Sunlight-driven water splitting in hematite-based photoelectrochemical cells

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Division for Chemical Physics, Applied Physics Department

Group photo on a nice Swedish late-summer day

Outline

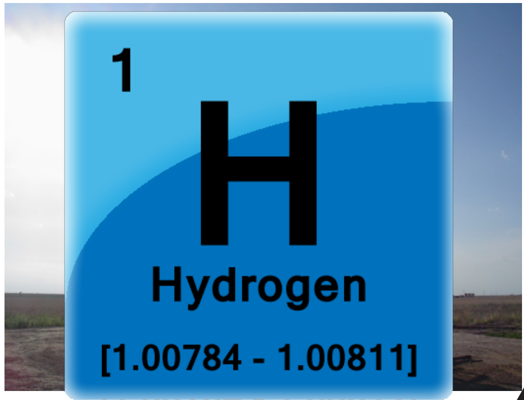
1. Plasmon-enhanced water splitting on hematite-based model photoanodes

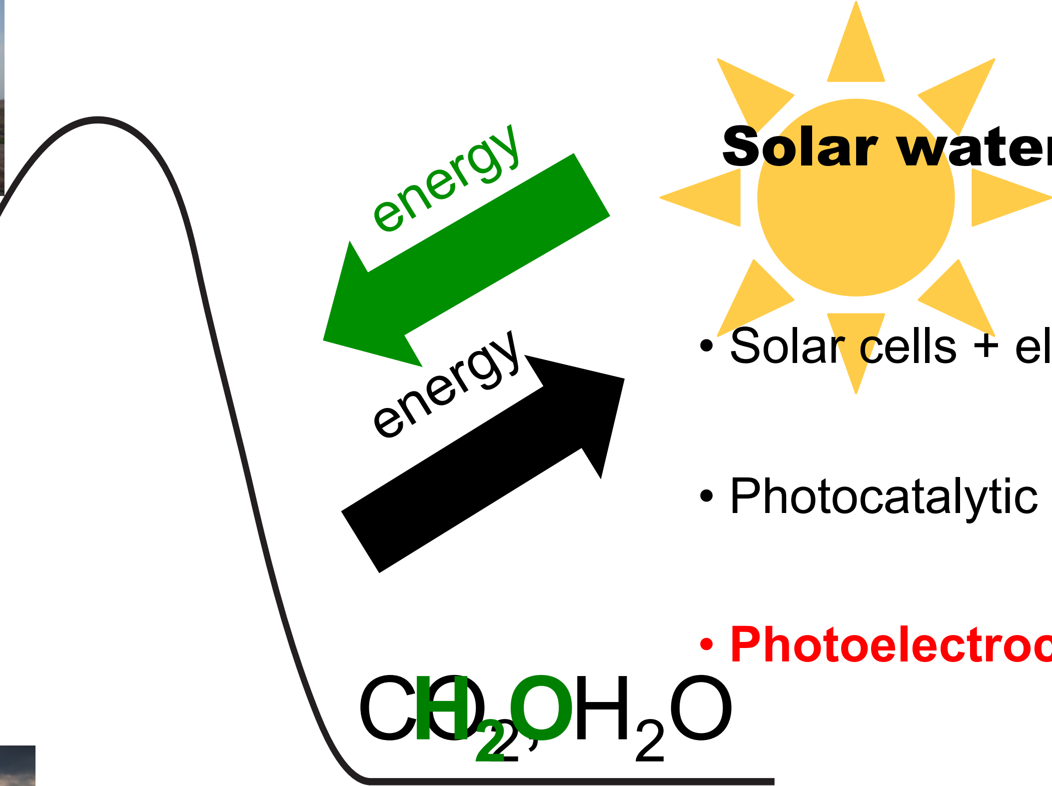
2. Faradaic efficiency of water splitting on hematite surface

3. Beyond plasmon-enhanced water splitting on hematite

1. Plasmon-enhanced water splitting on hematite-based model photoanodes

Background



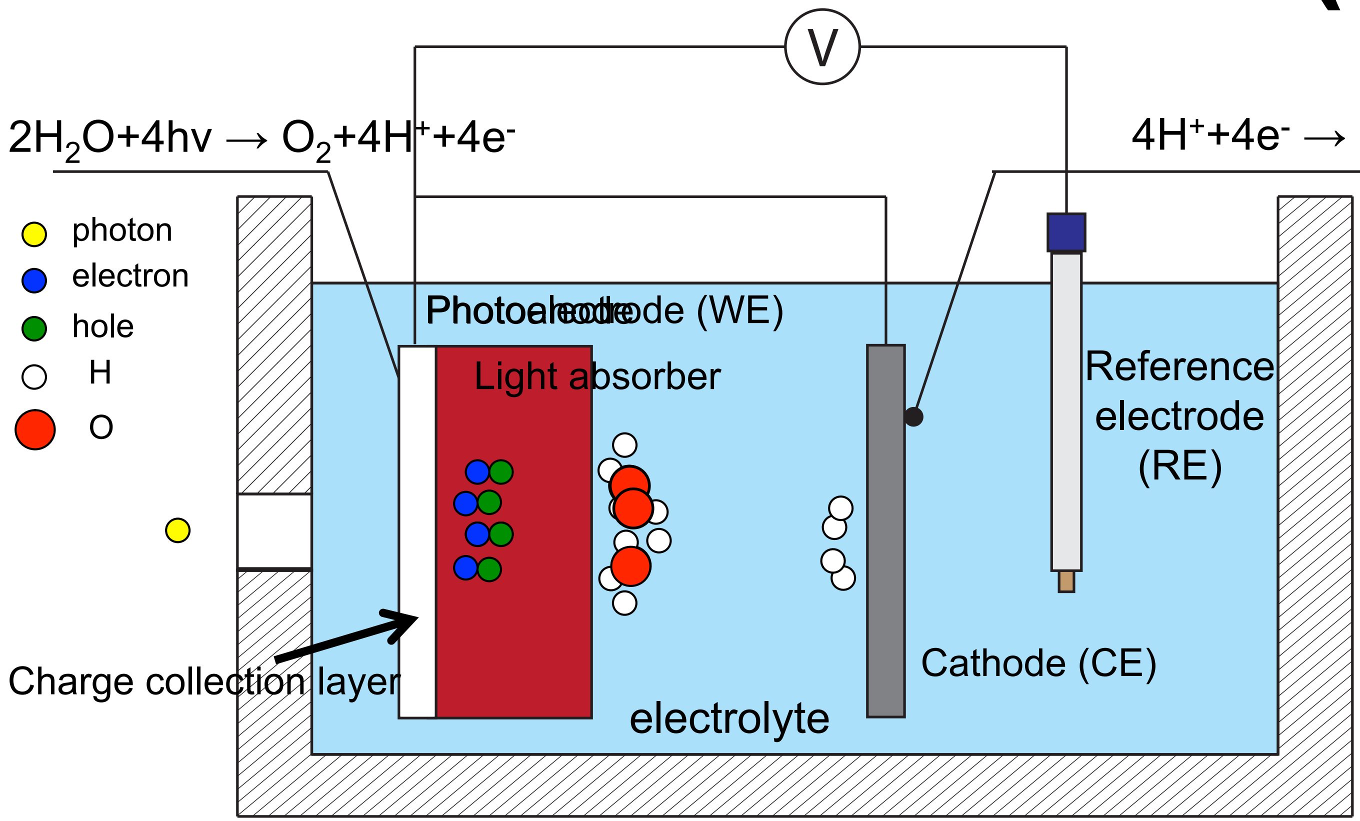


Solar water splitting:

- Solar cells + electrolyzers
- Photocatalytic cells
- **Photoelectrochemical cells**

- …**al (PEC) cell**: a *monolithic* device in which …gy is converted into chemical energy (H_2 and O_2) at …rent locations

Photoelectrochemical (PEC) cells



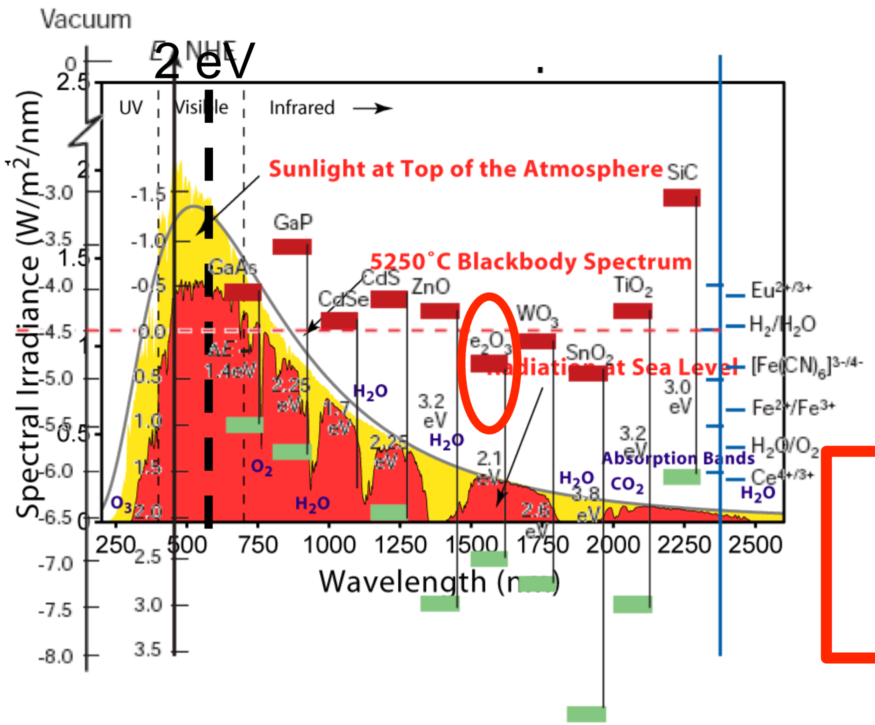
Solar-to-Hydrogen energy conversion efficiency

- light collection
- charge separation
- charge transport
- charge transfer
- reaction selectivity

Requirements on light absorber(s):

- efficiency
- durability
- fabrication costs

Hematite as photoanode for solar water splitting



Hematite (crystalline Fe_2O_3):

- ✓ absorbs visible light (E_g around 2 eV)
- ✓ inexpensive
- ✓ stable in aqueous environment for pH>3
- ✘ non-optimal alignment of conduction band edge and hydrogen evolution potential
- ✘ indirect bandgap → low $\eta_{absorption}$
- ✘ low conductivity, short hole diffusion length (4-5 nm) → low $\eta_{transport}$

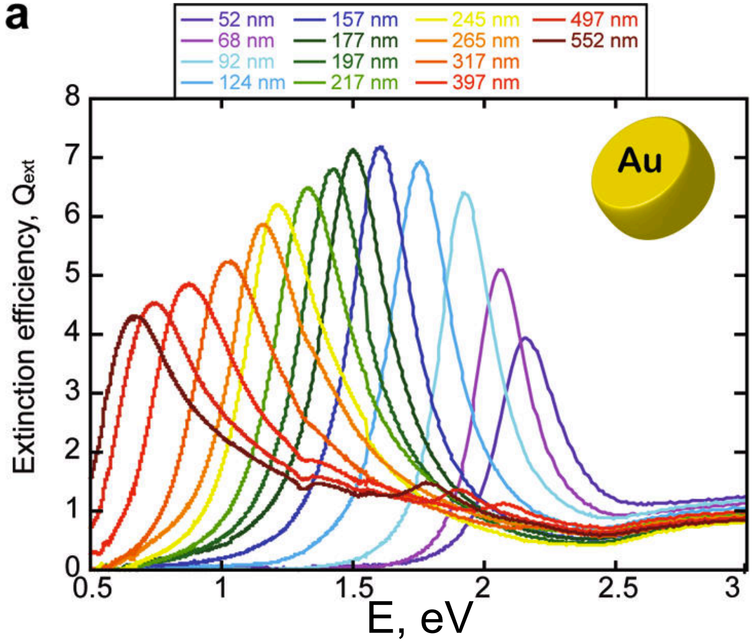
Physically **thin**, *optically* **thick** photoanodes:

- nanostructure absorber
- enhance light absorption

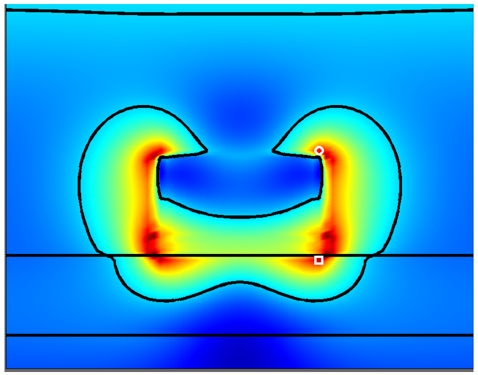
Metallic nanostructures supporting localized plasmonic resonances

Localized surface plasmon resonance (LSPR)

Lycurgus cup, 290-325 AD



Zorić et.al., ACS Nano 2011, DOI: 10.1021/nn102166t

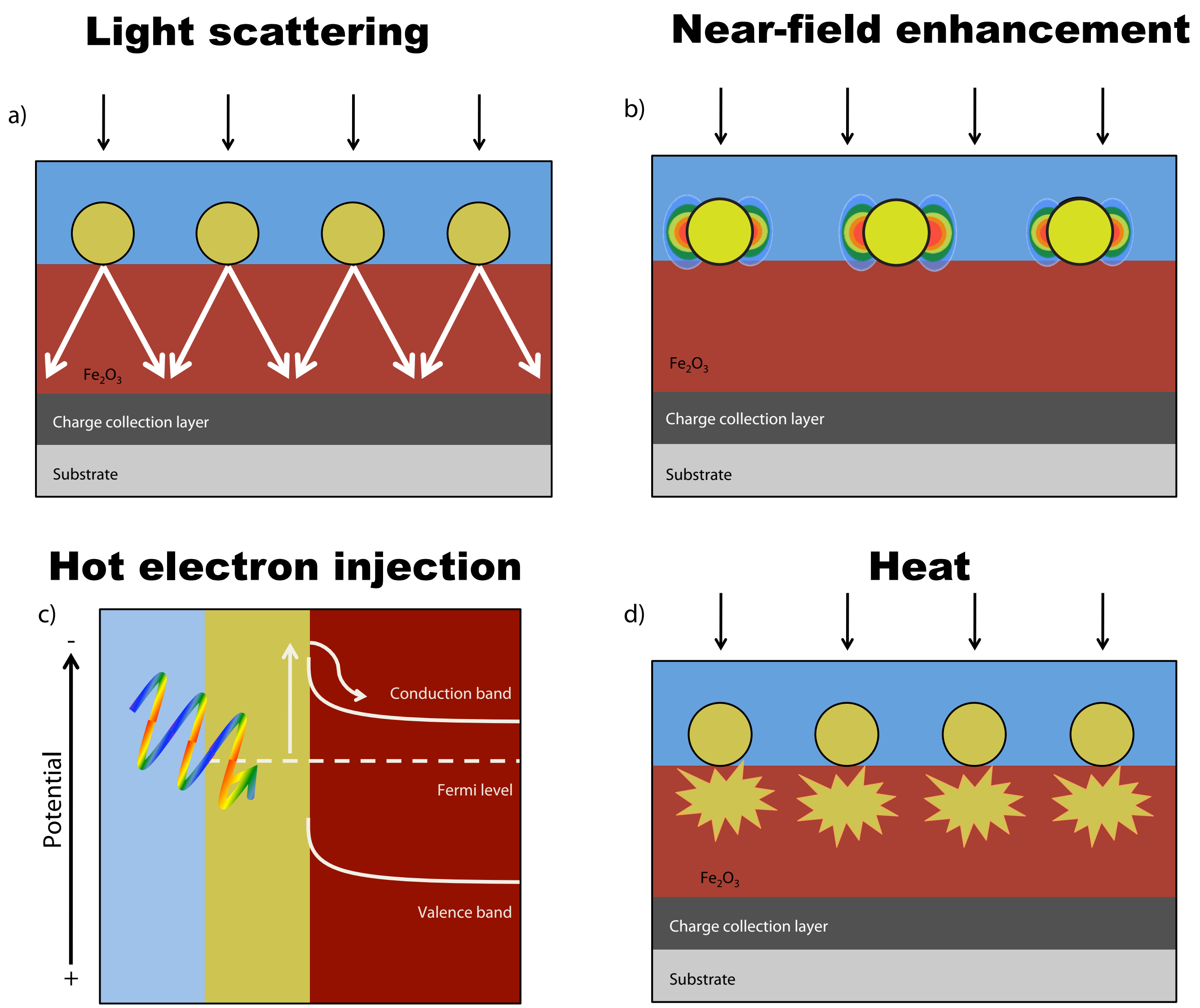


Electric field enhancement around nanodisk at resonance

E_{LSPR} depends on :

- metal
- shape
- size
- refractive index of the nanoenvironment

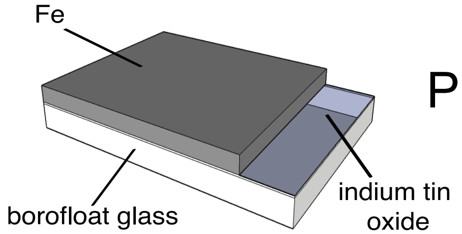
How can LSPR help?



Fabrication of hematite-based photoanodes

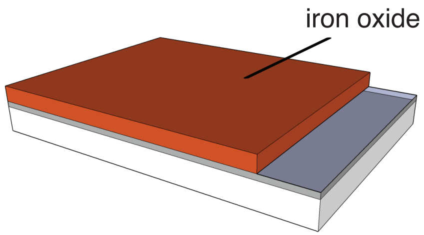
Model photoanodes, focus on process understanding

a)



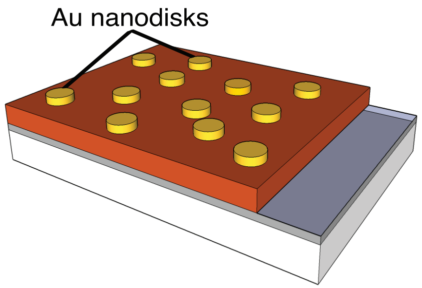
Physical Vapor Deposition of Fe thin films on indium tin oxide covered substrates

b)



Dry thermal conversion of Fe into Fe_2O_3

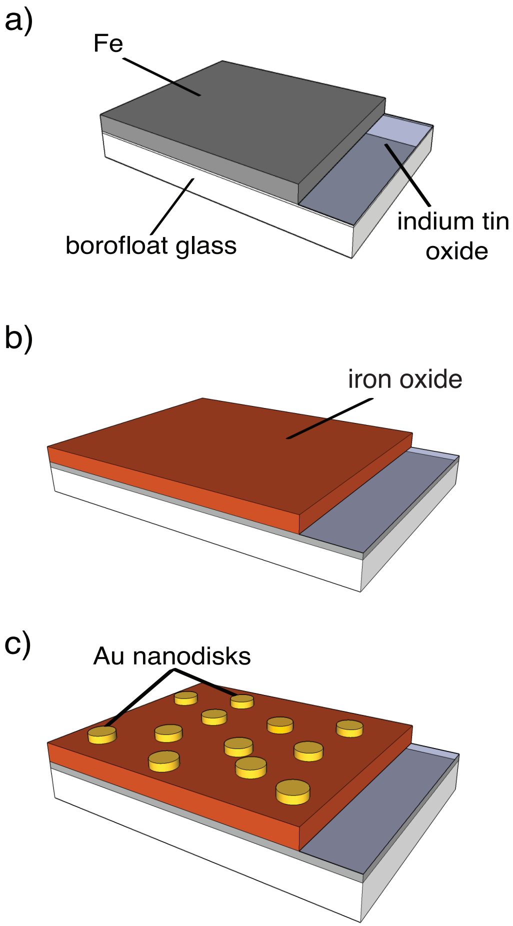
c)

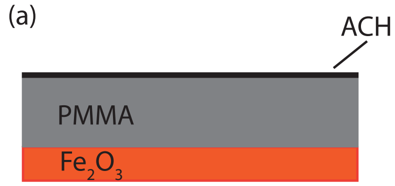


Functionalization of Fe_2O_3 with Au nanodisks

Fabrication of hematite-based photoanodes

Functionalization based on hole-mask colloidal lithography



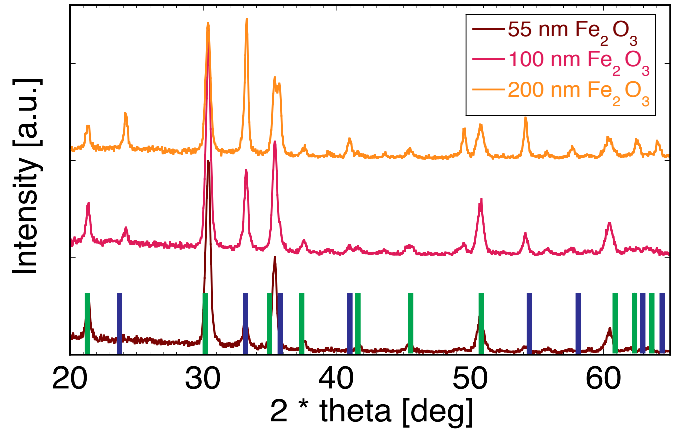


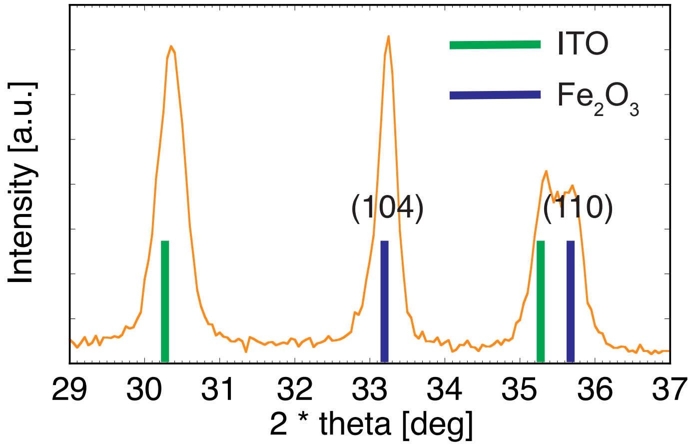
Short ordered arrays of nanostructures with control on **shape, size, surface coverage and chemistry**

H. Fredriksson *et. al*, *Adv. Mat.*, **19**, 4297-4302 (2007).

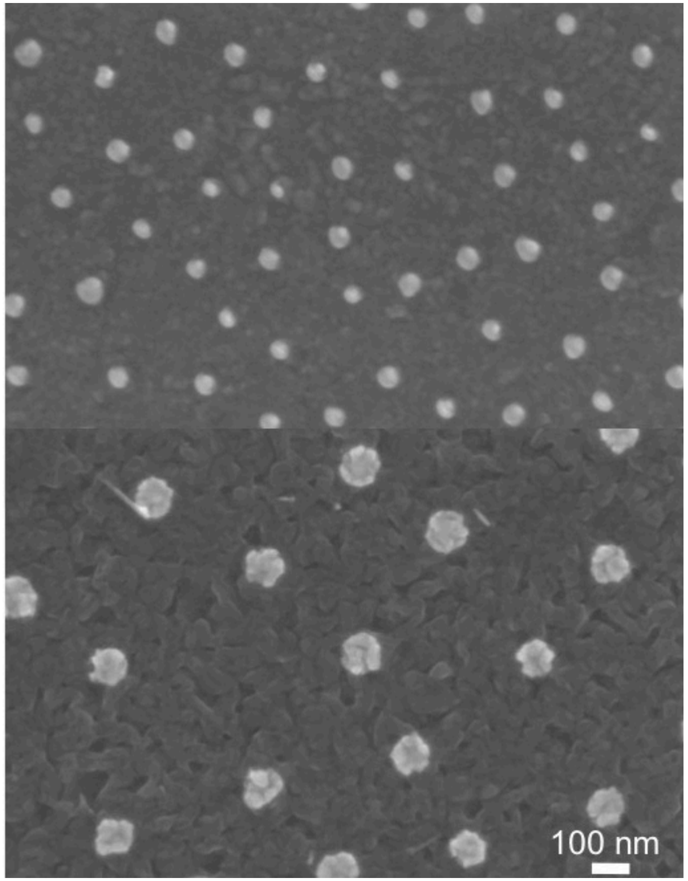
XRD and SEM characterization

XRD analysis





Top-view SEM

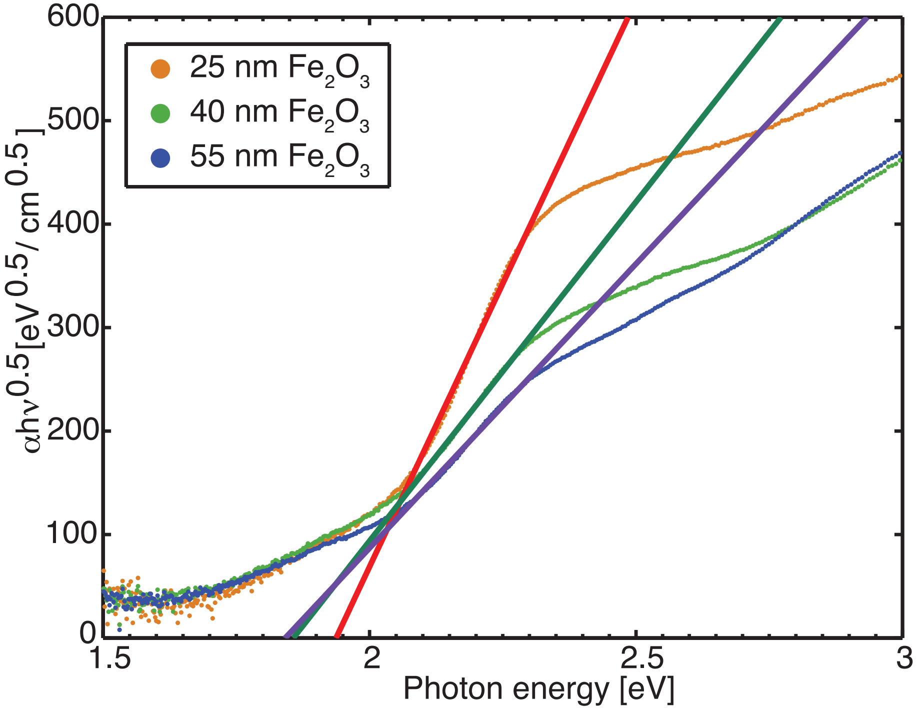


Fe_2O_3 is the only observable iron oxide phase

Optical characterization

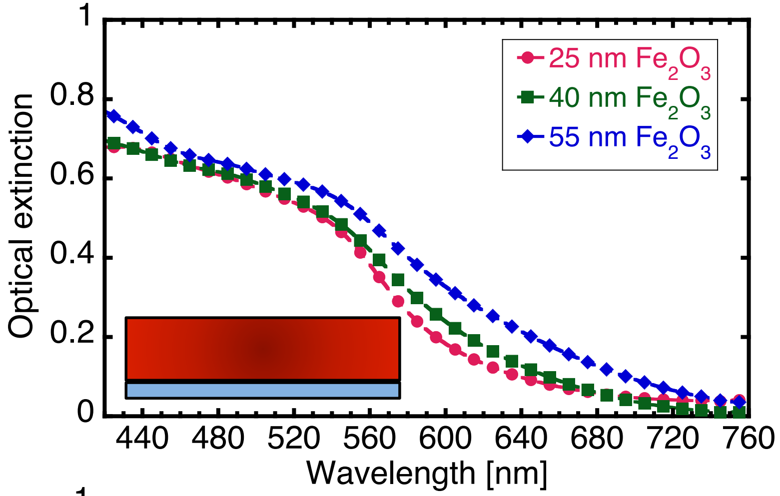
Determination of bandgap energy in hematite films

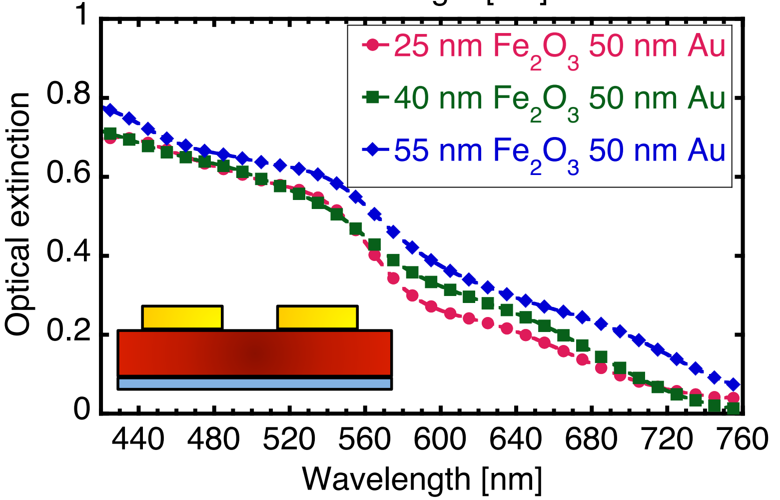
- Spectrophotometer with integrating sphere to measure extinction *E* and scattering *S*
- Optical theorem $E = A + S$ ➔ absorption $A = \alpha t$, t = thickness, α = absorption coefficient
- Tauc's formula: $(\alpha h\nu)^{0.5}=A(h\nu-E_G)$, where:
  - hv: photon energy
  - E_G: bandgap energy
  - A: constant
  - 0.5: exponent denoting indirect transiton
- Plot $(\alpha h\nu)^{0.5}$ *versus hv* and fit the linear part

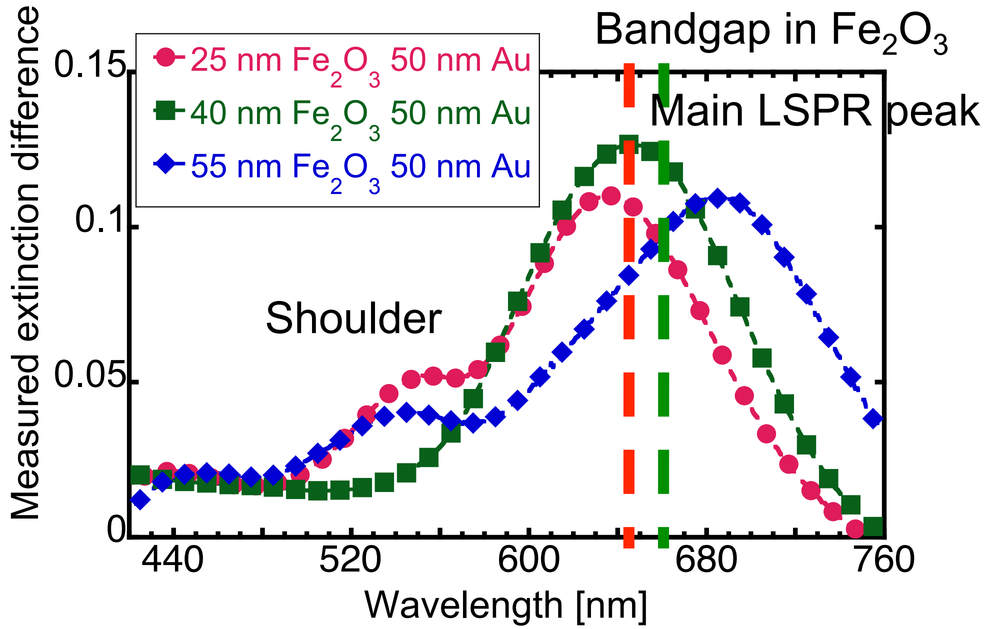


Optical characterization

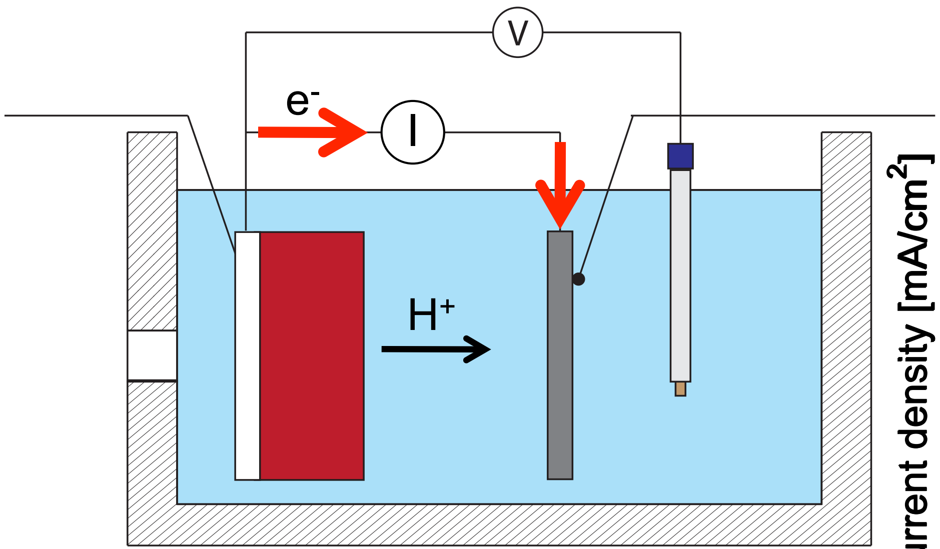
Increased light harvesting upon functionalization



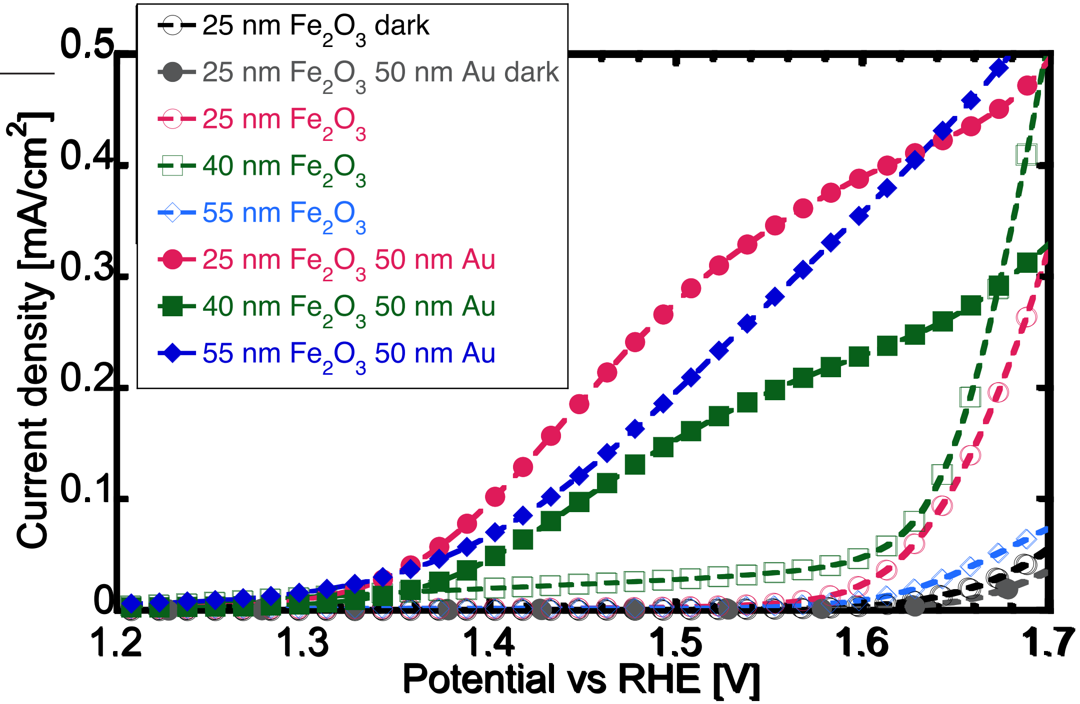




Photocurrent-potential (J-V) characteristics



- Pt wire counter-electrode,
- 1M KOH electrolyte (pH=13.6)
- Ag/AgCl reference electrode
- **solar simulated illumination**



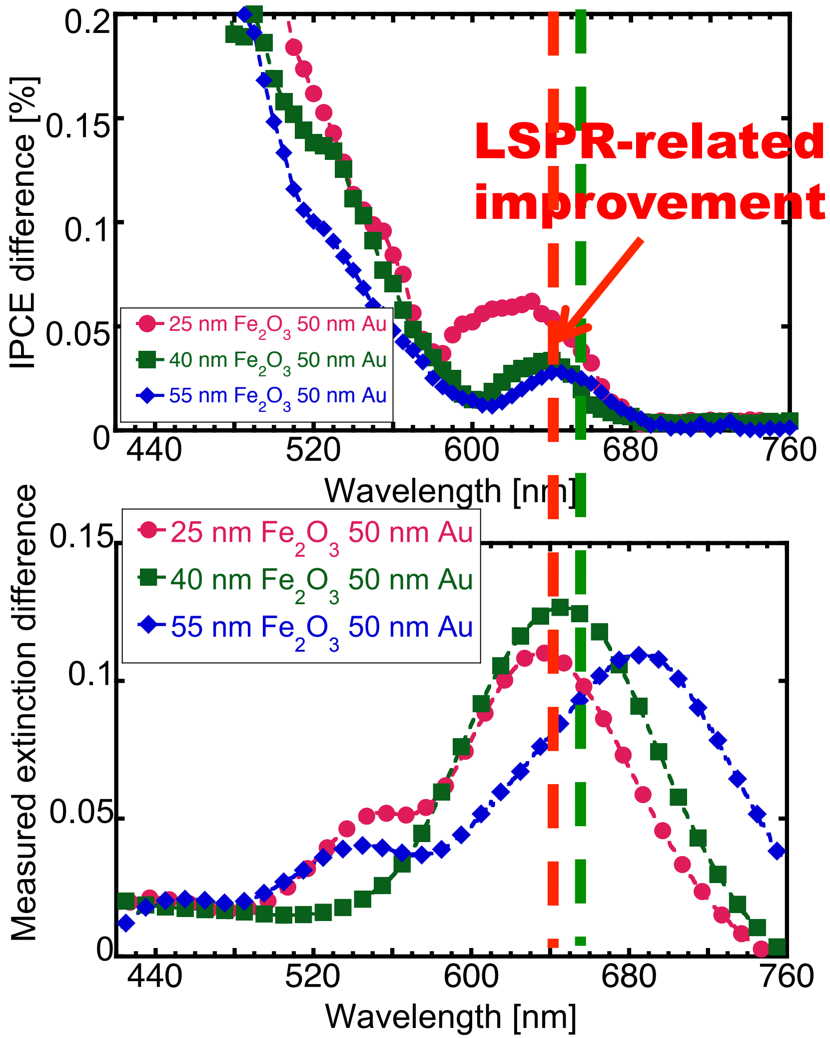
Conversion from Ag/AgCl to Reversible Hydrogen Electrode (RHE)

$$E_{RHE} = E_{Ag/AgCl} + E^0_{Ag/AgCl} + 0.059 * pH$$

Internal Photon-to-current Conversion Efficiency (IPCE)

$$IPCE = \frac{hc}{e\lambda}\frac{j_{ph}(\lambda)}{P(\lambda)}$$

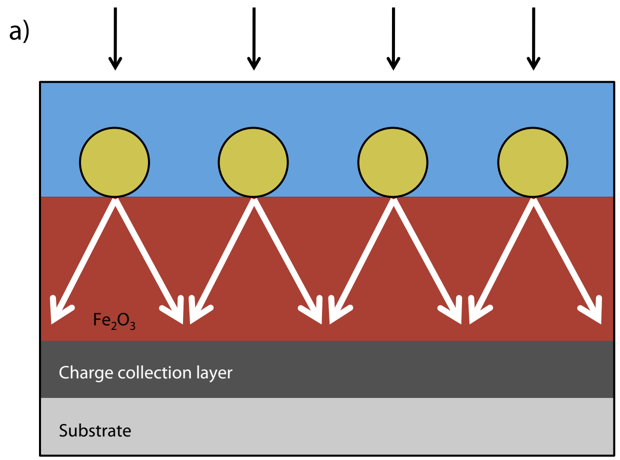
- Same 3-electrodes setup as before, constant potential of 1.5 V *versus* RHE



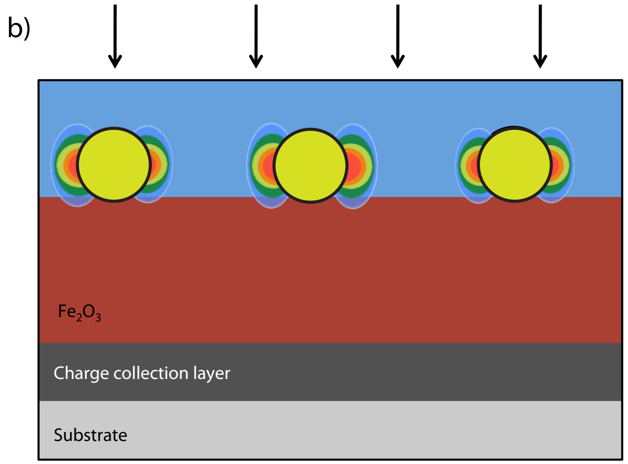
- **Increase in IPCE close to bandgap in Fe_2O_3**
  - Highest for 25 nm thick hematite
  - correlation between λ_{LPSR} and spectral position of relative ΔIPCE maximum

How did LSPR help?

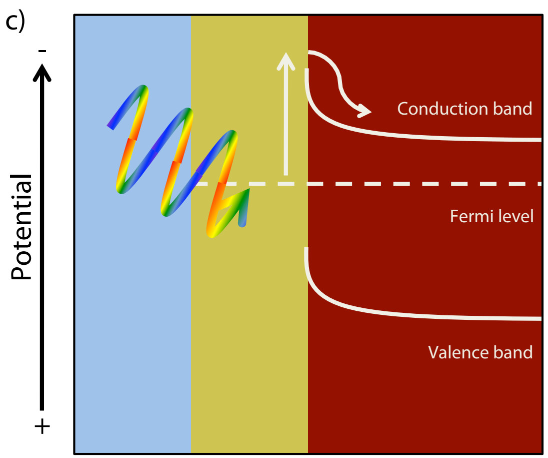
Light scattering



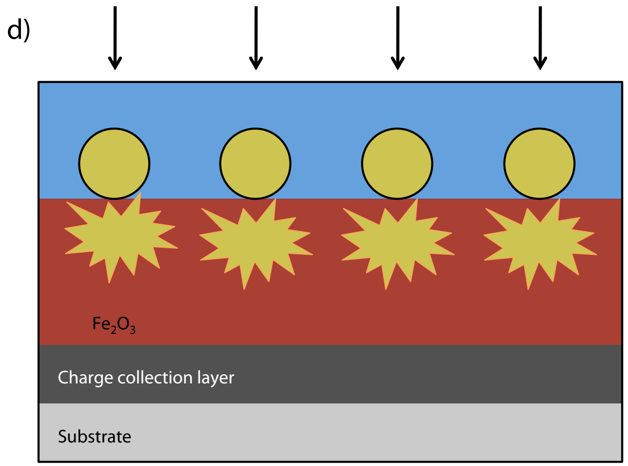
Near-field enhancement



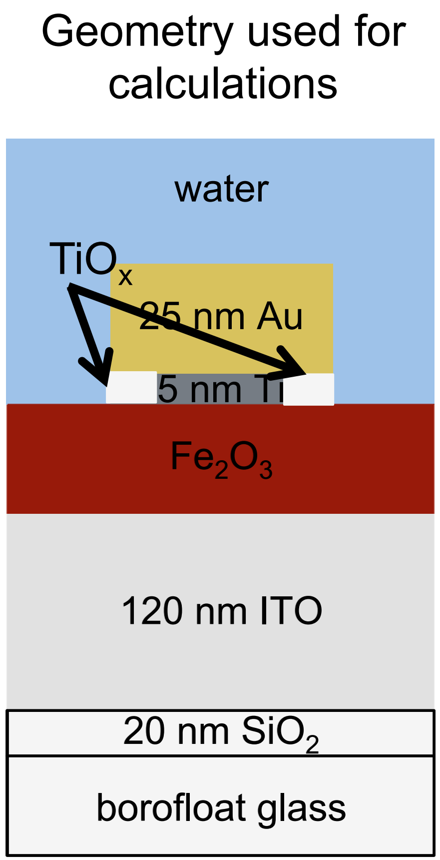
Hot electron injection

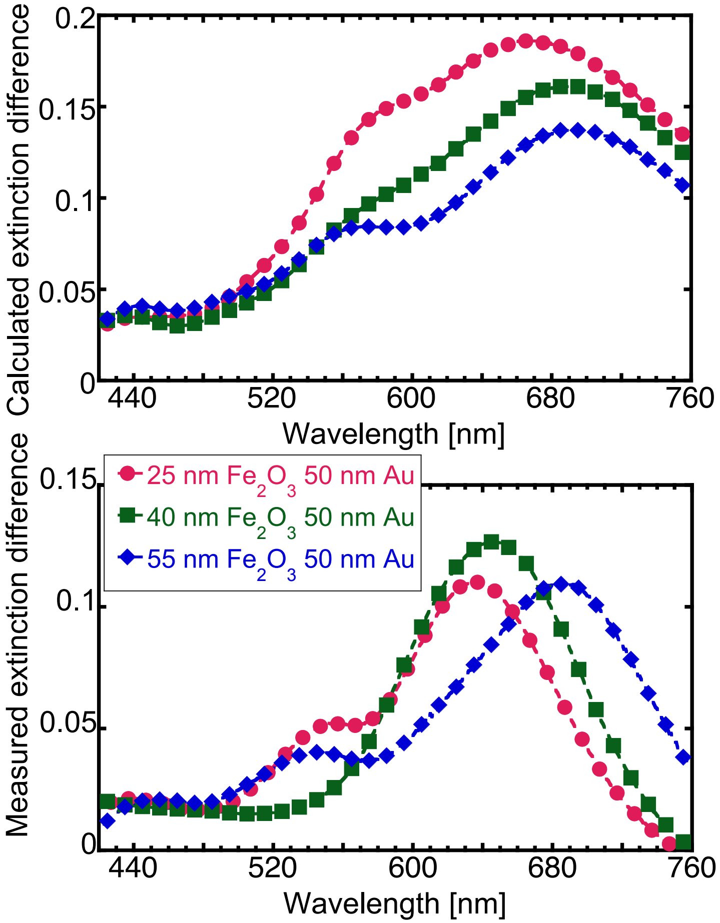


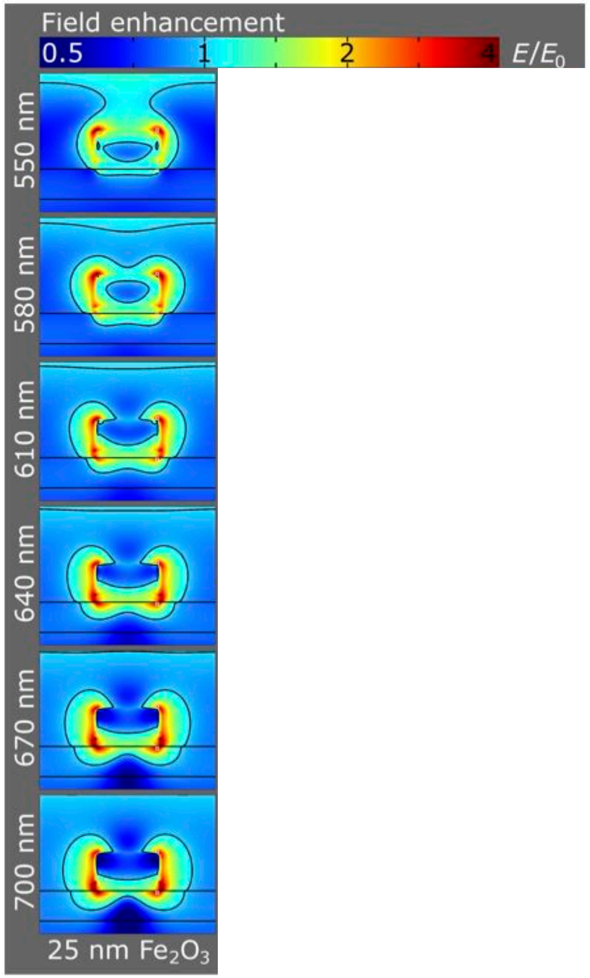
Heat



Spectrally resolved measurements and calculations

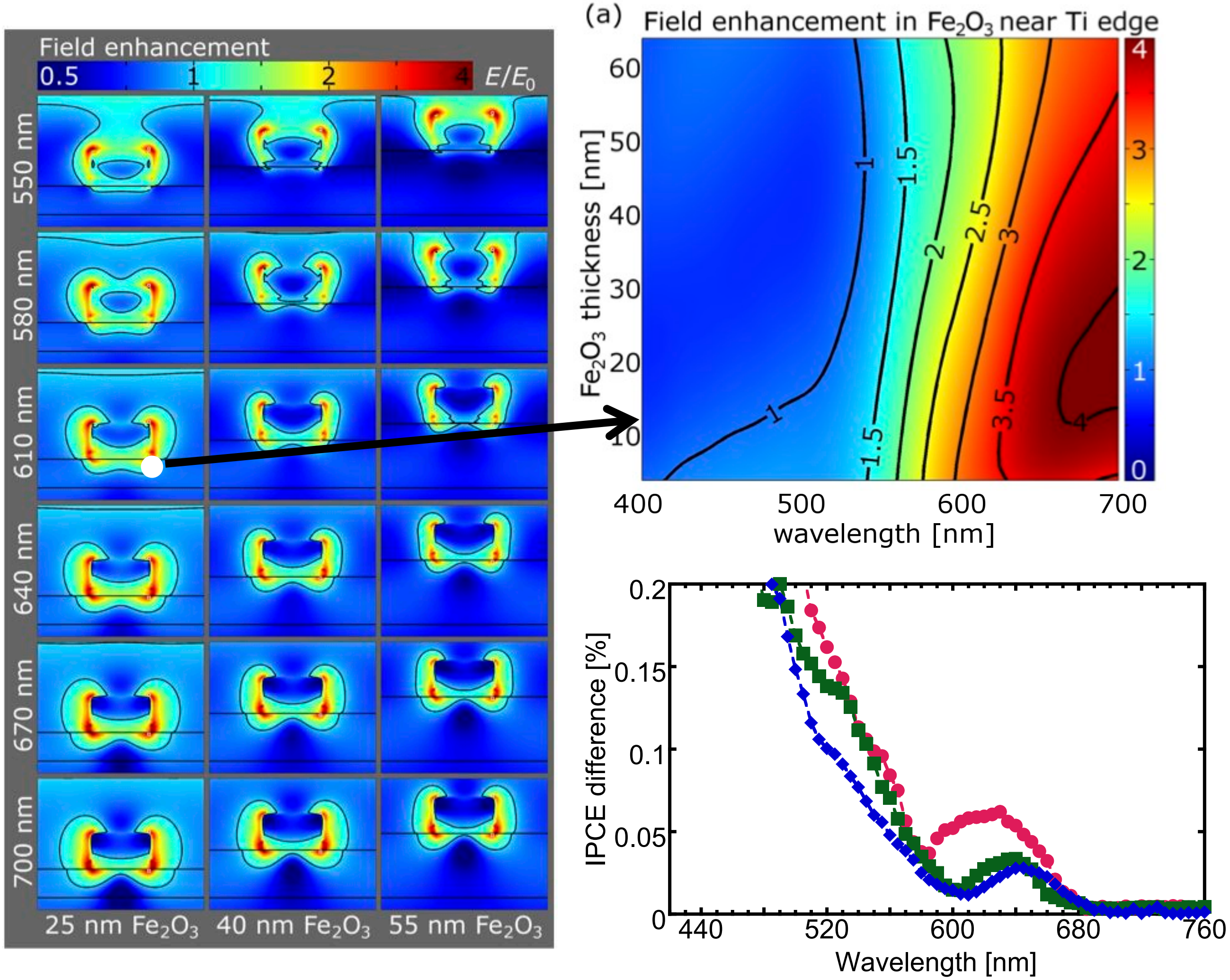






FDTD calculations by Tomasz J. Antosiewicz, Division for Condensed Matter Theory, Chalmers

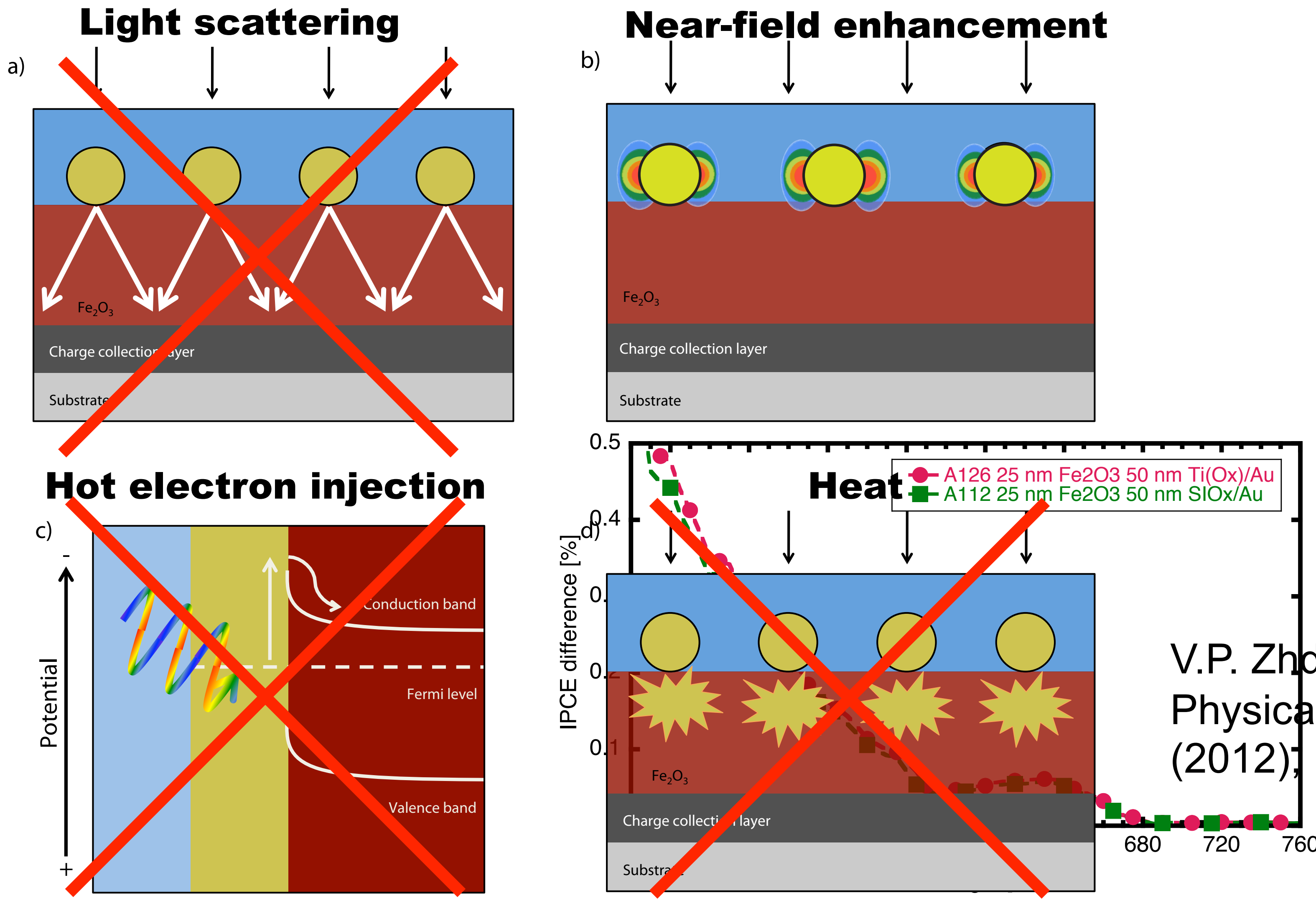
Mechanism of plasmonic IPCE increase



Evidence that the observed plasmonic improvement can be assigned to **enhanced charge generation in Fe_2O_3**

Iandolo *et al.*, PCCP (2013), 15, 4947--4954

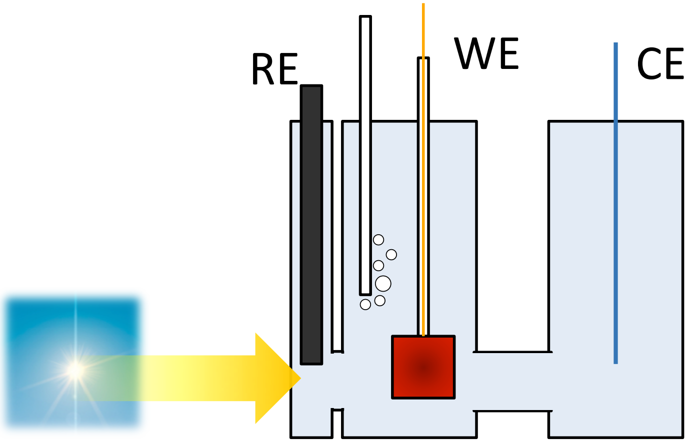
Mechanism of plasmonic IPCE increase



V.P. Zhdanov *et. al.*, Physica E 46 (2012), 113–118

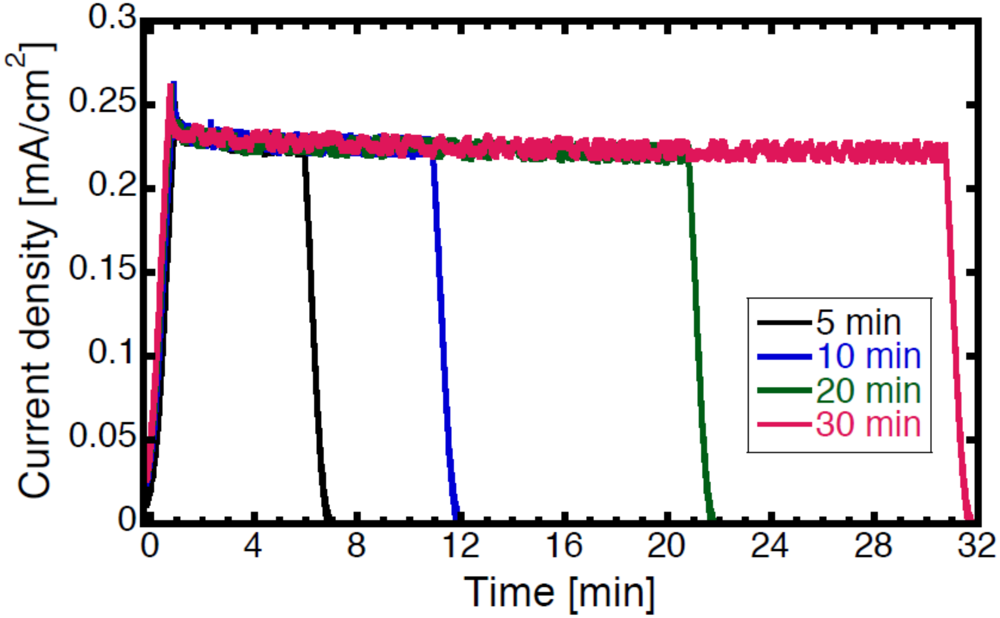
2. Faradaic efficiency of water splitting on hematite surface

Faradaic efficiency (FE) evaluation

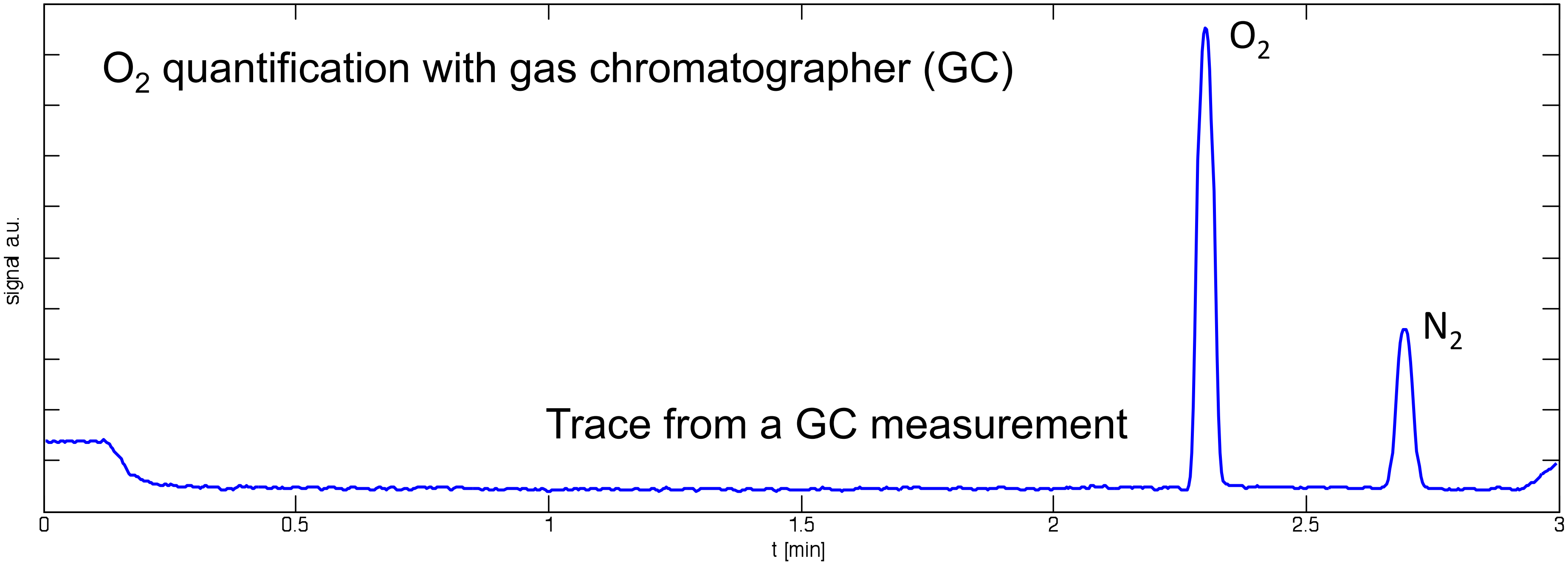


- Measure the total charge Q_{tot} from photocurrent integration
- Quantify evolved amounts of O_2 and obtain the corresponding Q_{O2}
- Determine FE as Q_{O2}/Q_{tot}

- 0.1 M KOH
- Calomel - RE
- Pt wire - CE
- Ar purged
- Solar simulated
- 1.56 V *vs.* RHE



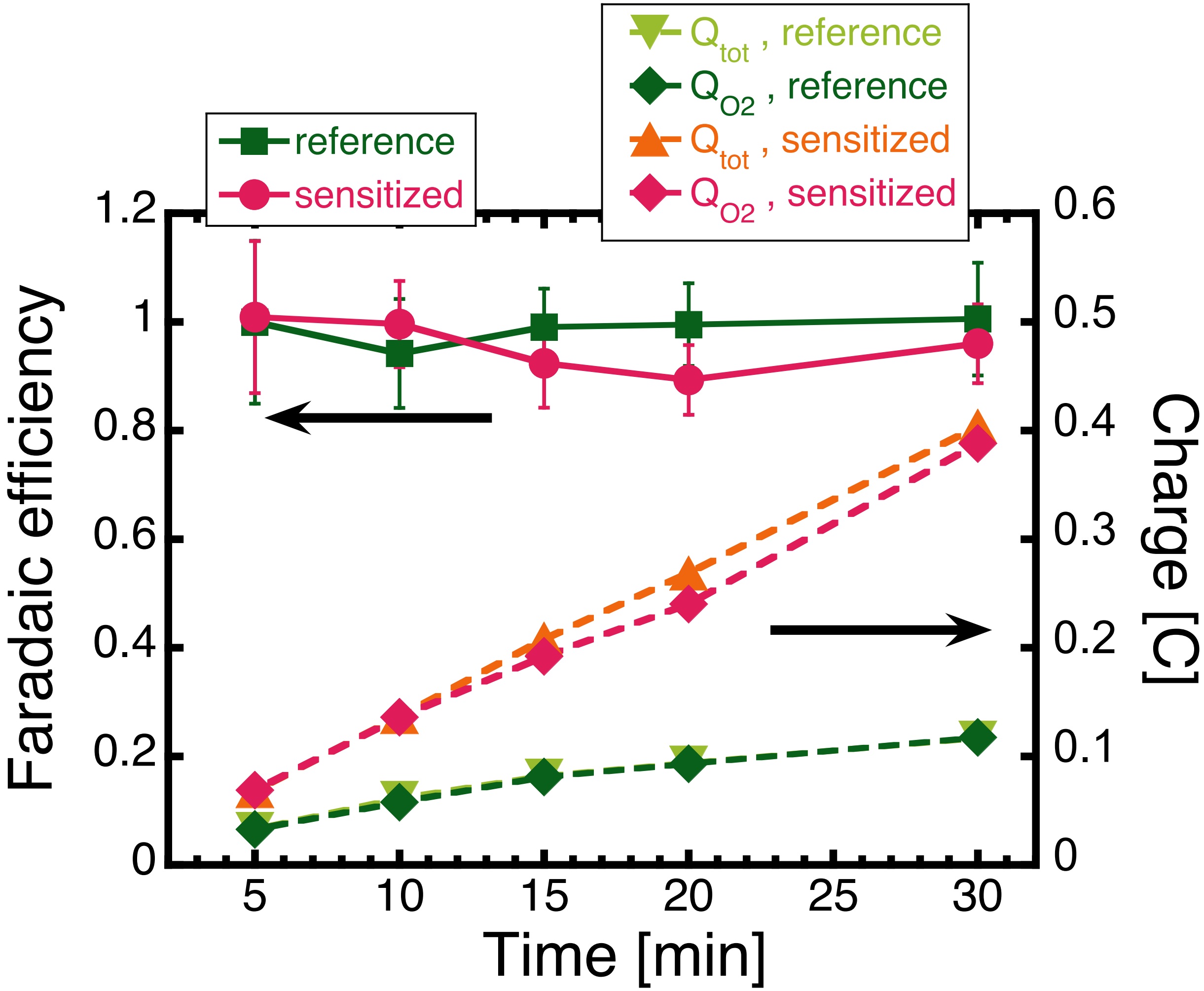
Faradaic efficiency (FE) evaluation



- Peak area → O_2-concentration (calibrated from known source)
- Subtraction of O_2 leaking in from the surrounding
- Volume (entire gas volume in system) determined electrochemically using HER

➢ **Total amount of O_2 evolved, charge Q_{O2}**

Faradaic efficiency (FE) evaluation



- FE=1 (within experimental error) for both samples
- for broadband illumination

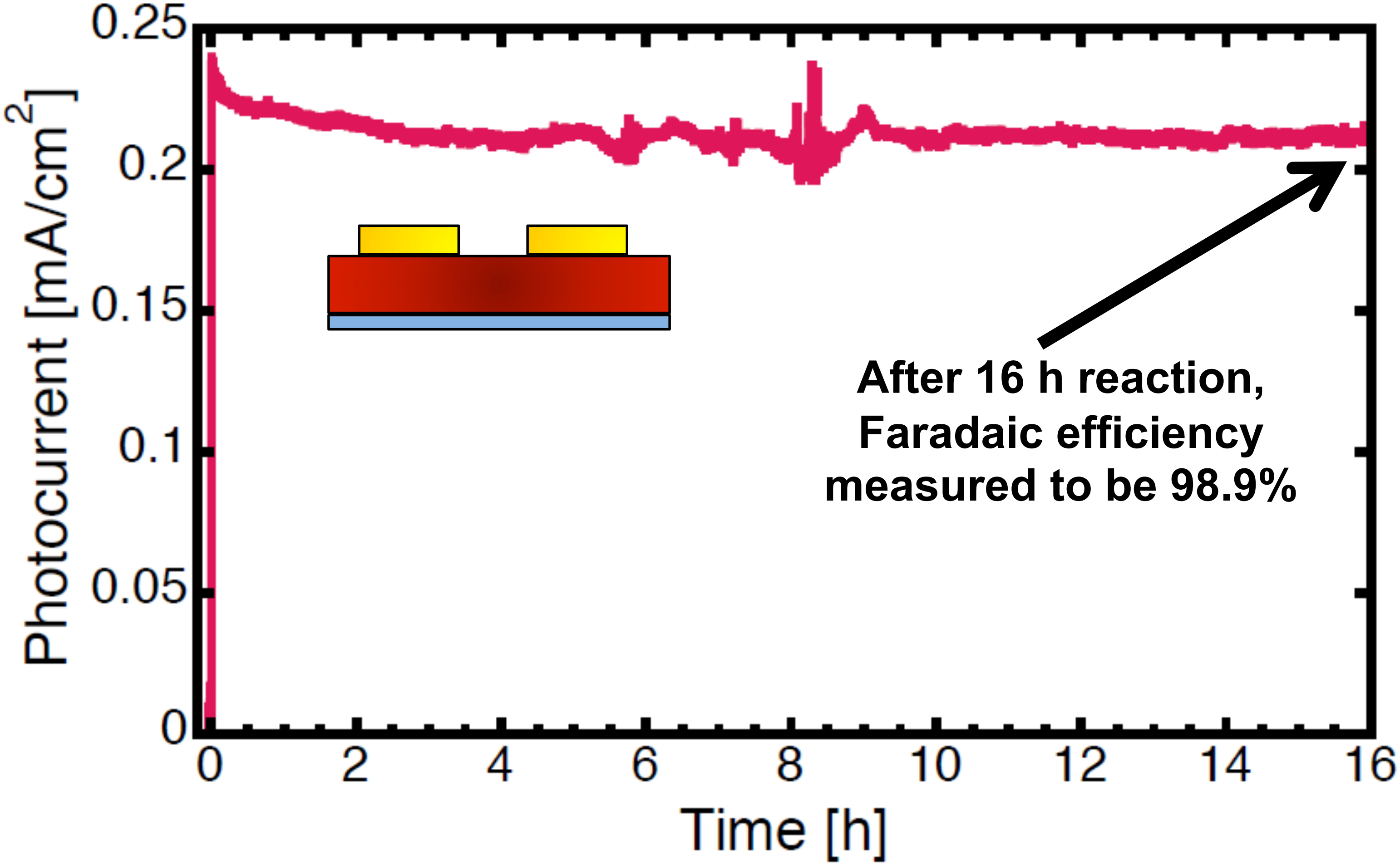
↓

also at plasmonic wavelengths

All the detected charge goes into O_2 evolution

Iandolo *et al.*, in manuscript

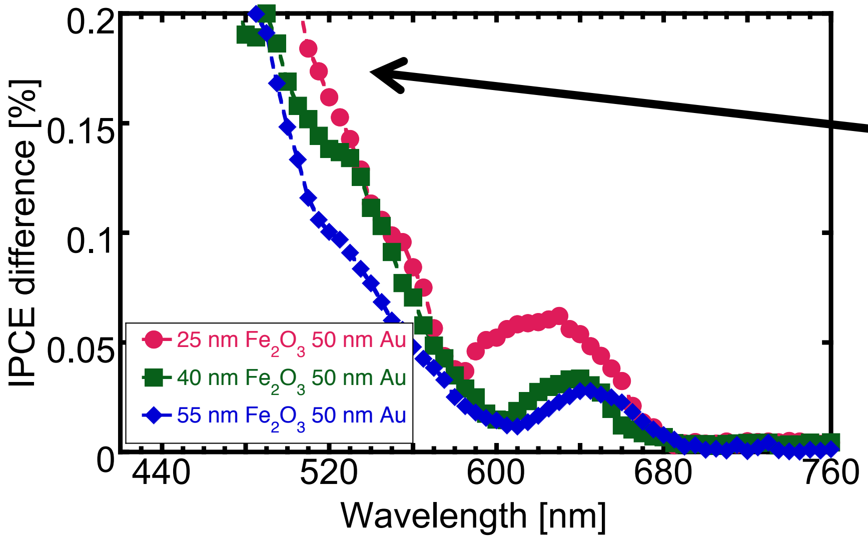
Stability test on functionalized hematite

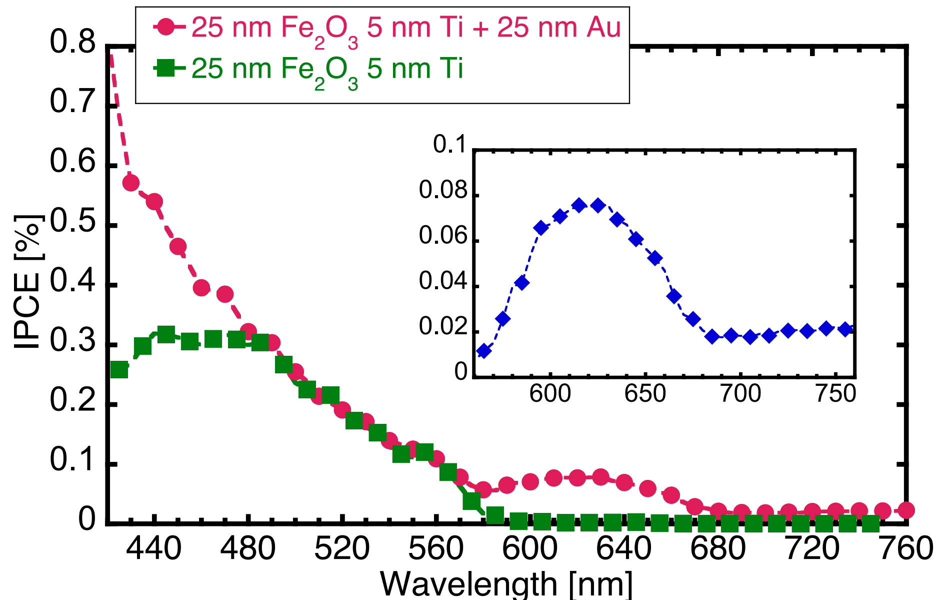


Iandolo *et al*., in manuscript

3. Beyond plasmon-enhanced water splitting on hematite

Beyond LSPR-induced improvement





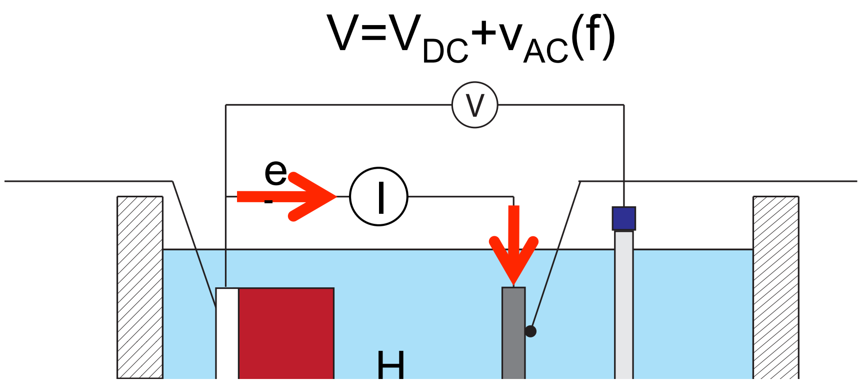
Which mechanism(s) behind IPCE increase at short wavelength?

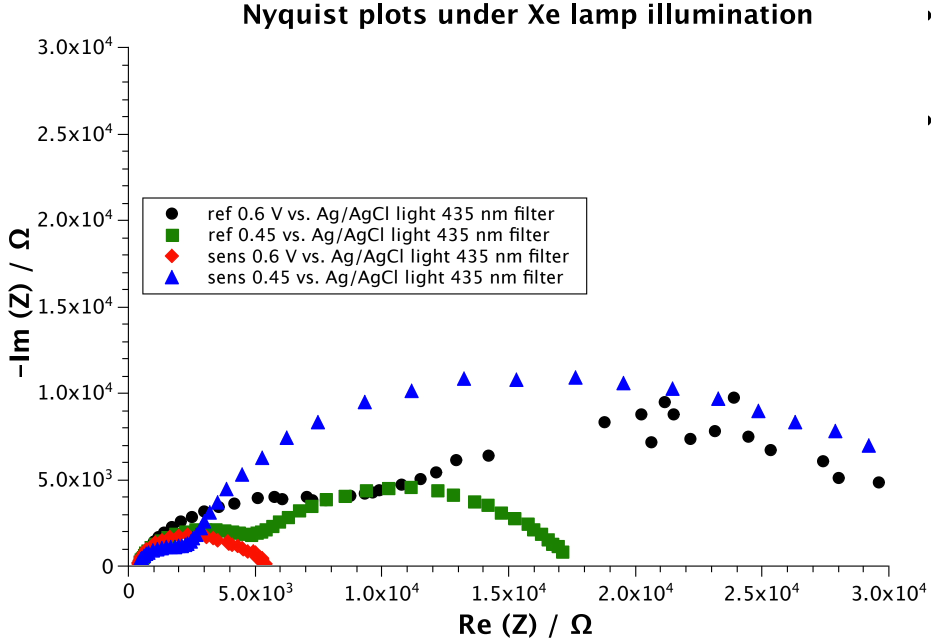
- Adhesion layer likely to be involved
- The interface properties are crucial:
  - semiconductor-metal
  - semiconductor-semiconductor
  - semiconductor-electrolyte
  - triple junctions

Electrochemical Impedance Spectroscopy (EIS)

How to study surface properties?

Electrochemical impedance spectroscopy (EIS)



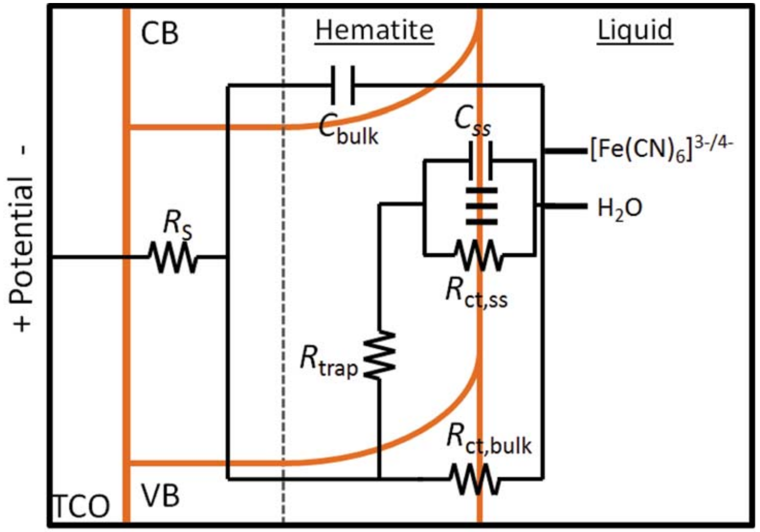


- a potential $V=V_{DC}+v_{AC}(f)$ is applied between working and reference electrodes
- the frequency of v_{AC} is swept keeping the same V_{DC} value
- for each f, the total complex impedance $Z(f)=Z'(f)+Z''(f)$ is recorded
- then, V_{DC} is changed and the sweep is repeated in the same frequency range

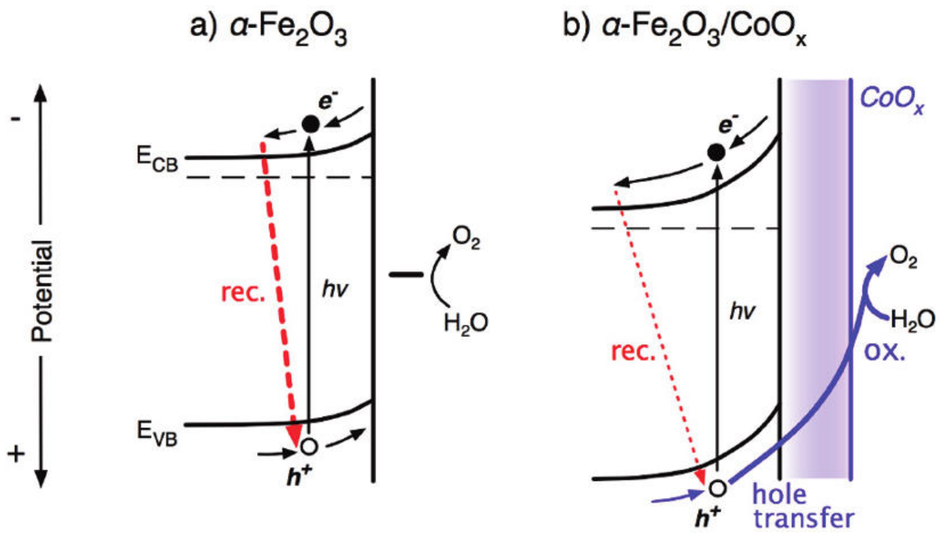
How to interpret the Nyquist plots data?

An equivalent circuit modeling is required

EIS on hematite photoanodes



Klahr *et.al.*, E&E Science, 2012, 5, 7626



Barroso *et.al.*, E&E JACS, 2011, 133, 14868–14871

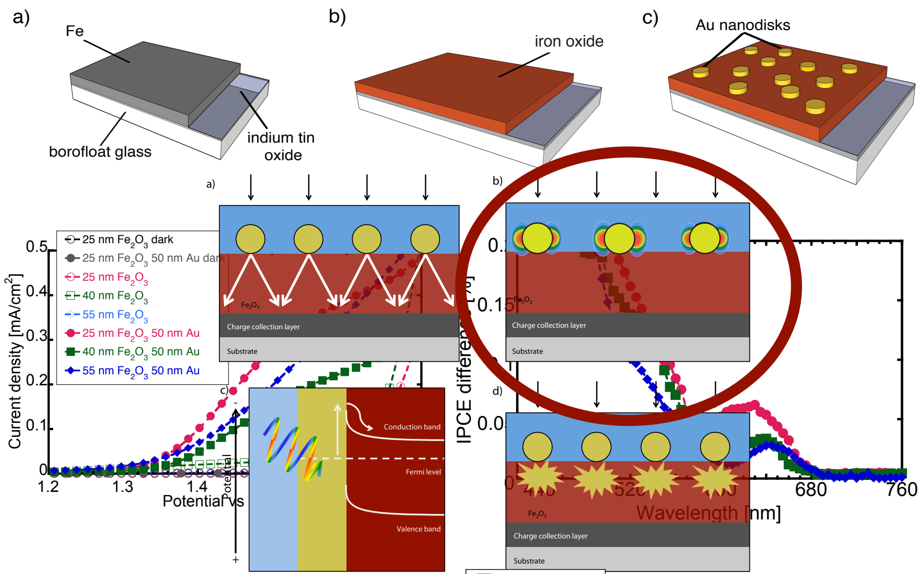
Surface states for holes at the hematite-electrolyte interface

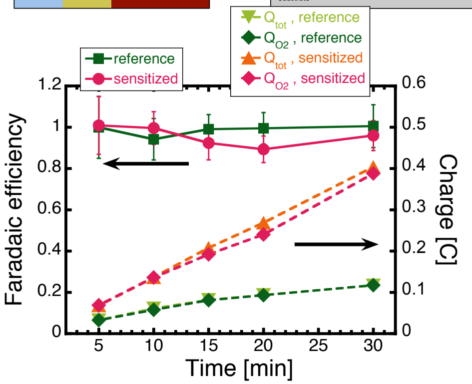
Increased band bending at semiconductor-semiconductor interface

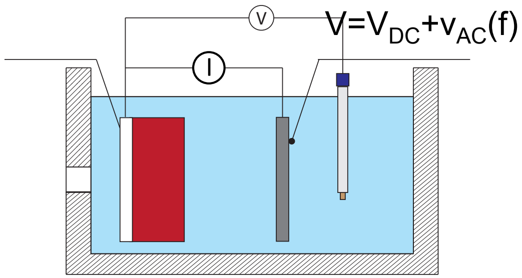
Systematic investigation on our model photoanodes:

- **chemistry (metals, oxides)**
- **surface coverage**
- **thickness**

Conclusions







- Model photoanodes were designed and fabricated
- Functionalization with Ti/Au nanodisks:
  - improves the photocurrent
  - improves IPCE close to the bandgap thanks to increased charge generation in Fe_2O_3
- FE of O_2 evolution is 1 for plasmon-functionalized hematite
- EIS investigation under process at SPREE (UNSW)

Acknowledgments

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