Solution-processed semiconductor oxide photoelectrodes for solar fuel production

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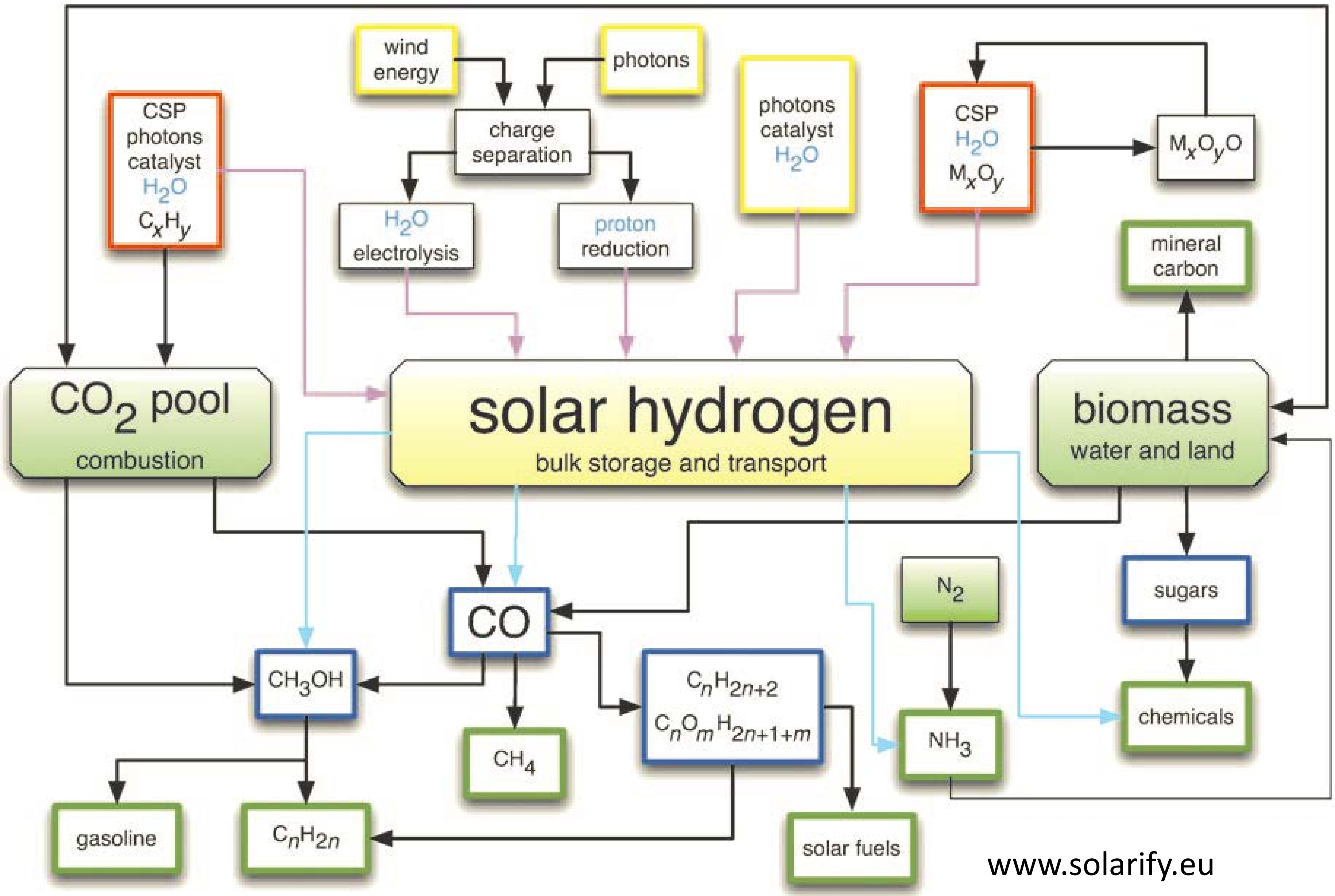
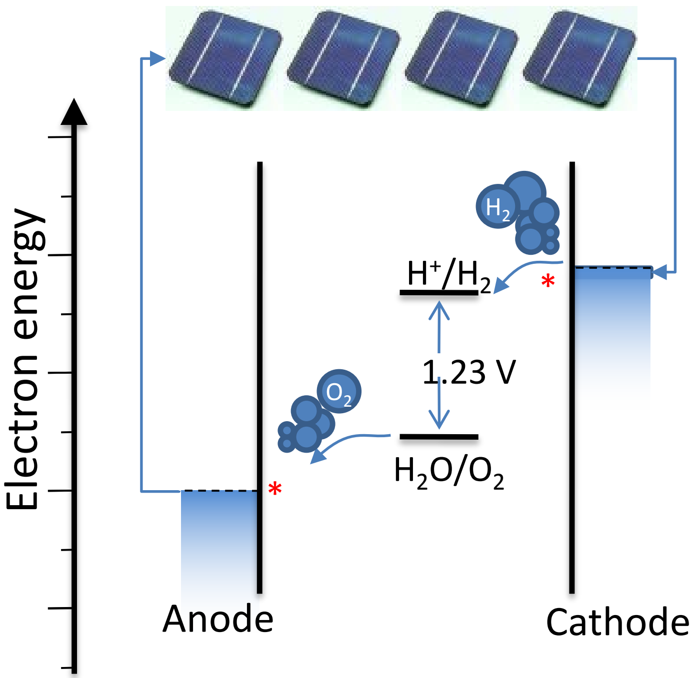
Chemical storage of solar energy



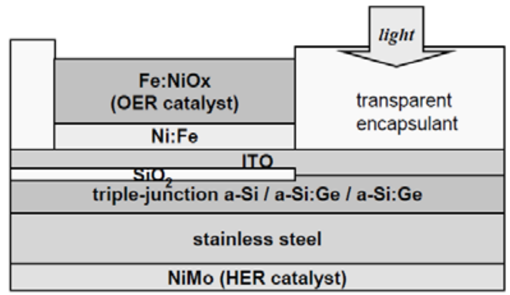
www.solarify.eu

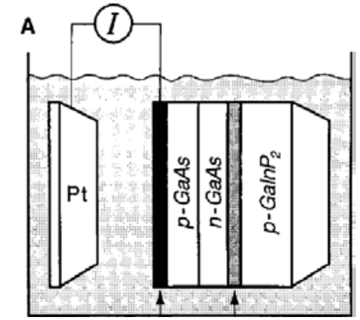
Technologies for Solar-to-chemical conversion

- Traditional photovoltaic + electrolyzer



- Direct water decomposition using a photoelectrochemical (PEC) device





Solar-to-Hydrogen efficiency = 7.8%	Solar-to-hydrogen efficiency = 12-16%

R. E. Rocheleau, E. L. Miller and A. Misra, *Energy and Fuels*, 1998, **12**, 3-10.

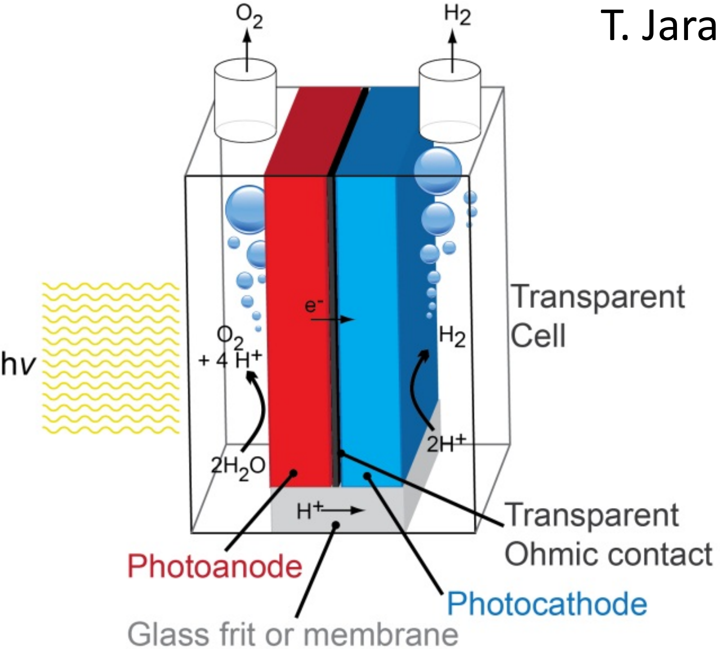
O. Khaselev, J. Turner. *Science*, **1997**, 280, 425.

D. G. Nocera, and coworkers *Science*, **2011**.

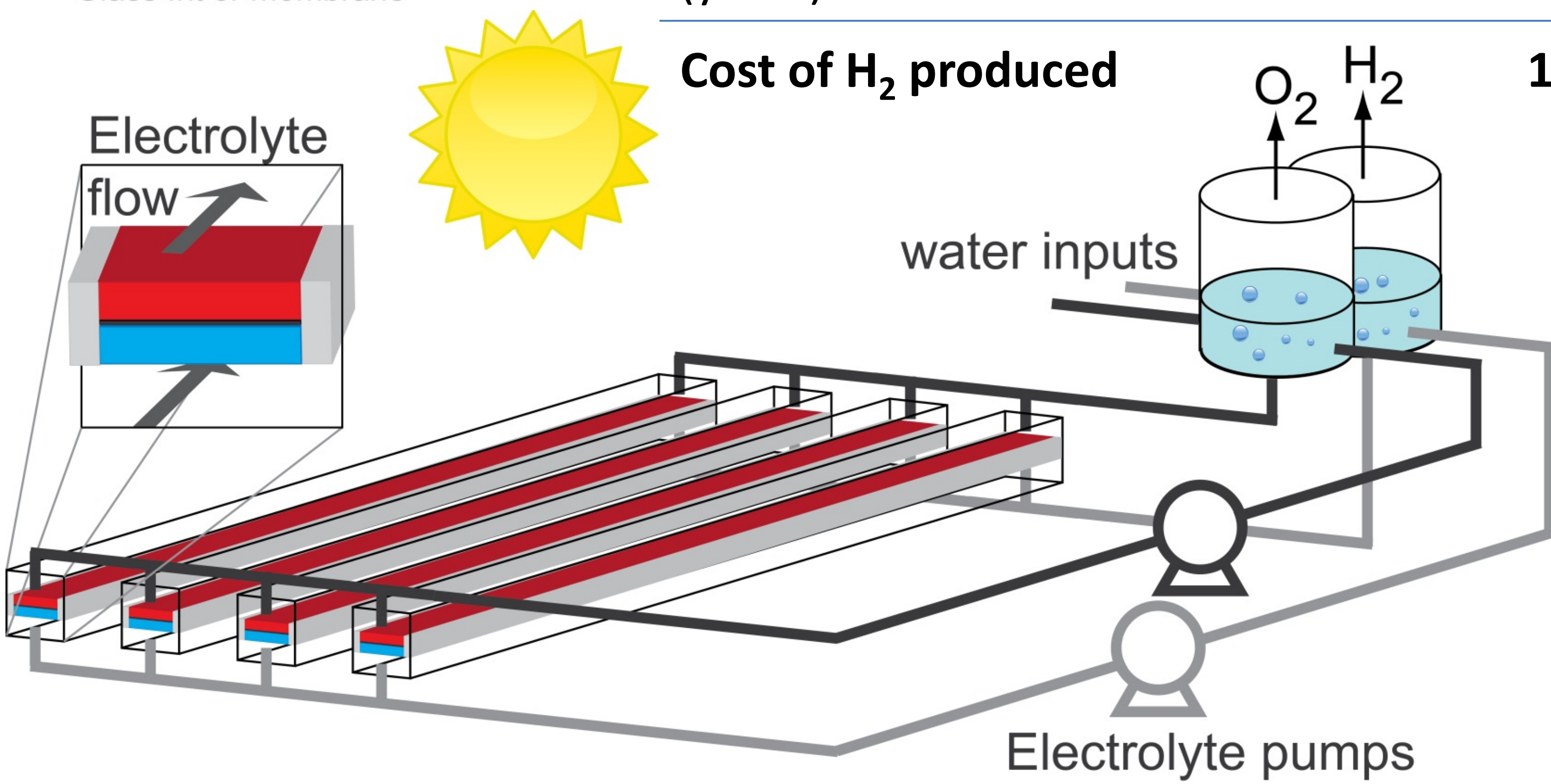
- Limited by price, availability of traditional photovoltaics
- Voltage output of Si PV strongly dependent on irradiation intensity
- Up to 50% energy loss
- Current cost under ideal conditions: ~$10/kg H_2 (Si PV costs ~$200-300/m^2)

- A direct semiconductor-liquid junction reduces losses and can increase conversion efficiency
- promising performance demonstrations have been achieved
- Remaining challenges are to meet cost competiveness with traditional approach
- $10/kg H_2 ~ 10% efficiency, 10 year lifetime and $100/$m^2$

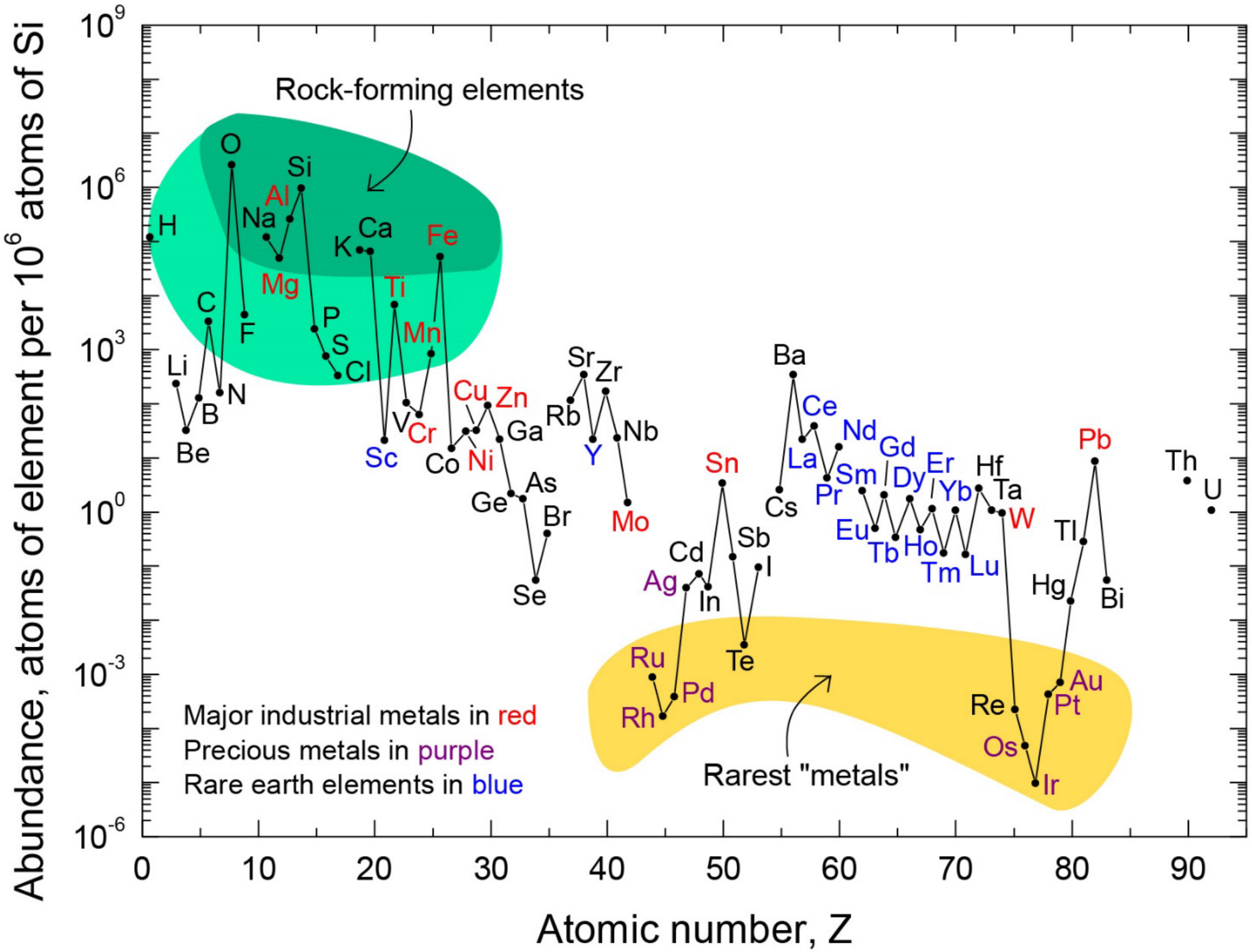
T. Jaramillo and coworkers ***Energy Environ. Sci.***, 2013,**6**, 1983-2002



Net production (kg H_2 per day, yearly average)	1000
PEC cell efficiency (solar to hydrogen %)	10 %
Cost of PEC cell (per m^2)	153 USD$
PEC cell lifetime (years)	10
Cost of H_2 produced	**10.40 $/kg**



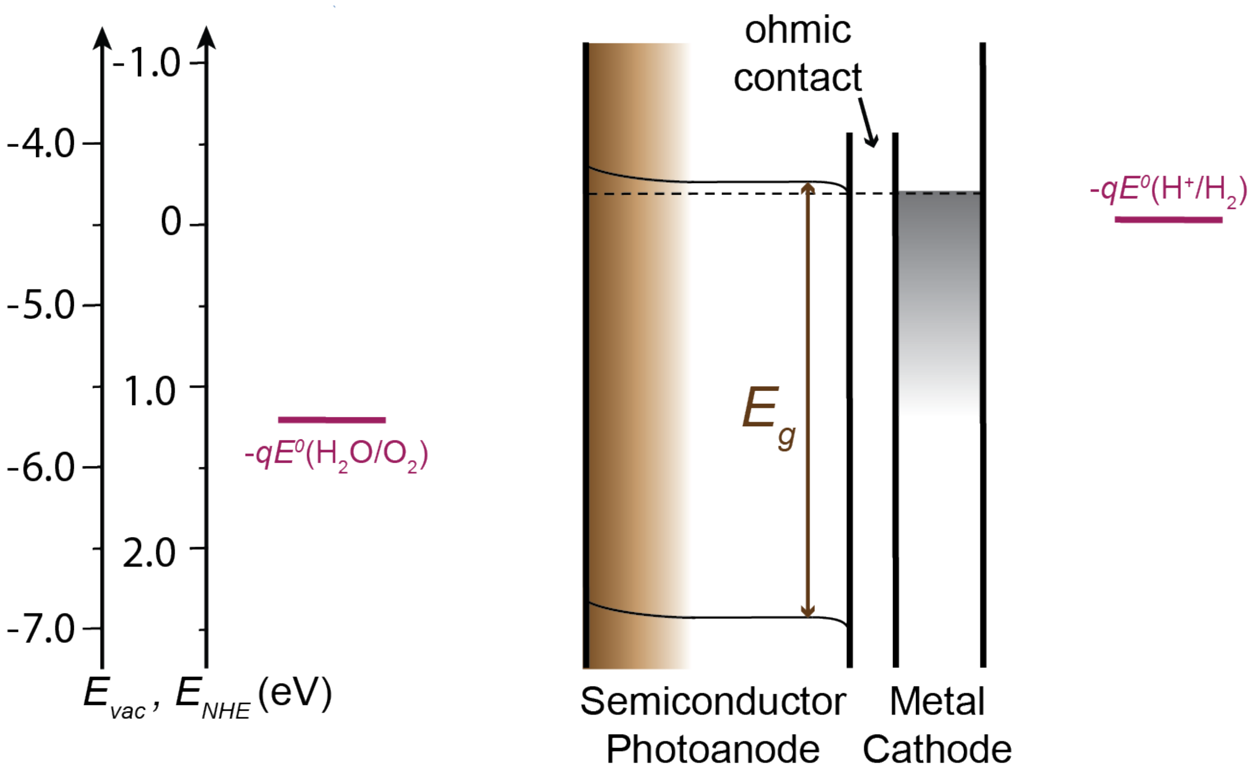
Strategy for inexpensive PEC cells



Solution based processing
Cost = $10/m²

Chemical storage of solar energy

- The brute force approach
- The direct water decomposition using photoelectrochemistry
- The integrated tandem cell approach



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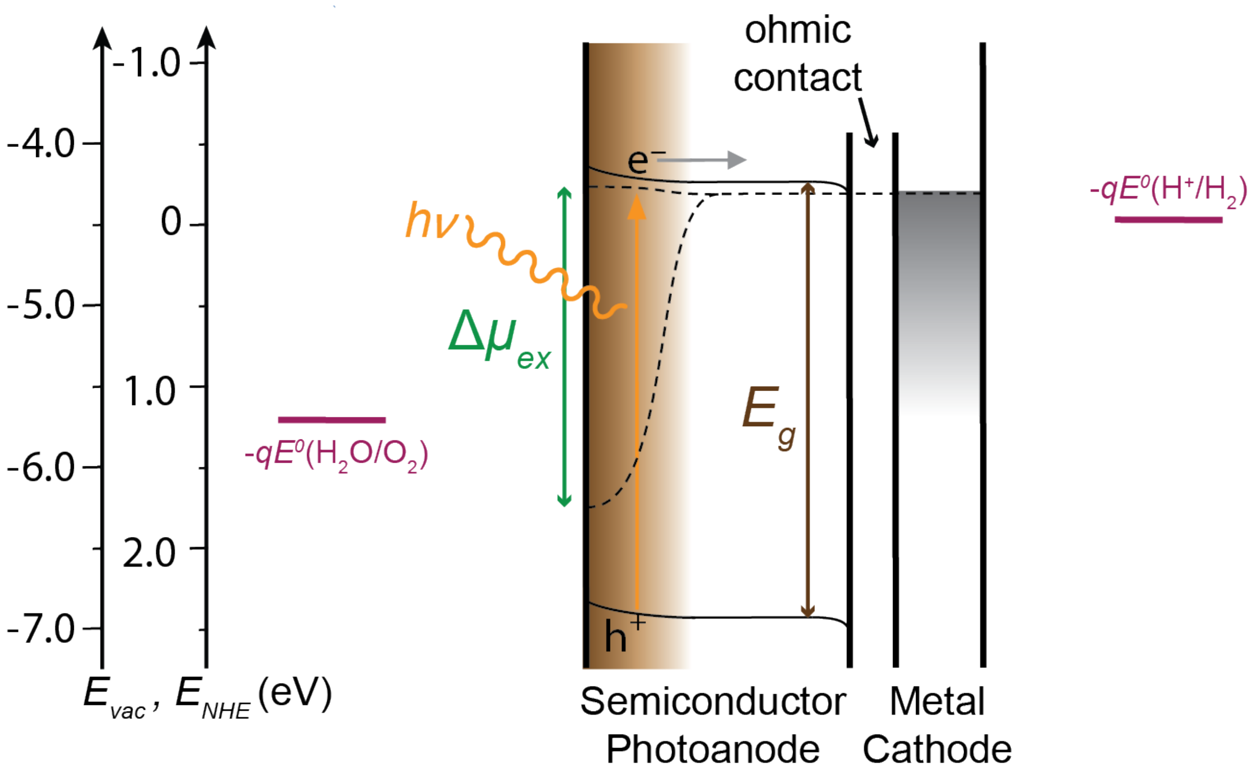

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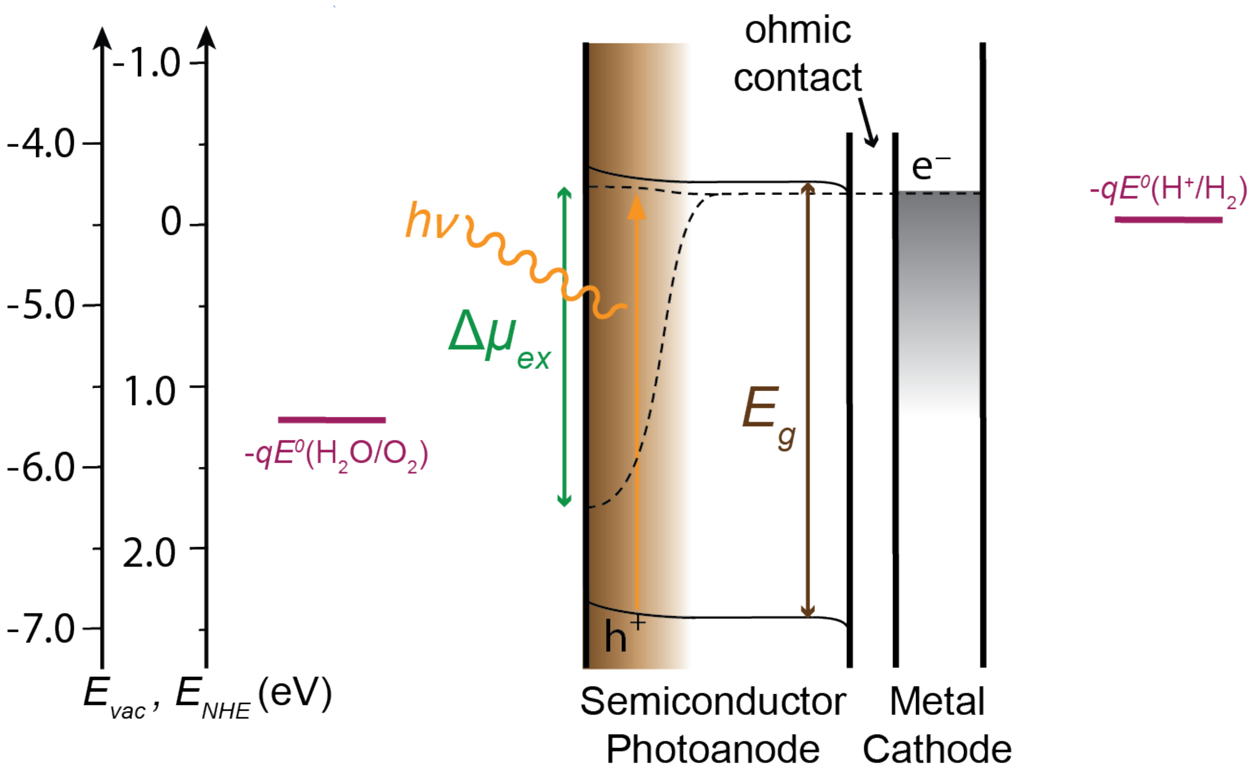

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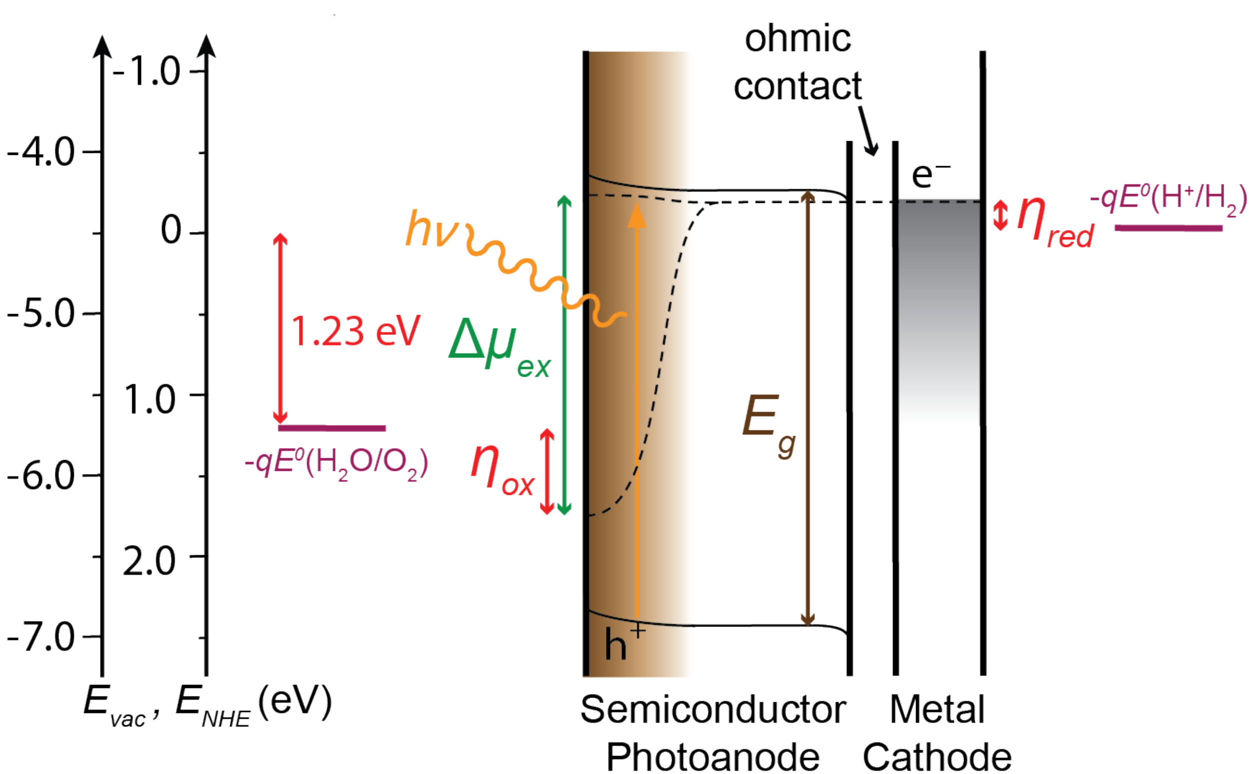

Chemical storage of solar energy

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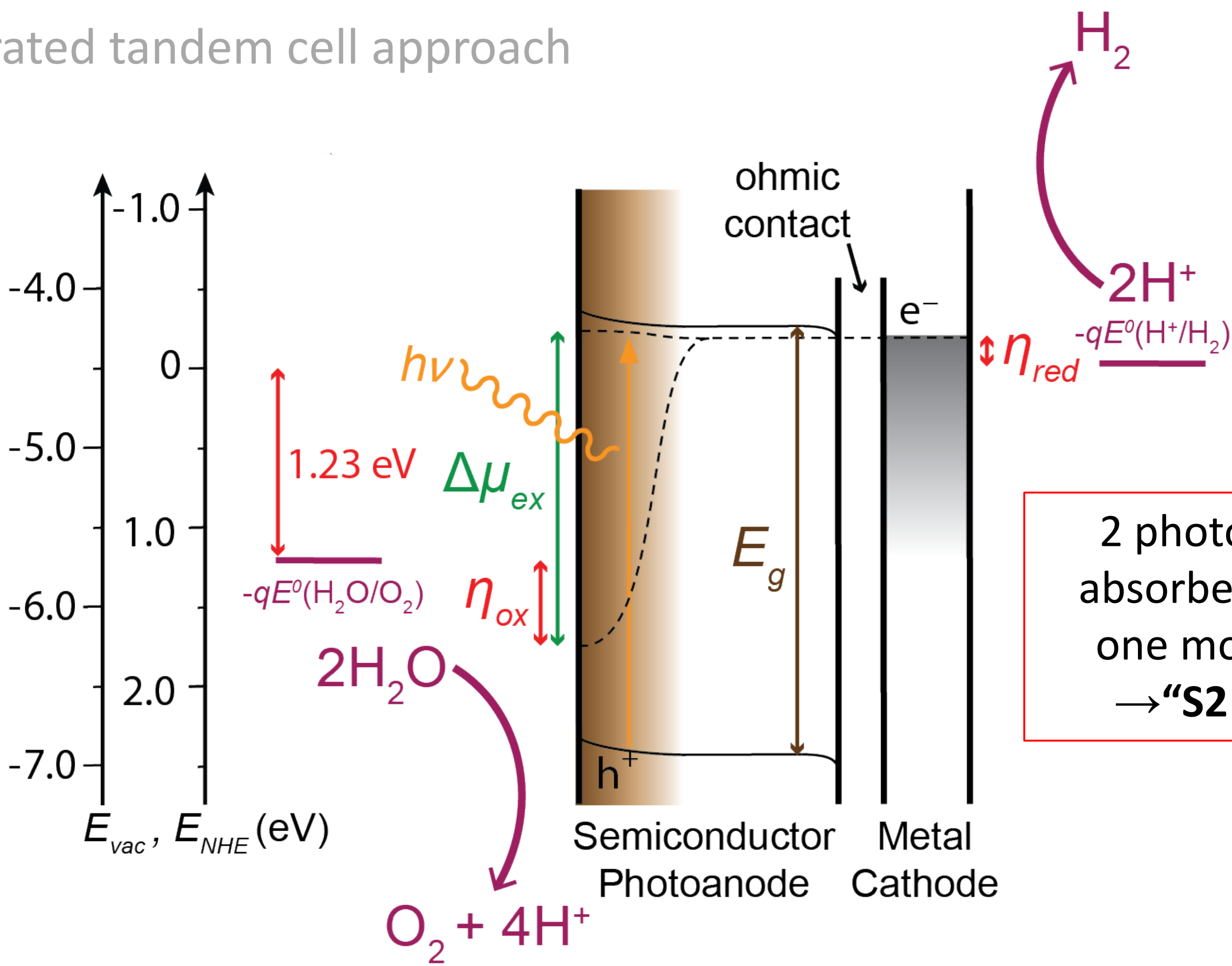
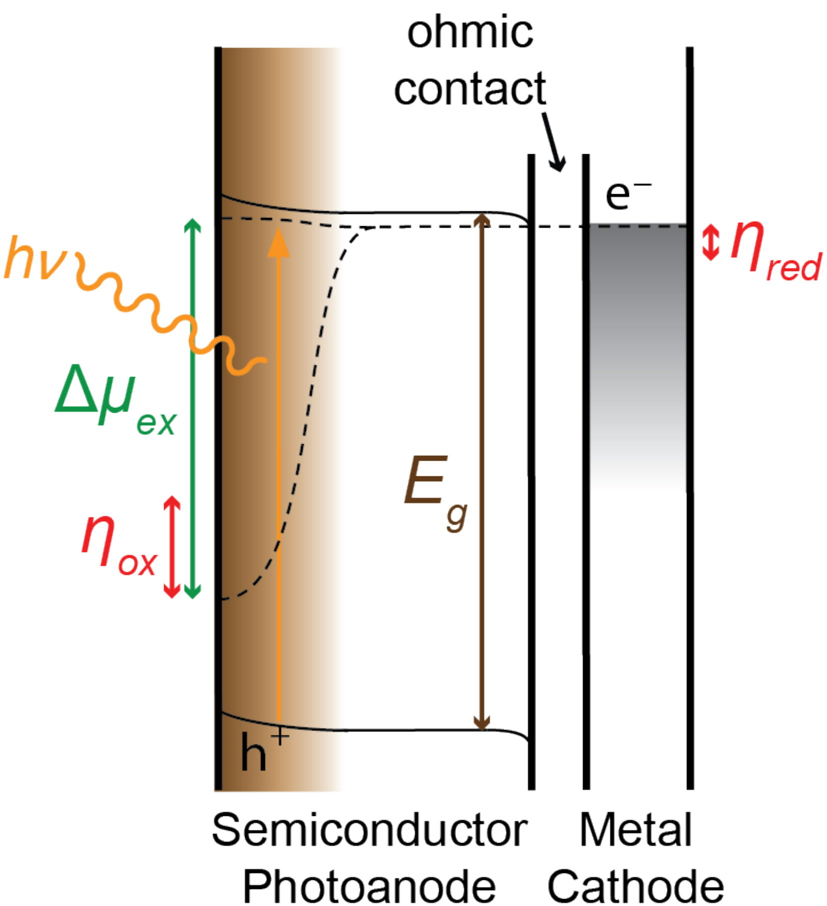


2 photons must be absorbed to produce one molecule of H_2
→**"S2 approach"**

Net Reaction: $2\,H_2O + 4h\nu \rightarrow 2H_2 + O_2$

Limitations of the S2 approach



Under 1 sun illumination:
$\Delta\mu_{ex} \approx 0.75\ E_g$.

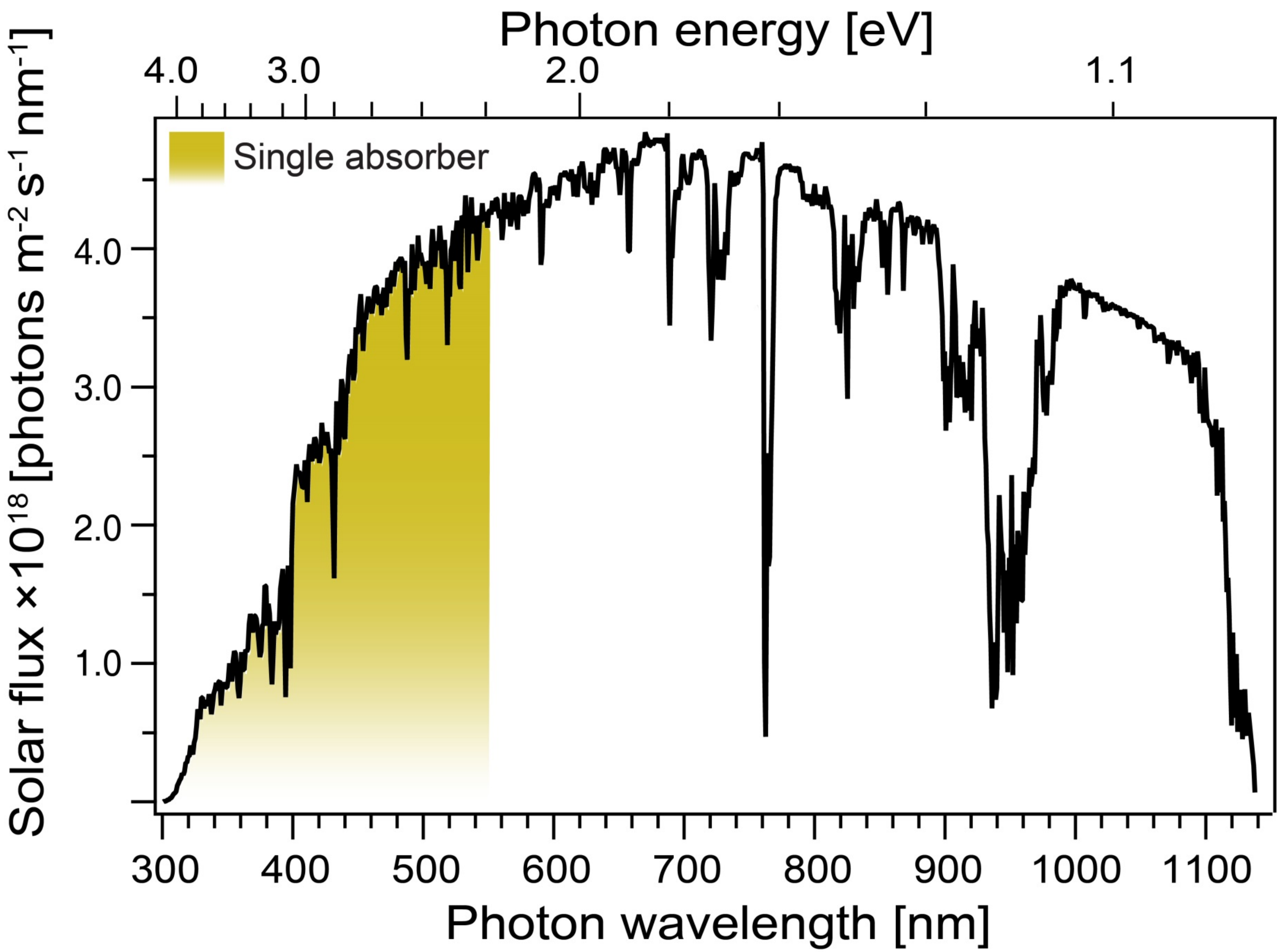
η_{ox} is large (0.2 – 0.4 eV) for ca. 10 mA cm^{-2}

U_{loss} can be up to 1.0 eV per photon

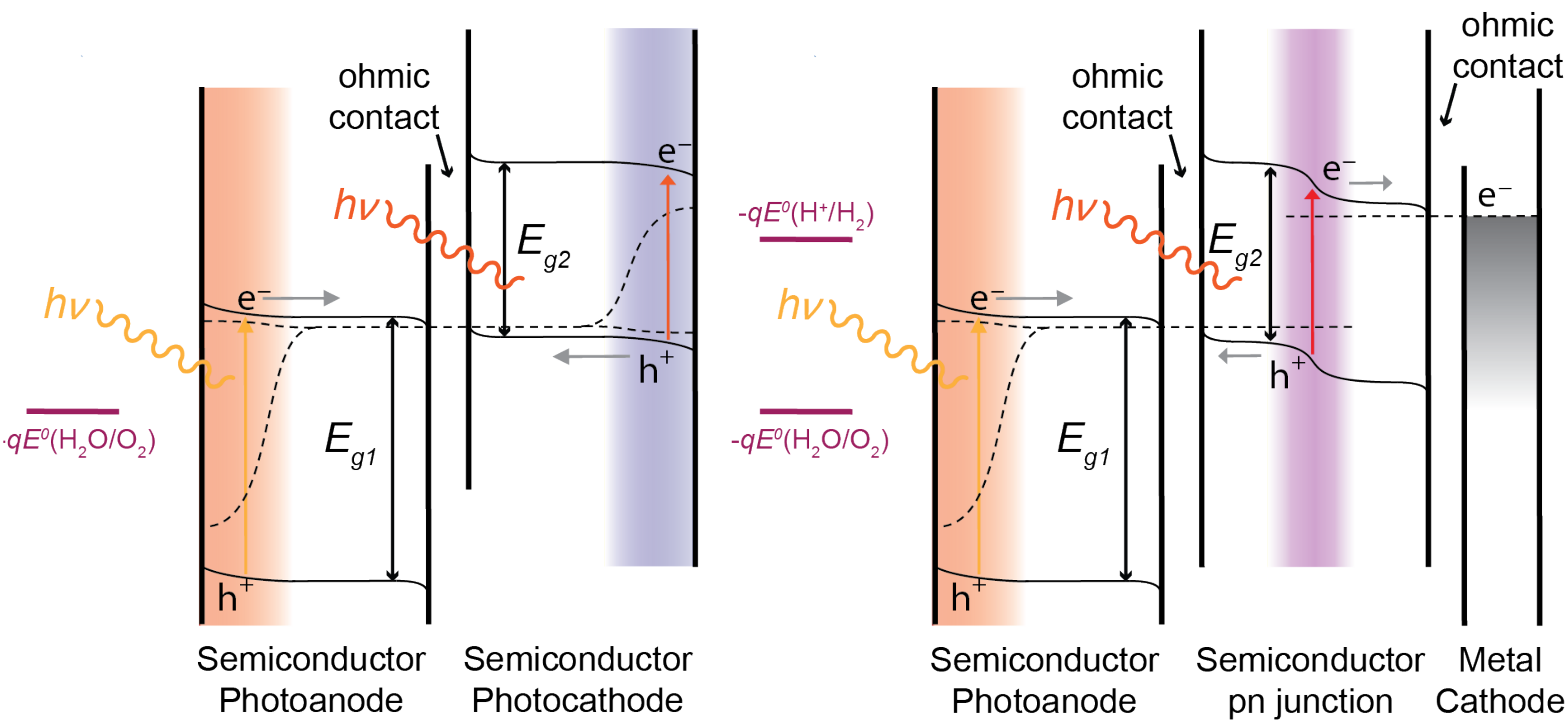
Maximum Solar to hydrogen conversion efficiency (STH) is 12.7 % (with E_g = 2.23 eV)

J.R. Bolton *Nature* **1985**, *316*, 495-500.

Limitations of the S2 approach



Tandem cell approach



4 photons must be absorbed to produce one molecule of H_2
→**"D4 approach"**

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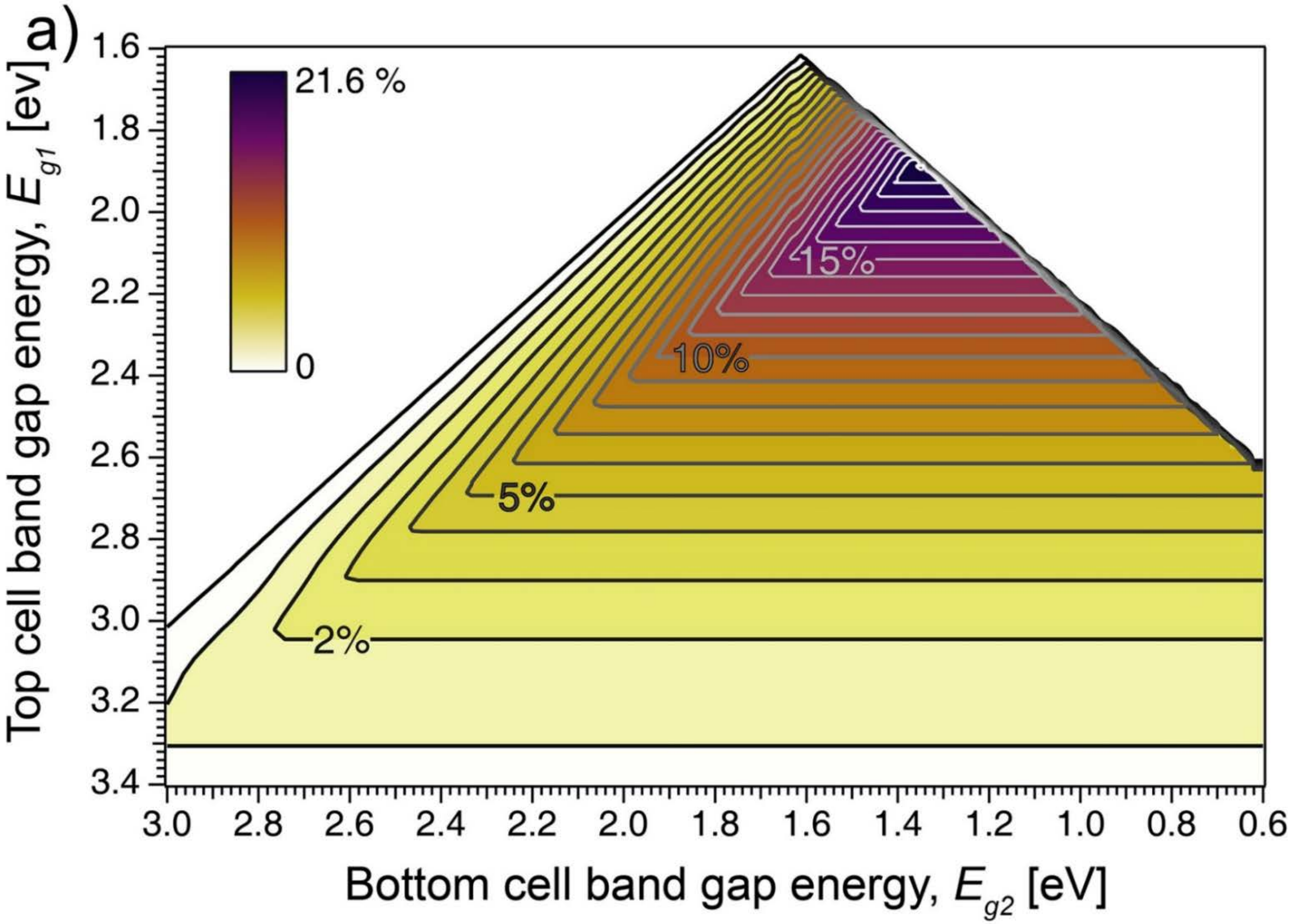
Limitations of the D4 approach

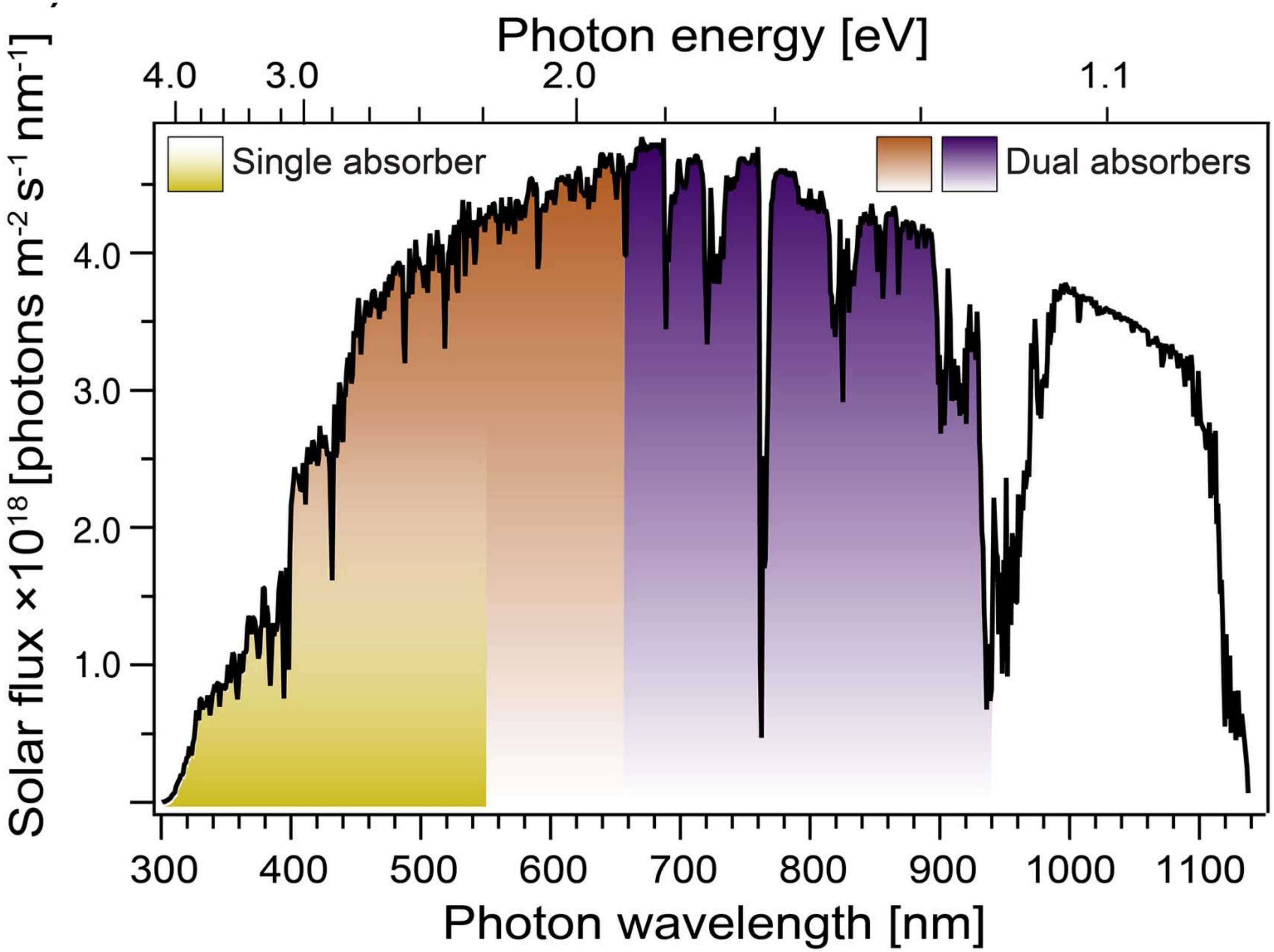
Assumption of 1.0 eV per photon energy loss



Prevot and Sivula *J. Phys Chem C.* **2013** 117, 17879-17893.

Limitations of the D4 approach

Using similar assumption of U_{loss} can be up to 1.0 eV per photon



Materials for the tandem cell

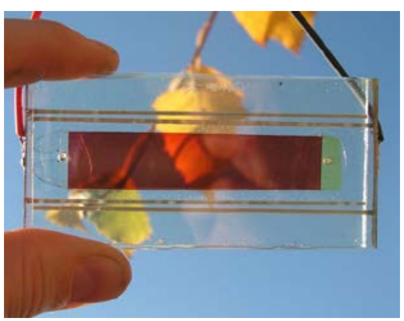
Photoanode

WO_3

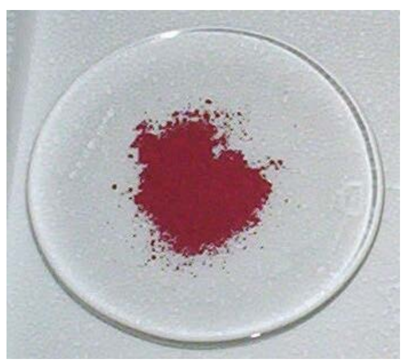
$BiVO_4$

$\alpha\text{-}Fe_2O_3$

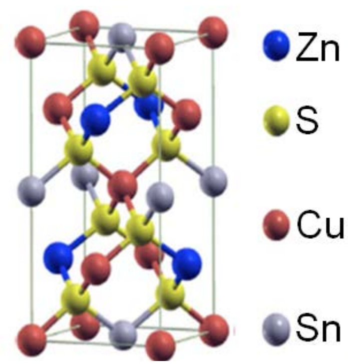
Photocathode



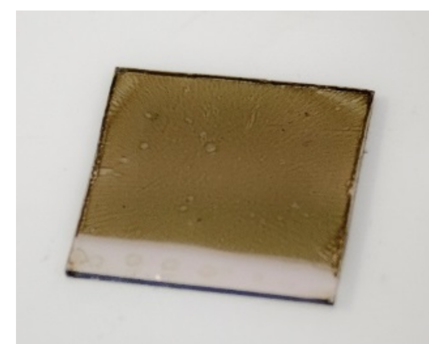
Dye sensitized solar cell



Copper(I) oxide



Cu_2ZnSnS_4



$CuFeO_2$

α-Fe_2O_3 (hematite) as a promising material

Advantages

Cheap and abundant

Stable

Environmentally benign

Absorbs over 16 % of AM1.5 solar spectrum

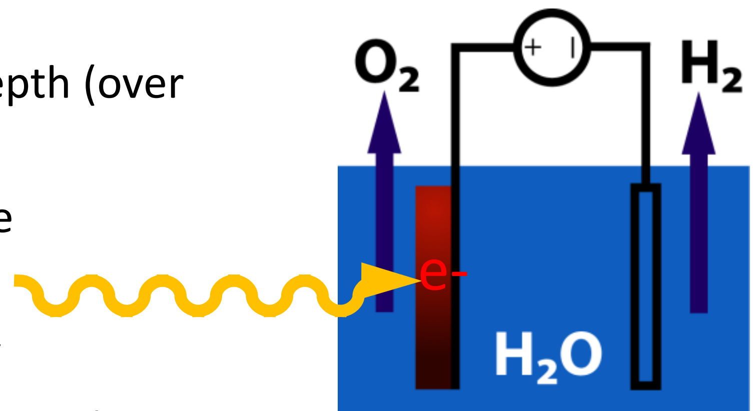
Challenges

Long photon penetration depth (over 100 nm @ 500 nm)

Short hole diffusion distance (L_D = 5 nm)

Poor electronic conductivity

High overpotential for water oxidation



Single Crystal
Hematite photoanode

12.6 mA/cm^2
Possible

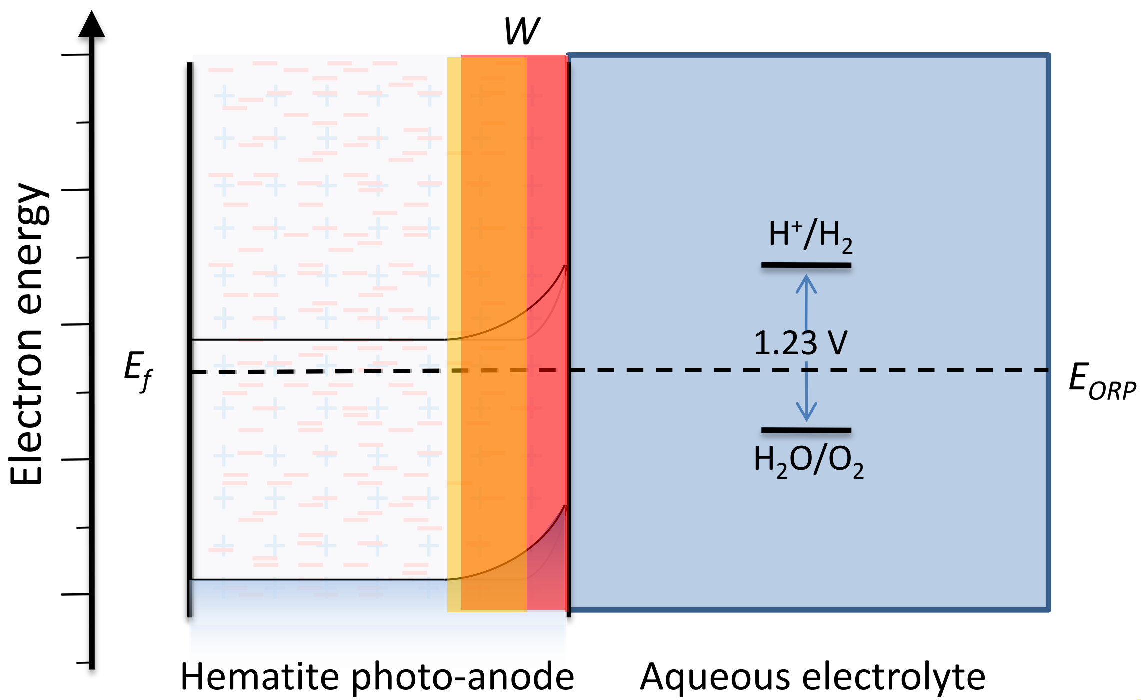
0.5 mA/cm^2
Observed*

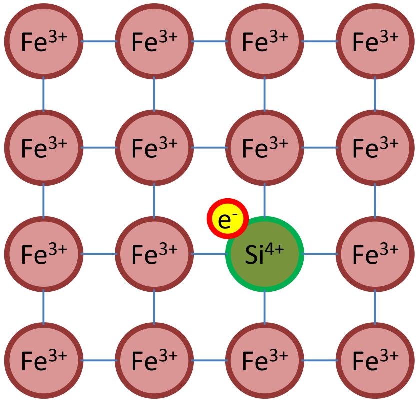
*Sanchez, et al., *J. Electroanal. Chem.* **1988**, *252*, 269-290.

Overcoming challenges of hematite

Challenge: Poor electronic conductivity

Resolution: Aggressive substitutional doping





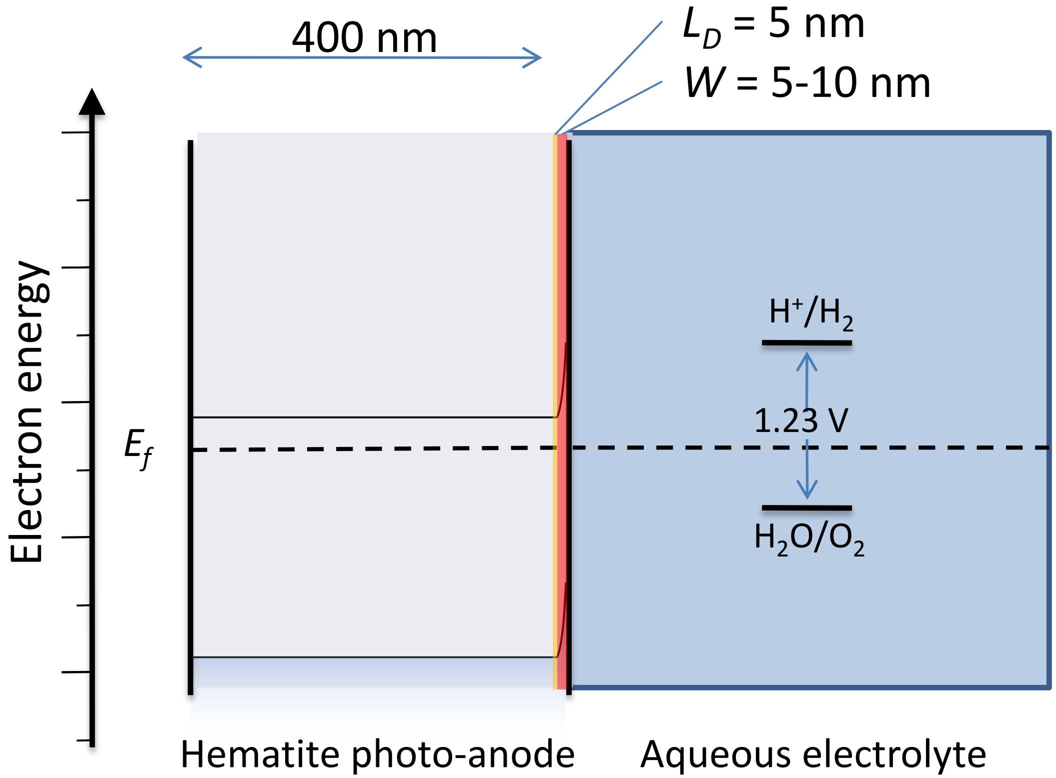
$$W = \sqrt{\frac{2\varepsilon\varepsilon_0(V - V_{fb})}{qN_d}}$$

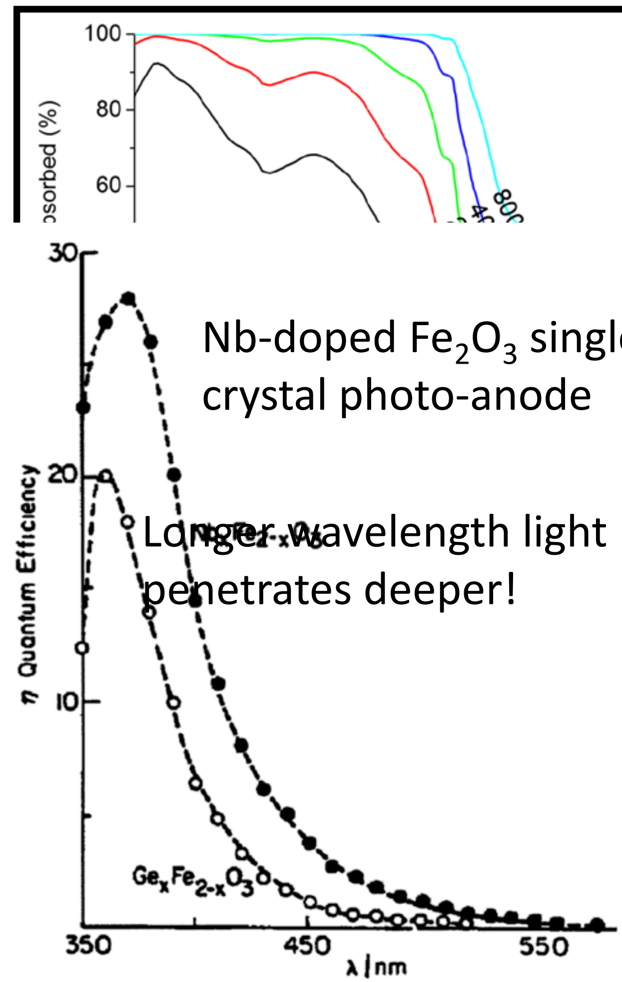
$$L_d = \sqrt{D\tau}$$

Overcoming challenges of hematite

Challenge: Poor electronic conductivity

Resolution: Aggressive substitutional doping





Nb-doped Fe_2O_3 single crystal photo-anode

Longer wavelength light penetrates deeper!

Sanchez, C.; Sieber, K. D.; Somorjai, G. A. *J. Electroanal. Chem.* ***1988,*** *252, (2), 269-290.*

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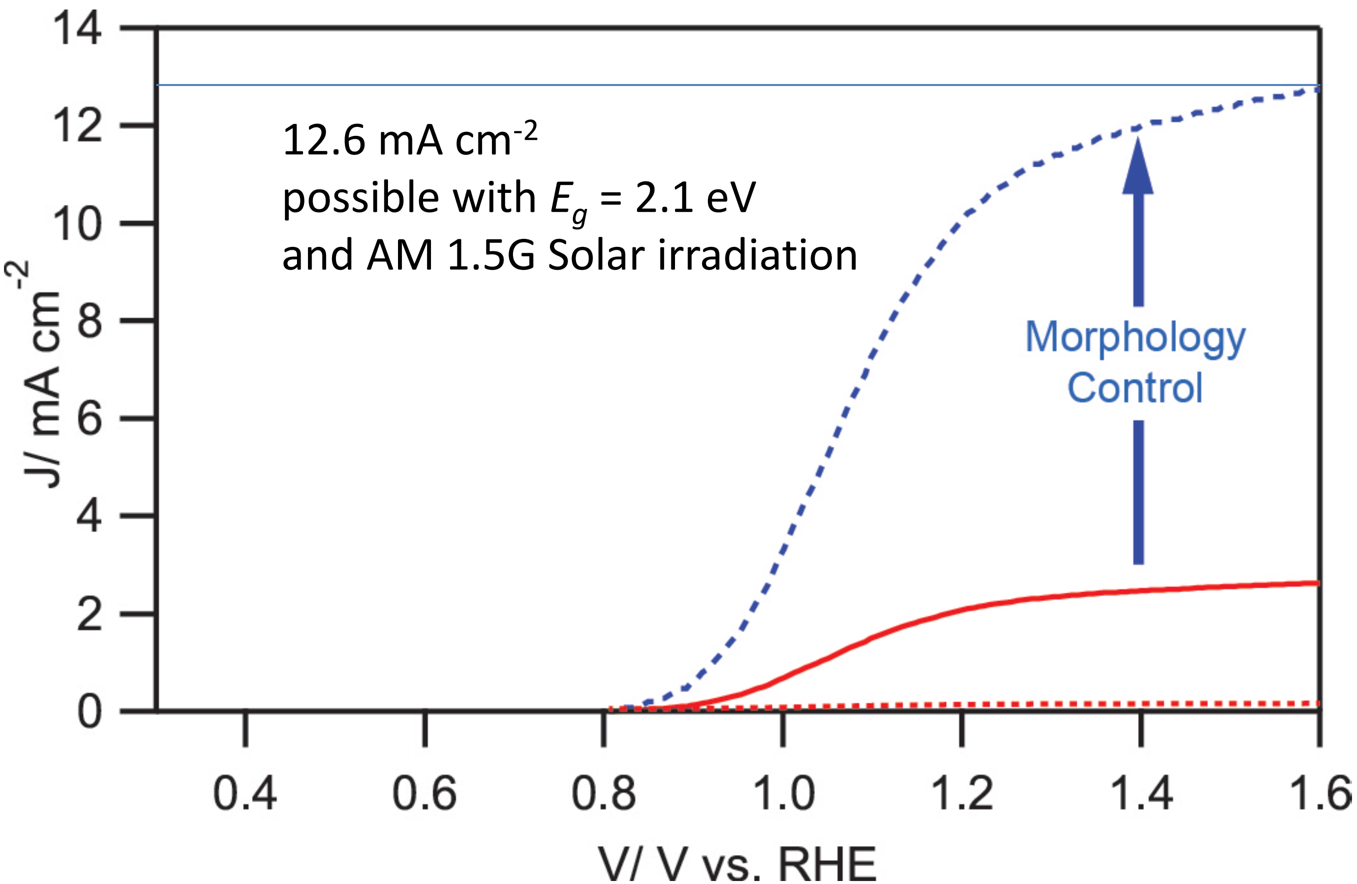
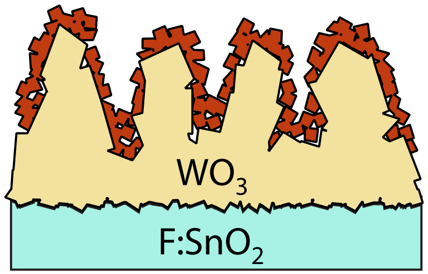
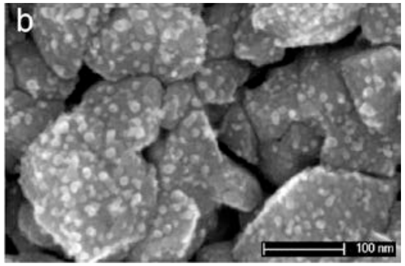
A strategy for improvement



Nanostructuring approaches for Fe_2O_3

Extremely thin absorber (ETA) approach





Demonstration with WO_3 scaffold

Chem. Mater. **2009**, *21*, 2862.

Employing buffer layers to enhance performance

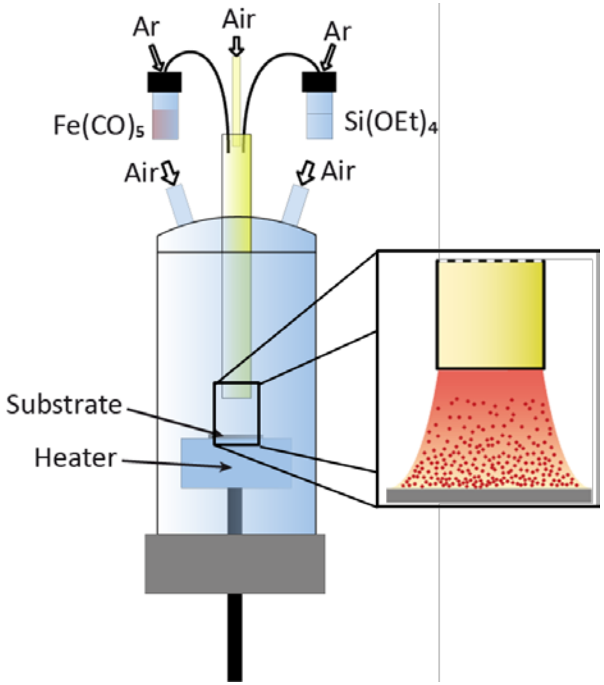
Adv. Funct. Mater. **2010**, *20*, 1099.

Adv. Mater. **2012**, 24, 2699.

Nb:SnO_2 Host

Nano Lett. **2012,** *12*, 5431.

Atmospheric pressure chemical vapor deposition.



Optimization of residence time

Angew. Chem. **2010,** *49*, 6405.

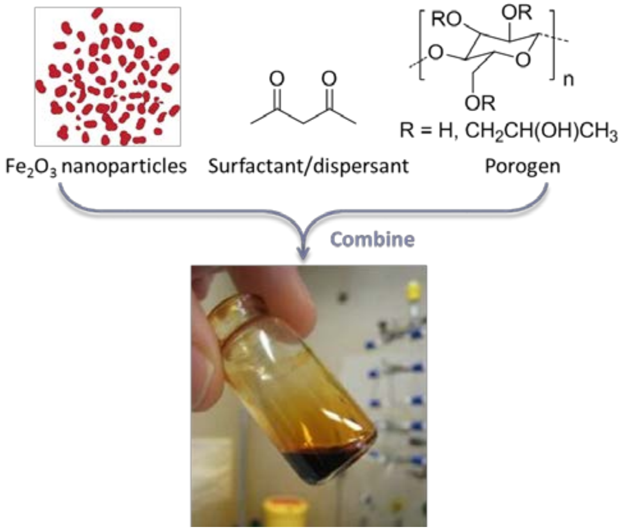
Preferential orientation

Chem. Vap. Dep. **2010**, *16*, 291

Identification of champion nanostructures

Nature mater. **2013**, *12*, 842

Mesoporous films by colloidal approach



Activation of dopant atoms

J. Am. Chem. Soc. ***2010***, *132*, 7436.

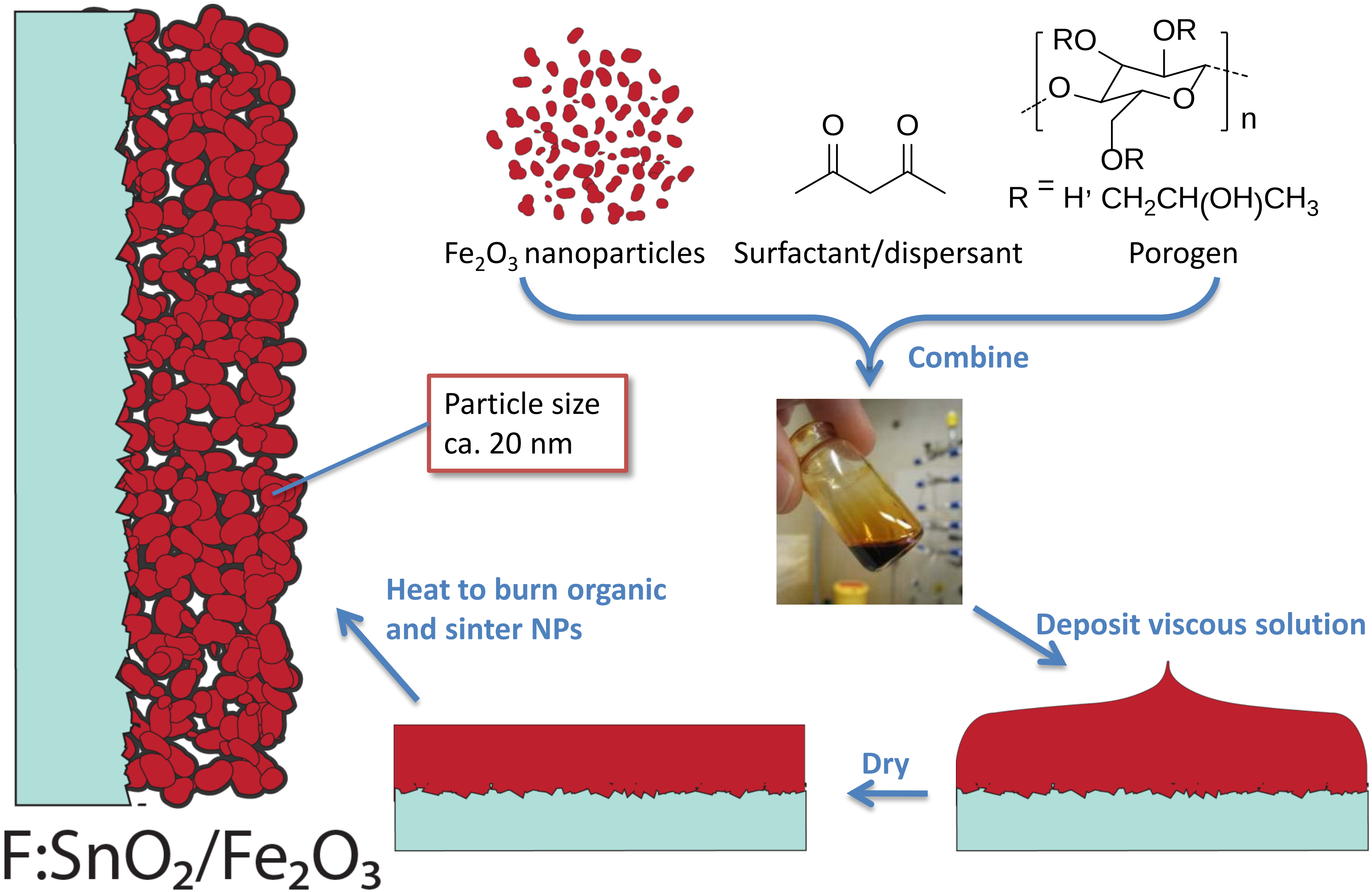
New strategy to control feature size

Nano Lett. ***2010,*** *10*, 4155-4160.

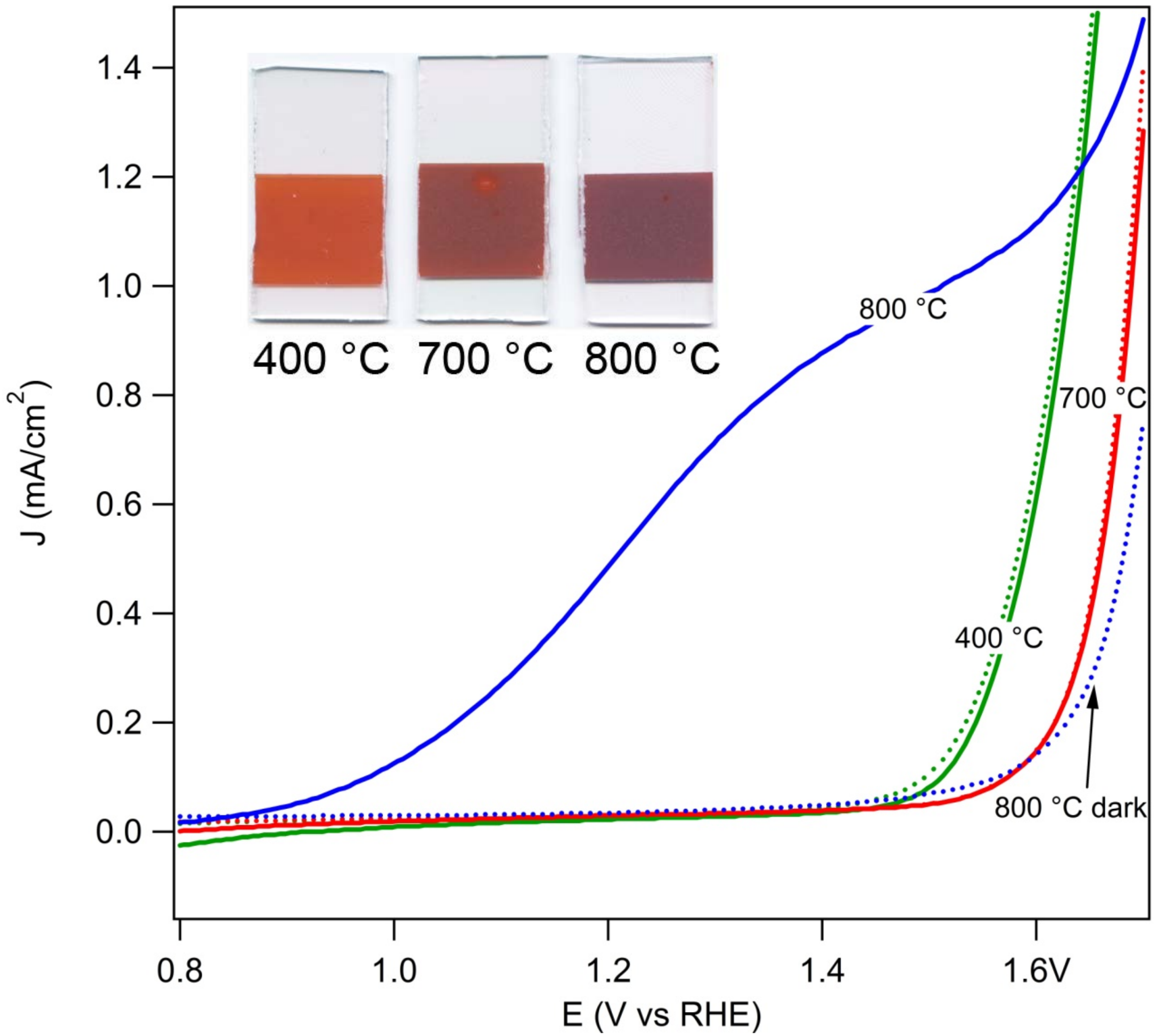
Low Temperature Sn^{4+} activation

J. Mater. Chem. **2012,** *22*, 23232.

Mesoporous films by colloidal approach

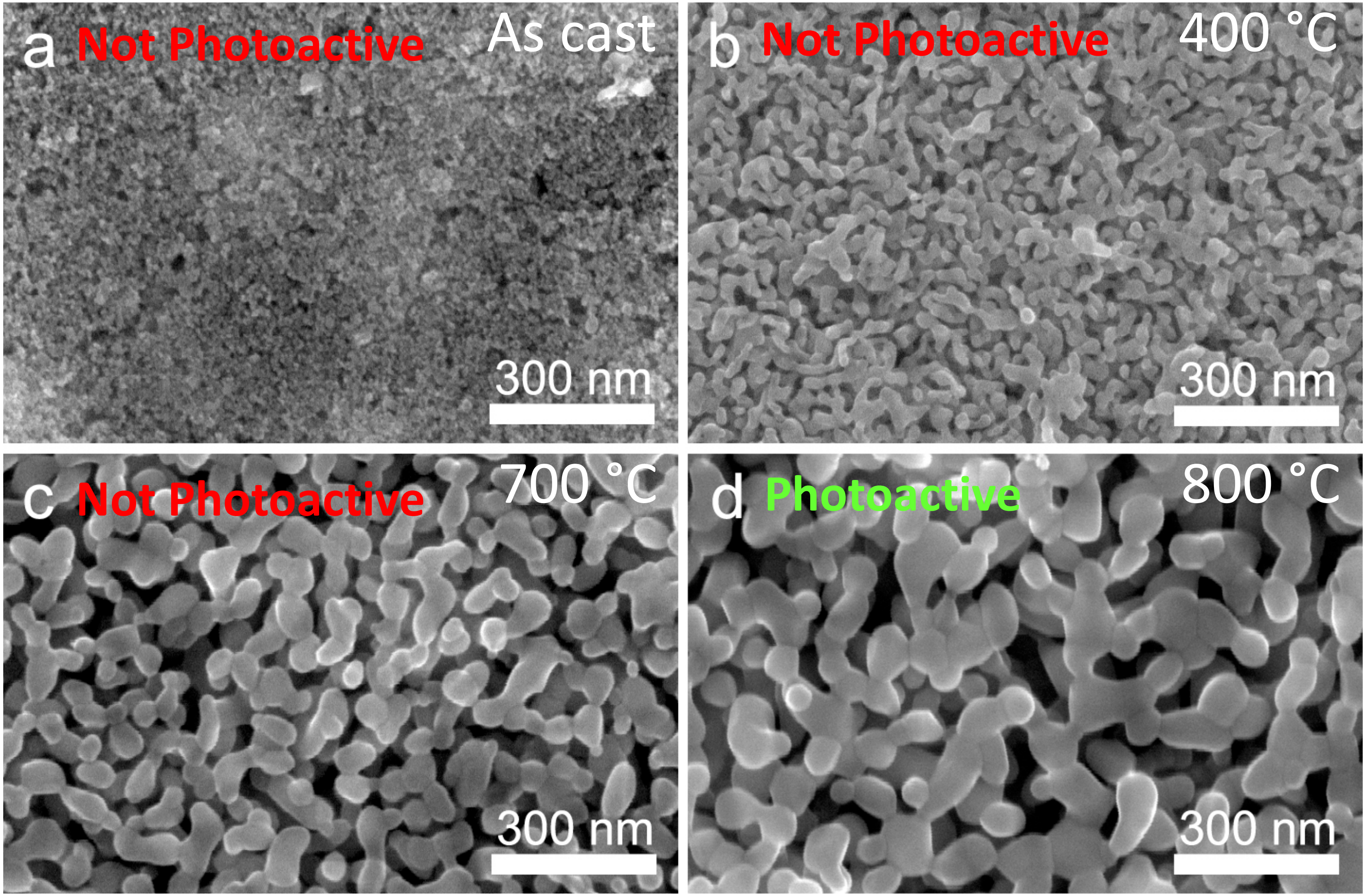


High temp sintering induces photo-activity



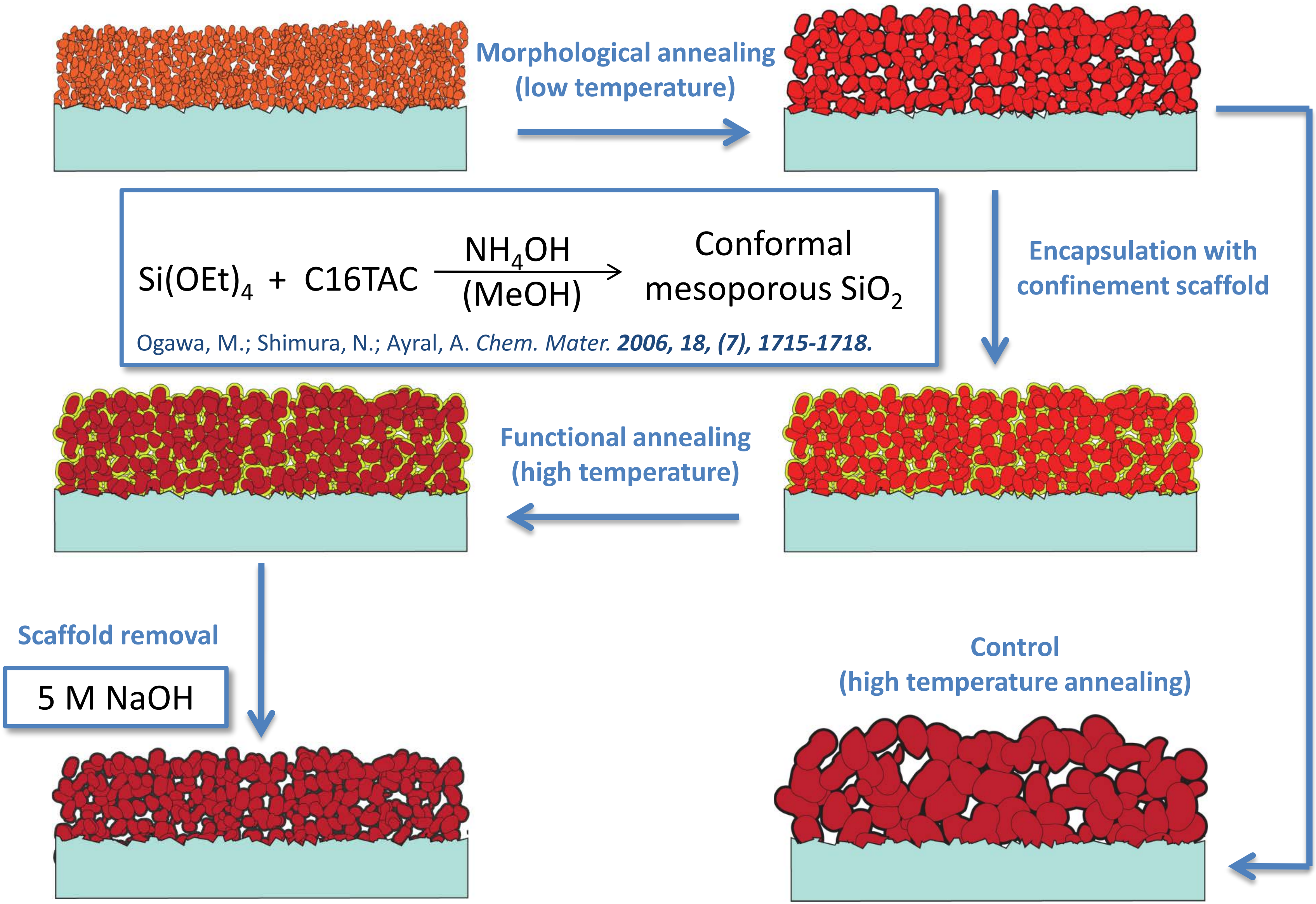
J. Am. Chem. Soc. ***2010,*** 132, 7436-7444***.***

Mesoporous morphology



J. Am. Chem. Soc. ***2010,*** 132, 7436-7444***.***

New confinement strategy



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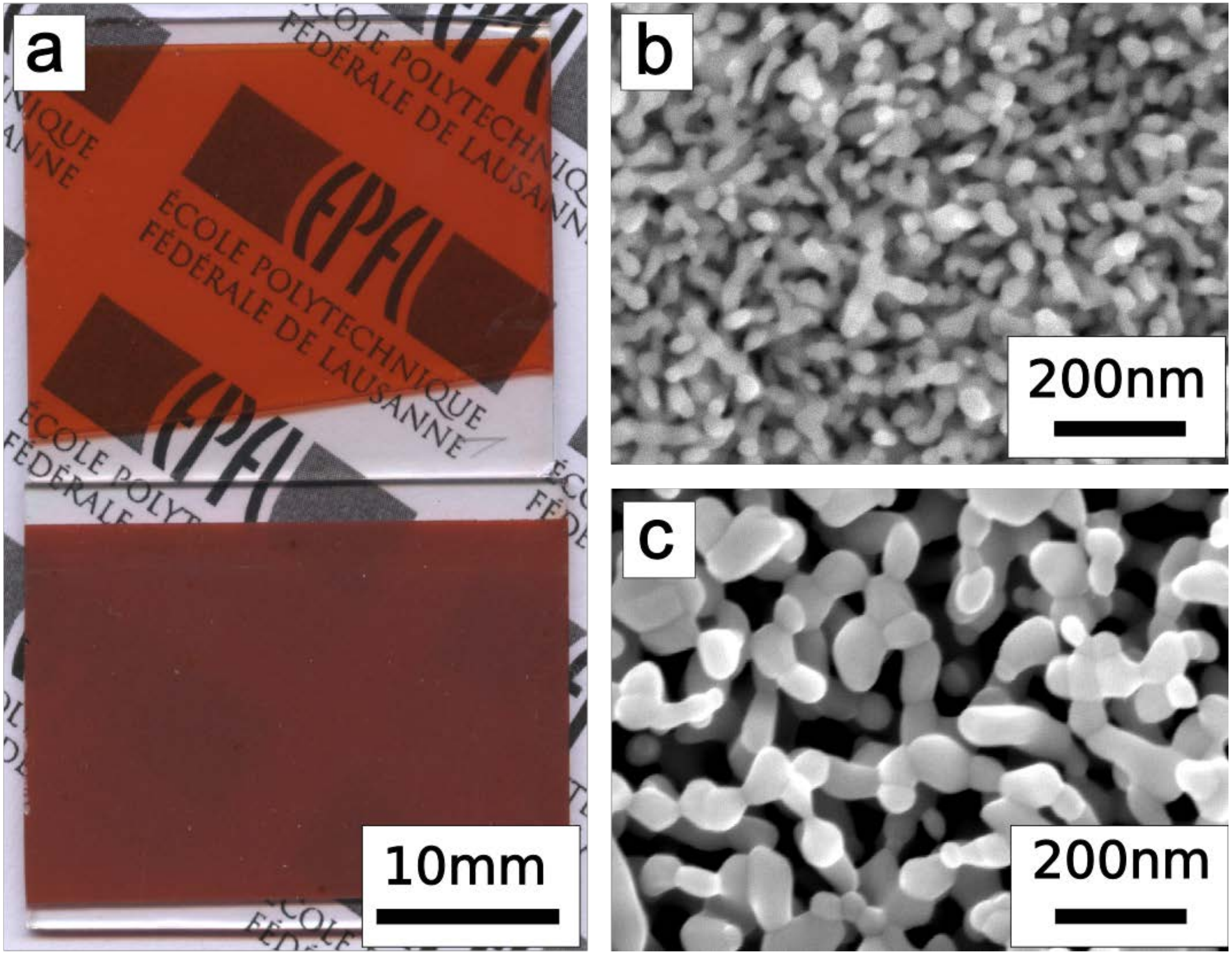
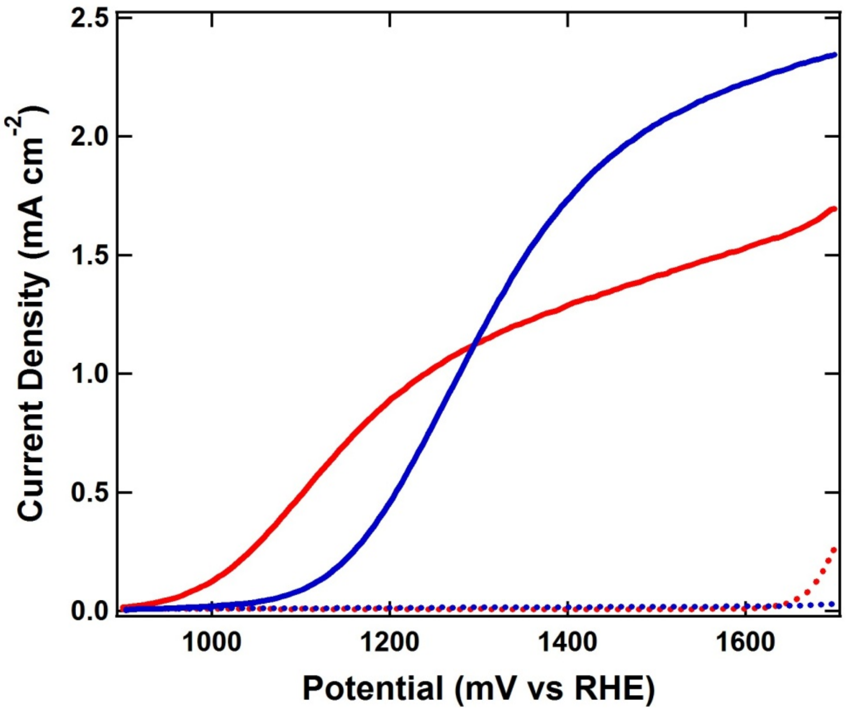
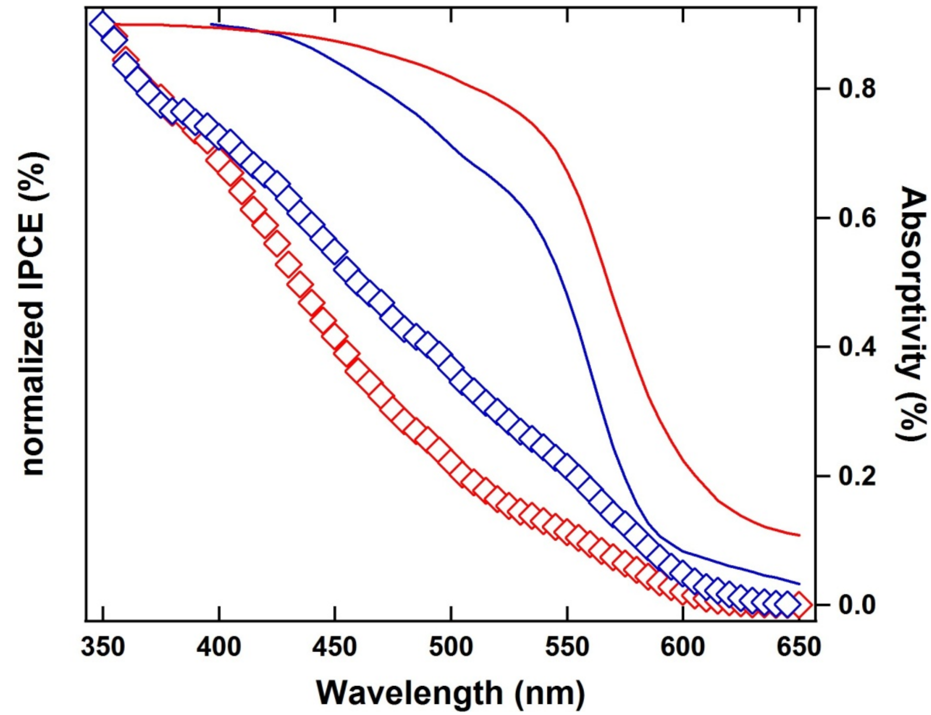
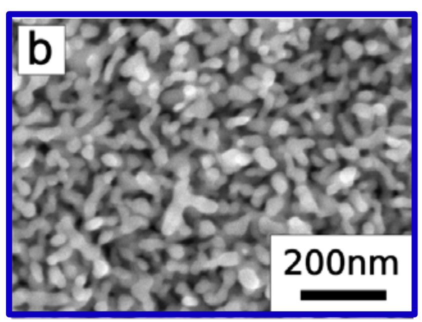


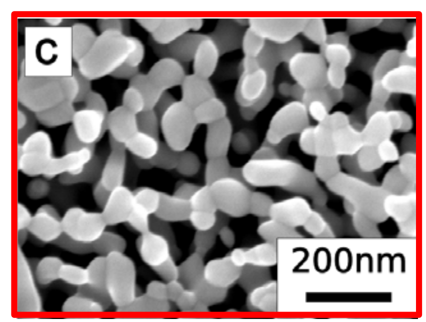
Nano Lett. ***2010***, 10, 4155.

Photoelectrochemical characterization









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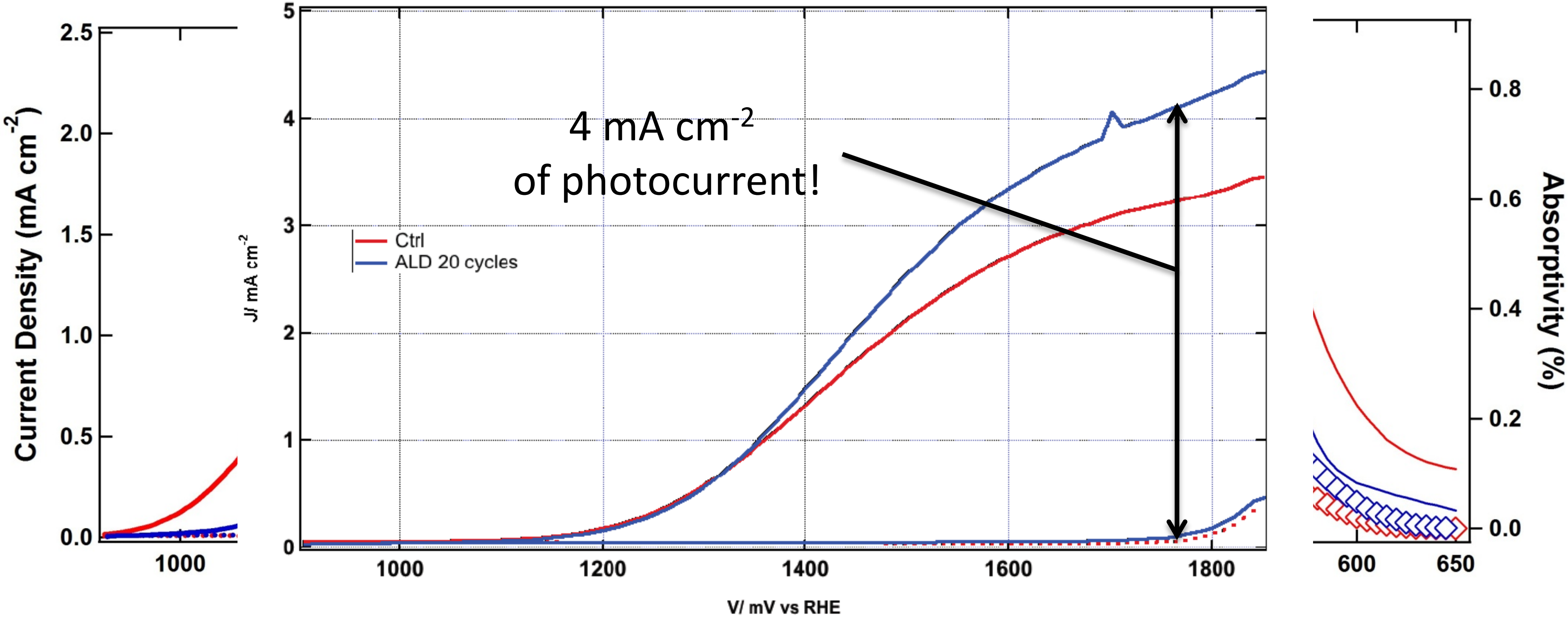
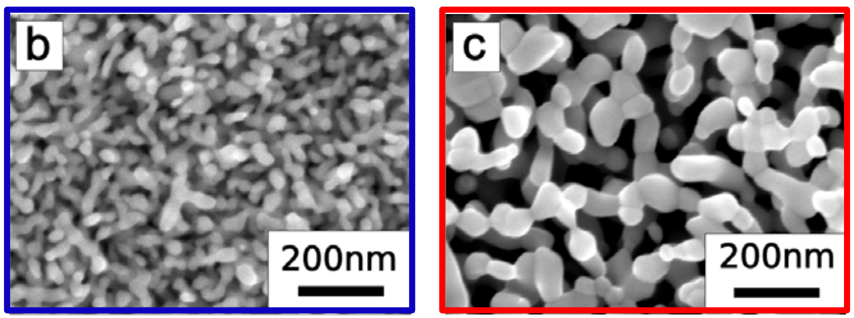
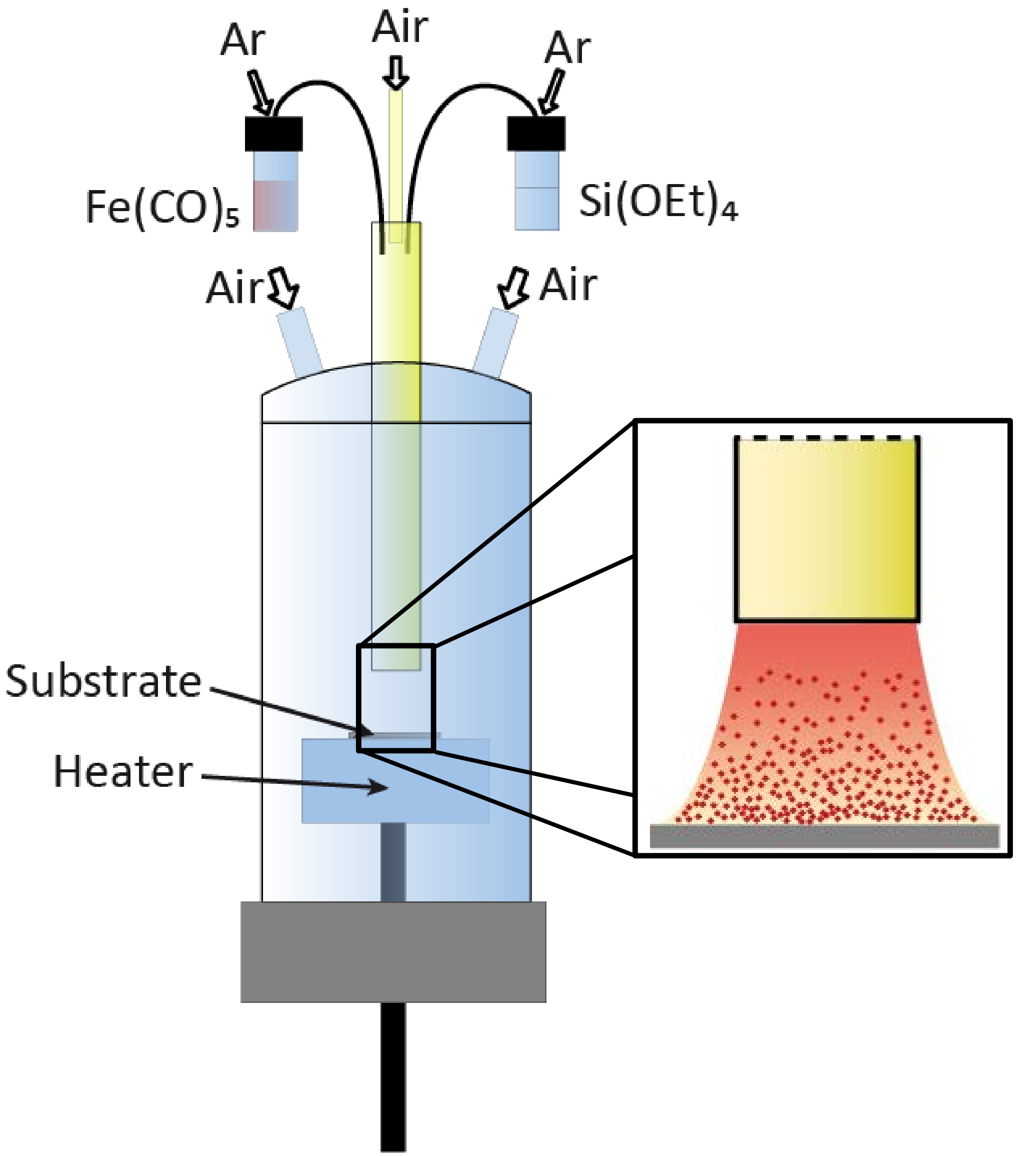
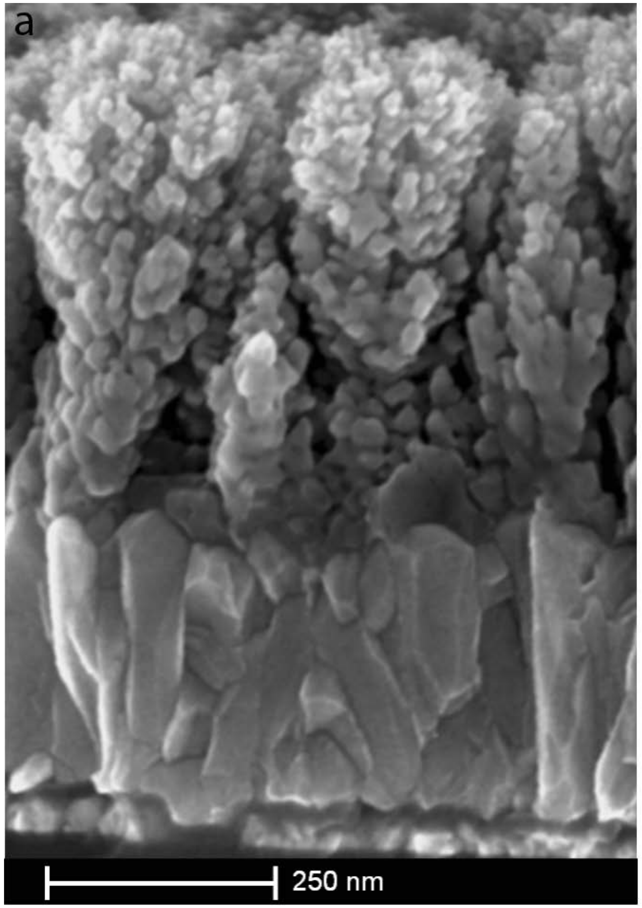




Nano Lett. ***2010***, 10, 4155.

Nanostructured films by APCVD

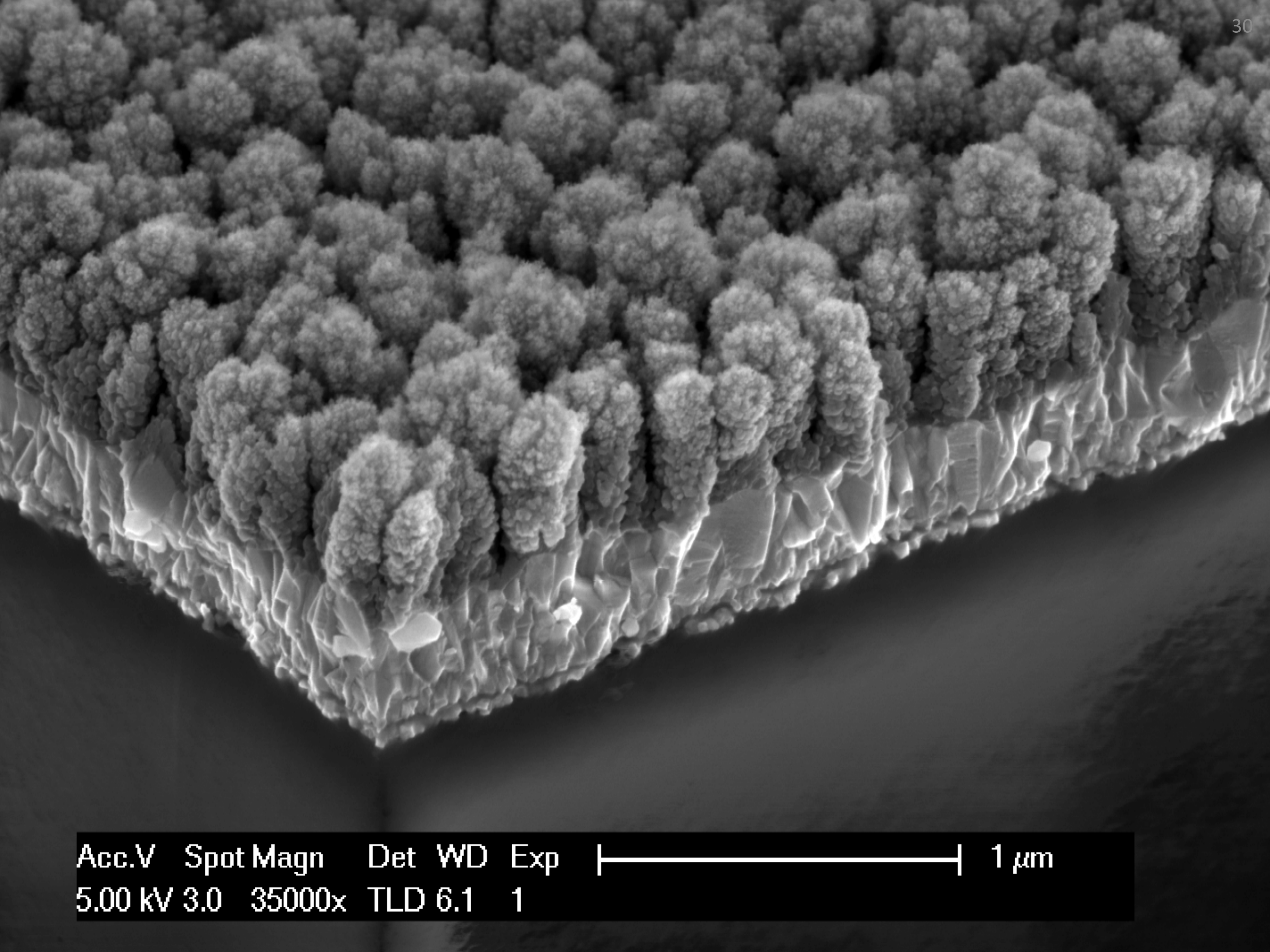




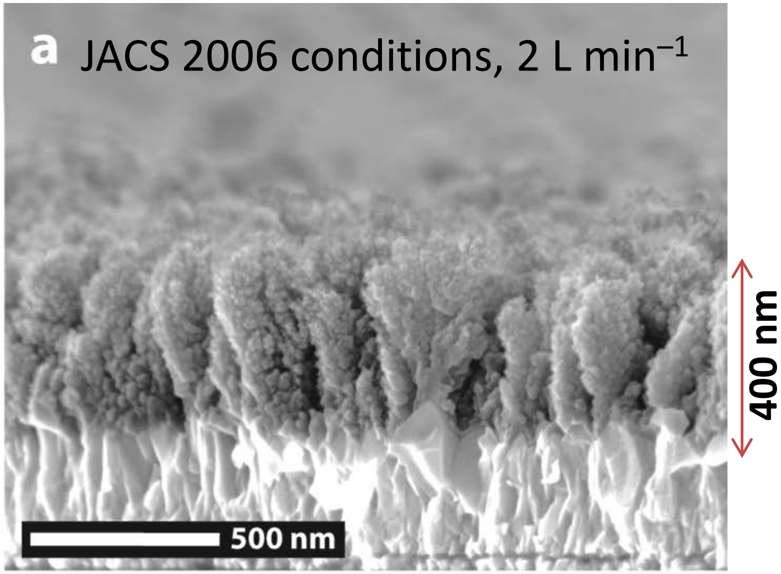
Si-doped Fe_2O_3

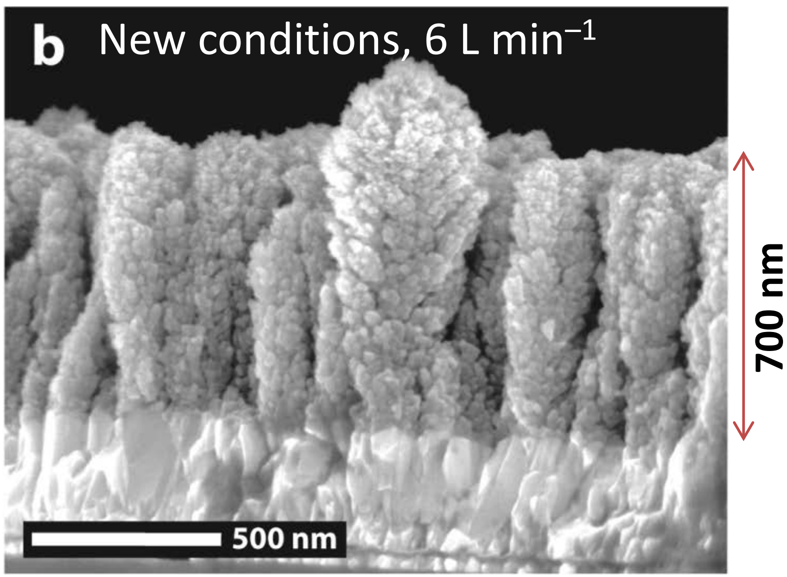
Substrate ($F:SnO_2$)

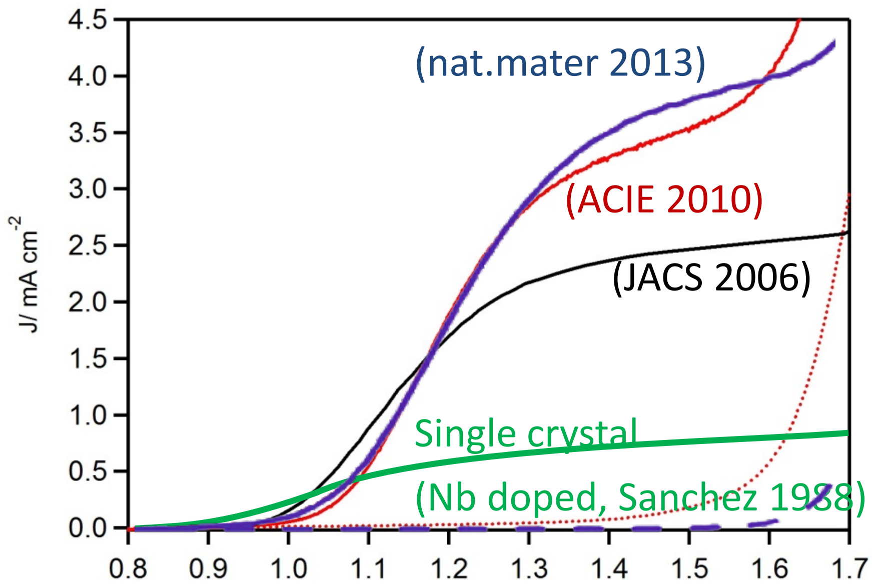
J. Am. Chem. Soc. ***2006,*** 128, 15714-15721.

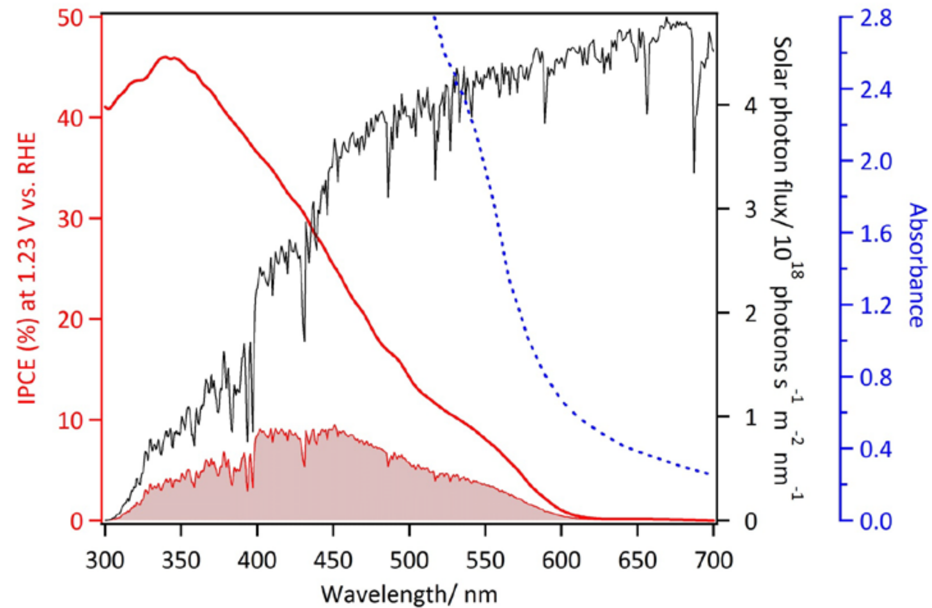

Acc.V Spot Magn Det WD Exp
5.00 kV 3.0 35000x TLD 6.1 1
1 μm

Controlling the particle/precursor ratio

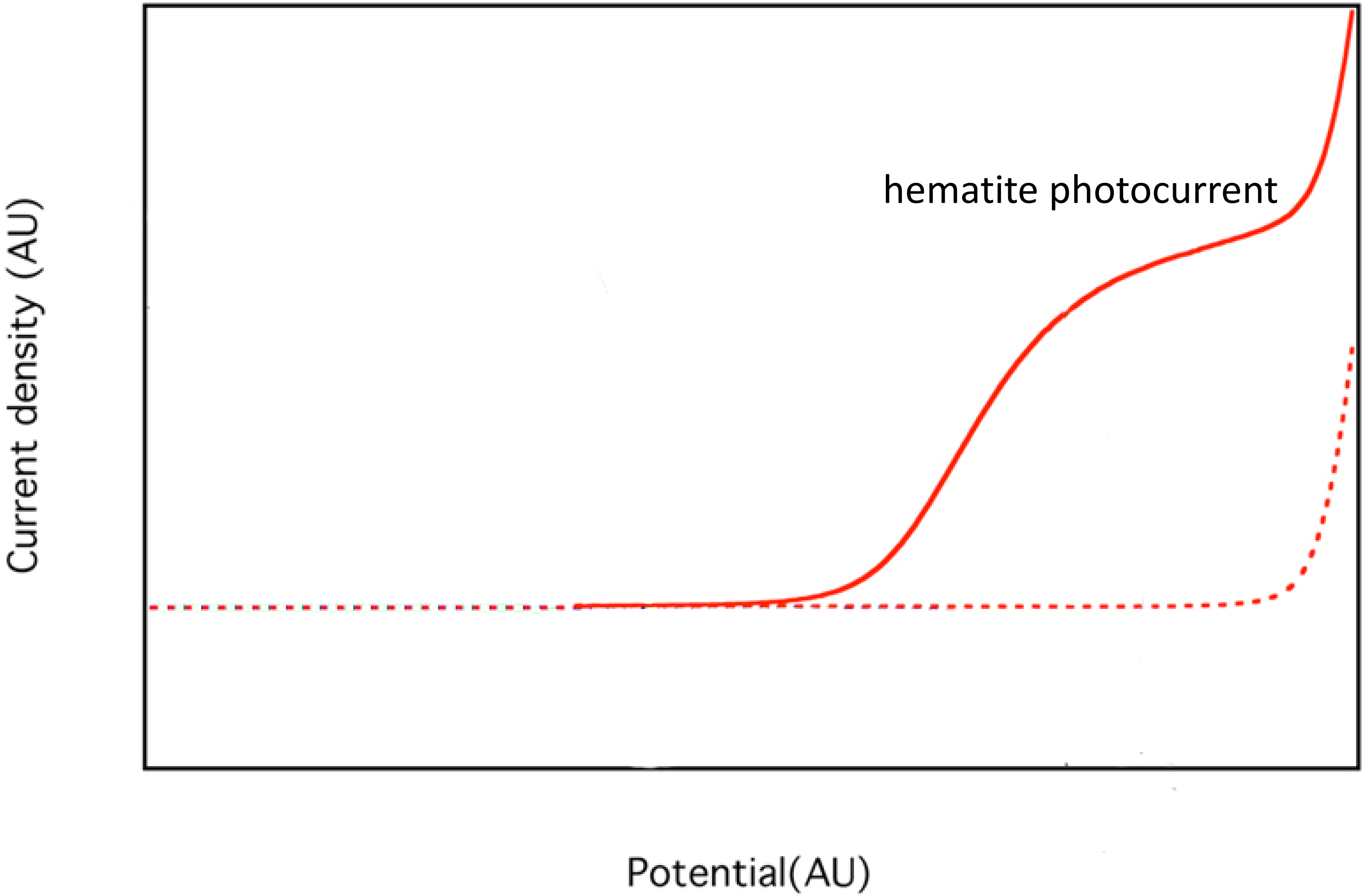








Photoanode/DSC tandem device



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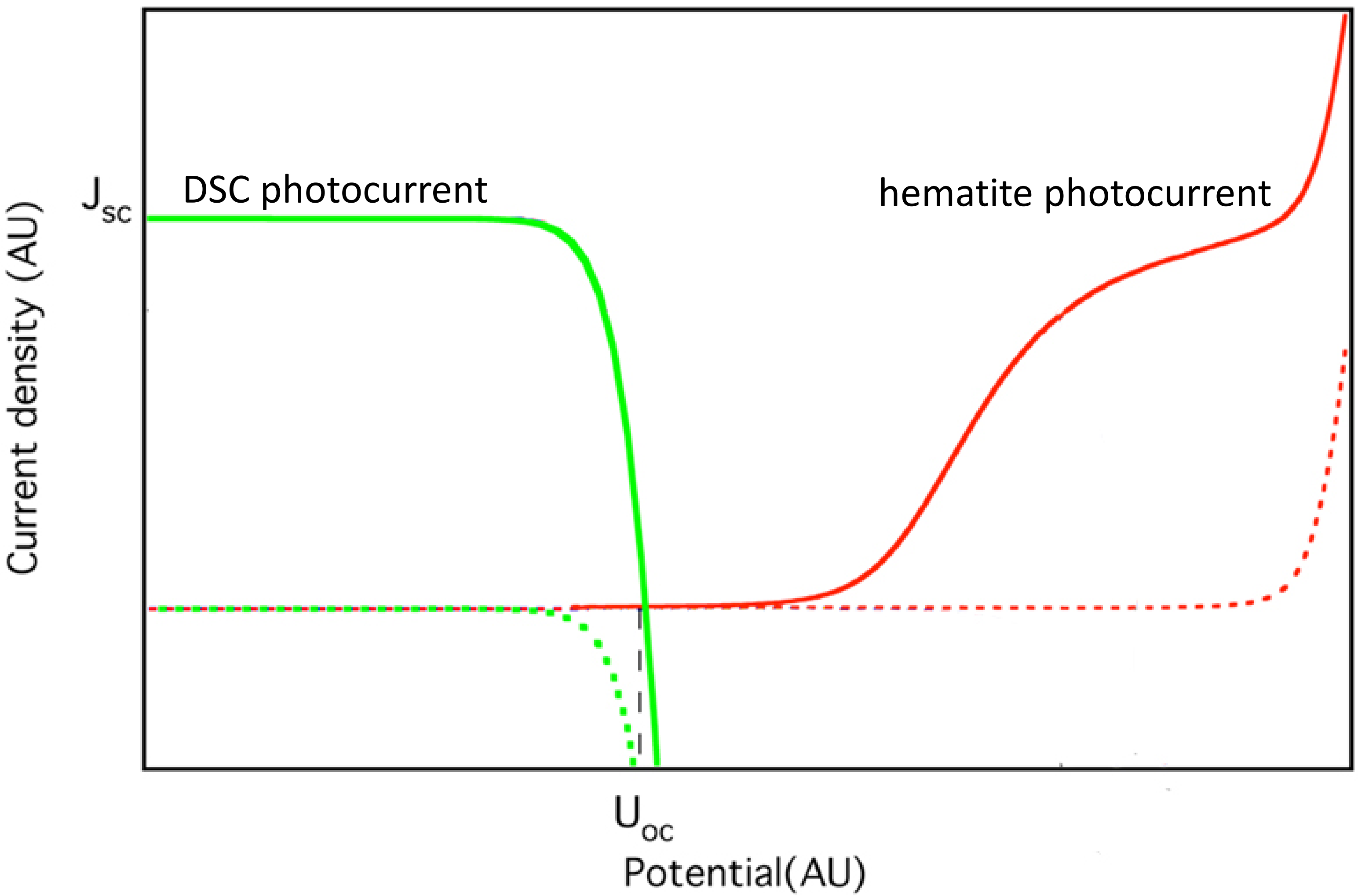
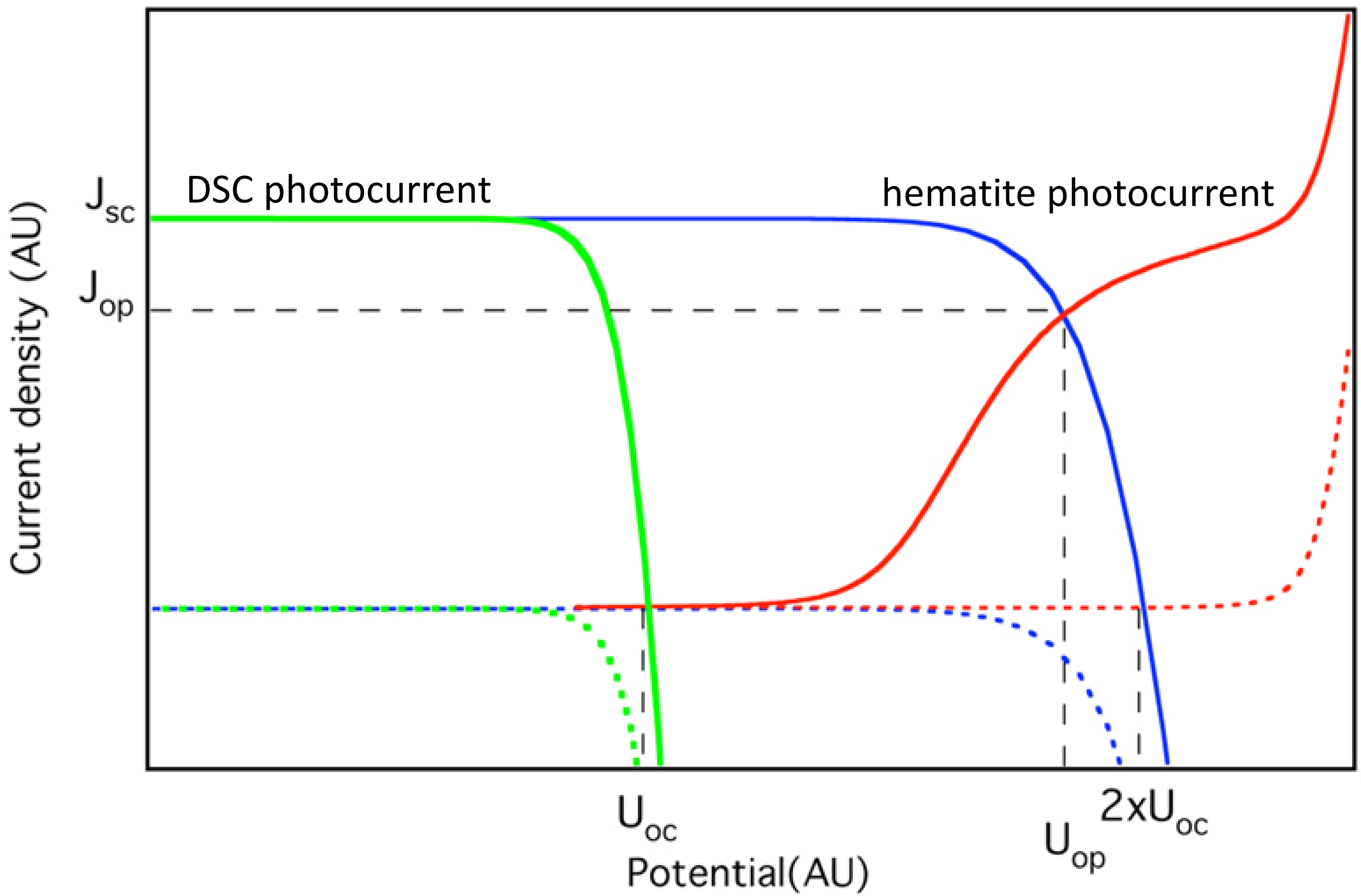
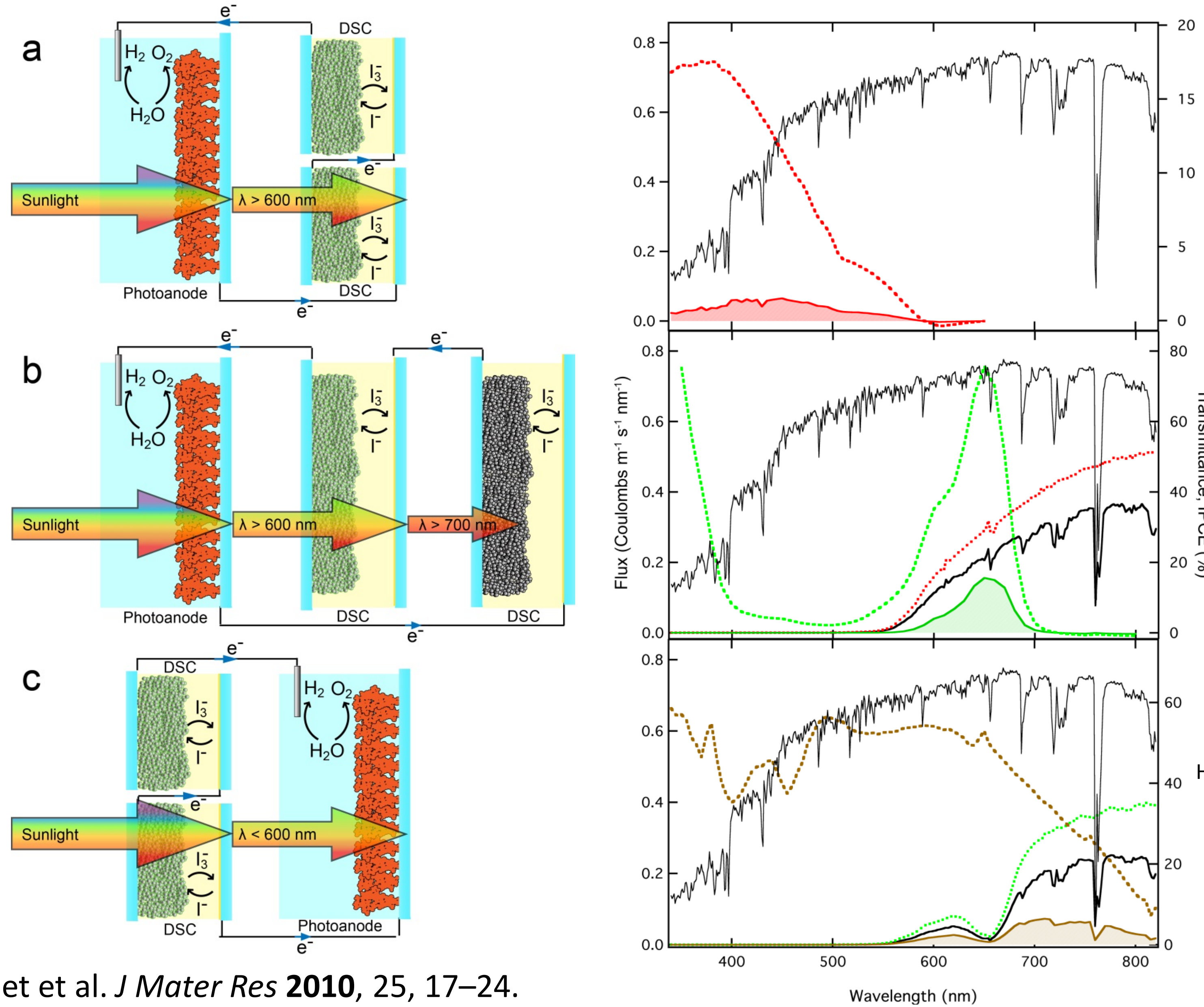
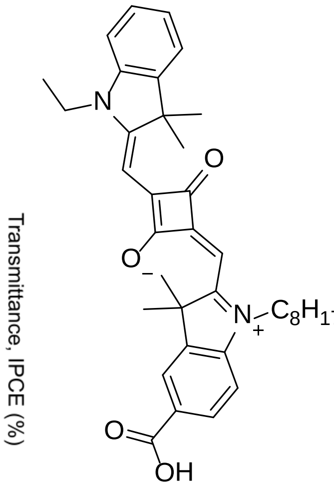


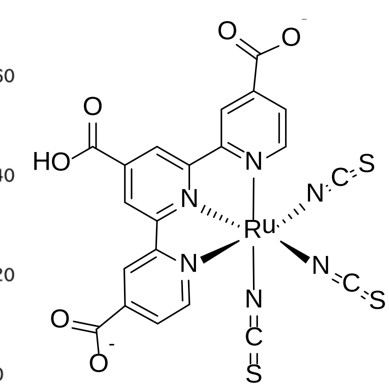
Photoanode/DSC tandem device



T6 tandem devices

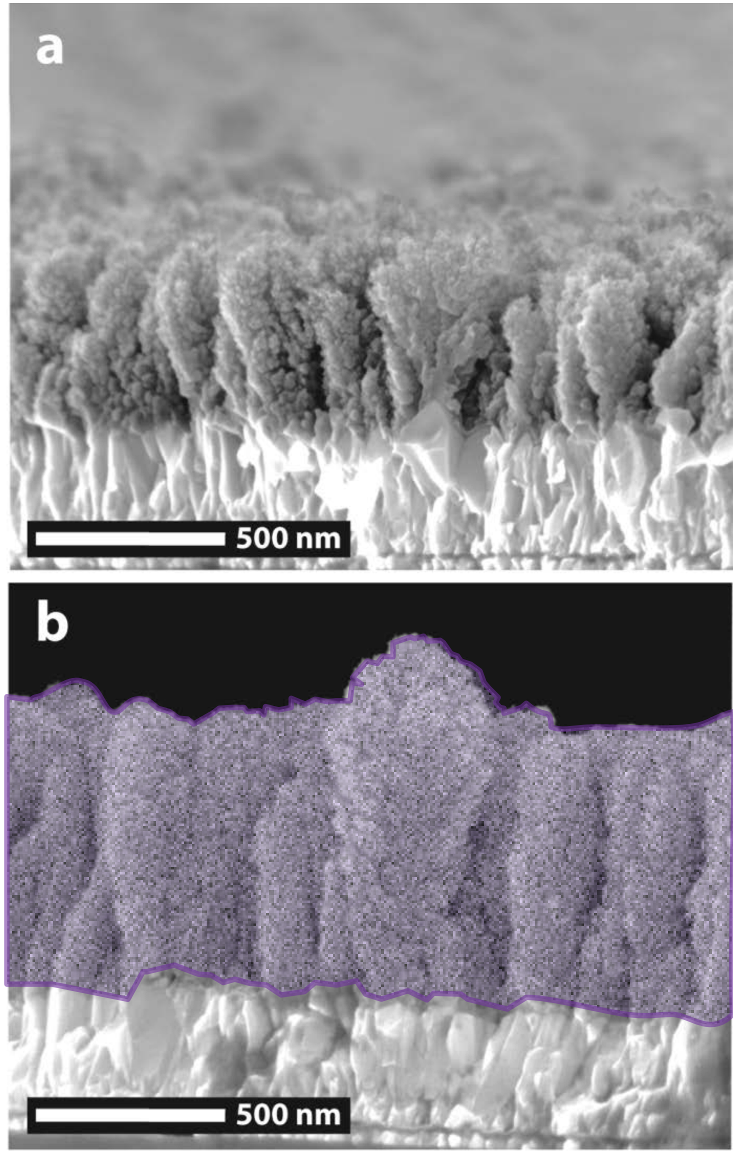




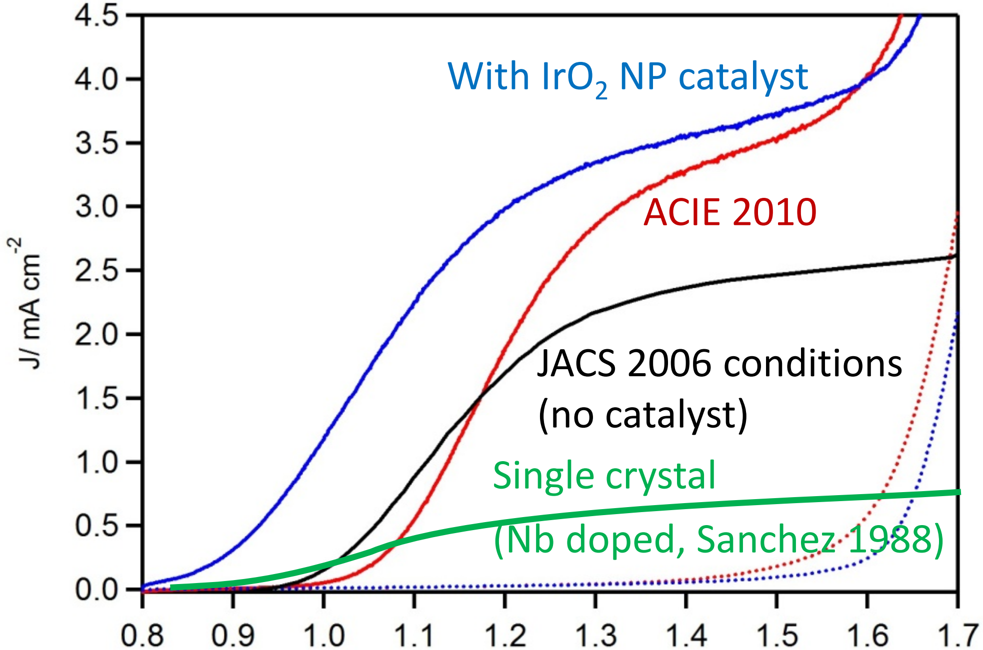


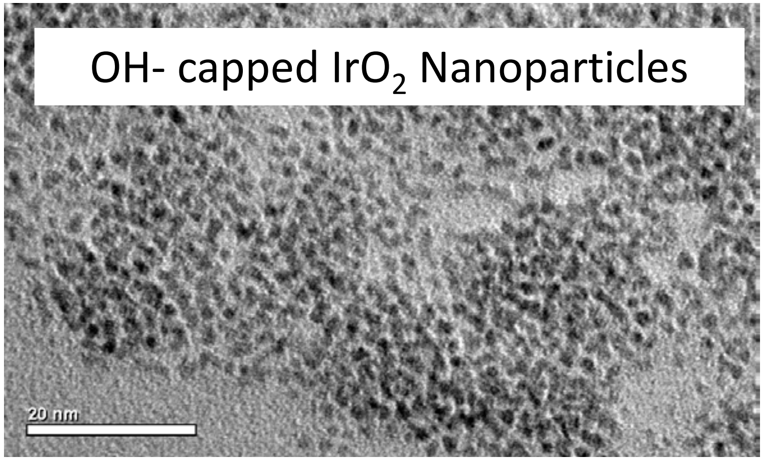
Brillet et al. *J Mater Res* **2010**, 25, 17–24.

Adding IrO_2 NP catalyst



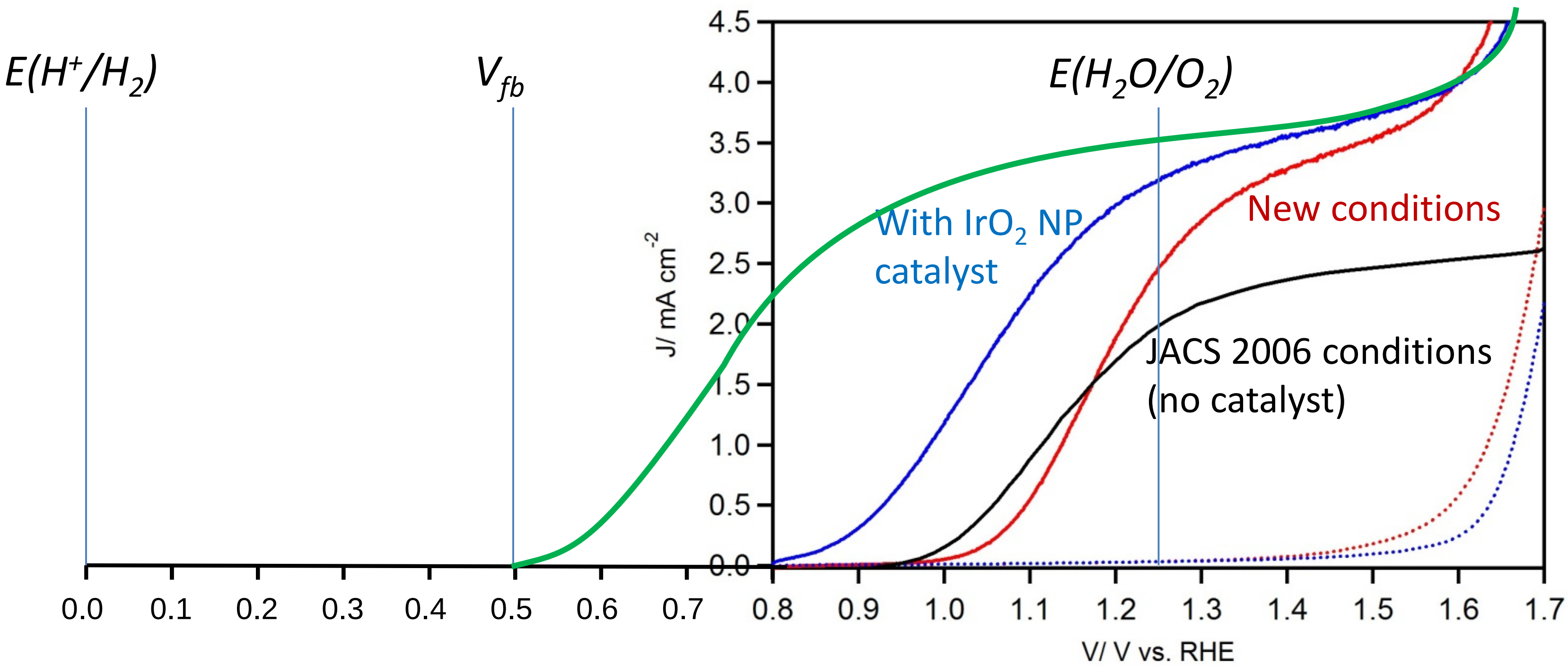
Electrophoretic deposition





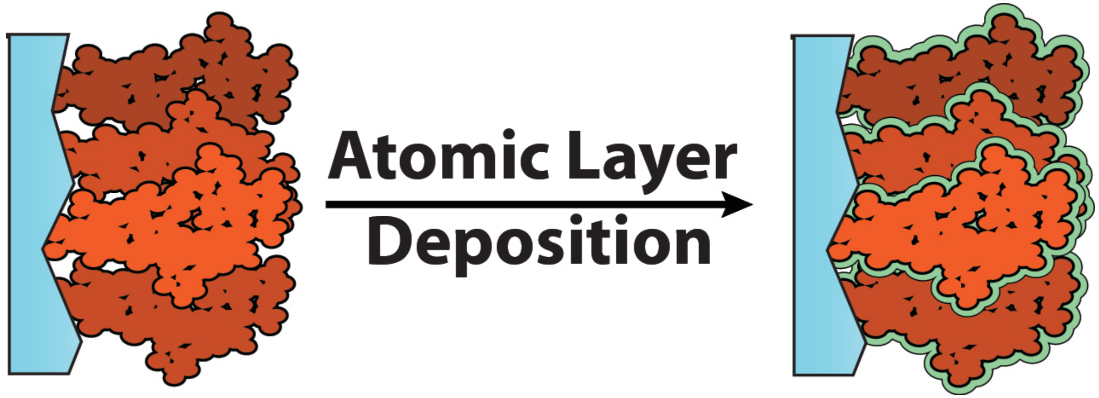
Angew. Chem. Int. Ed. ***2010***, 49, 6405.

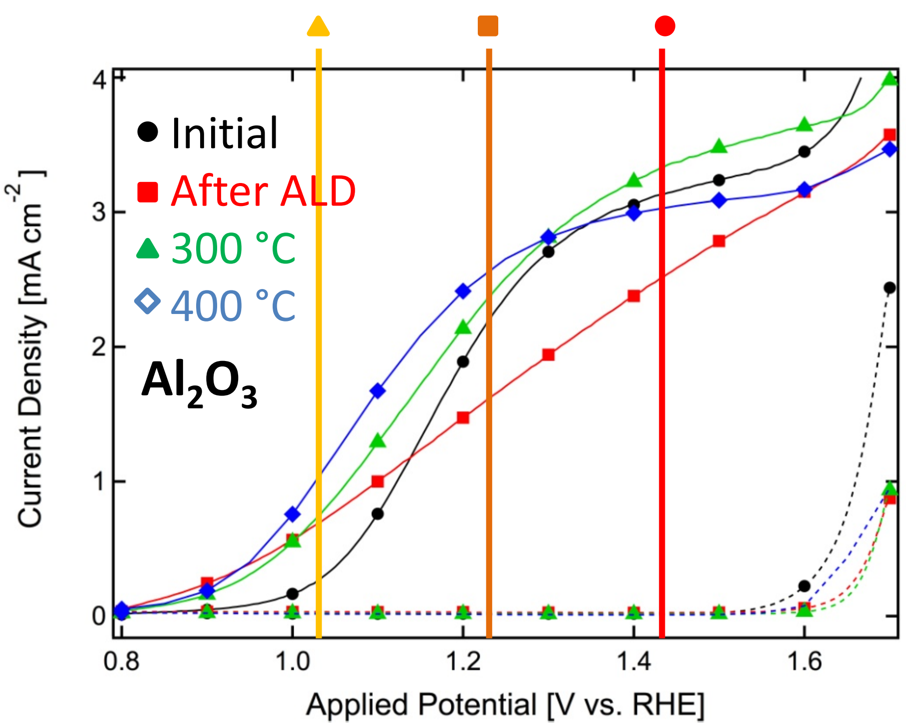
A large overpotential remains

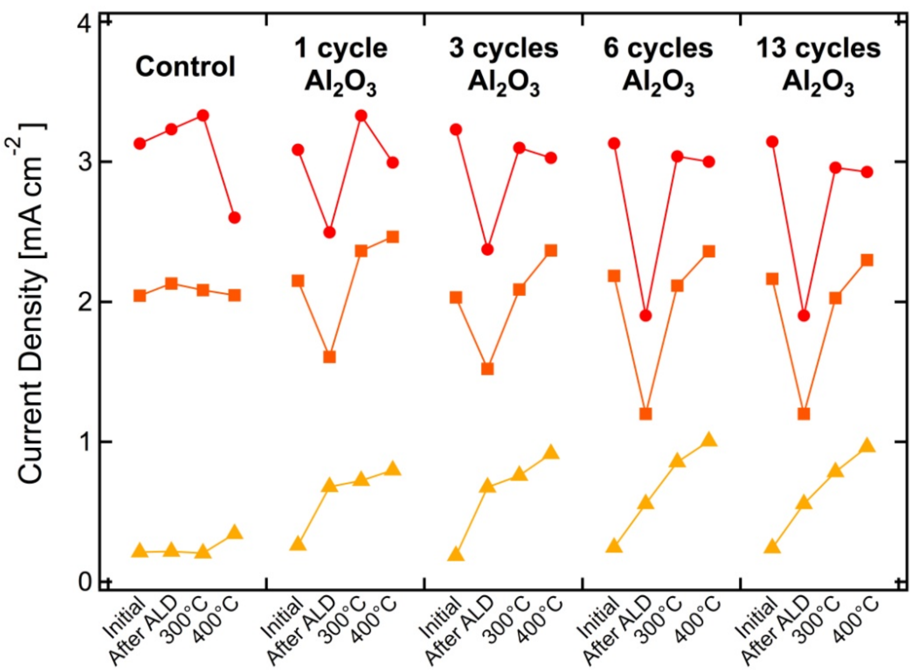


- Overpotential of 500 mV remains even with state of the art OER catalyst
- What else could be limiting the overpotential?

ALD surface treatment

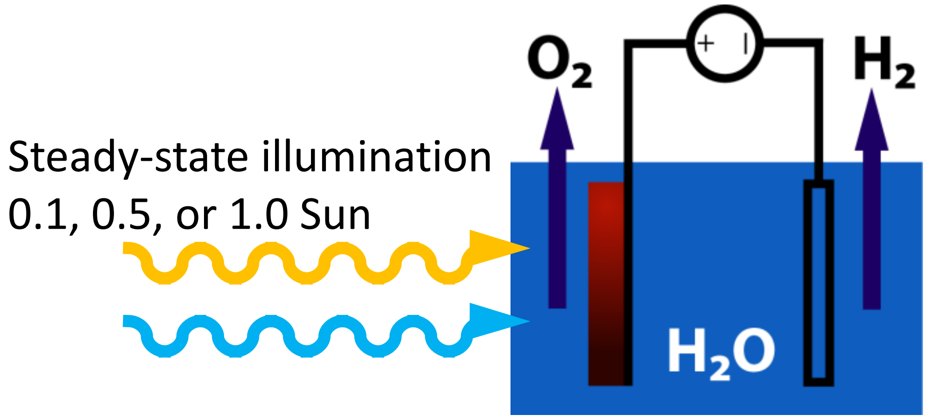


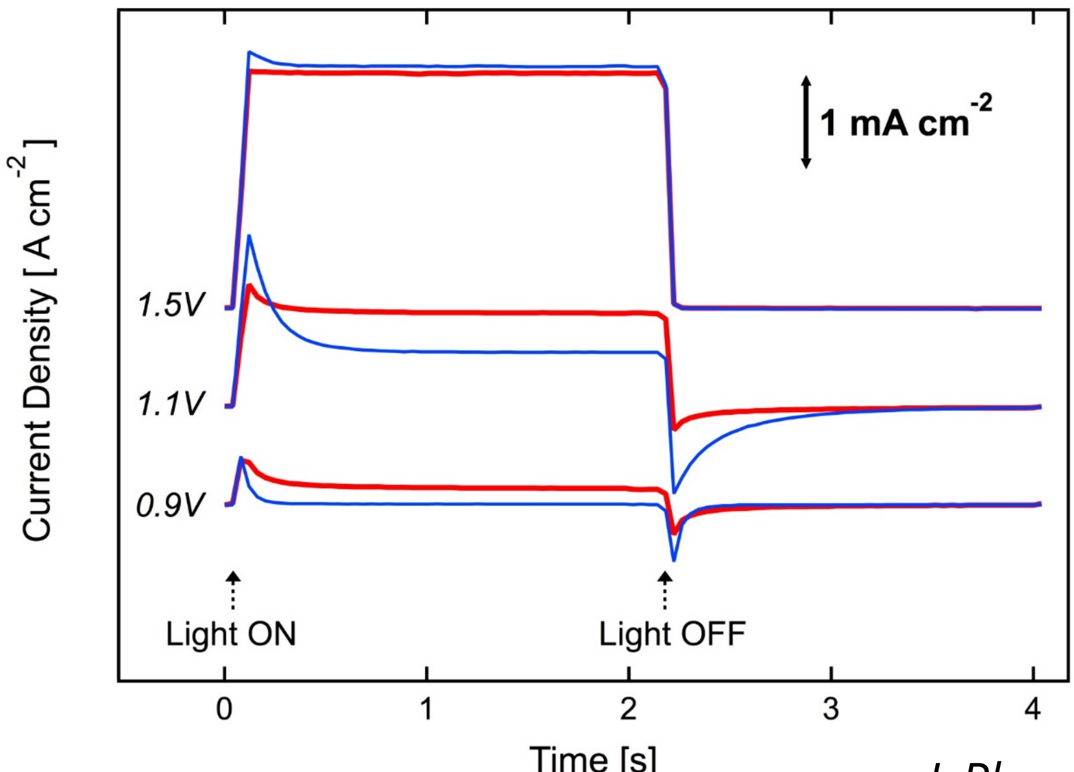


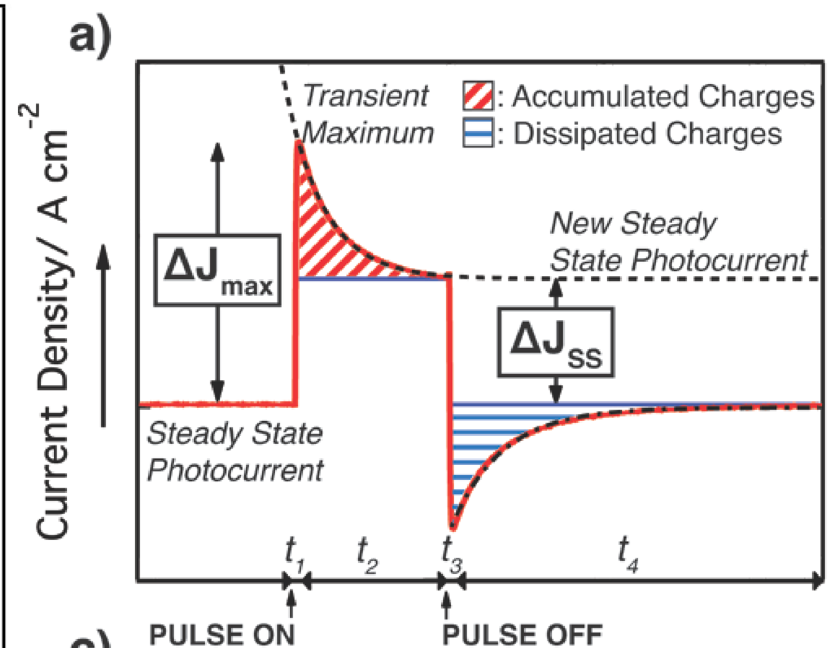


Chem. Sci. ***2011***, *2*, 737-743.

Transient photocurrent analysis

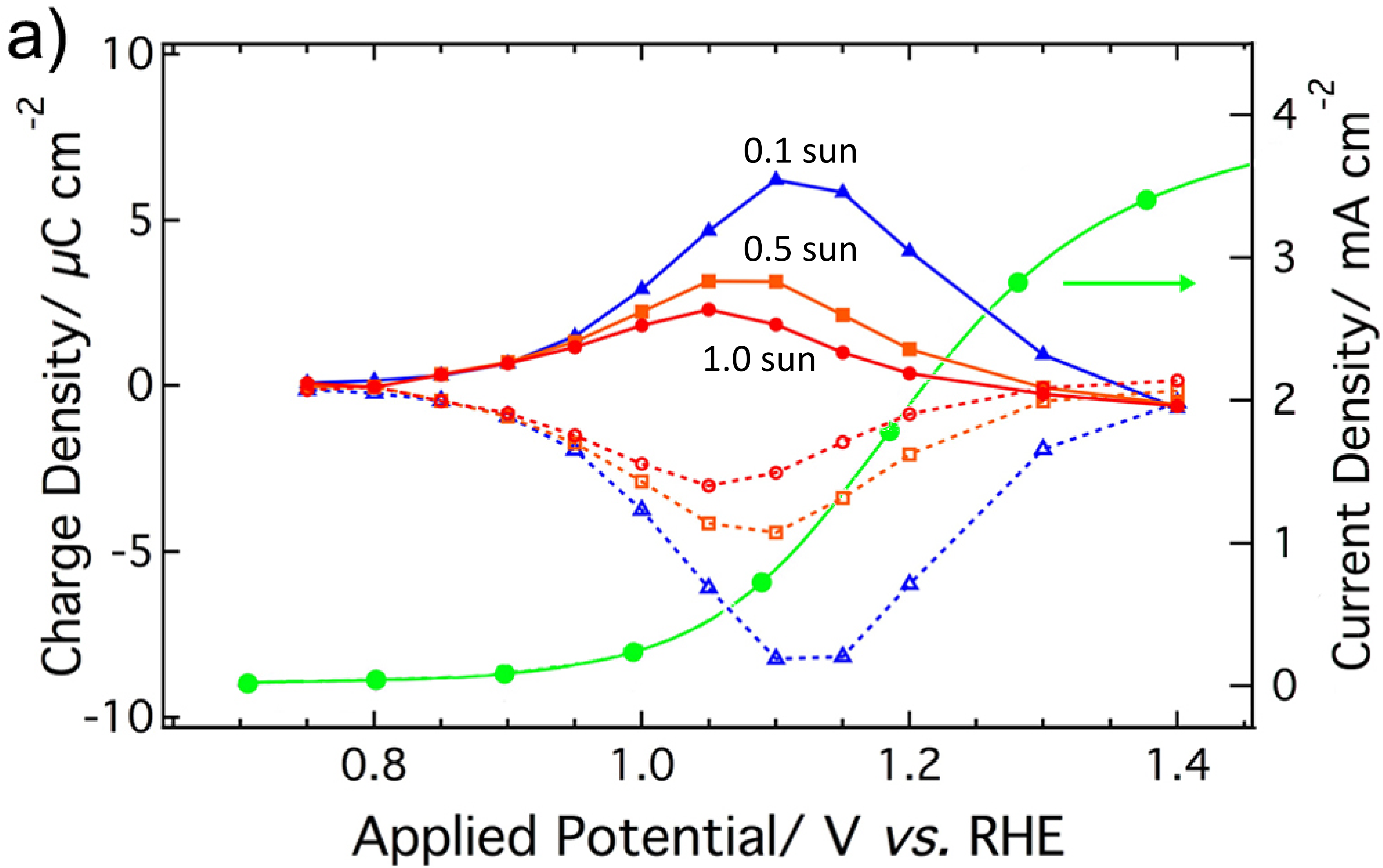






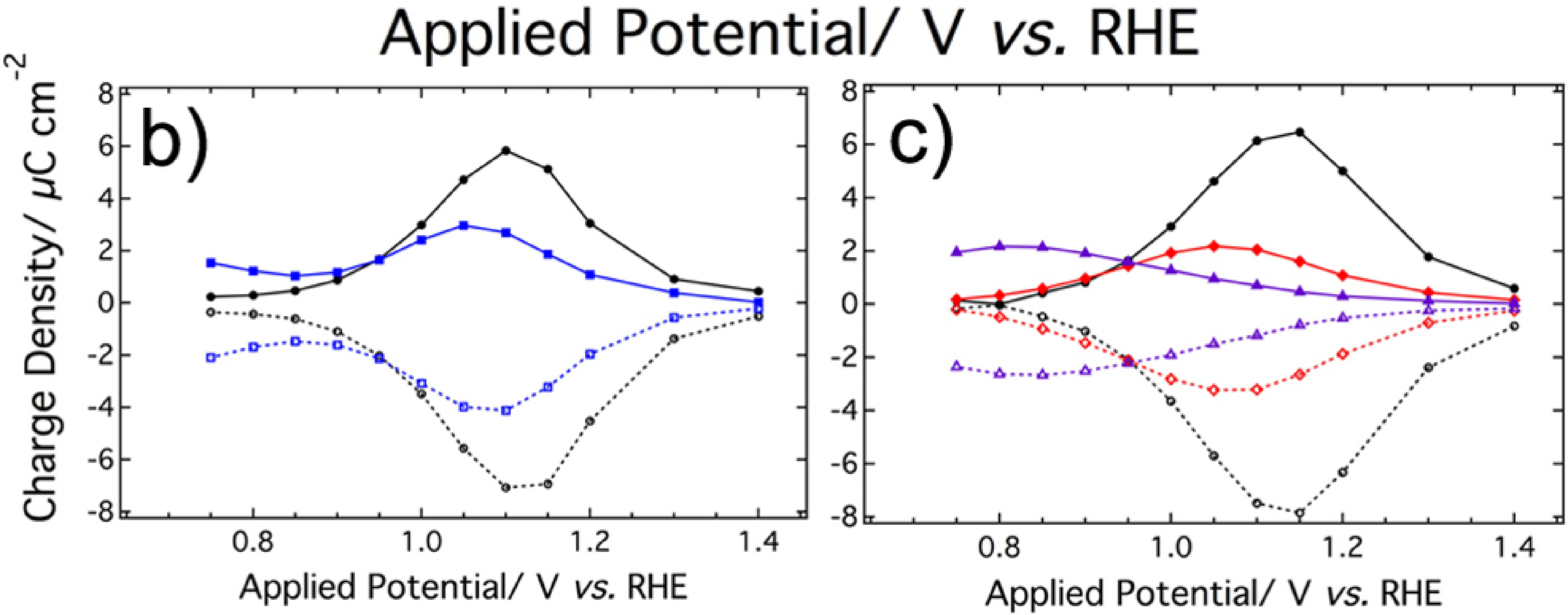
J. Phys. Chem. C **2012,** *116* (51), 26707-26720.

Catalysis versus surface state passivation



J. Phys. Chem. Lett. **2013**, *4*, 1624-1633.

Catalysis versus surface state passivation



- Indicates that 2 separate processes are causing the large overpotential in hematite photoanodes
- Suggests that surface electron traps are contributing to the large overpotential through "Fermi level pinning."

J. Phys. Chem. Lett. **2013**, *4*, 1624-1633.

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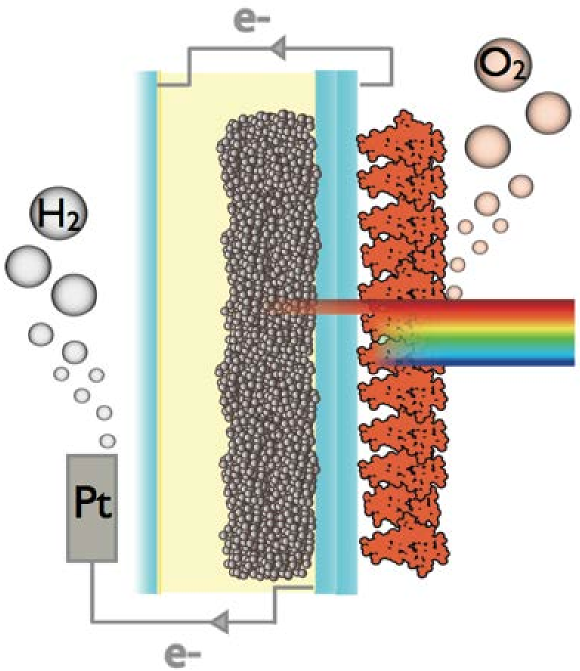
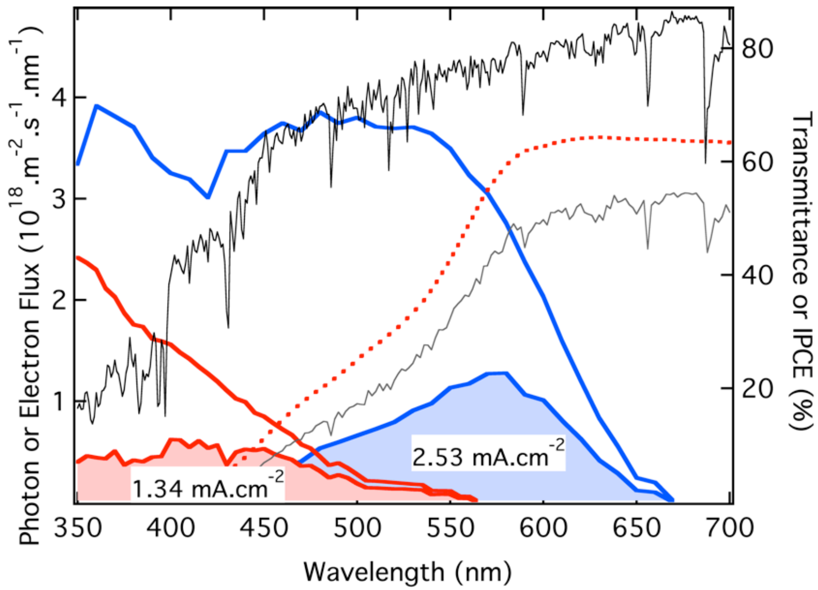
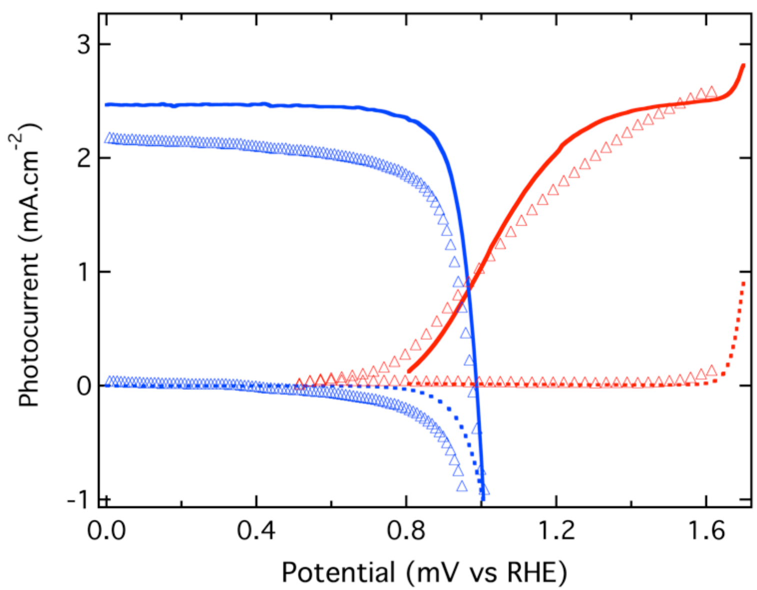
A D4 tandem cell with Hematite/DSC





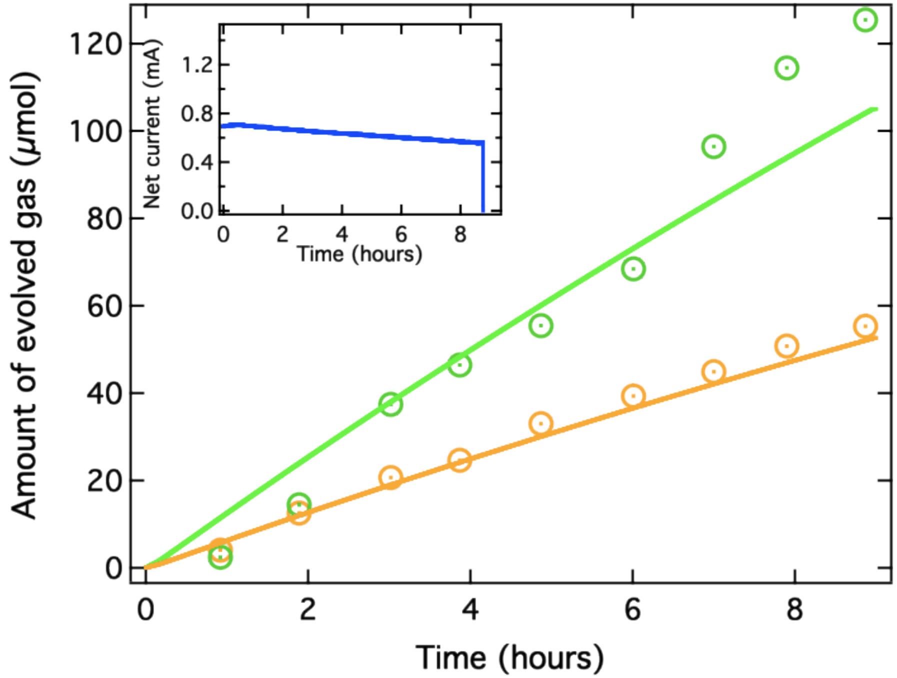


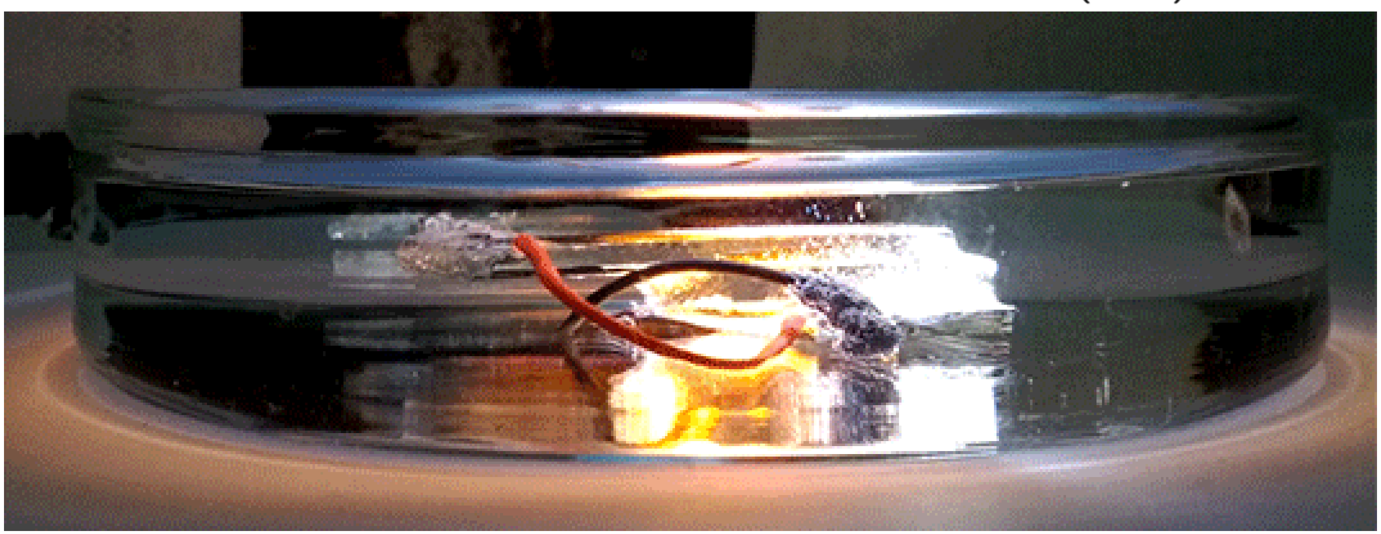
Fe_2O_3 - DSC tandem cell

- Predicted by calculation: **0.61 mA.cm^{-2}**
- Measurement *in situ* : **0.78 mA.cm^{-2}**
- Measured with ammeter: **0.95 mA.cm^{-2}**

Efficiency: 1.4 %STH

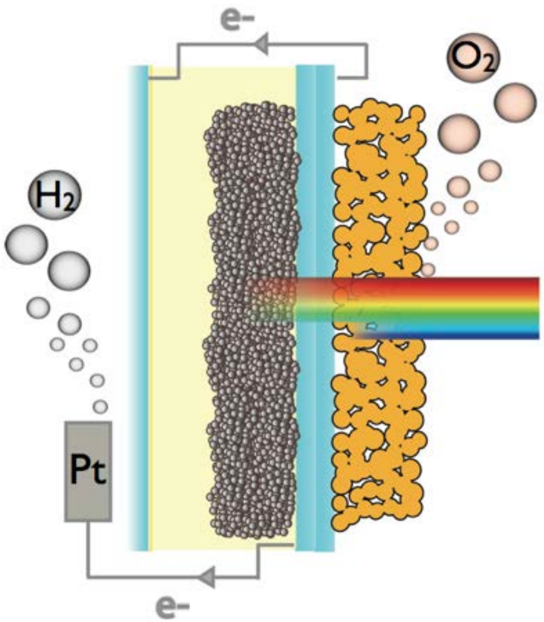
Tandem cell with Fe_2O_3 anode under operation

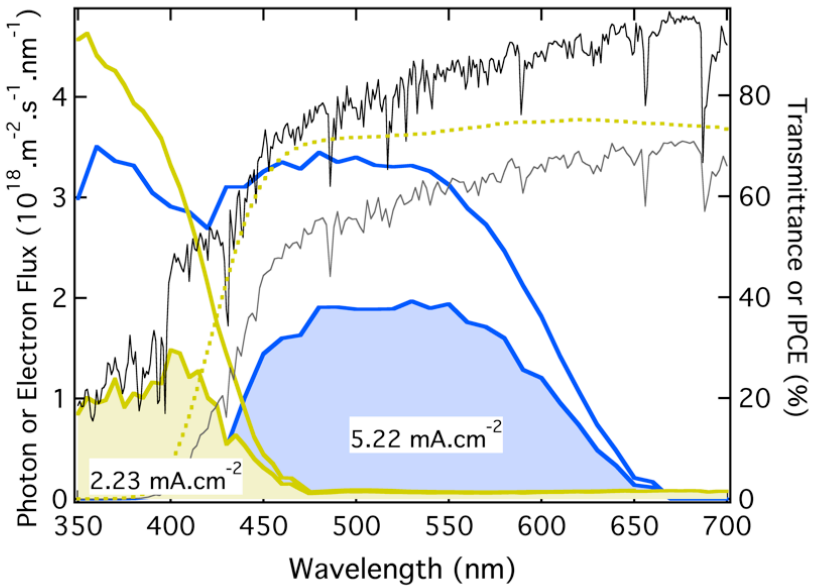


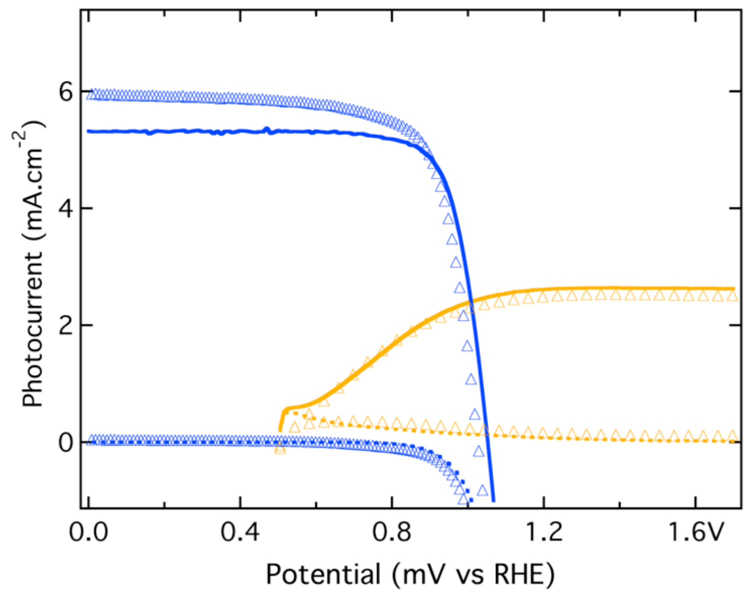


Nat. Photonics **2012**, *6*, 824-828.

WO_3 tandem device





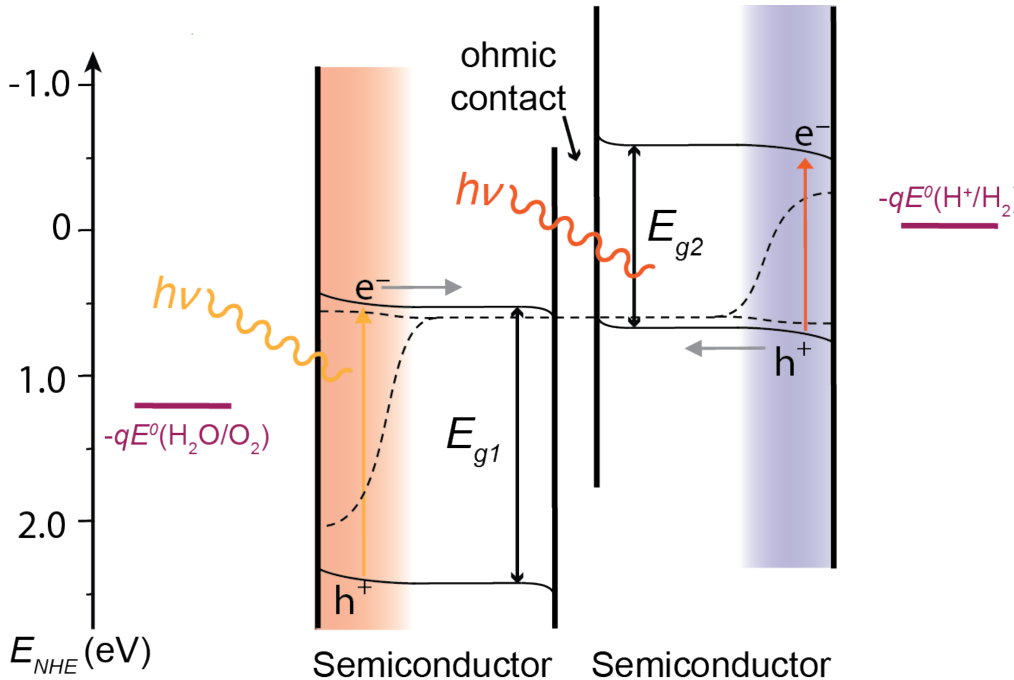


WO_3 - DSC tandem cell

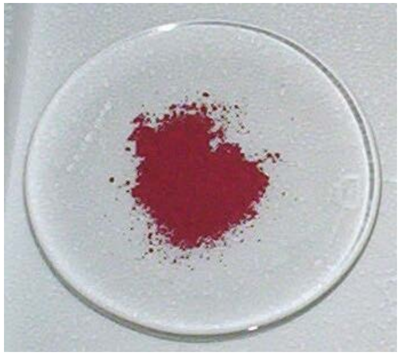
- Predicted by calculation: **2.35 mA.cm^{-2}**
- Calculation validated by in situ-measurement
- Measured with ammeter: **2.52 mA.cm^{-2}**

Efficiency: 3.6 %STH

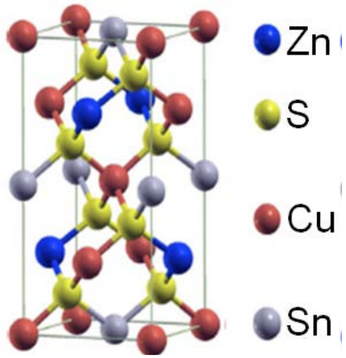
Photocathodes for hydrogen evolution



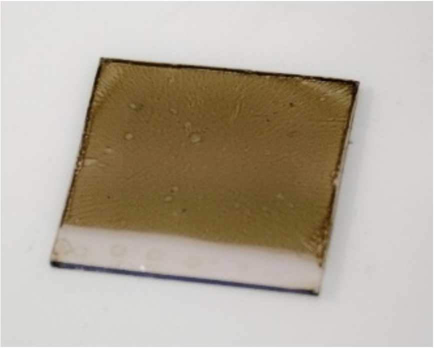
Photocathode materials



Copper(I) oxide

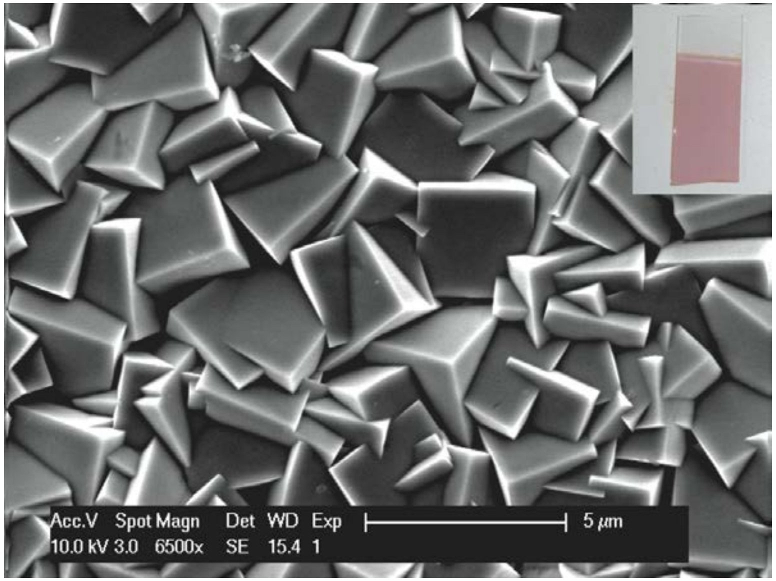


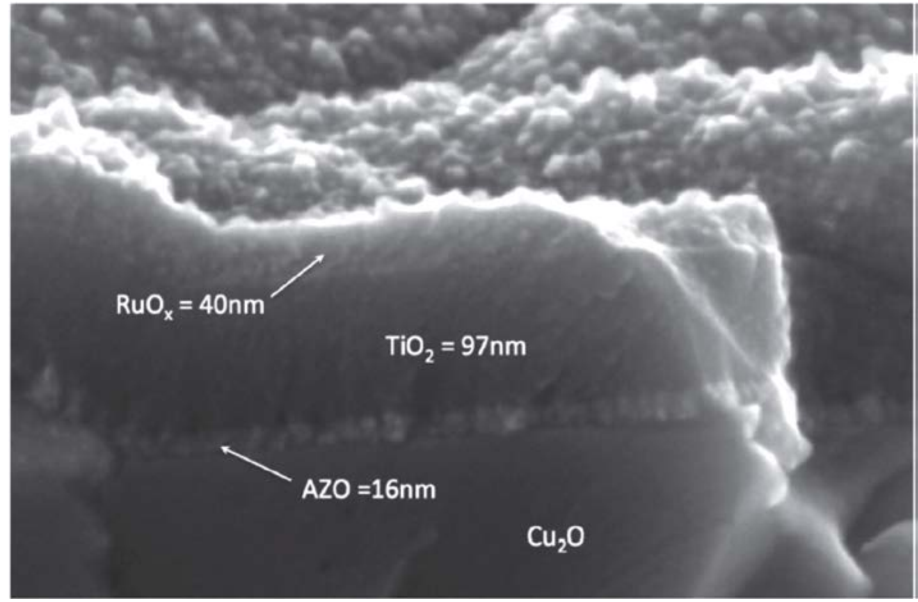
Cu_2ZnSnS_4



$CuFeO_2$

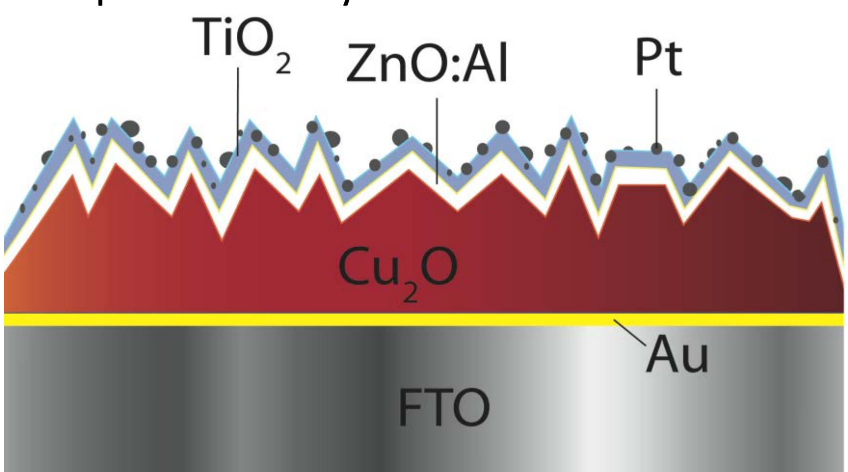
Protective layers enhance stability

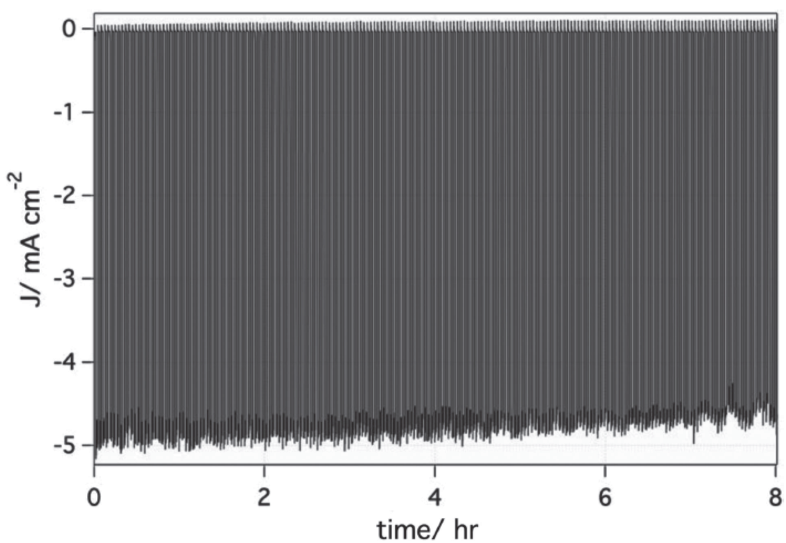




Electrodeposition (0.2 M $CuSO_4$, 3 M lactic acid with 0.5 M K_2HPO_4 buffer, pH 12, 2 M KOH)

ALD protective layers

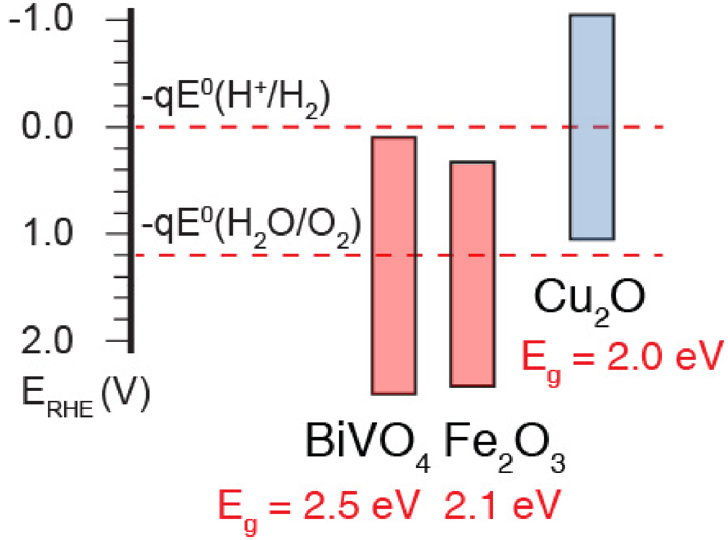


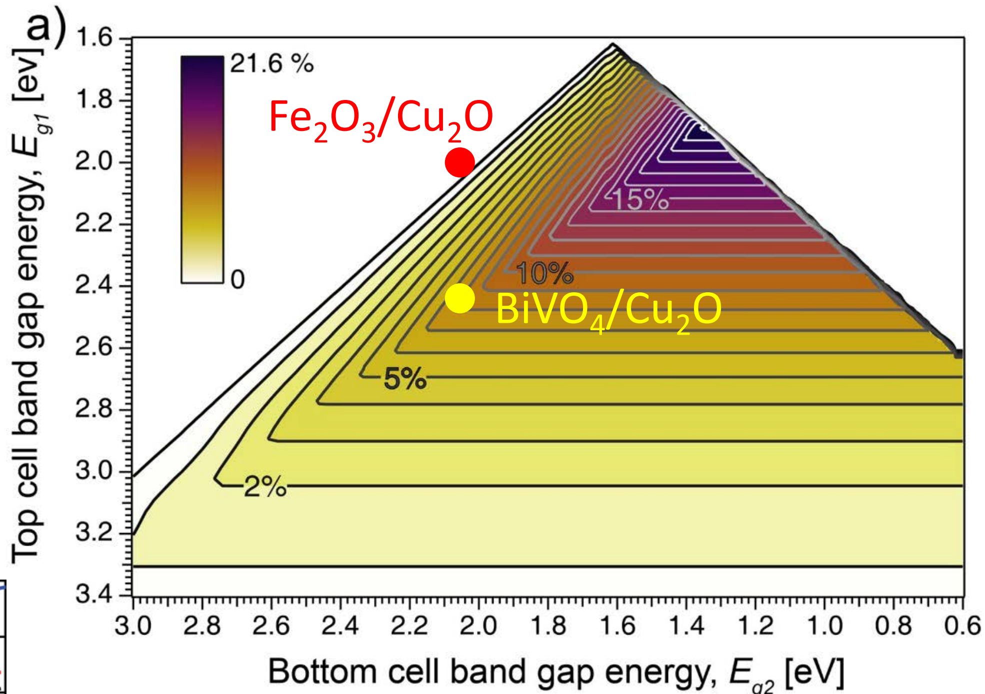


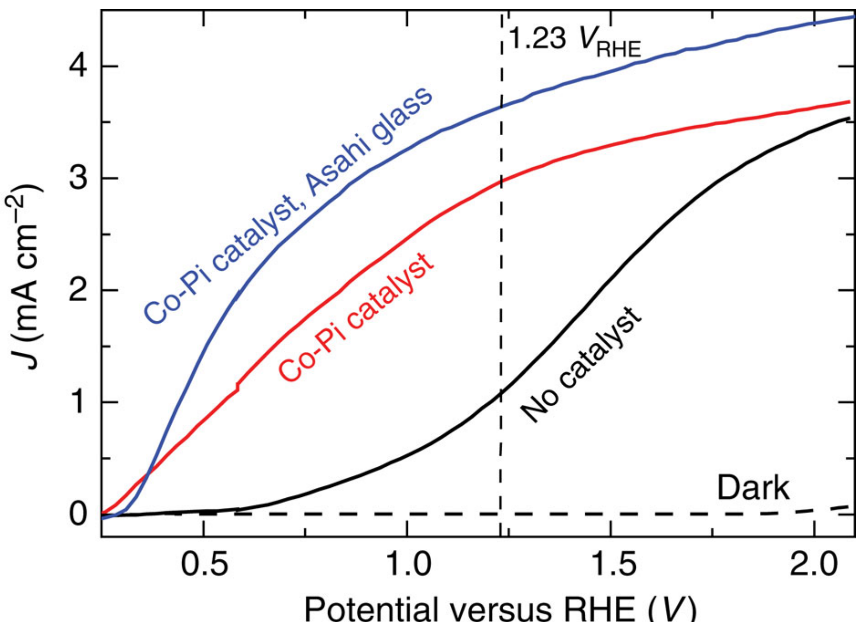
Nature Materials **2011**, *10, 456-461.*

S. David Tilley et al. *Adv. Funct. Mater.* **2014,** *24* (3), 303-311.

Copper oxide based tandem cells



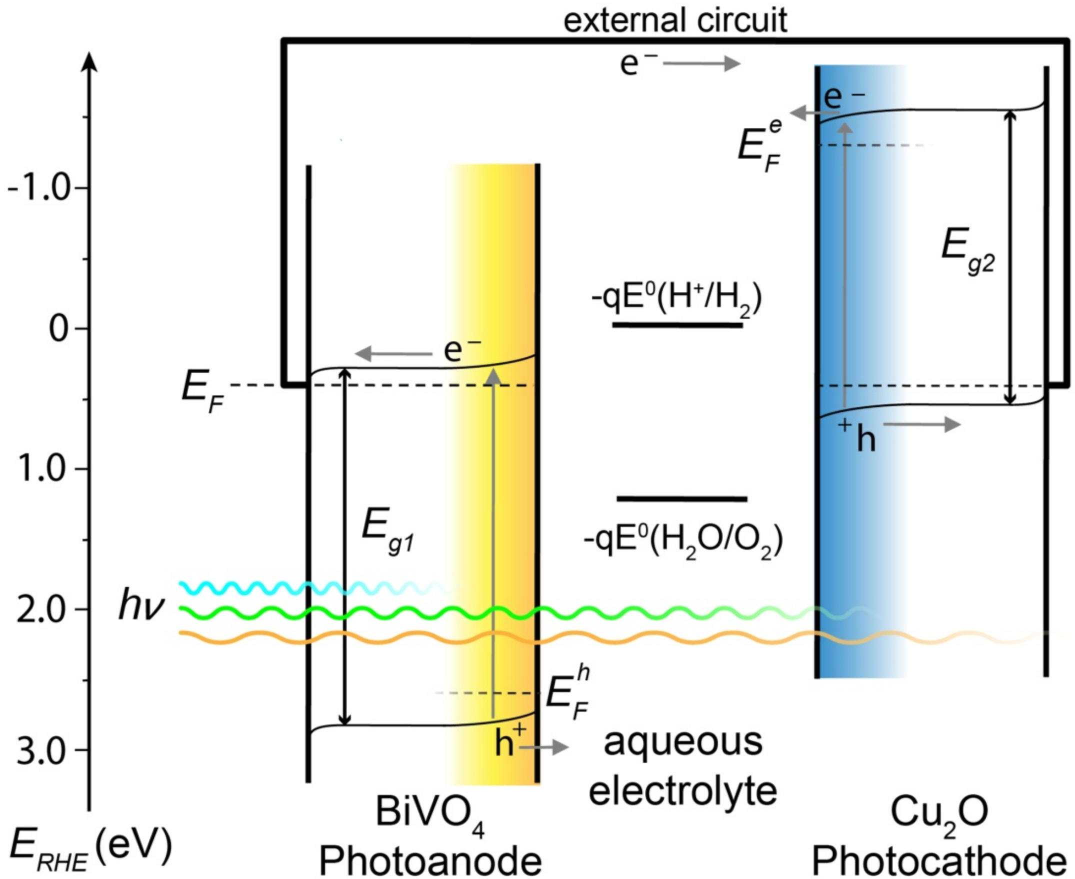




$BiVO_4$

F.F. Abdi, R. van der Krol et al. *Nature communications* **2013**, 4, 2195

$W:BiVO_4|Cu_2O$ Tandem cell configuration



FTO/W:$BiVO_4$/Co-Pi

W:$BiVO_4$ deposited by spray pyrolisis

***Cat*: Co-Pi potentiostatic photodeposition**

van de Krol's group

FTO/Au/Cu_2O/Al:ZnO/TiO_2/RuO_x

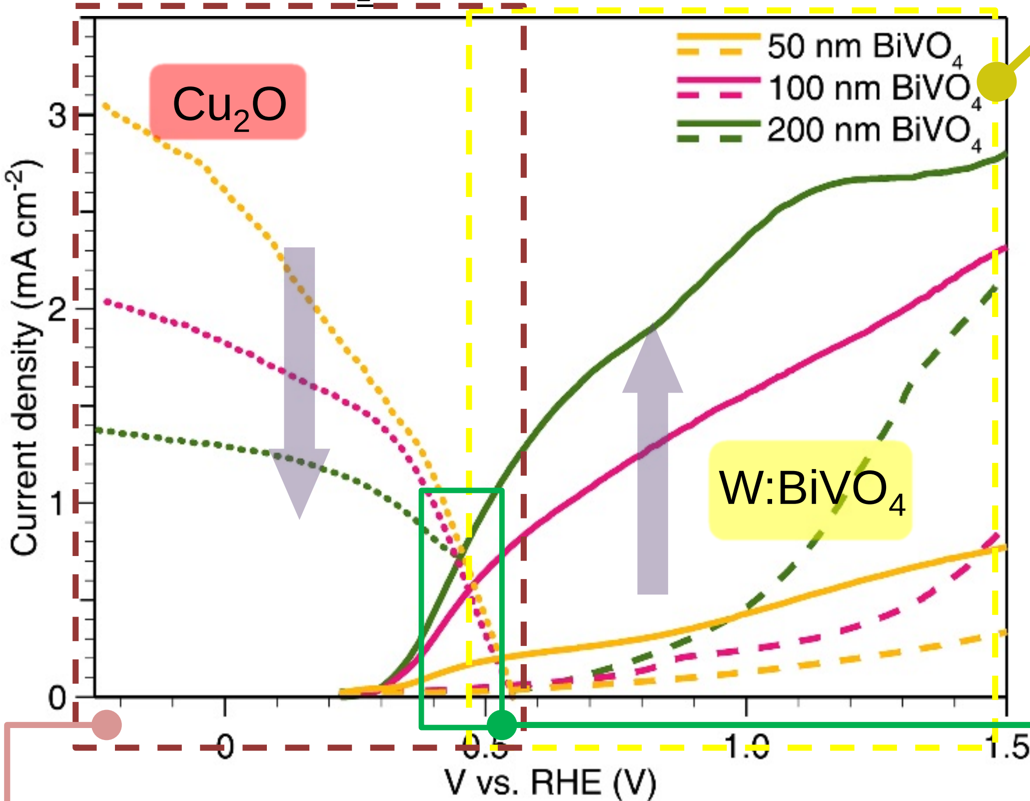
Electrodeposited Cu_2O

AZO and TiO_2 Atomic Layer deposition

***Cat*: RuO_x galvanostatic photodeposition**

$W:BiVO_4|Cu_2O$ Tandem cell analysis

Performance of Cu_2O with light restrictions imposed by $W:BiVO_4$



J-V (3-electrode cell)

-Thicker films give rise to higher activity (better light harvesting)

- CoPi deposition drastically enhances the photocurrents

- Onset photocurrent :+ 0.3 V vs RHE (E_{fb}=0.1 V)

J-V (3-electrode cell)

- The thicker the $BiVO_4$ layer, the lower the performance (limited light transmission)

- Onset photocurrent :+ 0.5 V vs RHE (E_{fb}=0.8 V)

Expected operating current density (intersection)

Thickness $BiVO_4$	**50 nm**	**100 nm**	**200 nm**
J_{sc} /$mAcm^{-2}$	0.20	0.55	0.71
STH / %	0.25	0.68	0.87

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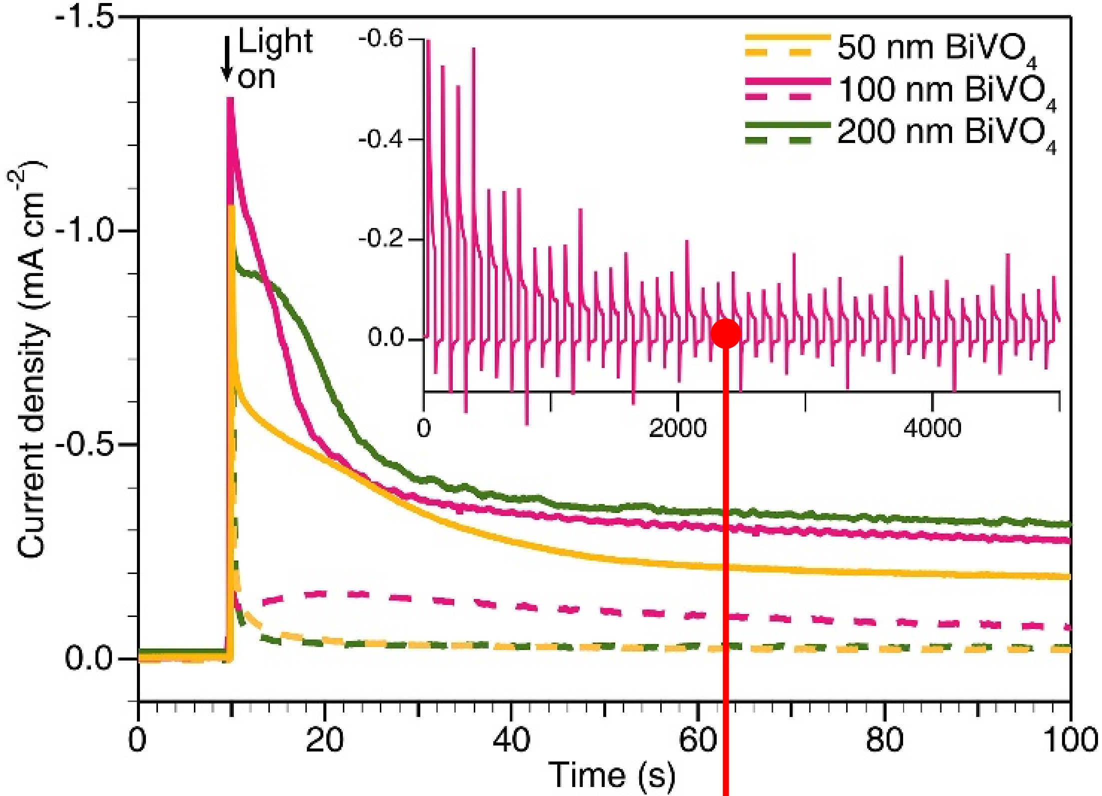
$W{:}BiVO_4|Cu_2O$ Tandem cell performance

Performance of a (2-electrode) TANDEM cell



Without Co-Pi

Spikes decay fast, low currents

Fast recombination

With Co-Pi

Slower spike decay, higher steady currents.

Improved charge separation kinetics

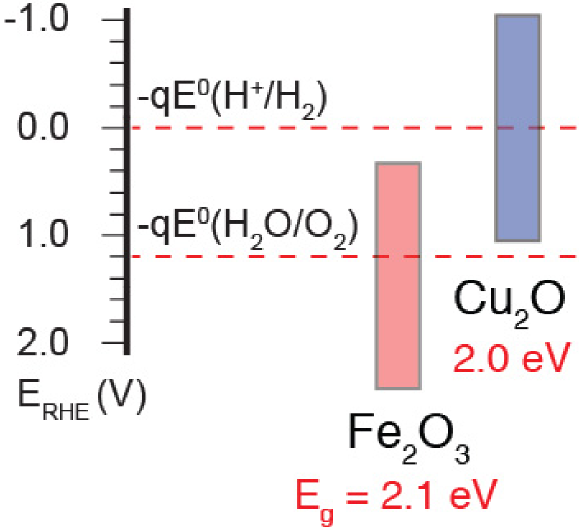
Stability issues

Decrease in photocurrent due to *dissolution of Co-Pi overlayer*

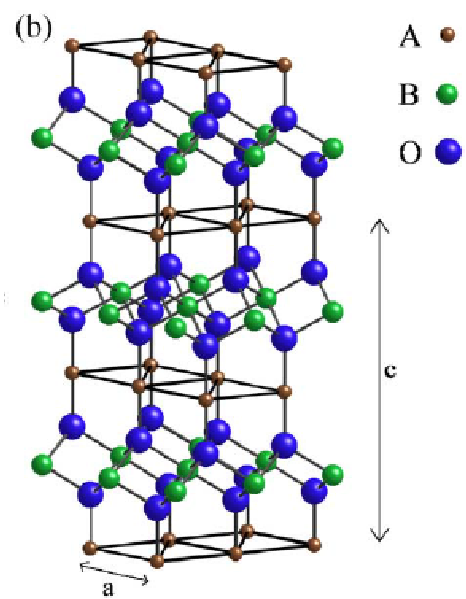
Co-Pi **stable** only at high operating voltages (~ 1 V vs RHE) in pH 6 electrolyte (Nocera and co workers *J. Am. Chem. Soc.* **2012,** *134*, 6326-6336.)

Co-Pi *repair mechanism* (oxidation and reposition of liberated Co^{2+}), the lower the voltage the slower the rate (dissolution favoured).

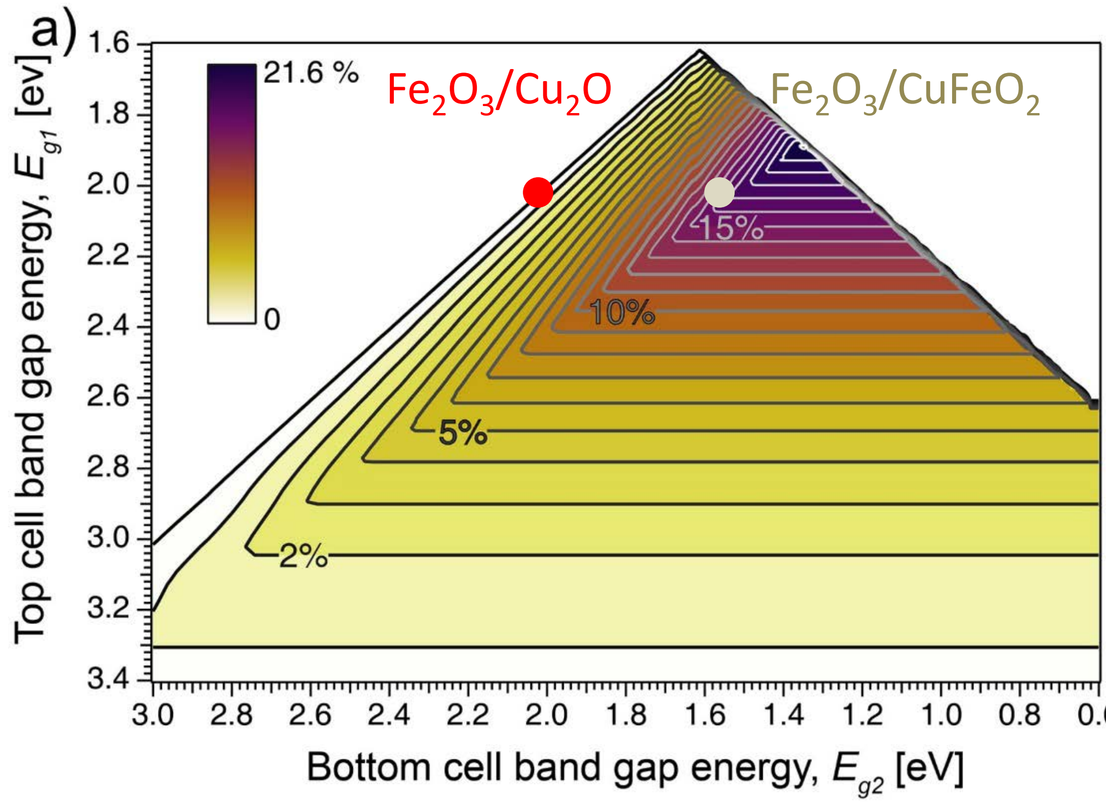
Photoanode/photochathode tandem cells



Delafossites



Thin Solid Films, **2006**, *496*, 146.



Advantages of $CuFeO_2$:
- Strong light absorption (Band-gap 1.5 eV)
- Made of inexpensive materials
- Robust, high stability (protection not needed)
- E_{fb}: +0.95-1.01V vs RHE

Weakness → Difficulties in processing

$CuFeO_2$ preparation: *the prospect of solution processability*

Solid state reaction

$$Cu_2O + Fe_2O_3 \xrightarrow[> 700°C]{N_2} 2CuFeO_2$$

Ball milled

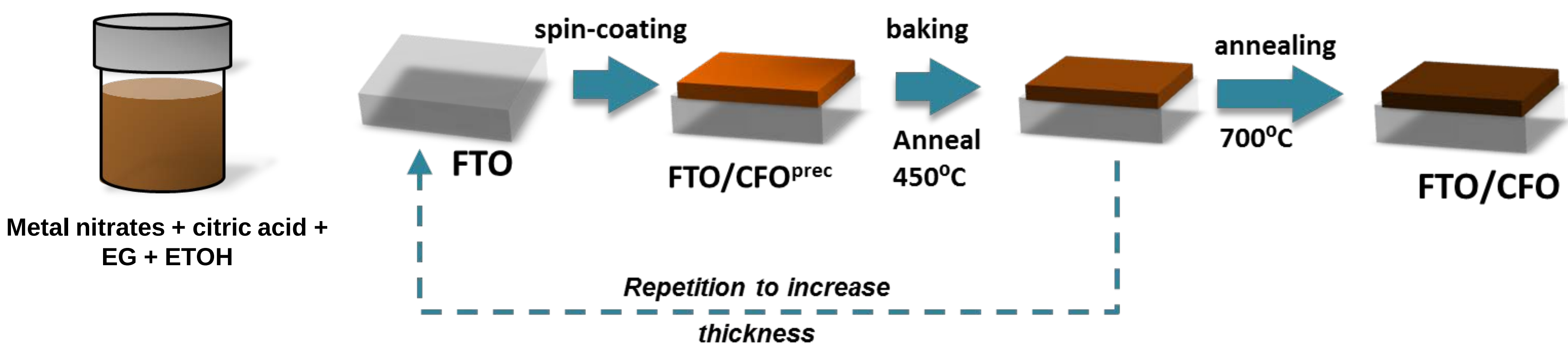
Difficult processing of the $CuFeO_2$ powder for preparing films

Electrodeposition

$$Cu(NO_3)_2 + Fe(ClO_4)_3 \xrightarrow[DMSO]{-0.3\ V} Cu\text{-}Fe\text{-}O \xrightarrow[650°C]{Ar} CuFeO_2$$

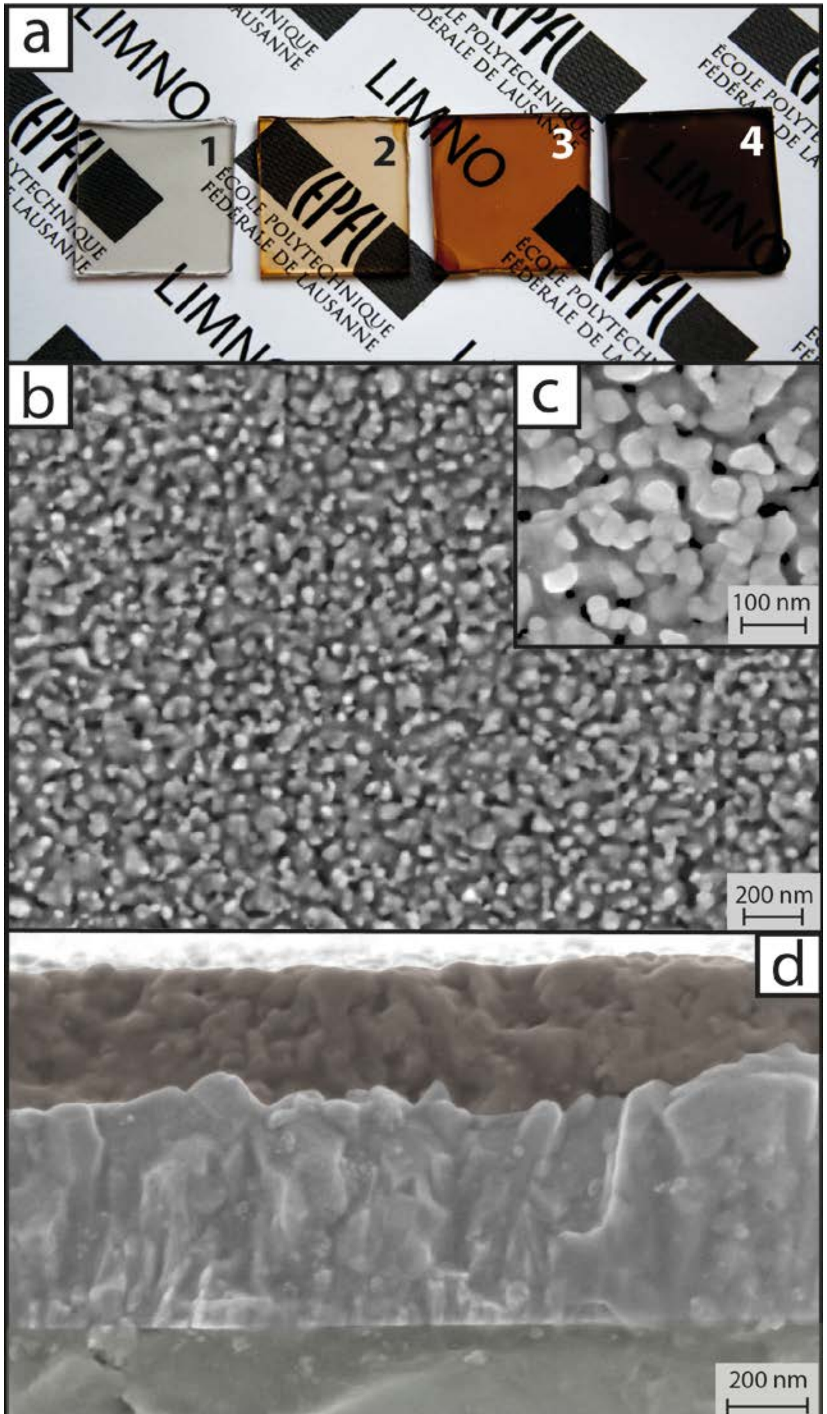
Electrode thickness limited by the electroactivity of the substrate and deposited precursor

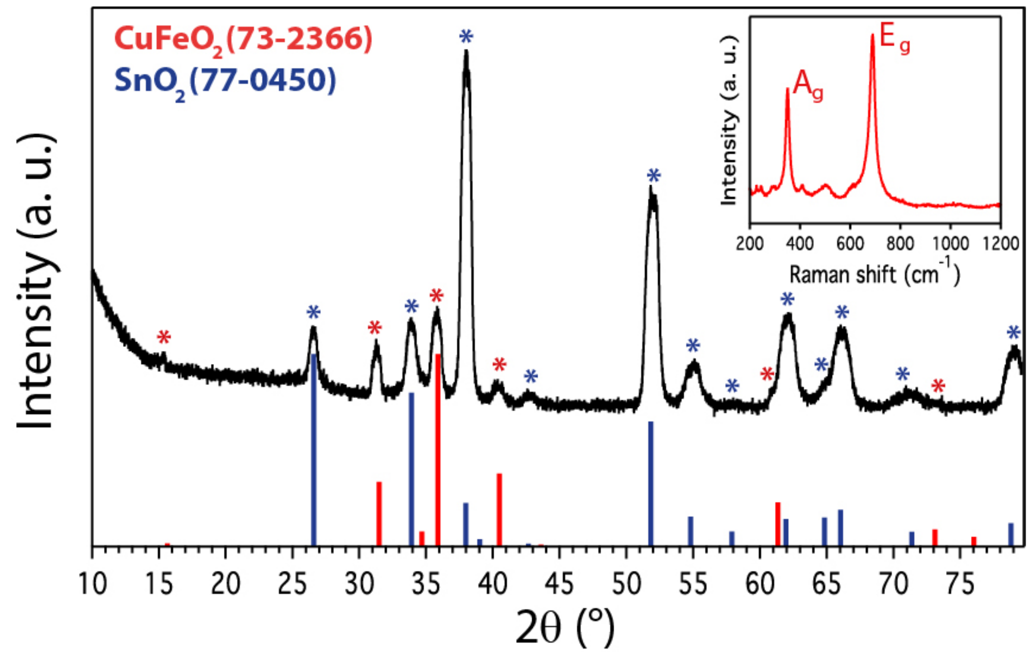
SOL-GEL approach

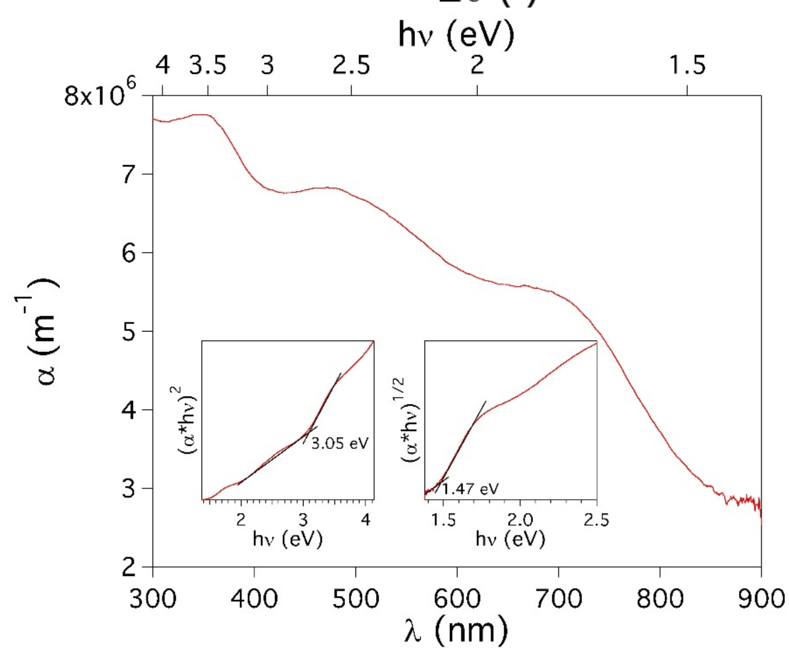


Straightforward scaled up, solution processable and easy control on the film thickness

$CuFeO_2$ characterization







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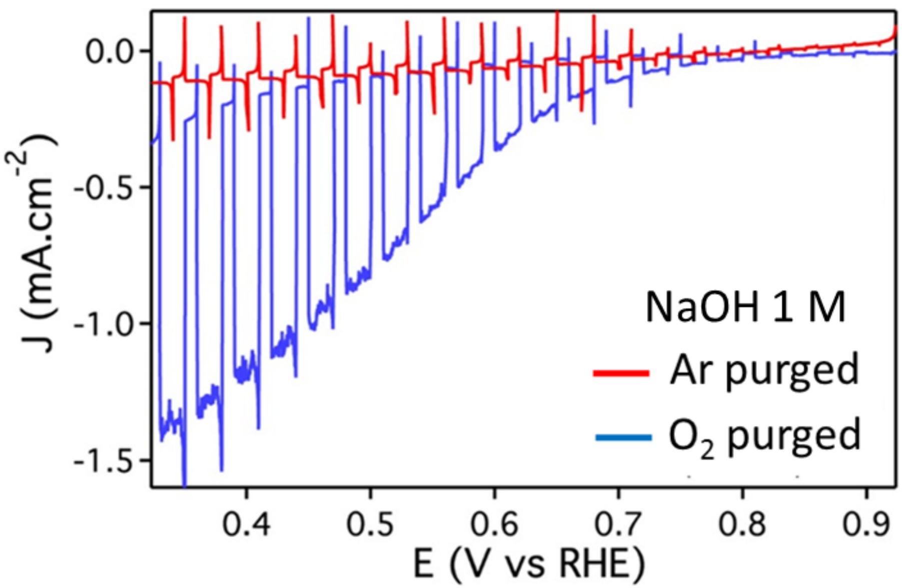
$CuFeO_2$ PEC performance



Optimum 6-layer sample

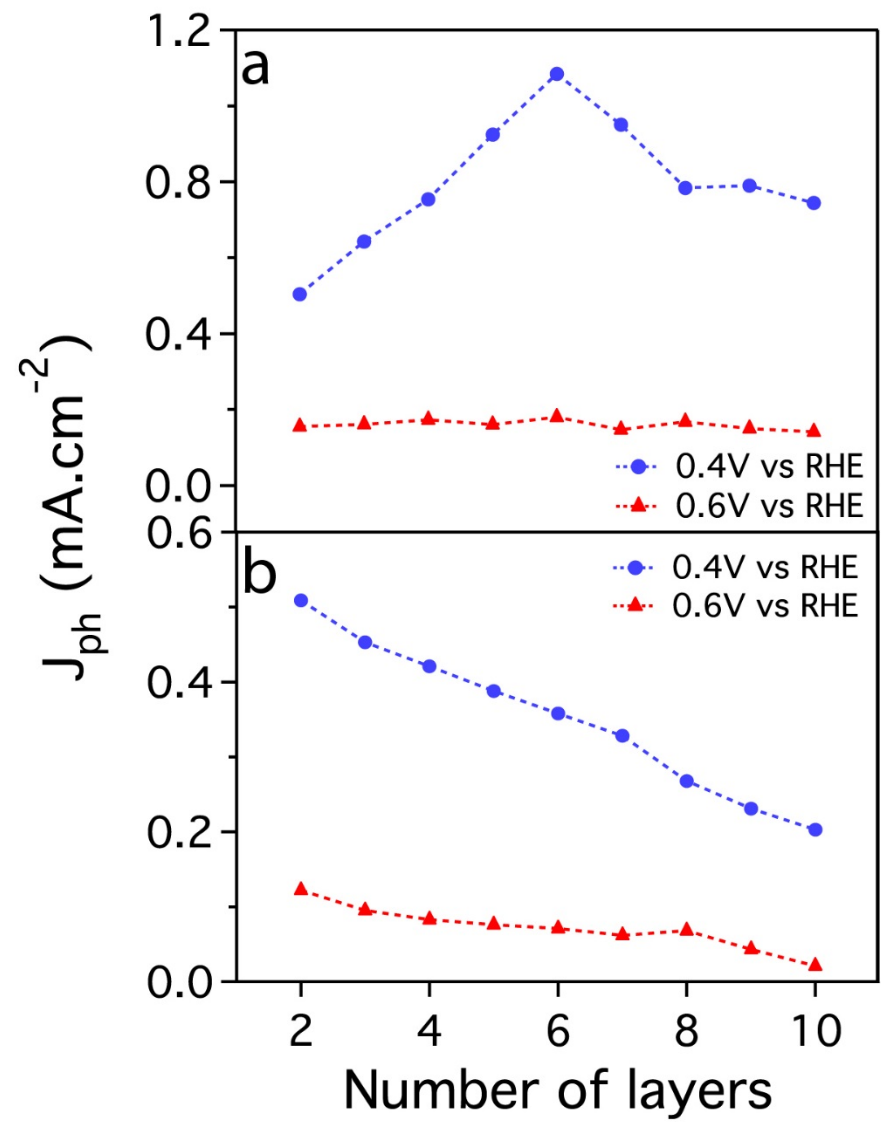
Ar-purged electrolyte

- Poor charge injection into electrolyte
- *Surface modification with co-catalyst is necessary*

With O_2 (good electron scavenger)

- Photocurrents larger than 1.0 mA cm^{-2} at 0.4 V *vs* RHE

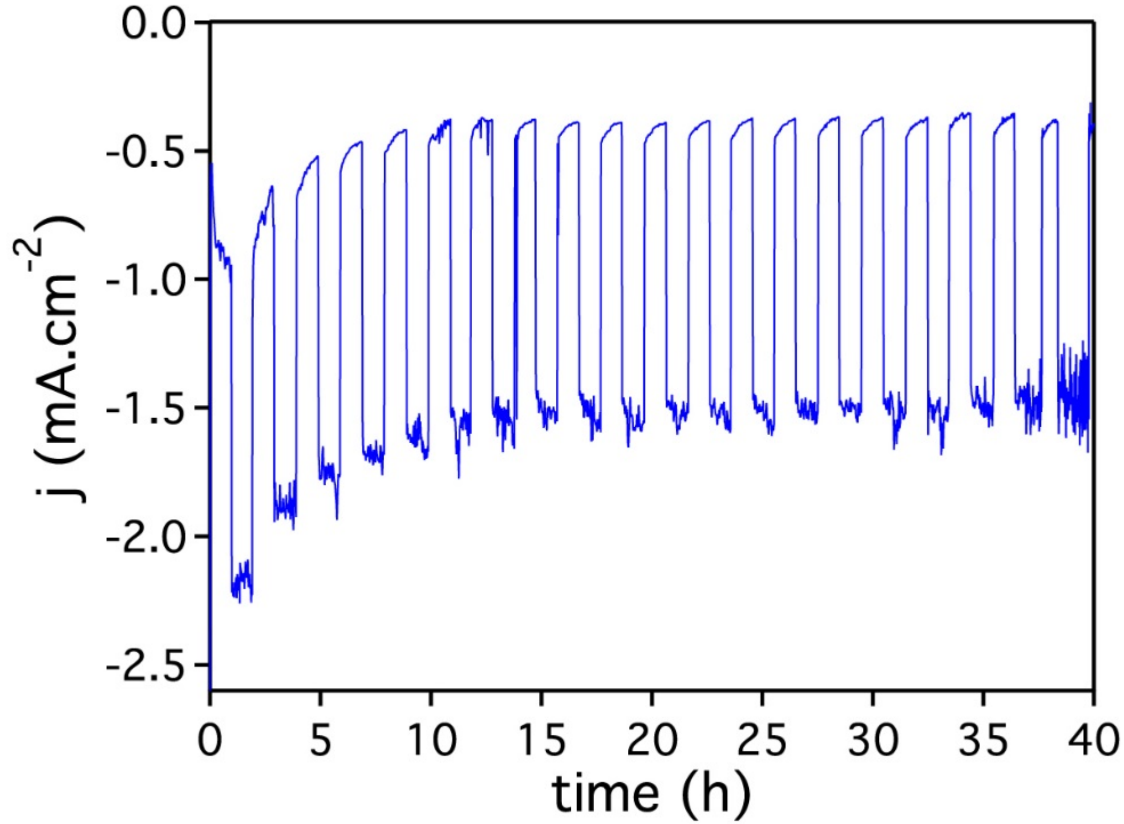
Onset photocurrent of 0.9 V vs RHE

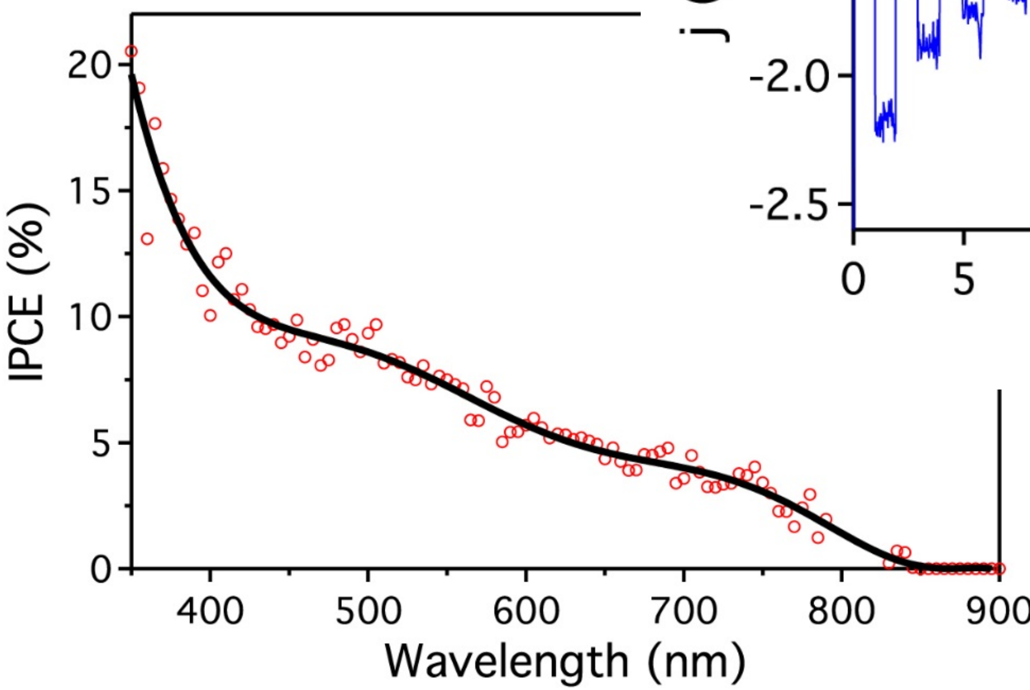


M. Prévot, N. Guijarro, K. Sivula *Submitted* **2014**

$CuFeO_2$ PEC performance

In 1 M NaOH
O_2 purged electrolyte

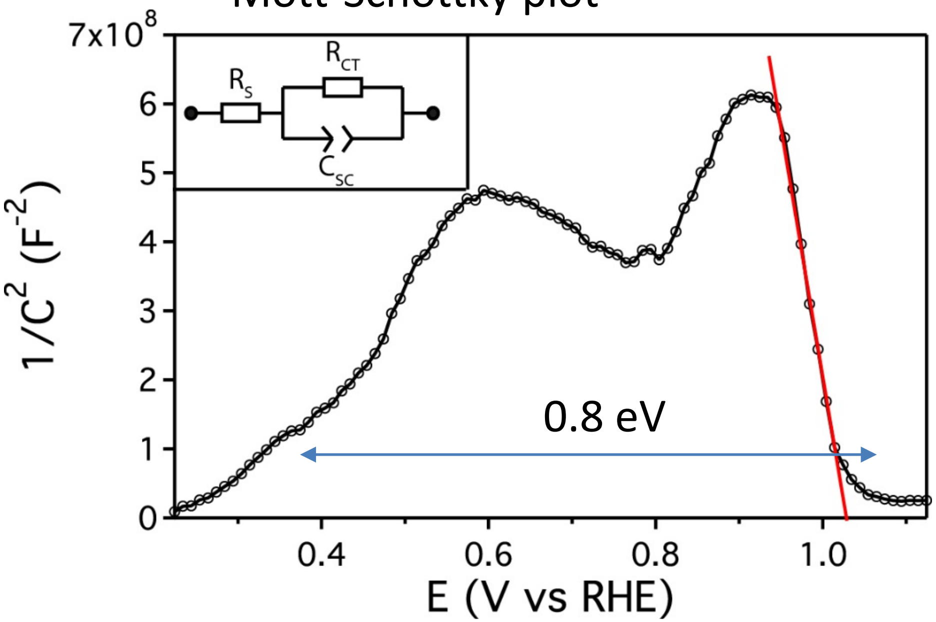




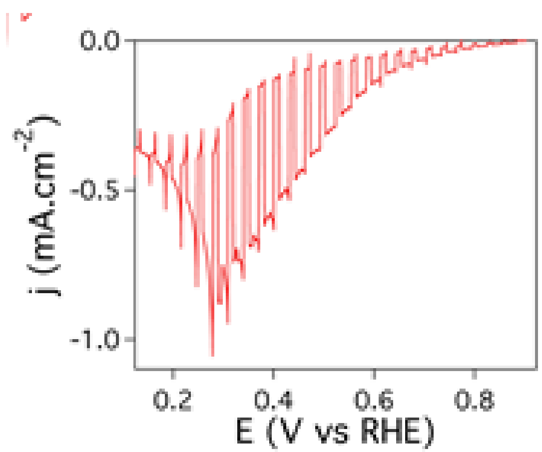
M. Prévot, N. Guijarro, K. Sivula *Submitted* **2014**

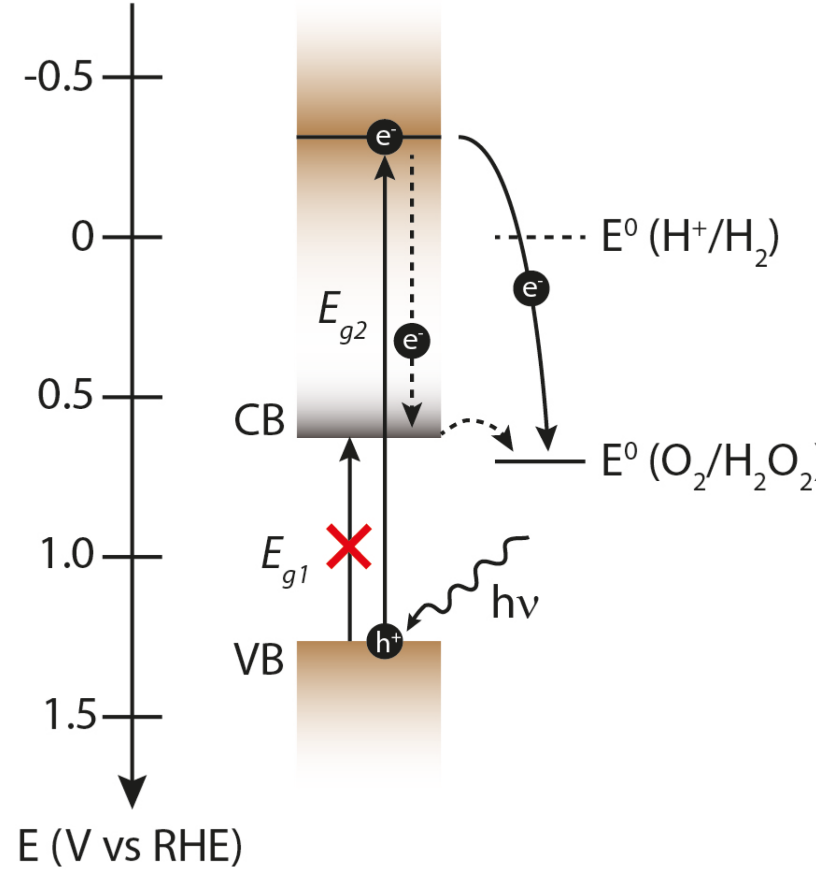
$CuFeO_2$ Electronic structure

Mott-Schottky plot



Anomalous photocurrent behavior





Optically forbidden gap previously predicted by DTF calculations

K. P. Ong, K. Bai, P. Blaha and P. Wu, *Chemistry of Materials*, 2007, **19**, 634-640.

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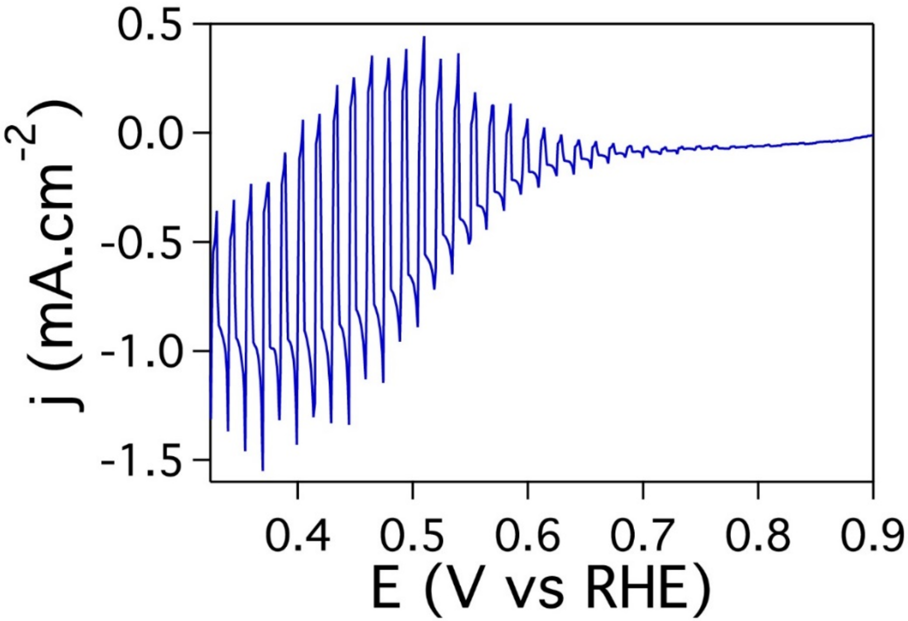
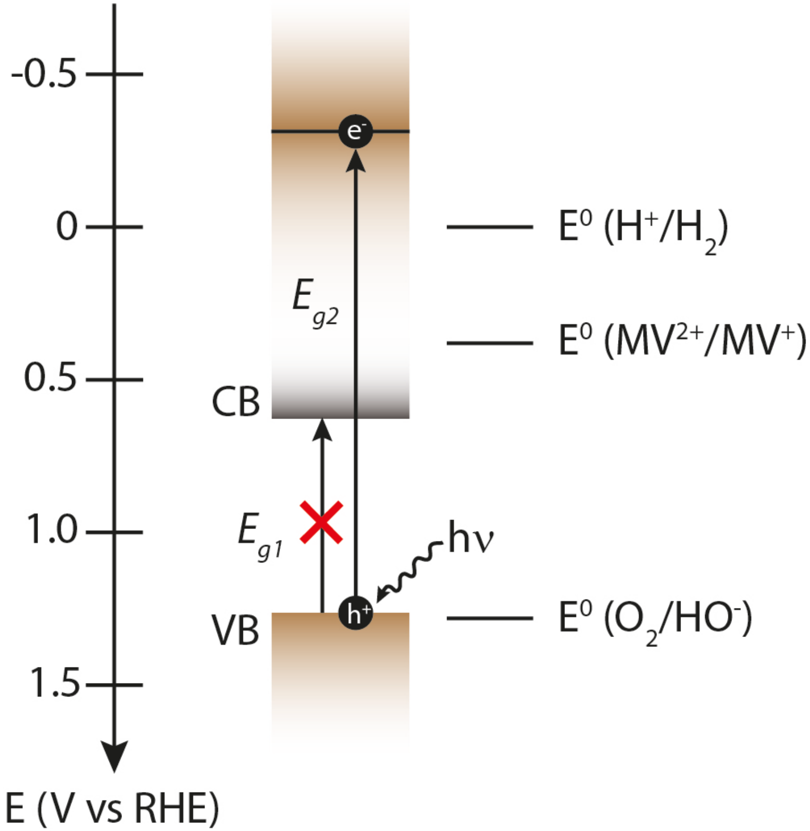
$CuFeO_2$ Electronic structure

With MV $^{2+}$ (Methyl viologen)

Ar purged electrolyte





$CuFeO_2$ conclusions

- Feasible solution-based approach for preparing p-type $CuFeO_2$ photocathodes.
- **Highly robust**, onset at **+0.9 V vs RHE**, photocurrent above 1mAcm^{-2} at 0.4 V $_{\text{vs RHE}}$
- Low photocurrent in absence of electron scavenger (Mv^{2+} or O_2)
- Improve performance by extrinsic doping or nanostructuring

Materials for the tandem cell

Photoanode

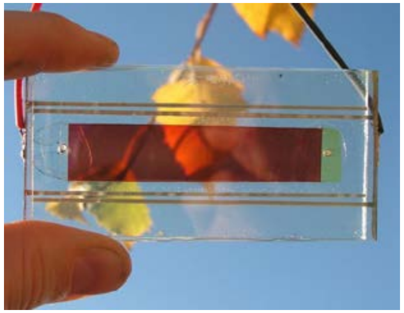
WO_3

$BiVO_4$

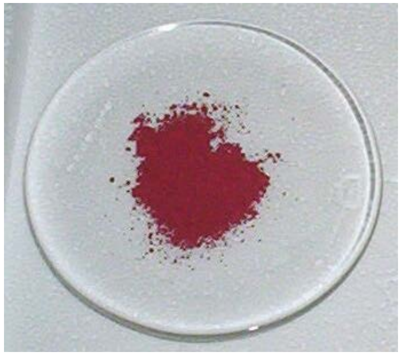
α-Fe_2O_3

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

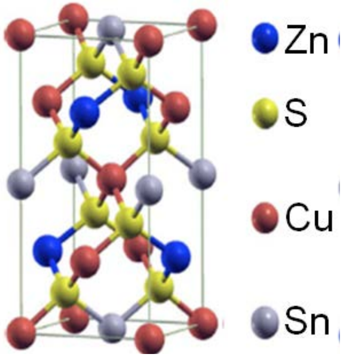
Photocathode



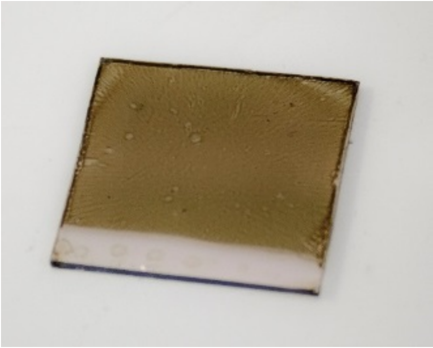
Dye sensitized solar cell



Copper(I) oxide

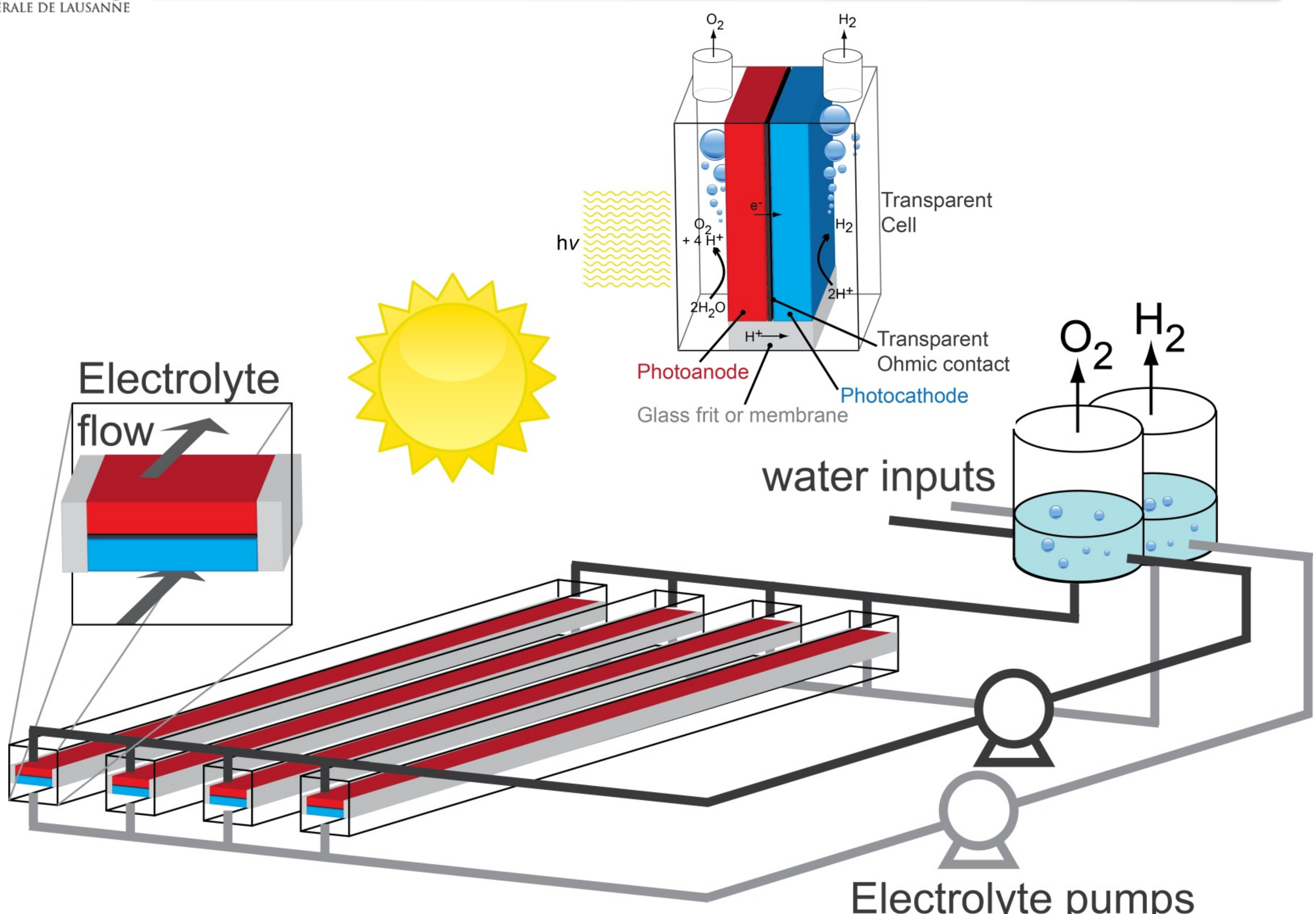


Cu_2ZnSnS_4



$CuFeO_2$

Scalable energy conversion systems



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Fe_2O_3:

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Cu_2O:

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- Elijah Thimsen (UMN)
- Adriana Paracchino

Tandem cells:

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- Pauline Bornoz

CZTS:

- Lorenzo Rivoli
- Nestor Guijarro

$CuFeO_2$:

- Mathieu Prévot
- Yang Li

External collaborators:

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PEC HOUSE PHOTO ELECTRO CHEMICAL

erc

MARIE CURIE ACTIONS

TOYOTA

EOS HOLDING

FNSNF
Fonds National Suisse
Schweizerischer Nationalfonds
Fondo Nazionale Svizzero
Swiss National Science Foundation

SEVENTH FRAMEWORK PROGRAMME