductivity (10^{-6} $\Omega^{-1}\text{cm}^{-1}$ for single crystal and 10^{-14} $\Omega^{-1}\text{cm}^{-1}$ for polycrystal)

Surface problems

- High overpotential for water oxidation kinetics (surface trap states)

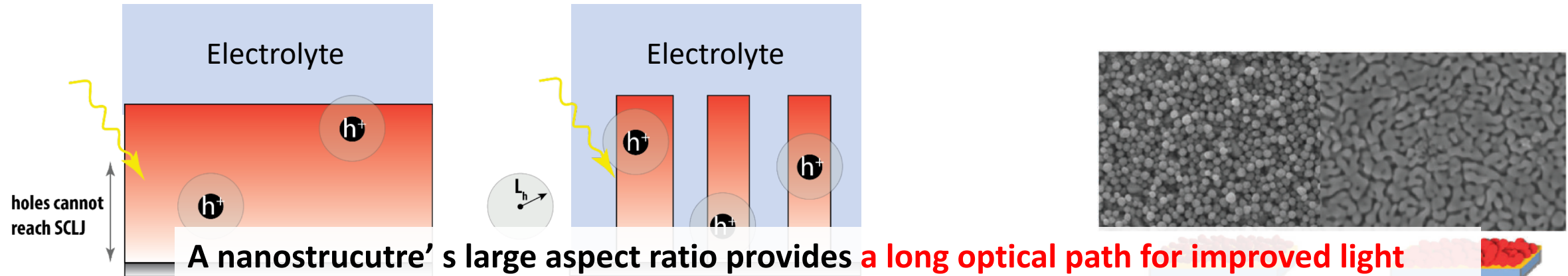


EPFL Bulk Problems in $\alpha\text{-Fe}_2\text{O}_3$ (hematite)

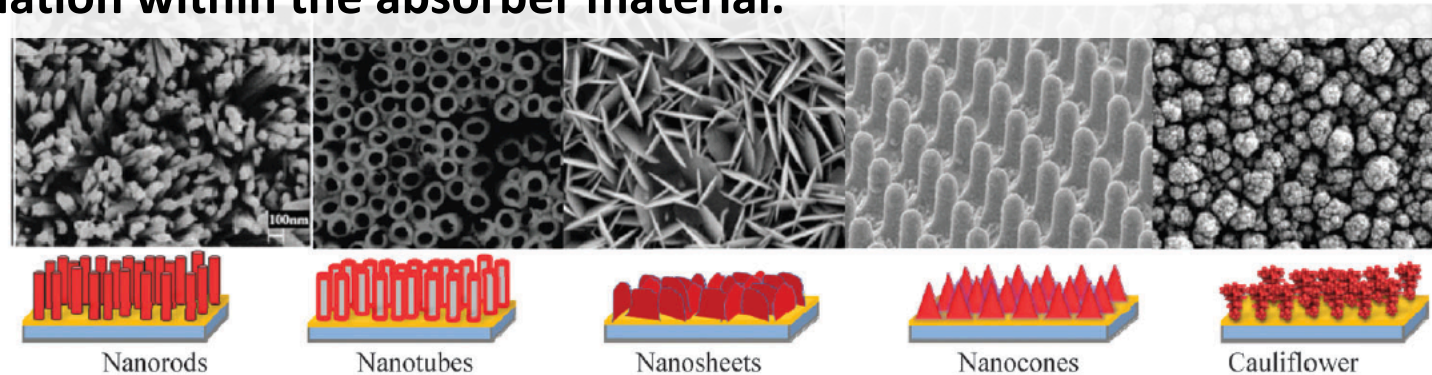


A. G. Tamirat et al., *Nanoscale Horiz.*, **1**, 243 (2016)

EPFL Bulk Problems in $\alpha\text{-Fe}_2\text{O}_3$ (hematite)

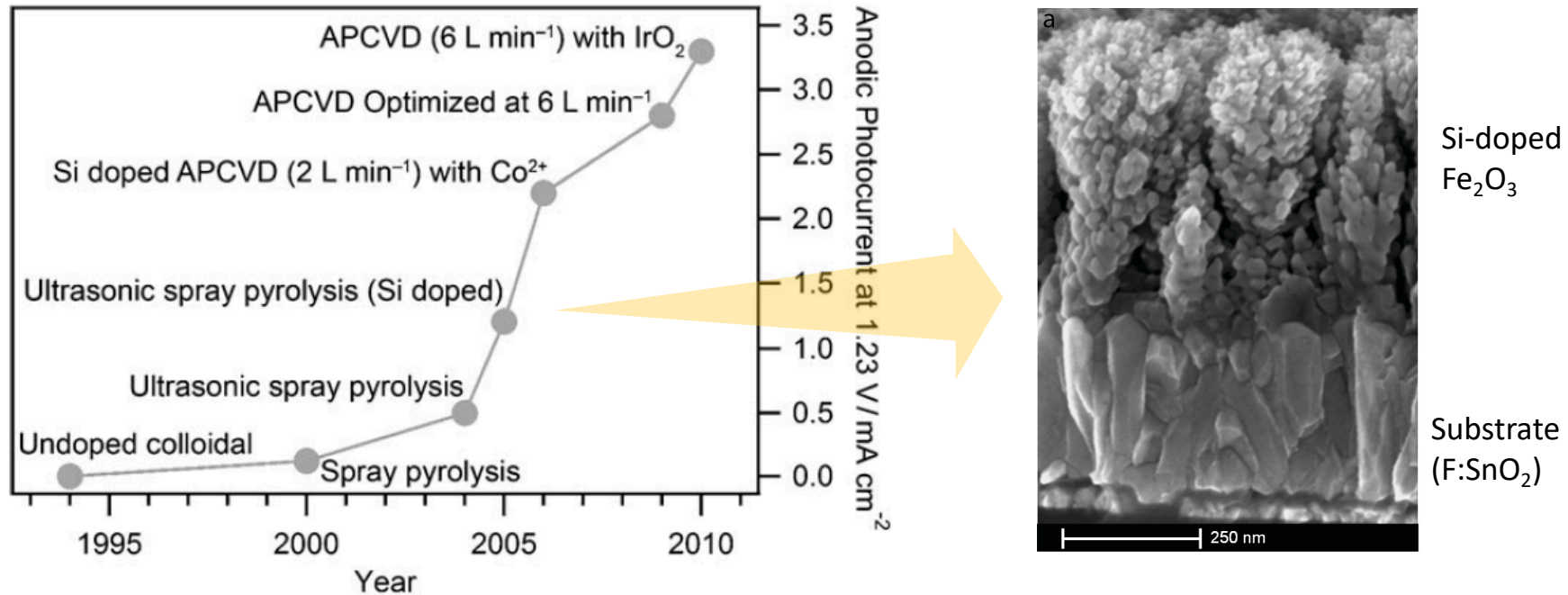


A nanostructure's large aspect ratio provides a long optical path for improved light absorption along the vertical axis, while its much smaller diameter facilitates collection of minority carriers over a shorter distance, minimizing the probability of recombination within the absorber material.



A. G. Tamirat et al., *Nanoscale Horiz.*, 1, 243 (2016)

EPFL Bulk Problems in $\alpha\text{-Fe}_2\text{O}_3$ (hematite)



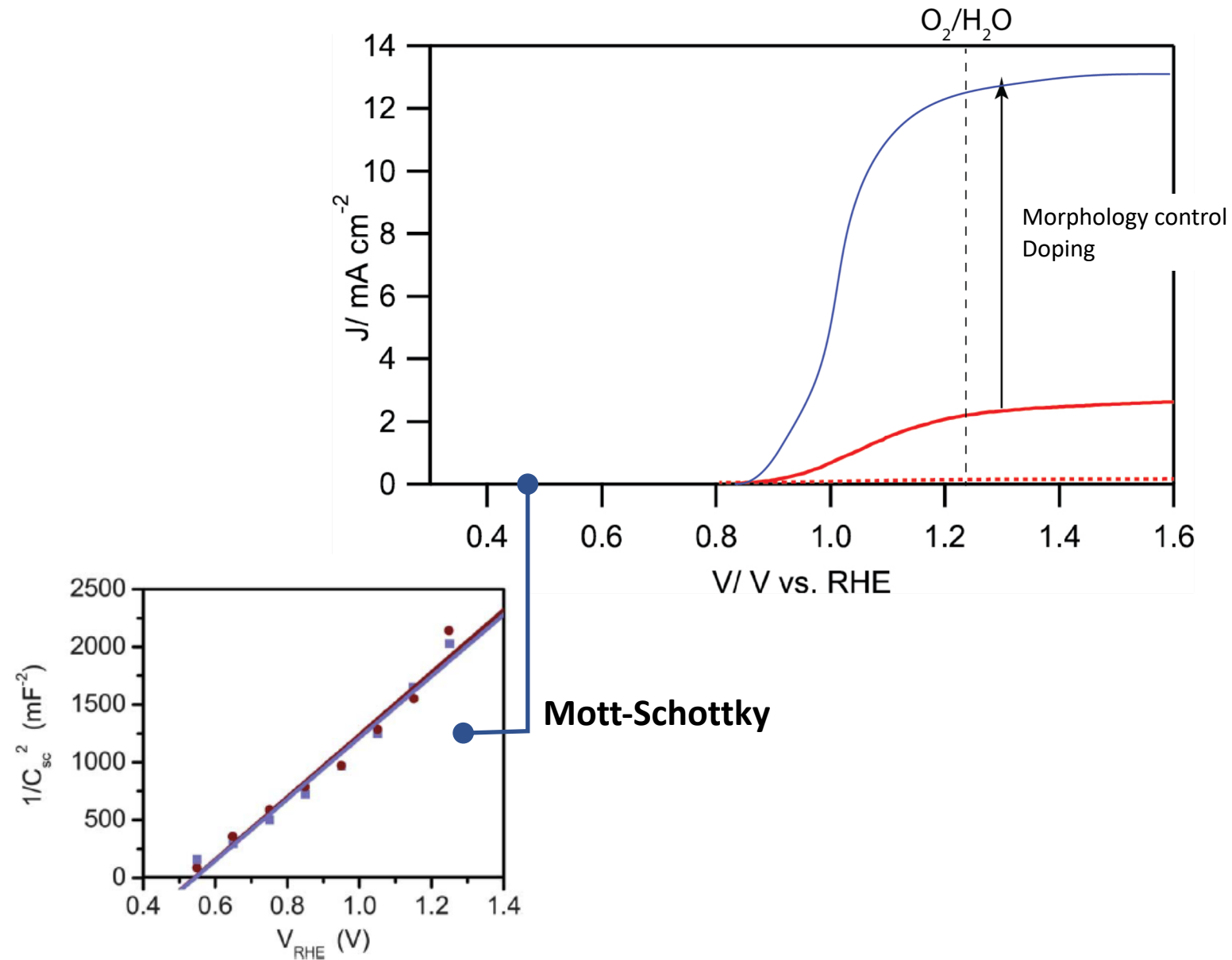
K. Sivula et al., *Chemsuschem*, **4**, 432 – 449 (2011)

- Ti⁴⁺, Sn⁴⁺, Zr⁴⁺, Nb⁵⁺ (n-type)
- Mg²⁺, Cu²⁺ (p-type)

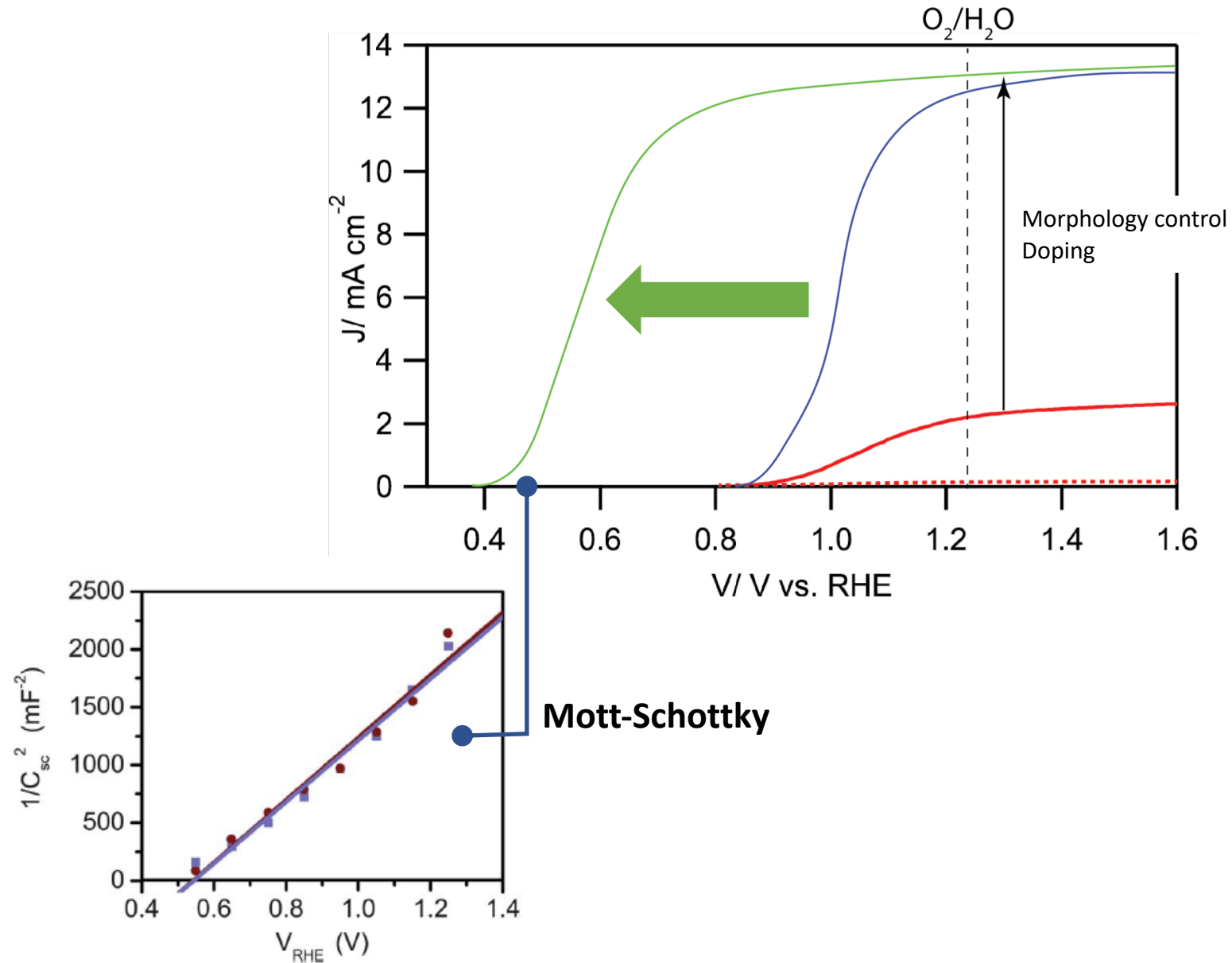
To promote charge transfer by increasing donor density and improve the electronic conductivity of hematite.

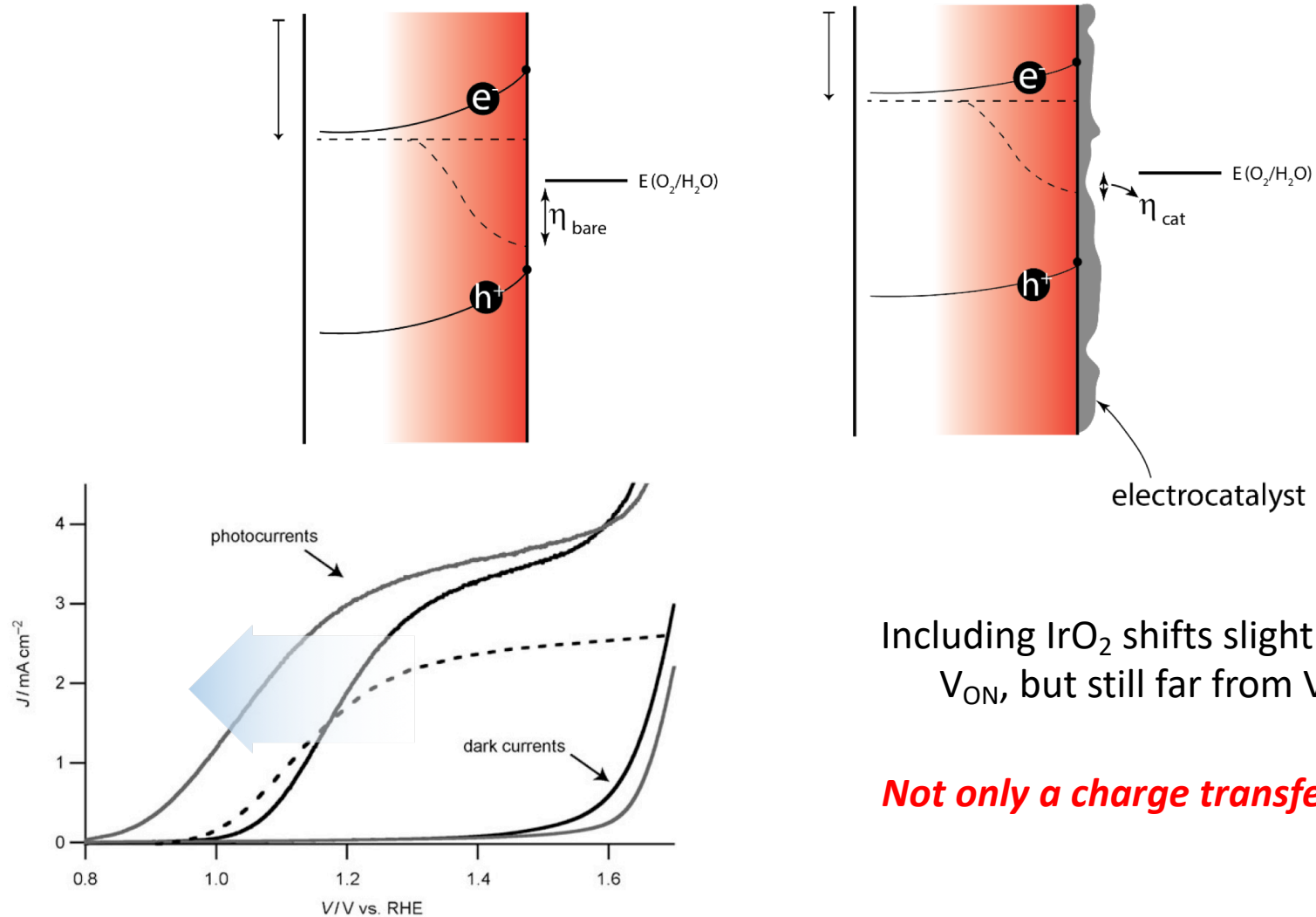
Ex) Zr⁴⁺ doped hematite: 0.1 $\Omega^{-1}\text{cm}^{-1}$ with 10^{19} cm^{-3} doping concentration

EPFL Bulk Problems in $\alpha\text{-Fe}_2\text{O}_3$ (hematite)



EPFL Bulk Problems in $\alpha\text{-Fe}_2\text{O}_3$ (hematite)

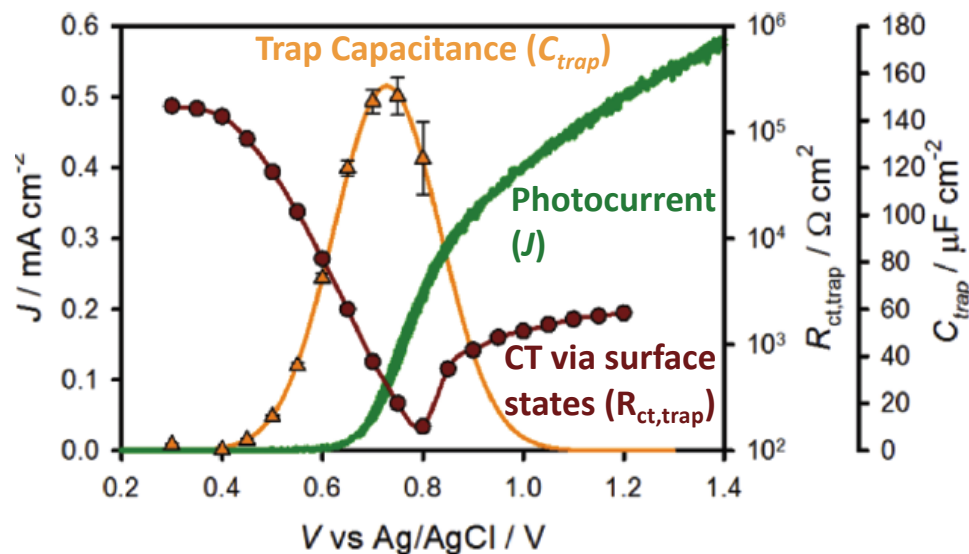
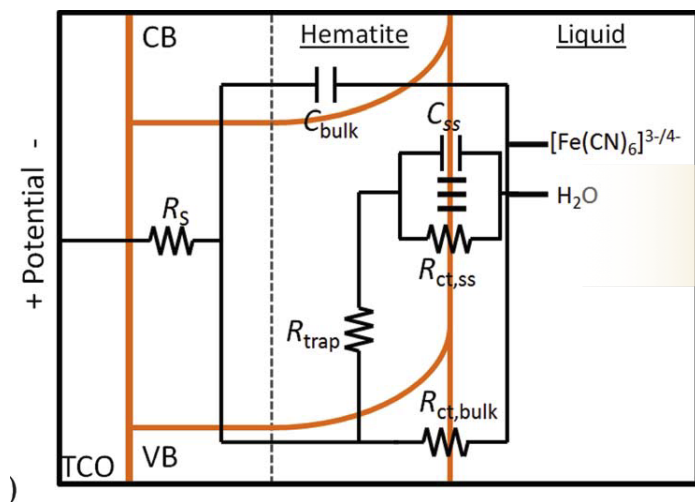


Coupling with an *electrocatalyst* $\downarrow$ = magnitude of applied potential vs. reference

Including IrO_2 shifts slightly the V_{ON} , but still far from V_{fb}

Not only a charge transfer issue?

Surface recombination. Examining the electrochemical properties of the SCLJ

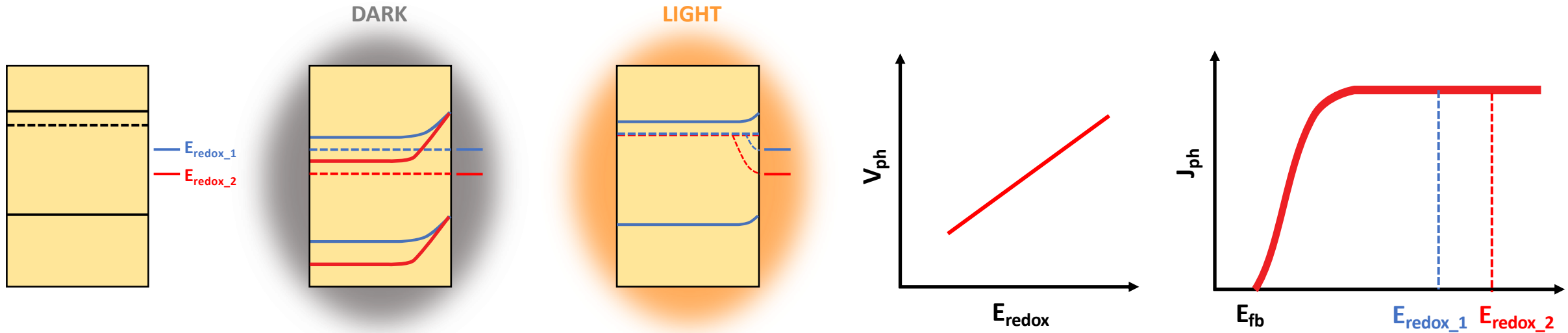


B. Klahr et al. *J. Am. Chem. Soc.*, **134**, 4294 (2012)

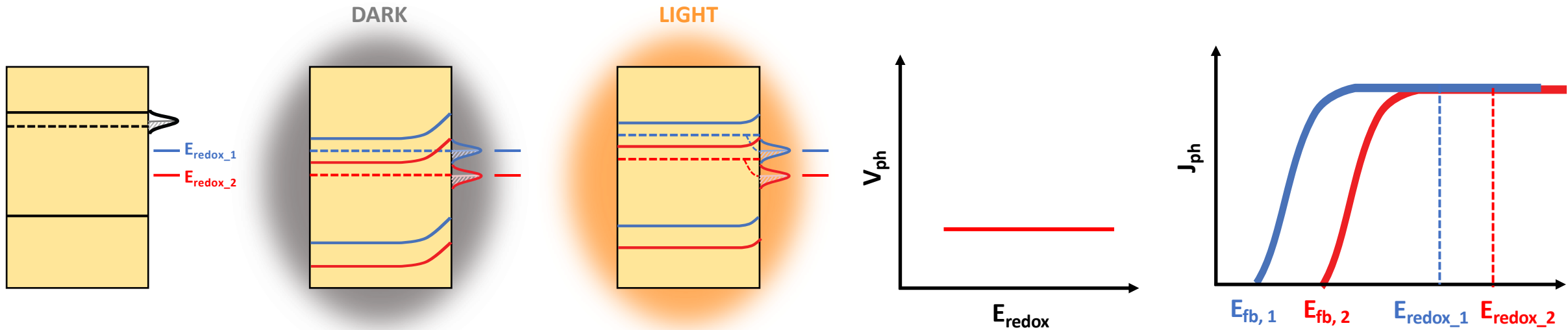
- C_{trap} indicate the **accumulation of charges at the SCLJ** just before the water oxidation starts.
- Charge transfer takes place from this surface state.
- Suggests that applying enough potential to overcome the strong surface recombination is necessary: “the delayed” onset of photocurrent is caused by **Fermi Level Pinning**.

EPFL Fermi Level Pinning (FLP)

No surface state / No FLP (band edge pinning)

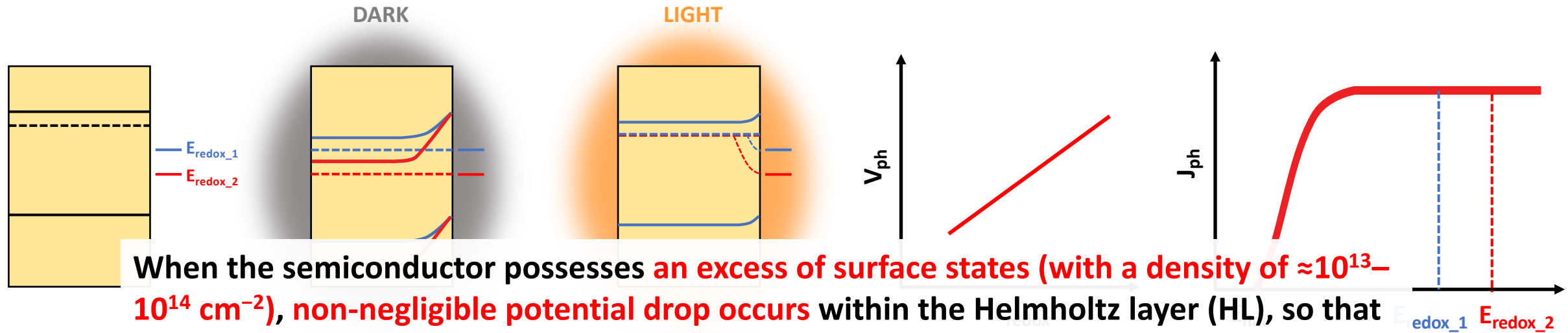


Presence of surface state/ Fermi Level Pinning



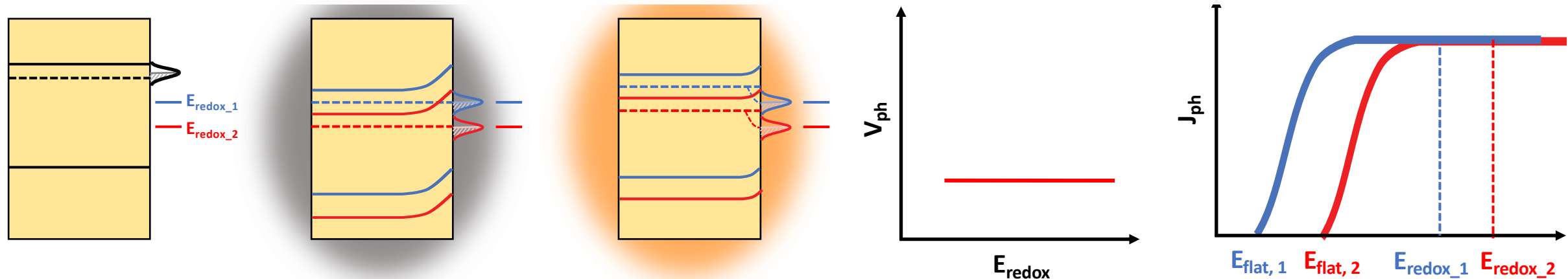
EPFL Fermi Level Pinning (FLP)

No surface state / No FLP (band edge pinning)

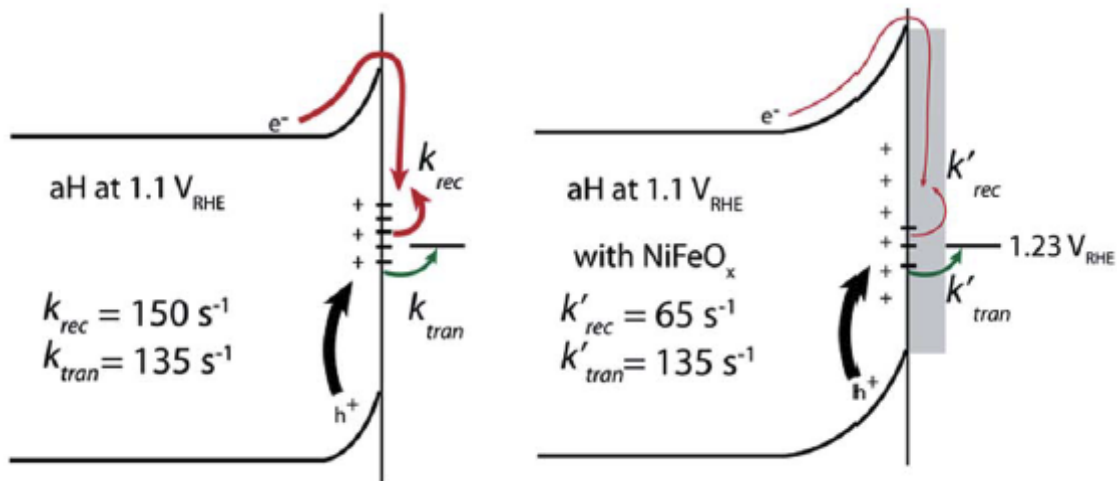


Presence of surface state / Fermi-level Pinning

Under Fermi-level pinning conditions, the degree of band bending remains unchanged.

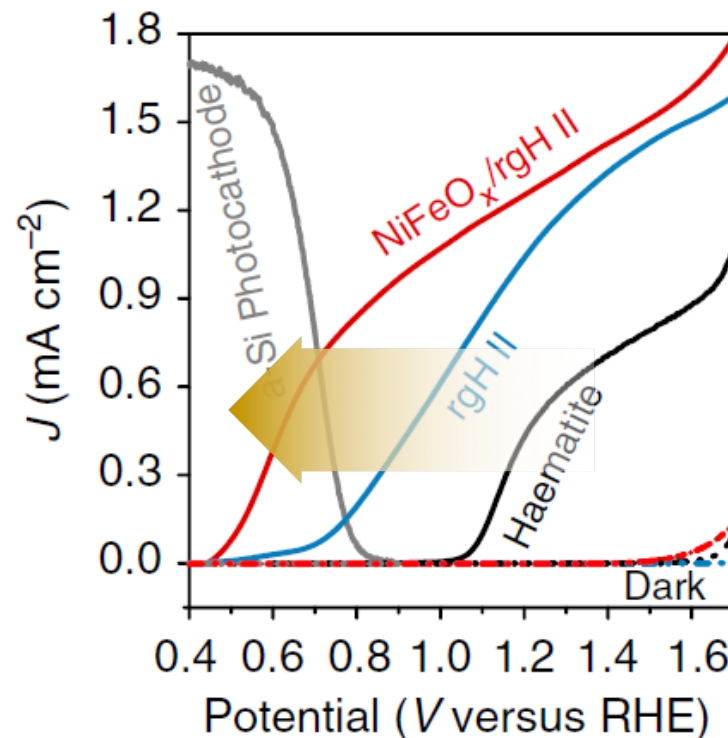


Surface recombination. Examining the electrochemical properties of the SCLJ



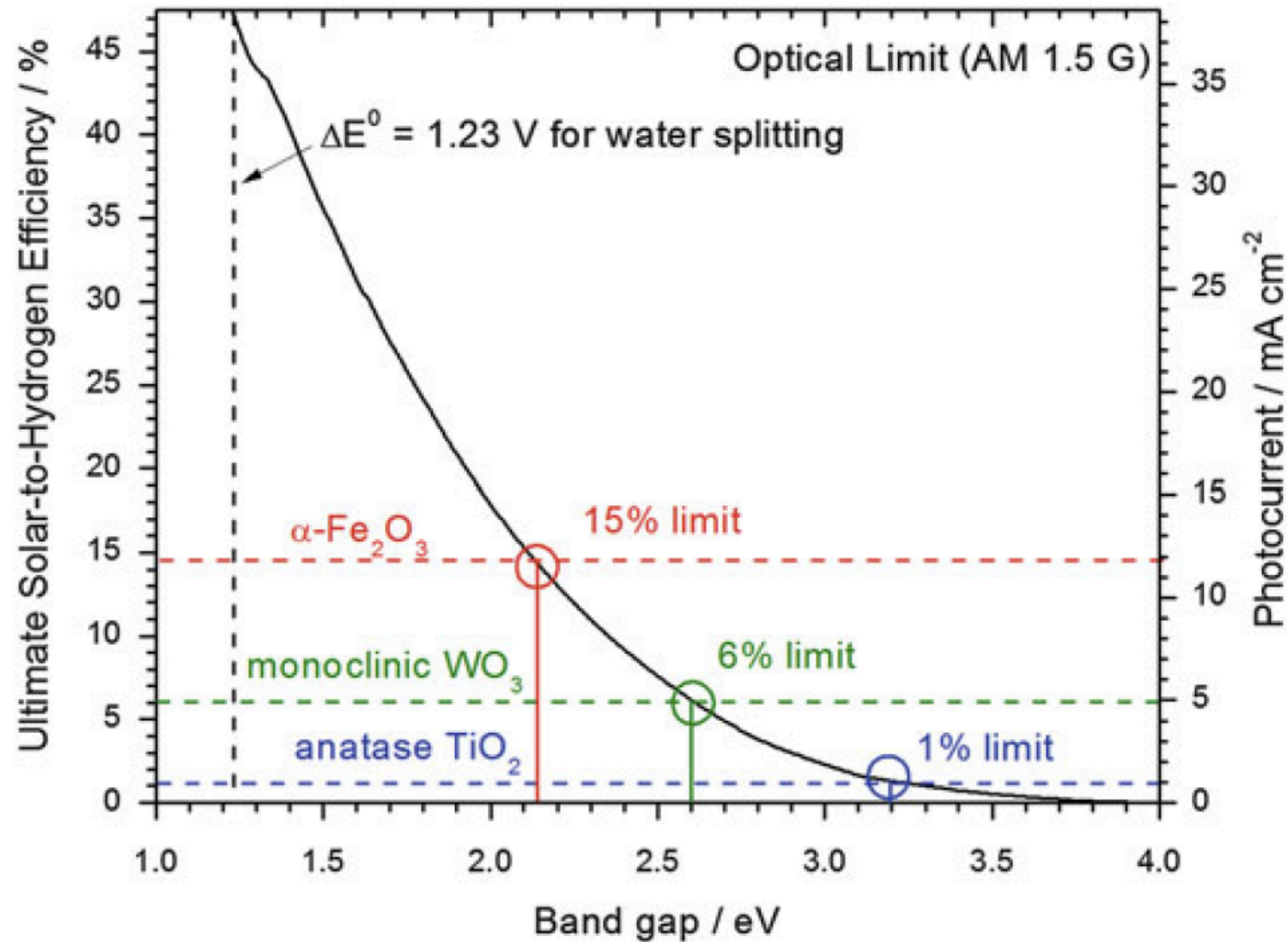
NiFeO_x **passivate** surface traps.

Thorne *et al. Chem. Sci.* **7**, 3347 (2016)



Deposition of NiFeO_x shifts V_{on}
 close to V_{fb} !!!

Jang *et al. Nature Commun.* **6**, 7447 (2015)



Advantages

- Cheap and abundant
- Stable
- Environmentally benign
- Theoretically 7.5 mA cm⁻² (2.5 eV)

Challenges

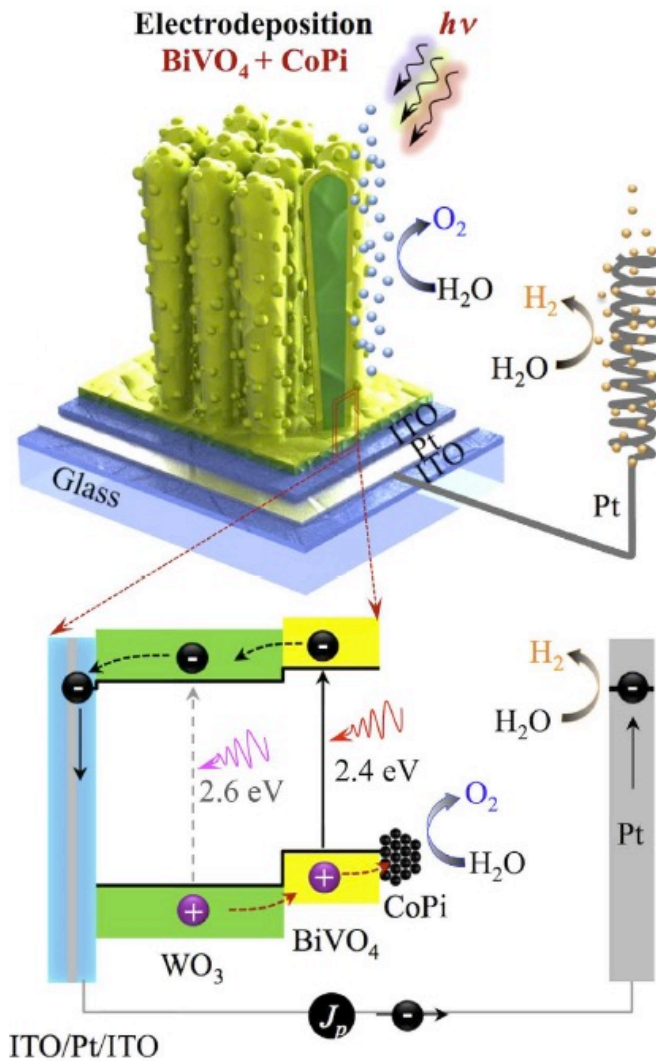
Bulk problems

- Short carrier diffusion length (**L_D = 70 nm**)

Surface problems

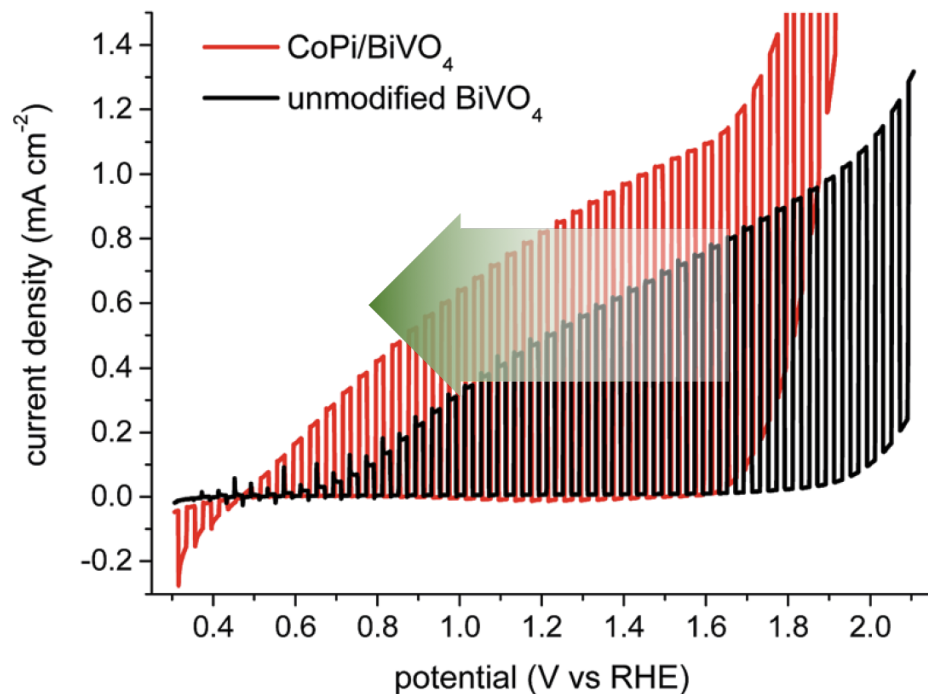
- Poor kinetics for water oxidation



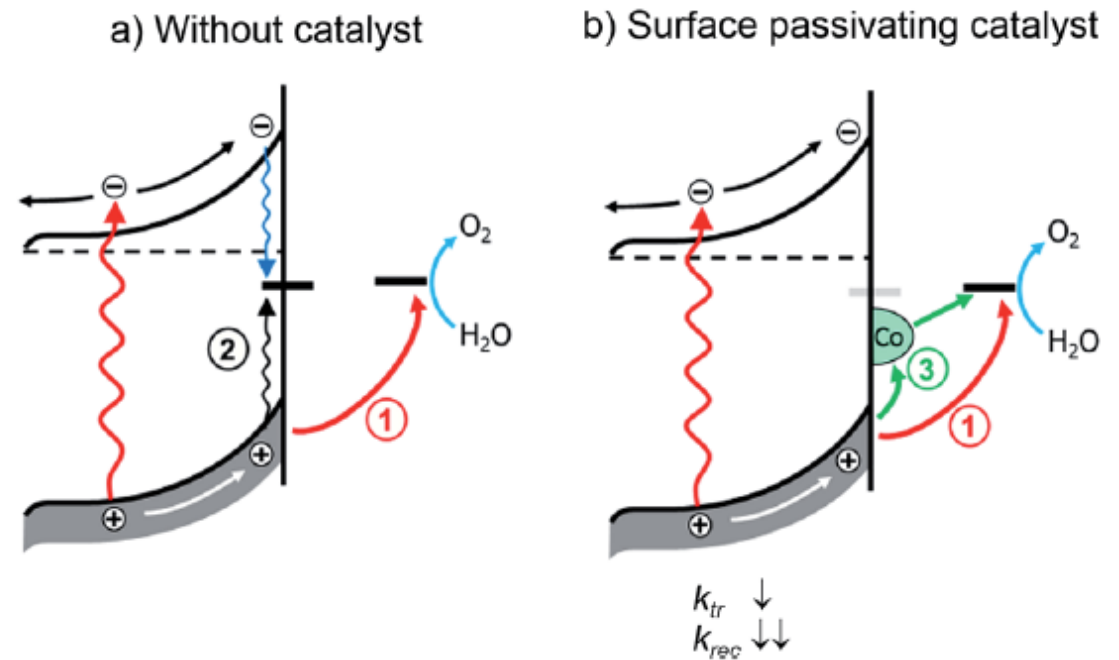


Compensate the short L using **extremely thin-absorber (ETA) heterojunction** structure

- BiVO_4 thin enough to ensure extraction of carriers
- *Nanostructure* with high-aspect ratio to ensure high light-absorption



Deposition of CoPi (Cobalt phosphate, *co-catalyst*) enhances performance.



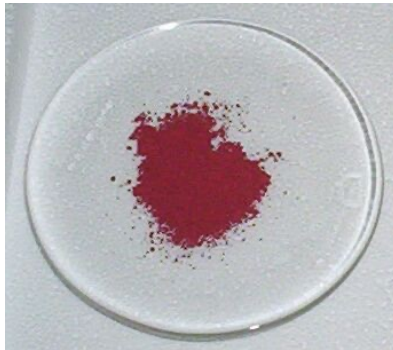
C. Zachäus *et al.* *Chem. Sci.* **8**, 3712 (2017)

Analysis of carrier dynamics of photogenerated holes in BiVO_4 suggests that the main role of CoPi on BiVO_4 is not to enhance the water oxidation kinetics, but to suppress surface recombination.

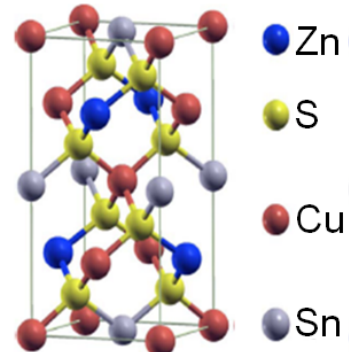
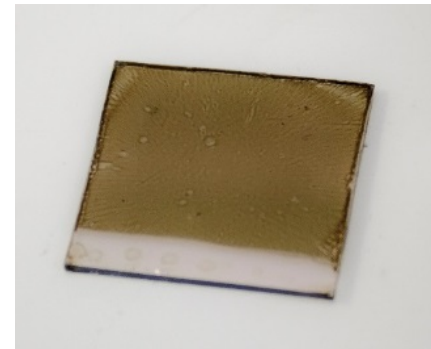
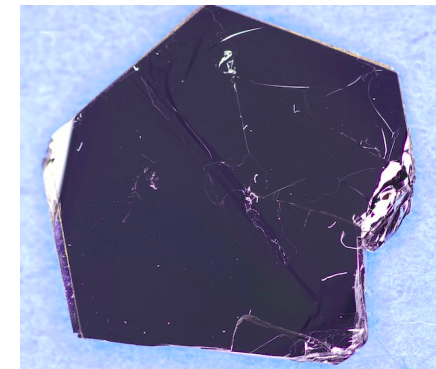
Photoanode

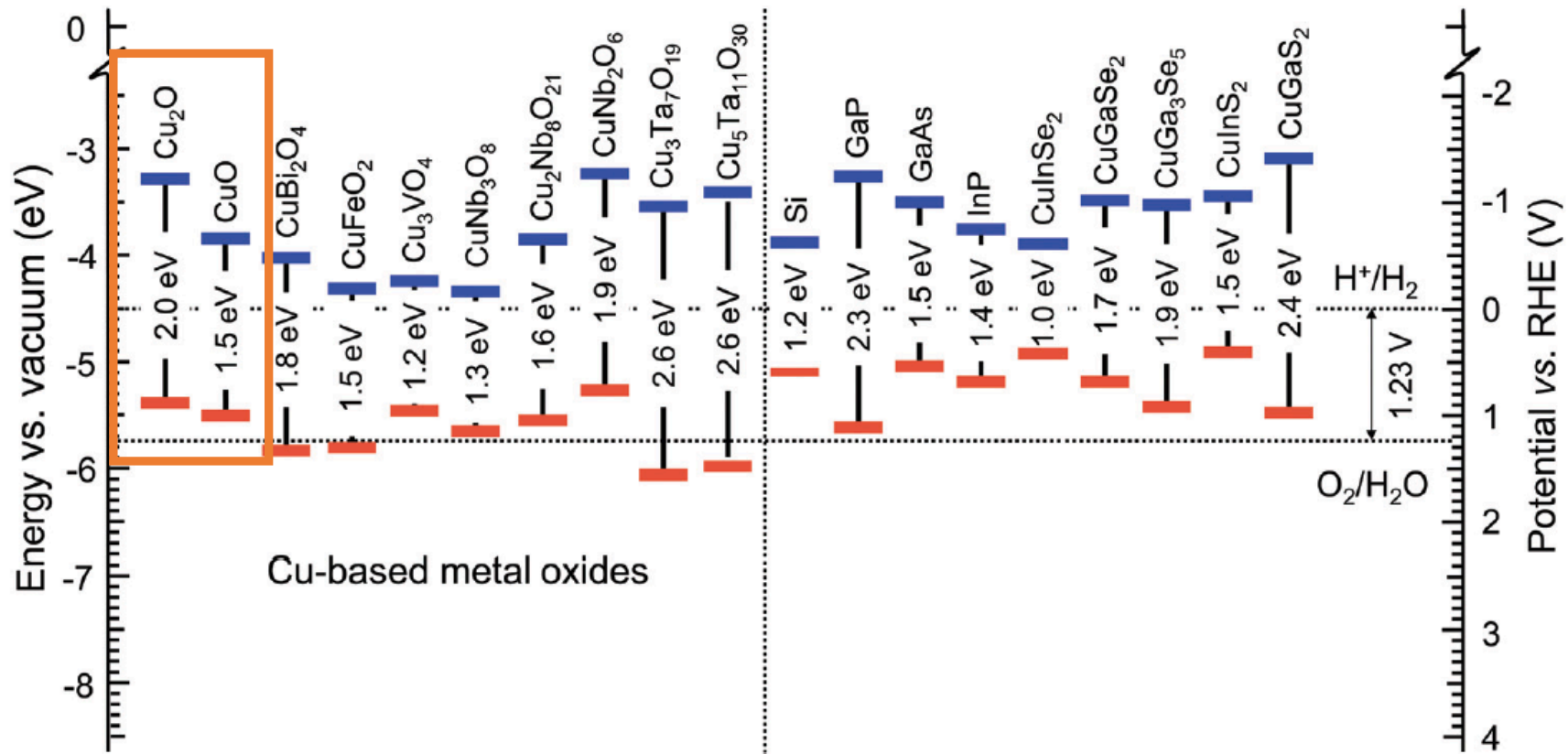
 WO_3  BiVO_4  $\alpha\text{-Fe}_2\text{O}_3$

Photocathode



Copper(I) oxide

 $\text{Cu}_2\text{ZnSnS}_4$  CuFeO_2  WSe_2



C. Li et al., *Energy Environ. Sci.*, **13**, 3269 – 3306 (2020)

Advantages

- Cheap and abundant
- Environmentally benign
- Band gap 2 eV

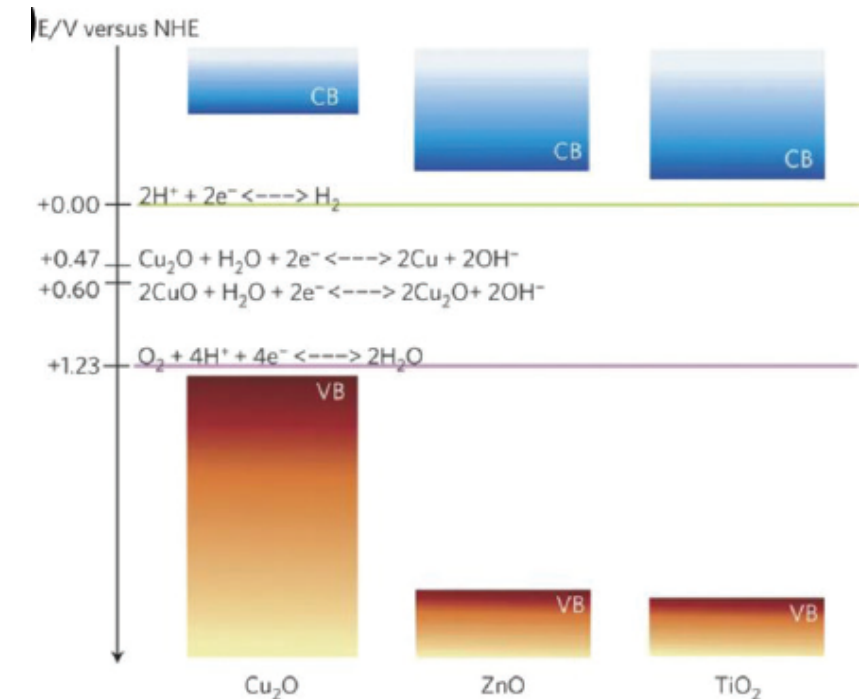
Challenges

Bulk problems

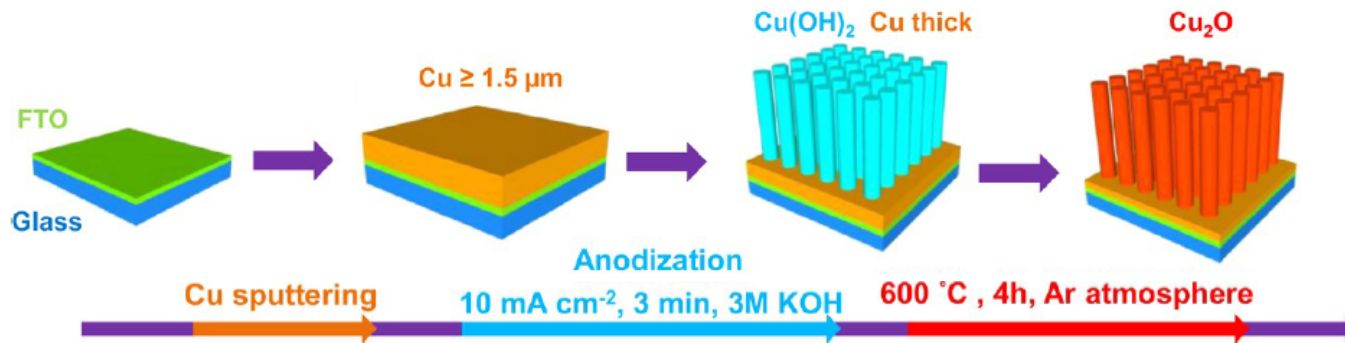
- Minority carrier diffusion length around 200 nm (light penetration depth 2.2 μm at 550 nm)

Surface problems

- Instability under operational condition (Facile reduction to Cu)

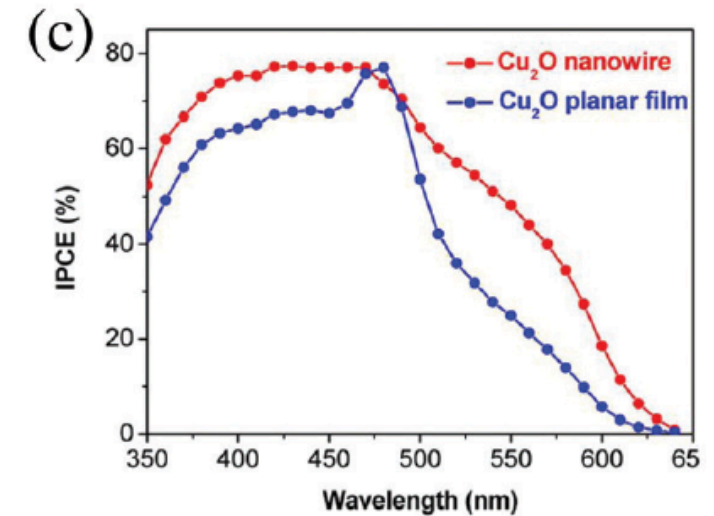
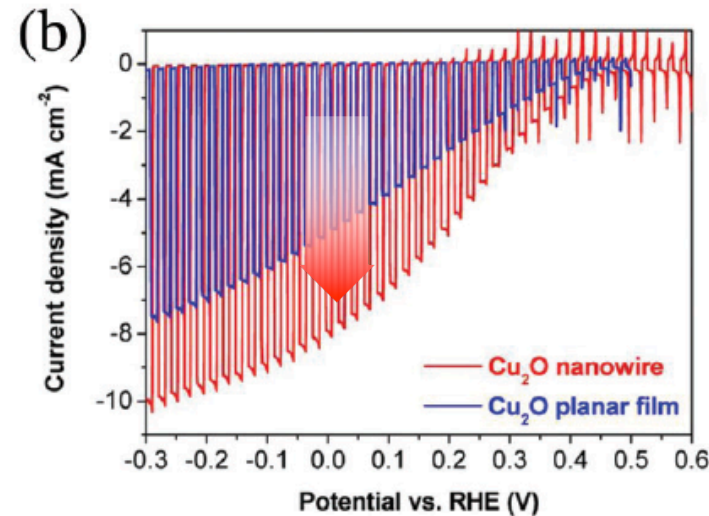
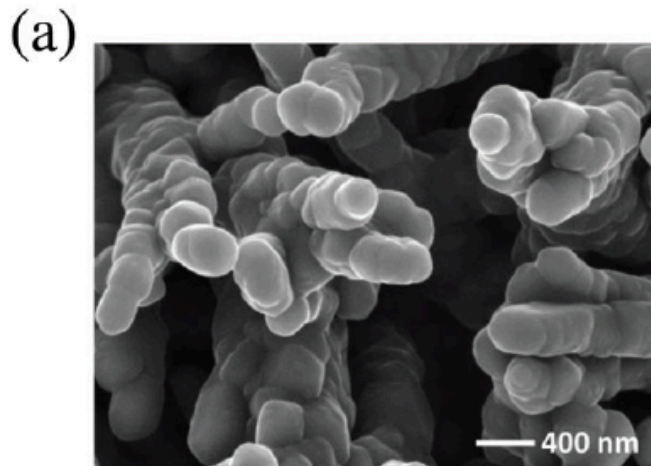


EPFL Nanostructuring Cu_2O as a photocathode



Photocathode: $\text{Cu}_2\text{O}/\text{AZO}/\text{TiO}_2/\text{RuO}_x$

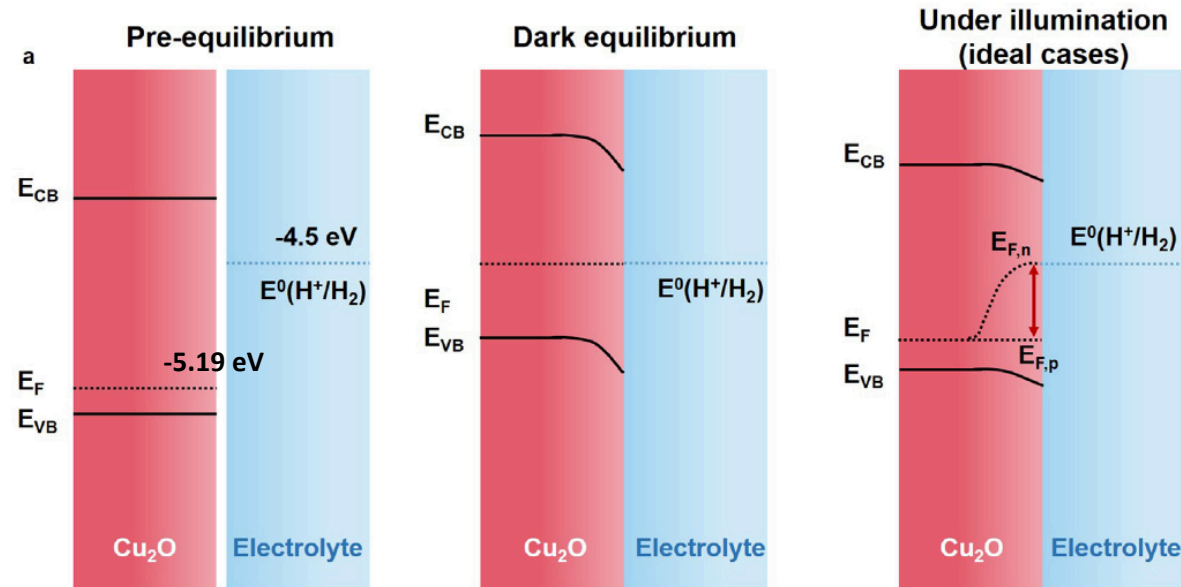
- Nanowire Cu_2O
- 20 nm Al-doped ZnO/100nm TiO_2 forms a buried p-n junction
- RuO_x catalyst



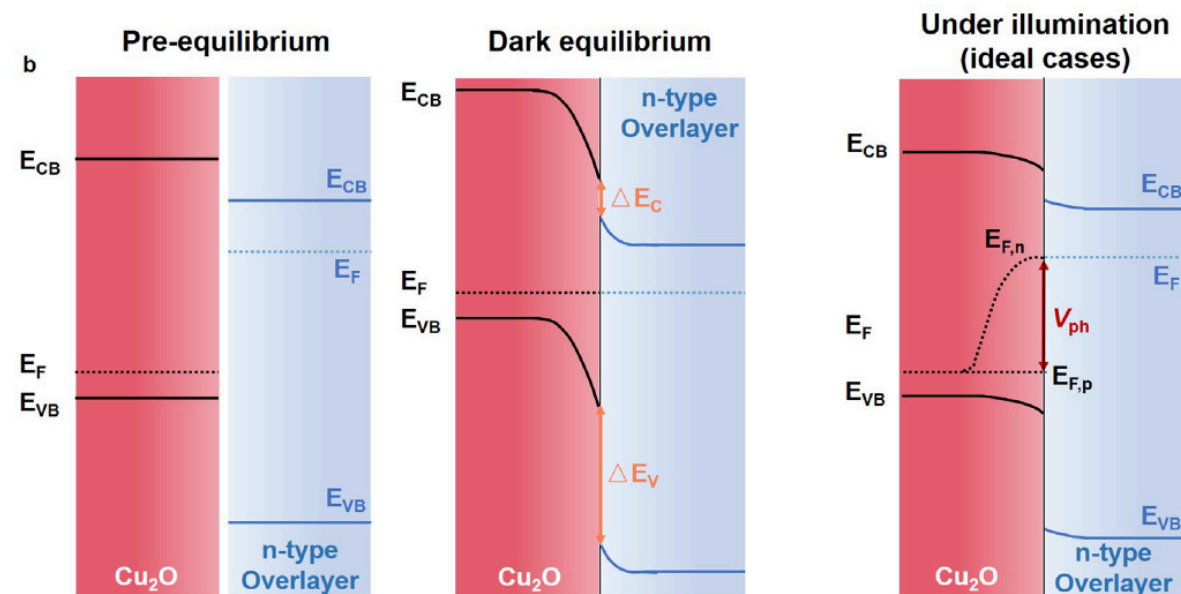
J. Luo et al., *Nano Lett.*, **16**, 1848 – 1857 (2016)

EPFL Improving the onset potential in Cu_2O photocathode

Cu_2O -liquid junction

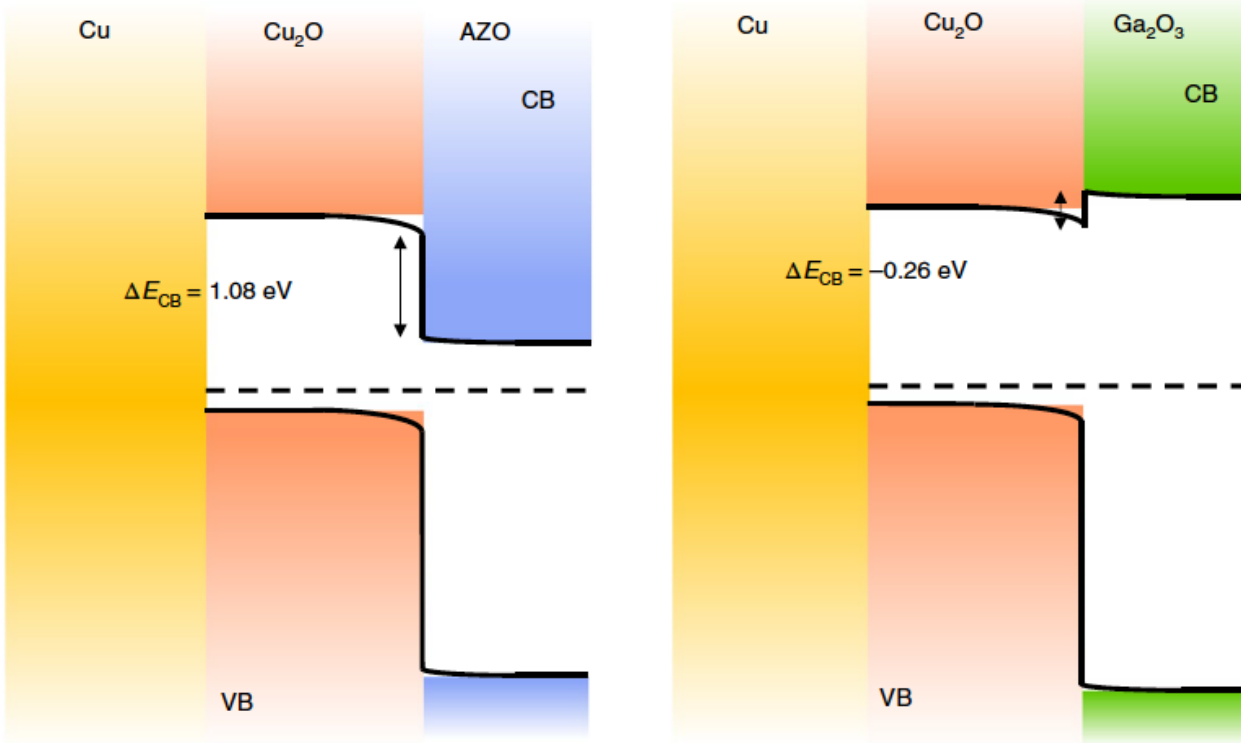


Cu_2O -n-type overlayer heterojunction (called buried junction)



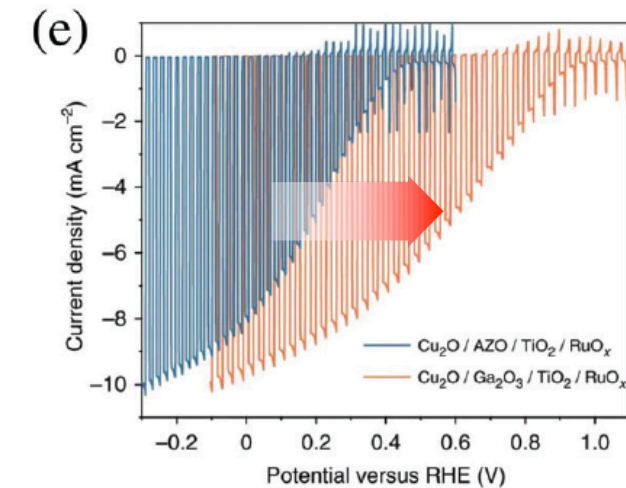
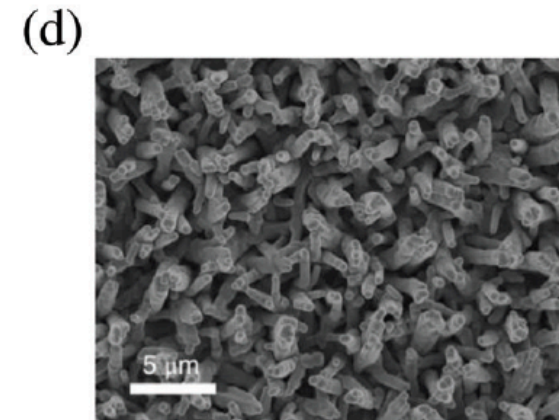
- Improved photovoltage
- Passivation against photocorrosion
- Still limited photovoltage due to a large conduction band offset

EPFL Improving the onset potential in Cu_2O photocathode



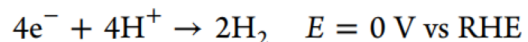
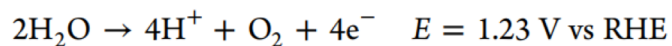
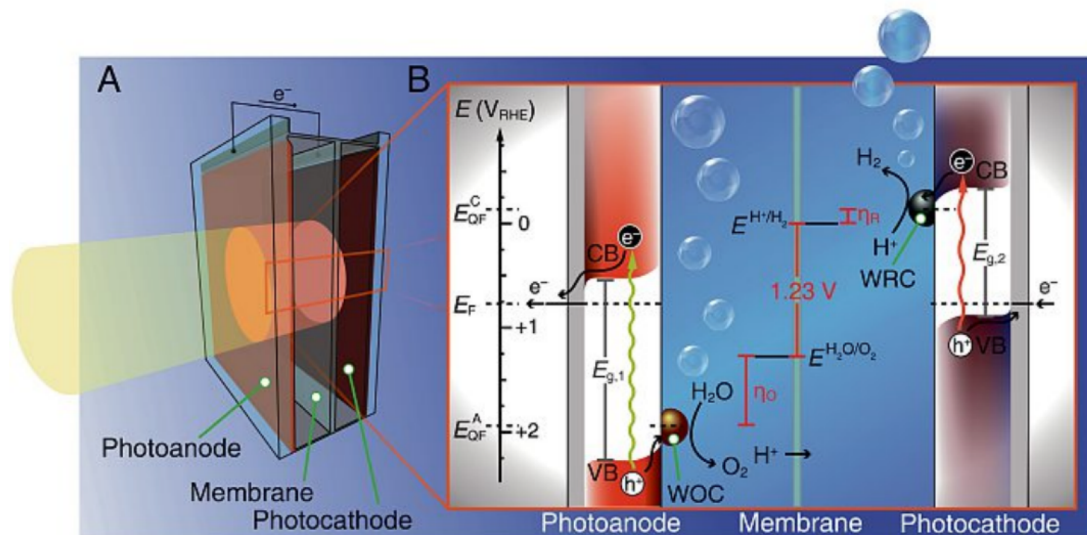
Photocathode: $\text{Cu}_2\text{O}/\text{Ga}_2\text{O}_3/\text{TiO}_2/\text{RuO}_x$

- The C.B. offset between Cu_2O and Ga_2O_3 is small.
- A build-up of a large photovoltage.



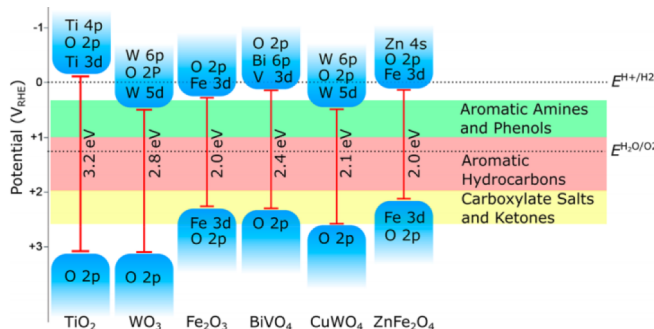
L. Pan et al., *Nature Catalysis*, **1**, 412 – 420 (2018)

- The formation of a **SEMICONDUCTOR-LIQUID JUNCTION (SCLJ)** can drive stand-alone photoelectrochemical reactions.
- There is still need for finding **NEW MATERIALS** for the design of tandem cells (complementary light absorption, robustness, excellent optoelectronic properties)
- Development of **NOVEL STRATEGIES** to effectively address issues like poor diffusion length, bulk recombination and/or surface recombination.



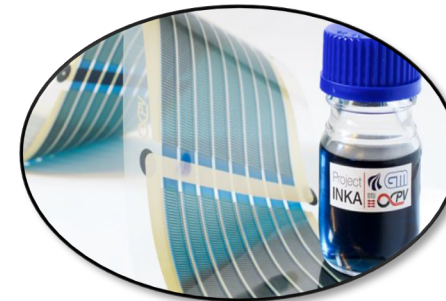
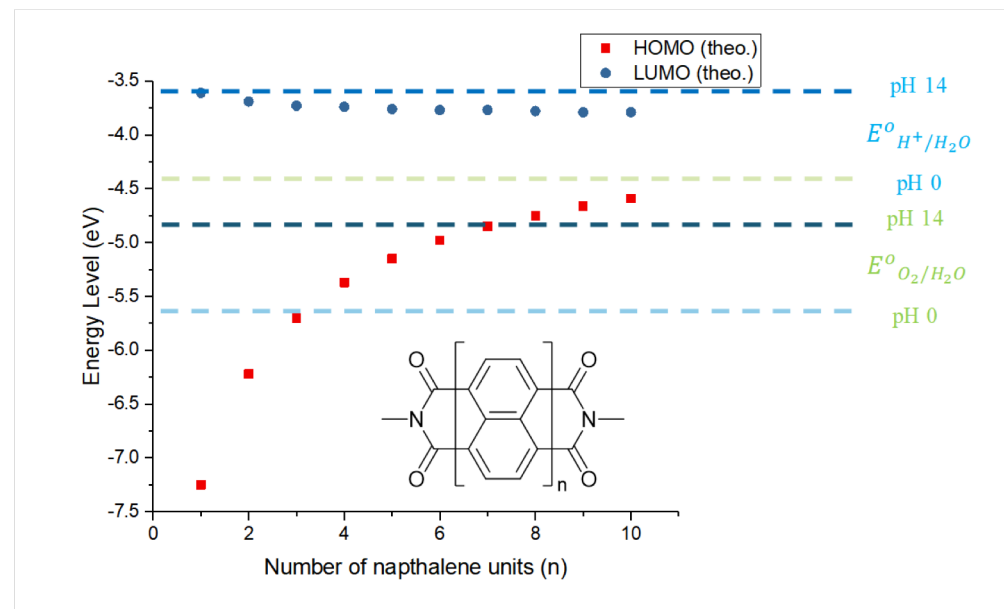
Inorganic semiconductors

- ✓ Harsh preparation condition
- ✓ Poor charge separation
- ✓ Fixed energy level



Organic semiconductors

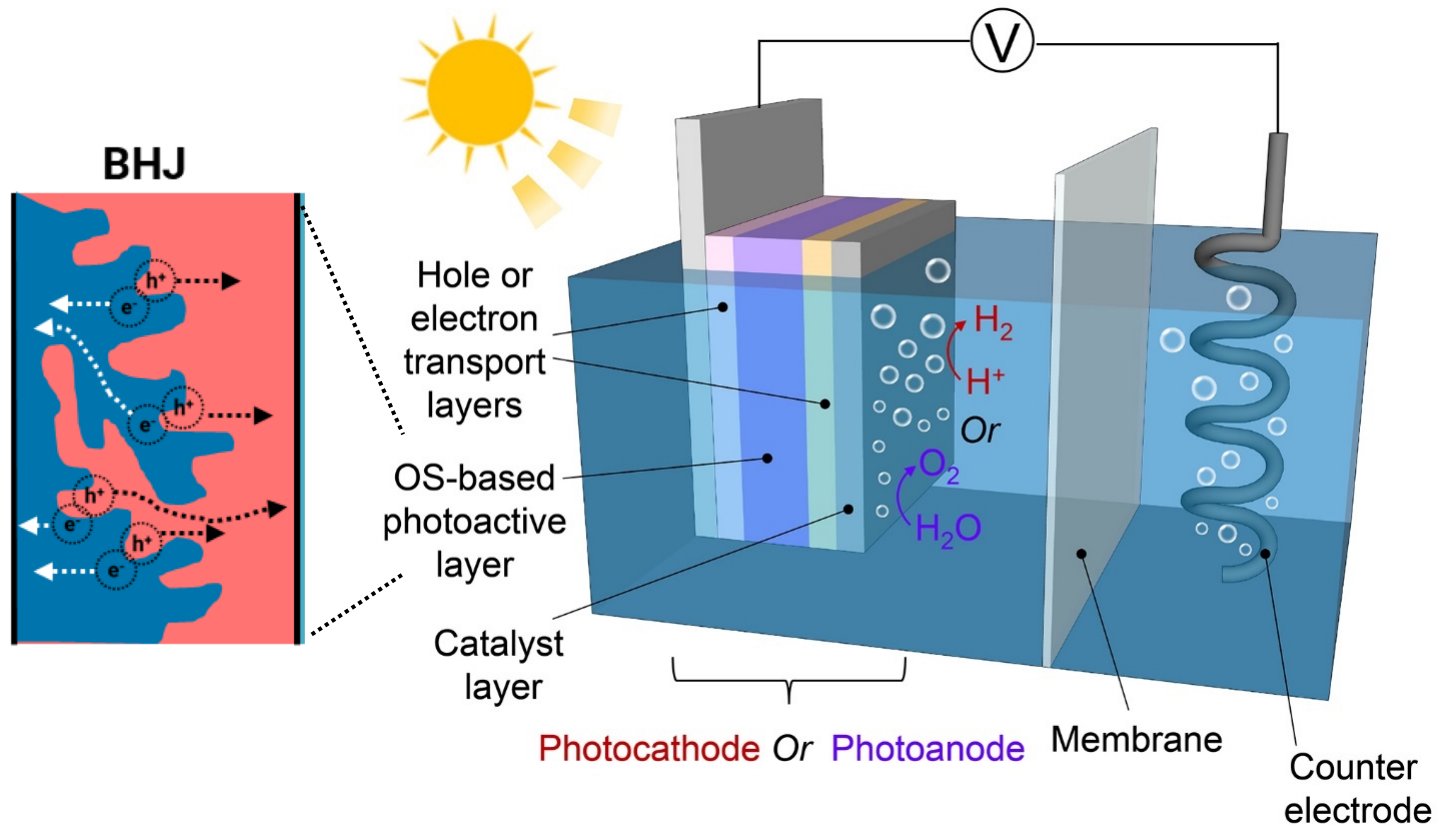
- ✓ Tunable energy levels
- ✓ Solution-processing & low temperature processing



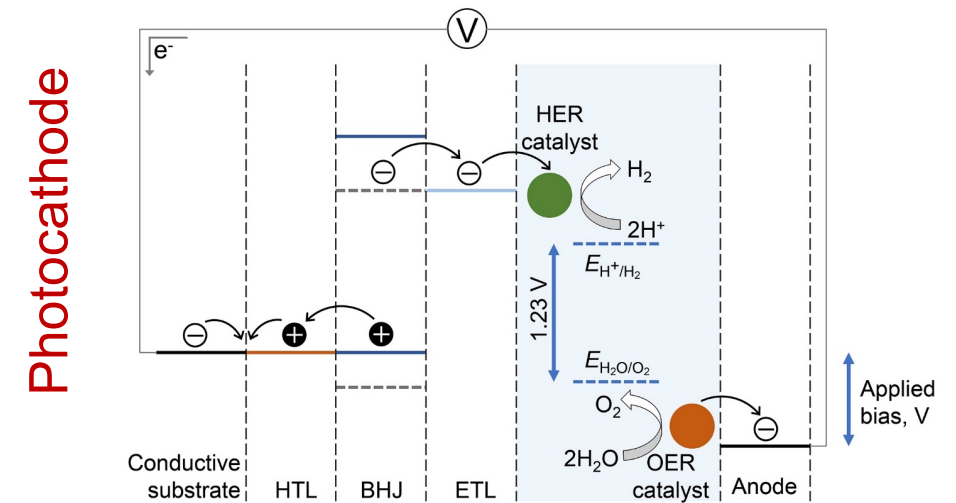
K. Sivula, *Chimia* **2017**, 71, 471-474

EPFL An Emerging Application for Organic Semiconductors

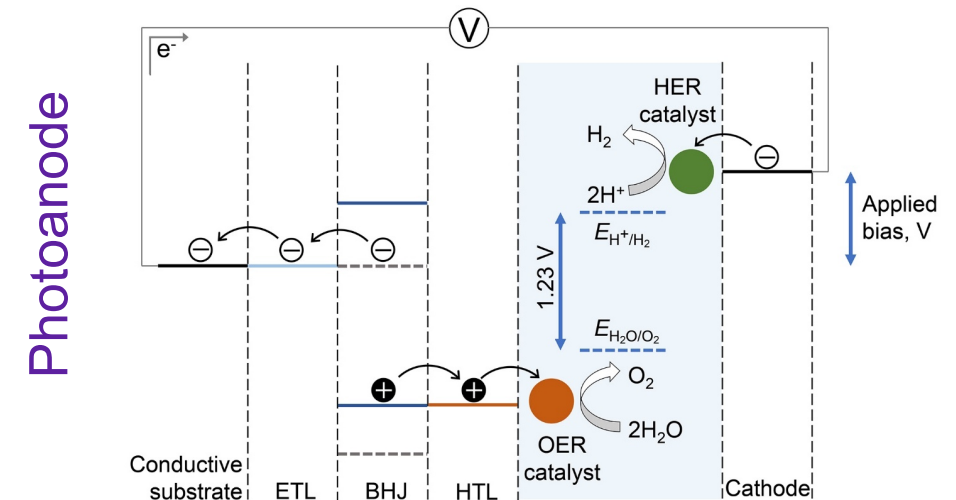
Solar-to-fuel conversion: "Artificial photosynthesis"



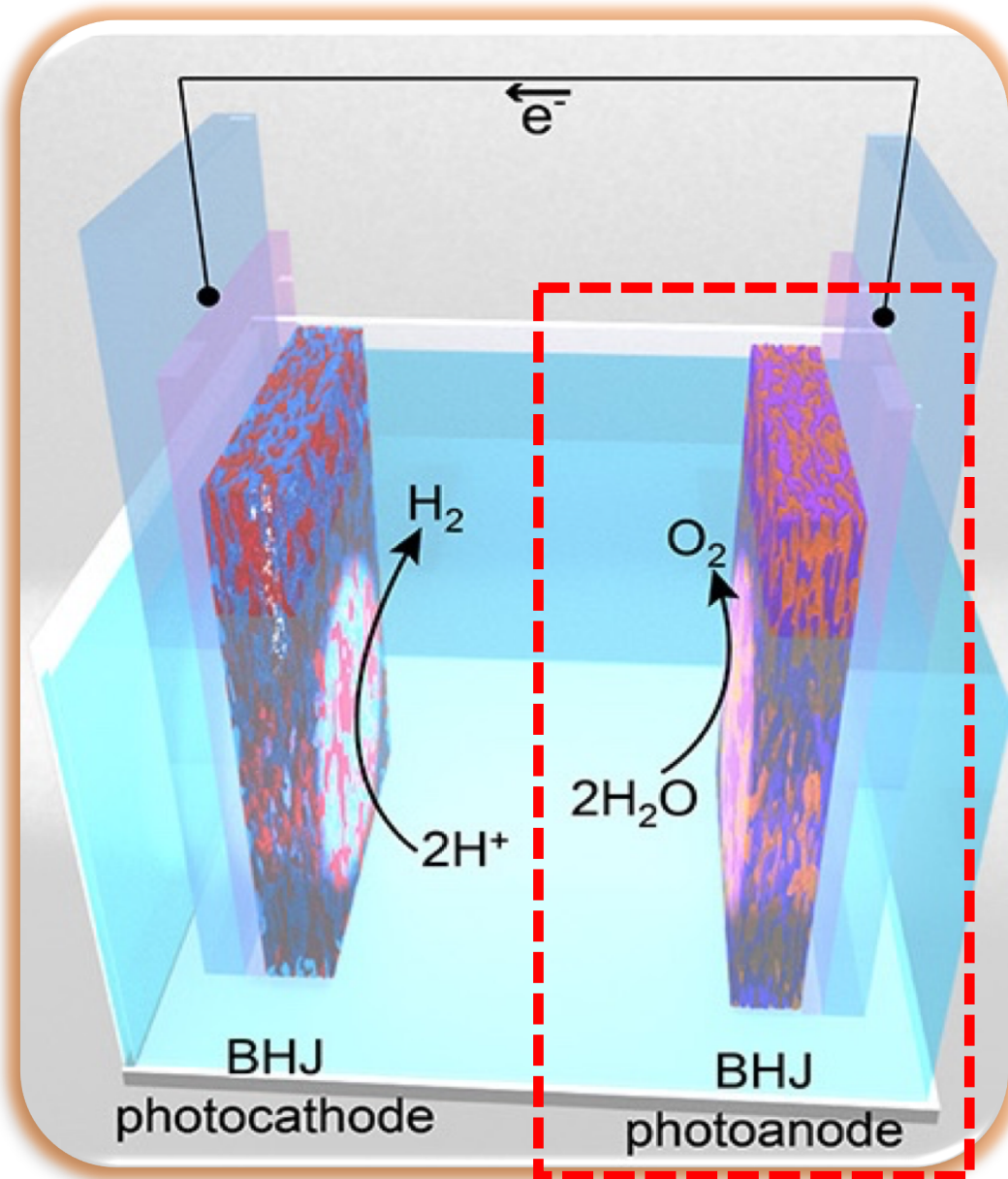
See review article: Yao et al. *Adv. Energy Mater.*, **2018**, 8, 1802585.



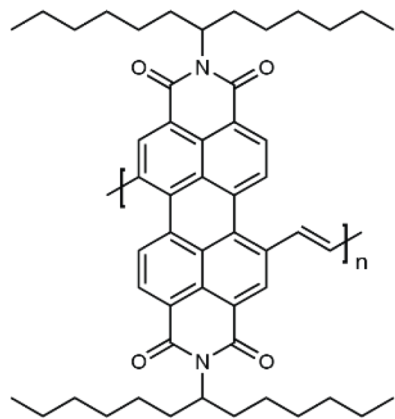
LUMO level of Acceptor higher than H^+/H_2 potential



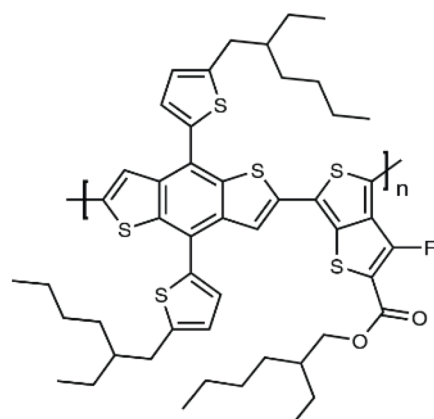
HOMO level of Donor lower than O_2/H_2O potential



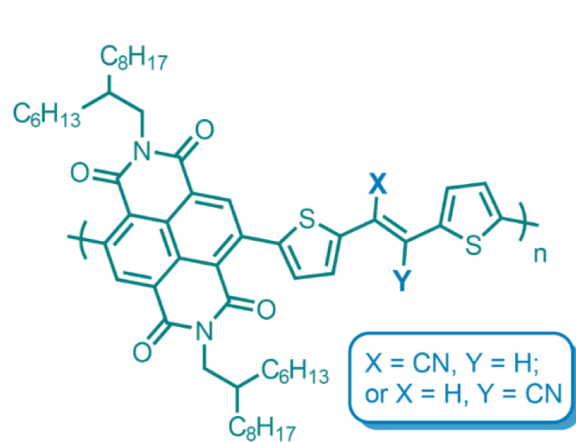
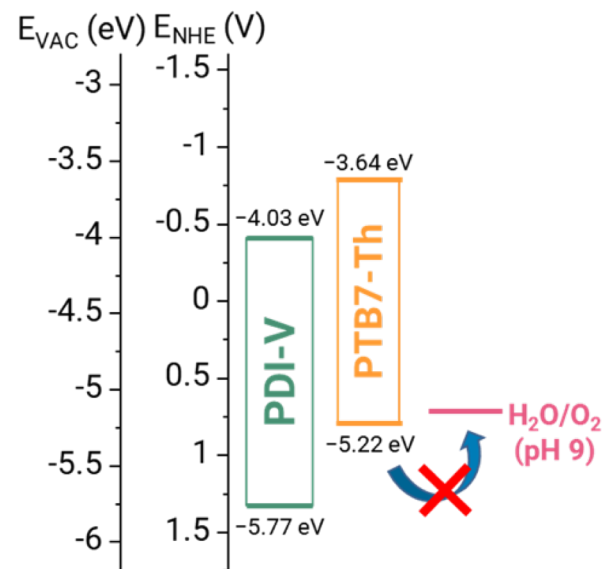
EPFL Identification of Ideal OS Materials: Photoanode



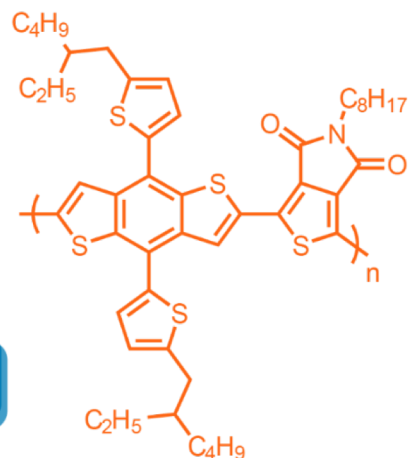
PDI-V (acceptor)



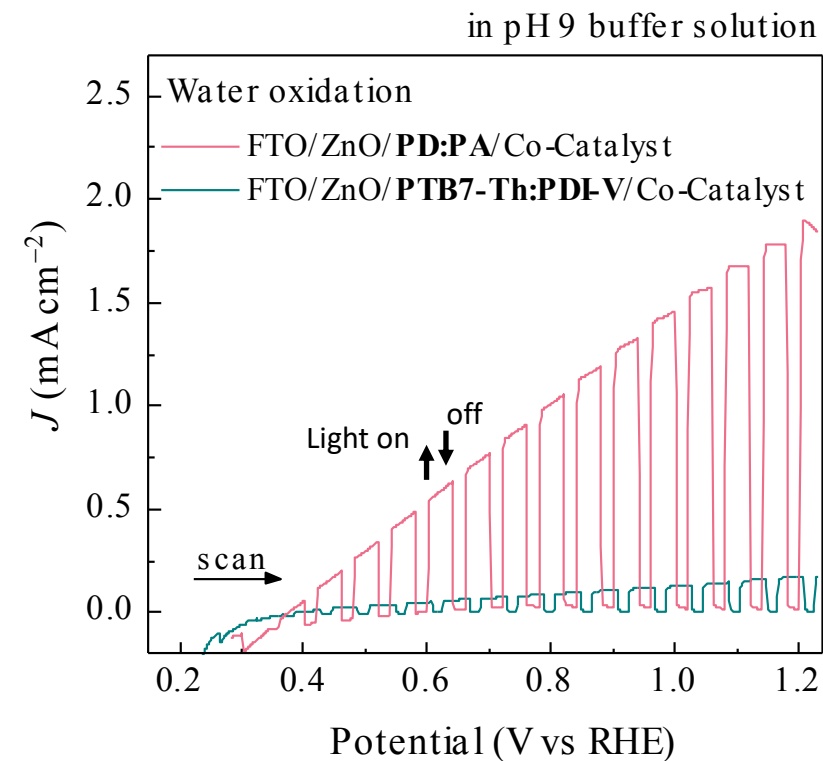
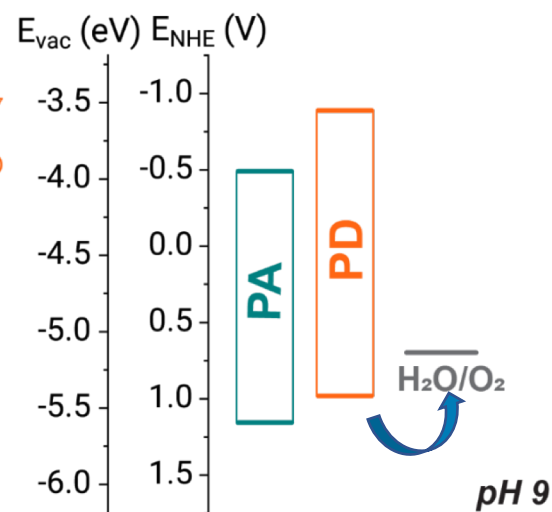
PTB7-Th (donor)



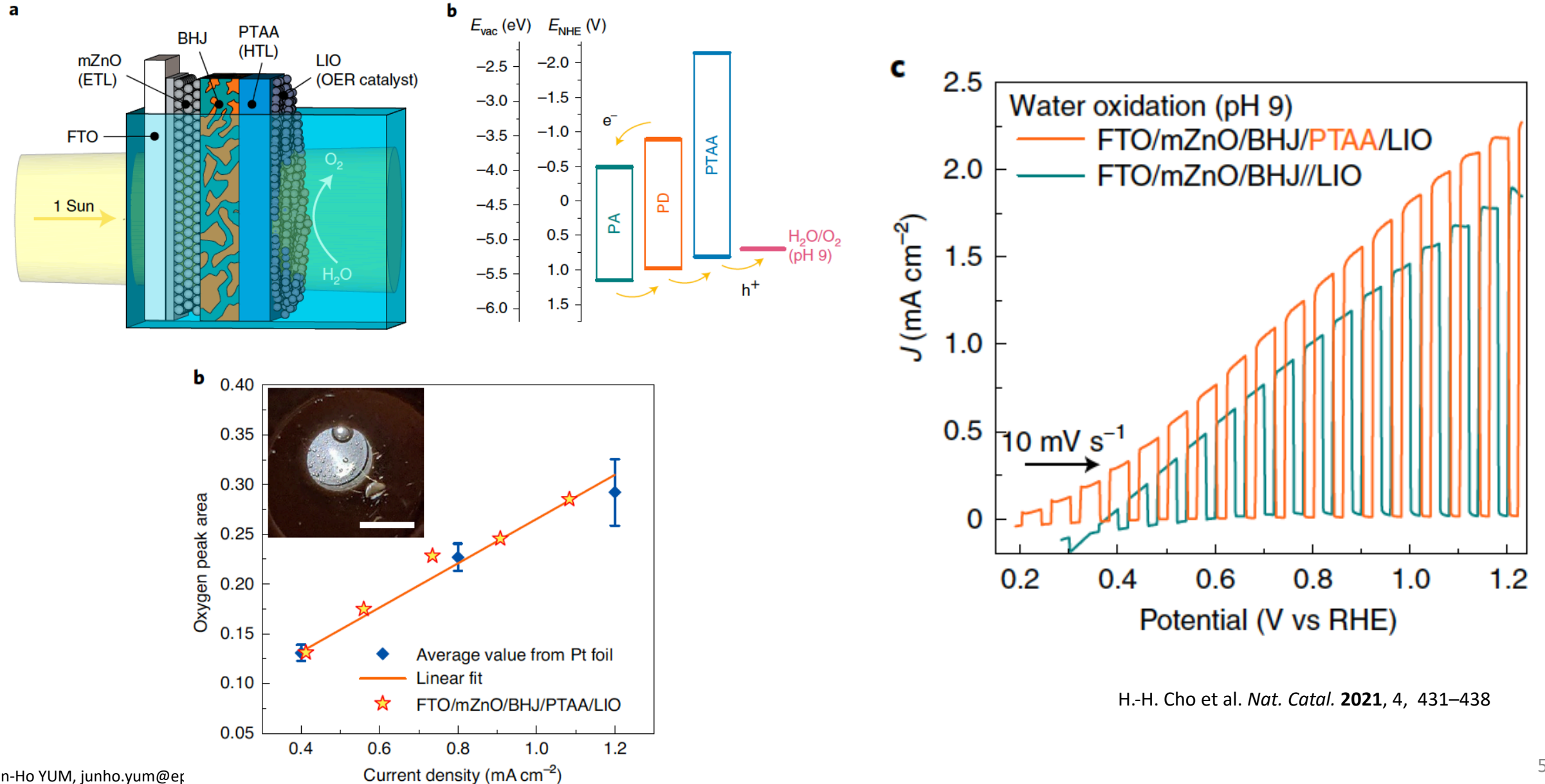
PNDITCVT (PA)



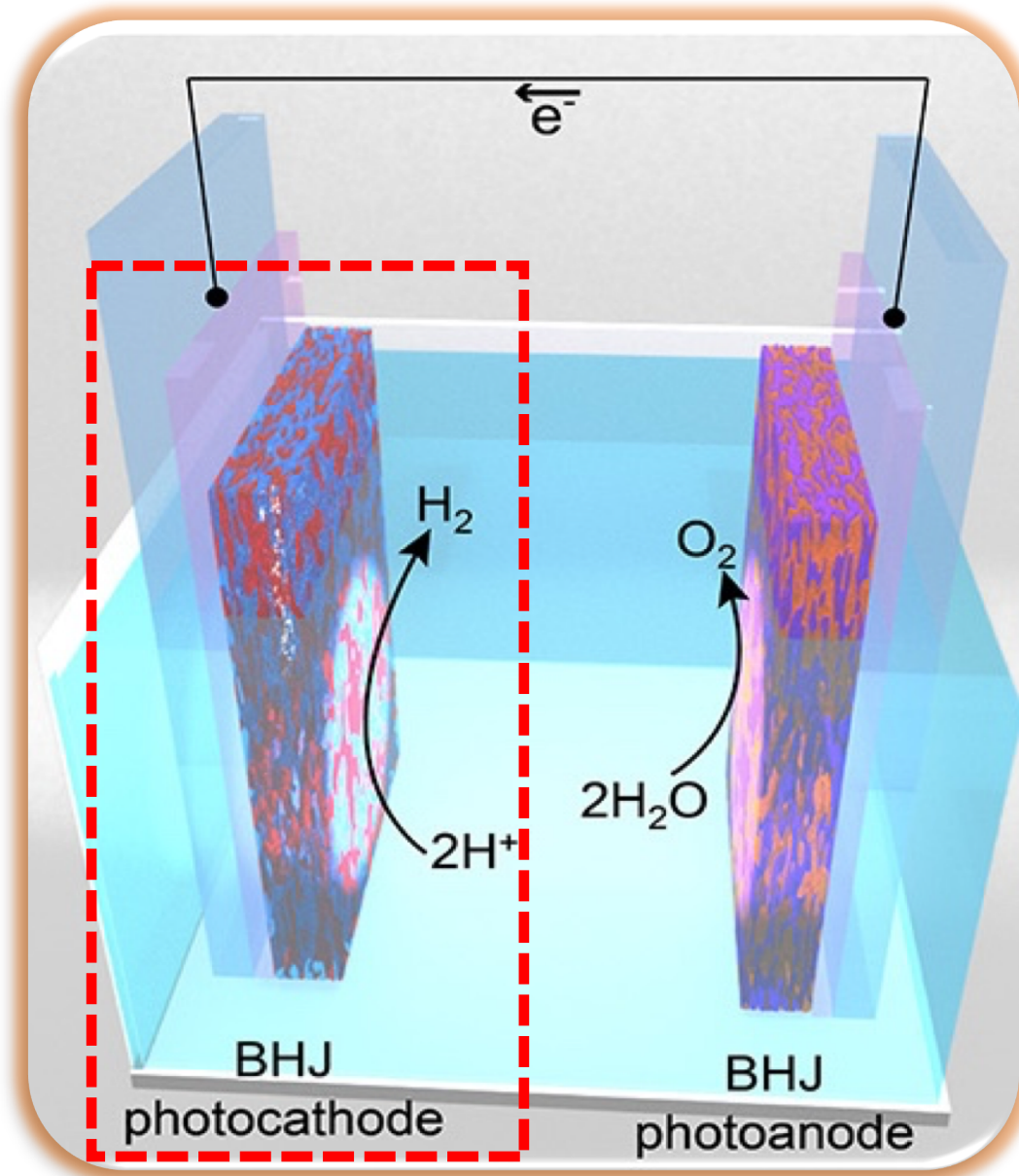
PBDTTTPD (PD)

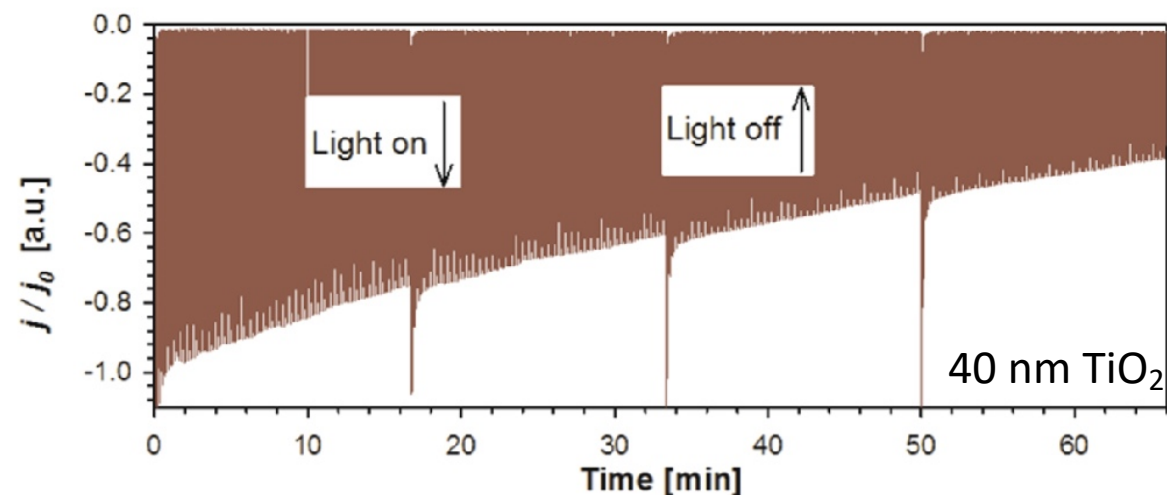
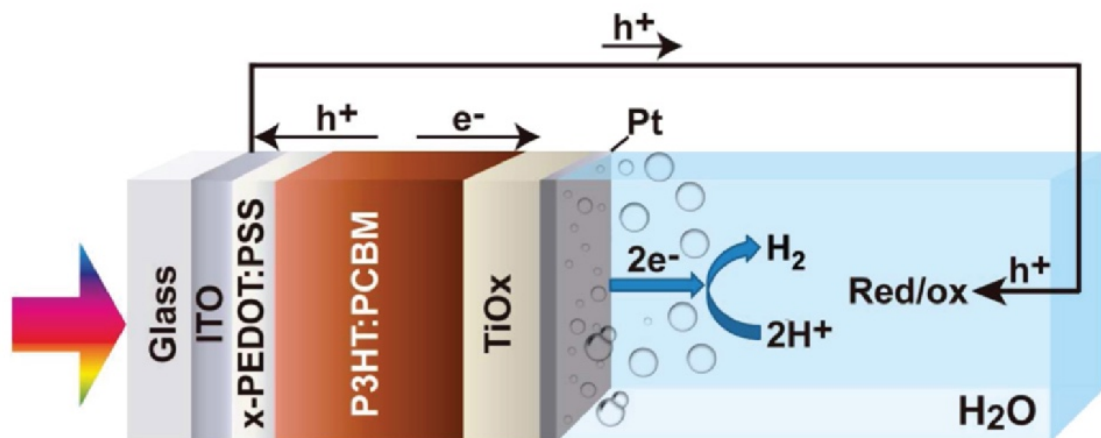


EPFL Polymer BHJ Photoanode for Solar Water Oxidation

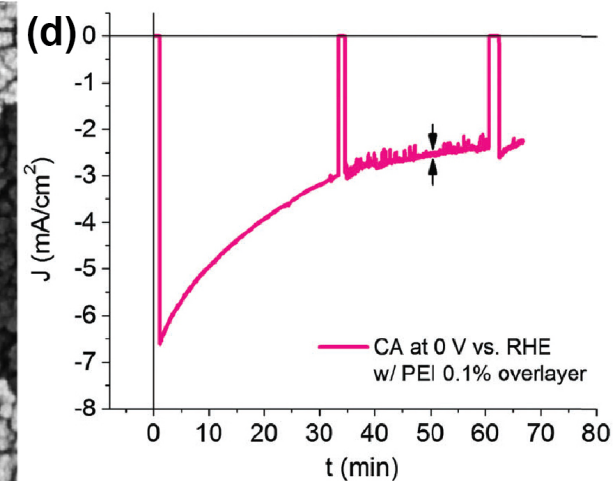
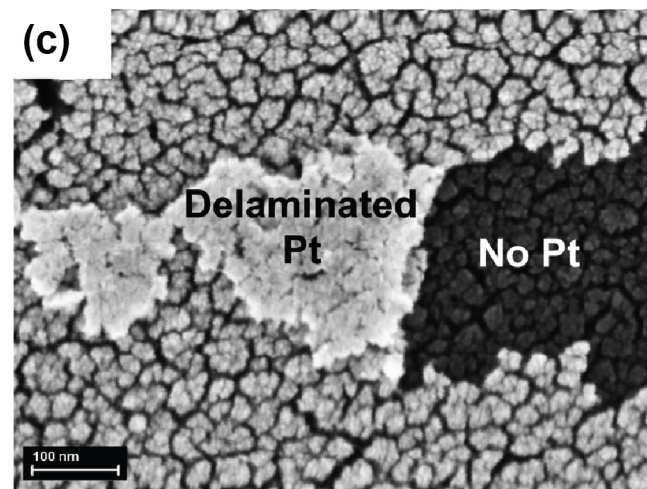
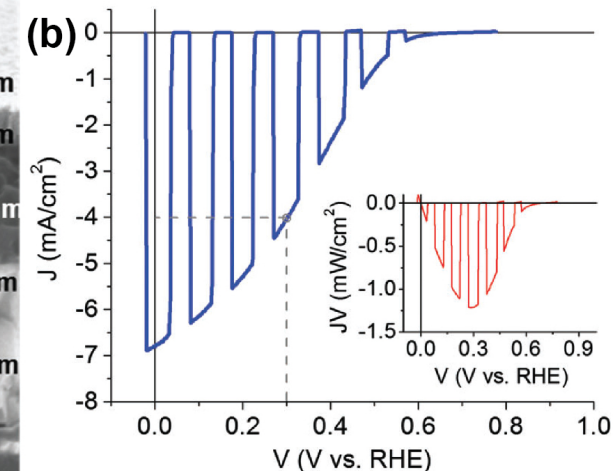
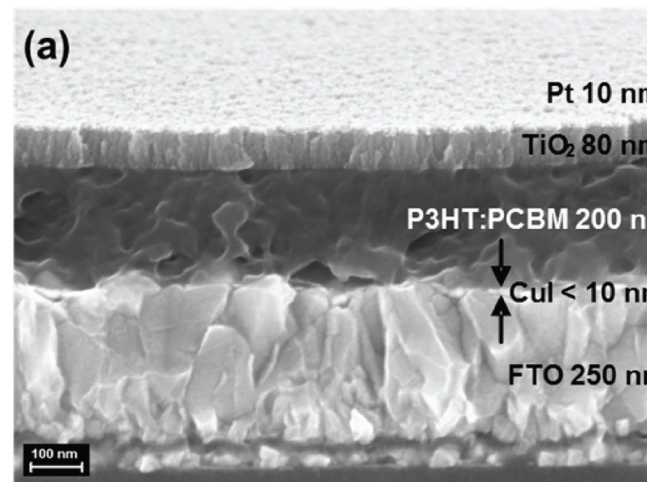


H.-H. Cho et al. *Nat. Catal.* **2021**, 4, 431–438





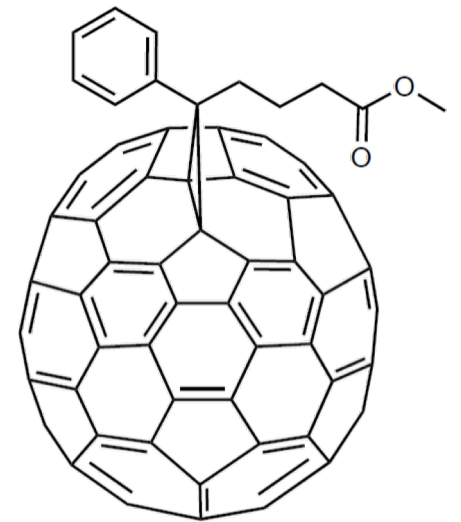
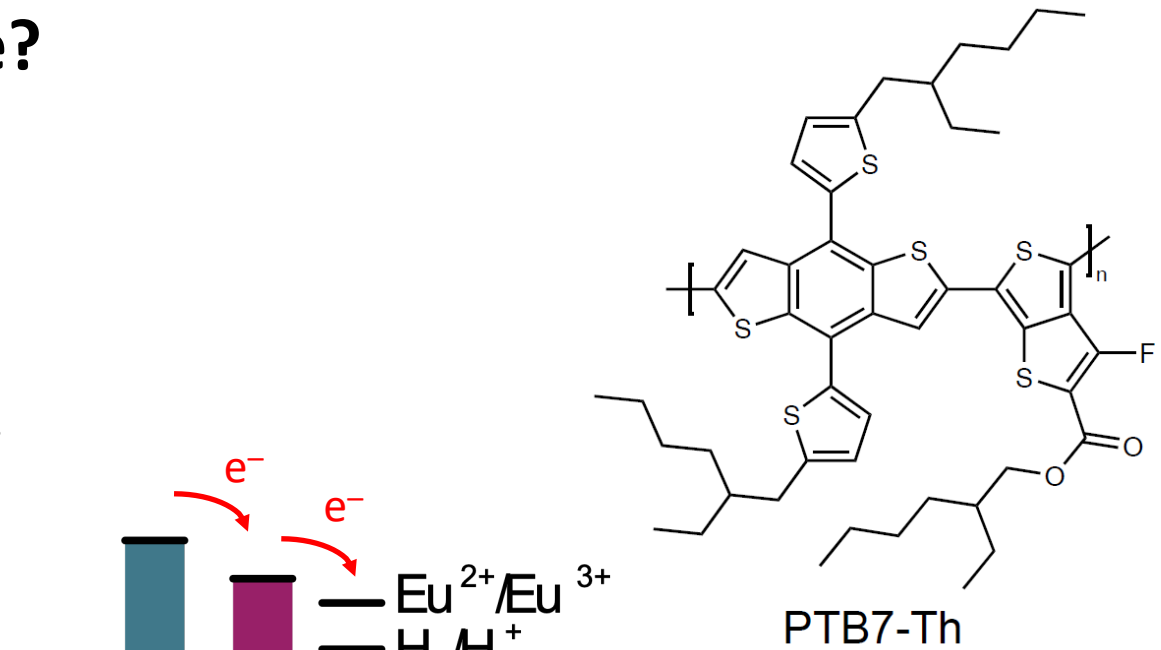
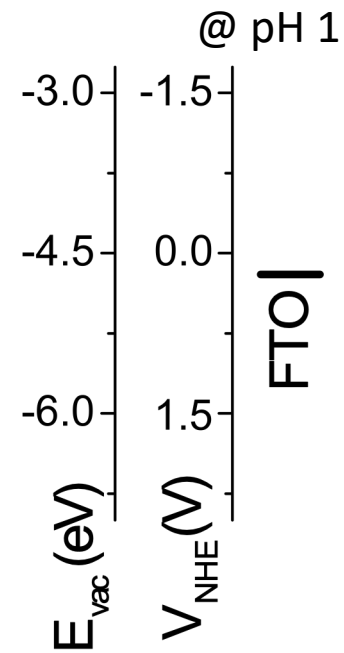
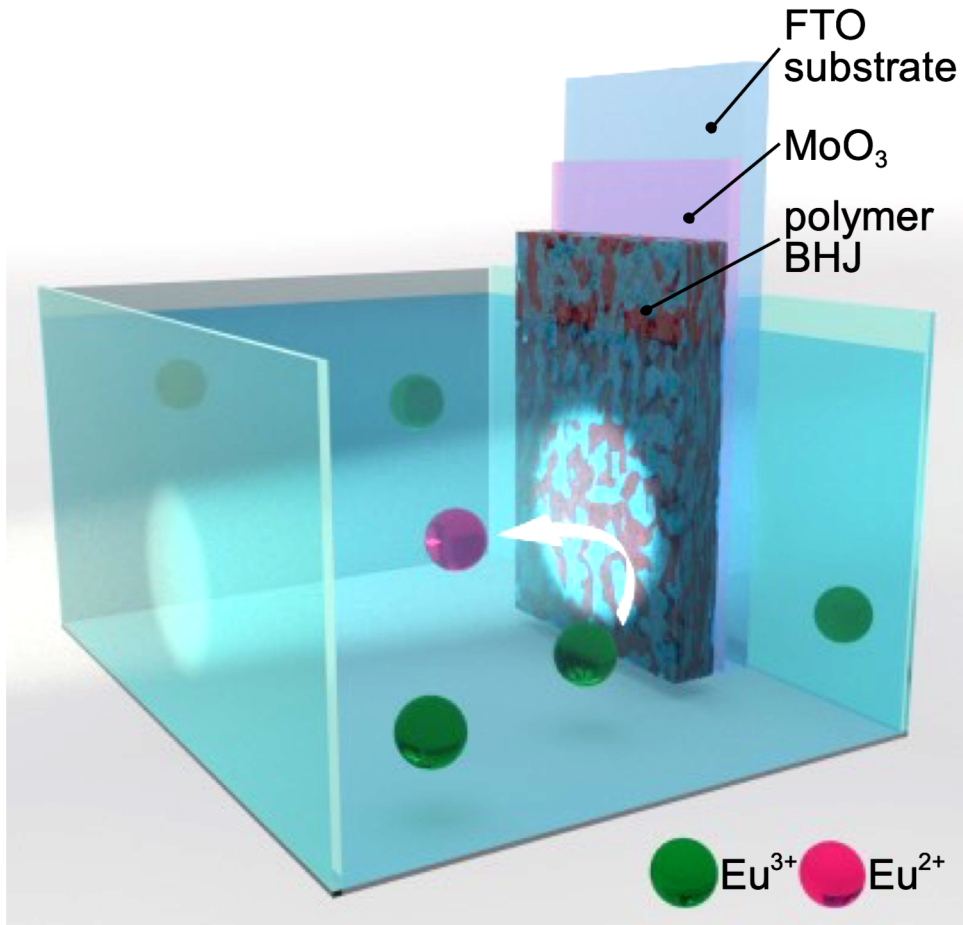
M. Haro et al., *J. Phys. Chem. C* **2015**, 119, 6488.



H. Comas Rojas et al., *Energy & Environmental Science* **2016**, 9, 3710.

EPFL Why is a BHJ in Water So Unstable?

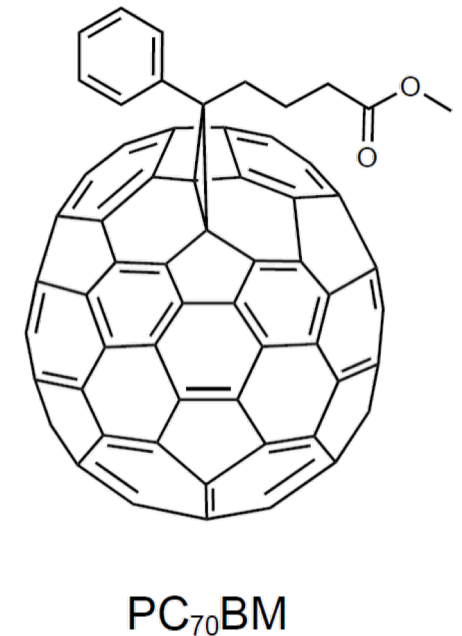
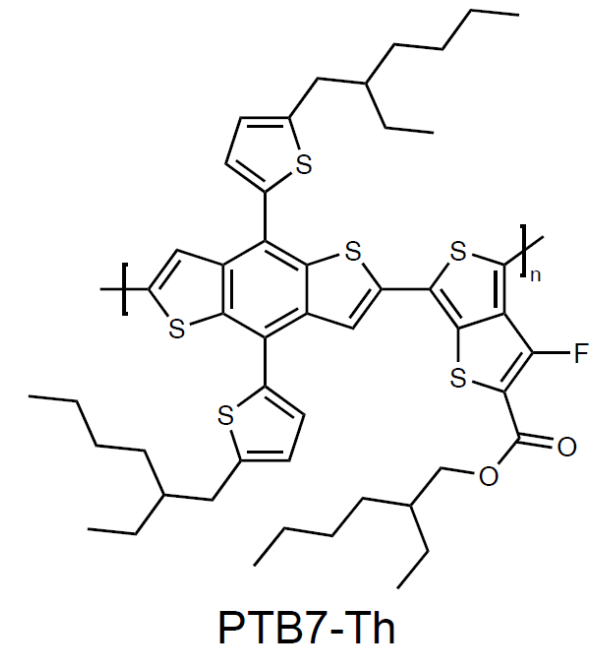
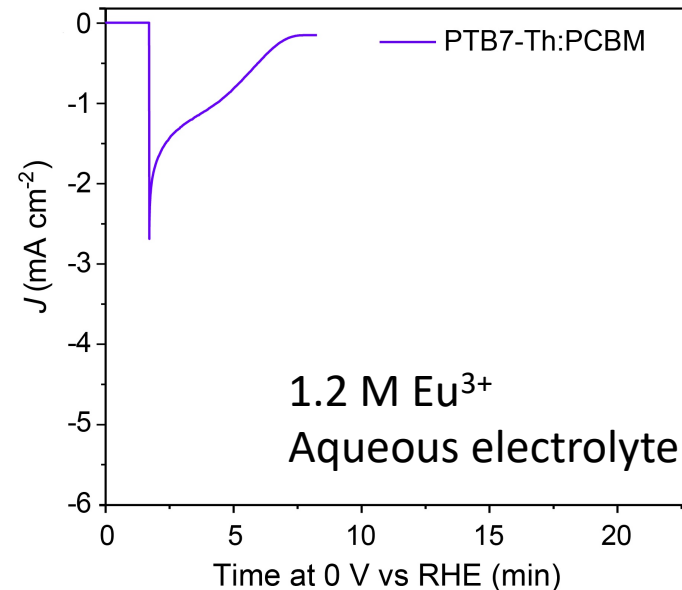
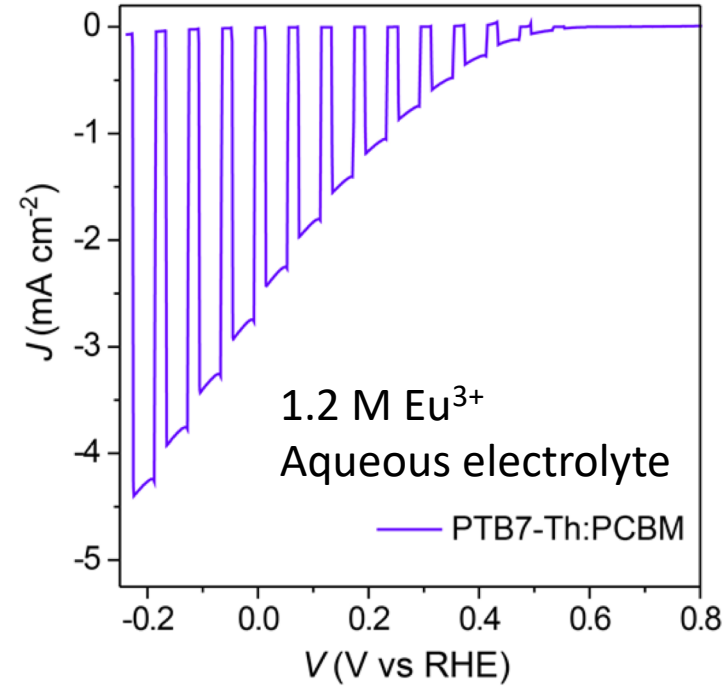
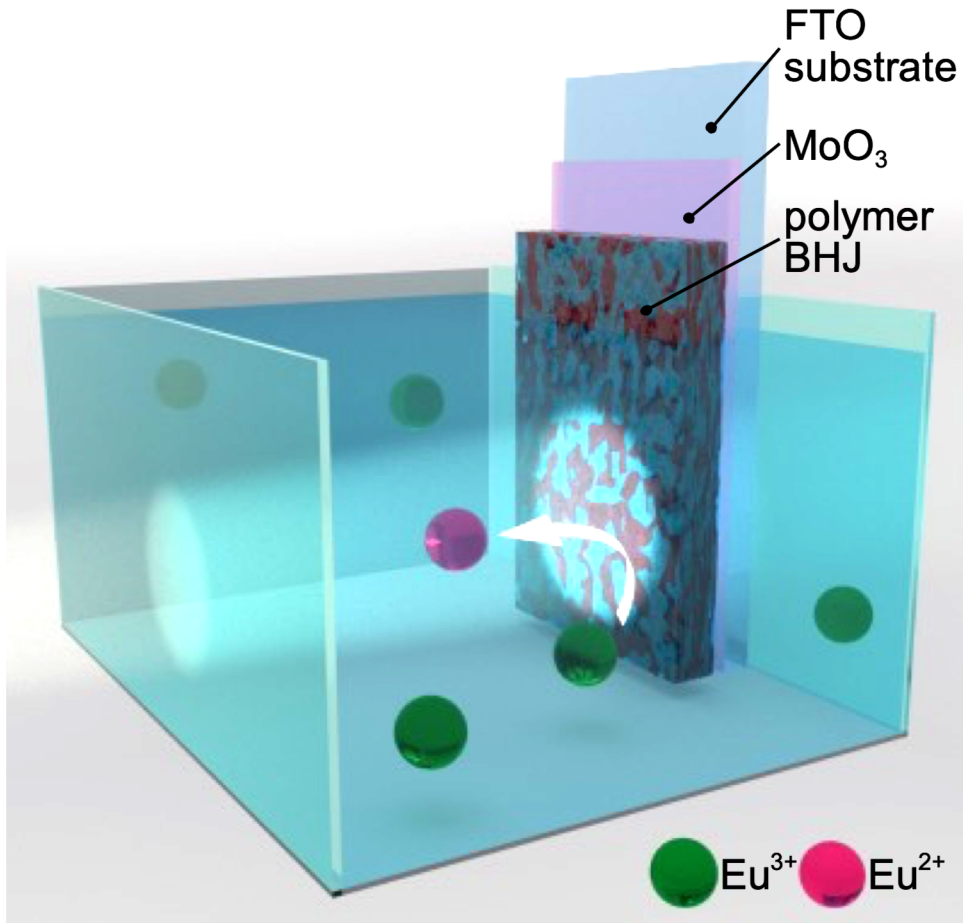
Or can a direct BHJ/water junction photocathode be stable?



PC₇₀BM

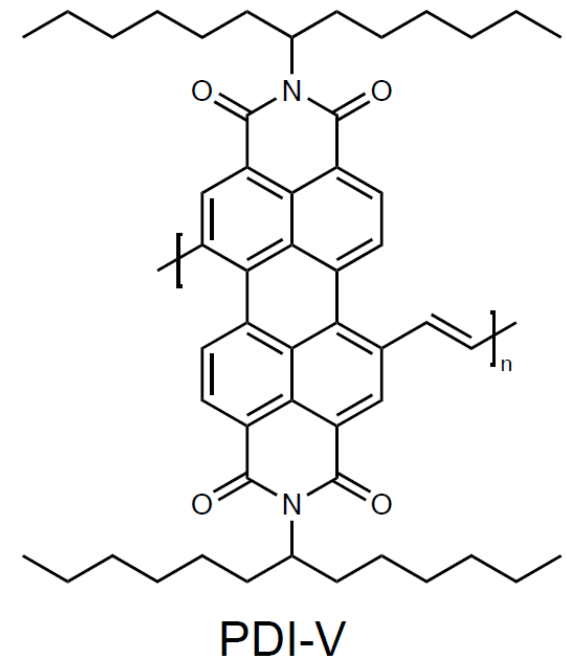
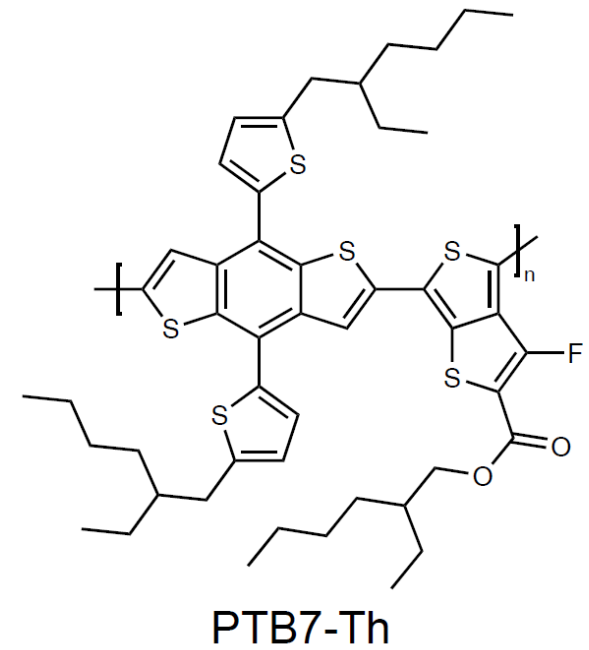
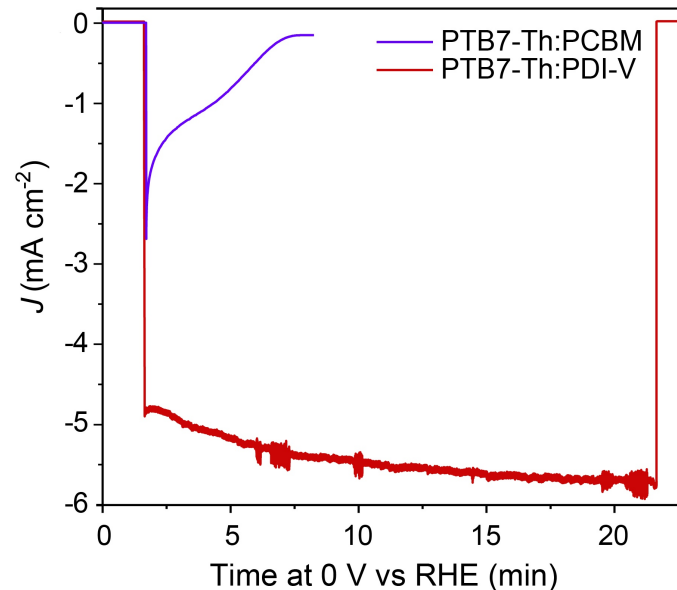
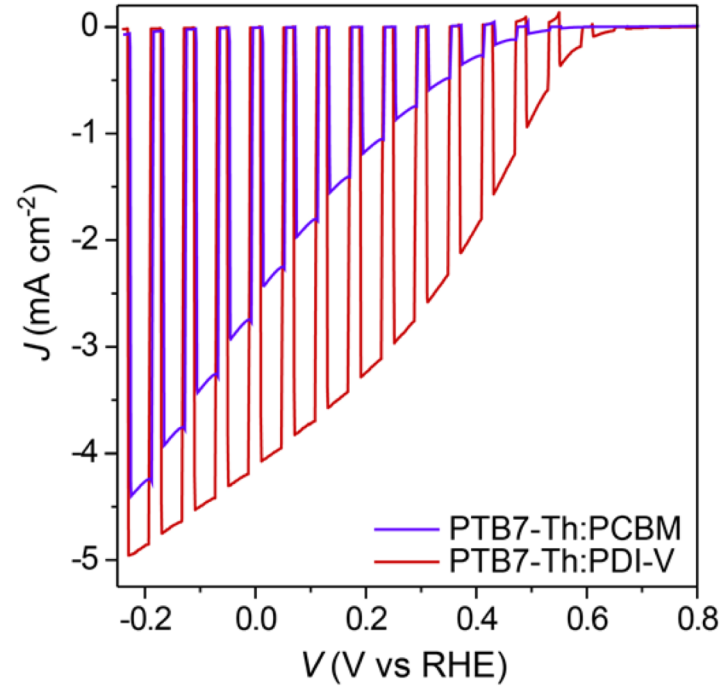
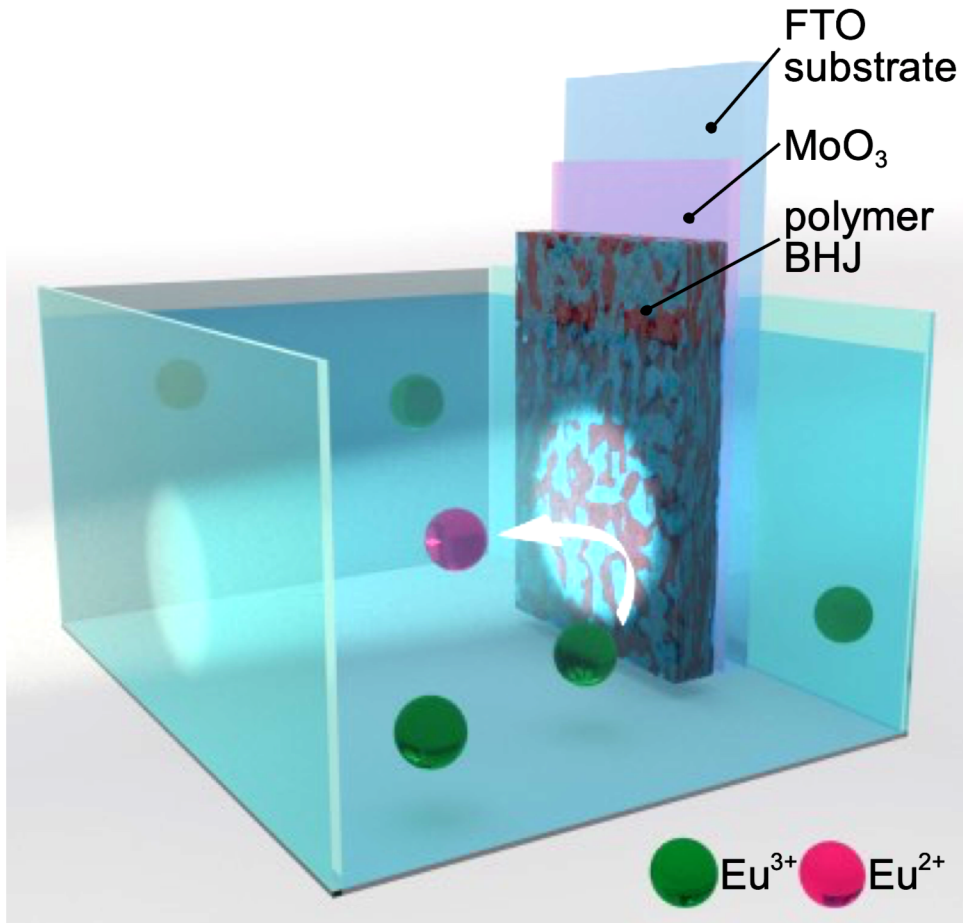
EPFL Why is a BHJ in Water So Unstable?

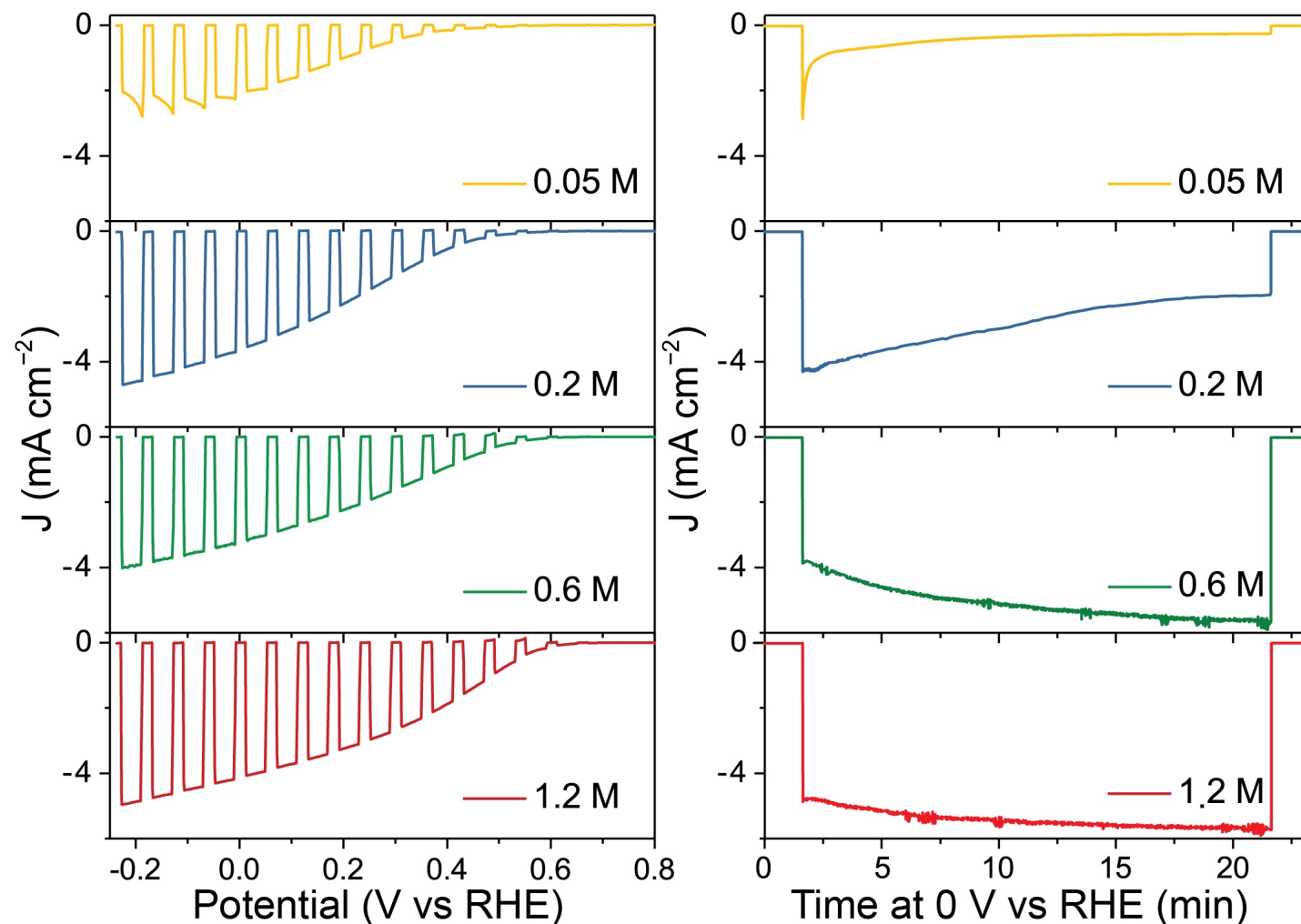
Or can a direct BHJ/water junction photocathode be stable?



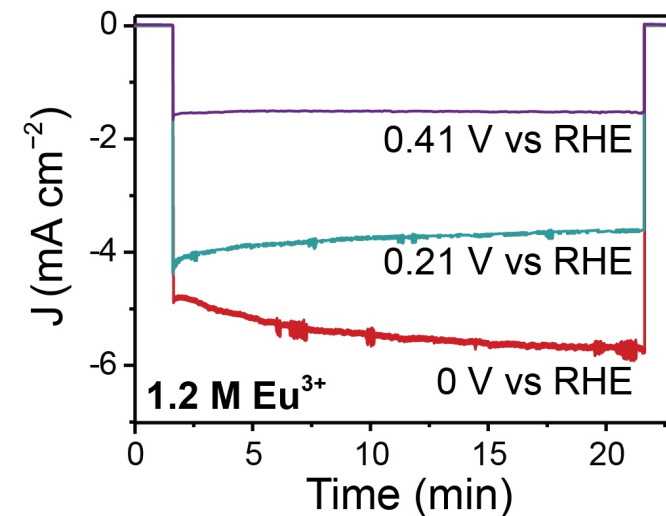
EPFL Why is a BHJ in Water So Unstable?

Or can a direct BHJ/water junction photocathode be stable?

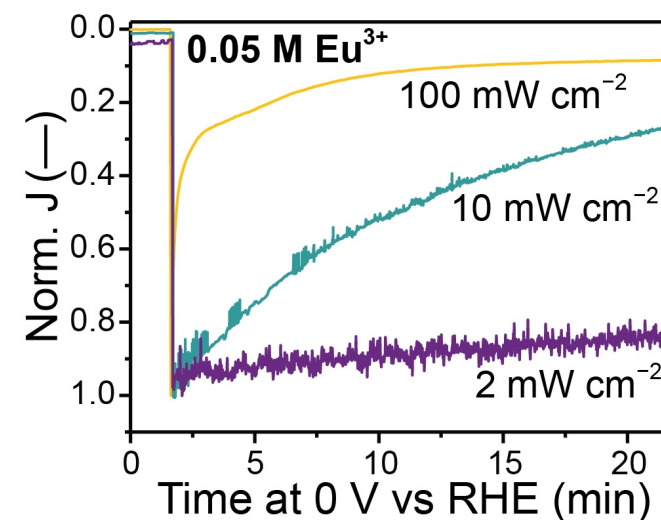


Changing the Eu^{3+} concentration:

Changing the applied potential:

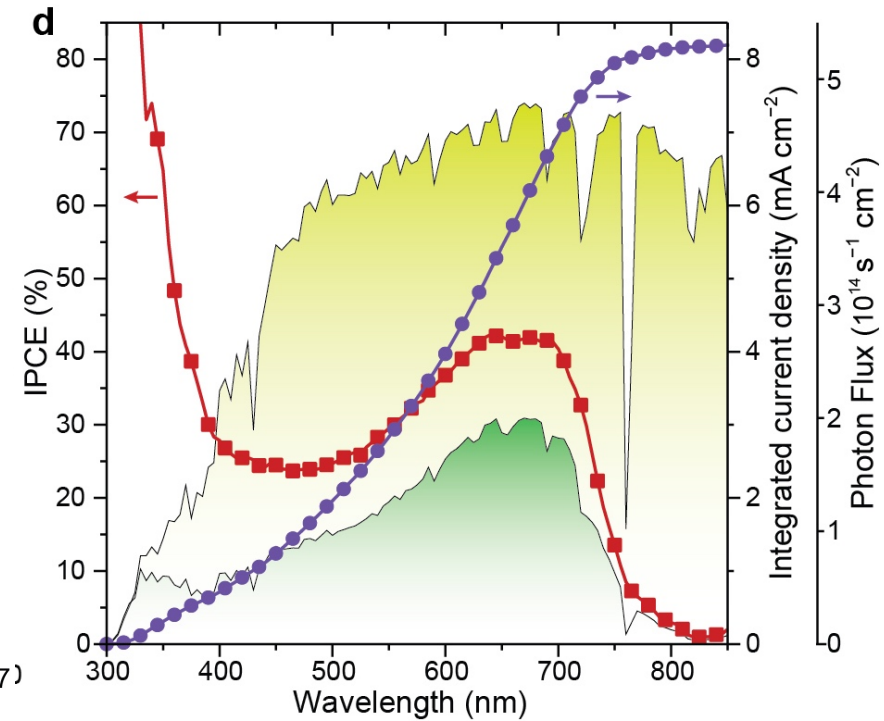
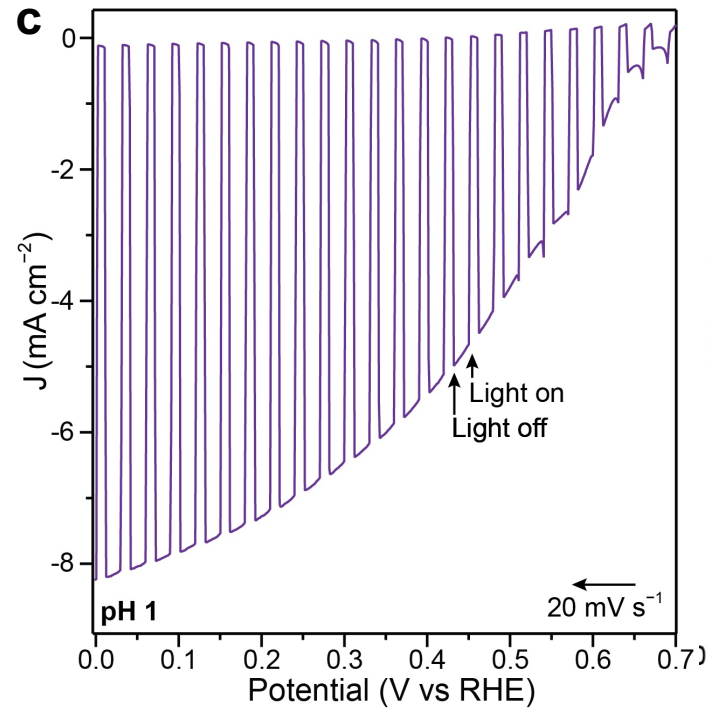
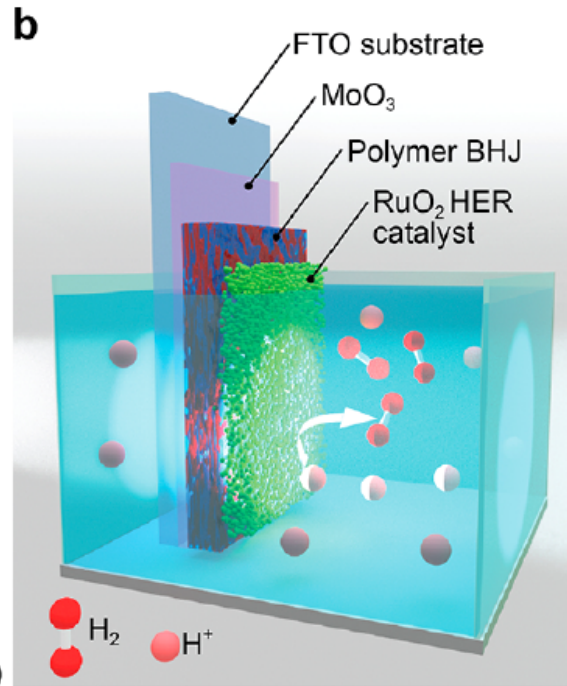
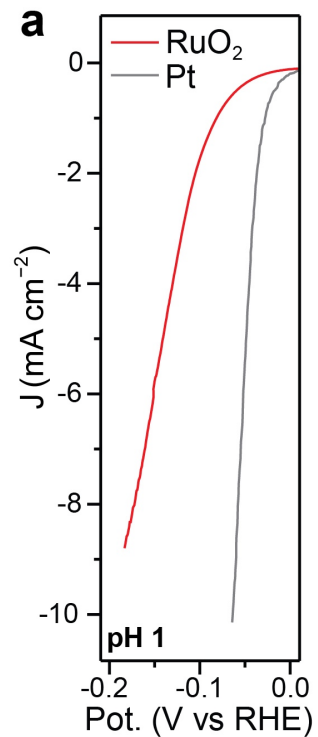


Changing the illumination intensity:

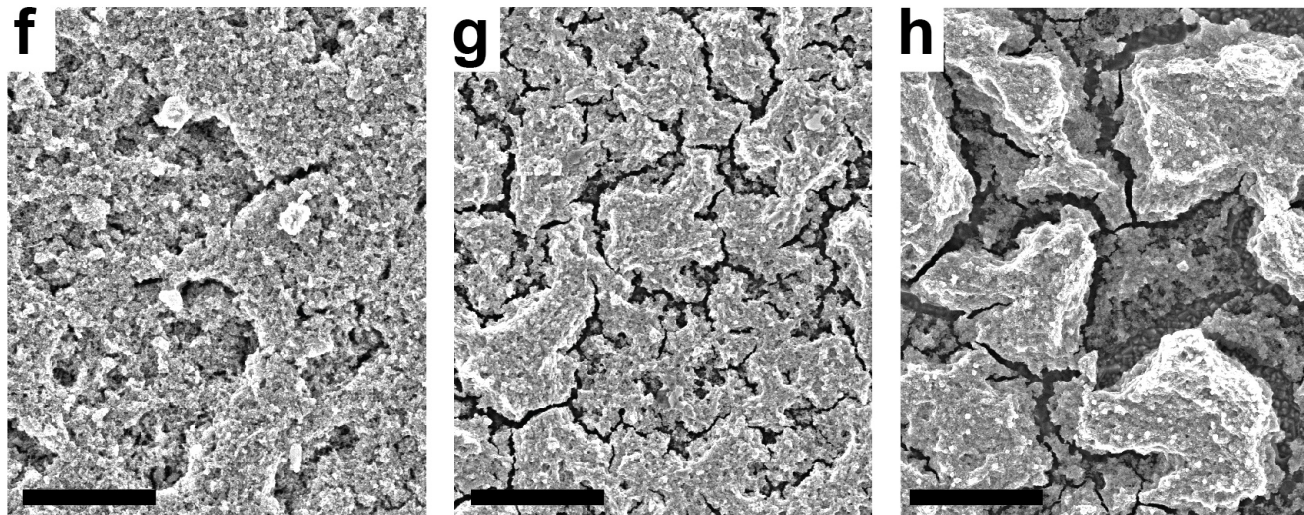
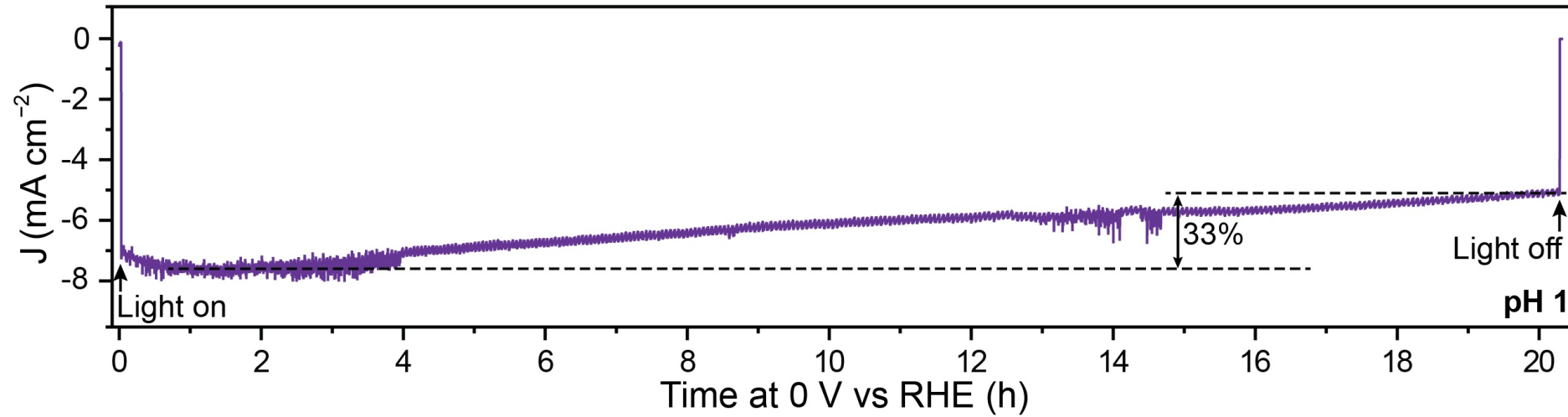


EPFL Adding a Catalyst to Drive H₂ Production

“Dark” electro-catalysis (on FTO)

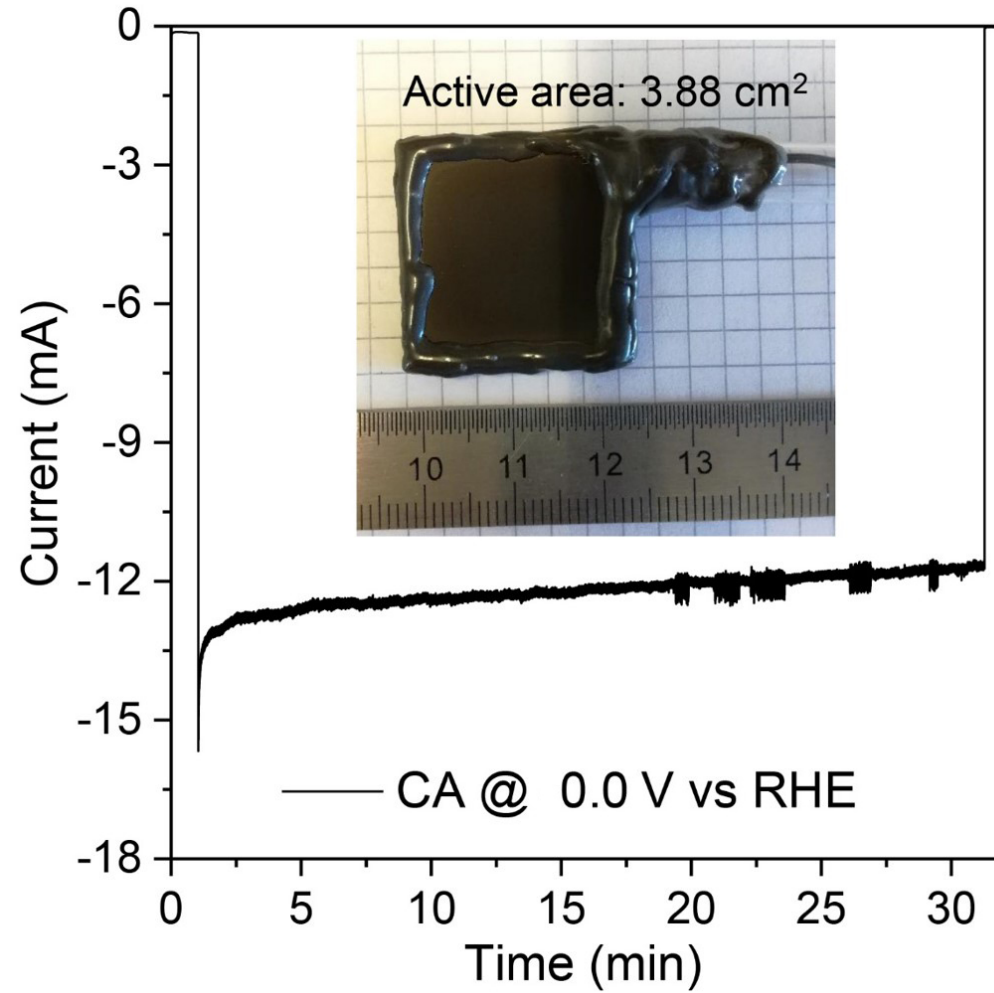


L. Yao et al. *J. Am. Chem. Soc.*, **2020**, 142, 17, 7795–7802

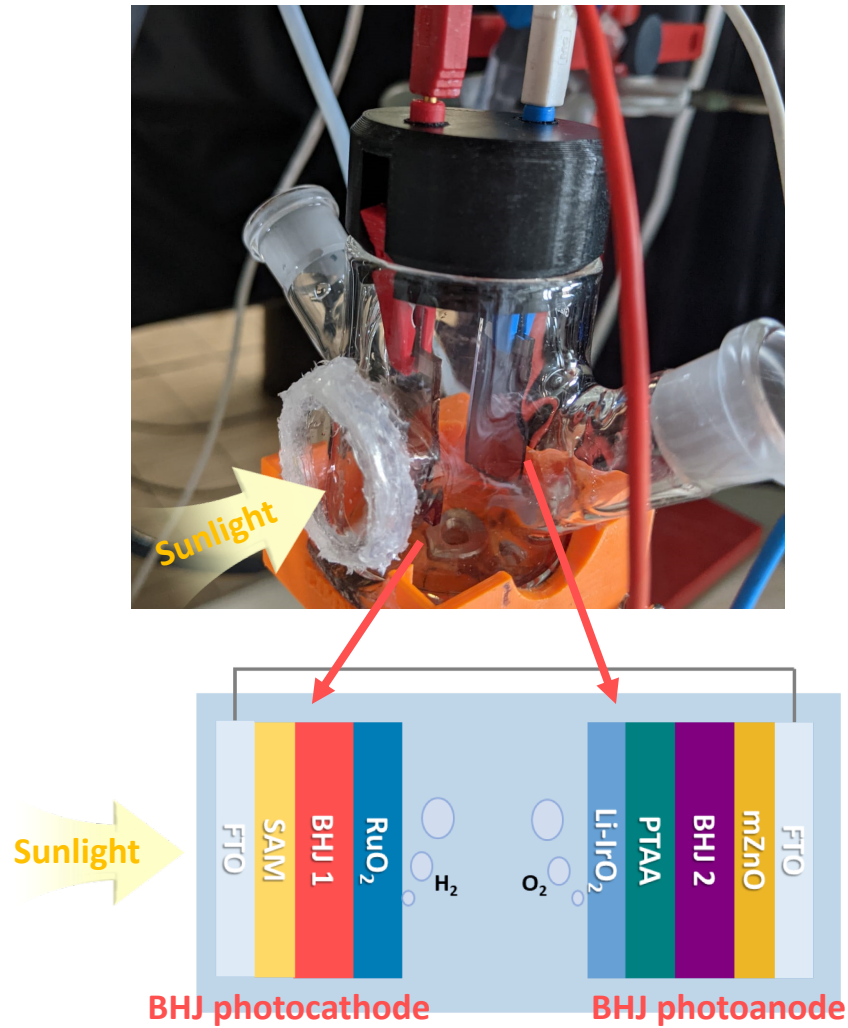


Scale bar: 1 μm

EPFL Large Area Demonstration

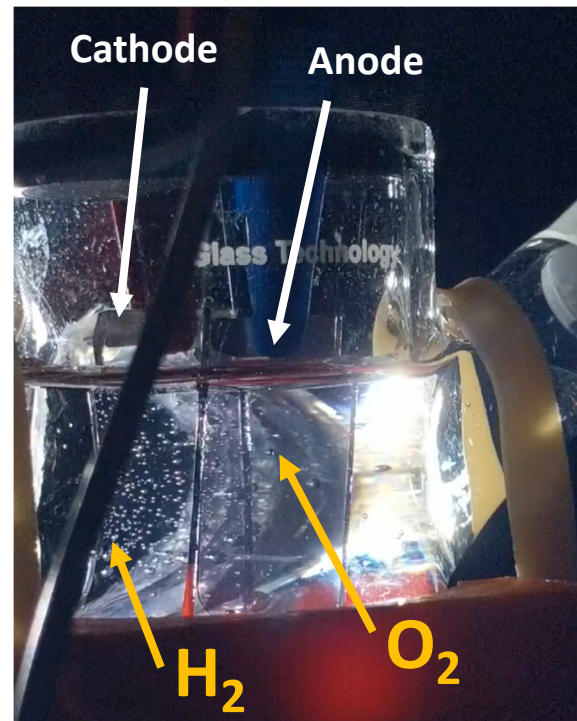


EPFL What is Next?

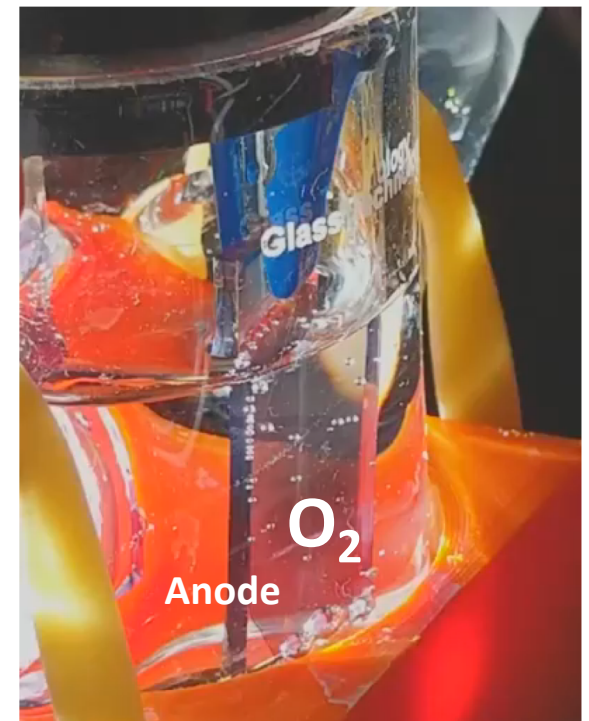


Complete solar water splitting at zero-bias
Without any capsulation or passivation

[Back]



[Side]



D. Zhang, et al., Adv. Energy Mater., **2022**, 2202363.