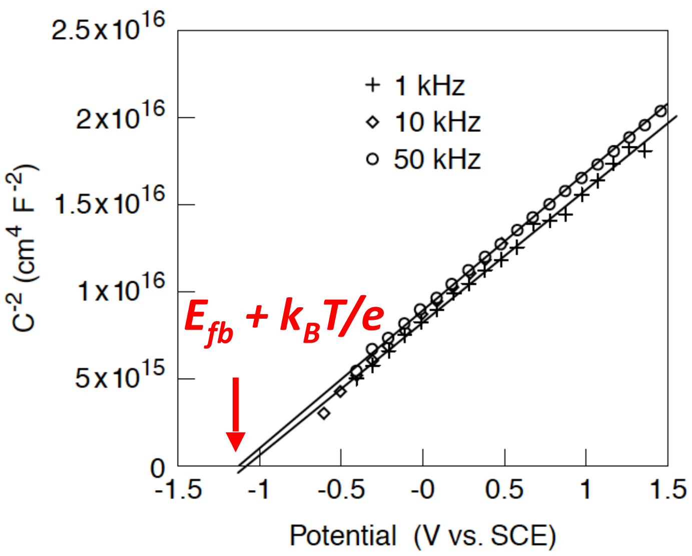
Energy Conversion by Semiconductor Devices

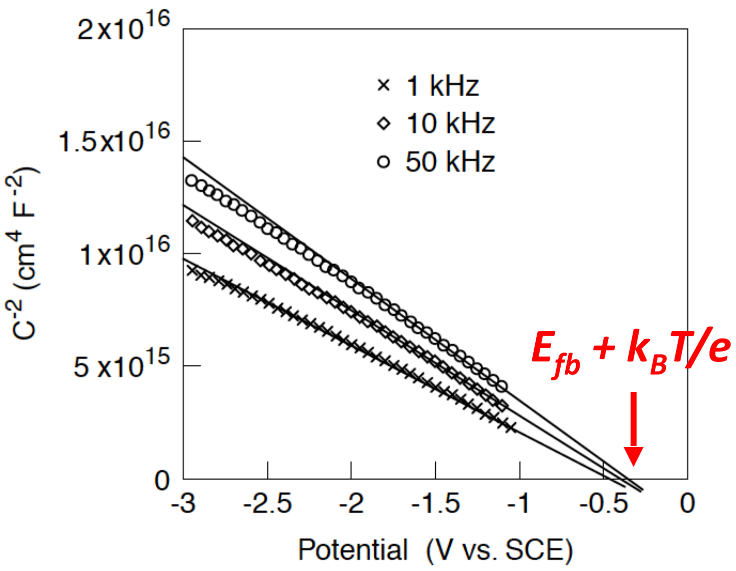
Jun-Ho YUM
junho.yum@epfl.ch

Recap: Mott-Schottky Equation

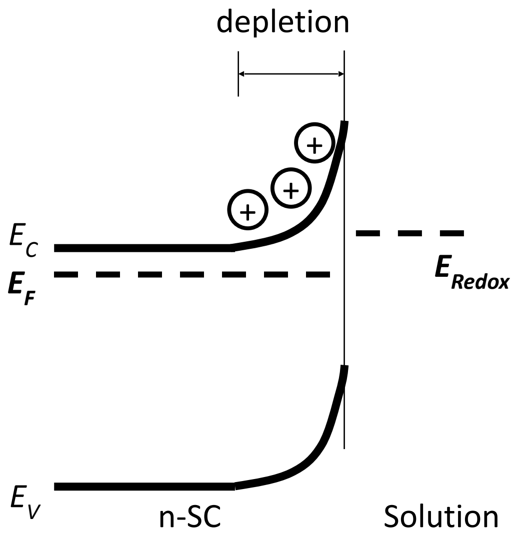
MS plot for an n-type silicon



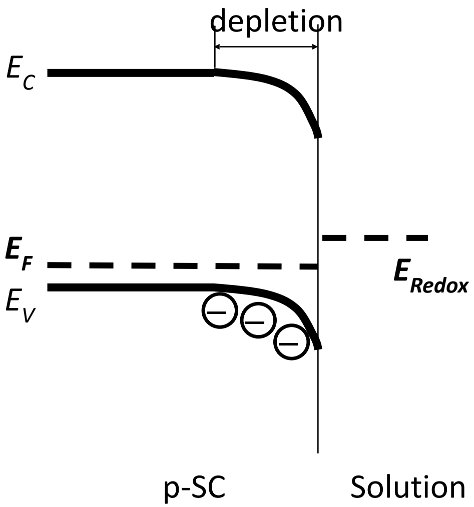
MS plot for an p-type silicon



$E > E_{fb}$

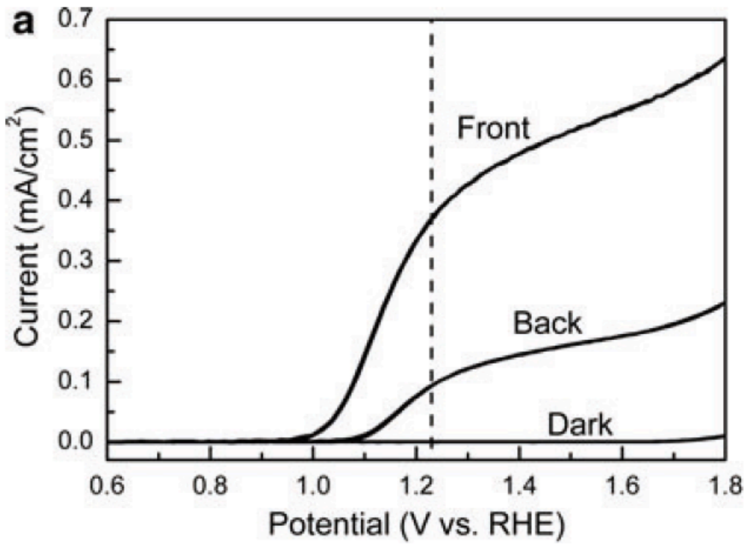


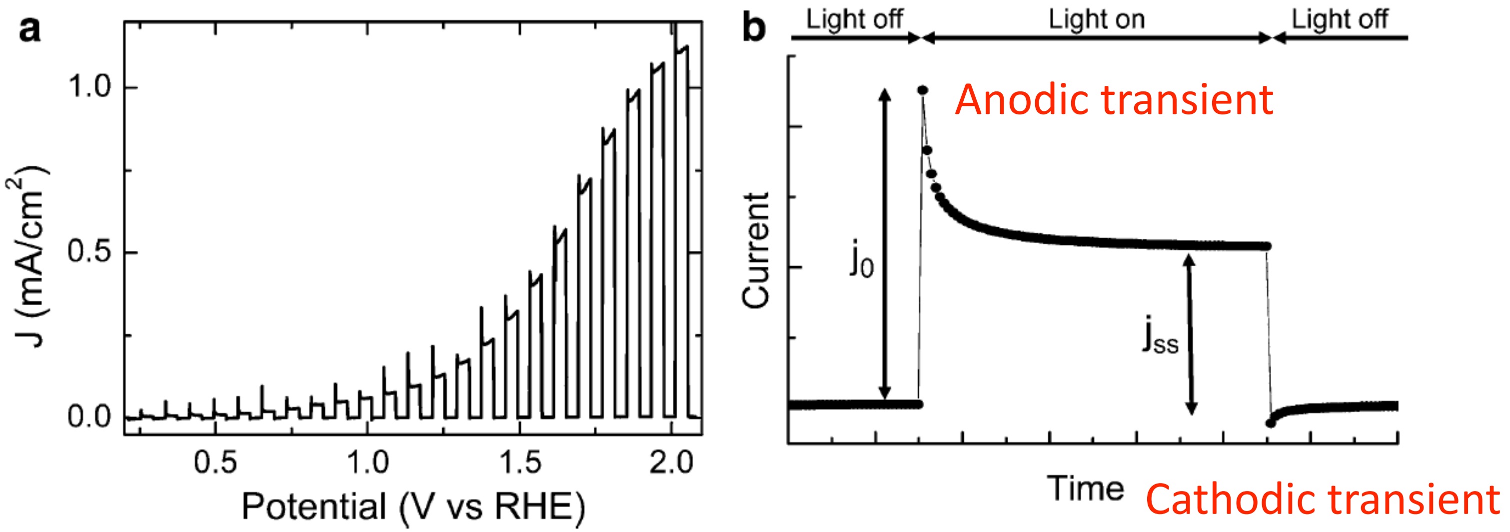
$E < E_{fb}$

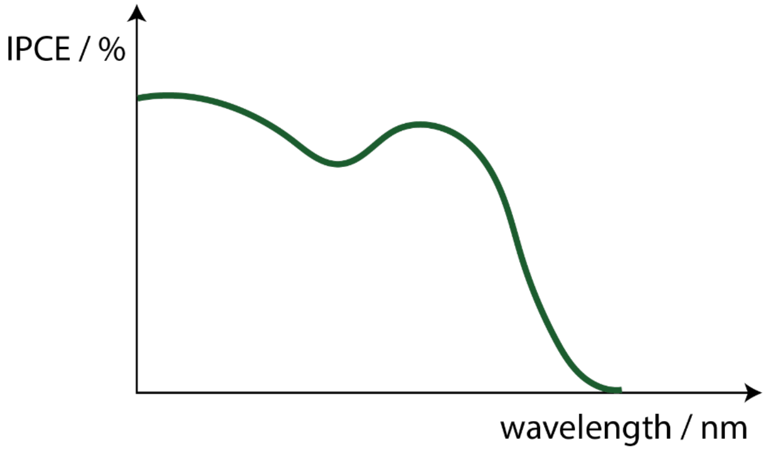


- Jun-Ho YUM, junho.yum@epfl.ch

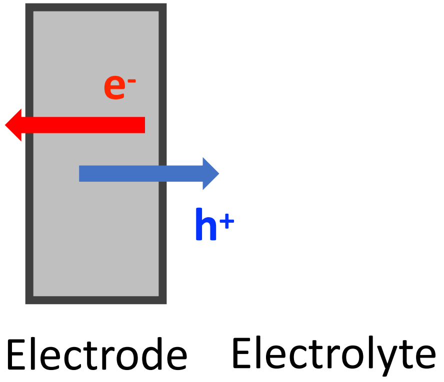
Photoelectrochemical Measurements





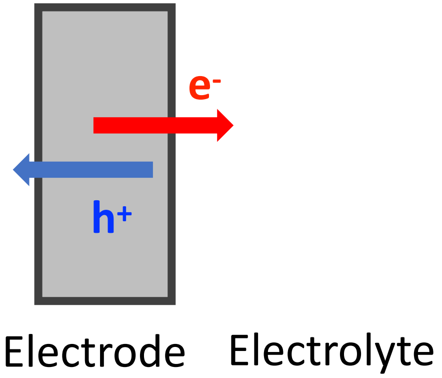


Oxidation



Electrode Electrolyte

Reduction



Electrode Electrolyte

Solar-To-Hydrogen Efficiency

- 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 H_2/s) multiplied by the change in Gibbs free energy per mole of H_2 ($\Delta G^0 =$ 237.2 kJ/mol at 25 °C).

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

This equation calculates the power output (numerator) based on the direct measurement of the true H_2 production rate by an analytical method such as gas chromatography or mass spectrometry.

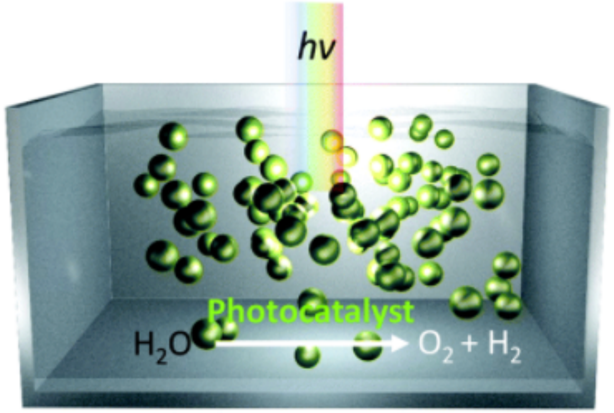
$$\boldsymbol{STH} = \left[\frac{(J_{sc}\ (mA/cm^2)) \times (1.23\ V) \times \eta_F}{P_{total}\left(\frac{mW}{cm^2}\right)}\right]_{AM1.5G}$$

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

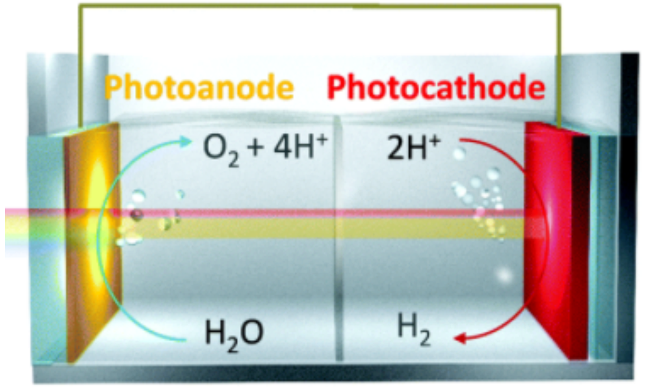
Jun-Ho YUM, junho.yum@epfl.ch

Solar-To-Hydrogen Efficiency

PC



PEC

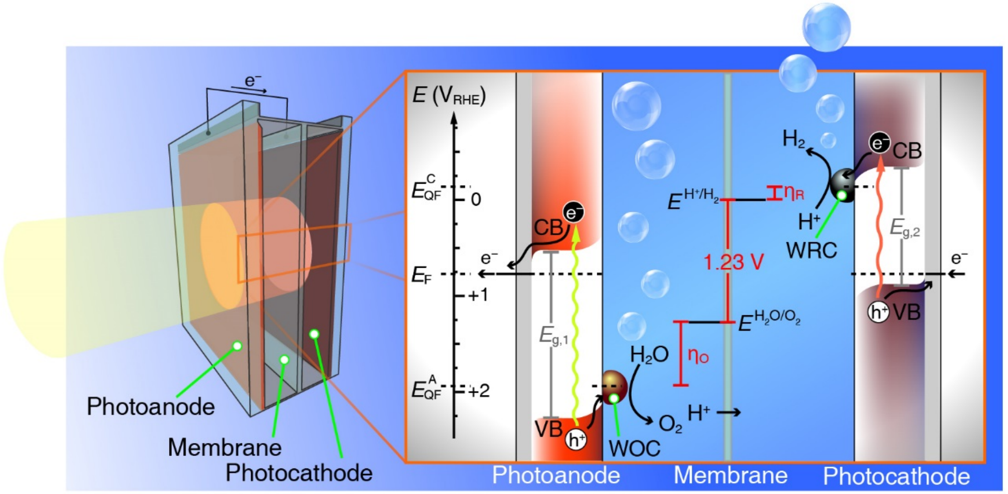


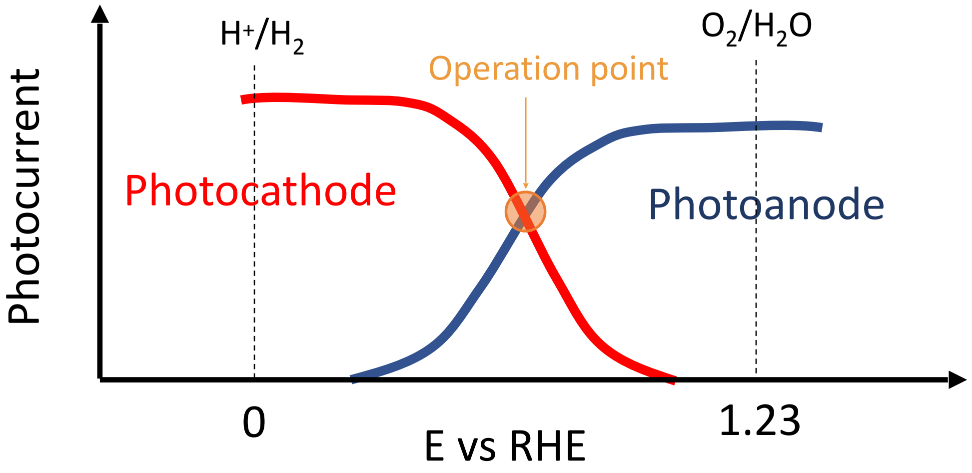
$$\boldsymbol{STH} = \left[\frac{(mmol\ H_2/s) \times (237{,}200\ J/mol)}{P_{total}\left(\frac{mW}{cm^2}\right) \times Area\ (cm^2)}\right]_{AM1.5G}$$

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

- Jun-Ho YUM, junho.yum@epfl.ch

Assessment of a Dual Tandem PEC Cell



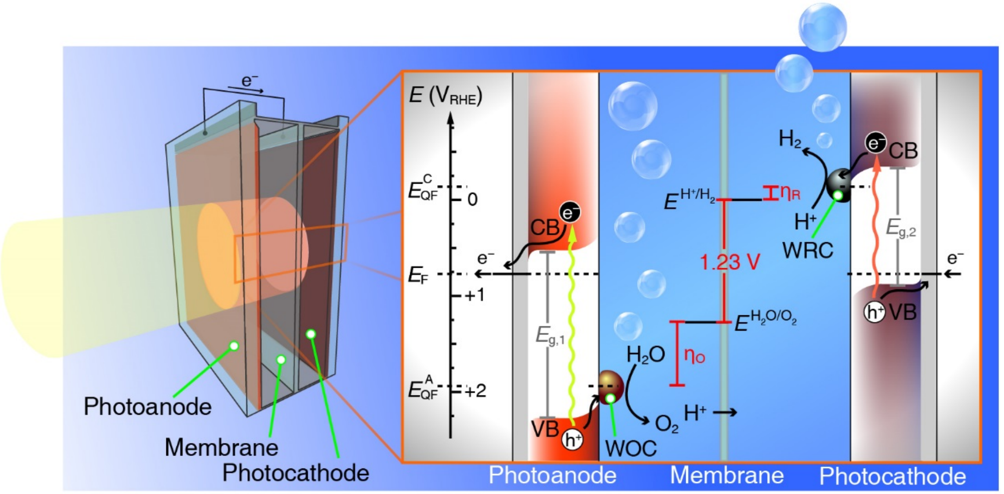


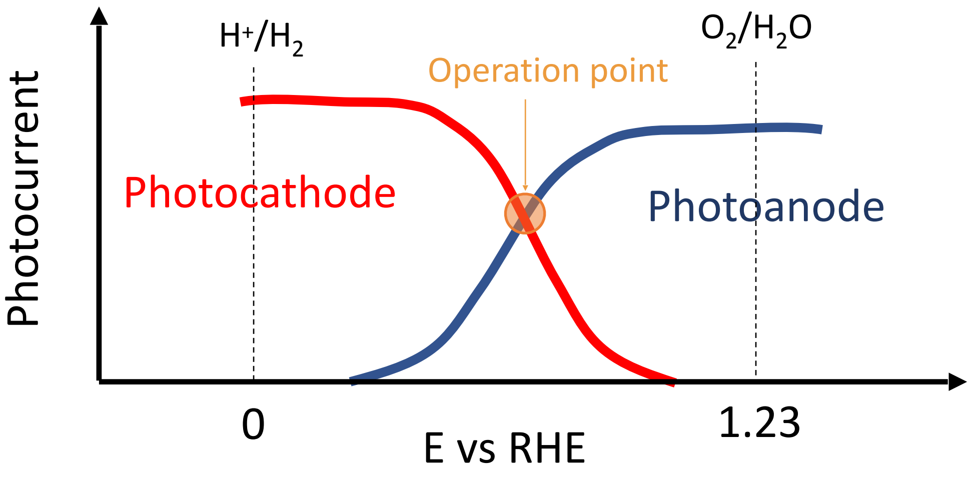
Examine separately photoelectrodes.

Predict ‘best’ performance (*overlapping of JV curves*)

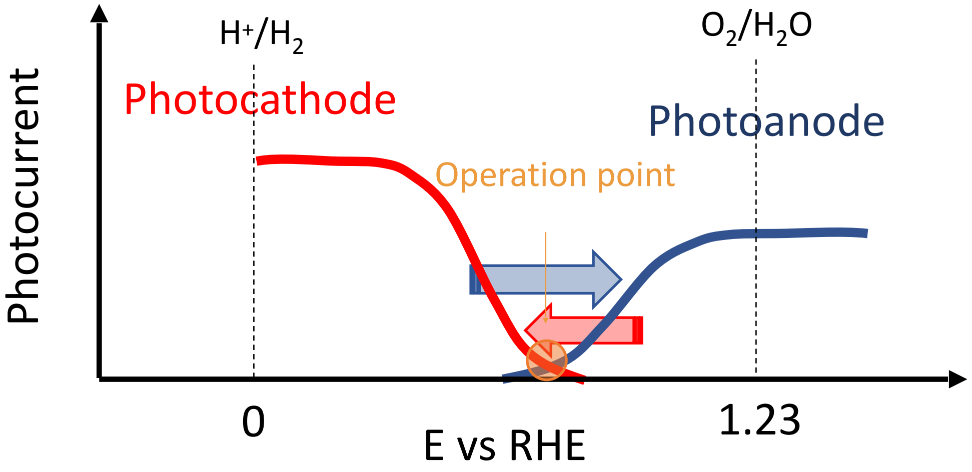
- Jun-Ho YUM, junho.yum@epfl.ch

Assessment of a Dual Tandem PEC Cell





Real

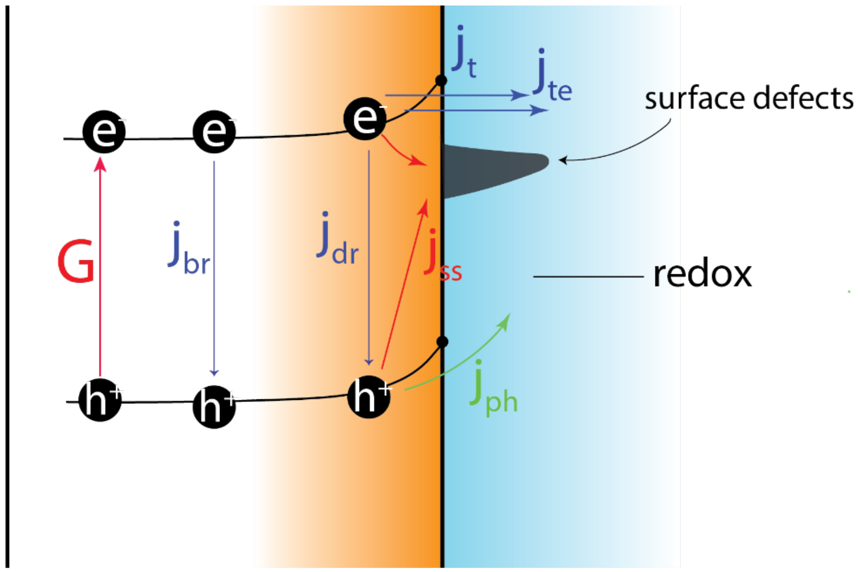


Today's low-cost PEC cells suffer from poor STH

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

- Jun-Ho YUM, junho.yum@epfl.ch

Challenges to Address



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

- 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

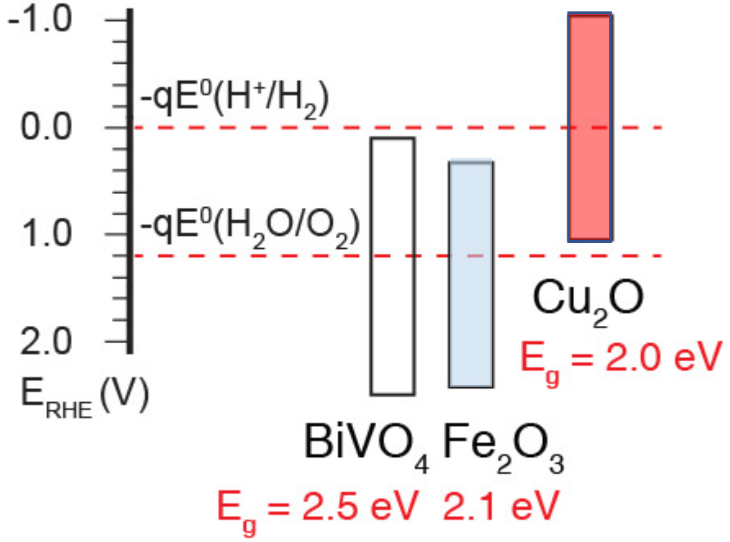
- Bulk defects (recombination)
- Carrier transport
- Doping density (conductivity, depletion depth)
- Morphology (charge collection)

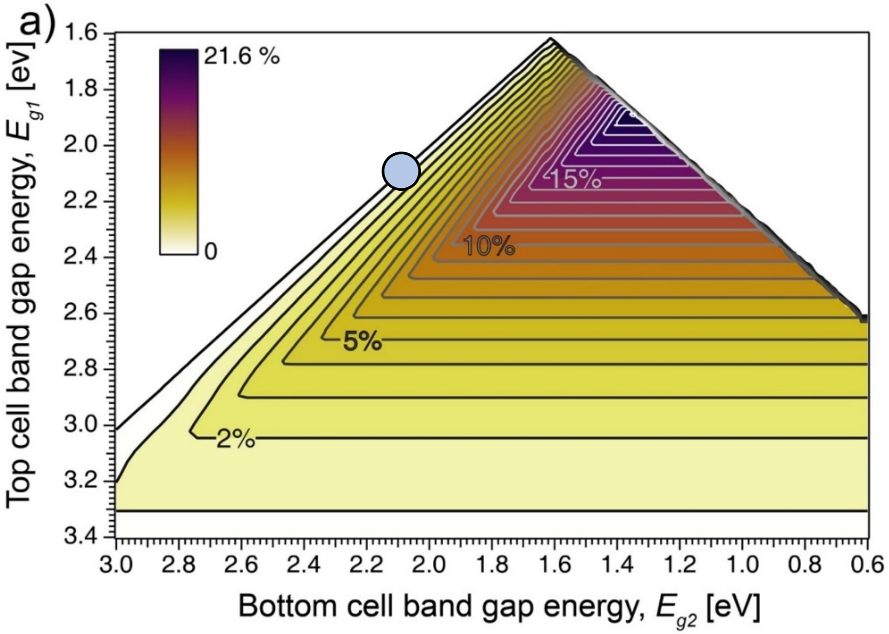
SURFACE PROPERTIES (Semiconductor-liquid junction)

- Surface defects (recombination)
- Catalytic properties
- Stability

- Jun-Ho YUM, junho.yum@epfl.ch

Assessment of a Dual Tandem PEC Cell

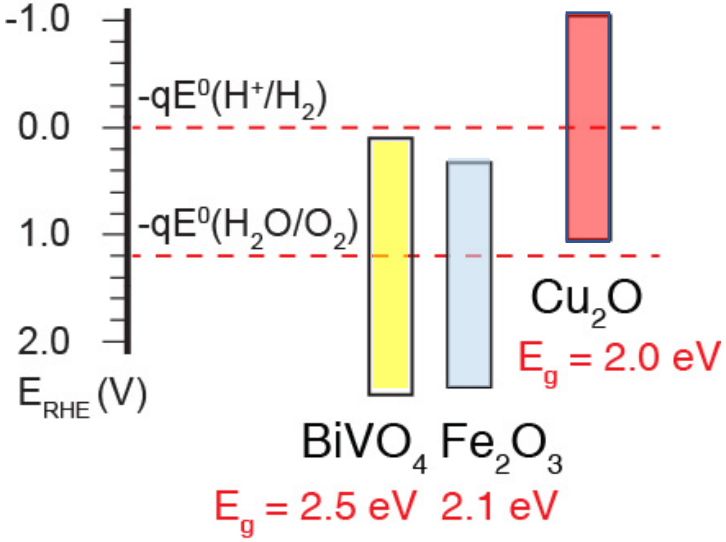


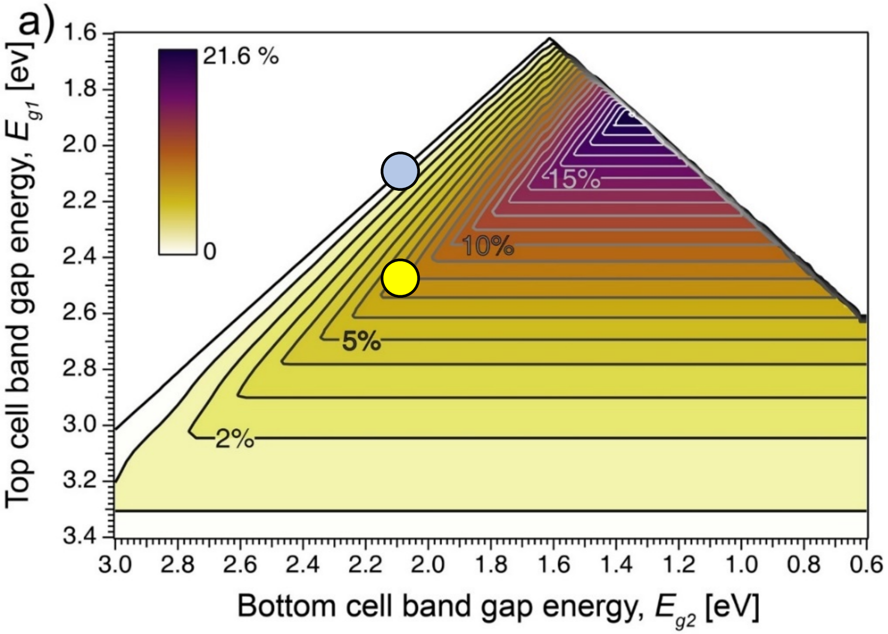


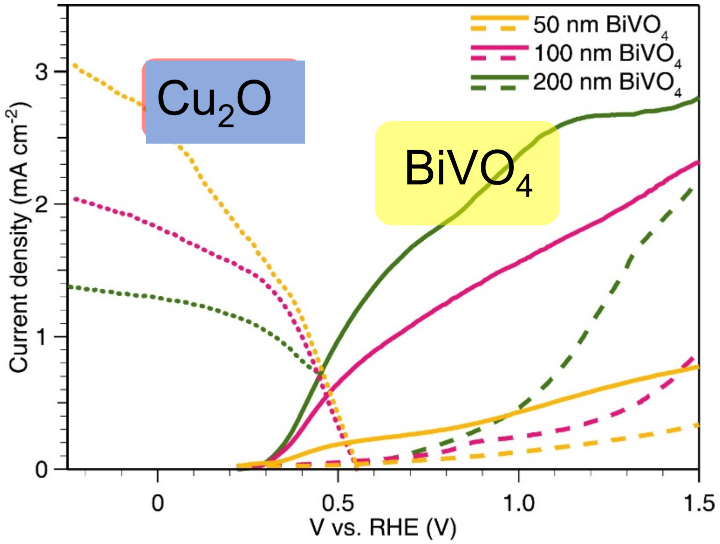
Low performance (non-complementary light absorption).

Hematite filters useful light for Cu_2O

Assessment of a Dual Tandem PEC Cell







Optimized combination of photoelectrodes (band gaps and thickness) are needed!

- Jun-Ho YUM, junho.yum@epfl.ch

Bornoz *et al. J.Phys. Chem. C.* **118**, 16959-16966 (2014).

Examples of Photoelectrodes

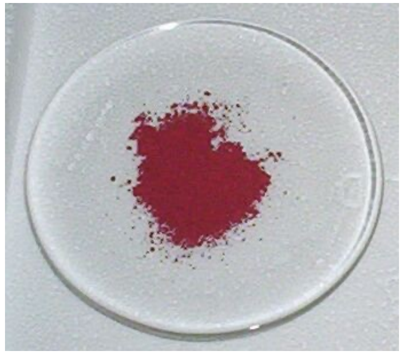
Photoanode (n-type SC)

WO_3

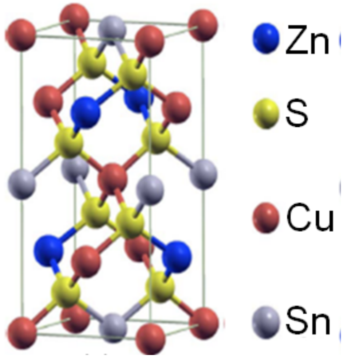
$BiVO_4$

$\alpha\text{-}Fe_2O_3$

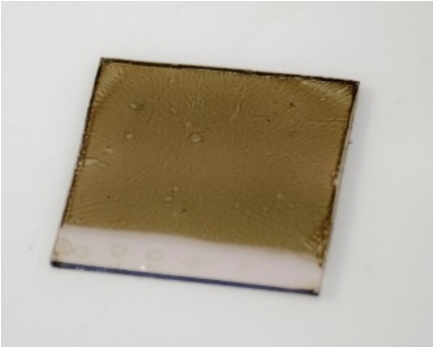
Photocathode (p-type SC)



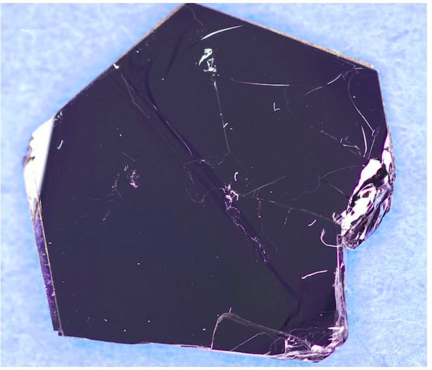
Copper(I) oxide



Cu_2ZnSnS_4



$CuFeO_2$

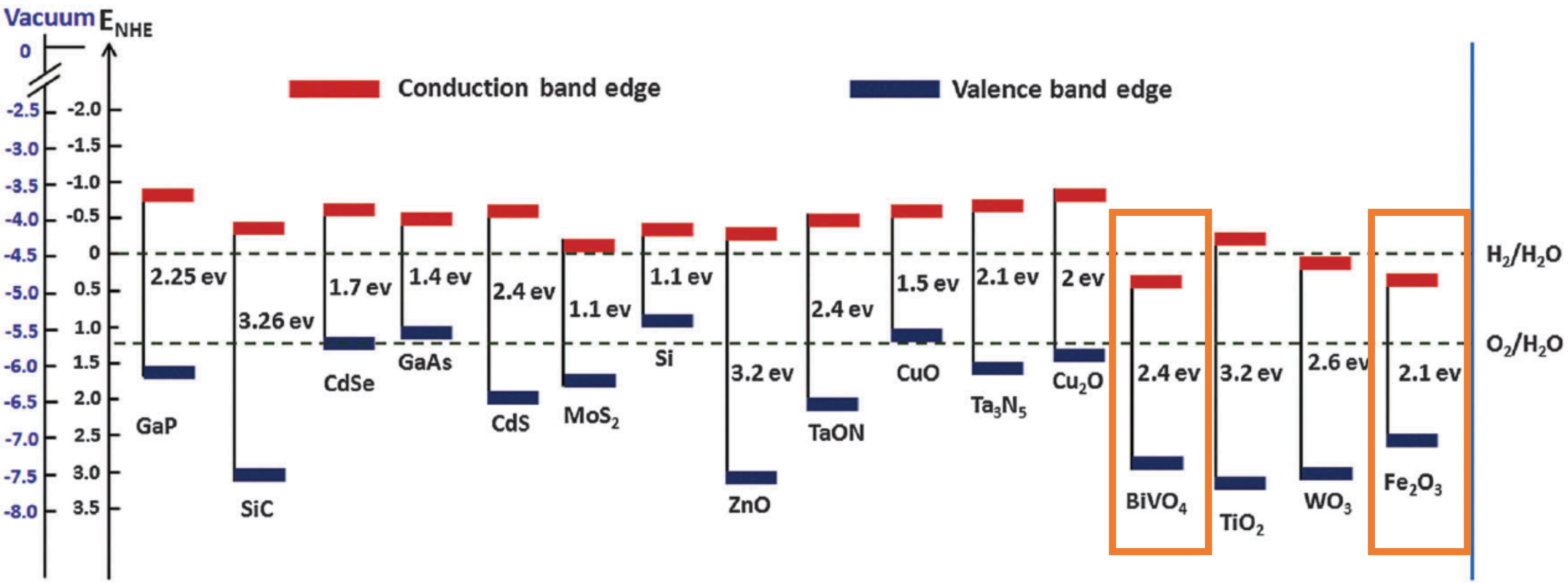


WSe_2

- Jun-Ho YUM, junho.yum@epfl.ch

Examples of Photoelectrodes

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



- Jun-Ho YUM, junho.yum@epfl.ch

α-Fe_2O_3 (hematite) as a Photoanode

Advantages

- Cheap and abundant (Fe in the earth crust, 5.6% 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/cm^2

Challenges

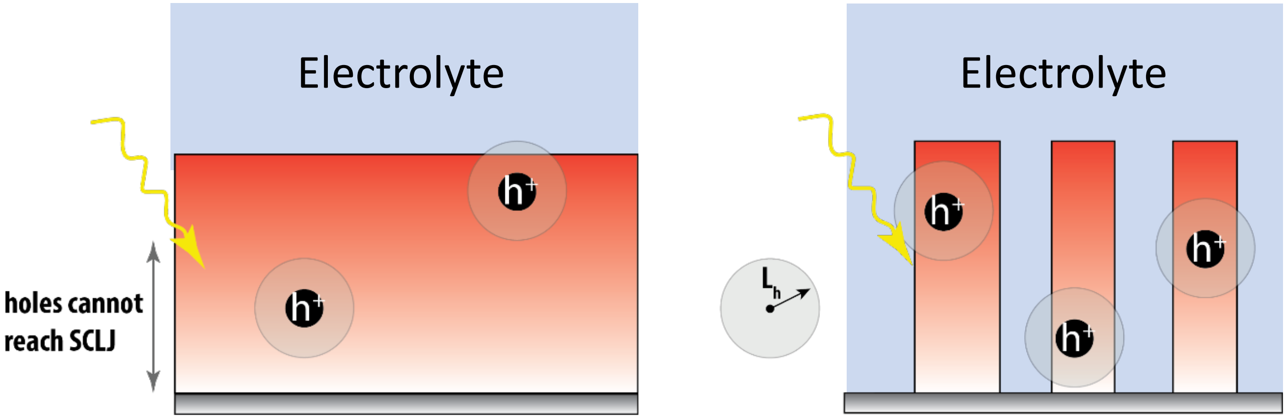
Bulk problems

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

Surface problems

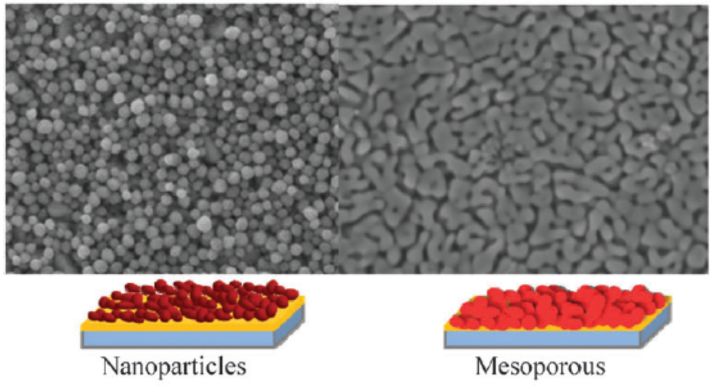
- High overpotential for water oxidation kinetics (surface trap states)

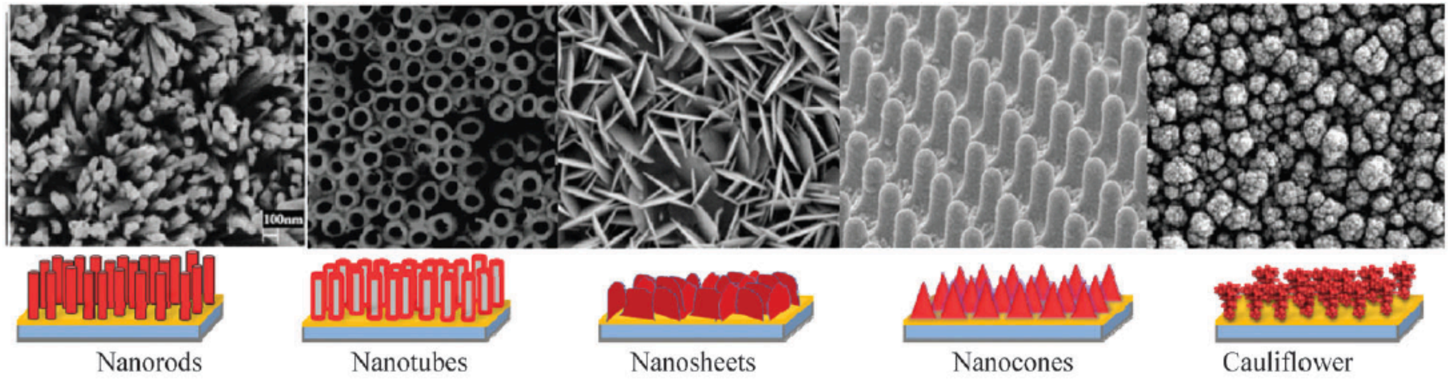
Bulk Problems in α-Fe_2O_3 (hematite)



Planar film

Nanostructured film

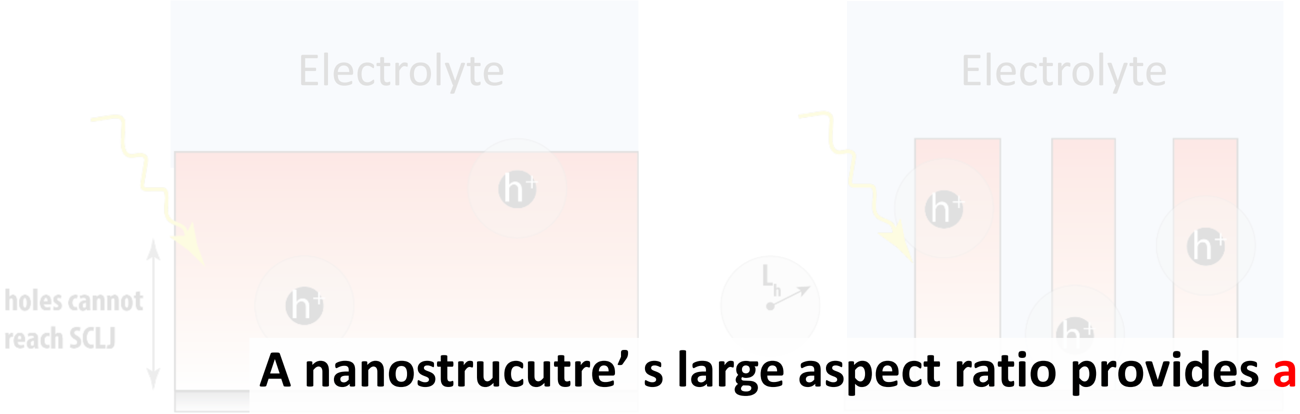


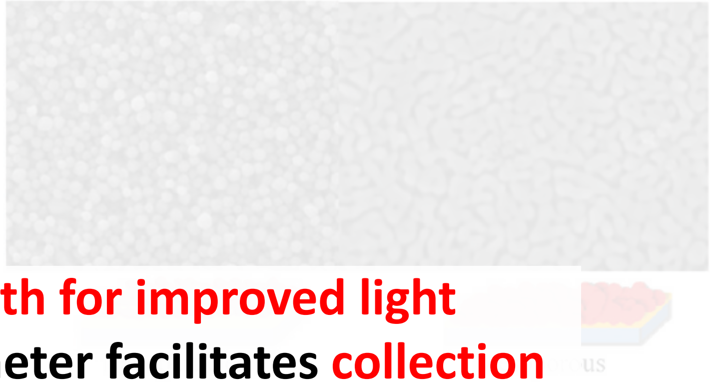


A. G. Tamirat et al., *Nanoscale Horiz.*, **1**, 243 (2016)

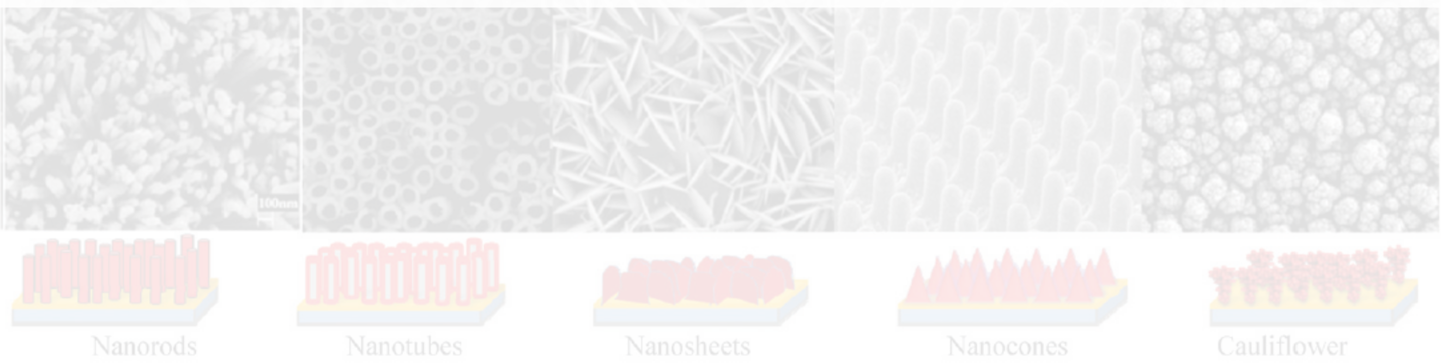
- Jun-Ho YUM, junho.yum@epfl.ch

Bulk Problems in α-Fe_2O_3 (hematite)





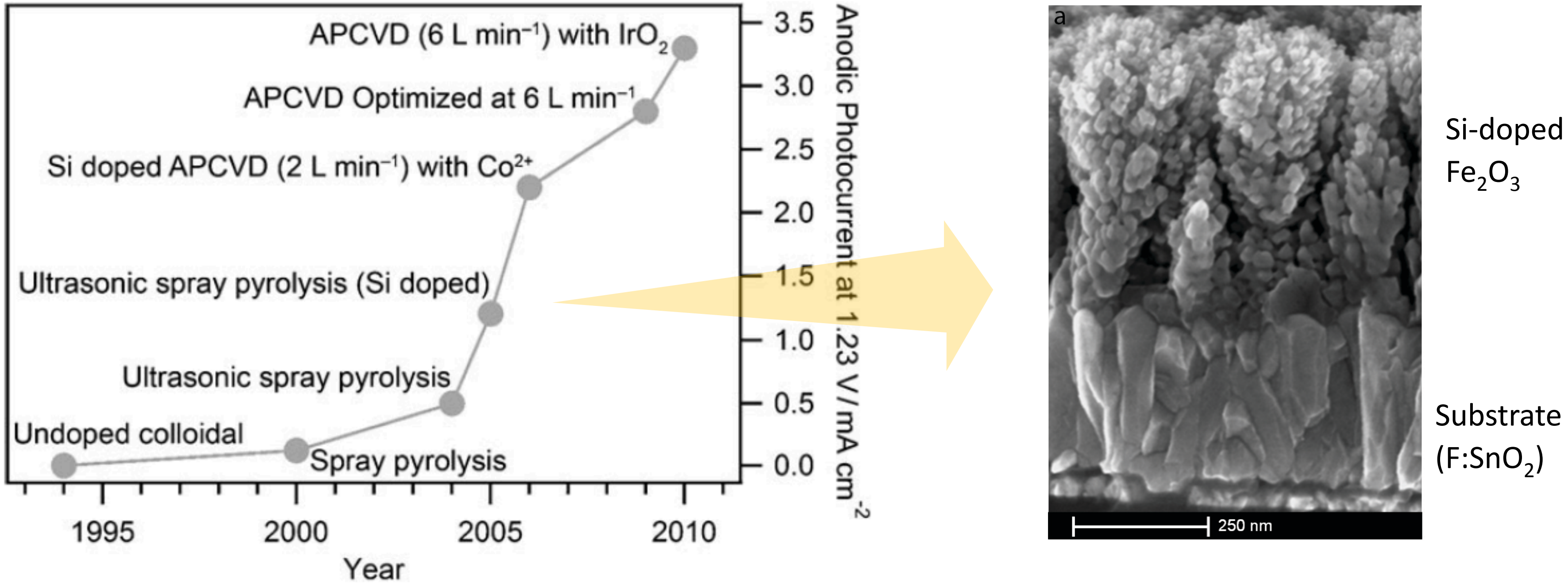
A nanostrucutre' s large aspect ratio provides a long optical path for improved light absorption along the vertical axis, while its much smaller diameter facilitates collection of minority carriers over a shorter distance, minimizing the probability of recombination within the absorber material.



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

- Jun-Ho YUM, junho.yum@epfl.ch

Bulk Problems in α-Fe_2O_3 (hematite)



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

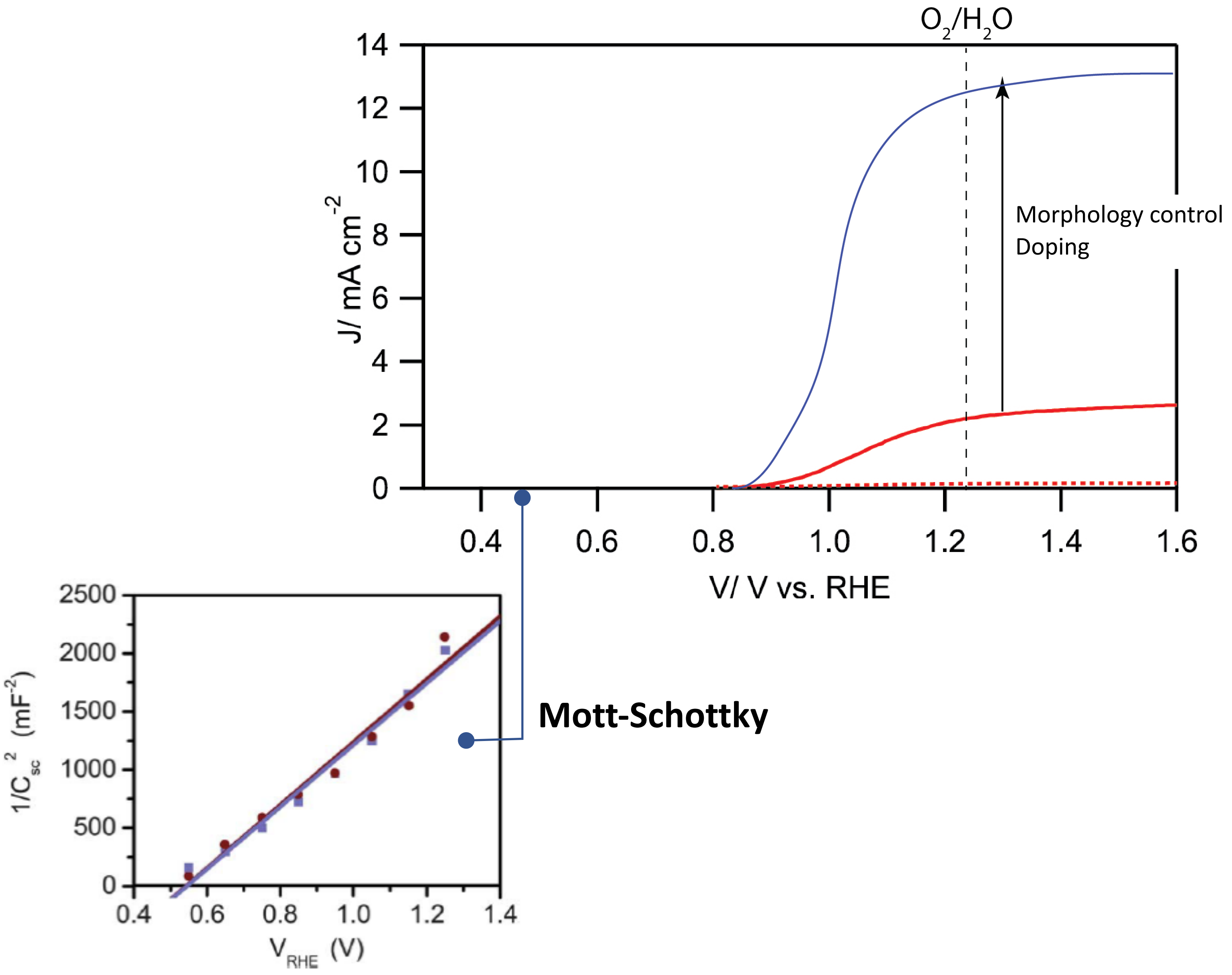
- Si^{4+}, Ti^{4+}, Sn^{4+}, Zr^{4+}, Nb^{5+} (n-type)
- Mg^{2+}, Cu^{2+} (p-type)

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

Ex) Zr^{4+} doped hematite: 0.1 $\Omega^{-1}cm^{-1}$ with 10^{19} cm^{-3} doping concentration vs 10^{-14} $\Omega^{-1}cm^{-1}$ for polycrystal

- Jun-Ho YUM, junho.yum@epfl.ch

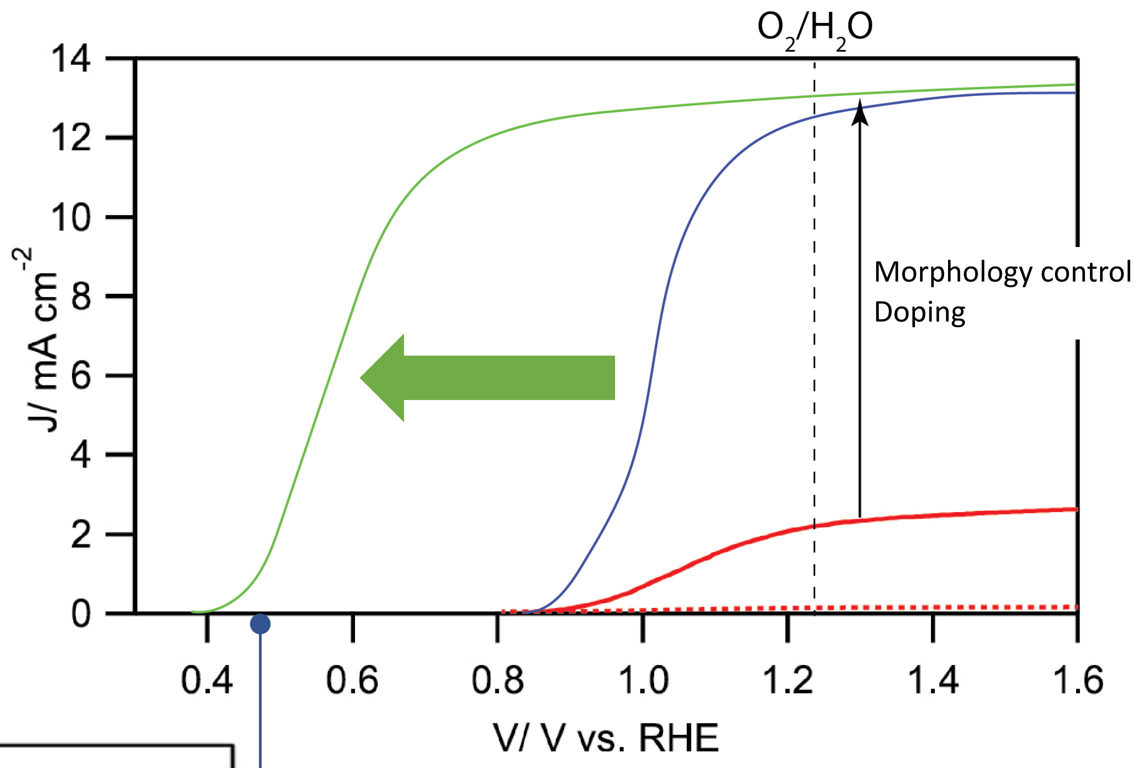
Bulk Problems in α-Fe_2O_3 (hematite)



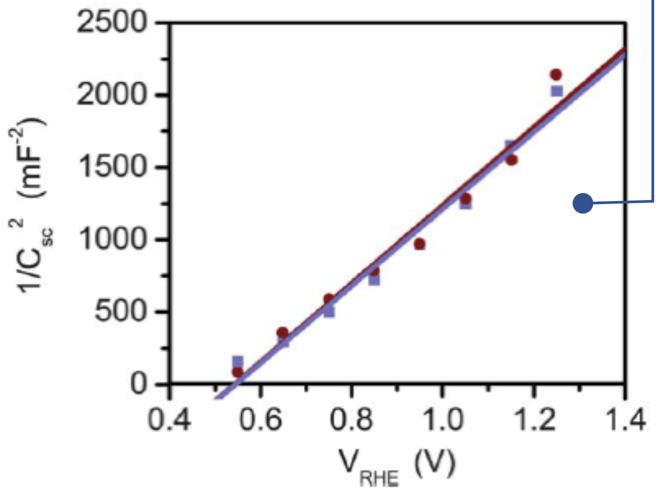
Mott-Schottky

- Jun-Ho YUM, junho.yum@epfl.ch

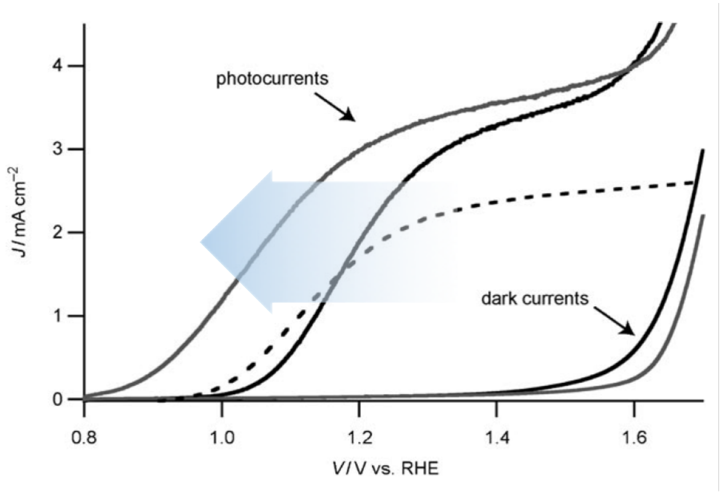
Overpotential Problems in α-Fe_2O_3 (hematite)



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



Mott-Schottky

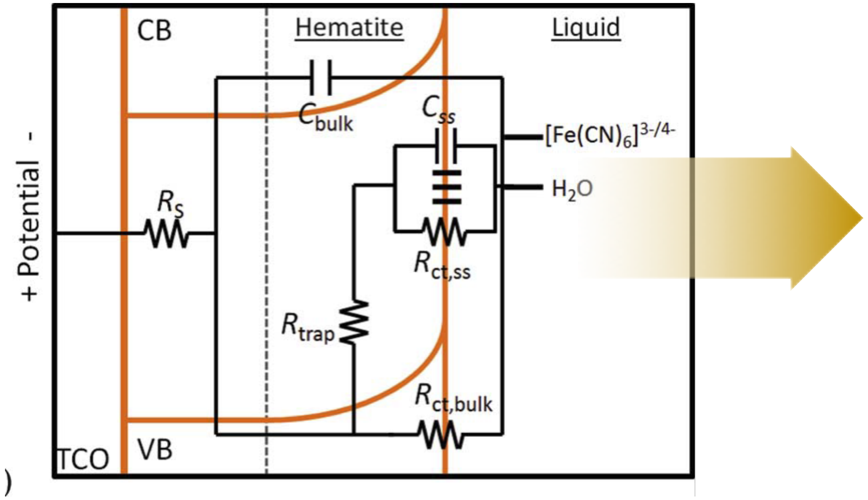


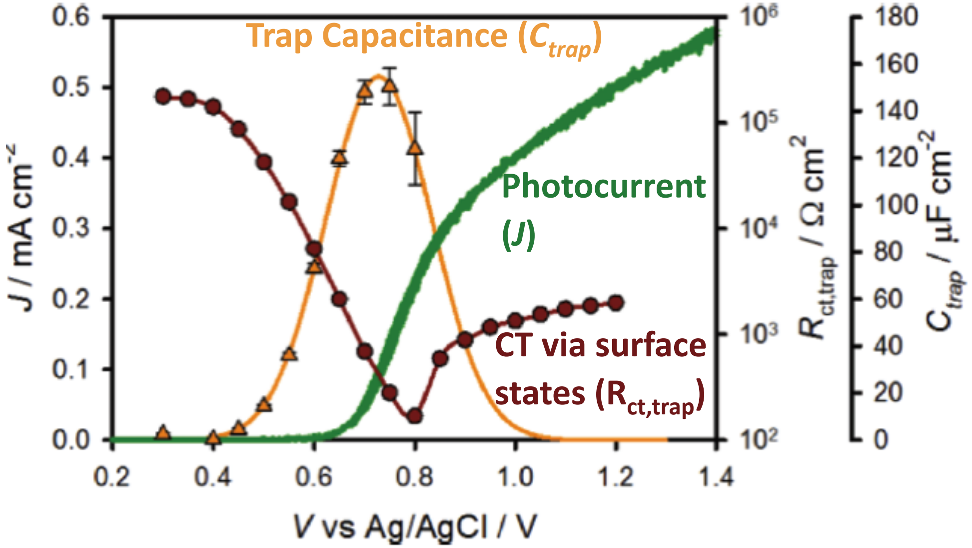
- Jun-Ho YUM, junho.yum@epfl.ch

Surface Problems in α-Fe_2O_3 (hematite) – Overpotential

Surface recombination. *Examining the electrochemical properties of the SCLJ*

equivalent electrical circuit



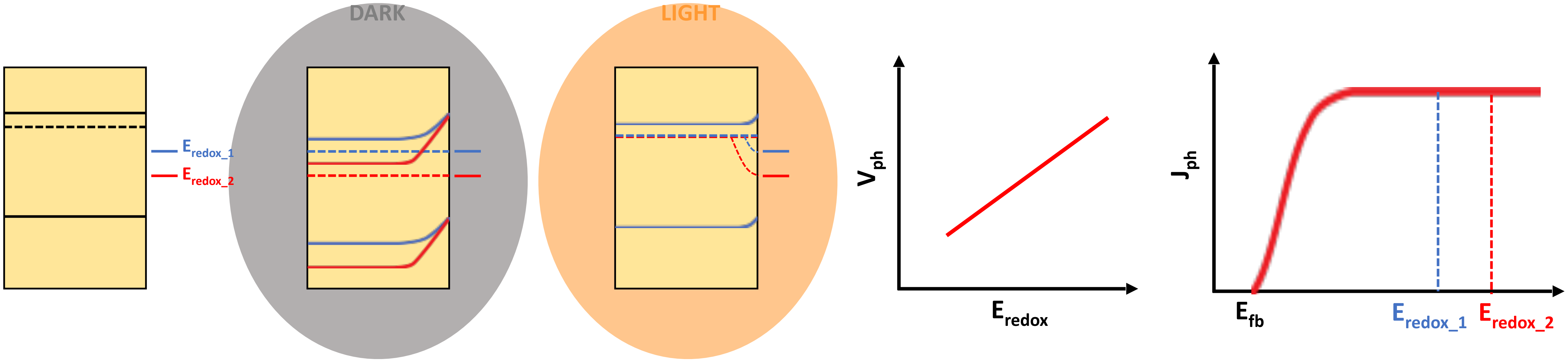


B. Klahr *et al. J. Am. Chem. Soc.*, **134**, 4294 (2012)

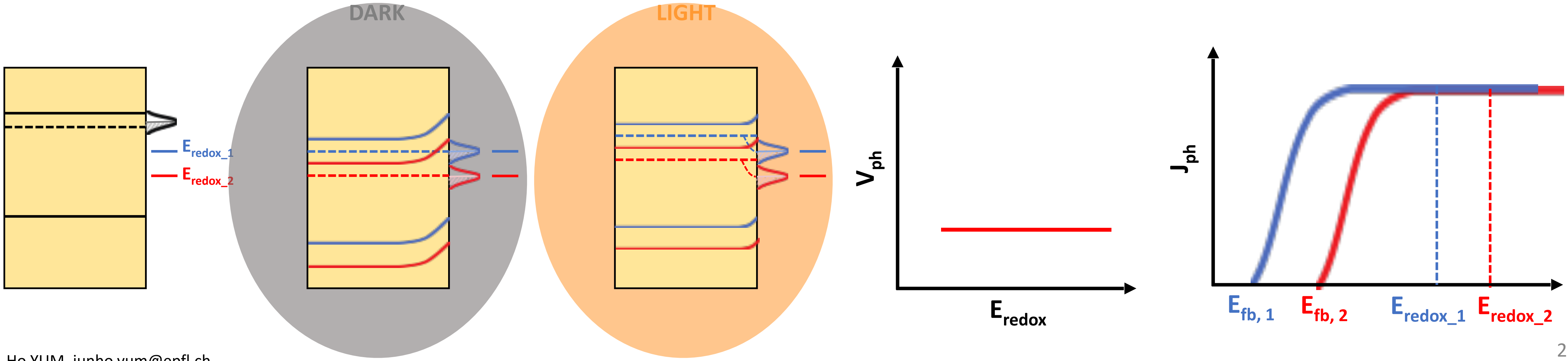
- **C_{trap}** indicate the accumulation of charges at the SCLJ just before the water oxidation starts.
- Charge transfer takes place from this surface state.
- Trapped charge carriers “pin” the Fermi level, Fermi Level Pinning, leading to reduced band bending and delayed onset of photocurrent (overpotential).

Fermi Level Pinning (FLP)

No surface state / No FLP (band edge pinning)



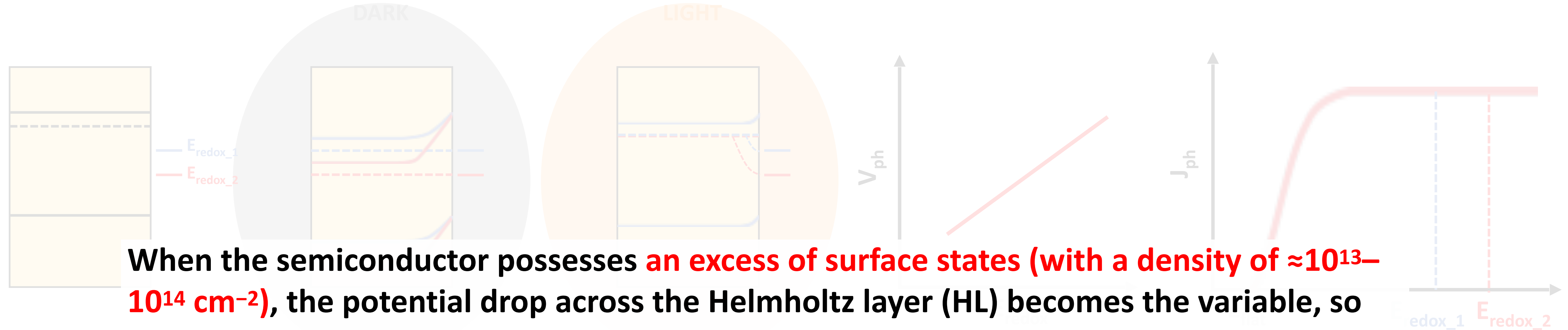
Presence of surface state/ Fermi Level Pinning



- Jun-Ho YUM, junho.yum@epfl.ch

Fermi Level Pinning (FLP)

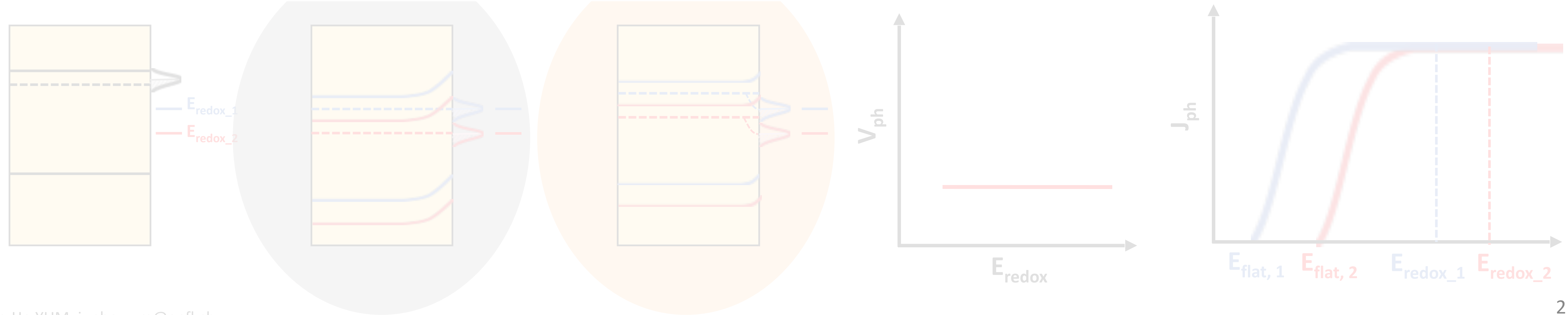
No surface state / No FLP (band edge pinning)



When the semiconductor possesses an excess of surface states (with a density of ≈10^{13}–10^{14} cm^{-2}), the potential drop across the Helmholtz layer (HL) becomes the variable, so that band bending degree in the space charge layer is greatly weaken and becomes independent of the applied bias. This effect is called Fermi-level pinning.

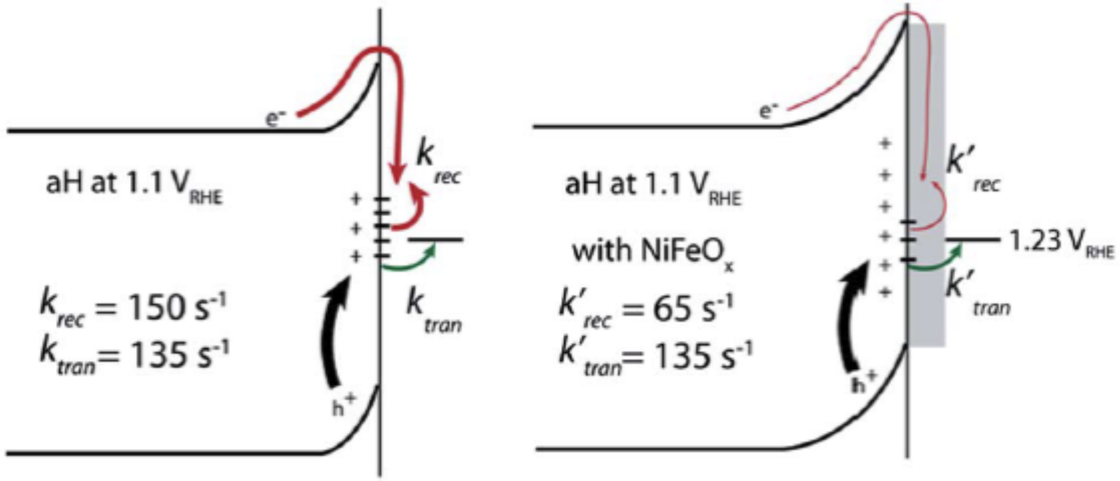
Under Fermi-level pinning conditions, the degree of band bending remains unchanged.

Presence of s



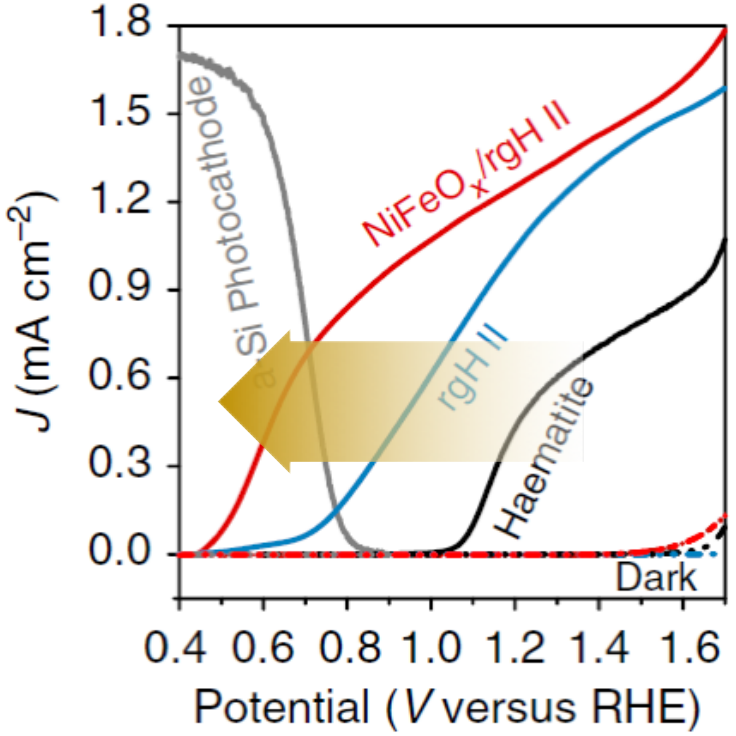
Surface Problems in α-Fe_2O_3 (hematite) – Overpotential

Surface recombination. *Examining the electrochemical properties of the SCLJ*



$NiFeO_x$ **passivate** surface traps.

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

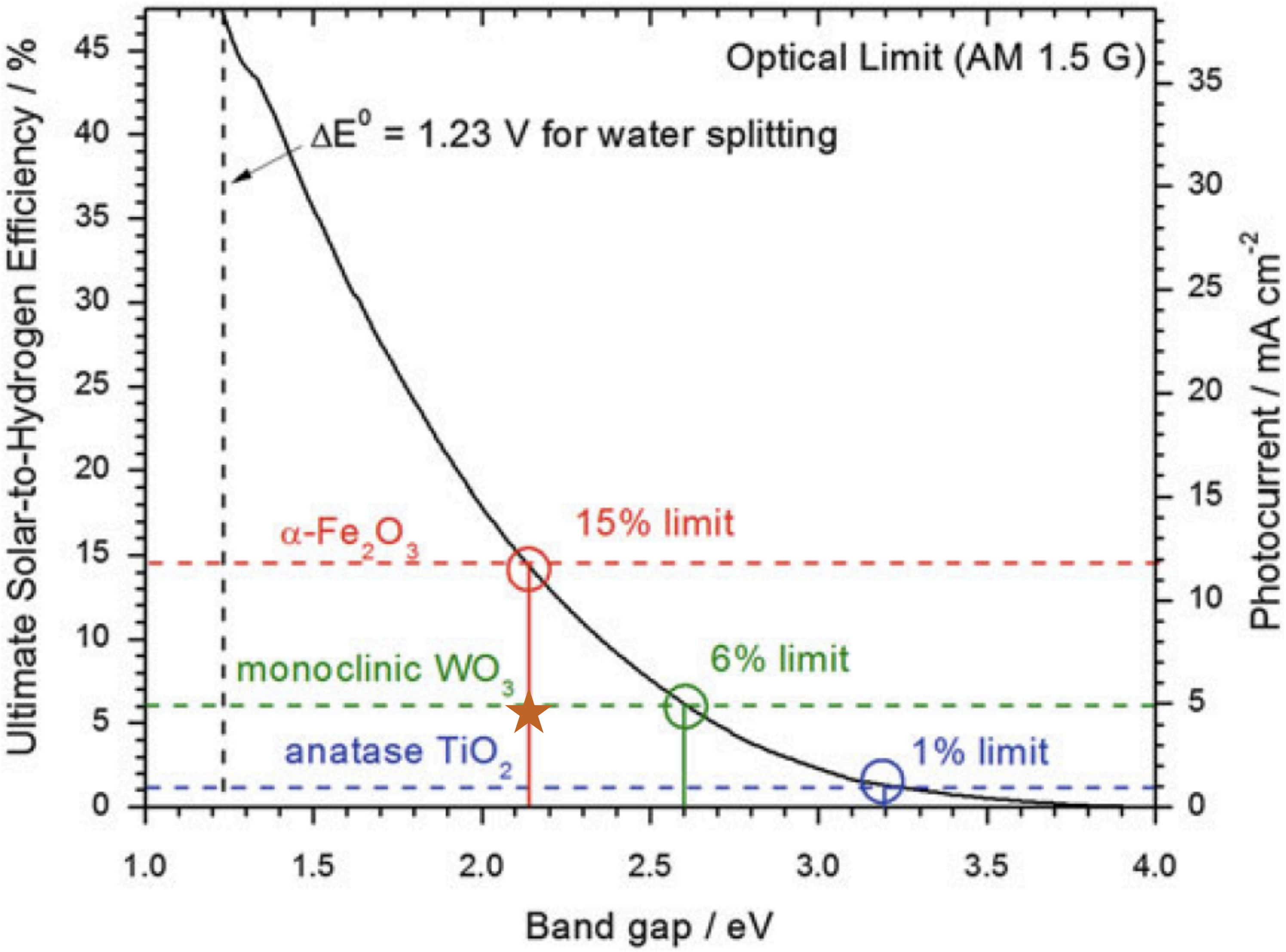


Deposition of $NiFeO_x$ shifts V_{on} close to V_{fb} !!!

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

- Jun-Ho YUM, junho.yum@epfl.ch

Theoretical Maximum Solar-To-Hydrogen Efficiency



- Jun-Ho YUM, junho.yum@epfl.ch

Examples of Photoelectrodes

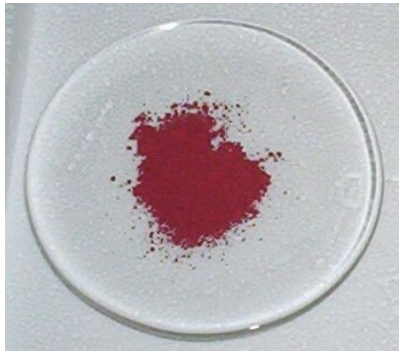
Photoanode (n-type SC)

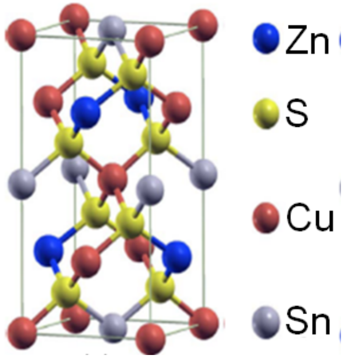

WO_3


$BiVO_4$

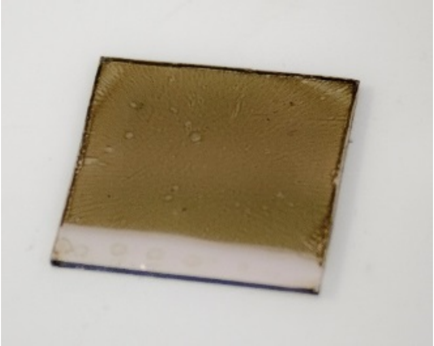

α-Fe_2O_3

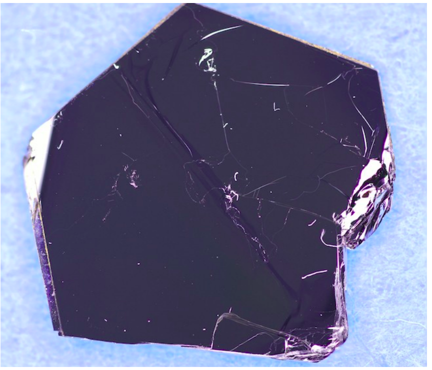
Photocathode (p-type SC)


Copper(I) oxide



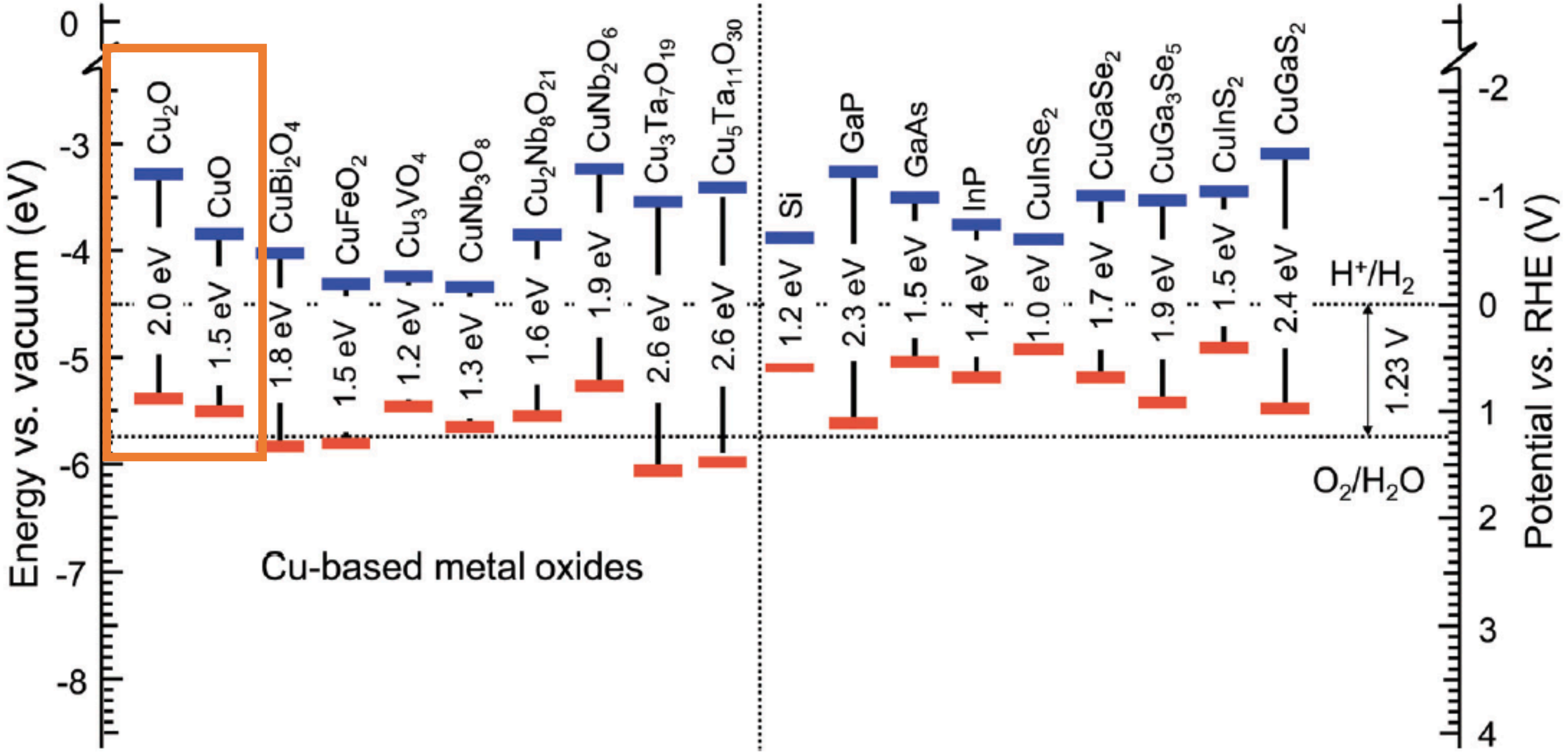
Cu_2ZnSnS_4


$CuFeO_2$


WSe_2

- Jun-Ho YUM, junho.yum@epfl.ch

Cu based Metal Oxides



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

Cu_2O (Cuprous oxide) as a photocathode

Advantages

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

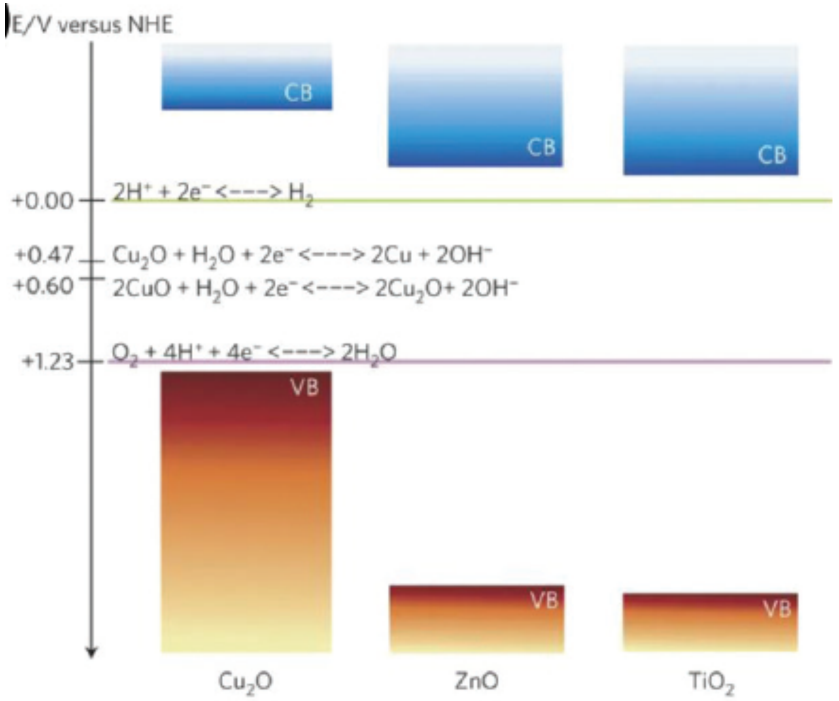
Challenges

Bulk problems

- Minority carrier diffusion length around 200 nm (light penetration depth over 1 µm at 550 nm)

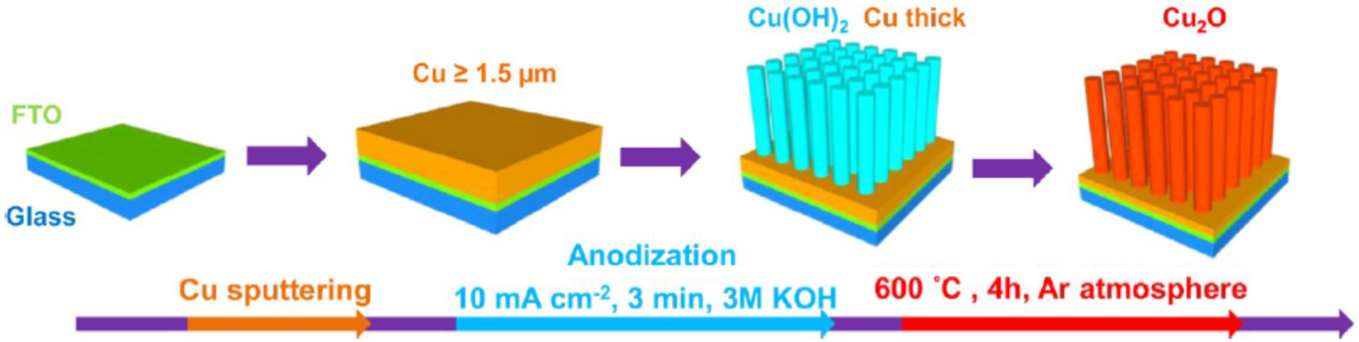
Surface problems

- Instability under operational condition (Facile reduction to Cu)



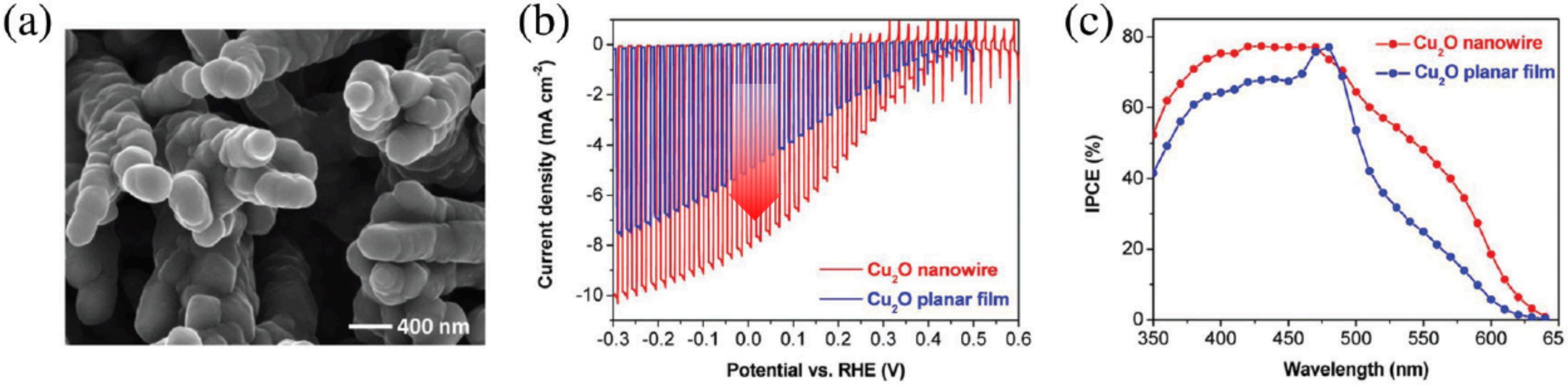
- Jun-Ho YUM, junho.yum@epfl.ch

Nanostructuring Cu_2O as a photocathode



Photocathode: $Cu_2O/AZO/TiO_2/RuO_x$

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

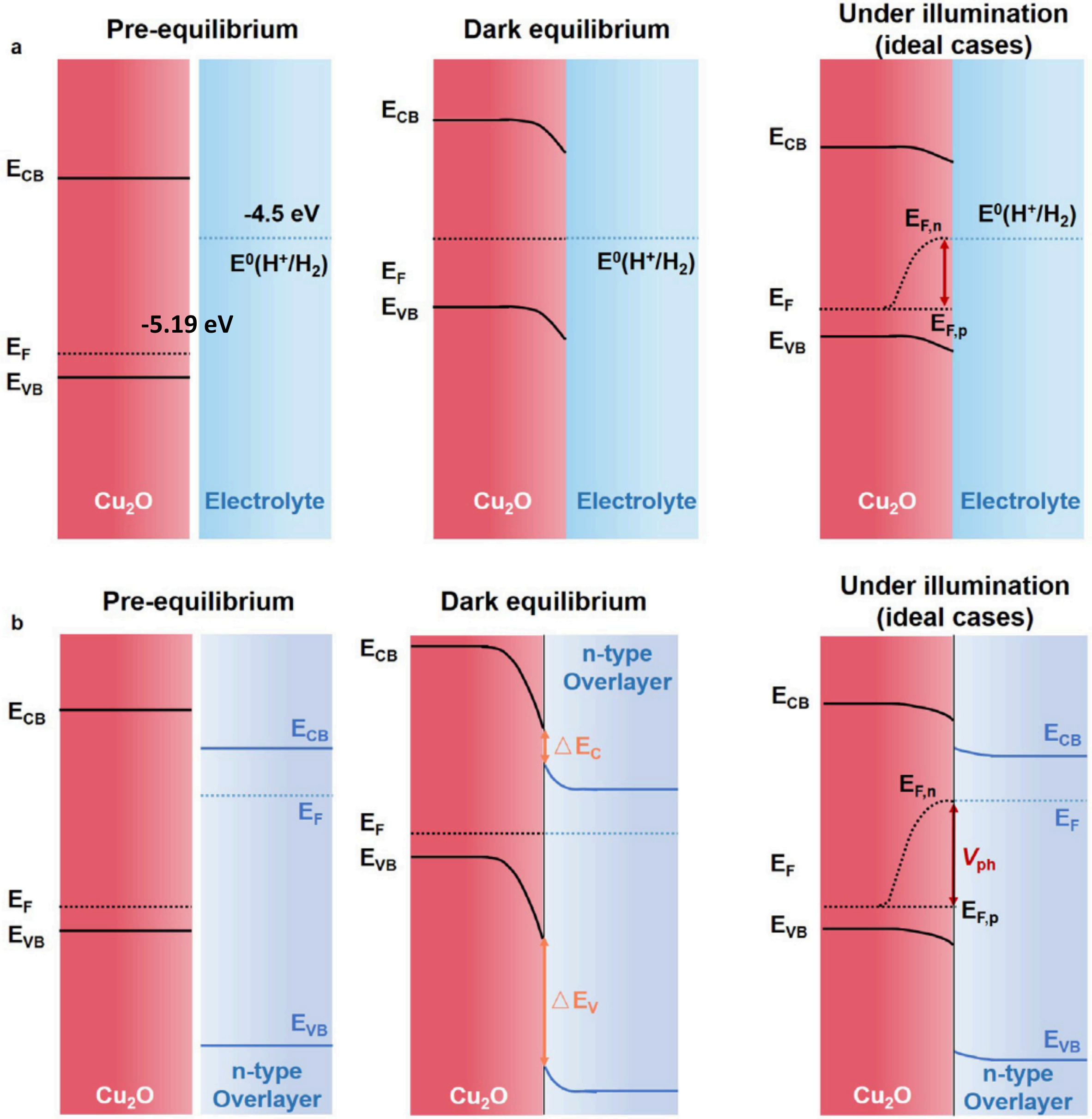


J. Luo et al., *Nano Lett.*, **16**, 1848 – 1857 (2016)

Improving the onset potential in Cu_2O photocathode

Cu_2O-liquid junction

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

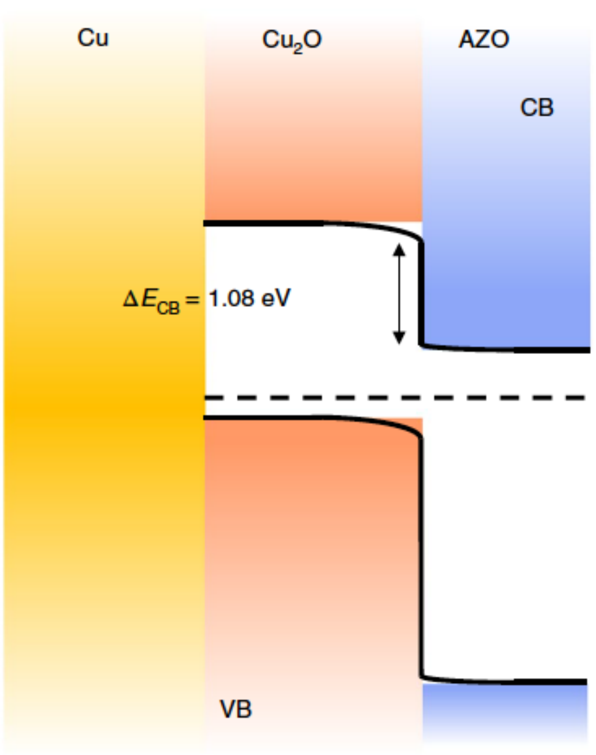


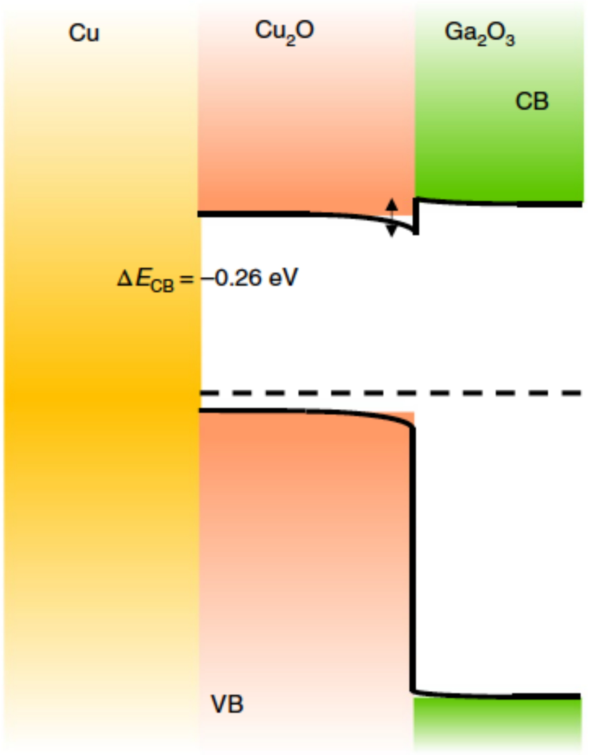
- Improved photovoltage
- Passivation against photocorrosion
- Still limited photovoltage due to a large conduction band offset

J. Cheng et al., *Chem. Phys. Rev.* , **3**, 031306 (2022)

- Jun-Ho YUM, junho.yum@epfl.ch

Improving the onset potential in Cu_2O photocathode

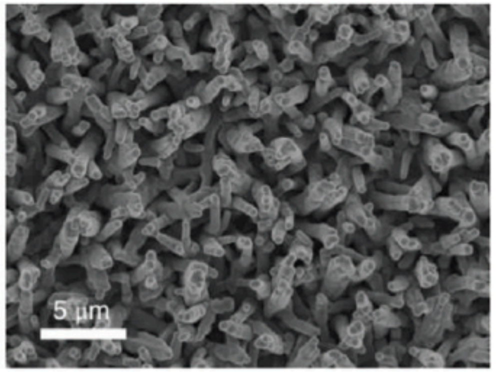




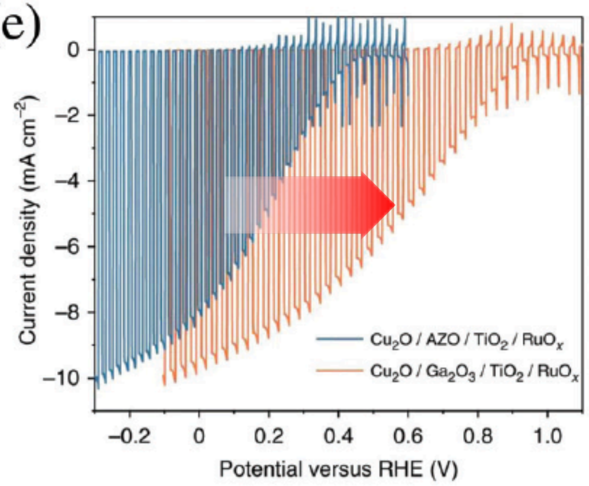
Photocathode: $Cu_2O/Ga_2O_3/TiO_2/RuO_x$

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

(d)



(e)



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

- Jun-Ho YUM, junho.yum@epfl.ch

Outlook on PEC Tandem Cells

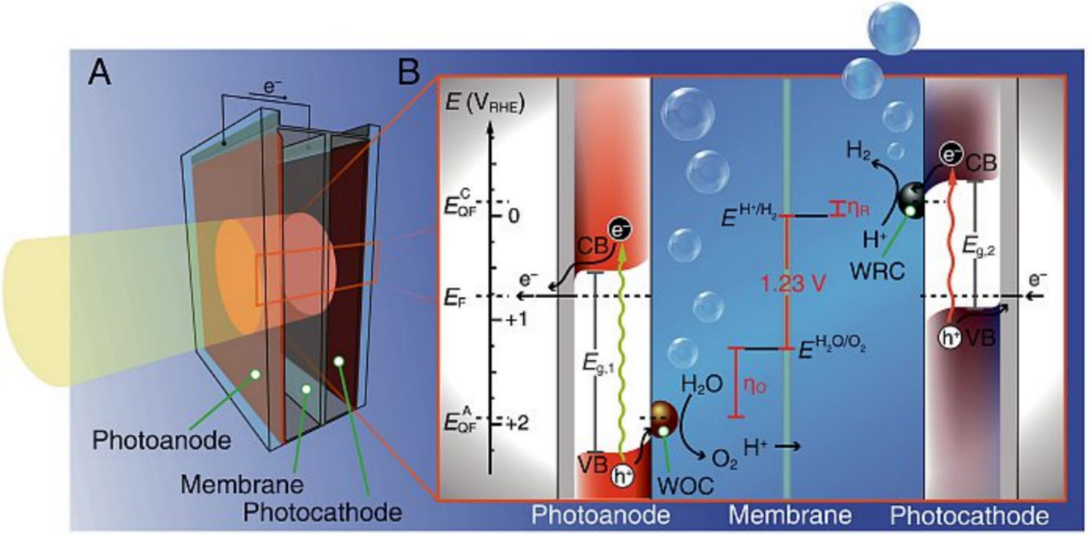
- **The formation of a SEMICONDUCTOR-LIQUID JUNCTION (SCLJ) can drive stand-alone photoelectrochemical reactions.**

- **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.**

- Jun-Ho YUM, junho.yum@epfl.ch

An Emerging Application for Organic Semiconductors

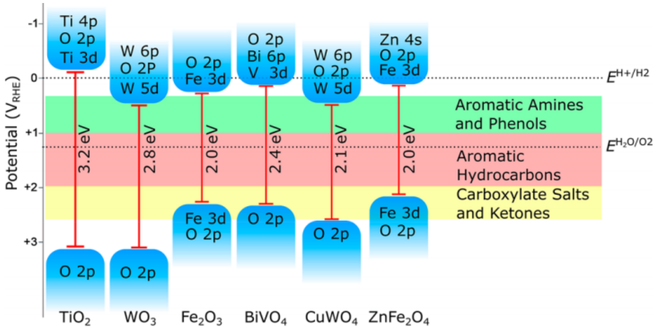


$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \quad E = 1.23\ \text{V vs RHE}$$

$$4e^- + 4H^+ \rightarrow 2H_2 \quad E = 0\ \text{V vs RHE}$$

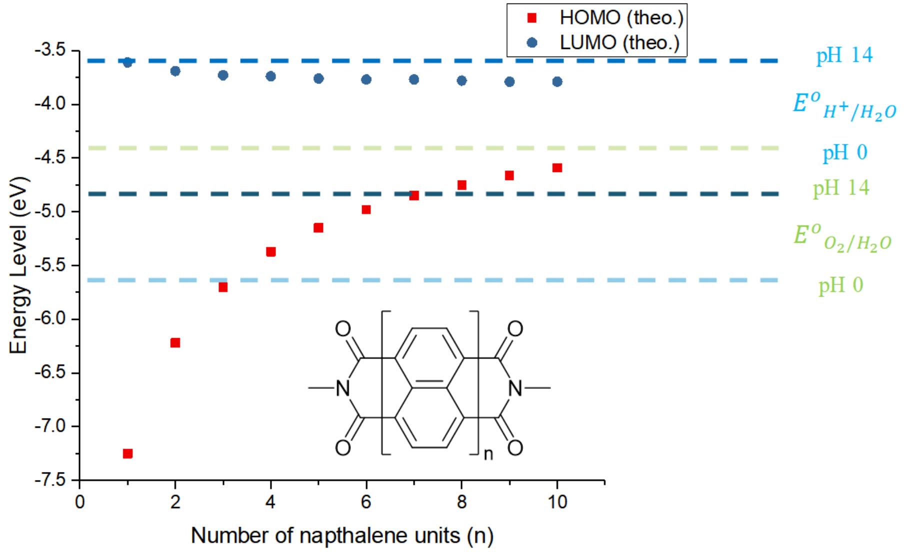
Inorganic semiconductors

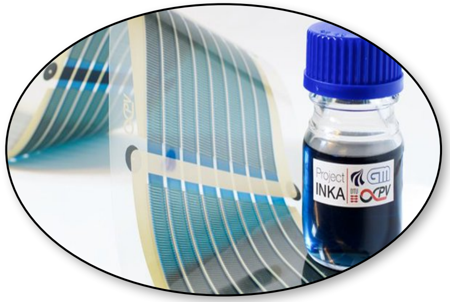
- ✓ Harsh preparation condition
- ✓ Poor charge separation
- ✓ Fixed energy level



Organic semiconductors

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



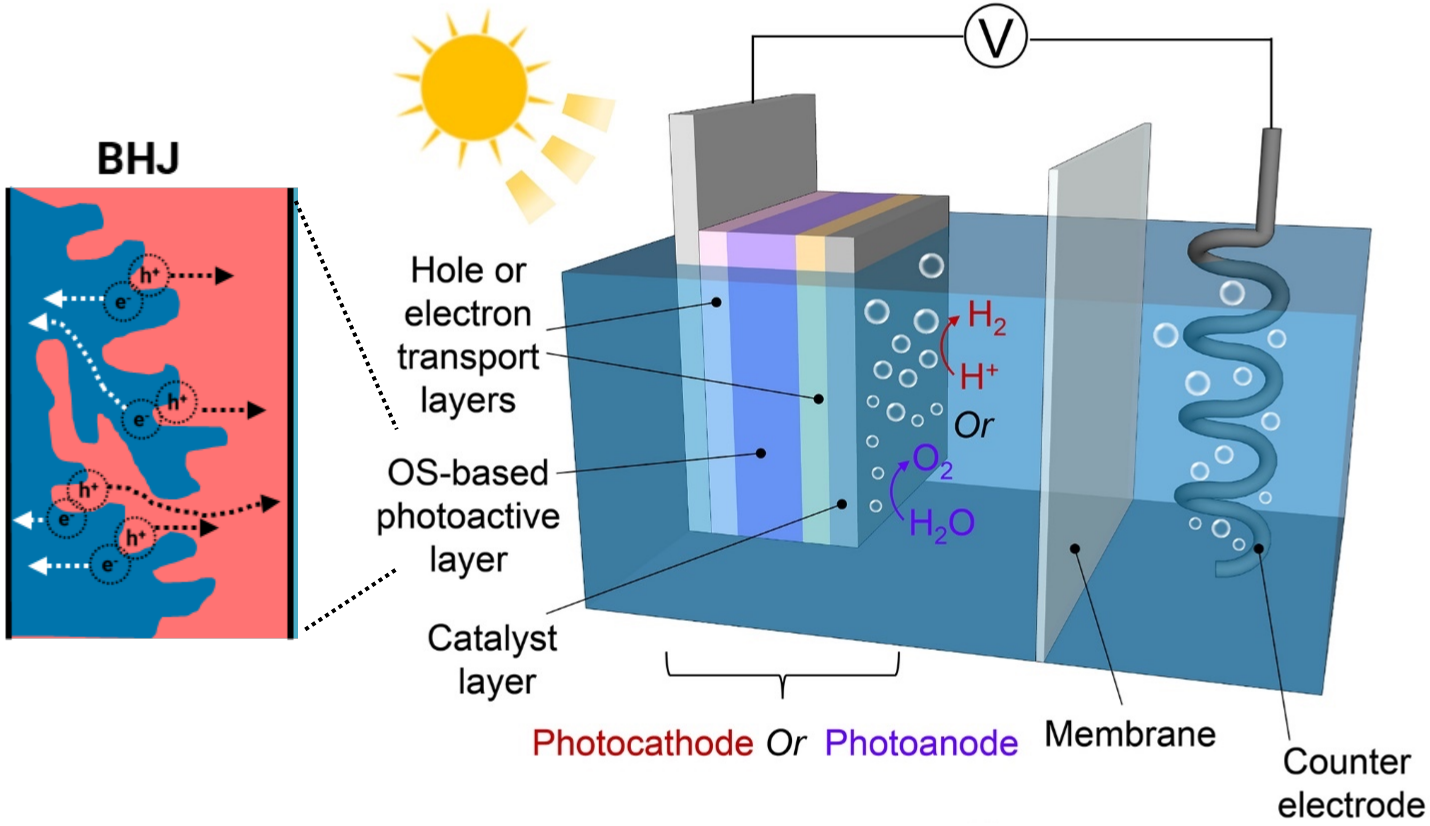


K. Sivula, *Chimia* **2017**, 71, 471-474

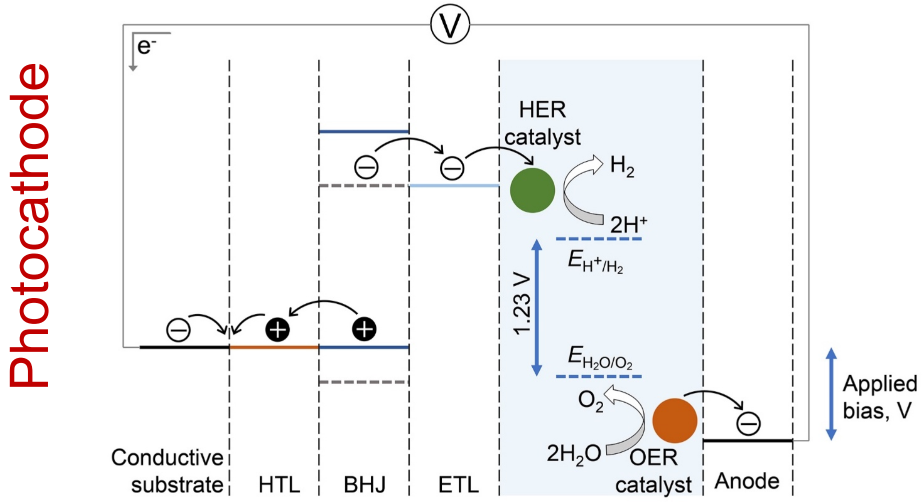
- Jun-Ho YUM, junho.yum@epfl.ch

An Emerging Application for Organic Semiconductors

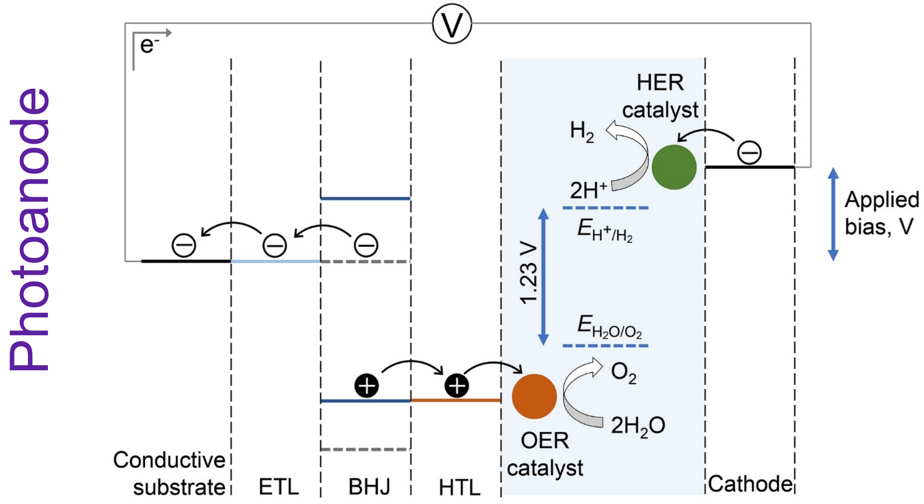
Solar-to-fuel conversion: “Artificial photosynthesis”



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



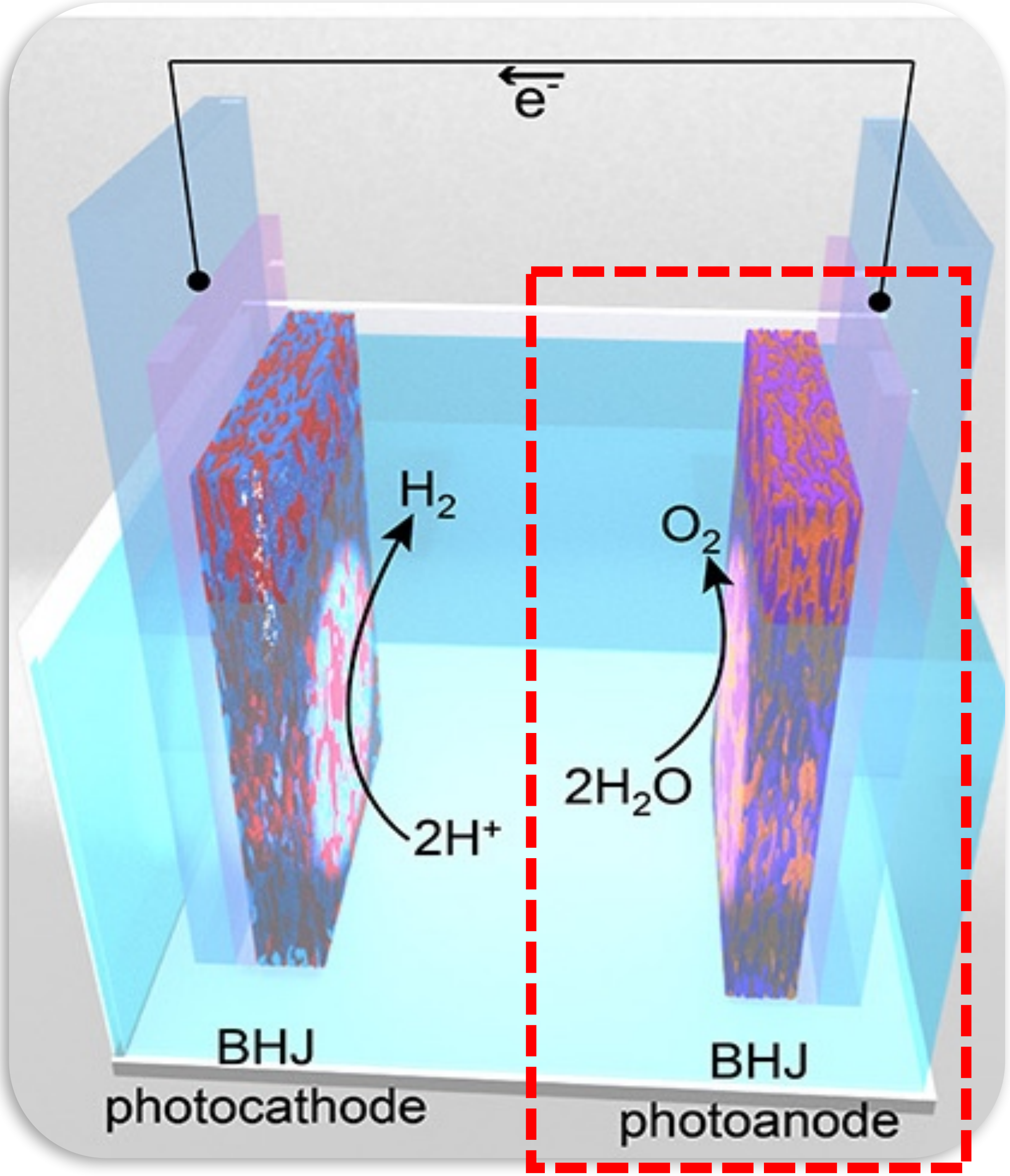
LUMO level of Acceptor higher than H^+/H_2 potential



HOMO level of Donor lower than O_2/H_2O potential

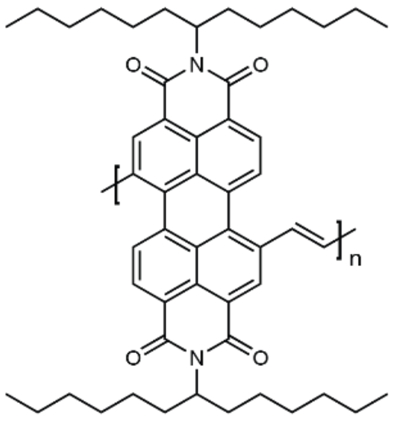
- Jun-Ho YUM, junho.yum@epfl.ch

Ultimate Goal

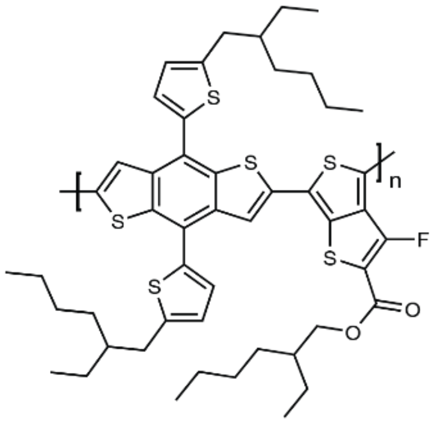


- Jun-Ho YUM, junho.yum@epfl.ch

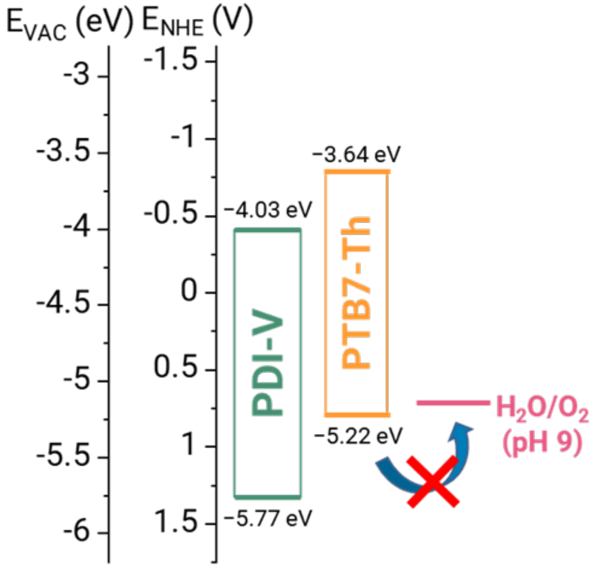
Identification of Ideal OS Materials: Photoanode

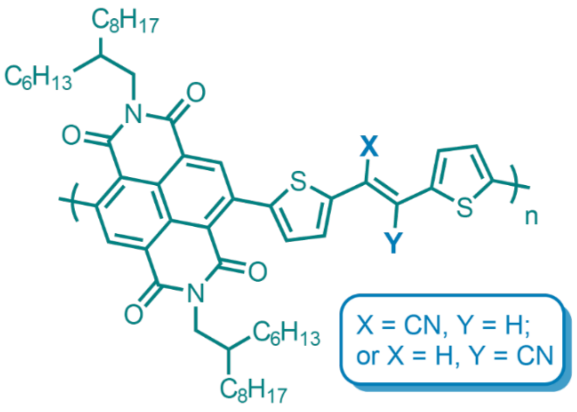


PDI-V (acceptor)

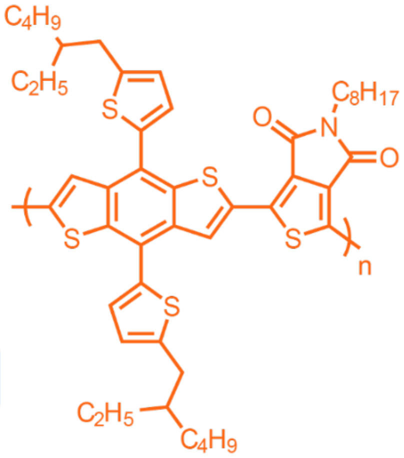


PTB7-Th (donor)

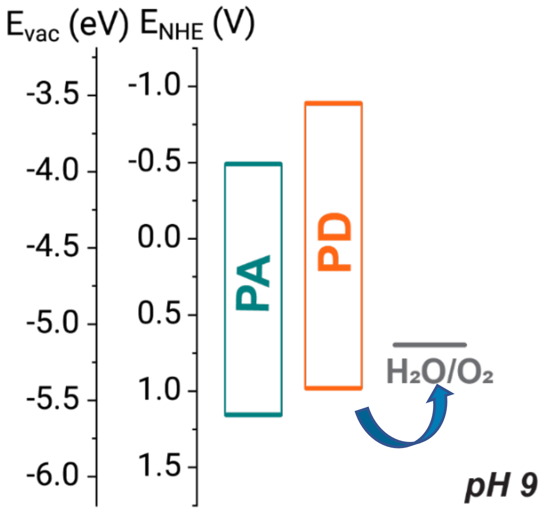


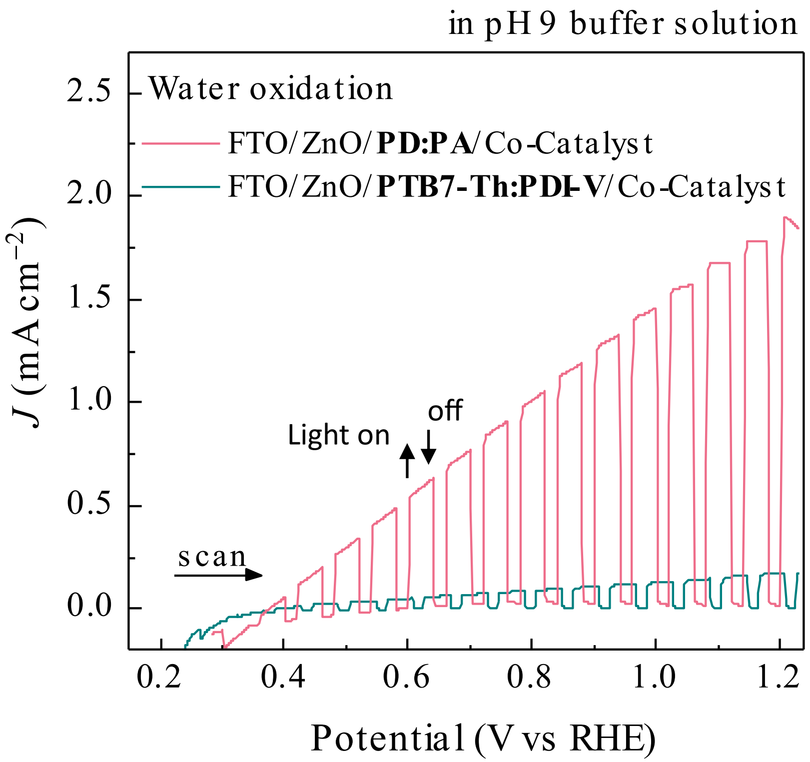


PNDITCVT (PA)



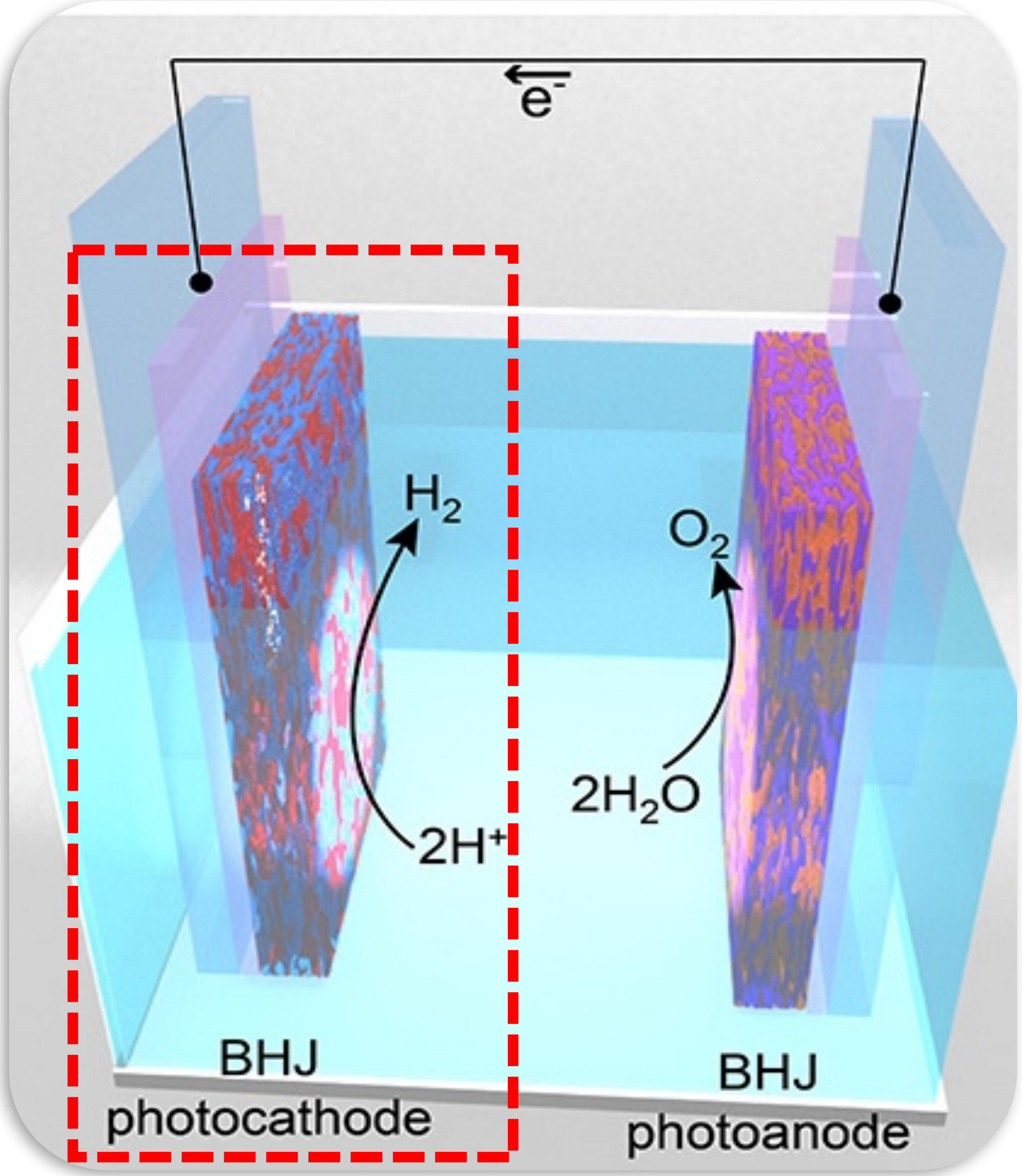
PBDTTTPD (PD)





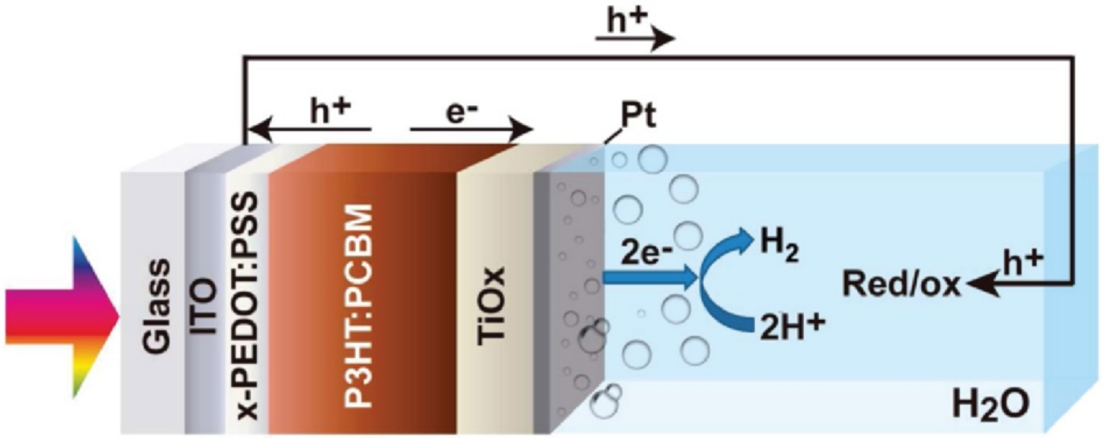
- Jun-Ho YUM, junho.yum@epfl.ch

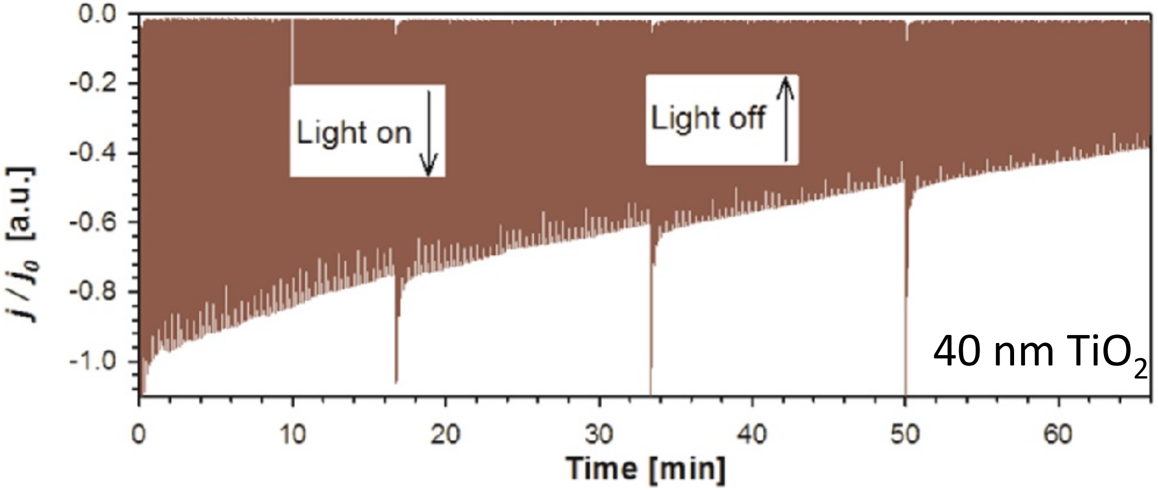
Ultimate Goal



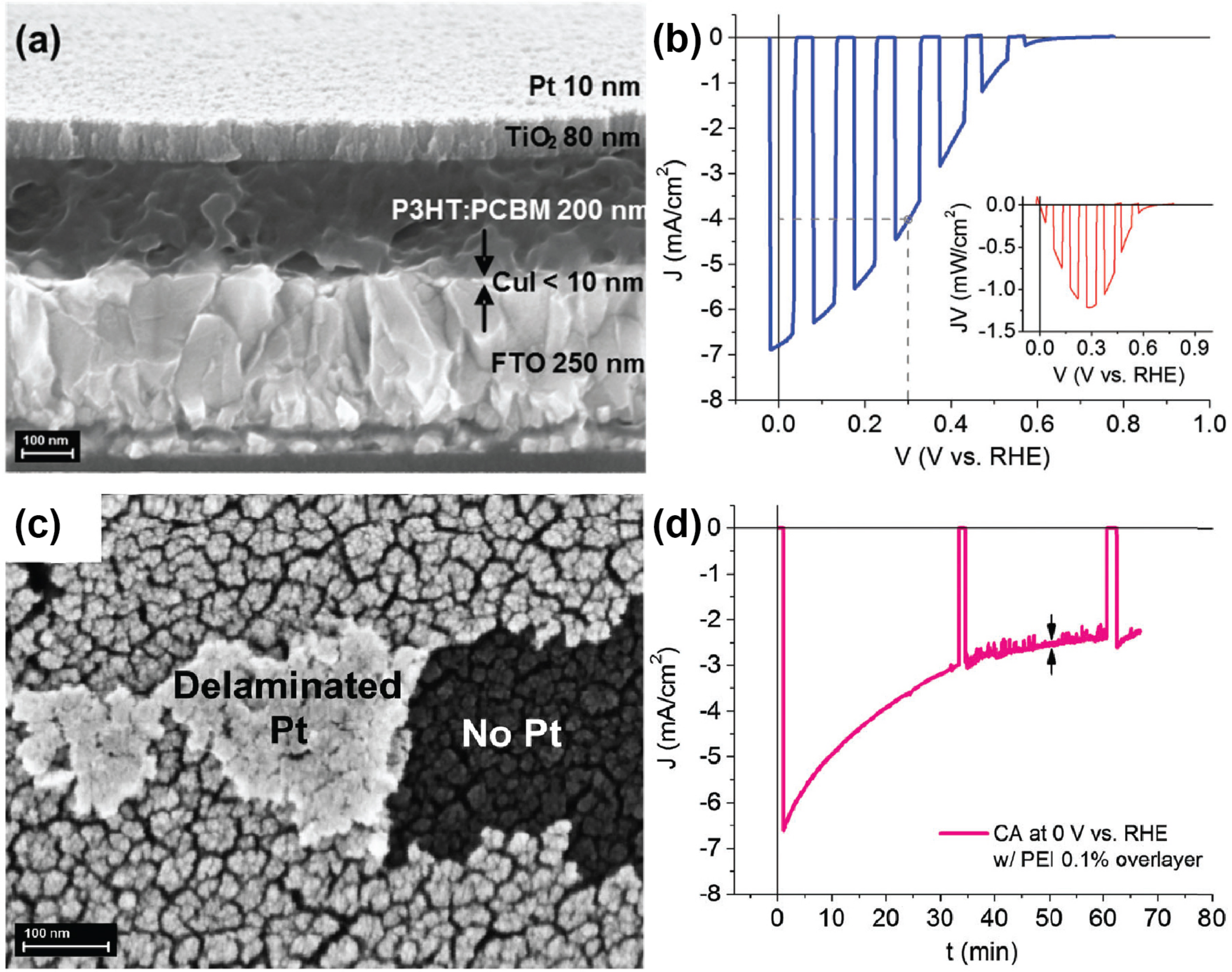
- Jun-Ho YUM, junho.yum@epfl.ch

Organic semiconductor photocathodes for direct H_2 production





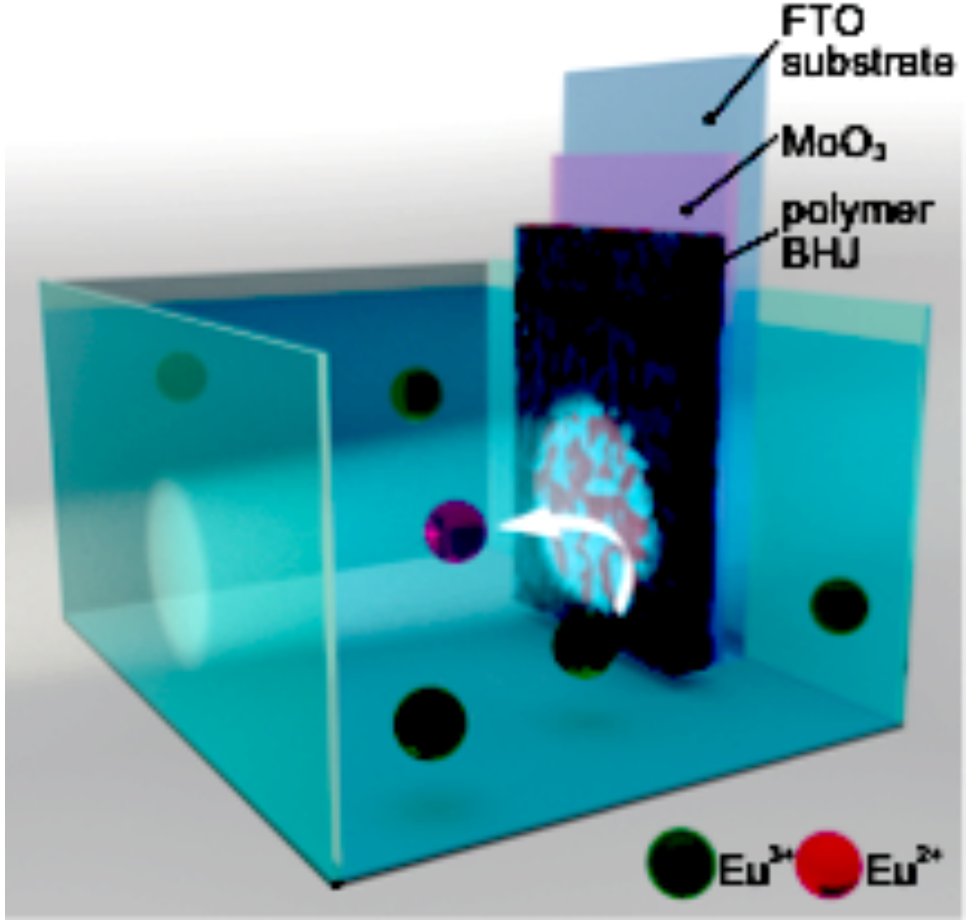
M. Haro et al., *J. Phys. Chem. C* **2015**, *119*, 6488.

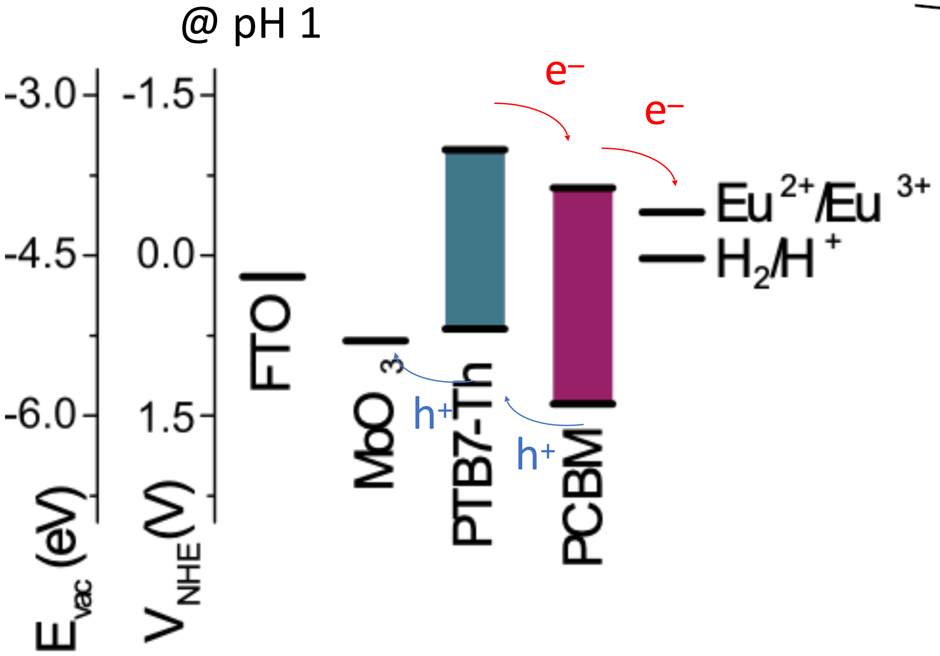


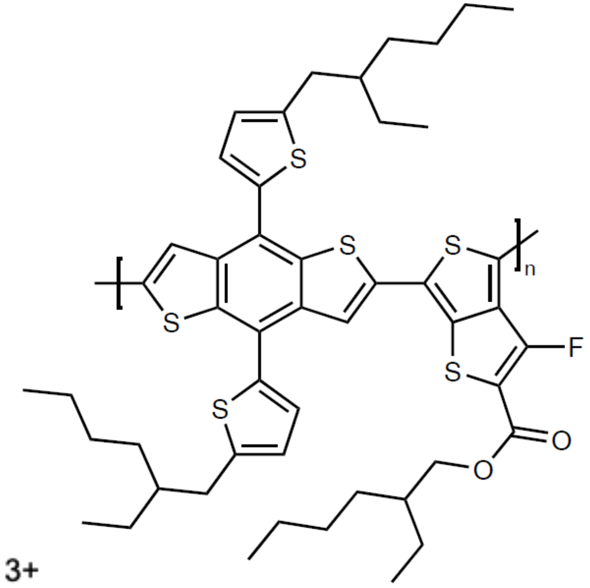
H. Comas Rojas et al., *Energy & Environmental Science* **2016**, *9*, 3710.

Why is a BHJ in Water So Unstable?

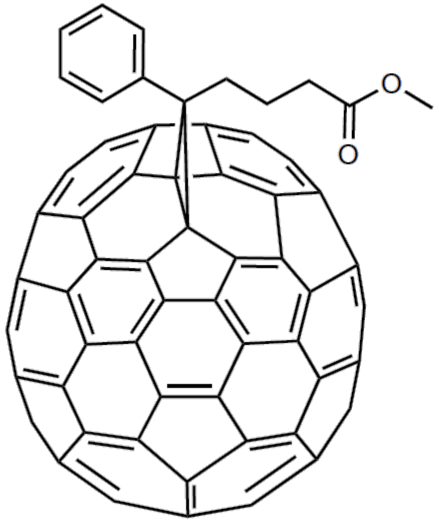
Or can a direct BHJ/water junction photocathode be stable?







PTB7-Th



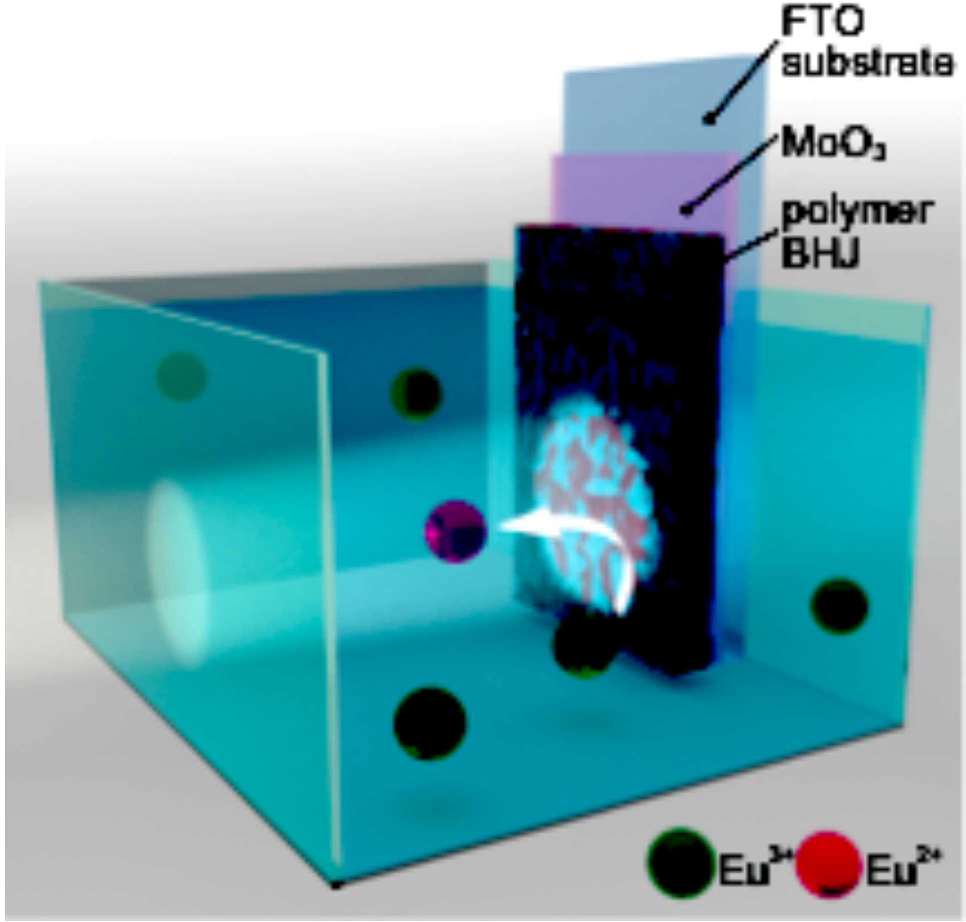
$PC_{70}BM$

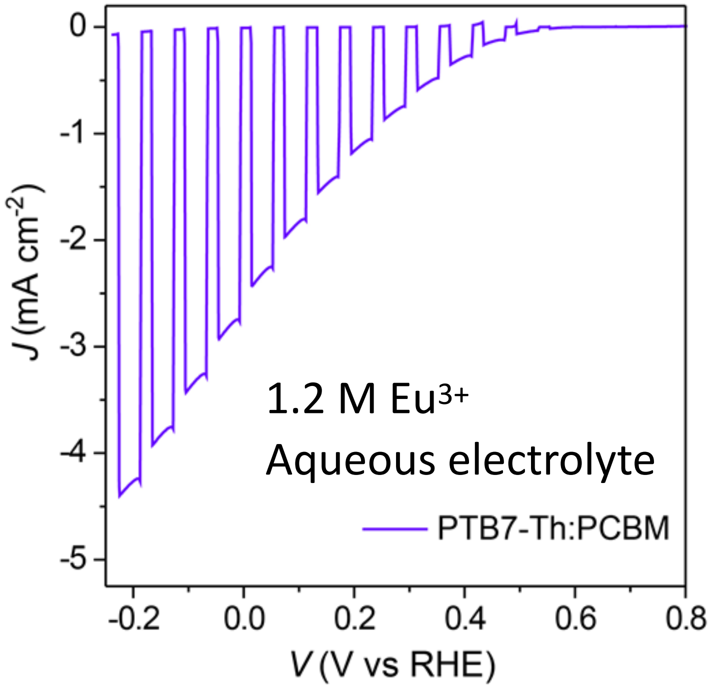
Study with sacrificial electrolyte (carrier scavenger that easily oxidised or reduced)

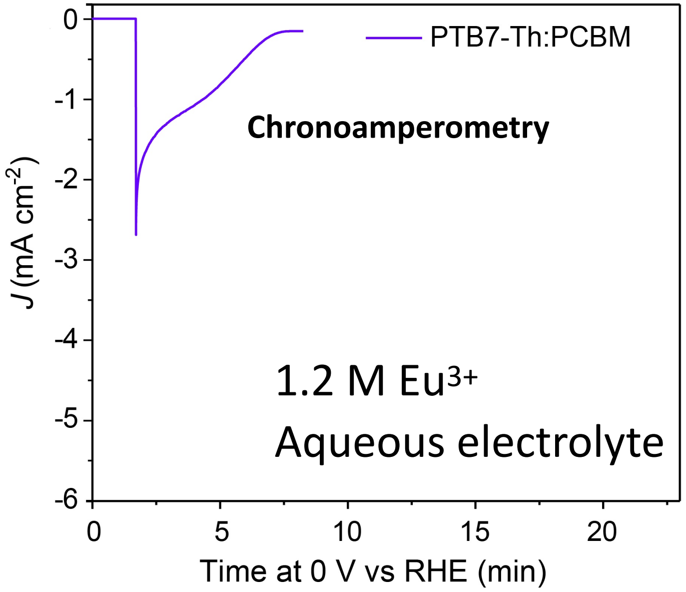
- Jun-Ho YUM, junho.yum@epfl.ch

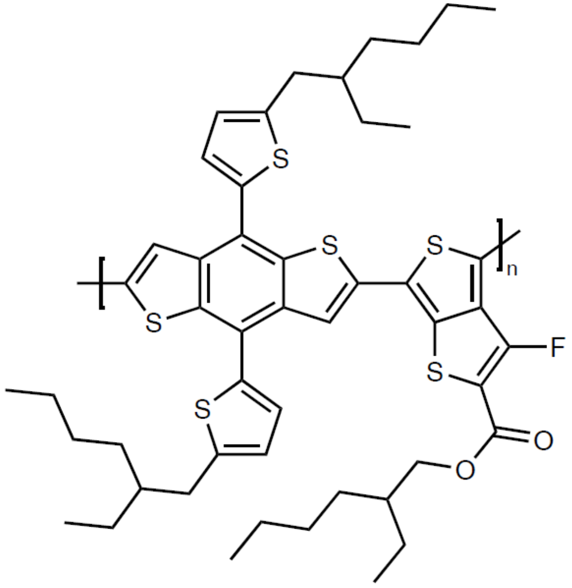
Why is a BHJ in Water So Unstable?

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

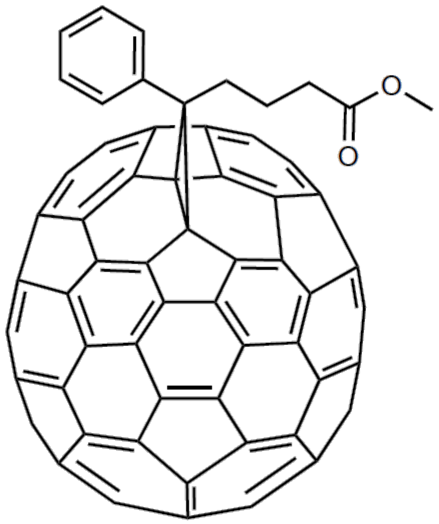








PTB7-Th

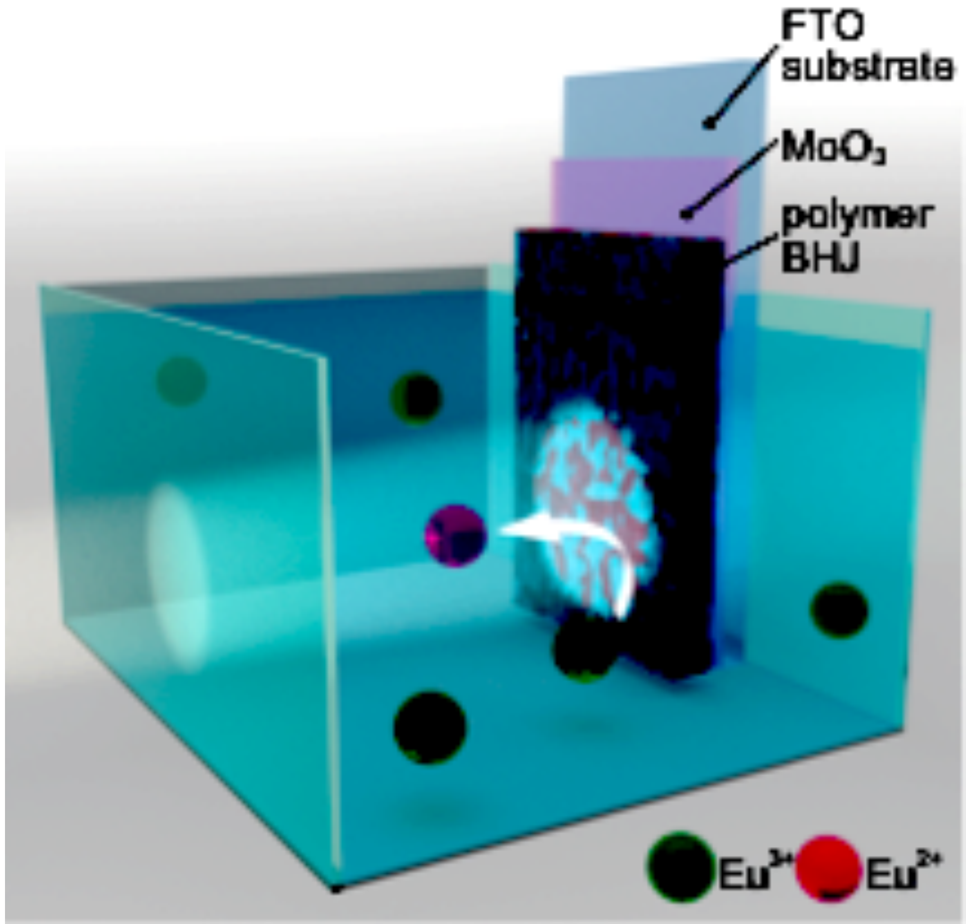


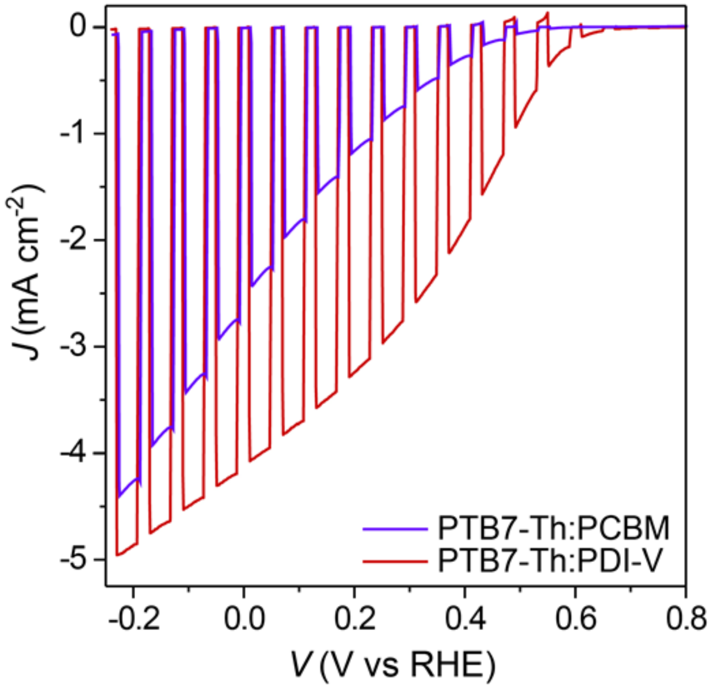
$PC_{70}BM$

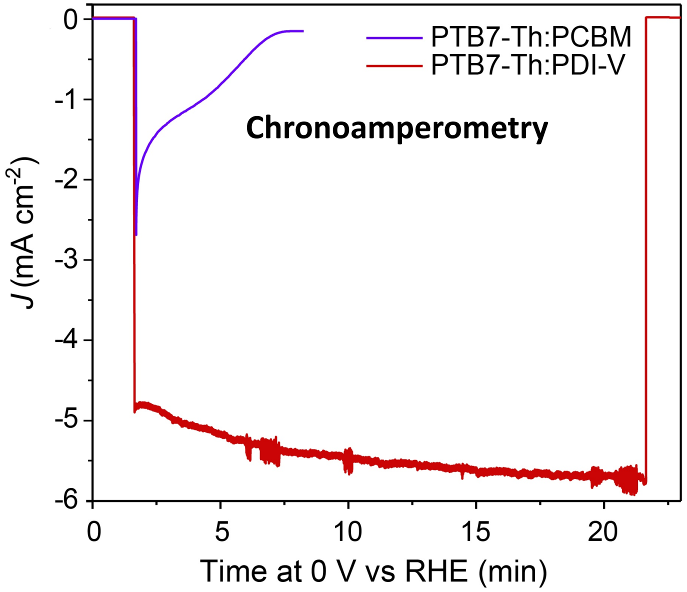
- Jun-Ho YUM, junho.yum@epfl.ch

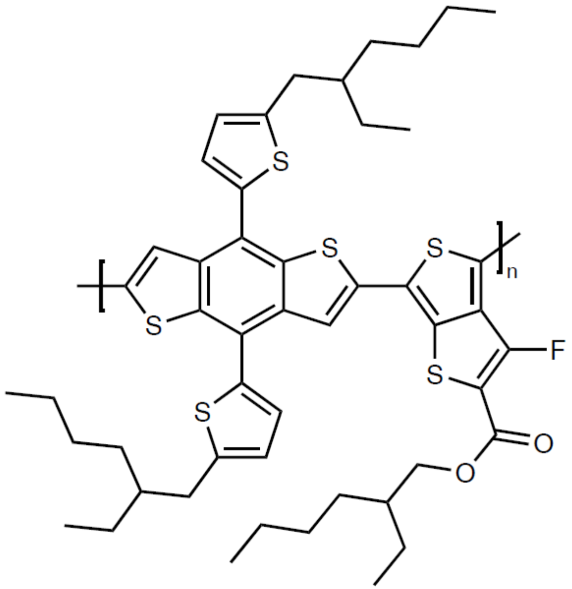
Why is a BHJ in Water So Unstable?

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

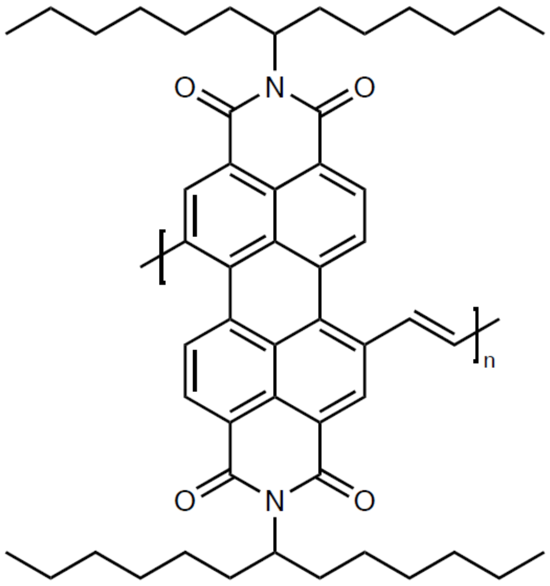








PTB7-Th

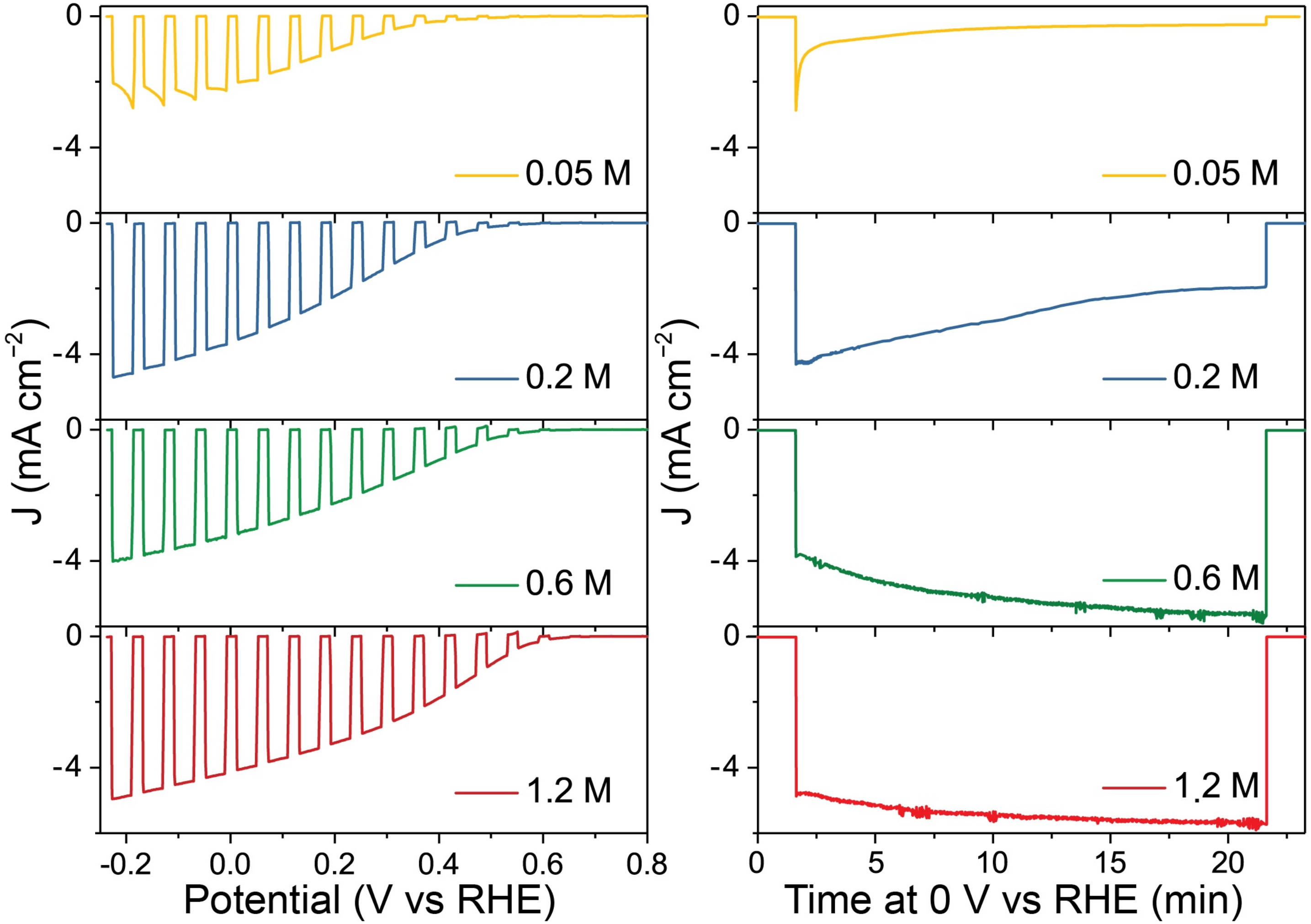


PDI-V

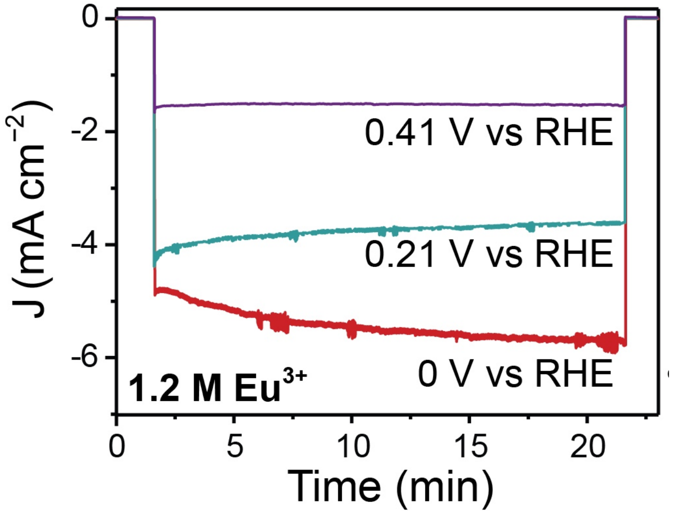
- Jun-Ho YUM, junho.yum@epfl.ch

Insight into Stability of NFA BHJ with Electron Scavenger

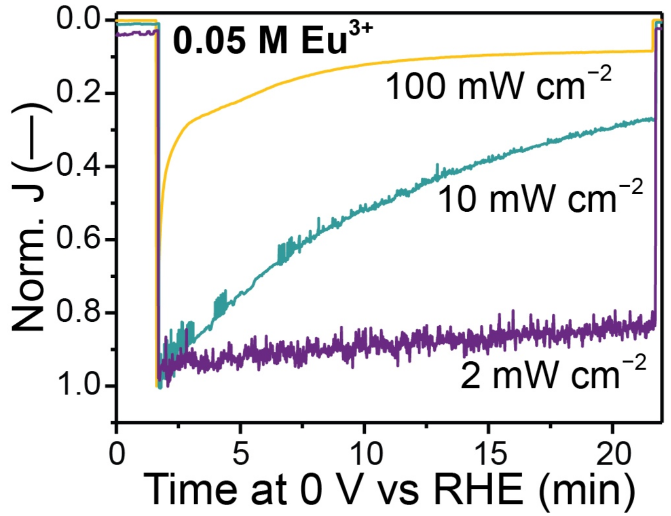
Changing the Eu³⁺ concentration:



Changing the applied potential:



Changing the illumination intensity:

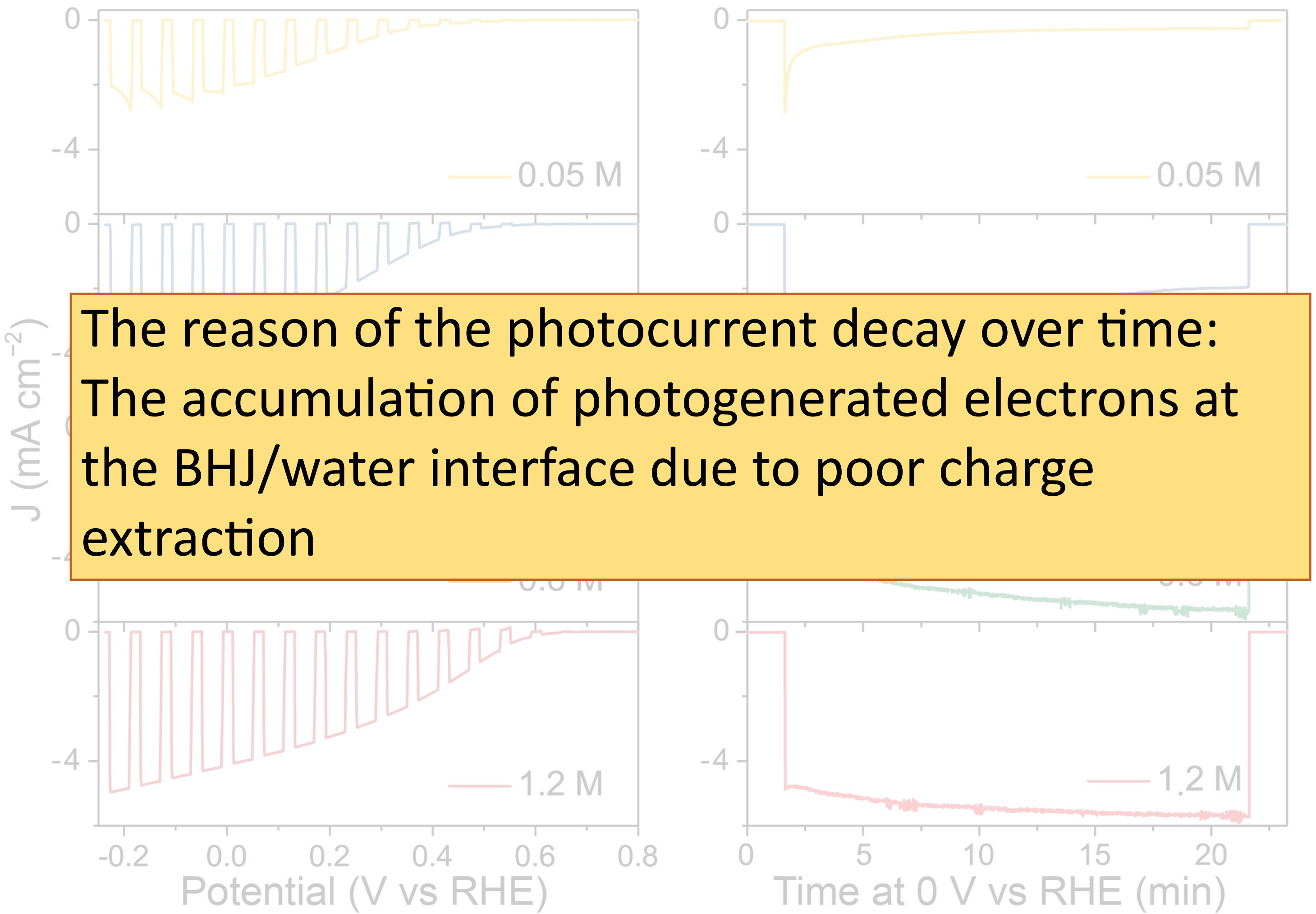


L. Yao et al. *J. Am. Chem. Soc.*, **2020**, 142, 17, 7795–7802

- Jun-Ho YUM, junho.yum@epfl.ch

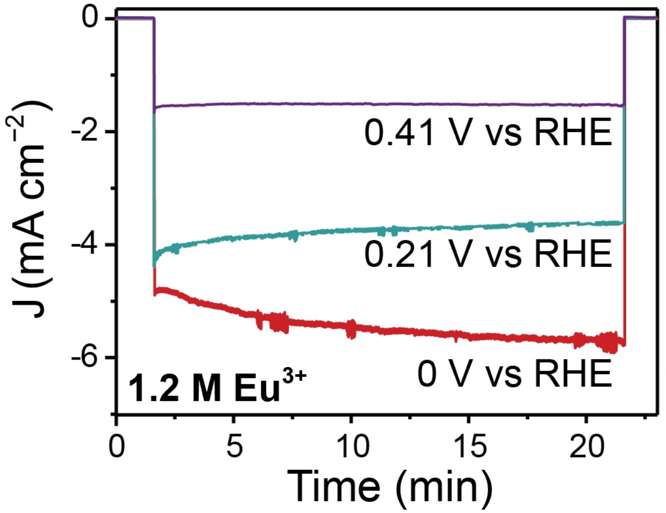
Insight into Stability of NFA BHJ with Electron Scavenger

Changing the Eu^{3+} concentration:

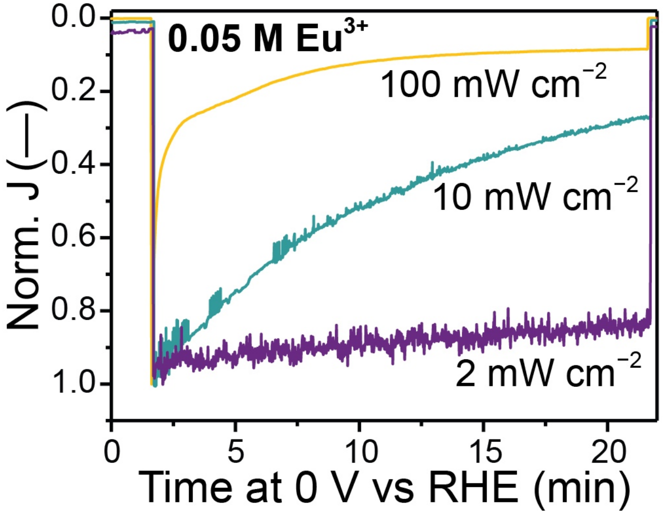


The reason of the photocurrent decay over time: The accumulation of photogenerated electrons at the BHJ/water interface due to poor charge extraction

Changing the applied potential:



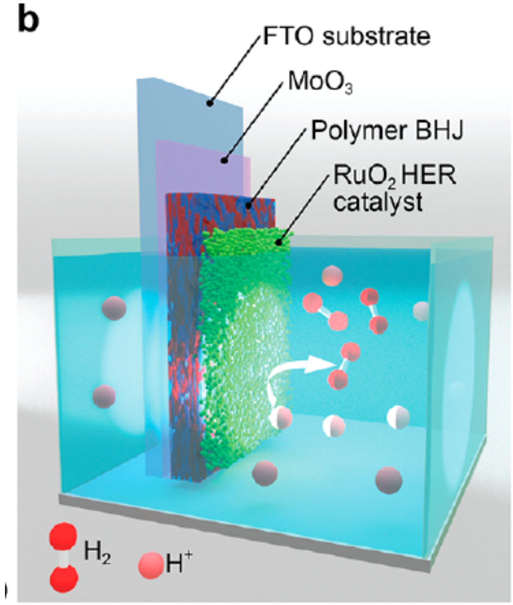
Changing the illumination intensity:

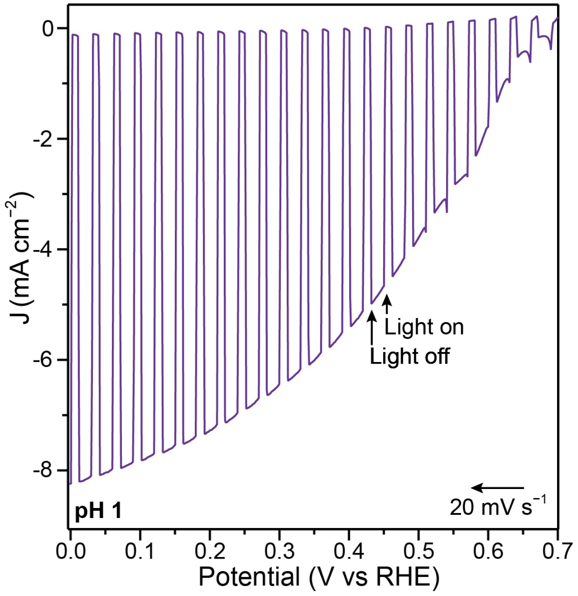


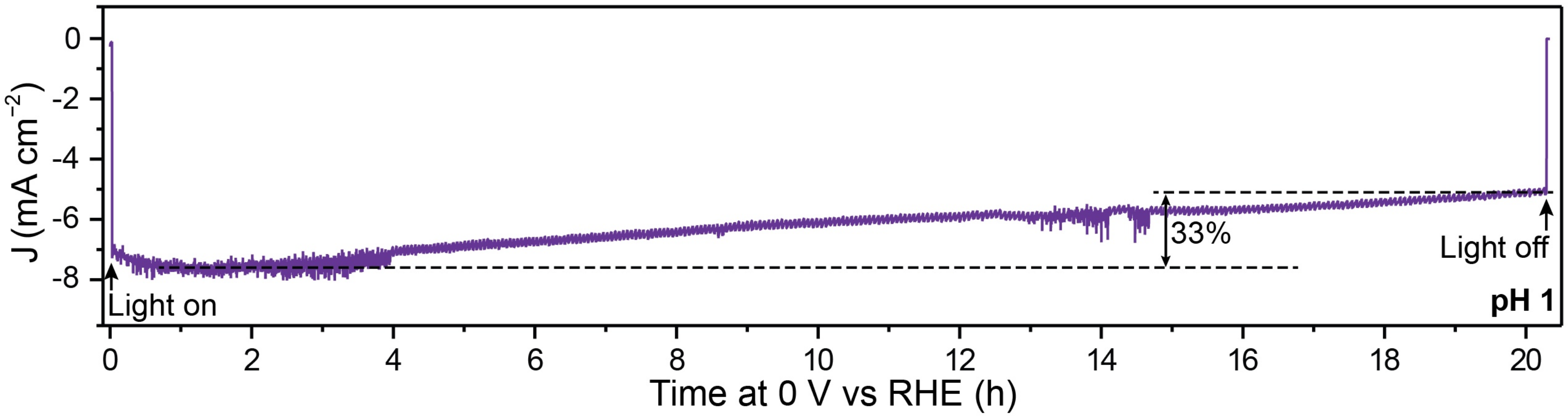
L. Yao et al. *J. Am. Chem. Soc.*, **2020**, 142, 17, 7795–7802

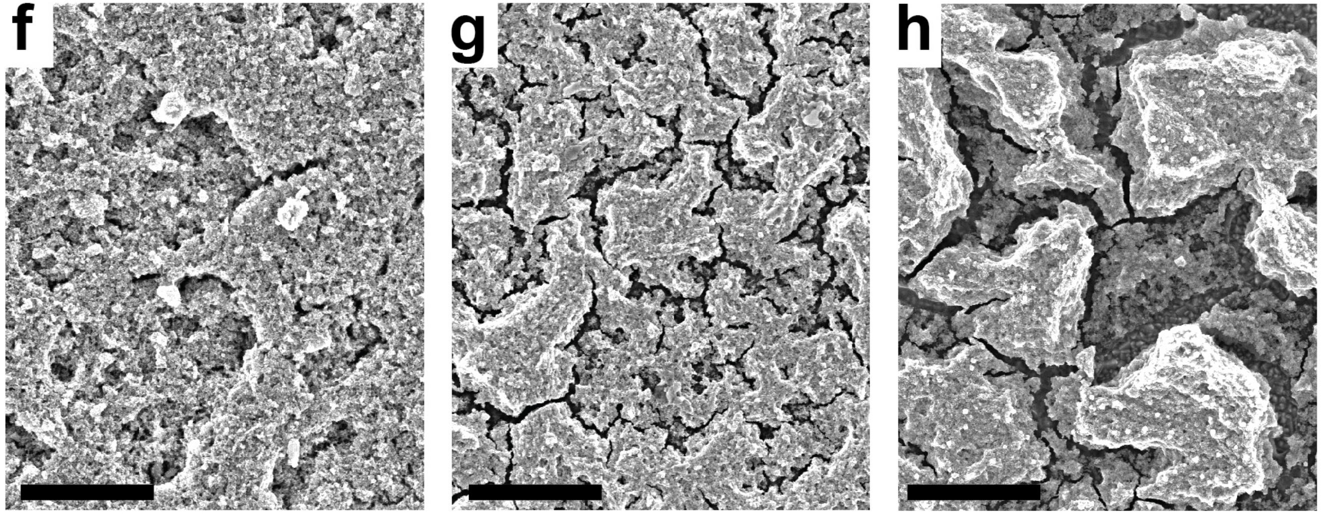
- Jun-Ho YUM, junho.yum@epfl.ch

Adding a Catalyst to Drive H_2 Production







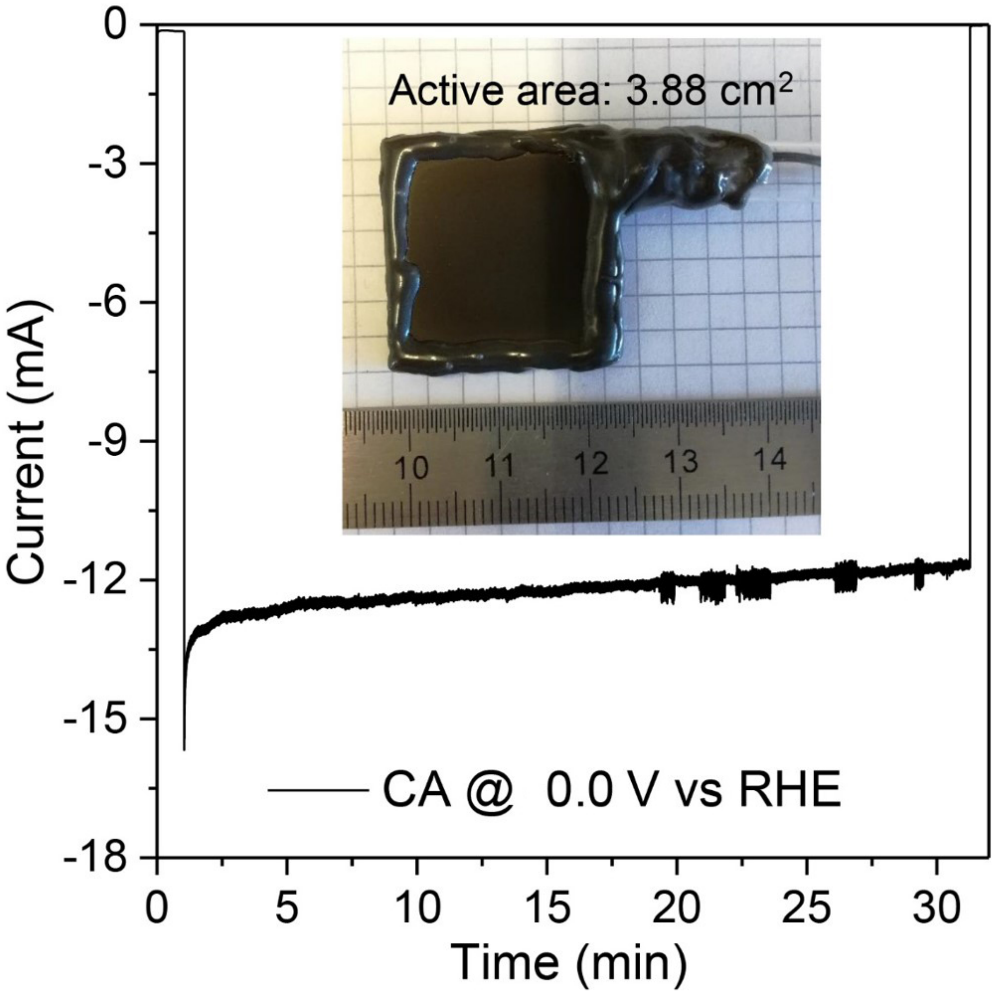


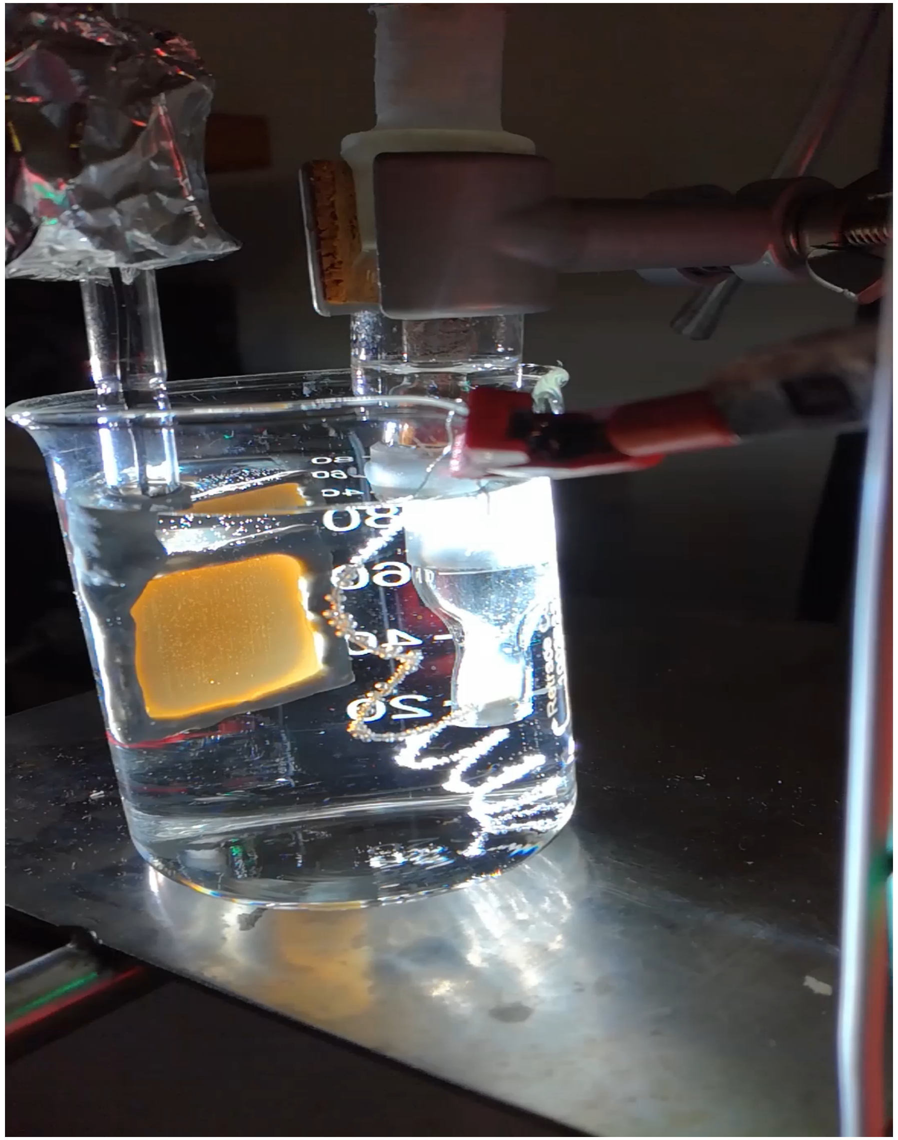
Scale bar: 1 µm

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

- Jun-Ho YUM, junho.yum@epfl.ch

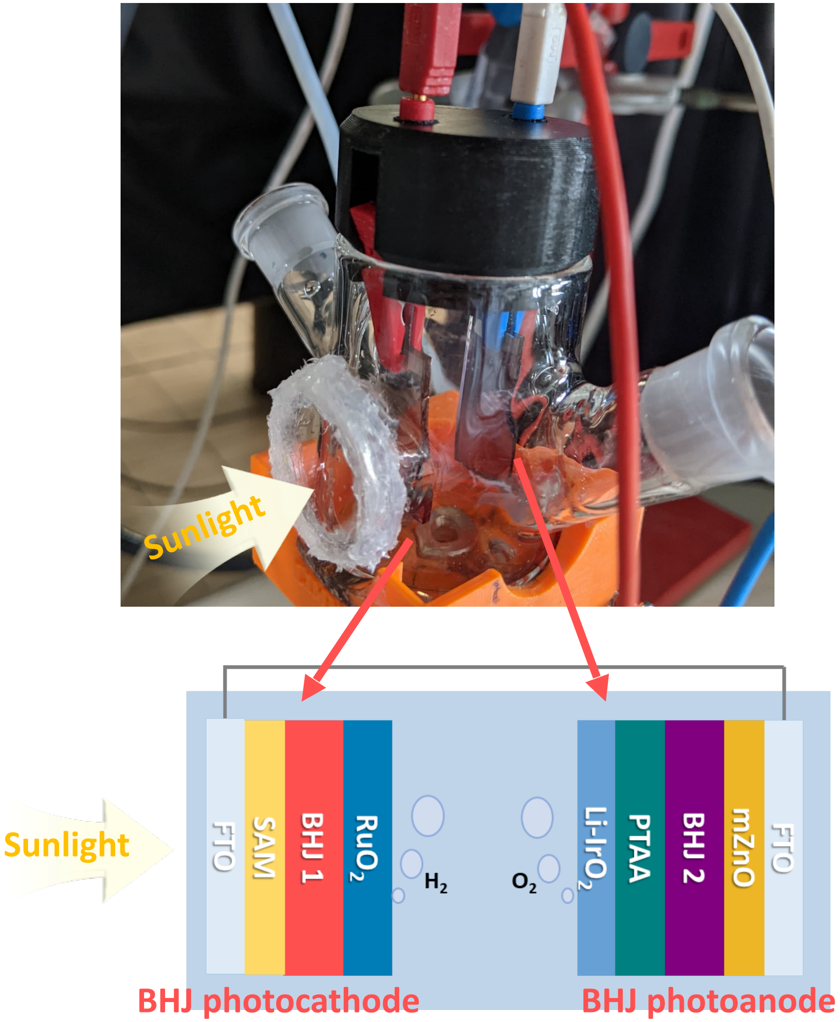
Large Area Demonstration



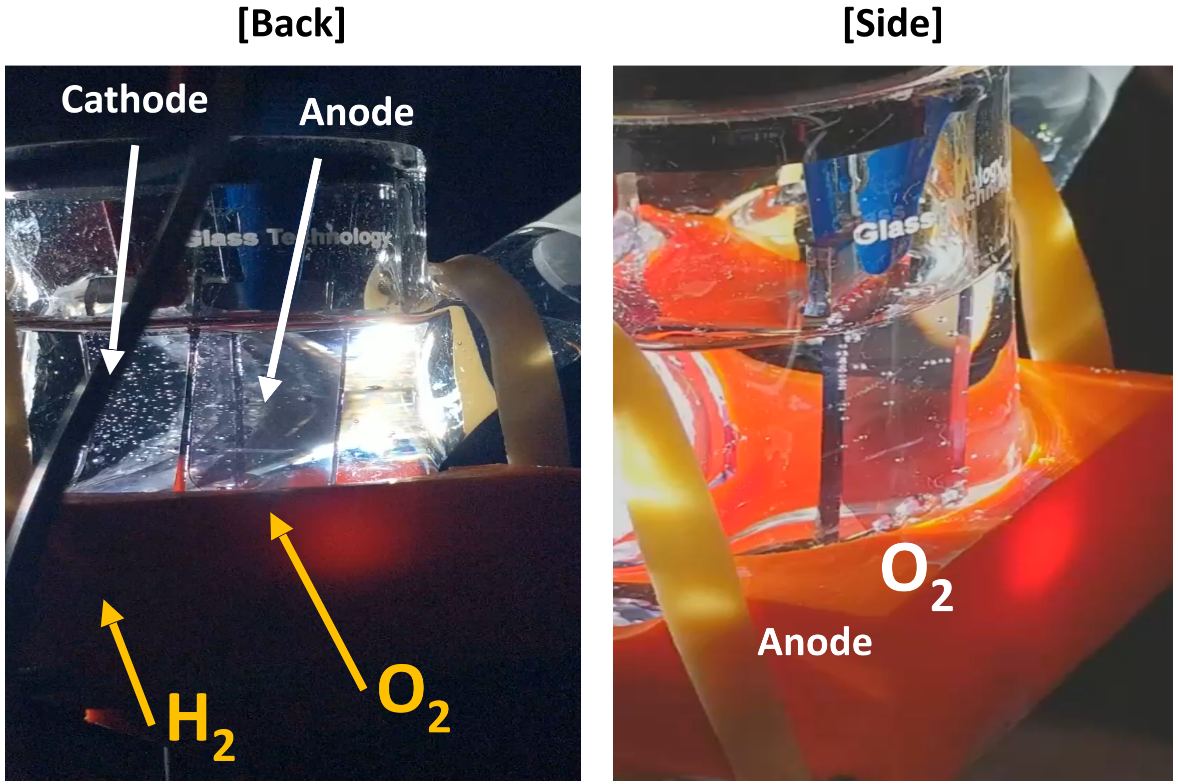


- Jun-Ho YUM, junho.yum@epfl.ch

What is Next?



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

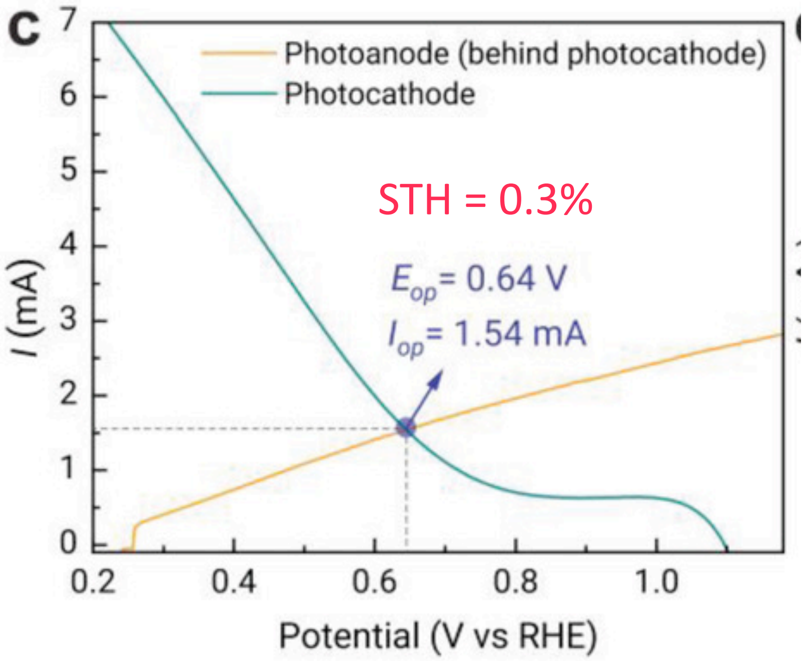

[Back]

[Side]

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

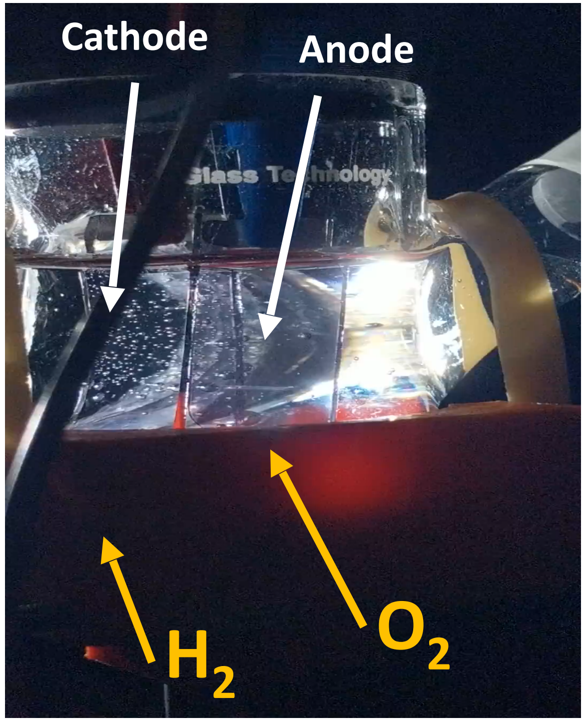
- Jun-Ho YUM, junho.yum@epfl.ch

What is Next?

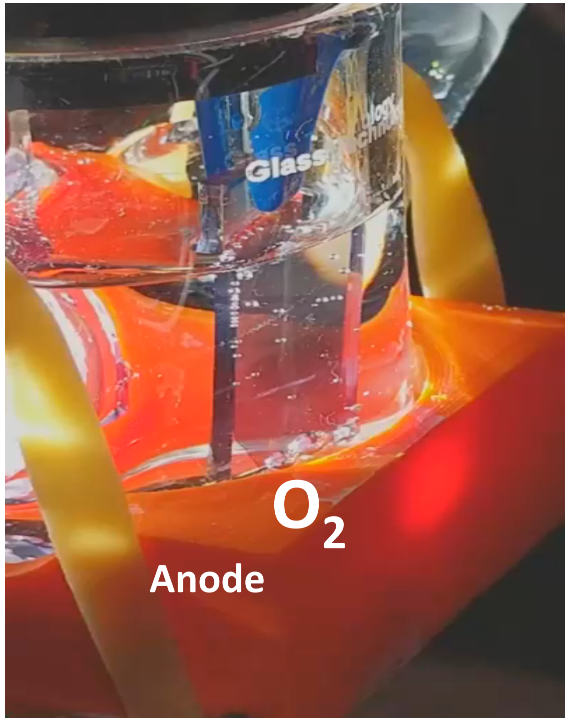


Complete solar water splitting at zero-bias
Without any capsulation or passivation

[Back]



[Side]



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

- Jun-Ho YUM, junho.yum@epfl.ch