Solar Photovoltaics & Energy Systems

Lecture 7 – Direct Solar-to-fuel Conversion: Photoelectrochemical and Photocatalytic systems

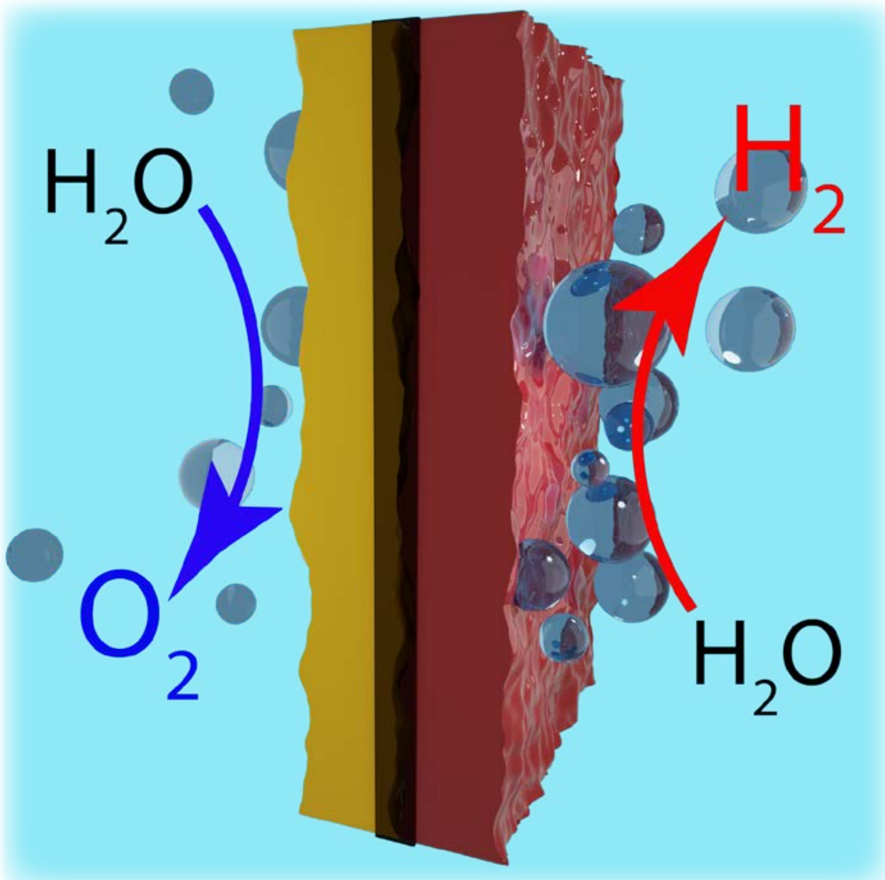
ChE-600

Néstor Guijarro Carratala, Spring 2018

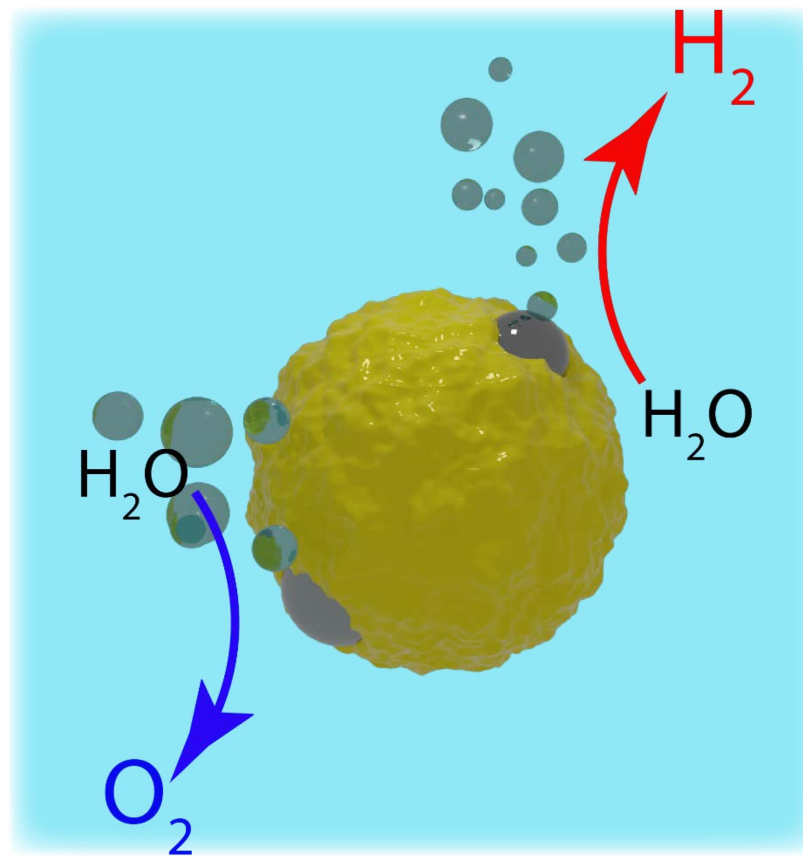
ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

Contents

Direct water splitting using *Photoelectrochemical cells*

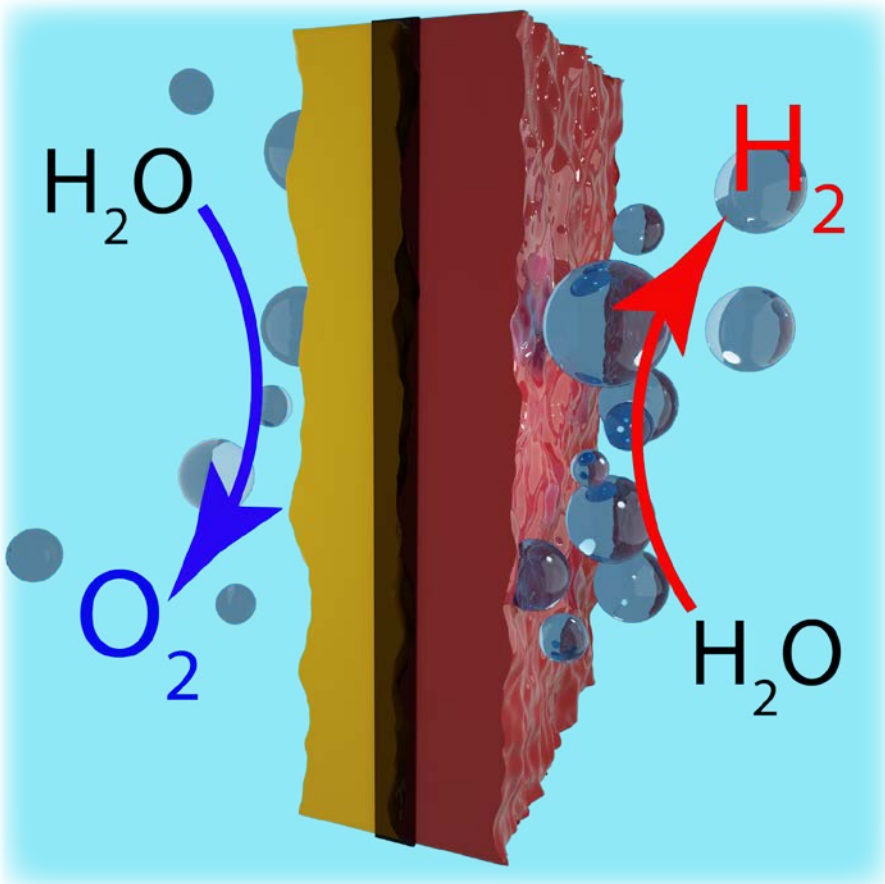


Direct water splitting using *Photocatalysts*



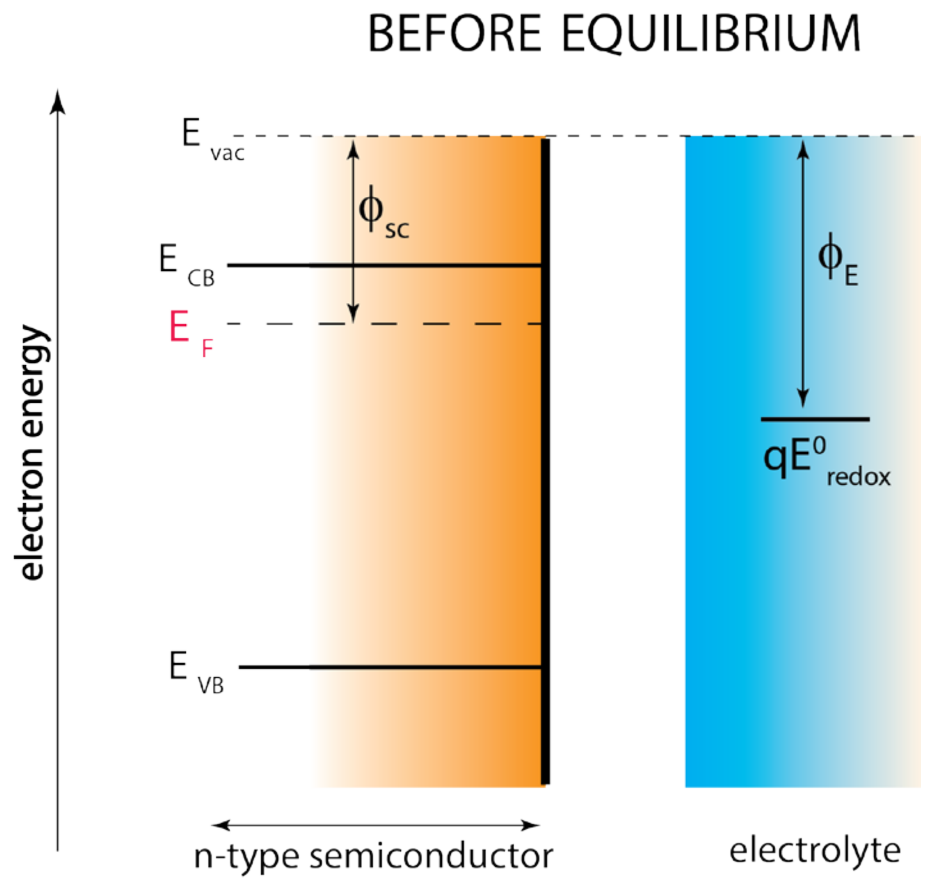
Contents

<u>**Direct water splitting**</u> using
Photoelectrochemical cells



- How does it work?
- Basic metrics
- Limitations of Tandem Cells
- Current approaches to understand and address intrinsic limitations

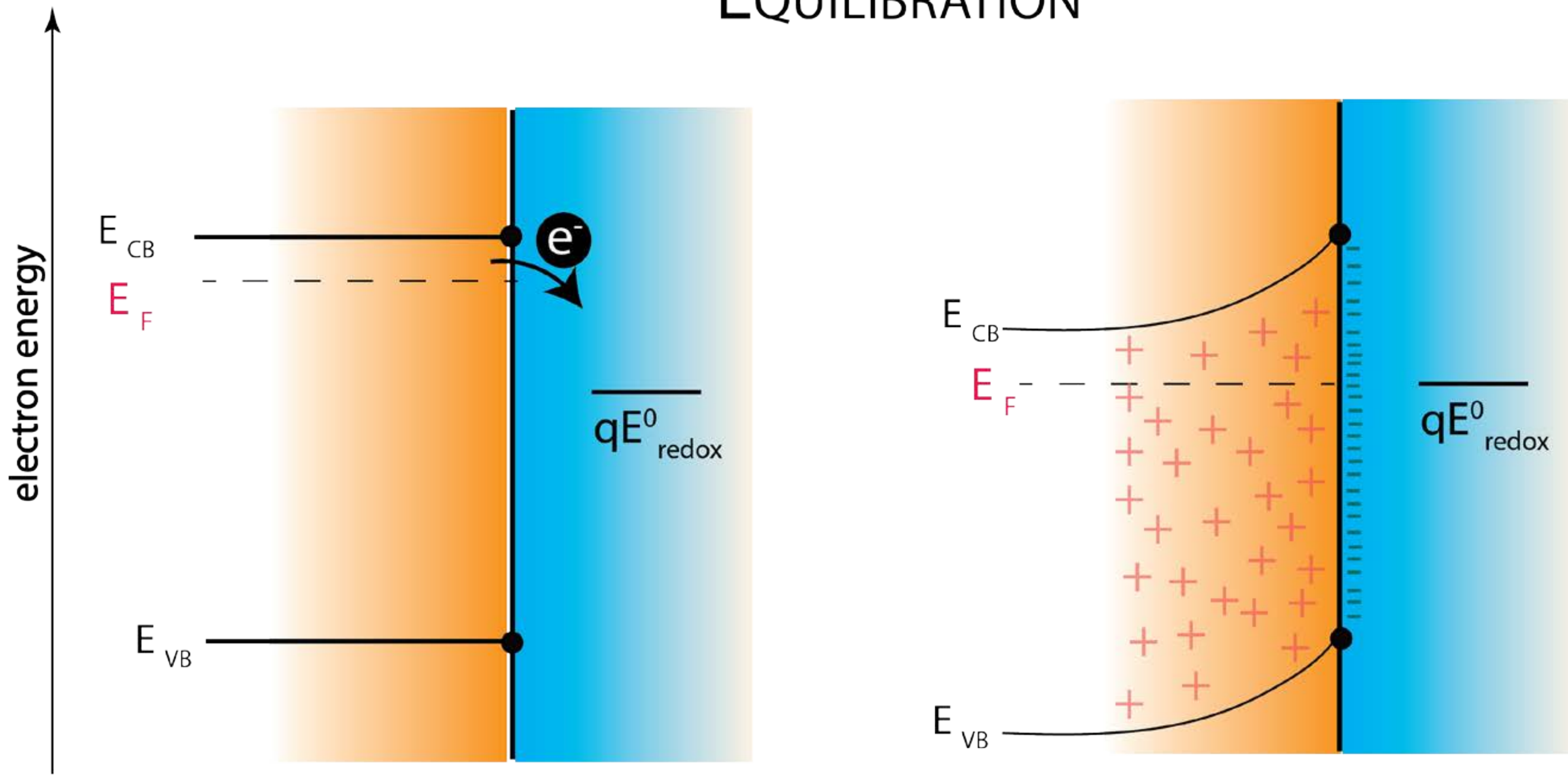
Semiconductor-liquid junction



$\phi_{sc}, \phi_E = workfunction\ of\ semiconductor$(SC) or redox

Semiconductor-liquid junction

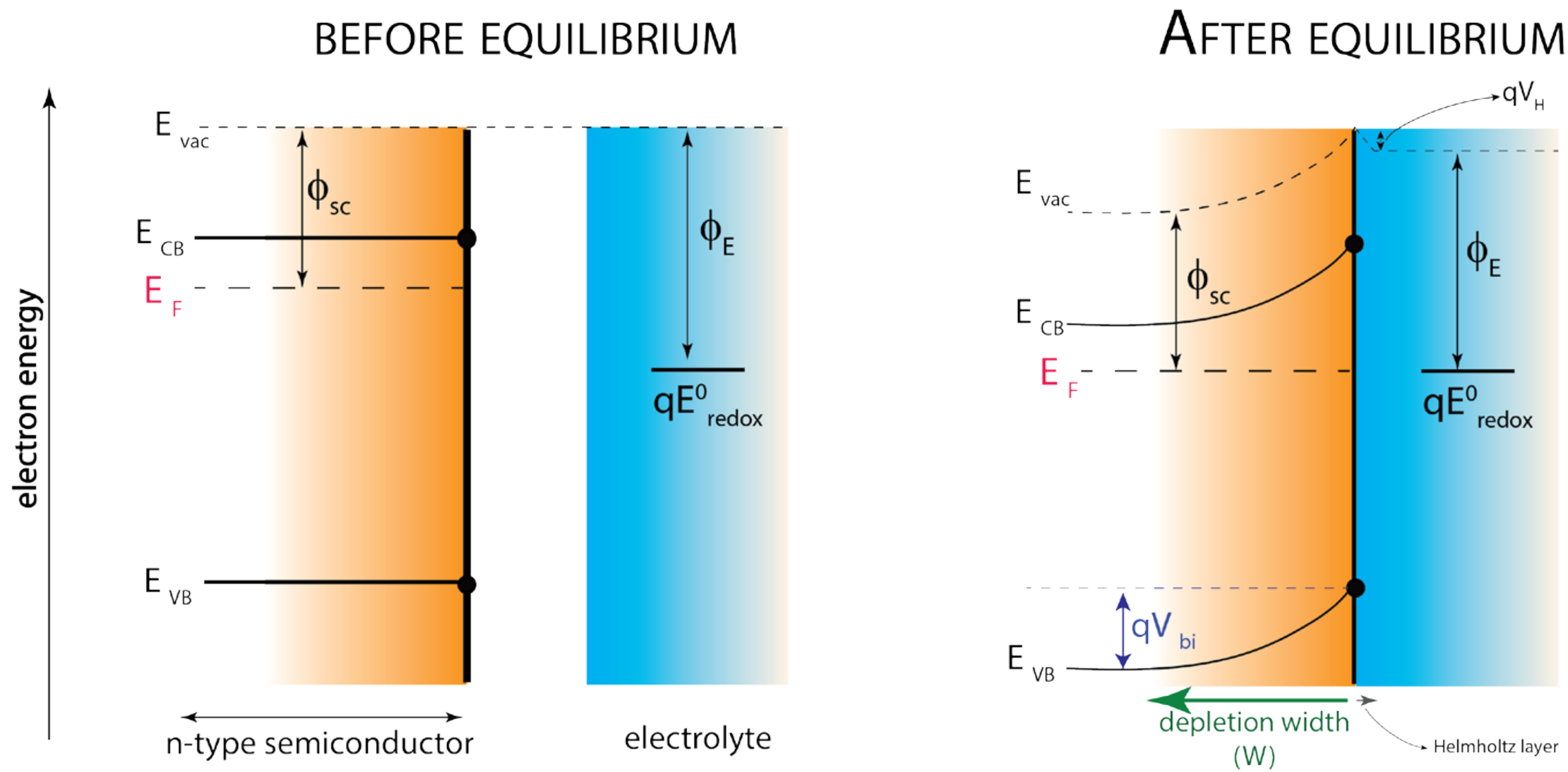
Equilibration



$\mu_e^{SC} \neq \mu_e^{redox}$ $\mu_e^{SC} = \mu_e^{redox}$

Flow of charge between phases to equalibrate the "chemical potential" of electrons in all the phases

Semiconductor-liquid junction



Built-in voltage $V_{bi} = |E_F - qE_{redox}|/q$

$$E_F = E_{CB} - kTln\left(\frac{n}{N_c}\right)$$

$n: electron\ concentration = n_i + N_d \approx N_d$

$N_c: effective\ density\ of\ states\ in\ the\ conduction\ band$

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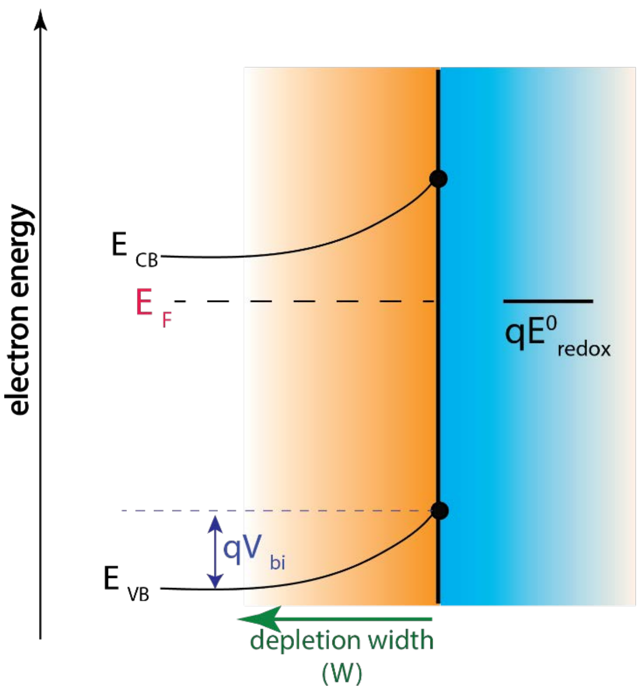
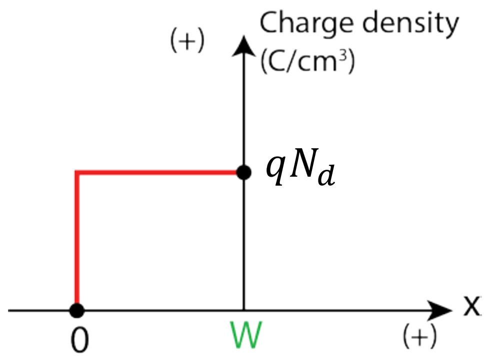
Semiconductor-liquid junction

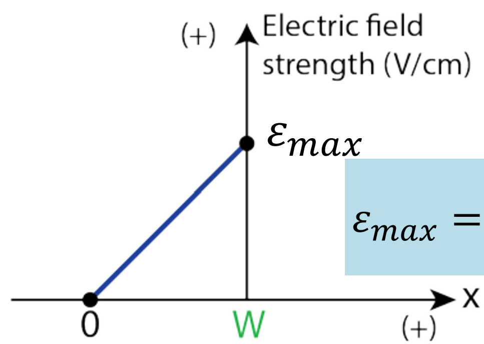
Depletion region





Poisson's equation

$$\frac{d^2\phi}{dx^2} = -\frac{d\varepsilon}{dx} = -\frac{\rho(x)}{\varepsilon_0\varepsilon_r}$$



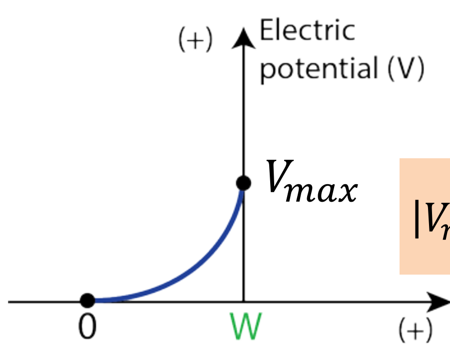
$$\varepsilon_{max} = \left(\frac{qN_d}{\varepsilon_0\varepsilon_r}\right)W$$

ϕ : *electrostatic potential*

ε : *electric field*

ρ : *charge density*

N_d: *dopant density*



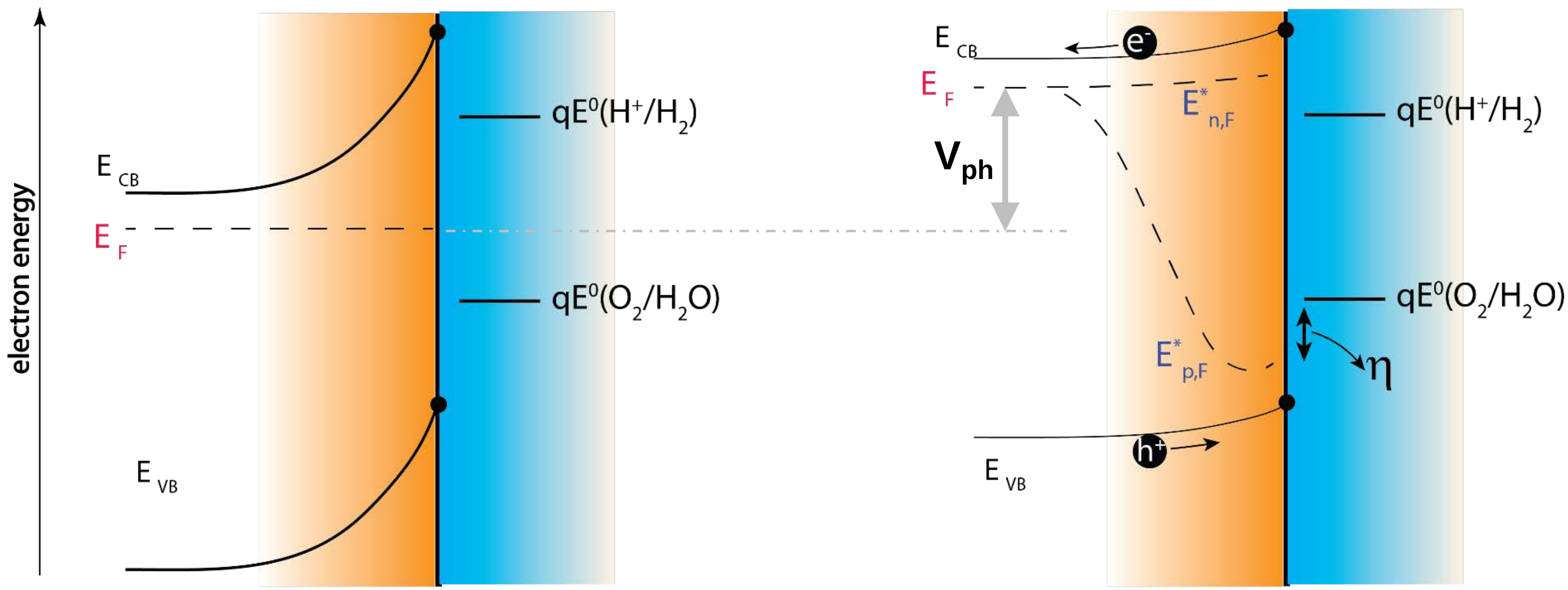
$$|V_{max}| = V_{bi} = \left(\frac{qN_d}{2\varepsilon_0\varepsilon_r}\right)W^2$$

$$W = \sqrt{\frac{2\varepsilon_0\varepsilon_r V_{bi}}{qN_d}}$$

Semiconductor-liquid junction under illumination

Dark

Light (open circuit conditions)



photoanode electrolyte

$$E^*_{n,F} = E_F + kTln\left(\frac{n+\Delta n^*}{n}\right)$$

$$E^*_{p,F} = E_F + kTln\left(\frac{p+\Delta p^*}{p}\right)$$

If n-type semiconductor

$$n \gg p$$

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

$$\boldsymbol{E^*_{n,F} \sim E_F}$$

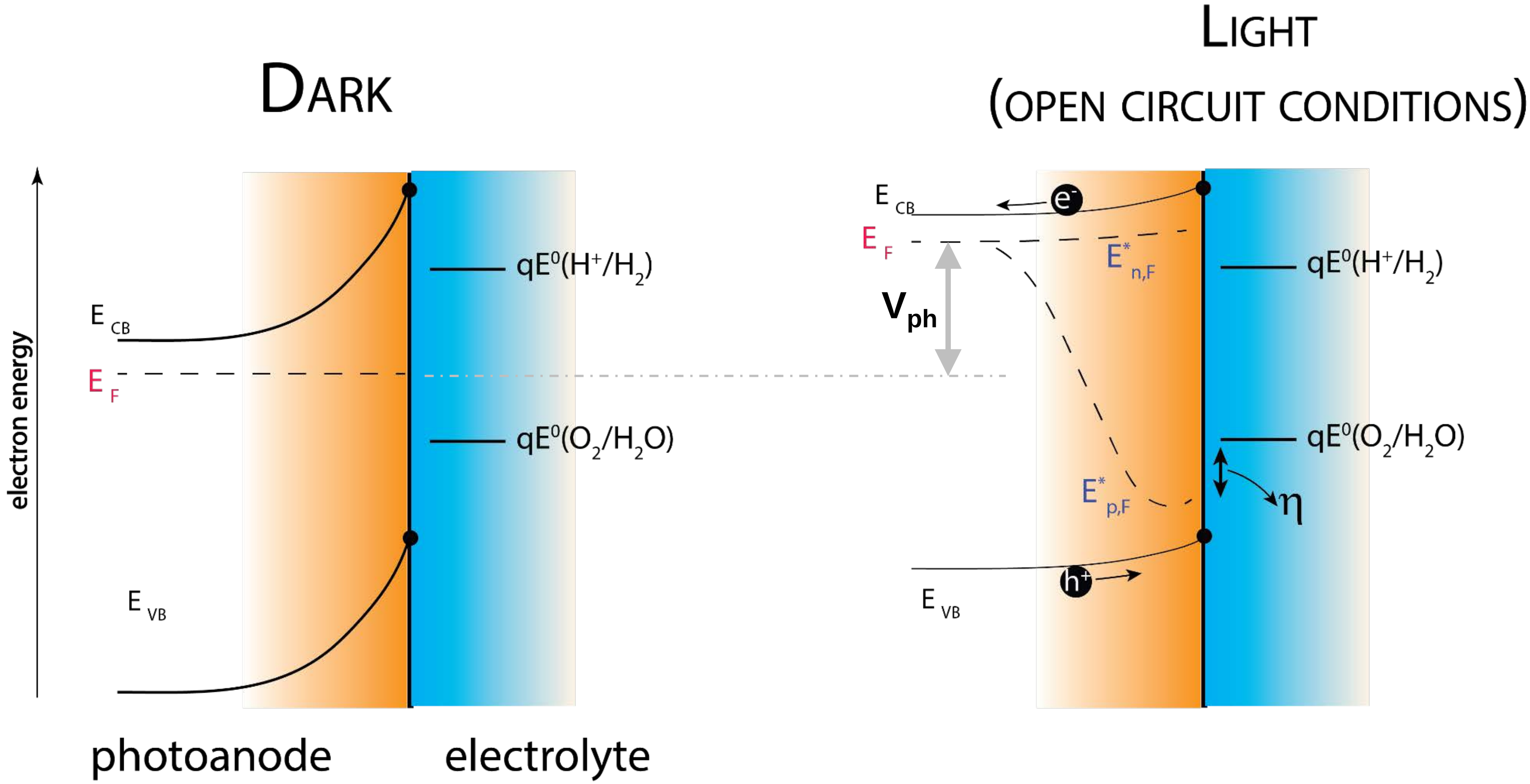
Photostationary *concentration* of carriers

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

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

light dark Increase by light

Semiconductor-liquid junction under illumination

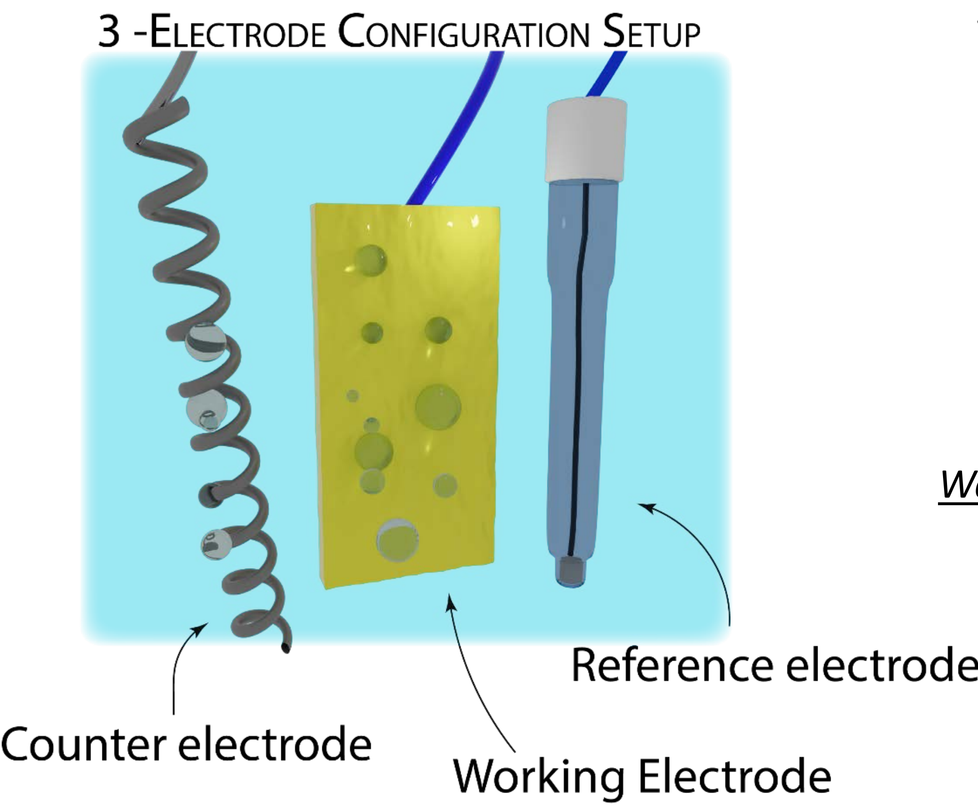


$$E^*_{p,F} < qE^0_{O2/H2O} + \eta_{ox} \qquad \textit{anodic hole transfer proceed}$$

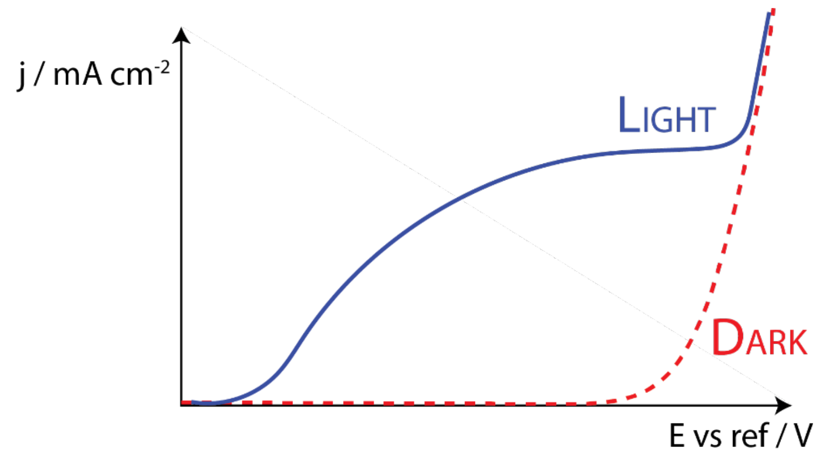
$$E^*_{n,F} > qE^0_{H2O/H2} + \eta_{red} \qquad \textit{cathodic hole transfer proceed}$$

If bands flatten under illumination (OCP) the E_F will equal the so-called V_{fb}

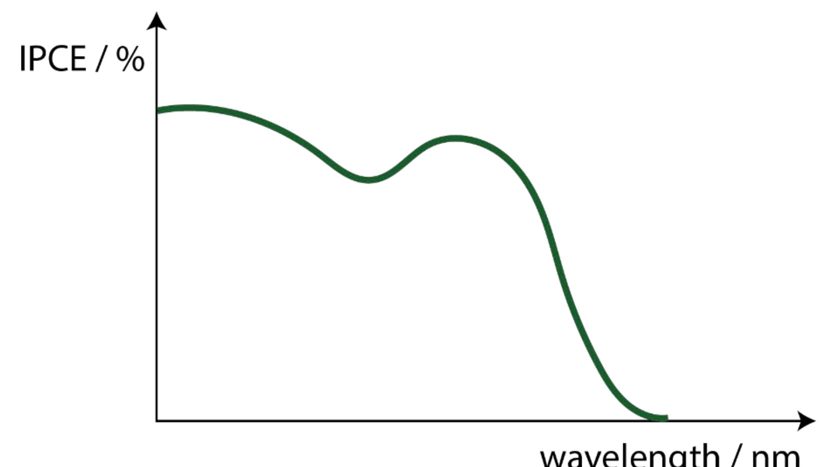
Metrics in Photoelectrode Development



Photocurrent measurements

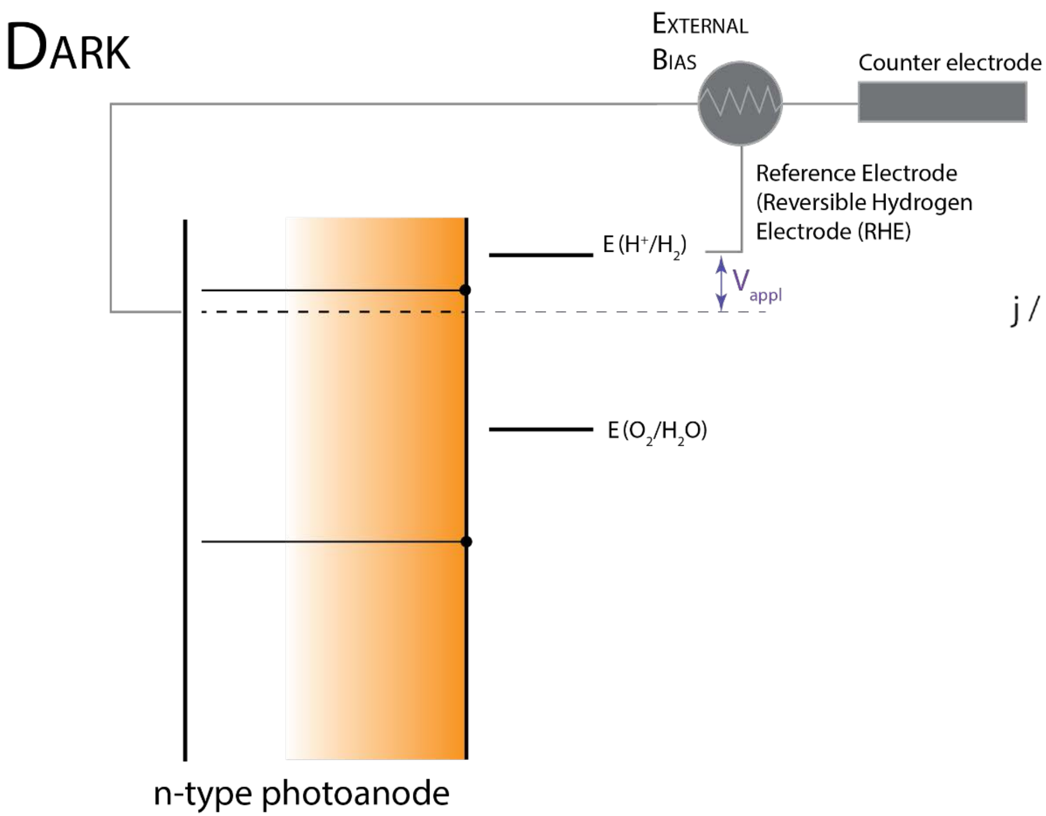


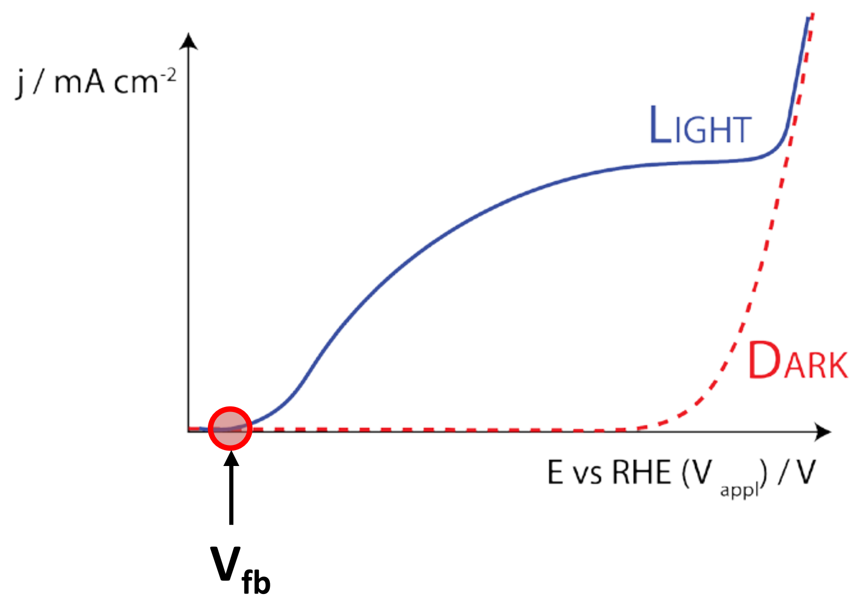
Wavelength-dependent photocurrent response



Metrics in Photoelectrode Development

Photocurrent measurements

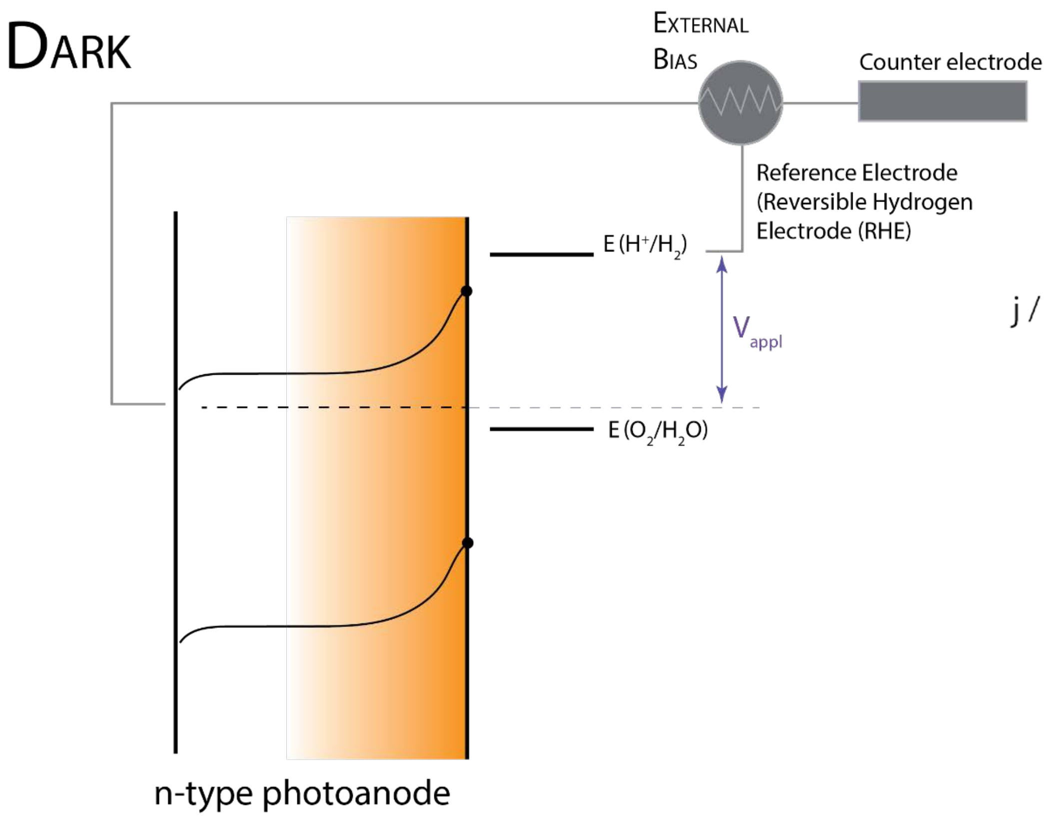


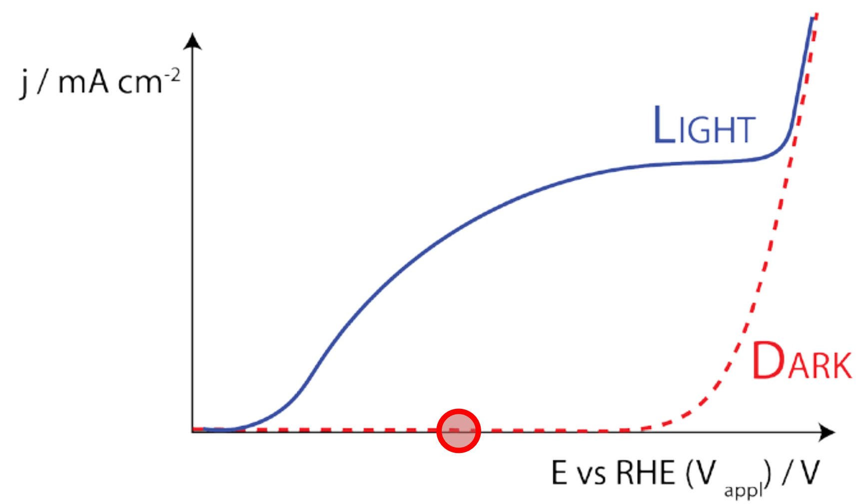


Flat band potential

Metrics in Photoelectrode Development

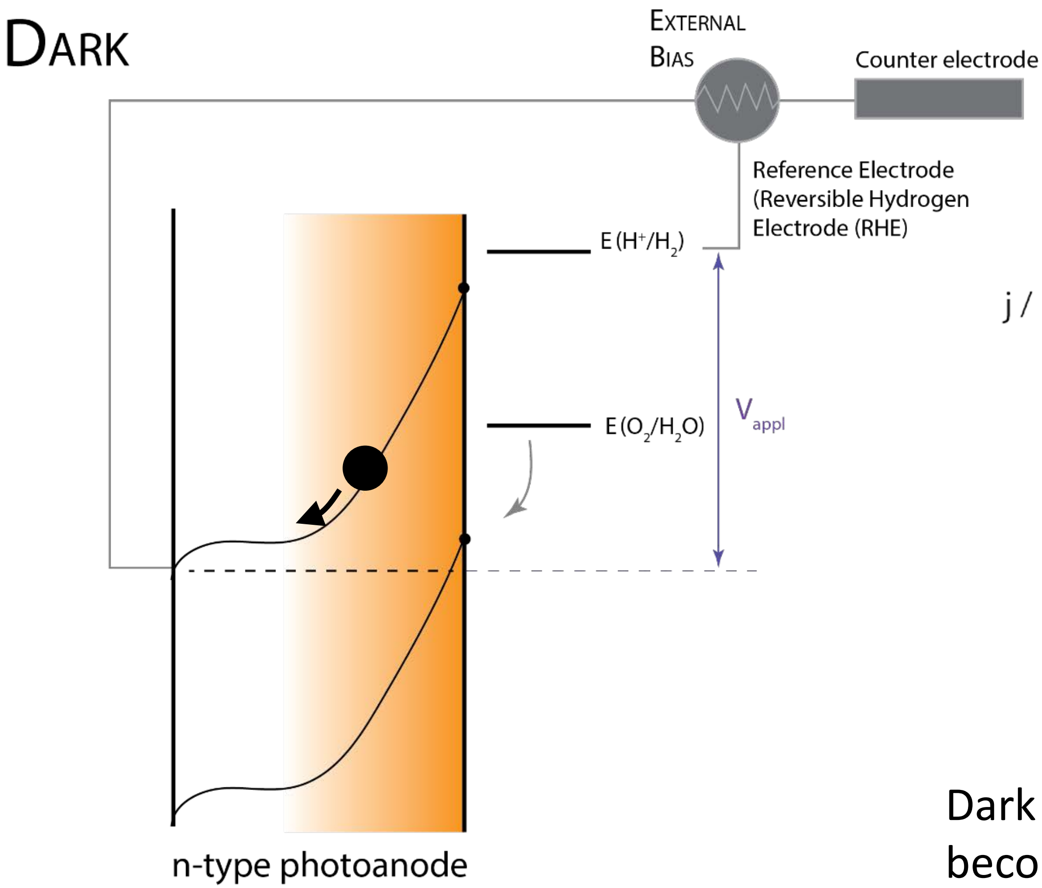
Photocurrent measurements

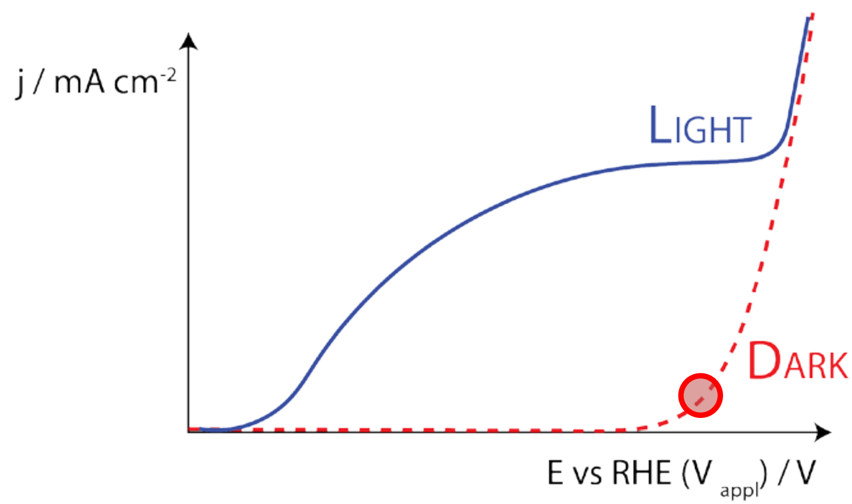




Metrics in Photoelectrode Development

Photocurrent measurements

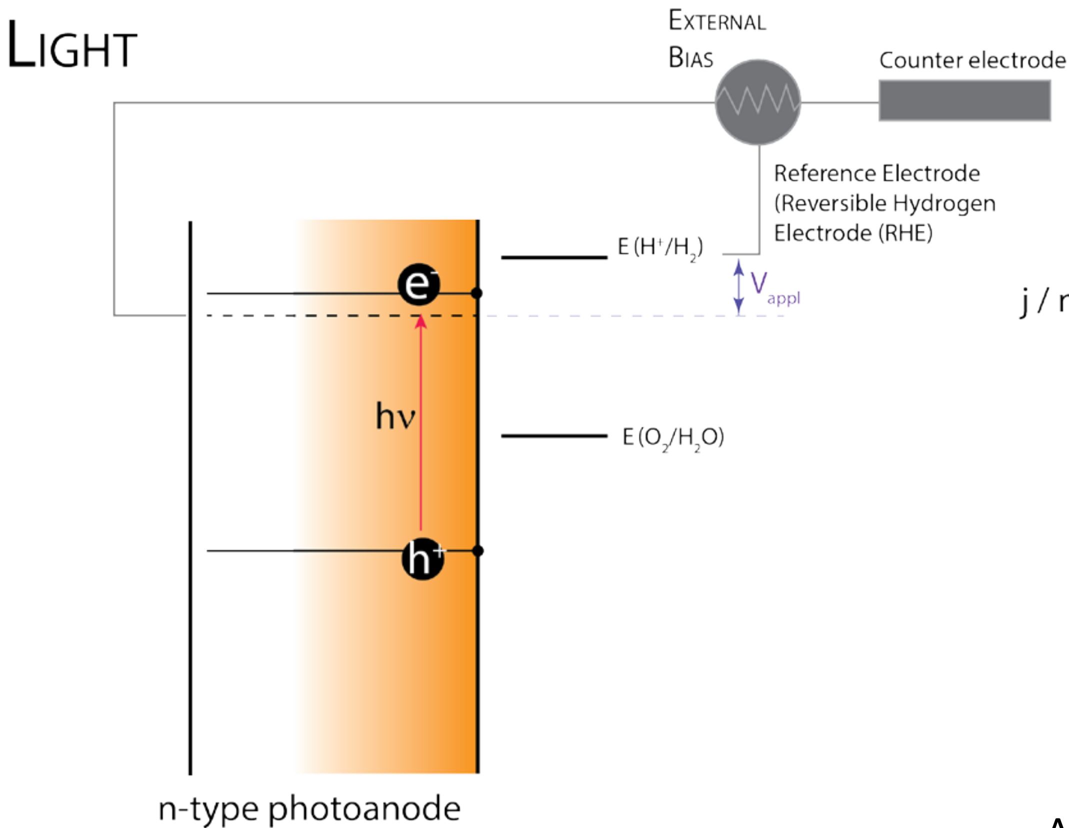


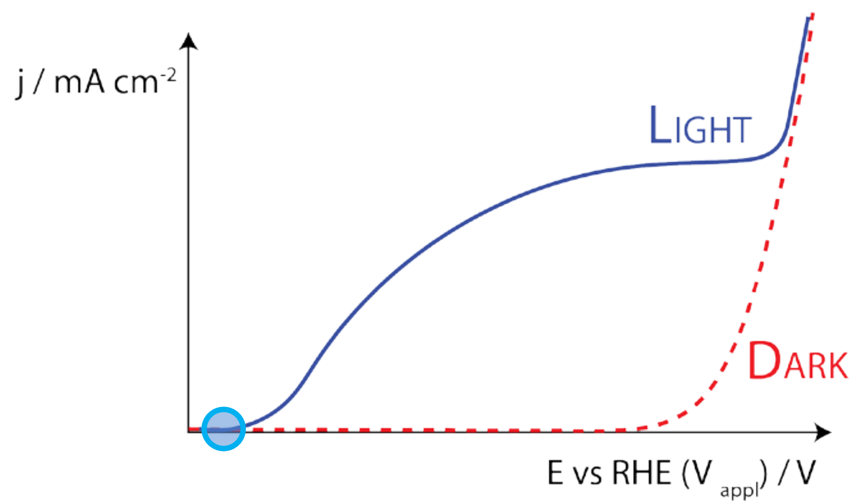


Dark current increases when energy states become available in conduction band.

Metrics in Photoelectrode Development

Photocurrent measurements

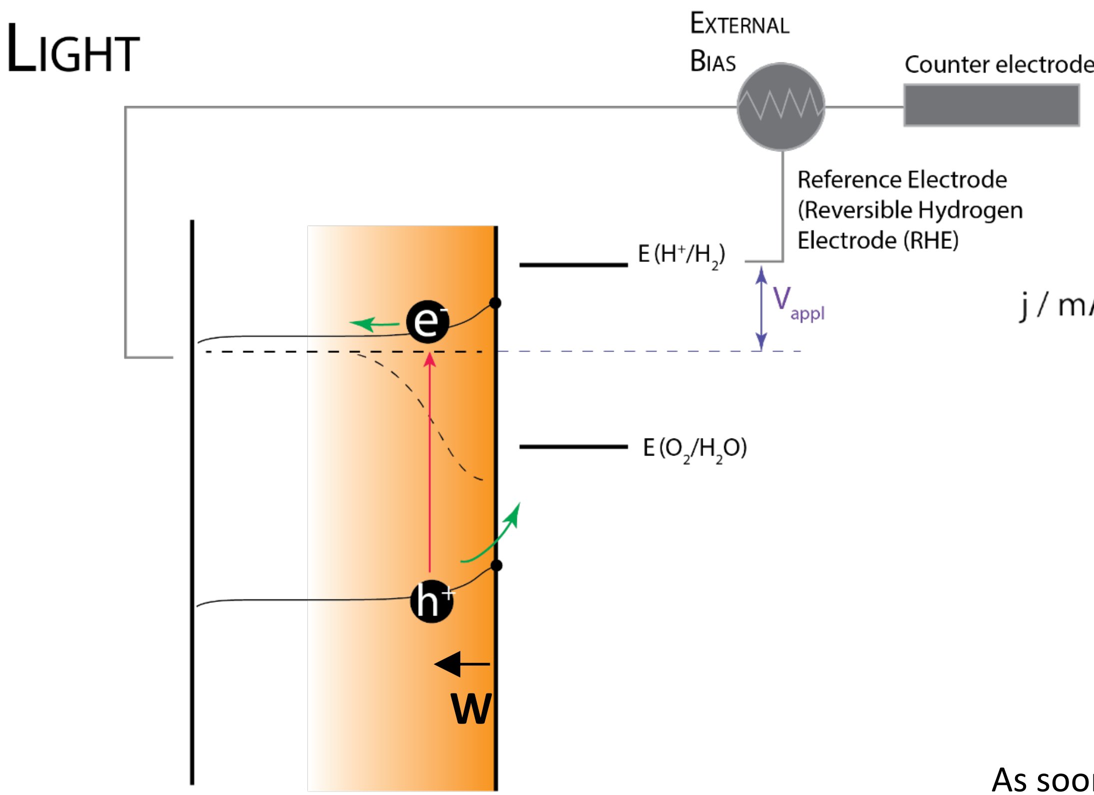




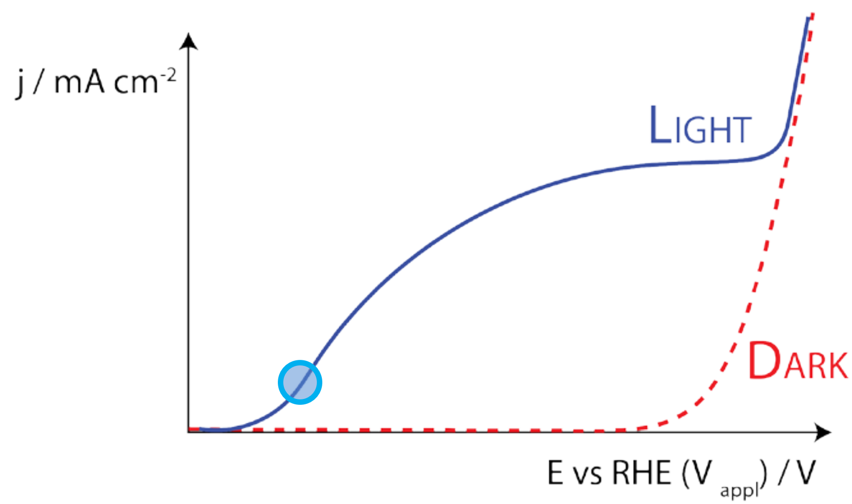
At the V_{fb}, there is no electric field to separate the photoexcited electron-hole pairs.

Metrics in Photoelectrode Development

Photocurrent measurements



n-type photoanode



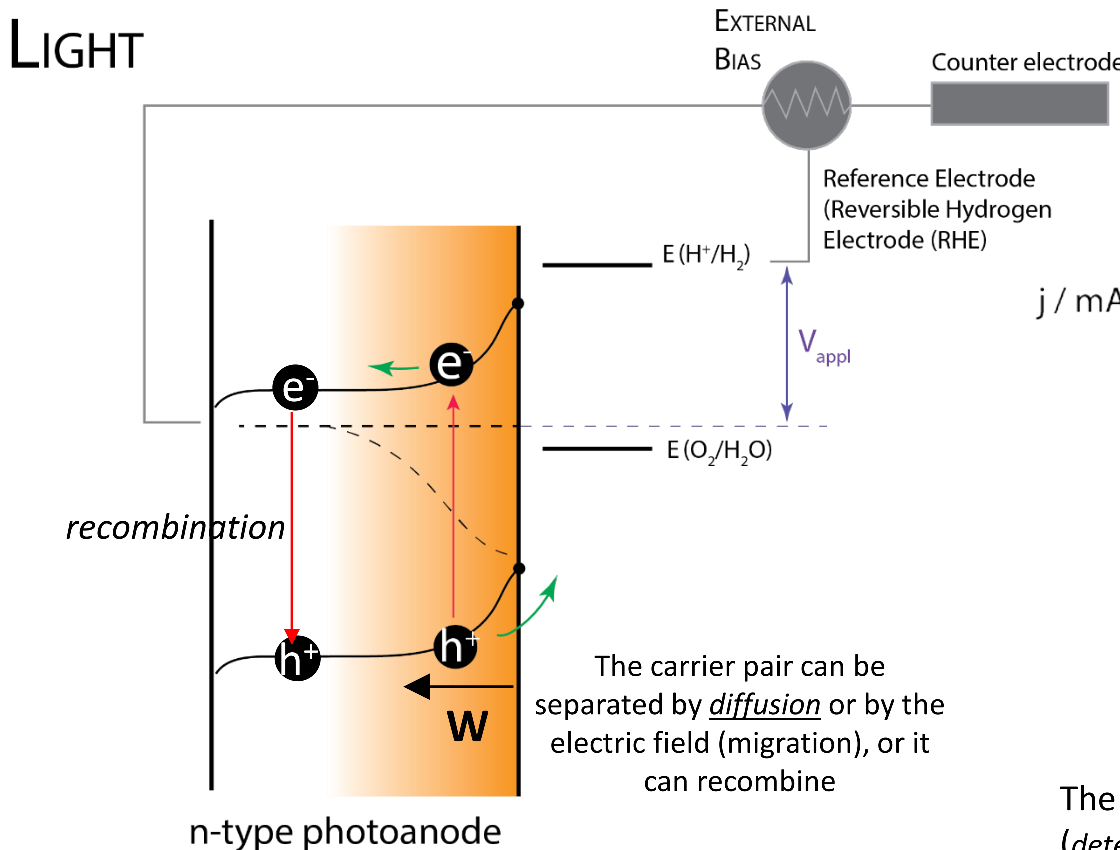
Photoexcited electrode reaction can occur at potentials at which the same electrode reactions are impossible in the dark.

As soon as the *band bending* is generated, the charge-separation withing the depletion width is possible and holes are accumulated at the interface (SCLJ).

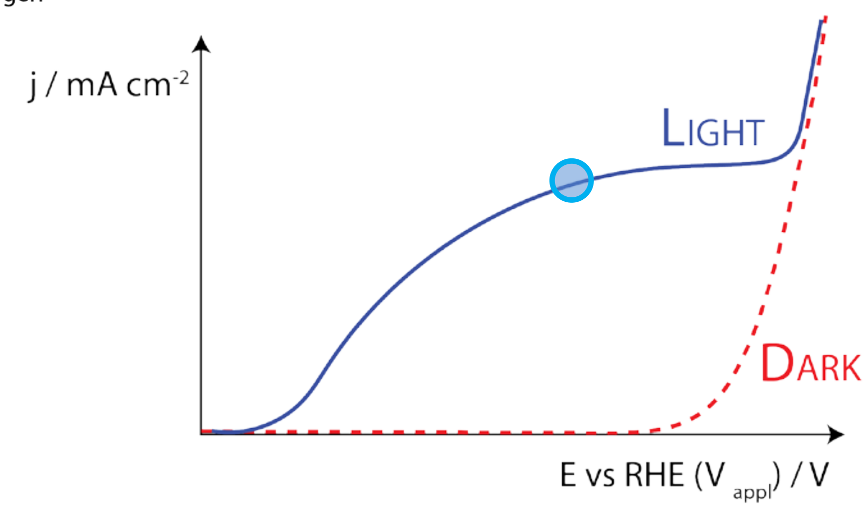
At potentials more positive than the V_{fb} (if the $E_{p,F}$ is positive enough), photo-induced charge transfer could occur to the electrolyte.

Metrics in Photoelectrode Development

Photocurrent measurements



The carrier pair can be separated by *diffusion* or by the electric field (migration), or it can recombine



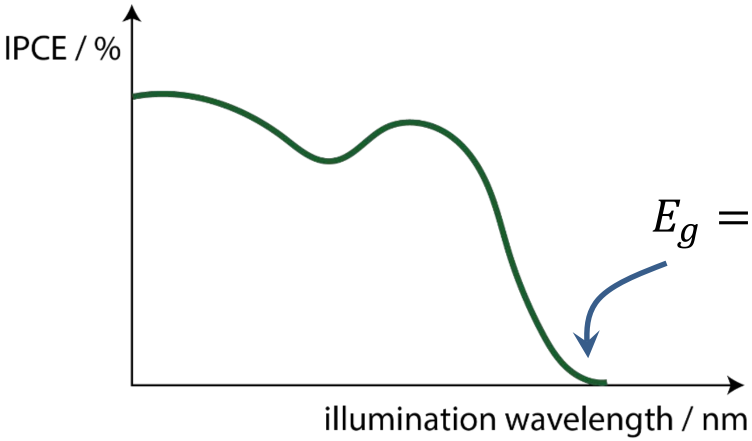
The photocurrent increases and reaches a plateau (*determined by Light absorption, Surface kinetics, carrier transport, etc.*).
Eventually, the dark current sets in.

In field-free region, ***minority carrier*** diffusion length before recombine

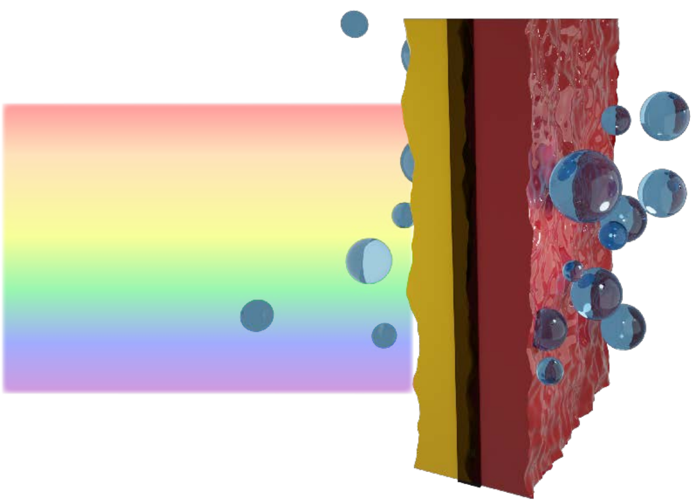
$$L_{min} = \sqrt{D_{min}\tau_{min}} = \sqrt{\frac{k_B T}{q}\mu_{min}\tau_{min}}$$

Metrics in Photoelectrode Development

Wavelength-dependent photocurrent response



$$E_g = \frac{hc}{\lambda_{on}}$$



Complementary light absorption

Record the photocurrent as a function of the wavelength of the incident light

Contains crucial information on the light-response of the sample (*typically agrees with the light-absorption properties*)

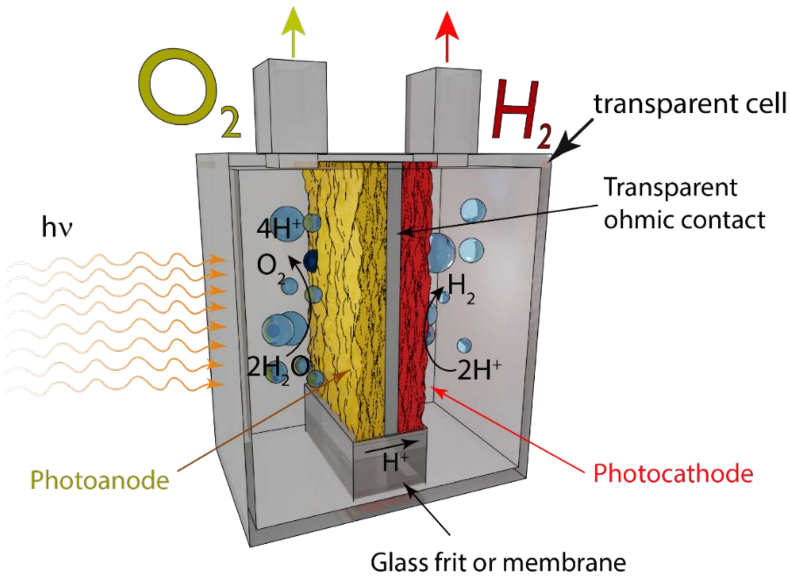
Incident photon to current efficiency (IPCE)
((External Quantum Efficiency))

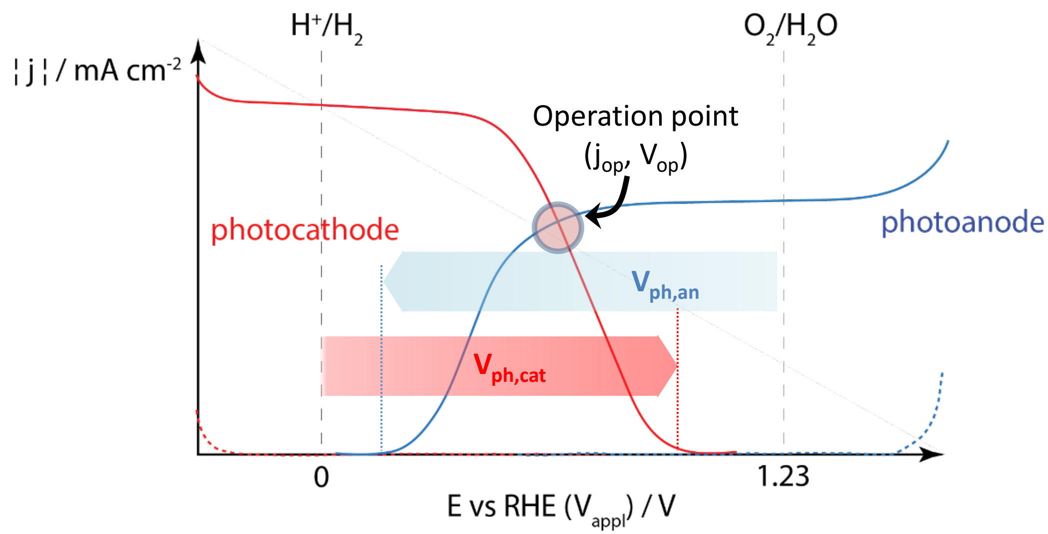
$$IPCE = \frac{(photo)electrons\ measured}{Photons\ incident\ on\ sample}$$

Absorbed photon to current efficiency (APCE)
((Internal Quantum Efficiency))

$$APCE = \frac{(photo)electrons\ measured}{Photons\ absorbed\ by\ sample}$$

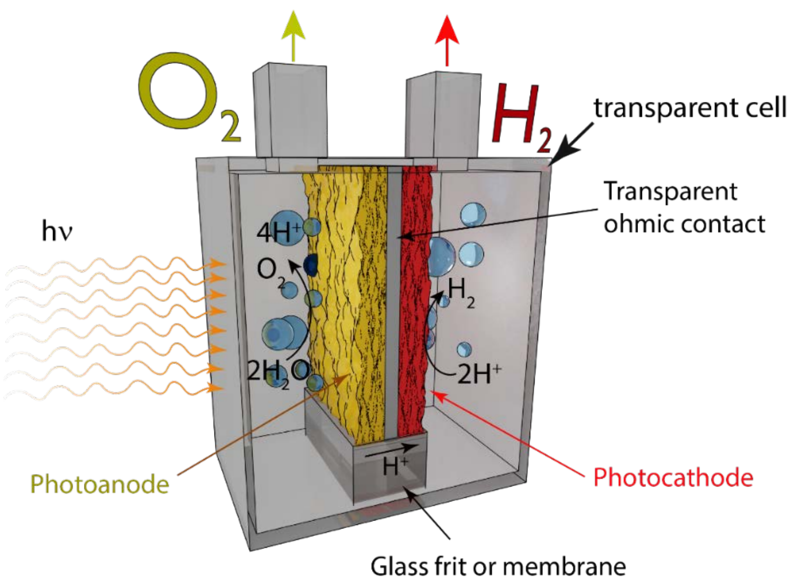
Assessment of a Dual Tandem PEC cell

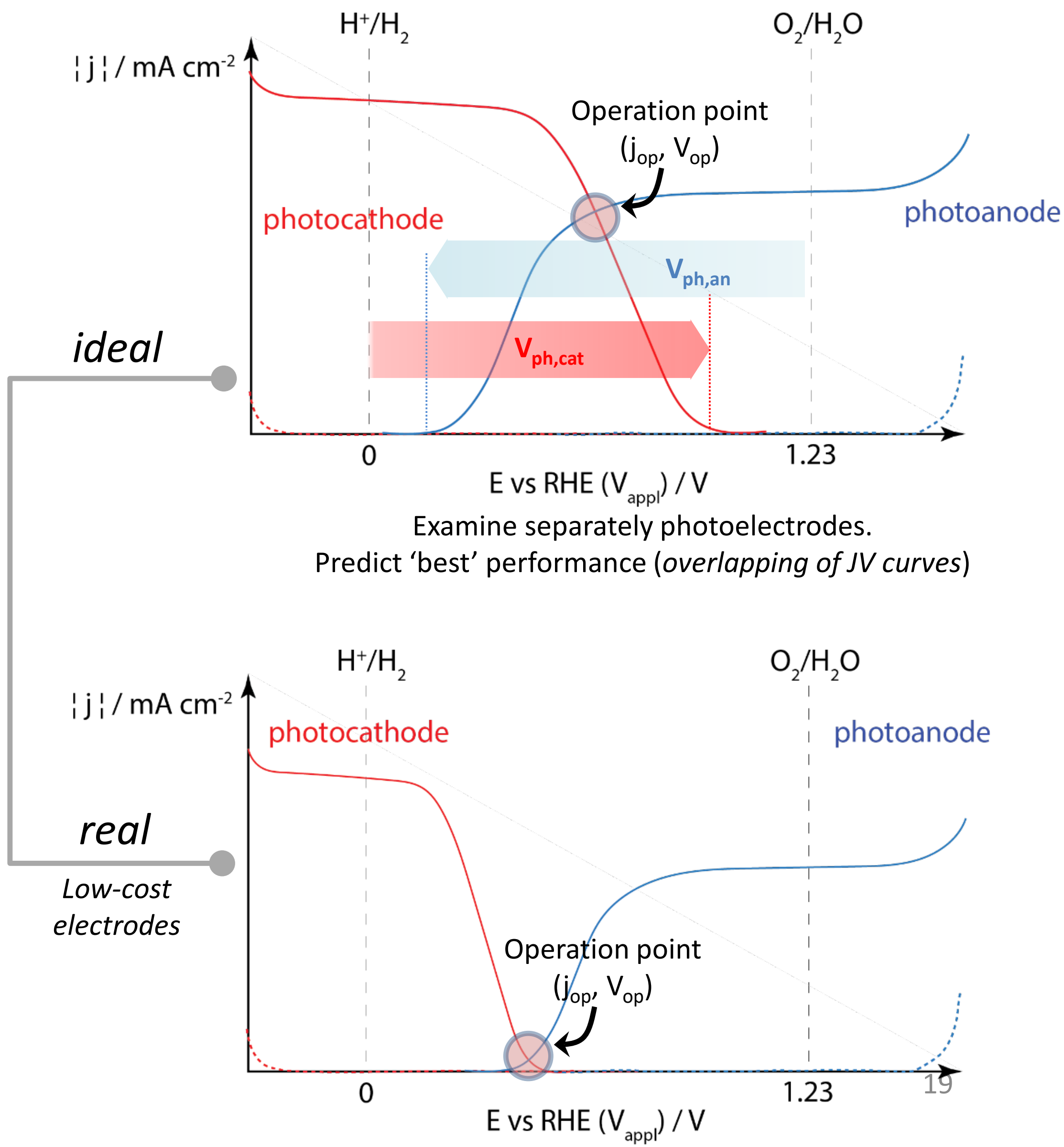




Examine separately photoelectrodes.
Predict 'best' performance (*overlapping of JV curves*)

Assessment of a Dual Tandem PEC cell

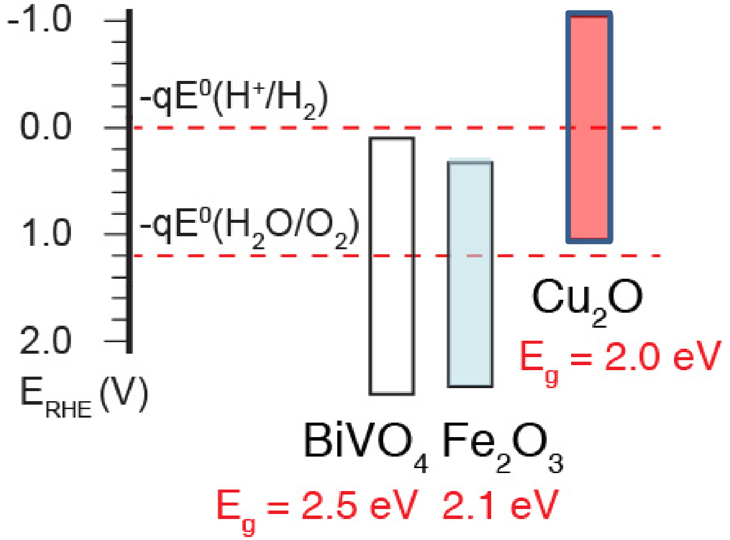


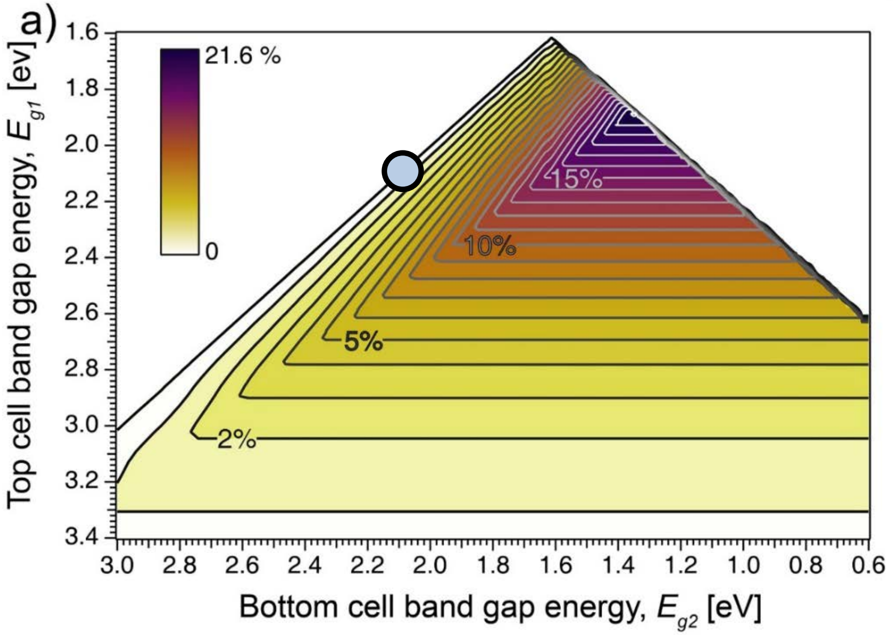


Today's low-cost PEC cells suffer from poor STH

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

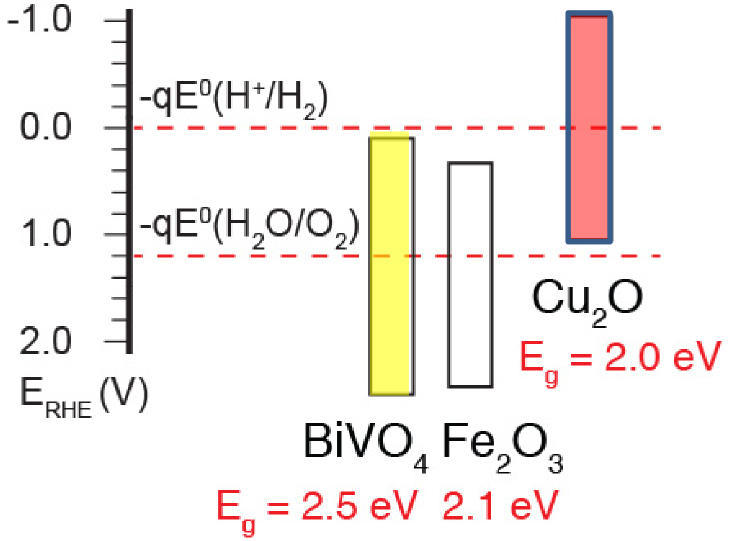
Assessment of a Dual Tandem PEC cell

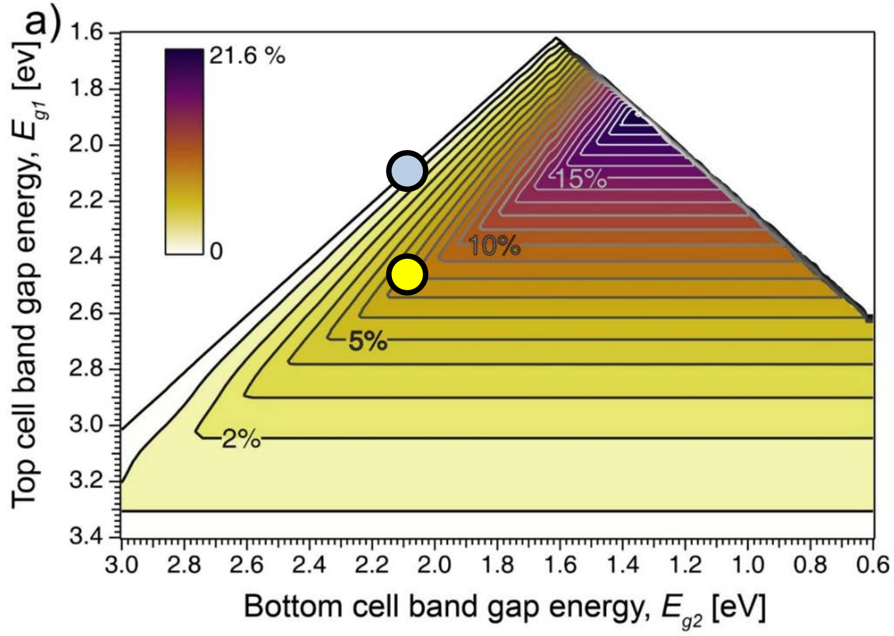


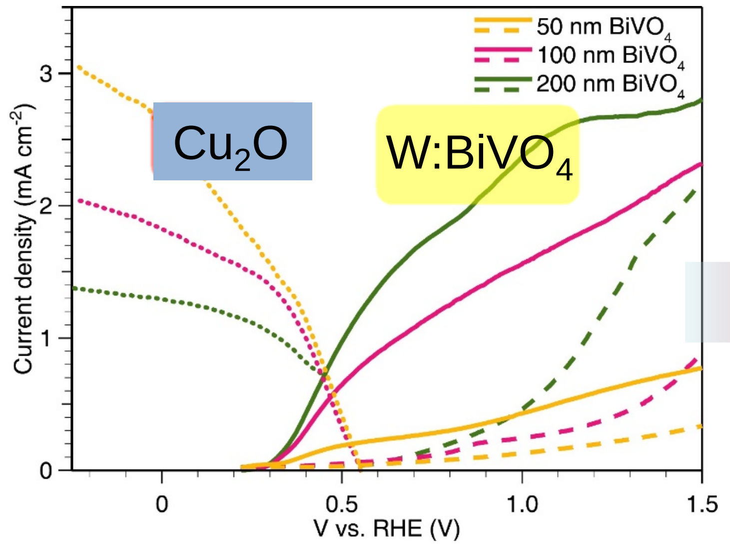


Low performance (non-complementary light absorption). *Hematite* filters useful light for Cu_2O

Assessment of a Dual Tandem PEC cell







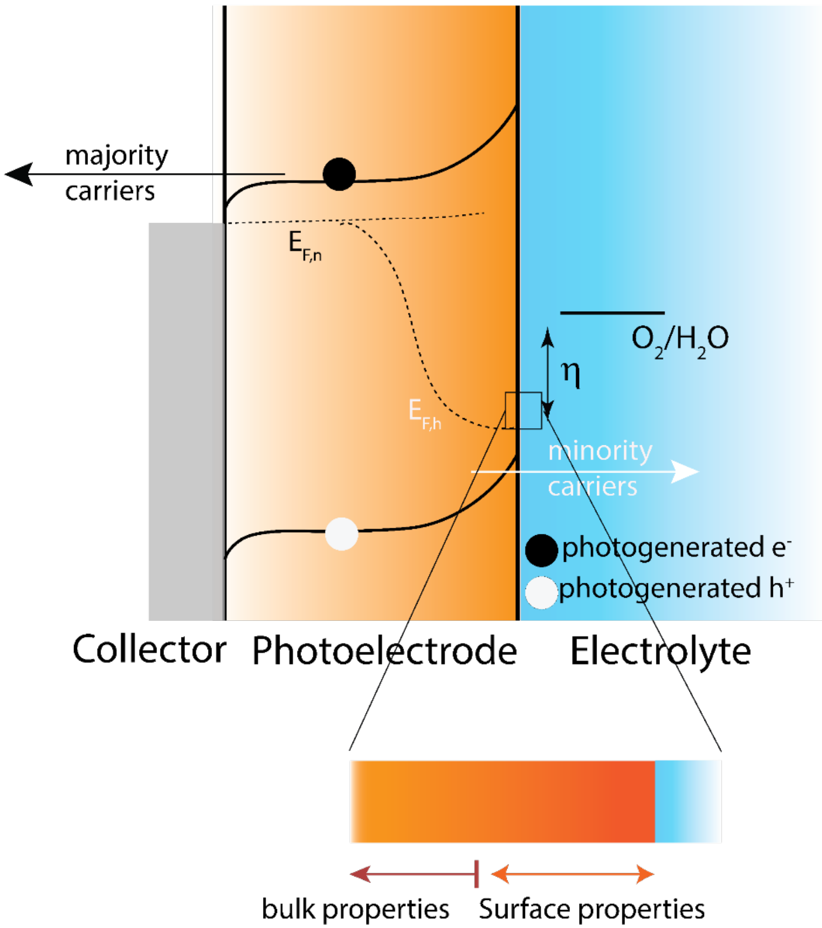
1) Performance of photoelectrodes, far from the maximum

- $BiVO_4$ ~7 mA cm^{-2} (for 1 sun)
- Cu_2O ~ 14 mA cm-2 (for 1 sun)

2) Light-scattering effects from $BiVO_4$ film prevents optimum light harvesting of Cu_2O

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

Challenges to address



BULK PROPERTIES

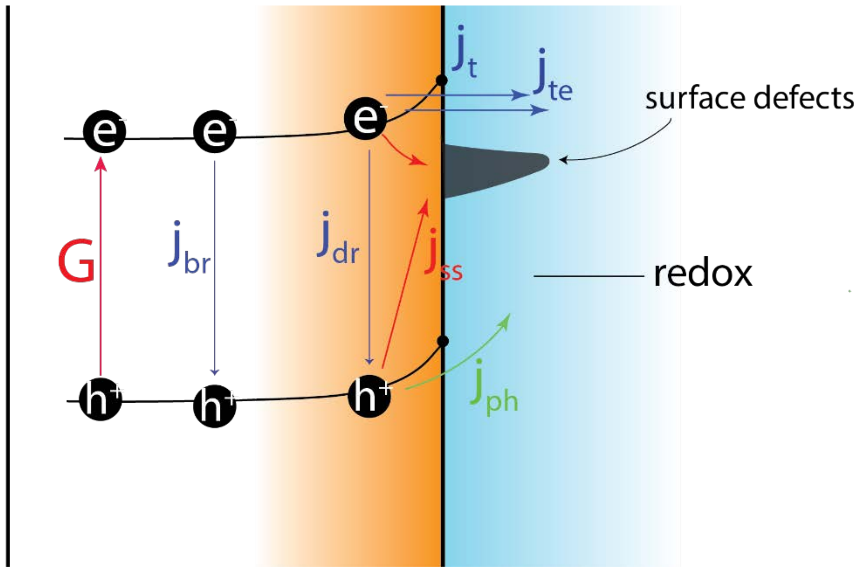
- Bulk defects (recombination)
- Carrier transport
- Doping density (conductivity, W)
- Morphology

SURFACE PROPERTIES (Semiconductor-liquid junction)

- Surface defects (Fermi level pinning)
- Catalytic properties
- Stability

Characterize/understand these parameters to design strategies to enhance the performance of photoelectrodes

Challenges to address



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

Bulk properties

- Bulk defects (recombination)
- Carrier transport
- Doping density (conductivity, W)
- Morphology

Surface properties (Semiconductor-liquid junction)

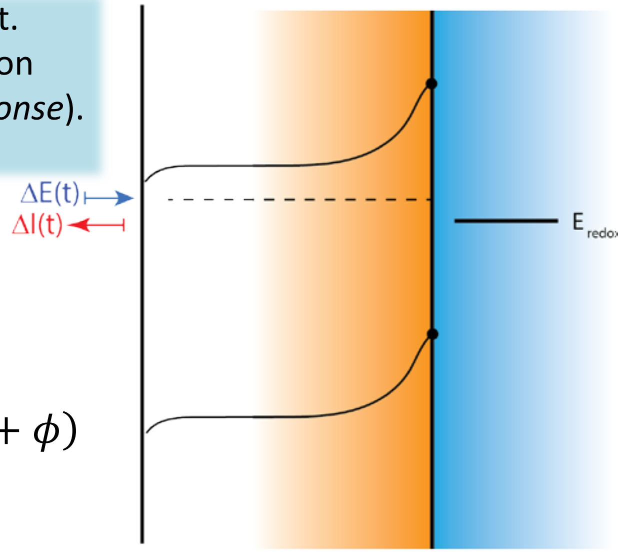
- Surface defects (Fermi level pinning)
- Catalytic properties
- Stability

Characterize/understand these parameters to design strategies to enhance the performance of photoelectrodes

Characterization by electrochemical tools

(Photo)Electrochemical Impedance Spectroscopy (PEIS)

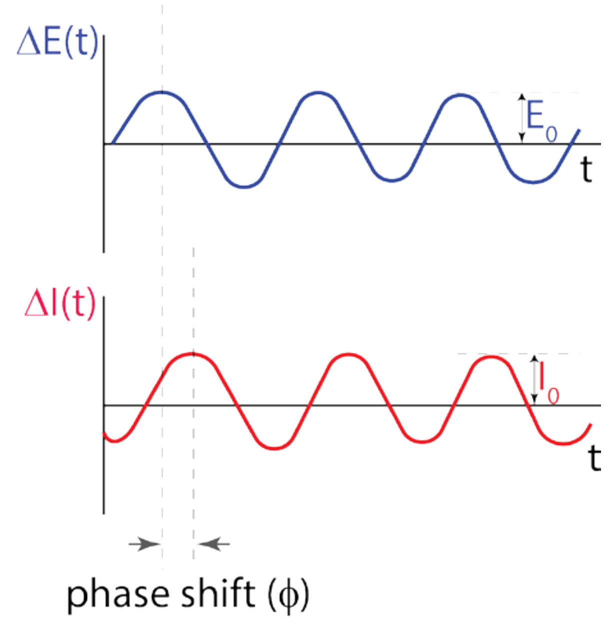
- **Frequency-domain** measurement.
- Small perturbation (small deviation from the equilibrium: *linear response*).
- Sinusoidal (AC) perturbation



$$Apply \rightarrow \Delta E(t) = E_0 sin(\omega t)$$

$$\omega = 2\pi f$$

$$Response \rightarrow \Delta I(t) = I_0 sin(\omega t + \phi)$$



$$impedance \equiv Z = \frac{\Delta E(t)}{\Delta I(t)} = \frac{E_0 sin(\omega t)}{I_0 sin(\omega t + \phi)} = Z_0 \frac{sin(\omega t)}{sin(\omega t + \phi)} = Z_0 e^{i\phi} = Z_0(cos\phi + isin\phi)$$

$$Z = Z' + iZ''$$

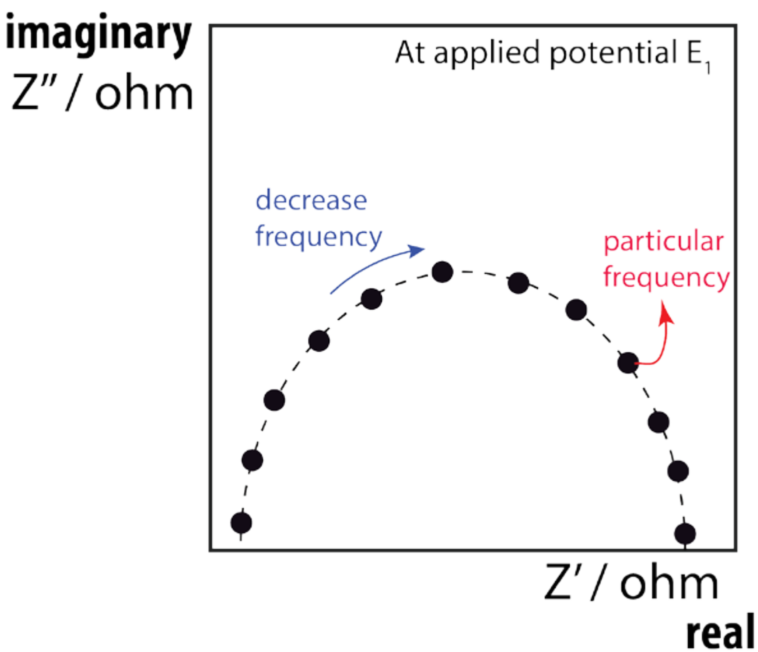
The ***impedance at a given frequency*** is related to the ***processes occurring at the timescales*** imposed by the frequency

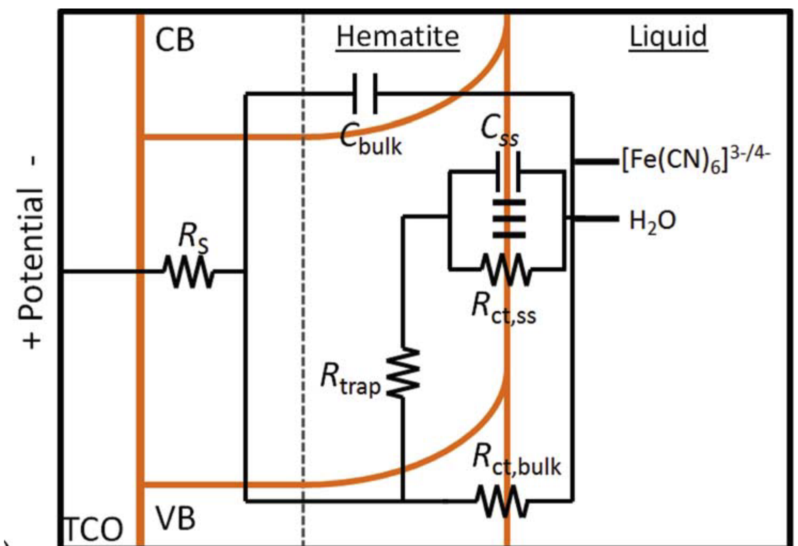
Characterization by electrochemical tools

(Photo)Electrochemical Impedance Spectroscopy (PEIS)

Nyquist Plot

$$Z = Z' + iZ''$$





Frequency not obvious

Contain valuable information on the electrochemical processes occurring on the electrode

Model the electrode with an ***equivalent circuit:*** Hypothetical network of electrical circuit elements that shows a behaviour similar to that of the electrode under study.

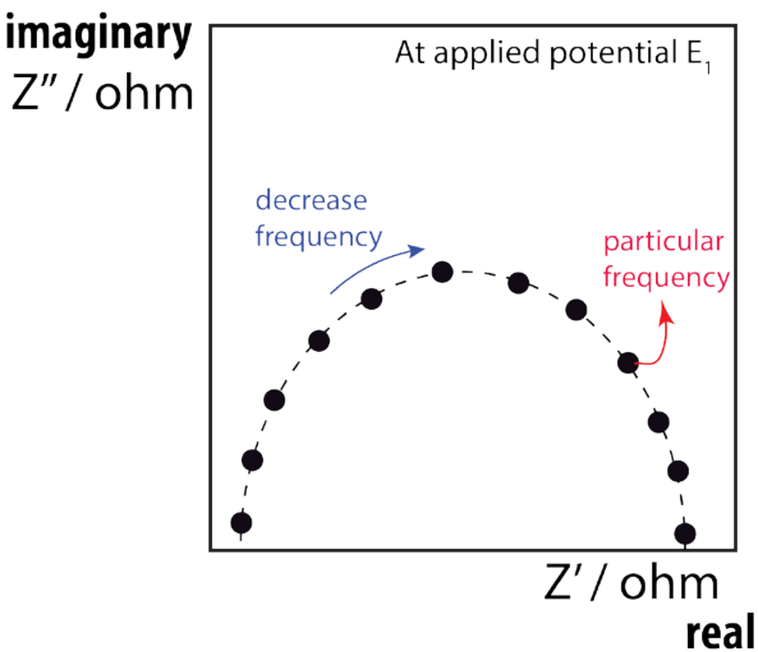
Derive information on the charge transfer resistance or surface capacitance.

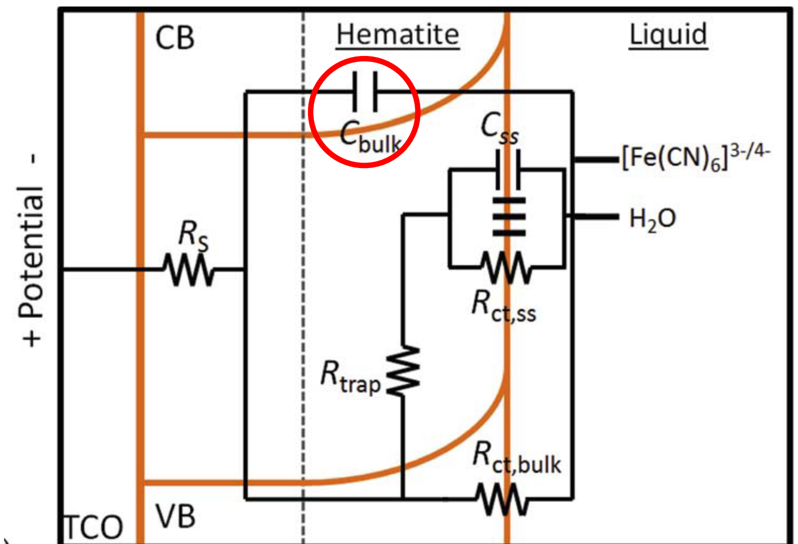
Characterization by electrochemical tools

(Photo)Electrochemical Impedance Spectroscopy (PEIS)

Nyquist Plot

$$Z = Z' + iZ''$$





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Characterization by electrochemical tools

(Photo)Electrochemical Impedance Spectroscopy (PEIS)

Nyquist Plot

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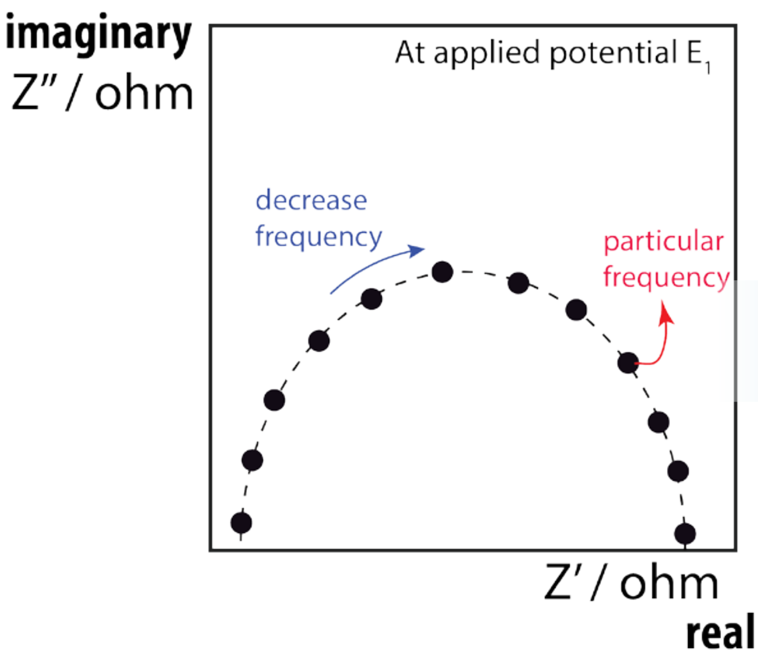
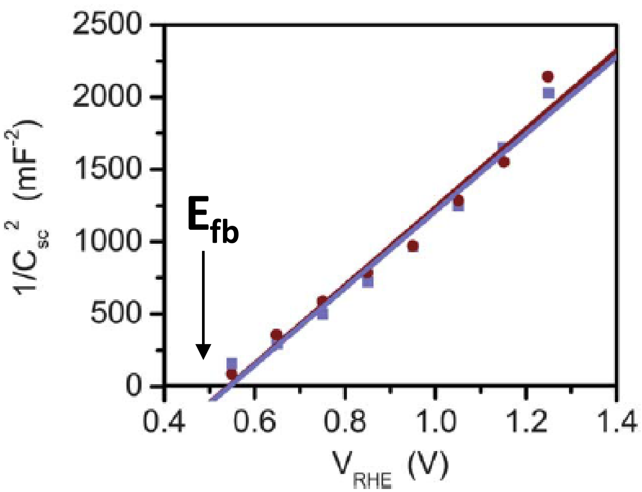


Frequency not obvious

Contain valuable information on the electrochemical processes occurring on the electrode

Mott-Schottky plot



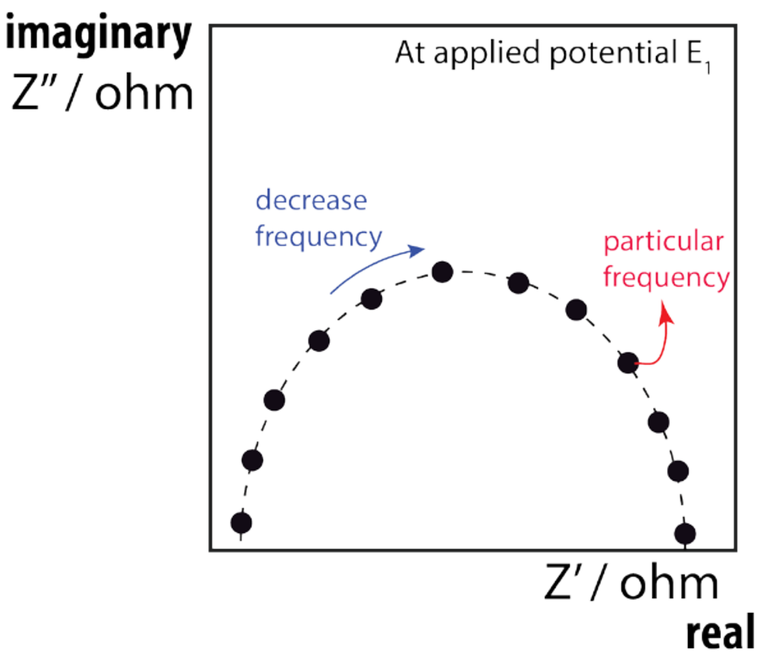
$$\frac{1}{C_{sc}^2} = -\frac{2}{\varepsilon_0 \varepsilon_r q N_d A^2}\left(E - E_{fb} - \frac{kT}{q}\right)$$

Characterization by electrochemical tools

(Photo)Electrochemical Impedance Spectroscopy (PEIS)

Nyquist Plot

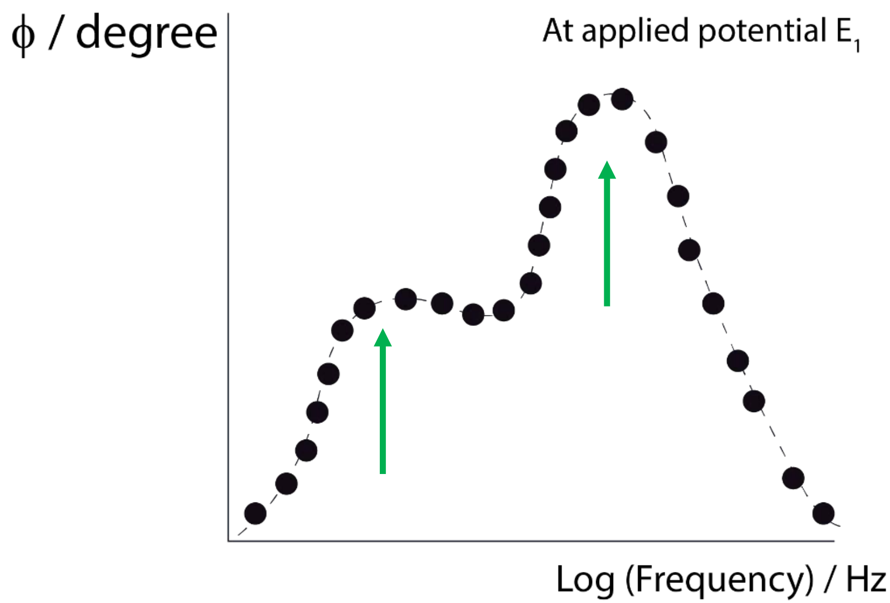
$$Z = Z' + iZ''$$



Frequency not obvious

Contain valuable information on the electrochemical processes occurring on the electrode

Bode plot



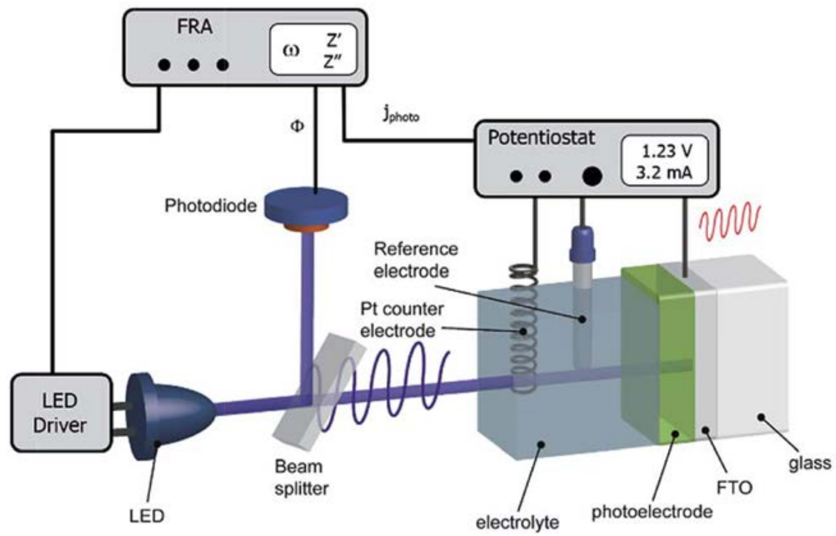
Frequency is explicit

Individual processes can be resolved in the frequency domain.

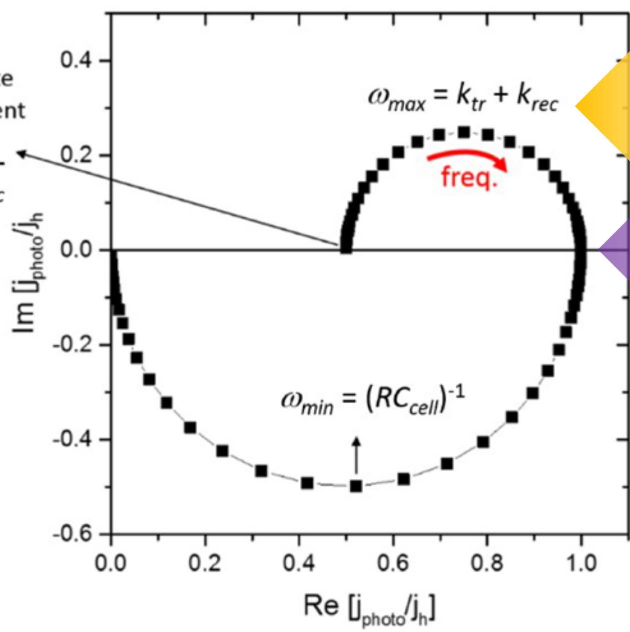
Characterization by electrochemical tools

Intensity-Modulated Photocurrent Spectroscopy (IMPS)

- **Frequency-domain** measurement.
- Small perturbation (small deviation from the equilibrium: *linear response*).
- Sinusoidal (AC) perturbation on the incident light



At a fixed potential, the modulation of the ***incident light*** modulates the surface concentration of carriers (and the ***photocurrent***)



Nyquist plot: Imaginary vs. Real parts of the photocurrent

SIMPLE MODEL

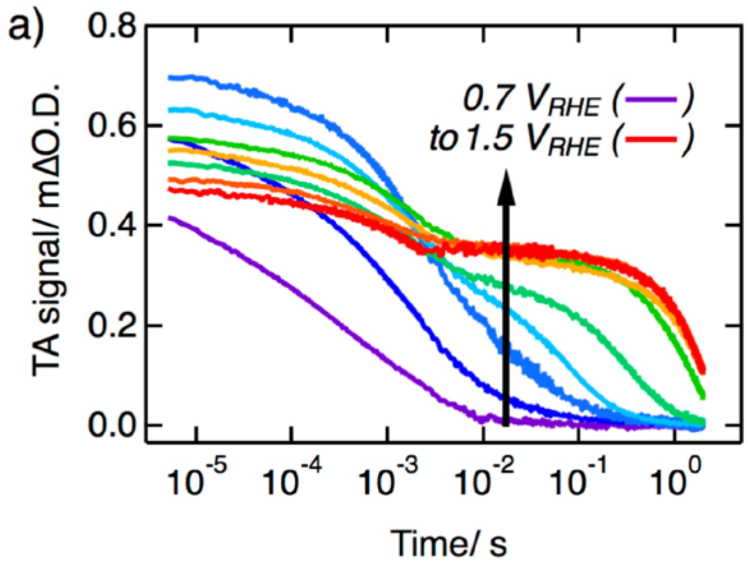
Extract information on the surface dynamics

By assuming
- Bulk processes are not detected
- A ***one-electron transfer process***
- Band bending remains constant

Zachaus *et al*. *Chem. Sci*. **2017**, 8, 3712

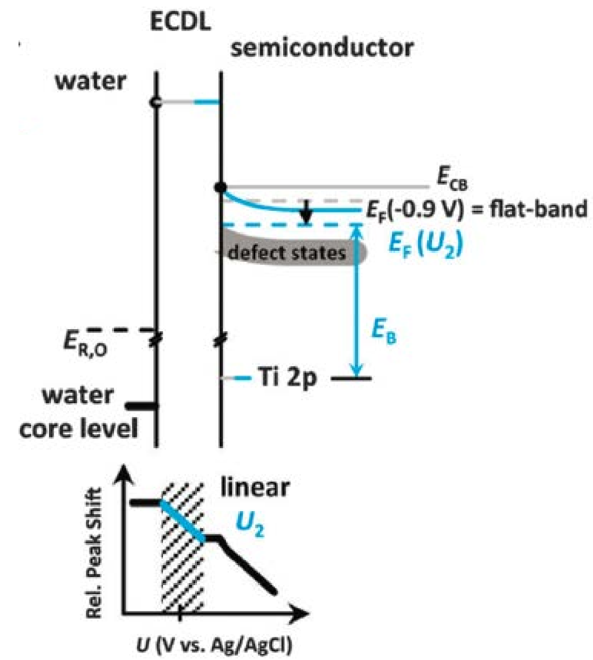
Other characterization techniques

Transient Absorption spectroscopy



- Specific information on the kinetics of the intermediates and reaction

In operando XPS



- Probe under operation the **chemical nature** of the surface species and band alignment

J. Am. Chem. Soc., 2014, **136**, 2564

EES, 2015, **8**, 2409

Examples of photoelectrodes

Photoanode

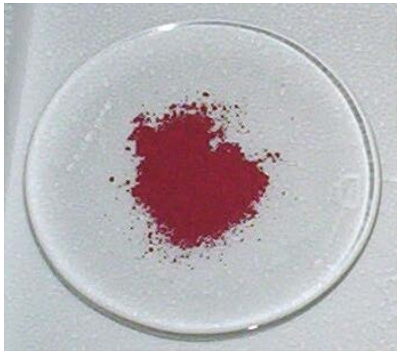
WO_3

$BiVO_4$

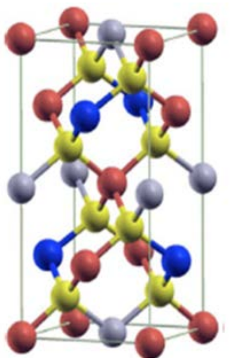
α-Fe_2O_3

Solution based processing
Cost = $\$10/m^2$

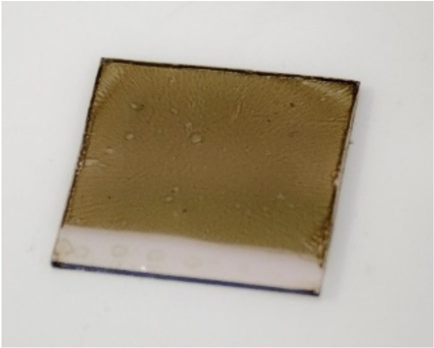
Photocathode



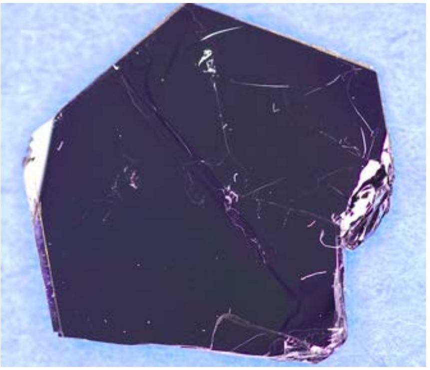
Copper(I) oxide



Cu_2ZnSnS_4



$CuFeO_2$



WSe_2

α-Fe_2O_3 (hematite) as a promising material

Advantages

- Cheap and abundant
- Stable
- Environmentally benign
- Absorbs over 16 % (AM 1.5 Solar spectrum)

Challenges

Bulk problems

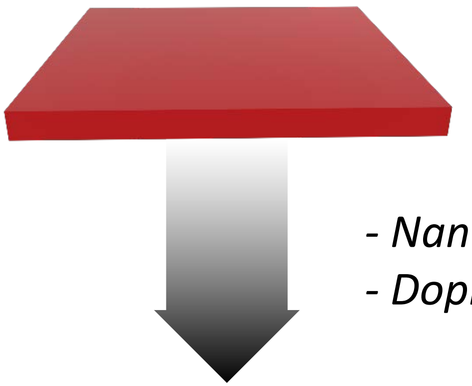
- Short hole diffusion length (**L_D = 5 nm**)
- Poor conductivity

Surface problems

- High overpotential for water oxidation

Bulk problems I – *Photocurrent*

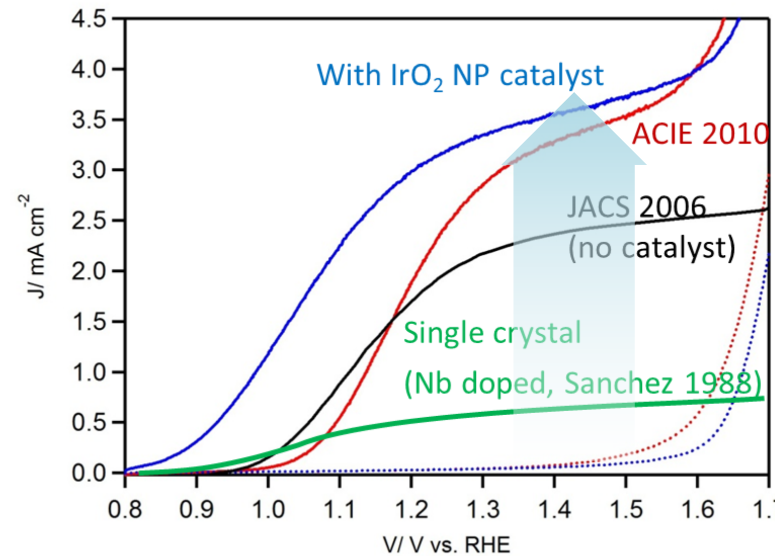
Single crystal α- Fe_2O_3

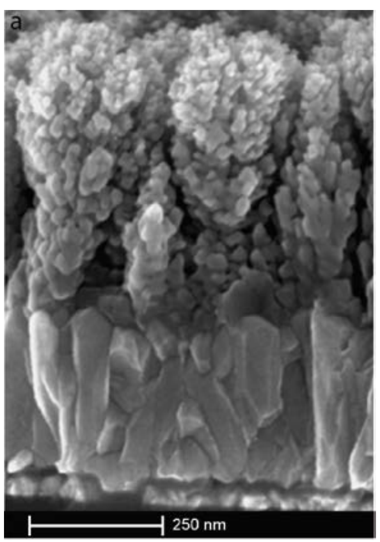


12.6 mA/cm^2

Possible

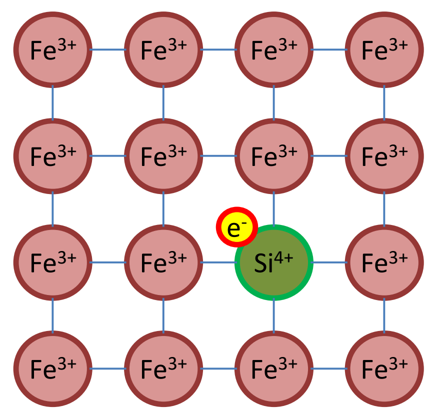
- *Nanostructure*
- *Doping*





Si-doped Fe_2O_3

Substrate ($F:SnO_2$)



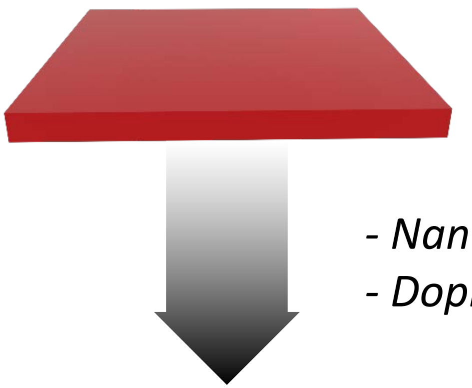
Improve conductivity and strengthen built-in field (reduce W)

*Sanchez, et al., *J. Electroanal. Chem.* **1988**, *252*, 269-290.

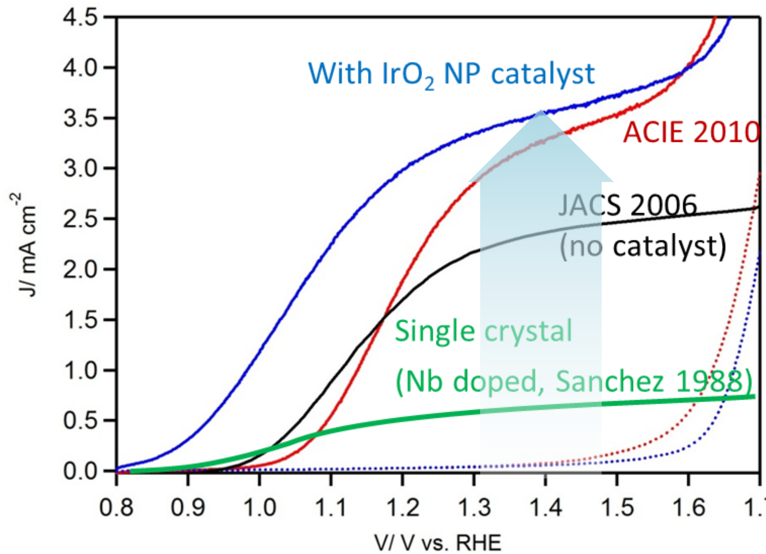
Bulk problems – *Photocurrent*

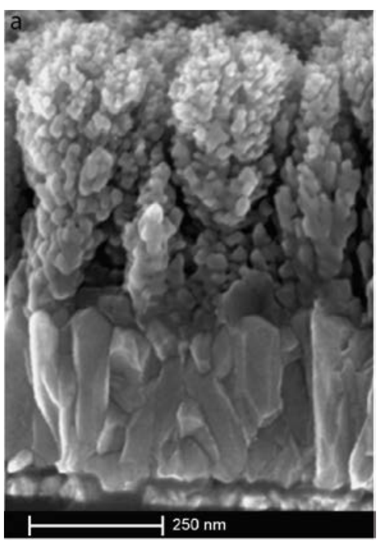
Single crystal α- Fe_2O_3

12.6 mA/cm^2
Possible



- *Nanostructure*
- *Doping*





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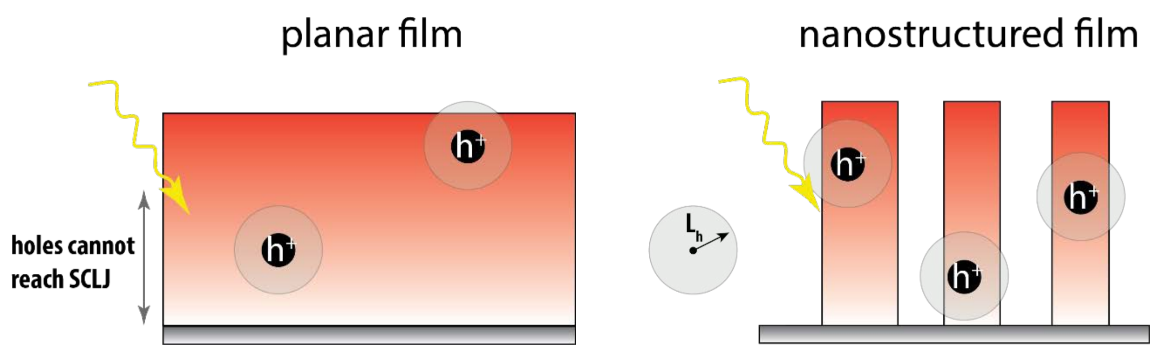
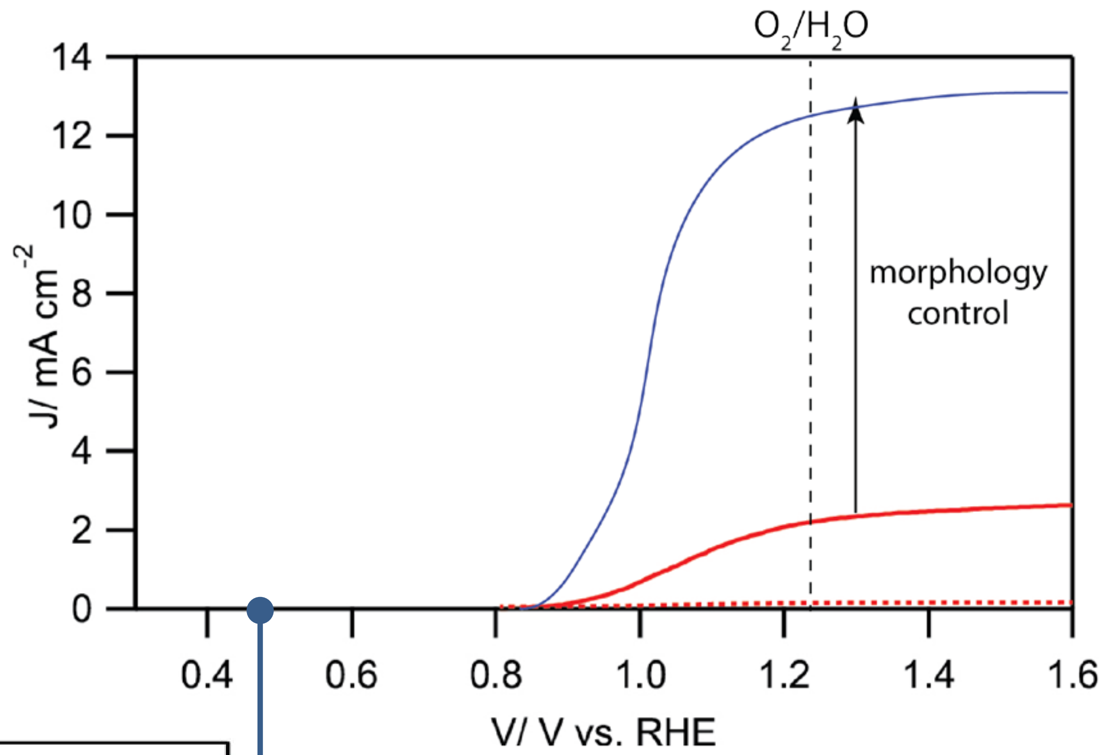
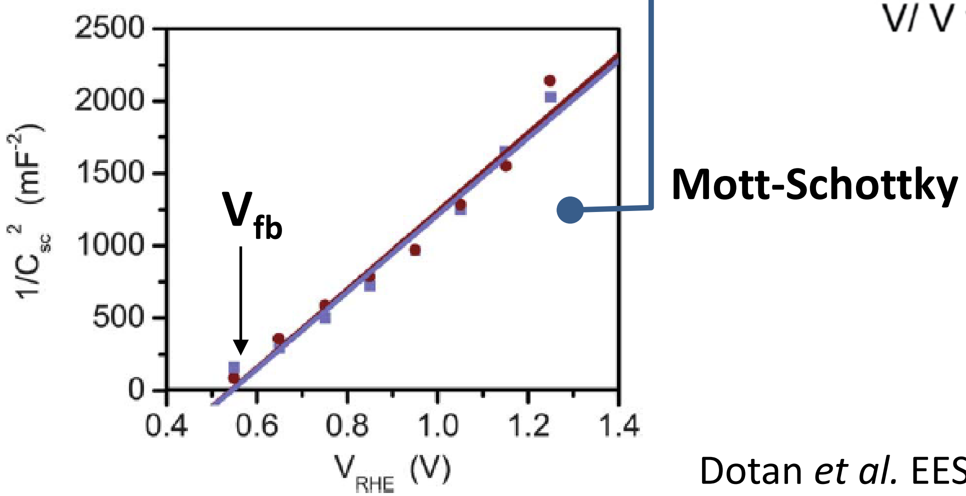


*Sanchez, et al., *J. Electroanal. Chem.* **1988**, *252*, 269-290.

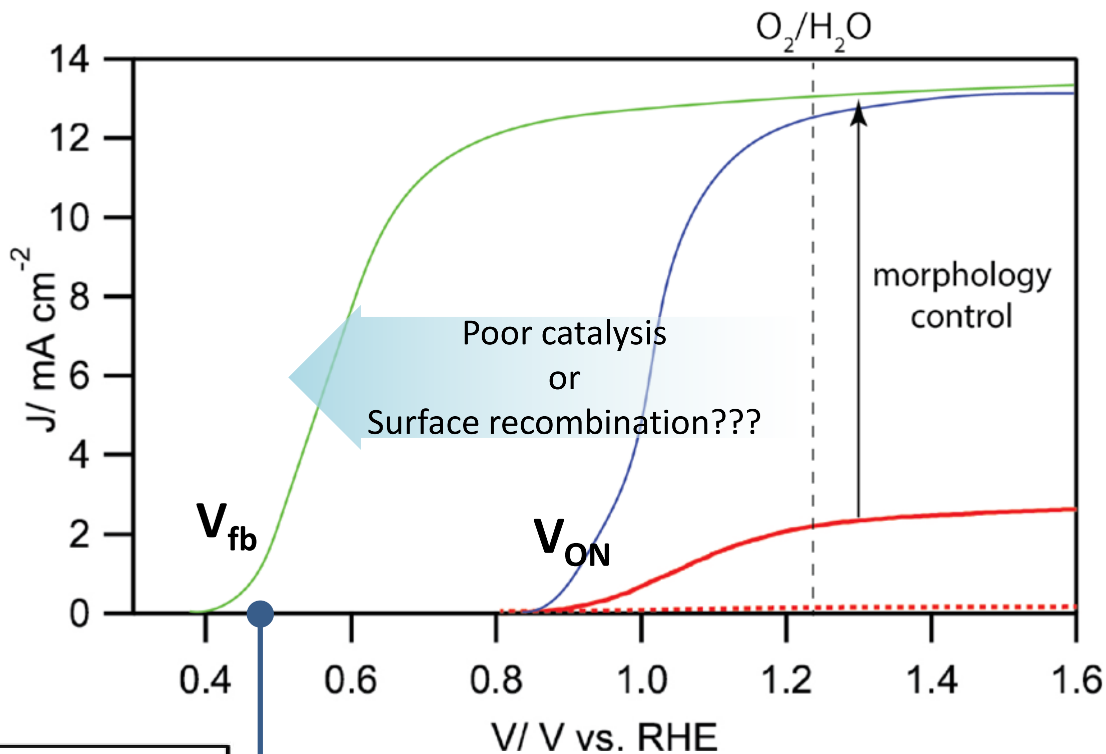
Surface issues – *Overpotential*

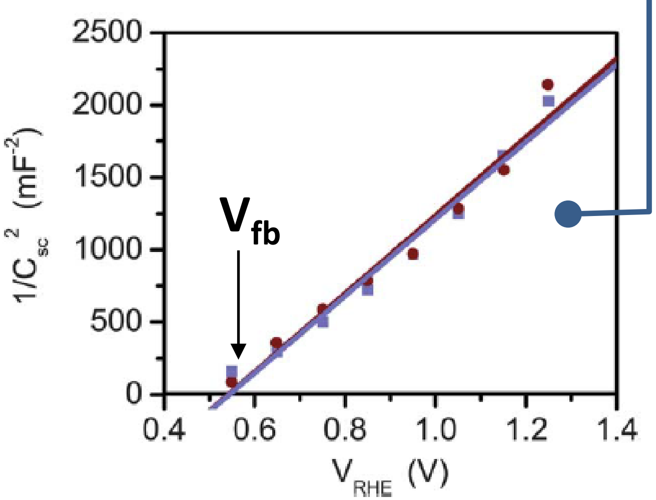




Dotan *et al.* EES 2011, 4, 958

Surface issues – *Overpotential*





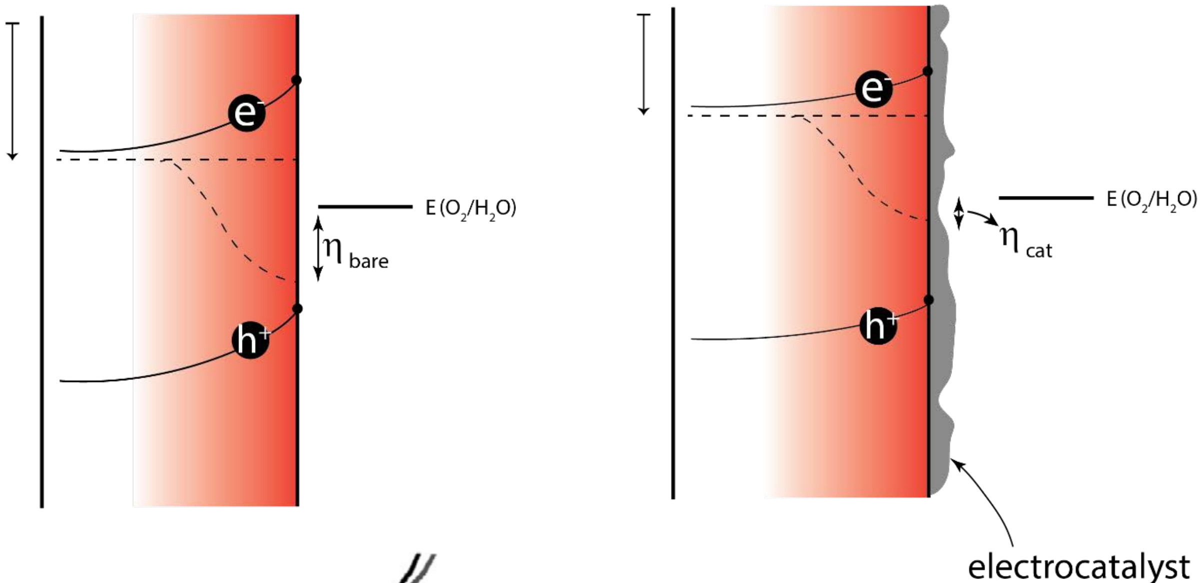
Mott-Schottky

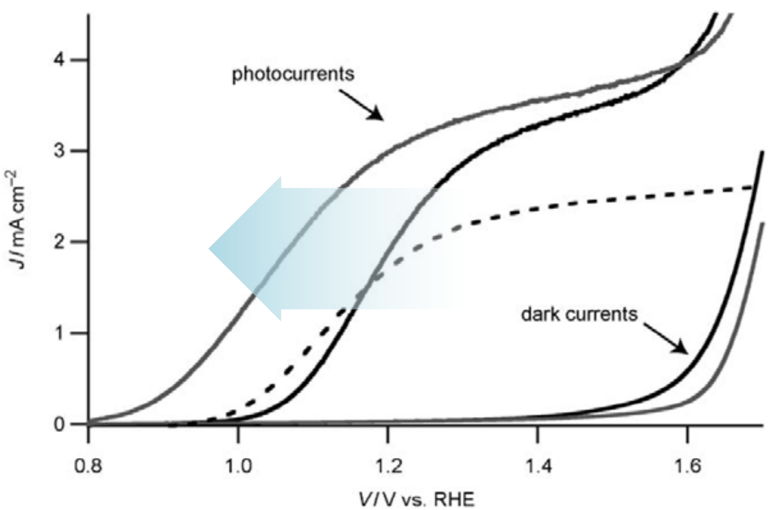
Dotan *et al.* EES 2011, 4, 958

Surface issues – *Overpotential*

Coupling with an ***electrocatalyst***

⫟ = magnitude of applied potential vs. reference





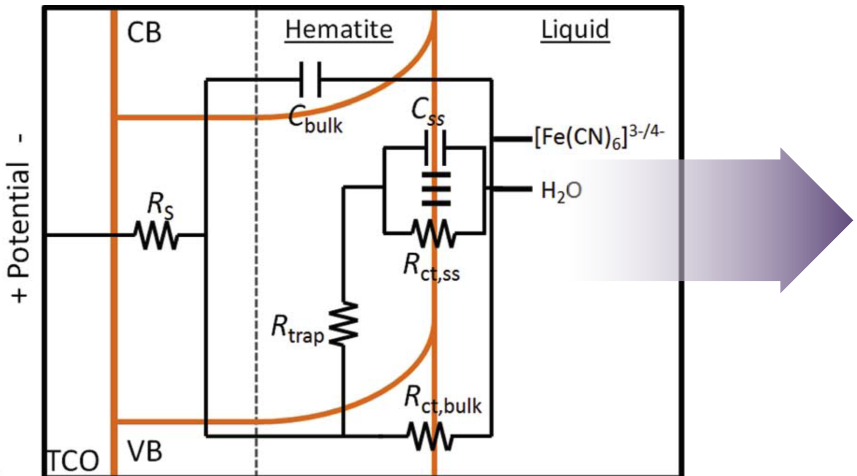
Including IrO_2 shifts slightly the V_{ON}, but still far from V_{fb}

Not a catalytic issue?

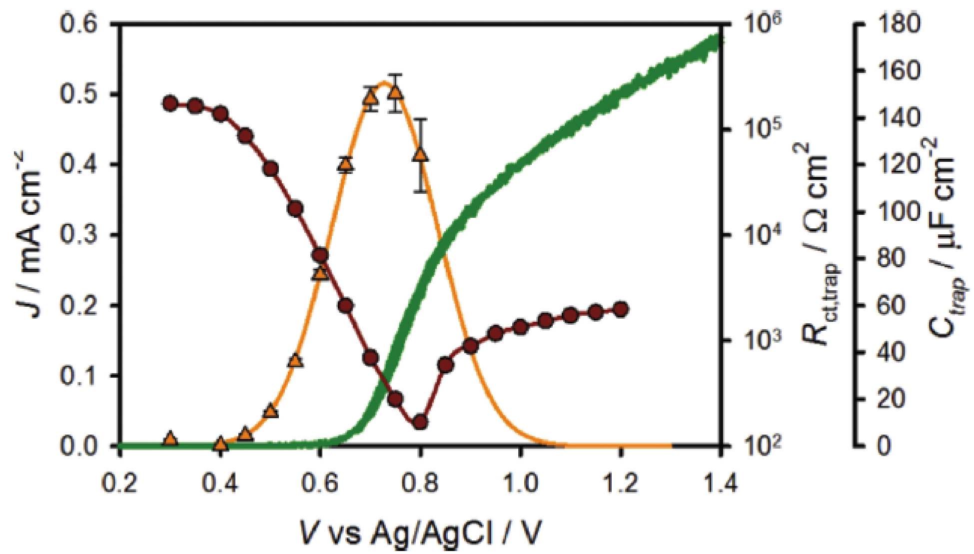
Surface issues – *Overpotential*

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

PEIS



)



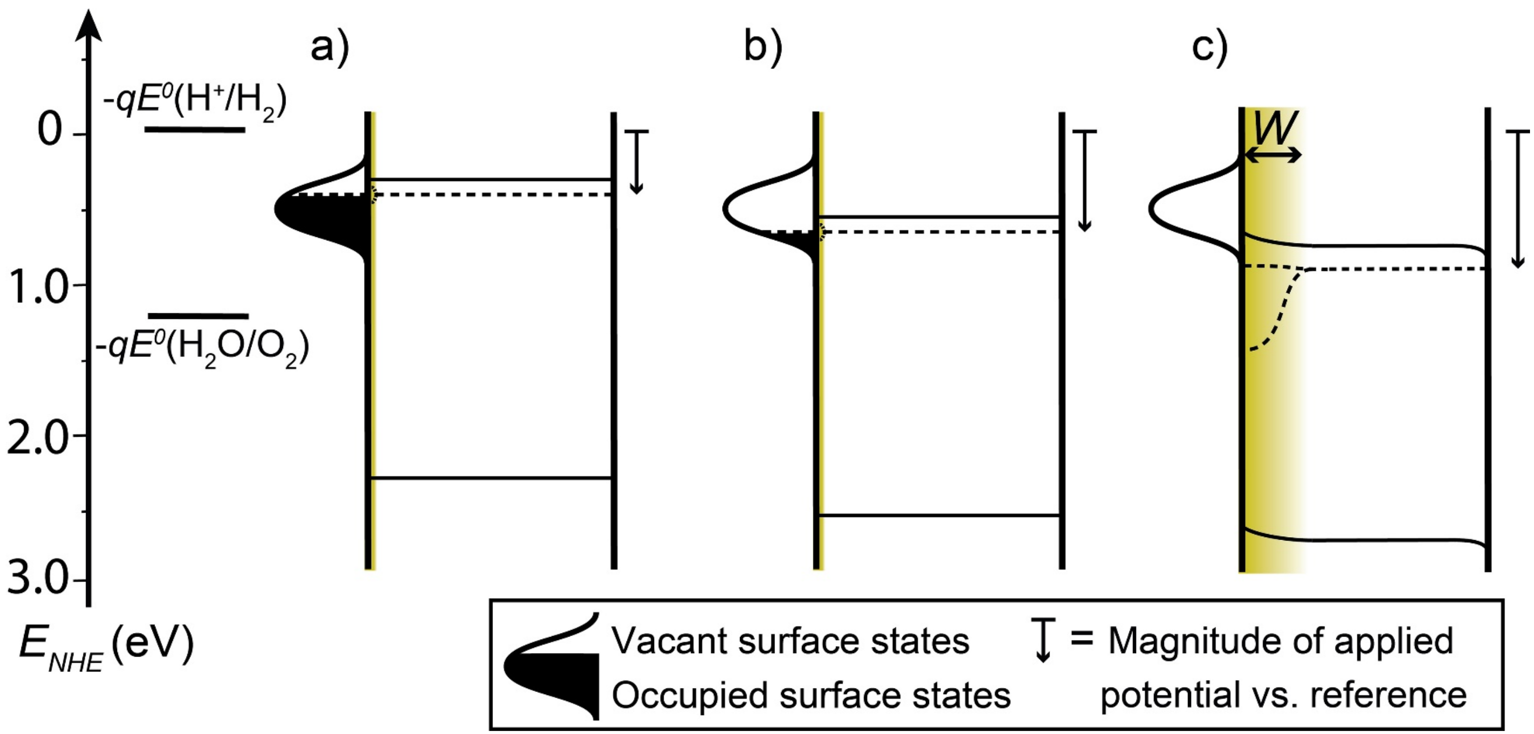
C_{trap} indicate the accumulation of charges at the SCLJ just before the water oxidation starts

Suggests that "the delayed" onset of photocurrent is caused by Fermi Level Pinning
(necessary to apply enough potential to overcome the strong surface recombination)

Surface issues – *Overpotential*

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

PEIS



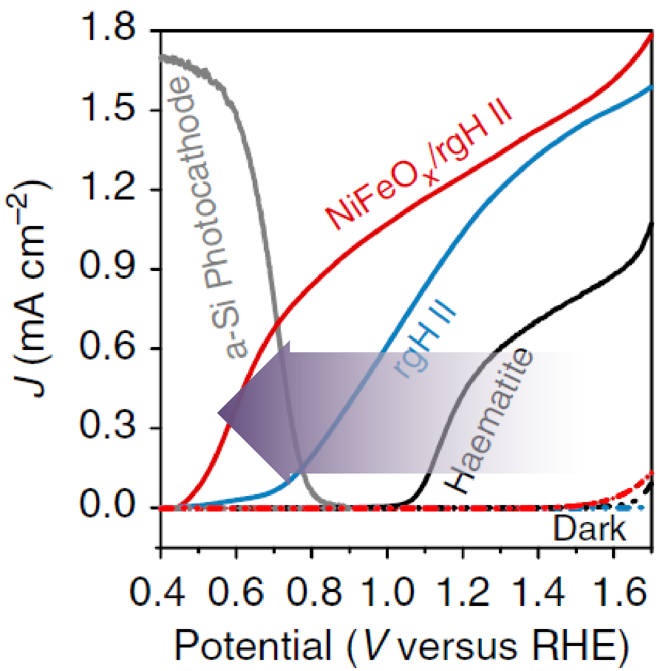
$$\Delta V_H = \frac{\Delta Q_{ss}}{C_H} = \frac{qN_{ss}}{C_H}$$

Fermi level pinning (band edge unpinning)

- the applied potential drops across the Helmholtz layer (charging-discharging Surface States) shifting the bands with respect the redox, instead of across the space charge region to create the band bending.

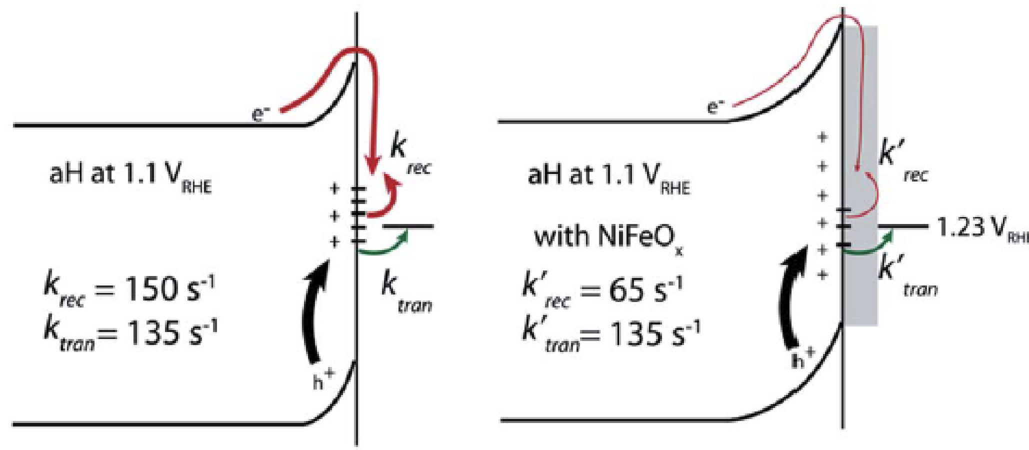
Surface issues – *Overpotential*

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



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

IMPS



$NiFeO_x$ **passivate** surface traps.
Mitigate the Fermi Level pinning

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

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

$BiVO_4$ as a potential photoanode

Advantages

- Cheap and abundant
- Stable
- Environmentally benign
- Theoretically 7.5 mA cm^{-2}

Challenges

Bulk problems

- Short carrier diffusion length (**L_D = 70 nm**)
    - Typically electrodes very thin (poor light absorption).

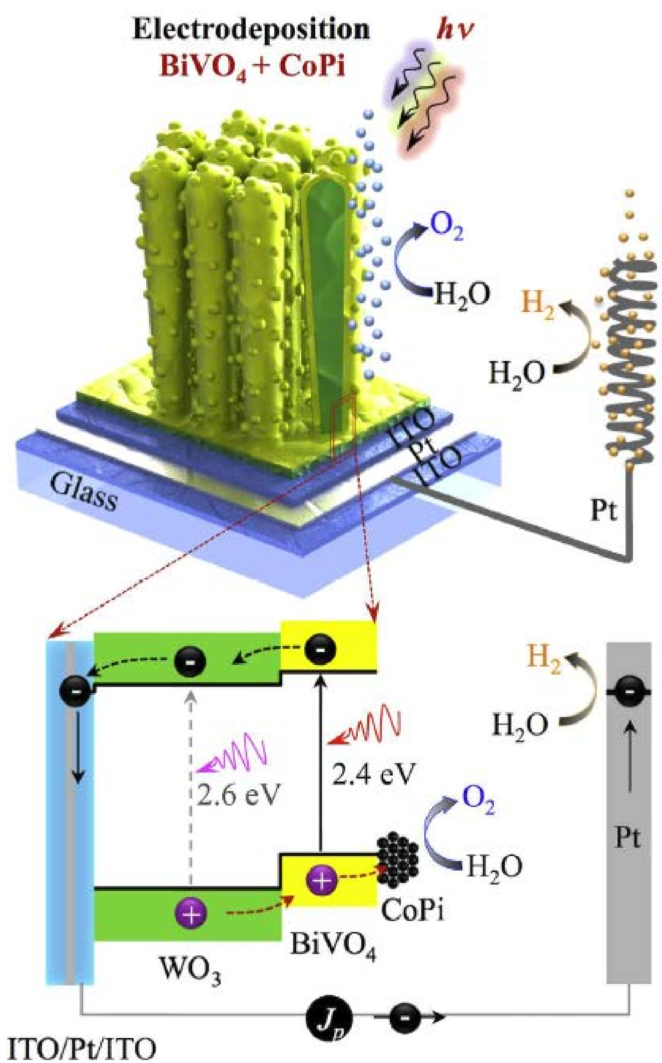
Surface problems

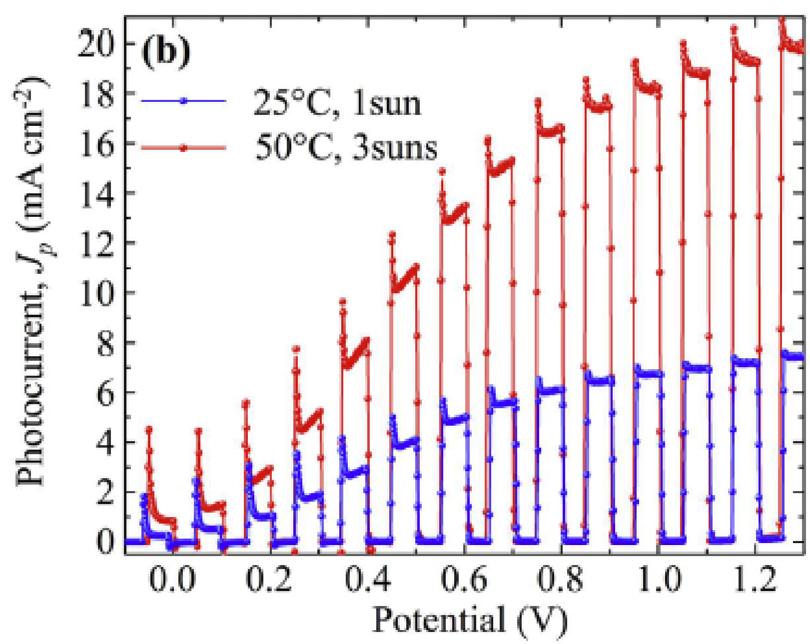
- Poor kinetics for water oxidation

Bulk problems

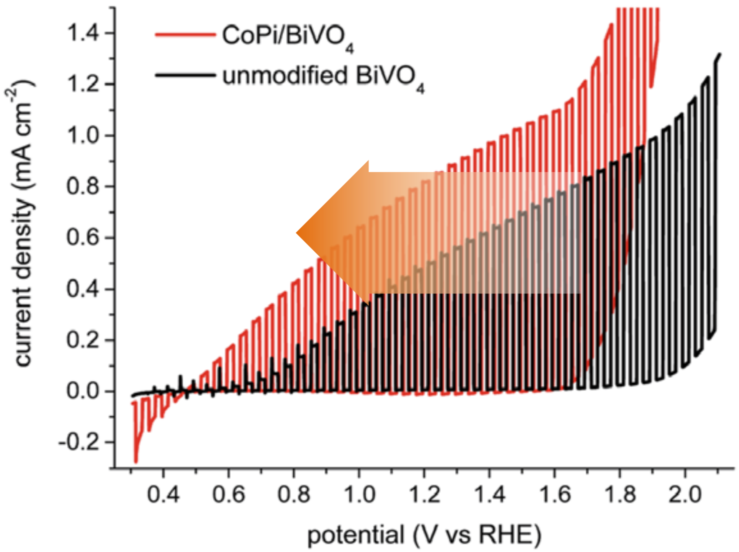
Compensate the short *L* using **extremely thin-absorber (ETA) heterojunction** structure

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



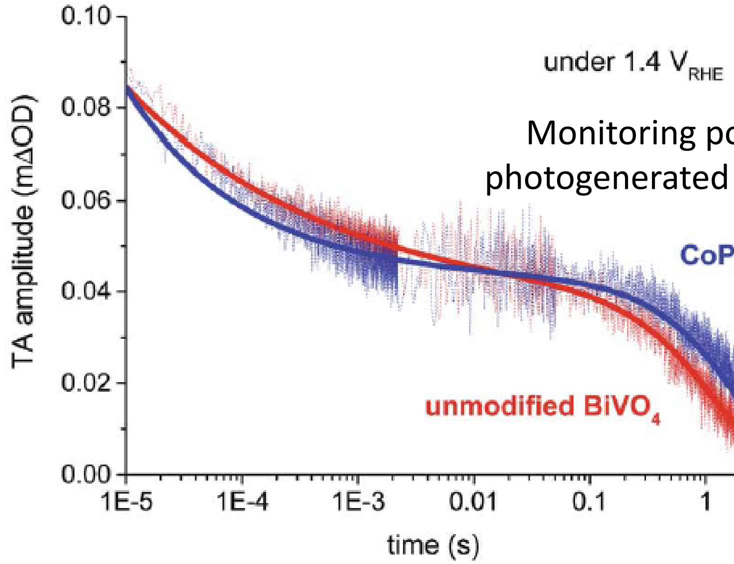


Surface issues

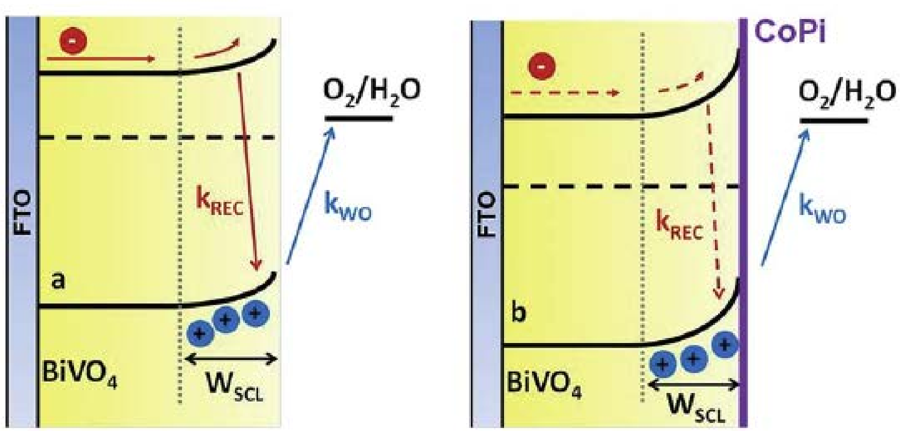


Deposition of CoPi (*electrocatalyst*) enhances performance

Transient Absorption spectroscopy



Monitoring population of photogenerated holes in $BiVO_4$



Analysis of carrier dynamics of photogenerated holes in $BiVO_4$ suggests that CoPi does not function as co-catalyst but reduces recombination of surface-accumulated holes with bulk electrons.

Outlook on PEC tandem cells

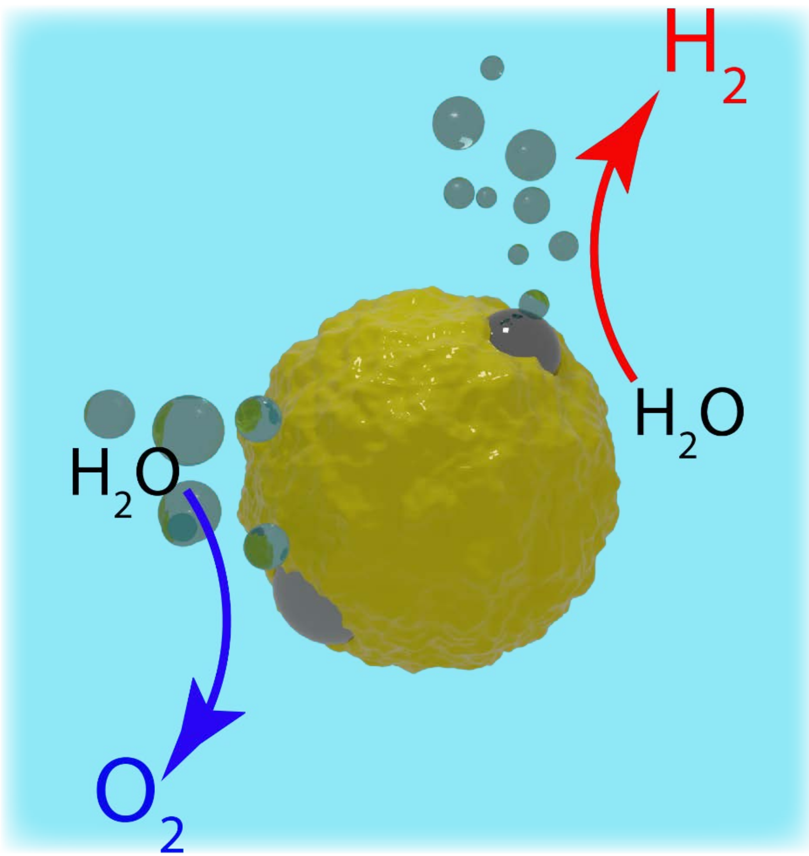
- The formation of a SEMICONDUCTOR-LIQUID JUNCTION (SCLJ) can drive stand-alone photoelectrochemical reactions.

- 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.

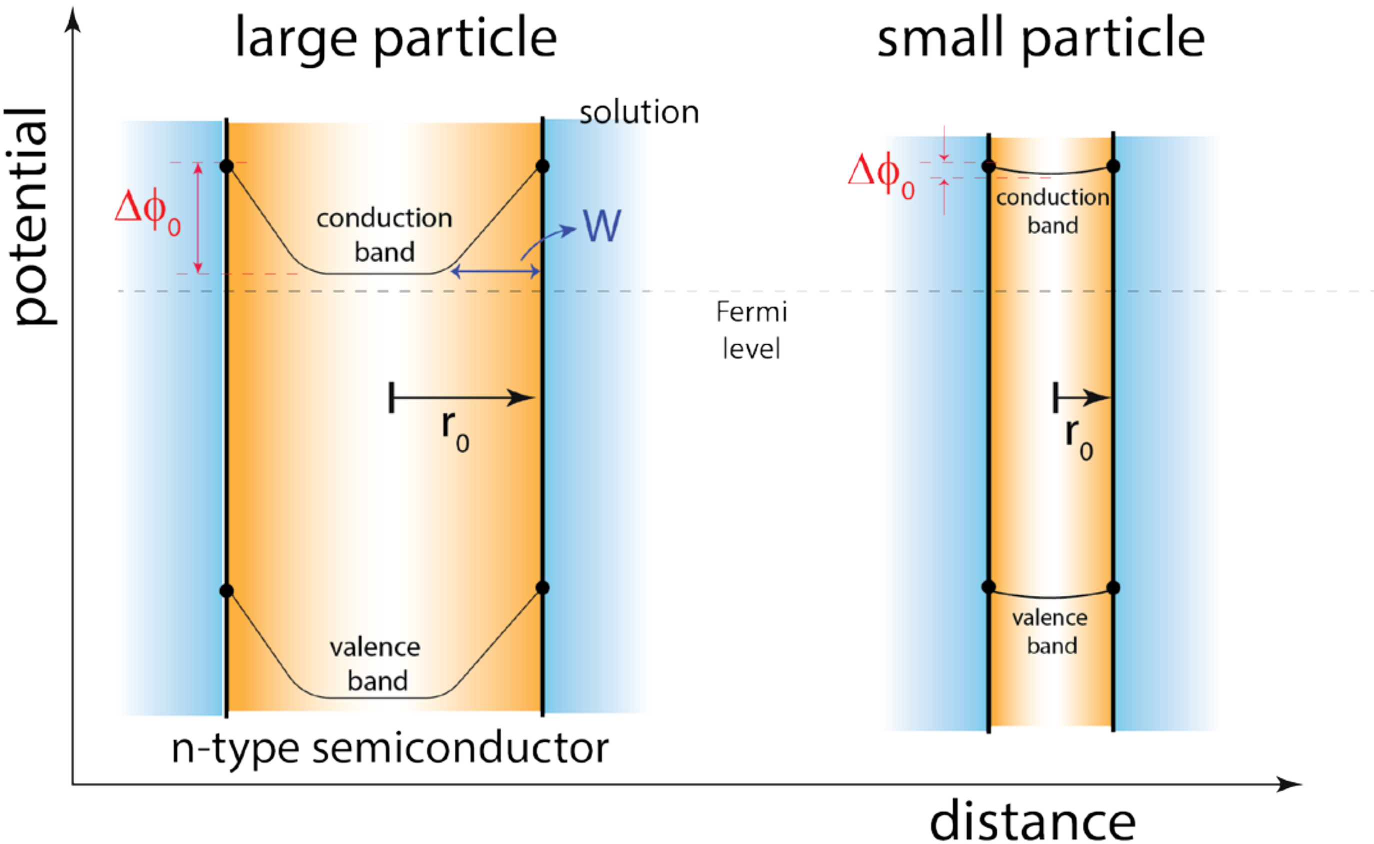
Contents – Part II

<u>**Direct water splitting**</u> using
Photocatalysts



- Which is the driving force for charge separation?
- Basic metrics
- Examples on how to improve the performance

Charge separation: drift *vs.* diffusion



Large particles ($r_0 >> W$)

$$\Delta\phi_0 = \frac{kT}{2q}\left(\frac{W}{L_D}\right)^2$$

Small particles

$$\Delta\phi_0 = \frac{kT}{6q}\left(\frac{r_0}{L_D}\right)^2$$

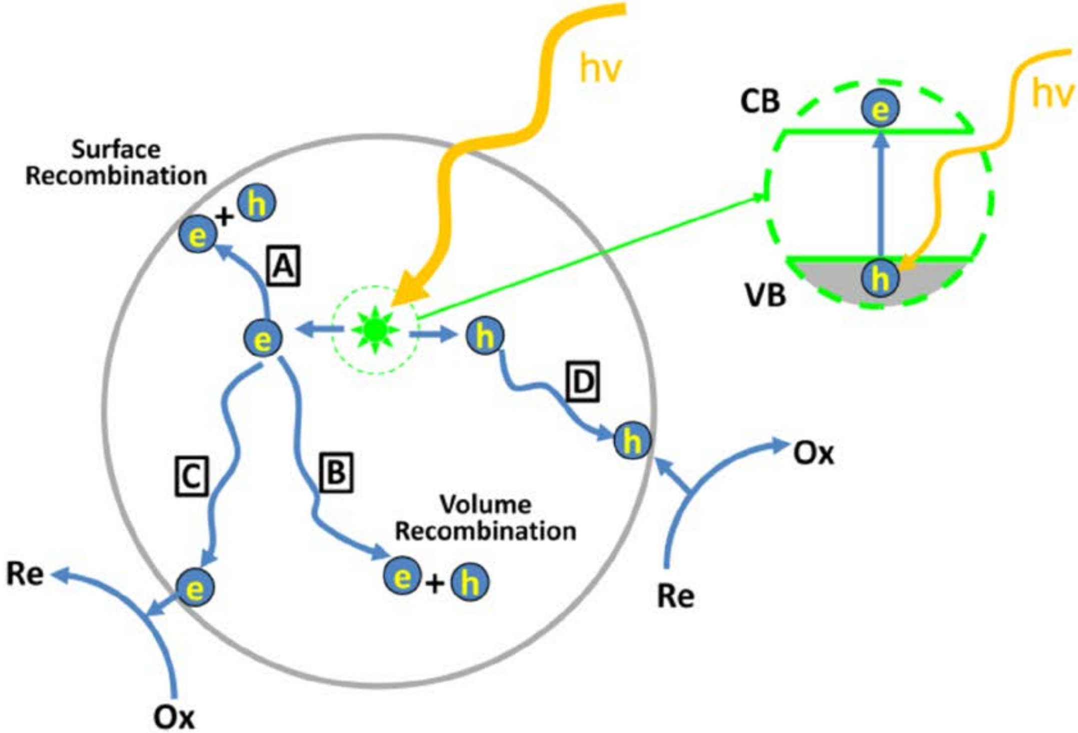
Electric field very small (required high doping density to develop potential difference between surface and center

$$\Delta\phi_{SC}(r) = \frac{kT}{6q}\left(\frac{r-(r_0-W)}{L_D}\right)^2\left(1+\frac{2(r_0-W)}{r}\right)$$

$$Debye\ Length\ \ L_D = \left(\frac{\varepsilon\varepsilon_0 kT}{2q^2 N_d}\right)^{1/2}$$

Hagfeldt *et al. Chem. Rev.* **1995**, 95, 49

Light-induced charge separation



Zhang *et al*. *Chem. Rev*. **2012**, 112, 5520

A. Electron and hole recombine at the surface (traps)

B. Electron and hole could recombine in the bulk.

C. and D. Electron or hole reach the surface and trigger photoreactions

Random walk model

$$\tau_d = \frac{r_0^2}{\pi^2 D}$$

Average transit time from the interior of the particle to the surface

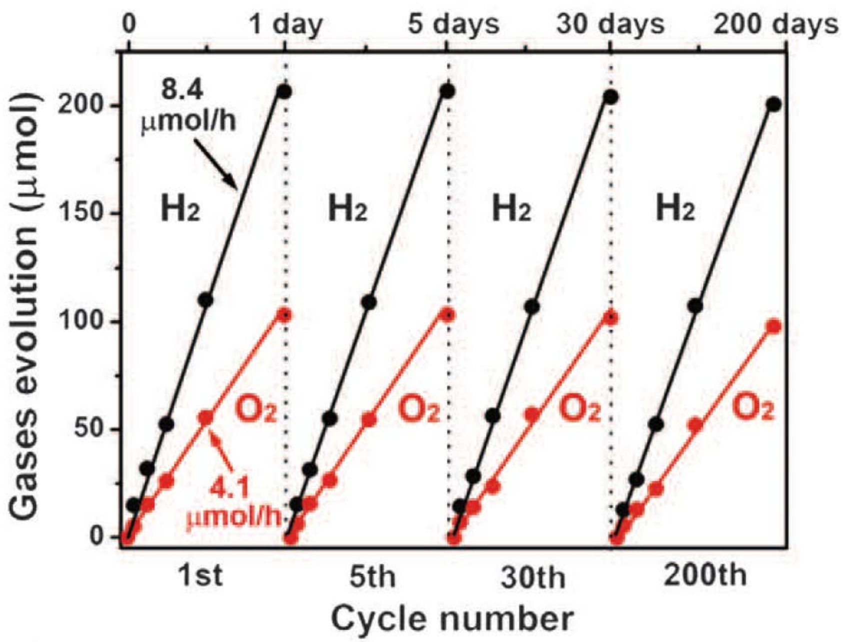
$$TiO_2\ 6\,nm\ \left(D_e = 2 \times \frac{10^{-2} cm^2}{s}\right) \rightarrow \tau_d = 3\,ps$$

If the band bending is small.
Charge separation occurs via diffusion

Typically diffusion can occurs more rapidly than recombination

Metrics in photocatalytic water splitting

Gas production over time

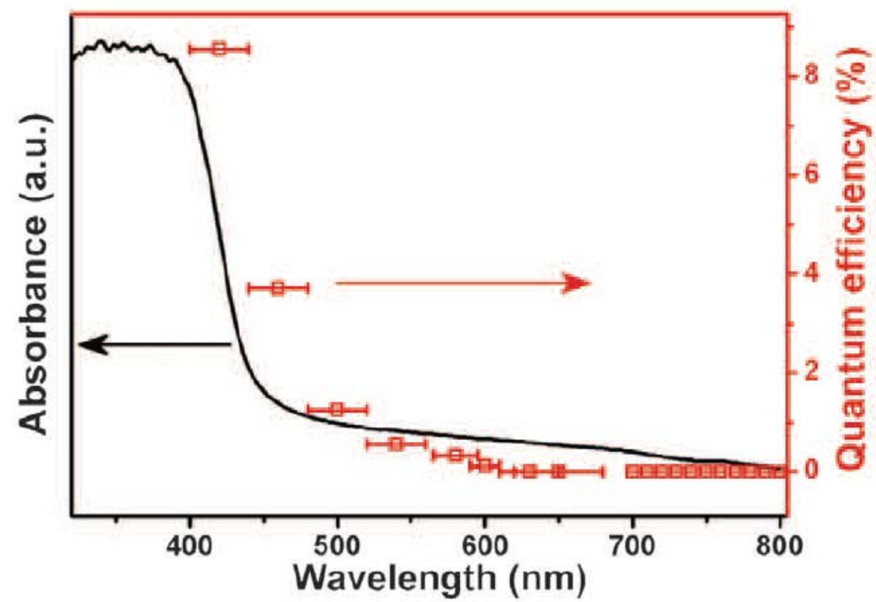


Cdots/C_3N_4 (1.6 x 10^{-5} g_{Cdots}/g_{C3N4})

Difficult comparison, effect of
- the amount of photocatalyst
- surface area (active sites)
- geometry cell (light path)

…

Quantum efficiency



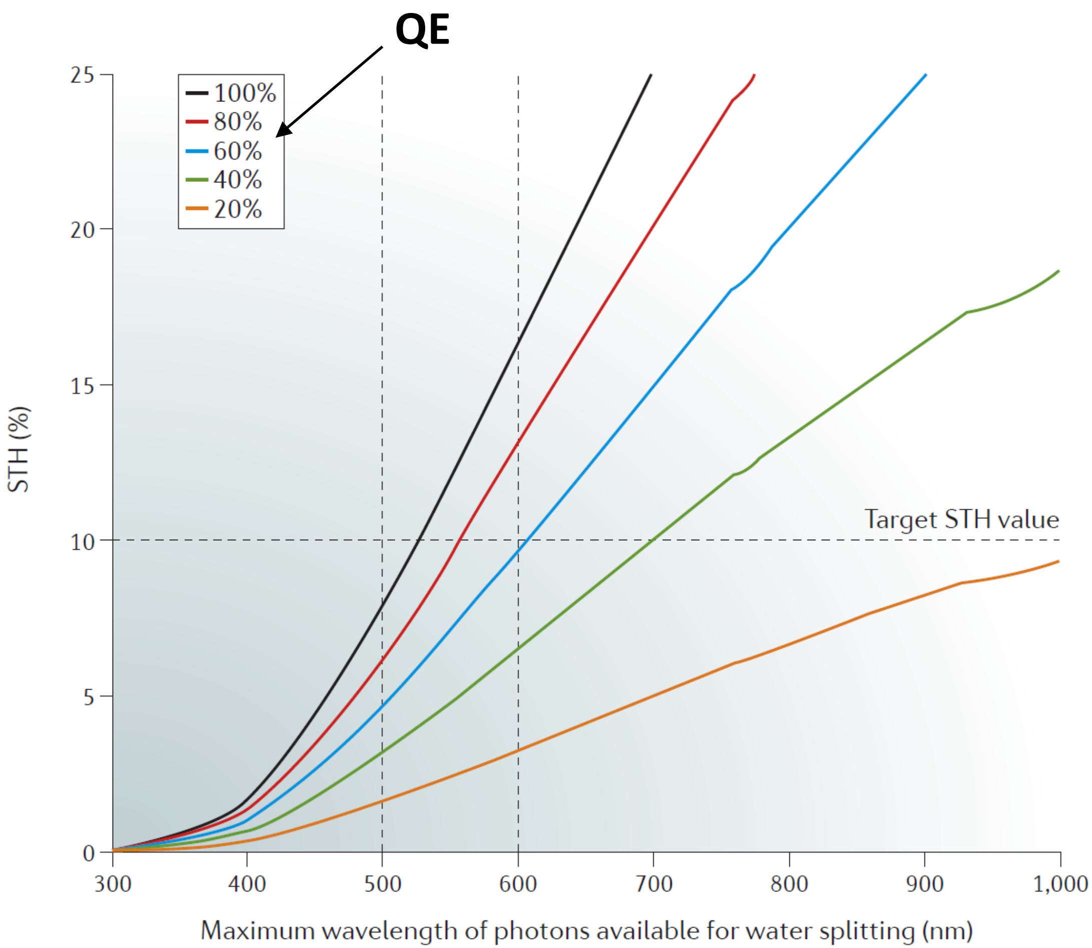
$$QE = \frac{2 \times number\ of\ evolved\ H_2\ molecules}{number\ of\ incident\ photons}$$

QE depends on the amount of catalyst

Very important to detail the experimental conditions to compare between studies

Liu *et al*. *Science* **2015**, 347, 970

Challenge in Photocatalyst systems



Today's main problems are:

- Large band gap of photocatalytic systems.
- Poor QE (20-30 % best cases)

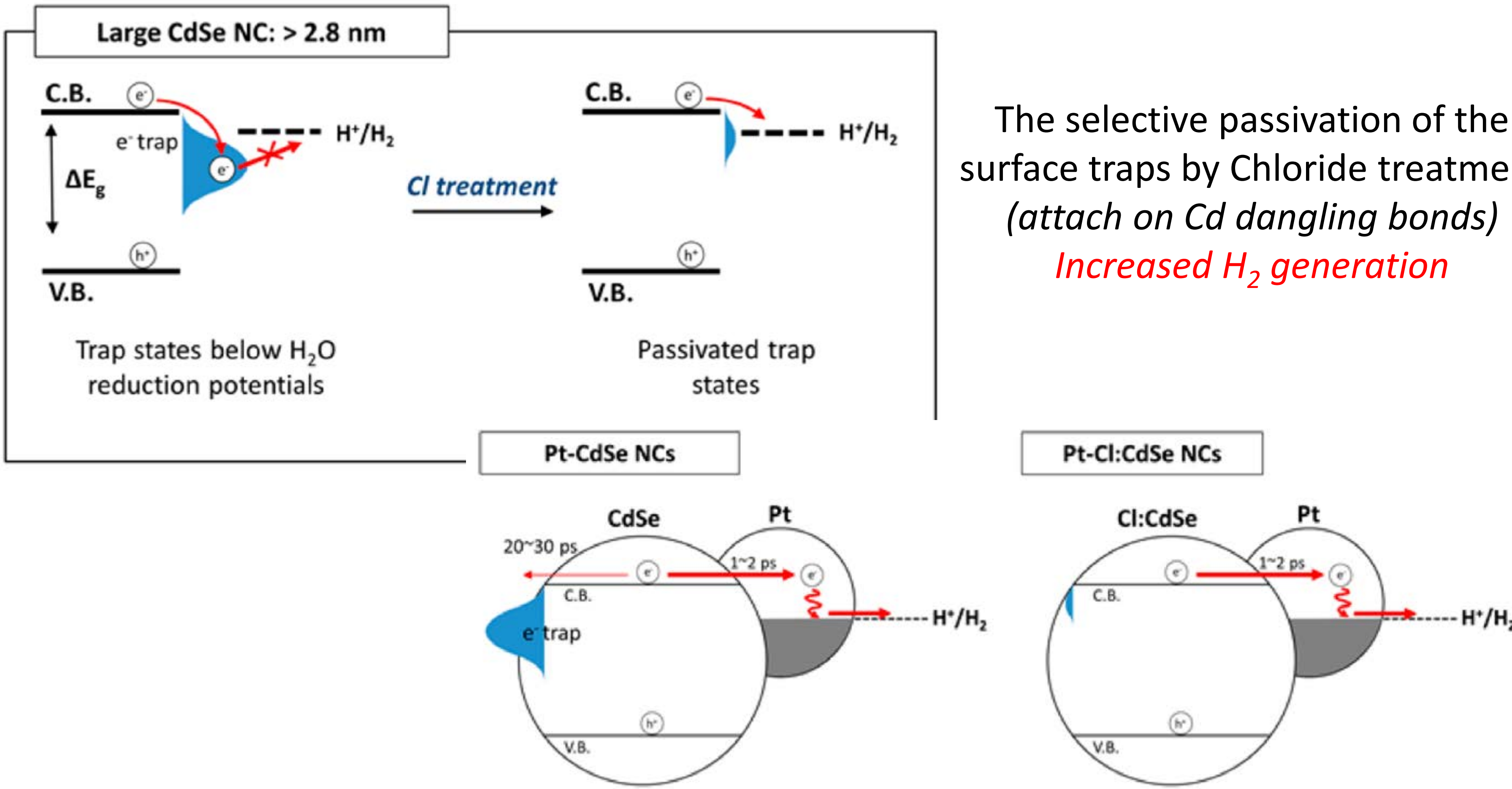
Poor light harvesting

Strong recombination (bulk / surface)

Chen *et al*. *Nature Reviews Materials* **2017**, 2, 17050

Examples improved photocatalytic activity

CdSe Nanocrystals (surface recombination)



The selective passivation of the surface traps by Chloride treatment *(attach on Cd dangling bonds)*

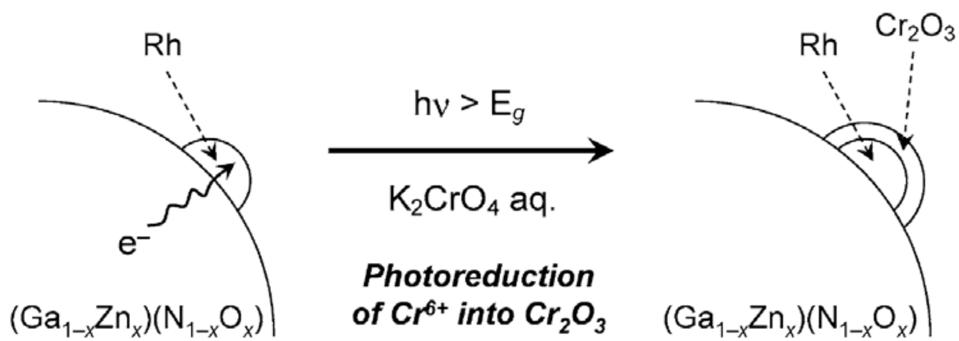
Increased H_2 generation

Kim et al. Chem. Mater. **2016**, 28, 962

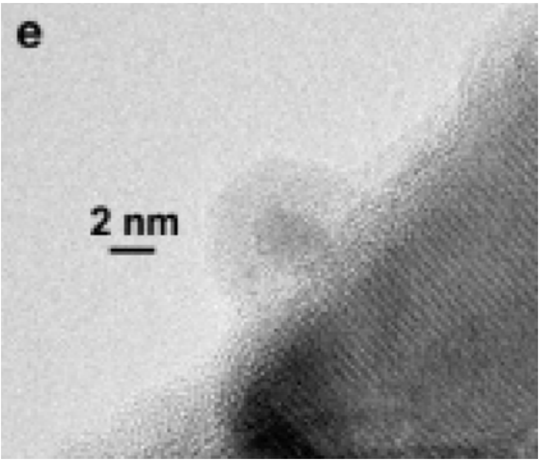
Examples improved photocatalytic activity

Surface engineering of co-catalyst (surface recombination)

$(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ (x=0.12, E_g = 2.68 eV)



[a] E_g is the band gap energy of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$.



Maeda et al. J. Phys. Chem C. **2007**, 111, 7554

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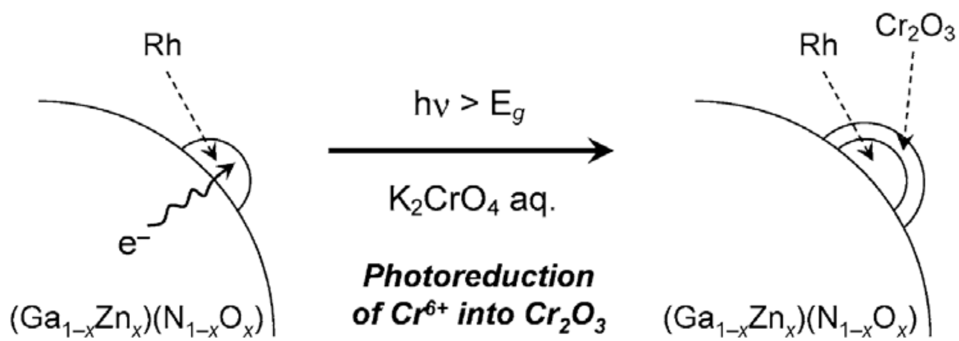

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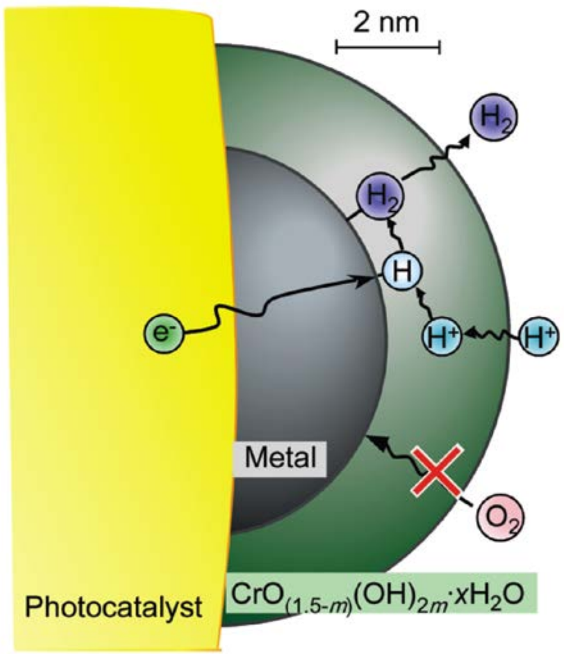

The selective coating prevents O_2 back reaction to water

O_2 generated in other part of the particle could reach the *Hydrogen evolution catalyst* where it could be reduced to H_2O, reducing overall solar-to-hydrogen yield.

Maeda et al. J. Phys. Chem C. **2007**, 111, 7554

Yoshida et al. J. Phys. Chem C. **2009**, 113, 10151

Outlook on Photocatalytic systems

- The POOR LIGHT ABSORPTION and INTENSE RECOMBINATION (surface/bulk) in nanoparticulate photocatalyst limits the achievable STH values.

- Design of NEW PHOTOCATALYTIC MATERIALS is necessary (enhance light harvesting).

- Development of surface engineering approaches to promote a FAST SURFACE CHARGE SEPARATION to mitigate the losses by recombination.