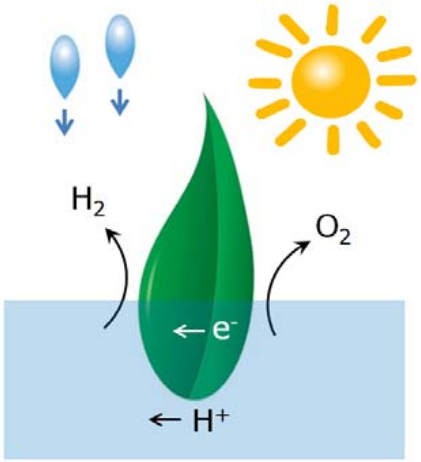
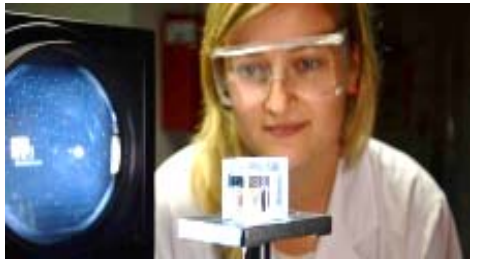


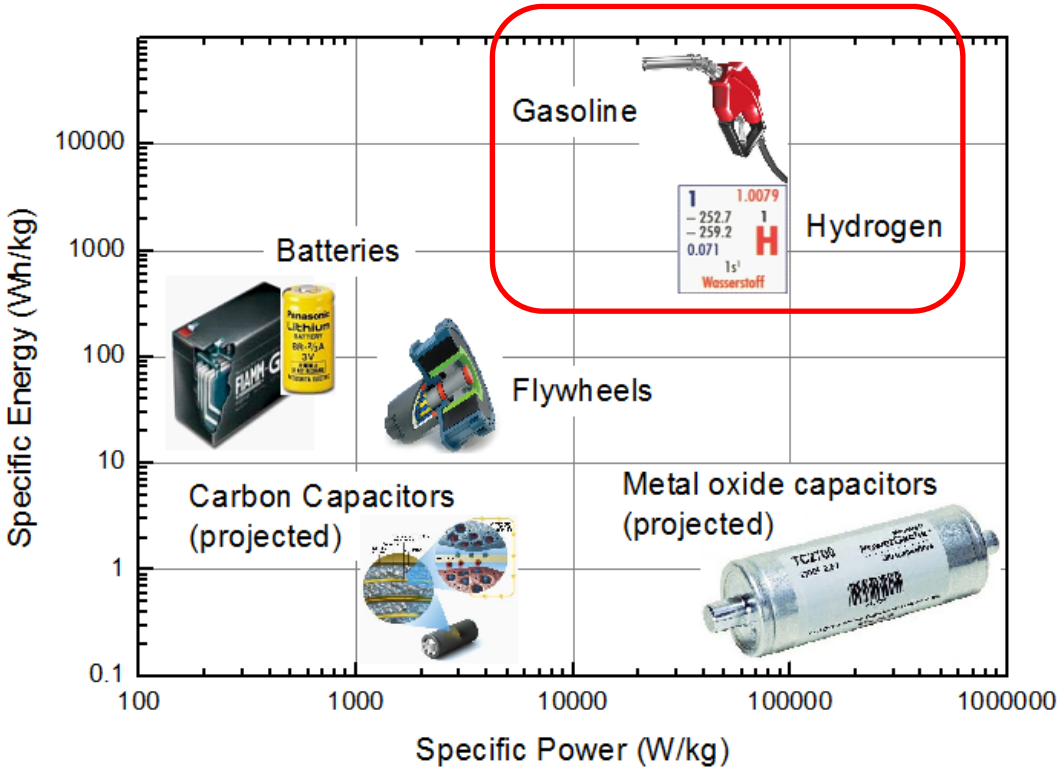


Solid State Photoelectrochemical Devices for Artificial Photosynthesis

Roel van de Krol
Institute for Solar Fuels
Helmholtz-Zentrum Berlin für Materialien und Energie GmbH
and Institut für Chemie, Technische Universität Berlin, Germany

Three „Hard“ Facts on Energy

- **Sunlight** is by far the most abundant and sustainable source of energy
- We need to **store** this energy on a GWh scale
- For long-term storage, **chemical fuels** are hard to beat

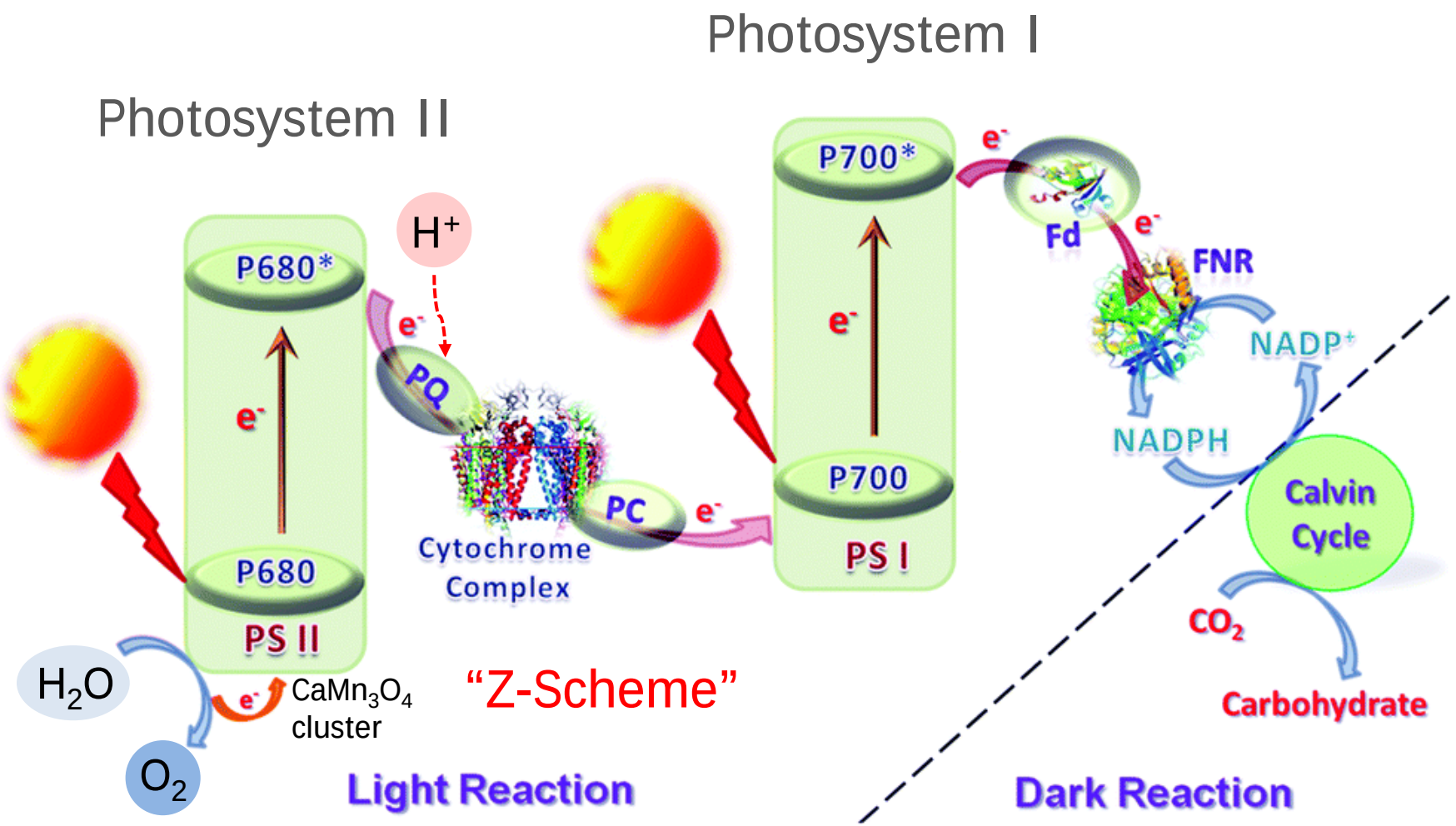


Importance of hydrogen:

- **All** fuels contain hydrogen
- Hydrogen is also needed for production of **food**, plastics, steel, etc.

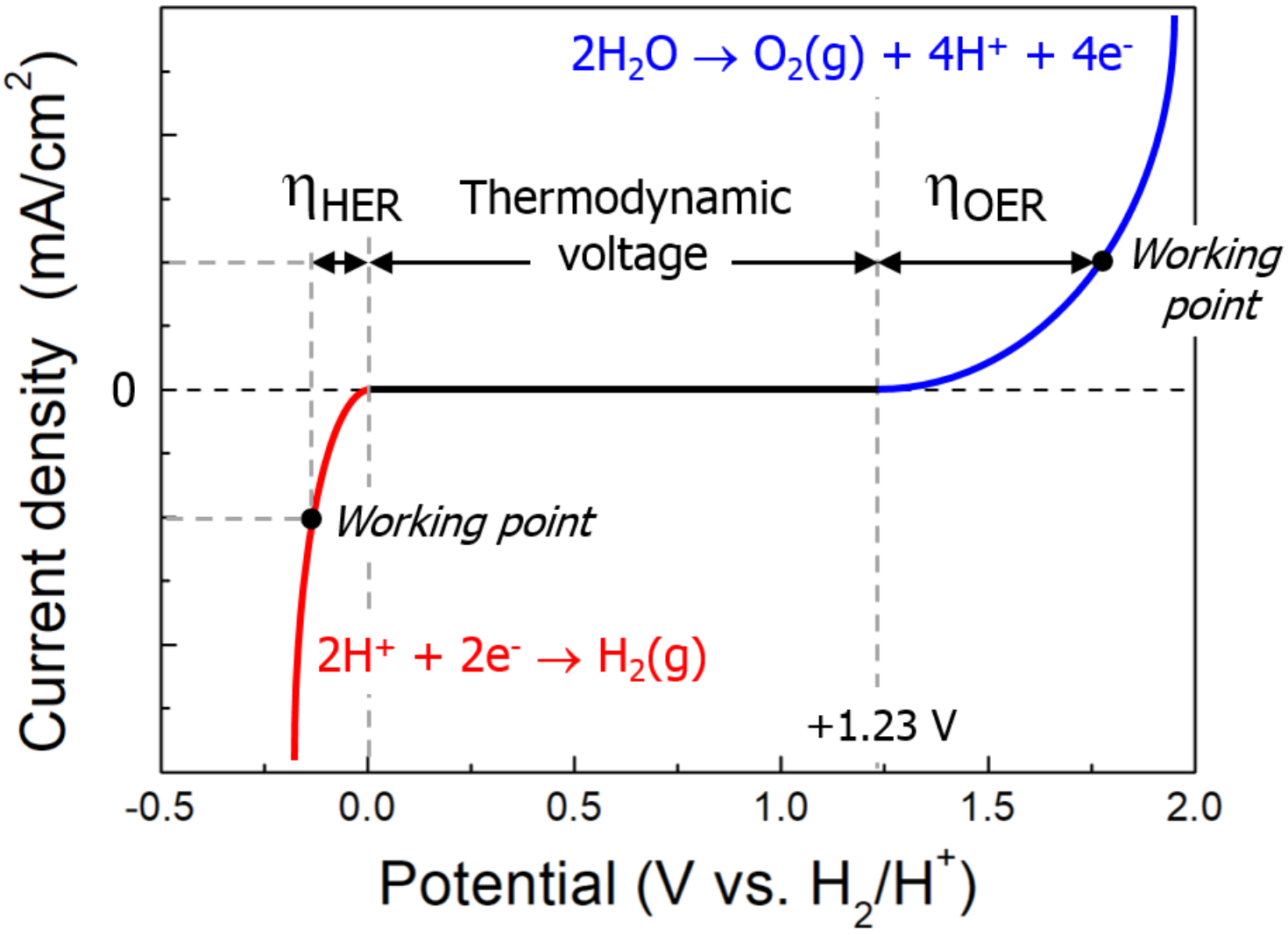
Only <u>one</u> sustainable source: water!

Water Splitting in Natural Photosynthesis



Adapted from: Choudhury et al., *Green Chem.* 16, 4389 (2014)

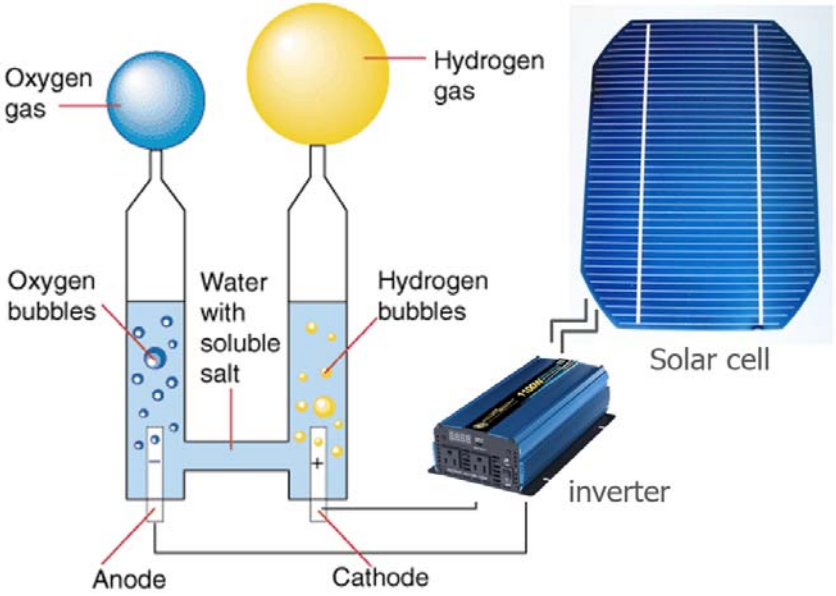
Electrochemical Water Splitting



Voltage required for water splitting is at least 1.5 V

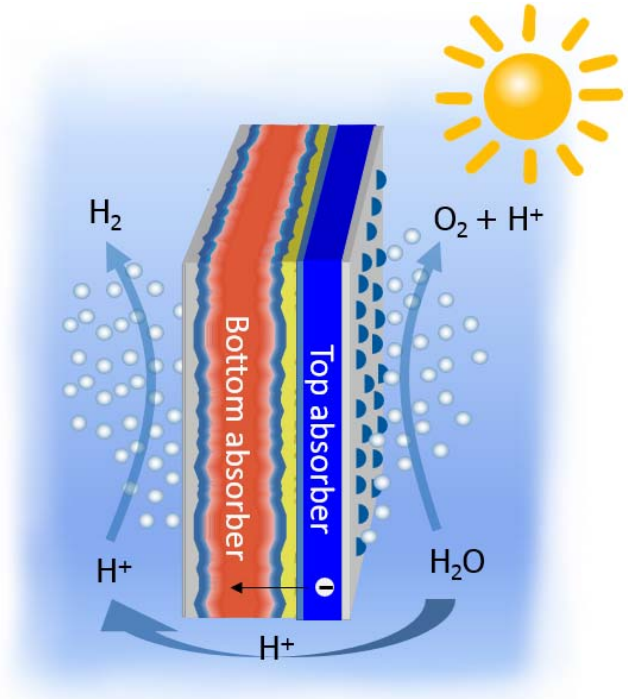
Clean Hydrogen Production

PV-Driven Electrolysis



- ✗ Many components ⇒ high costs
- ✓ Can be optimized individually
- ✗ Alkaline electrolysers corrode in the dark, PEM electrolyzers require noble metals
- ✓ Hydrogen can be produced at pressure

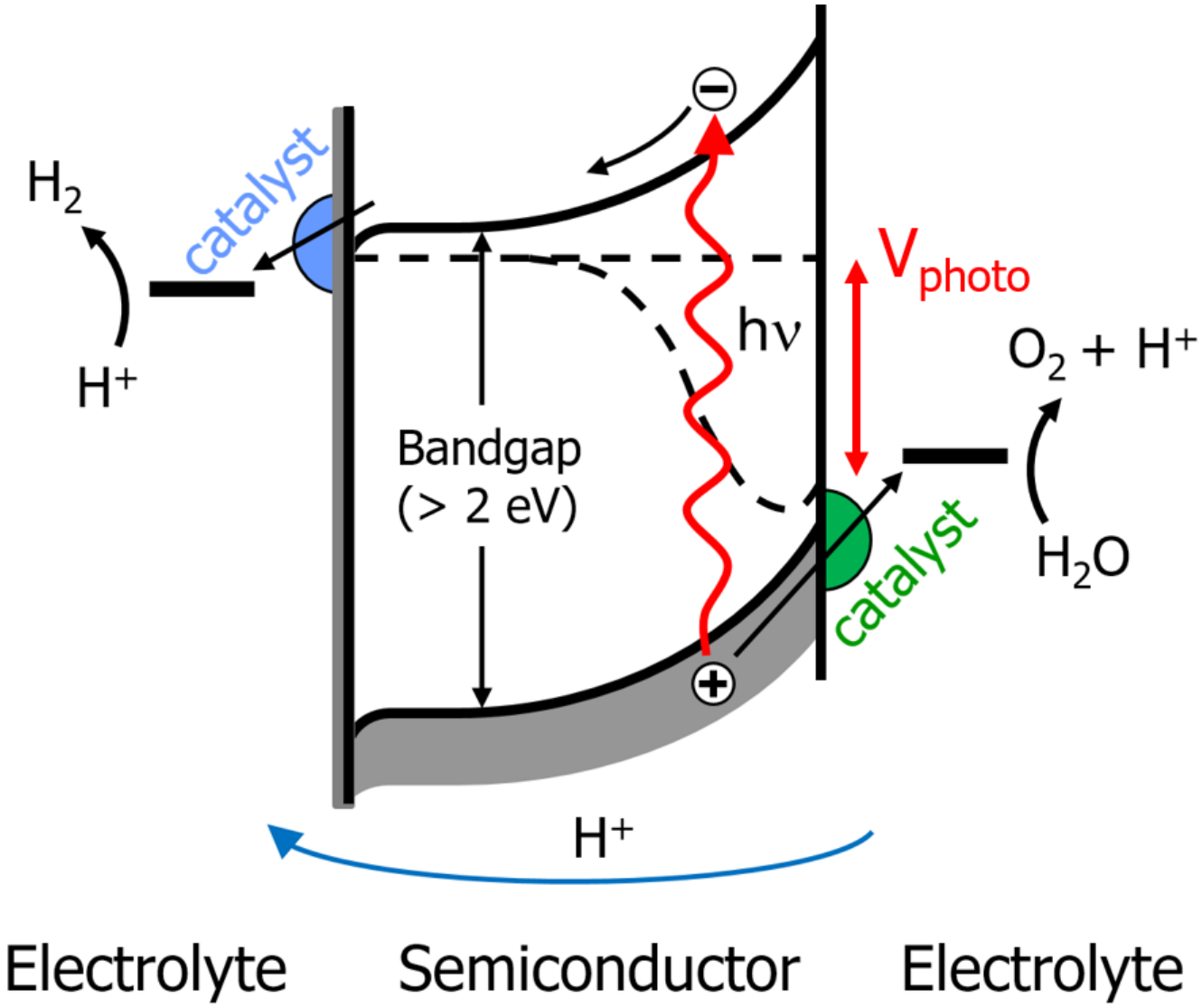
"Artificial Photosynthesis"



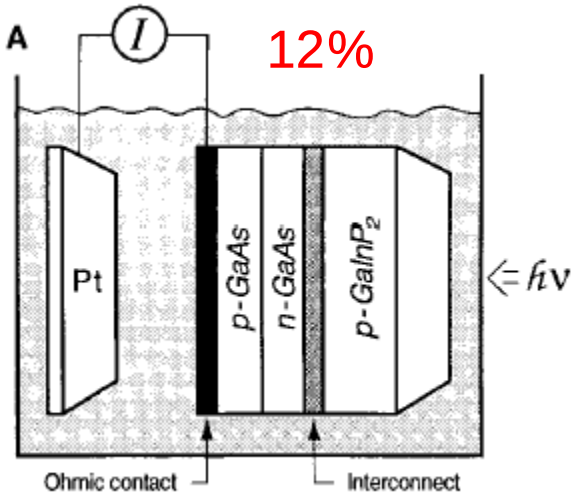
- ✓ Integrated device might be cheaper
- ✓ Heat easily used to accelerate reactions
- ✓ Current densities ~100x lower than in electrolyzers ⇒ earth-abundant catalysts
- ✗ Collection over large areas is challenging

Winning technology will be determined by Levelized Cost Of Hydrogen (€/kg H_2)

Photoelectrochemical Water Splitting at Semiconductor Surfaces

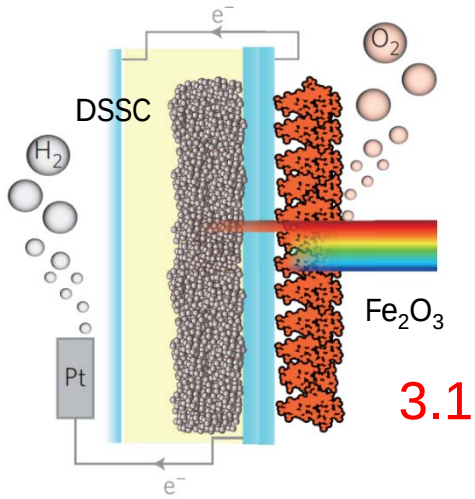


Unassisted PEC Water Splitting with SC / Liquid Junctions



12%

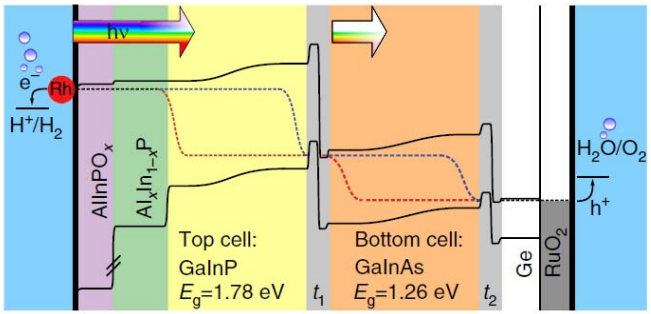
Turner, *Science (1998)*



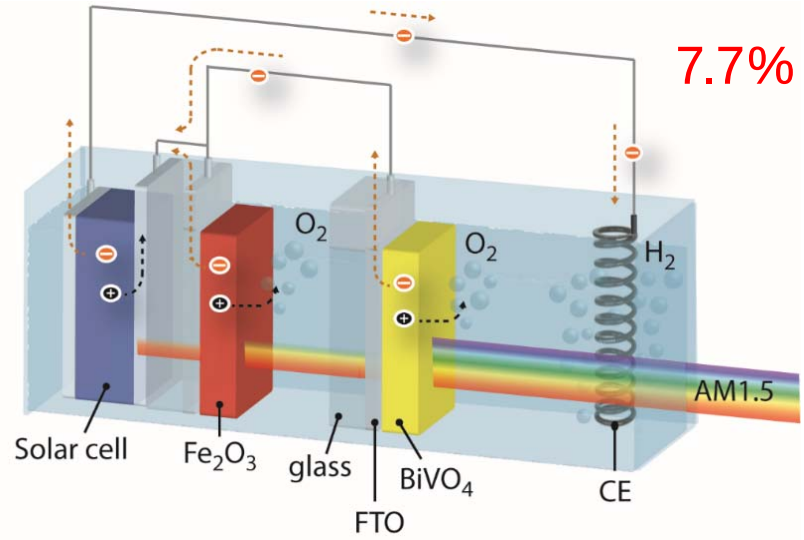
3.1%

Grätzel, *Nat. Photon. (2012)*

14%



May et al., *Nat. Commun. (2015)*

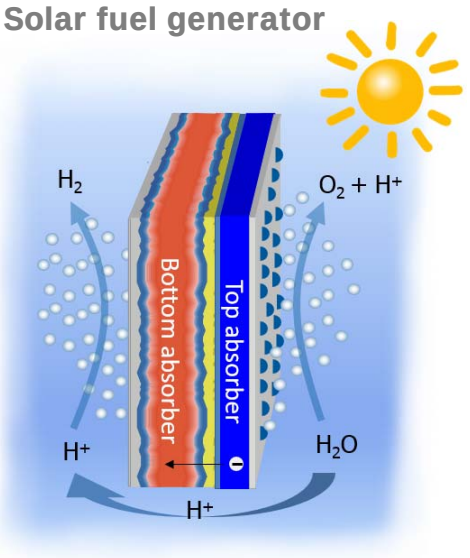


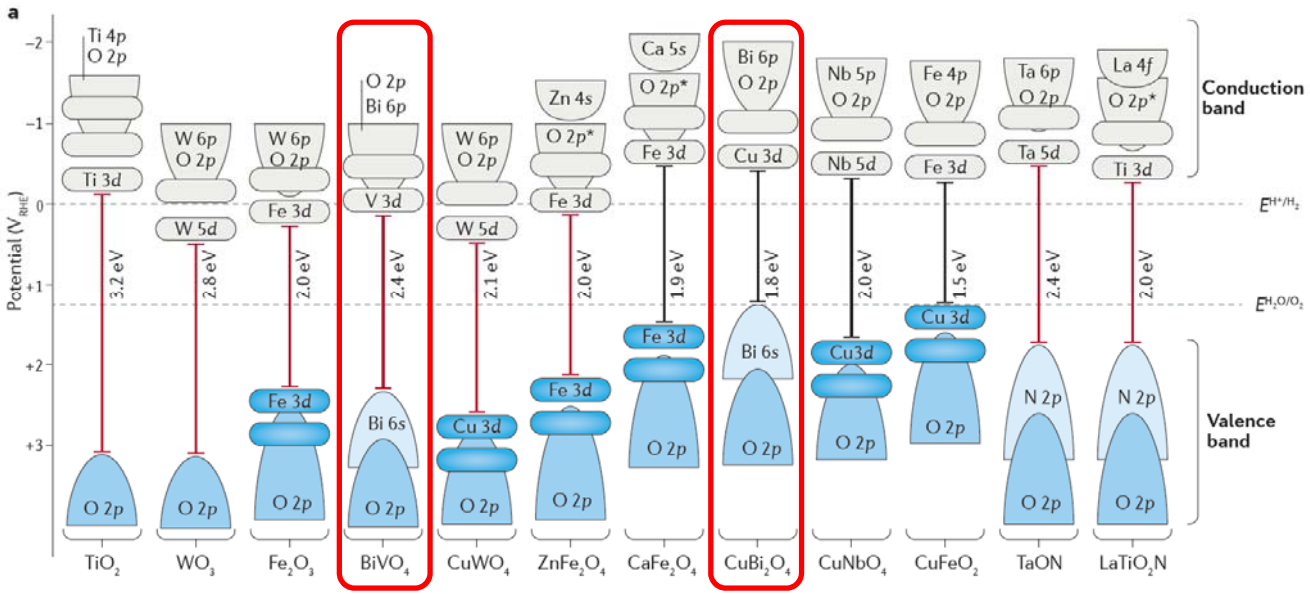
7.7%

HZB/POSTECH/UNIST, *Nat. Commun. (2016)*

The Need for New Light Absorbers

- Missing component for multijunction absorber: **stable** and **efficient** top absorber with a **1.5 – 2.1 eV** bandgap
- Combination with silicon offers path to solar-to-hydrogen (STH) efficiencies of ~20%
- Requirements: band gap, -positions, stability, carrier transport
- Our approach: focus on metal oxide absorbers



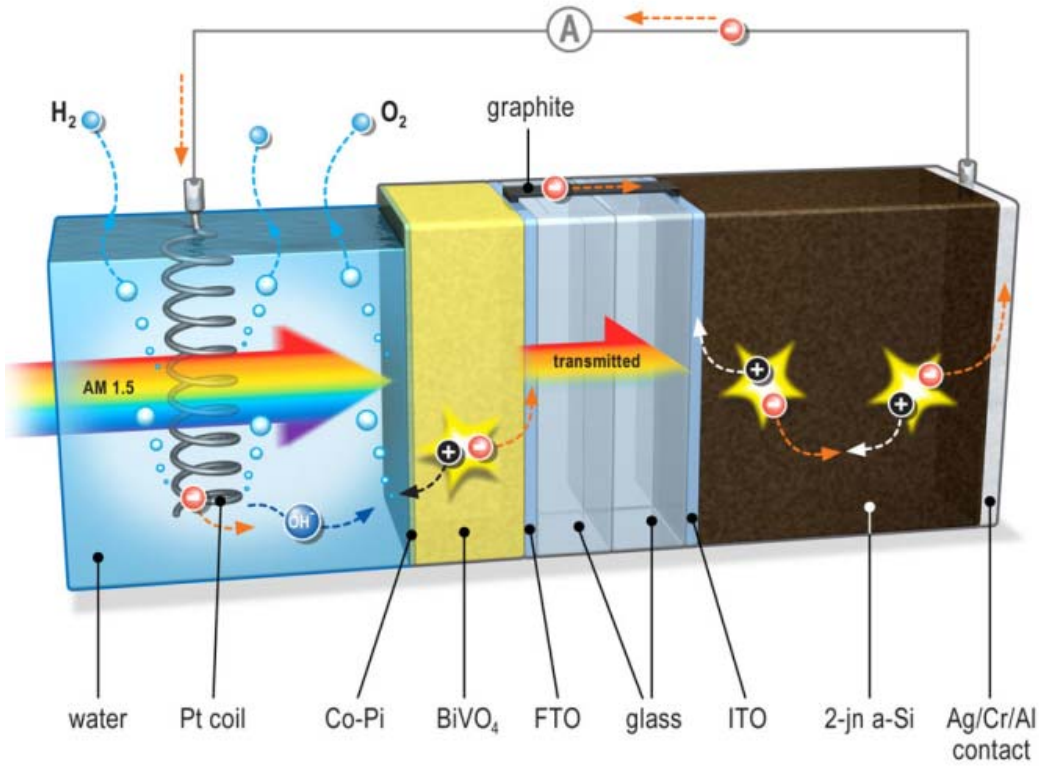


Multinary ('complex') oxides:

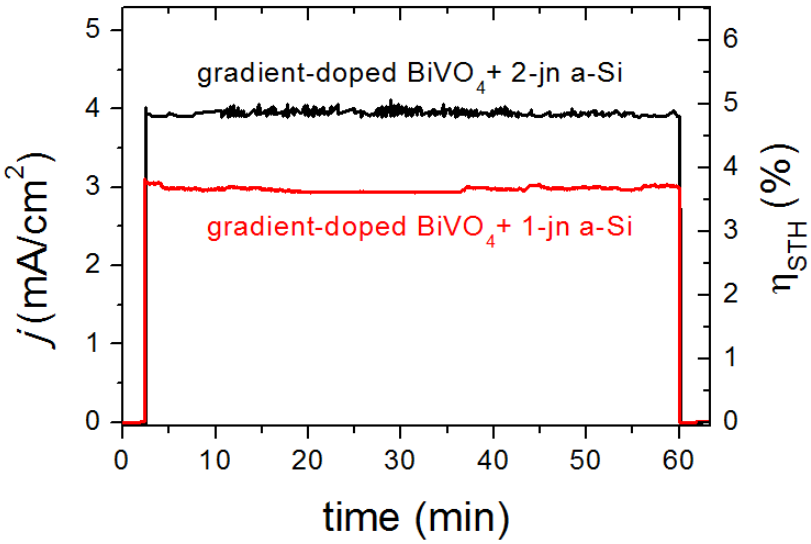
- Good stability
- Many candidates (>10^5)
- Few have been explored so far

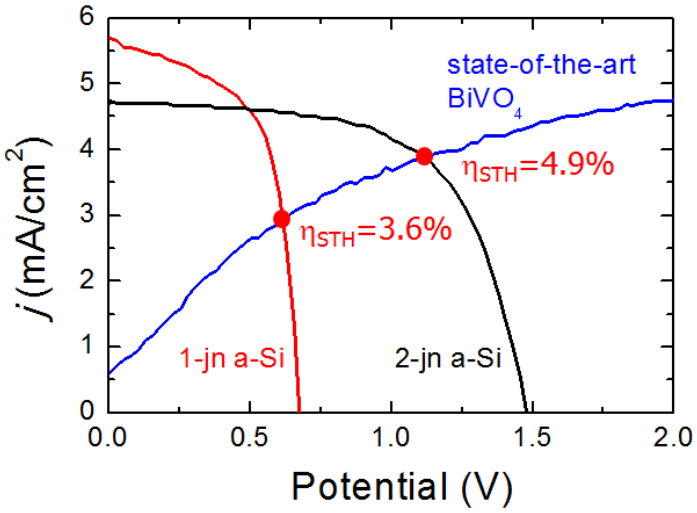
Nat. Rev. Mater. 1, 15010 (2016)

CoPi-$BiVO_4$ / a-Si / a-Si Tandem Water Splitting Device



Fatwa Abdi





Highest efficiency (5.2%*) ever reported for a metal oxide-based device (in 2013)

$$\eta_{STH} = \frac{j_{photo} \times V_{redox}}{P_{light}}$$

Nat. Commun. 4 (2013) 2195;
(*) *ChemSusChem* 7 (2014) 2832

TU Delft

HZB Helmholtz Zentrum Berlin

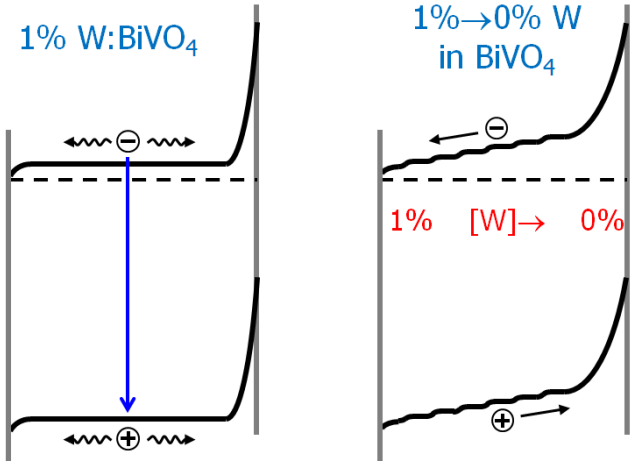
Towards Efficient $BiVO_4$ Photoanodes: Bottlenecks to Solve

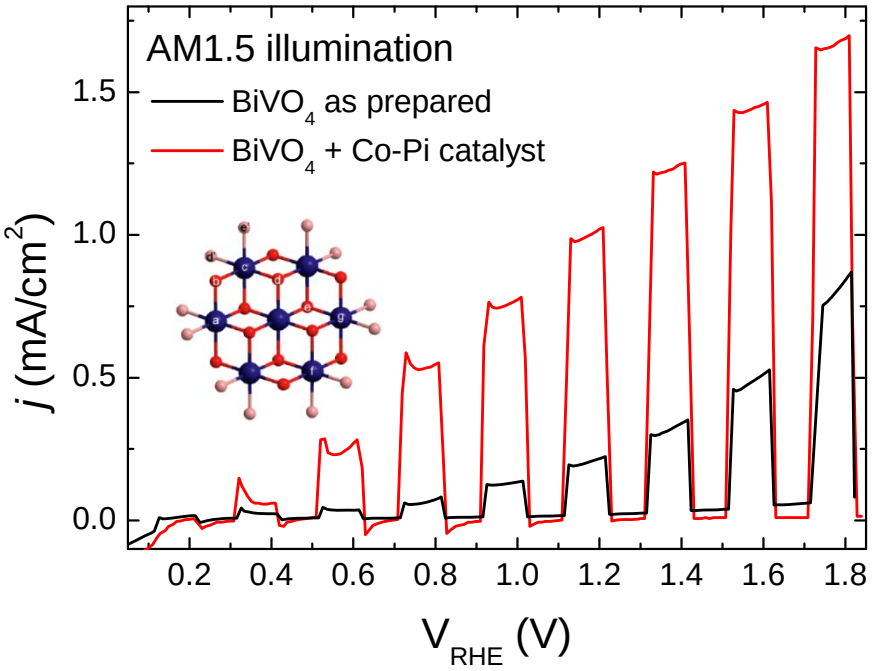
Performance limitations due to:

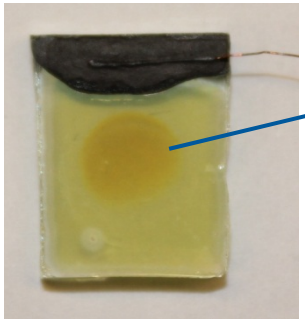
- **Slow water oxidation kinetics**
  → Solved by depositing CoPi OEC [1]
- **Low electronic conductivity**
  → Solved by doping with W: [2]

$$2WO_3 + Bi_2O_3 \xrightarrow{2BiVO_4} 2Bi_{Bi}^{x} + 2W_V^{\bullet} + 8O_O^{x} + \tfrac{1}{2}O_2(g) + 2e'$$

- **Poor charge carrier separation**
  → Solved by dopant gradient [3]







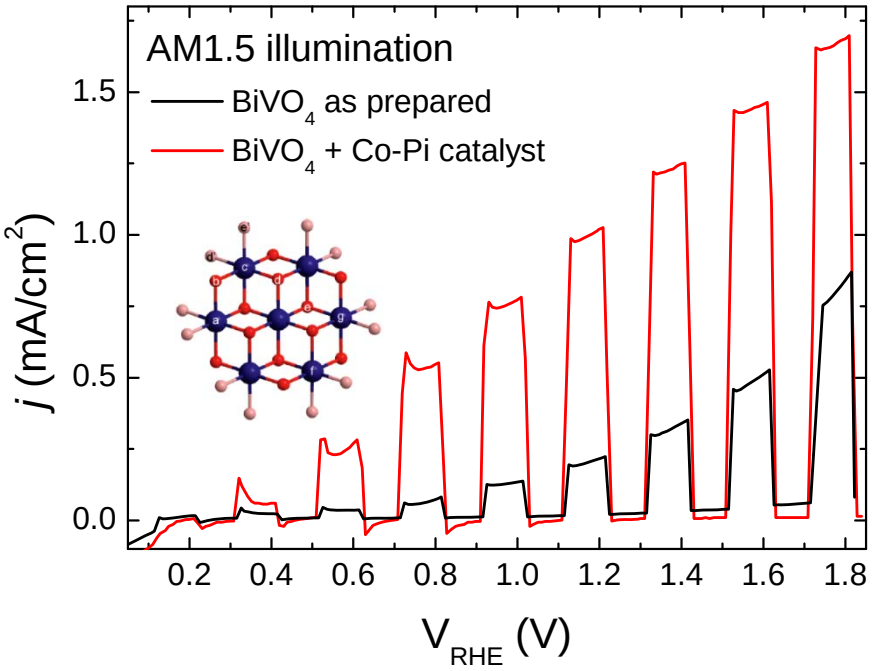
TU Delft

[1] *J. Phys. Chem. C* 116 (2012) 9398; [2] *ChemCatChem* 5 (2013) 490; [3] *Nat. Commun.* 4:2195 (2013)

What Happens at the Surface of $BiVO_4$?

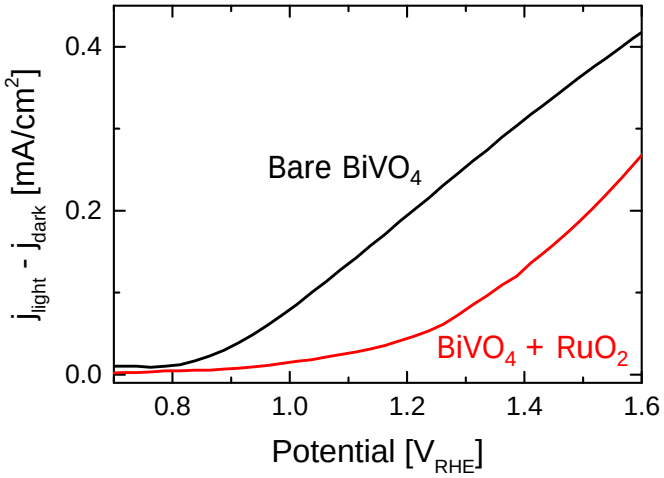
Performance limitations due to:

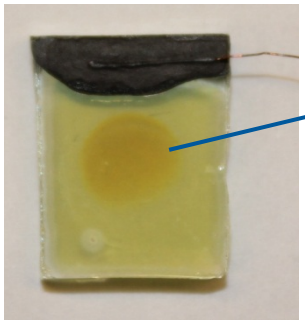
- **Slow water oxidation kinetics**
  → Solved by depositing CoPi OEC



Problem:

Modification of surface with traditional electrocatalysts does not always enhance the photocurrent:





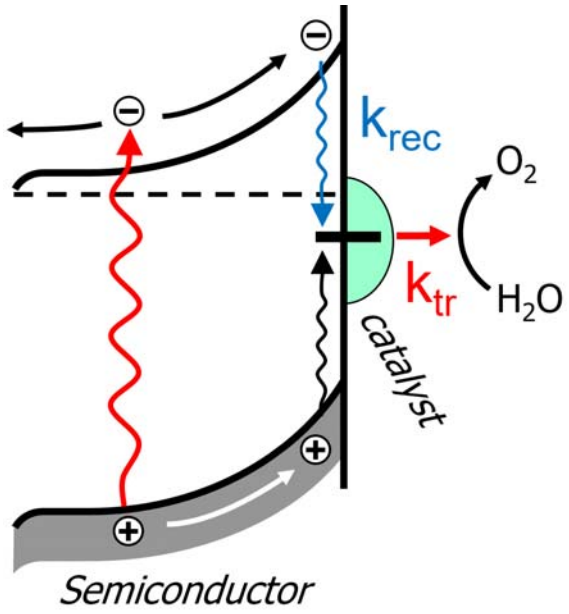
Electro-deposited CoPi

TU Delft

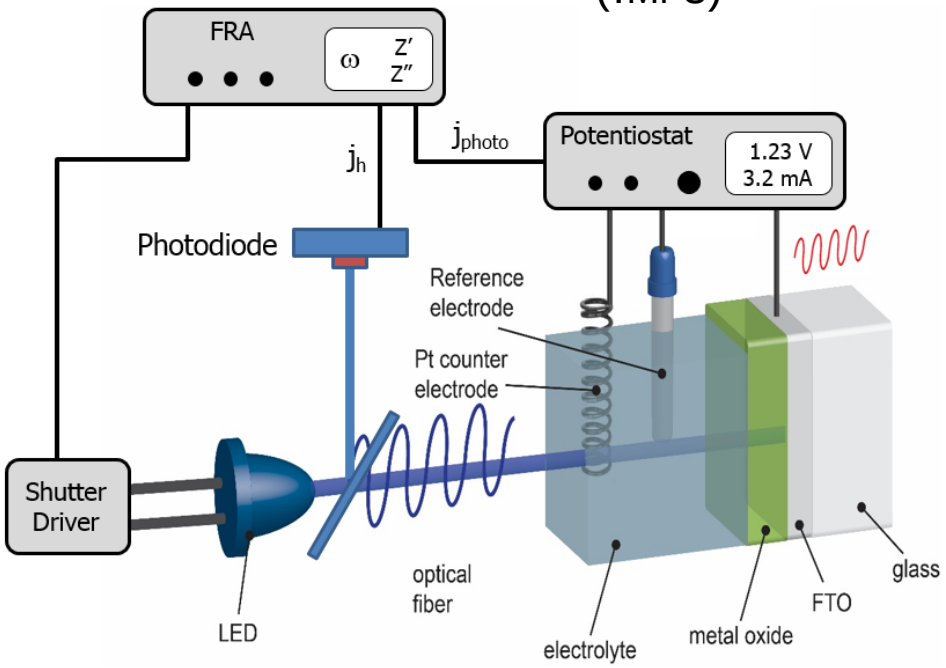
Understanding Semiconductor / Catalyst Interfaces


Fatwa Abdi


Carolin Zachäus



Intensity-Modulated Photocurrent Spectroscopy (IMPS)



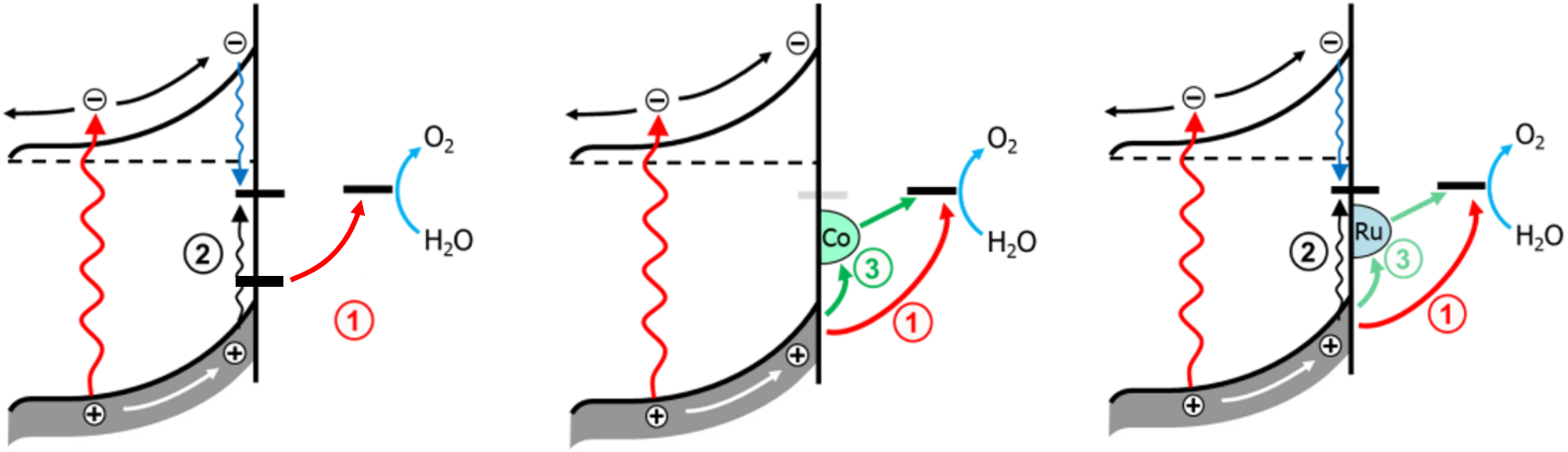
Possible functions of a “co-catalyst”:

- Improve water oxidation kinetics
- Passivate surface defects
- Modify band bending

- Charge transfer rate hardly affected by CoPi: unexpected for electrocatalyst!
- Instead, CoPi strongly reduces recombination at $BiVO_4$ surface

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

Tentative Description of $BiVO_4$ / CoPi / Electrolyte Interface



a) Without catalyst b) Surface passivating catalyst c) Non-passivating catalyst

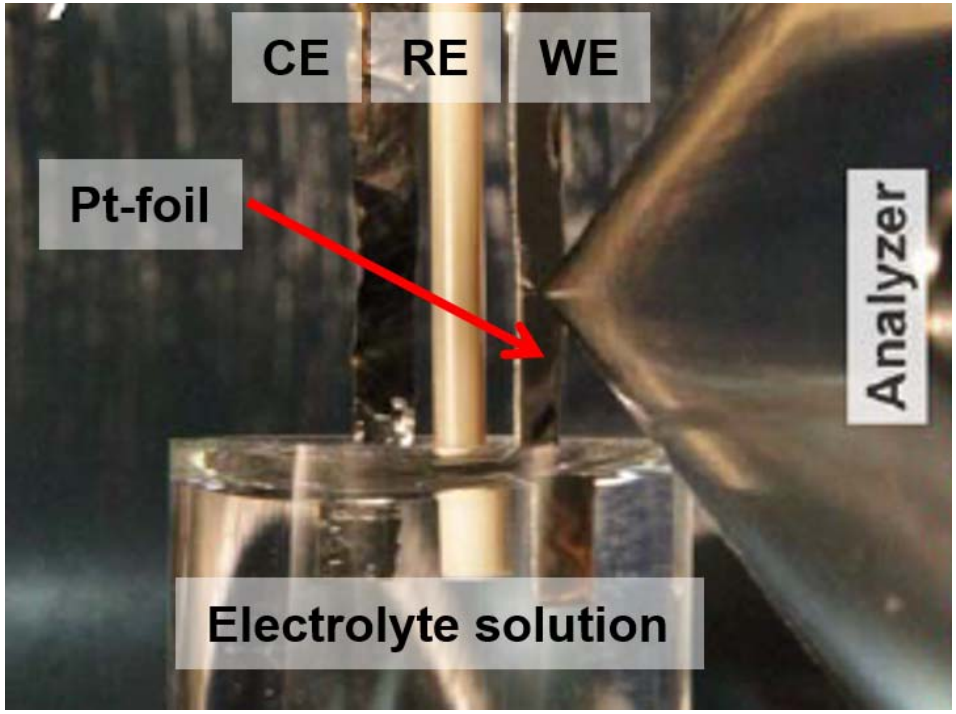
- Surface states affect both charge transfer *and* recombination in $BiVO_4$
- … what's the chemical nature of these states in $BiVO_4$?

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

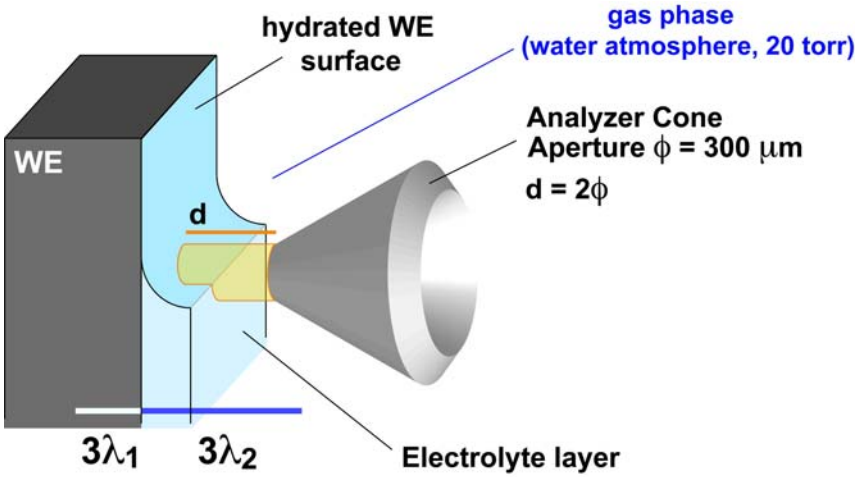
AP-HAXPES Experiments at ALS Beamline 9.3.1

Marco Favaro

David Starr



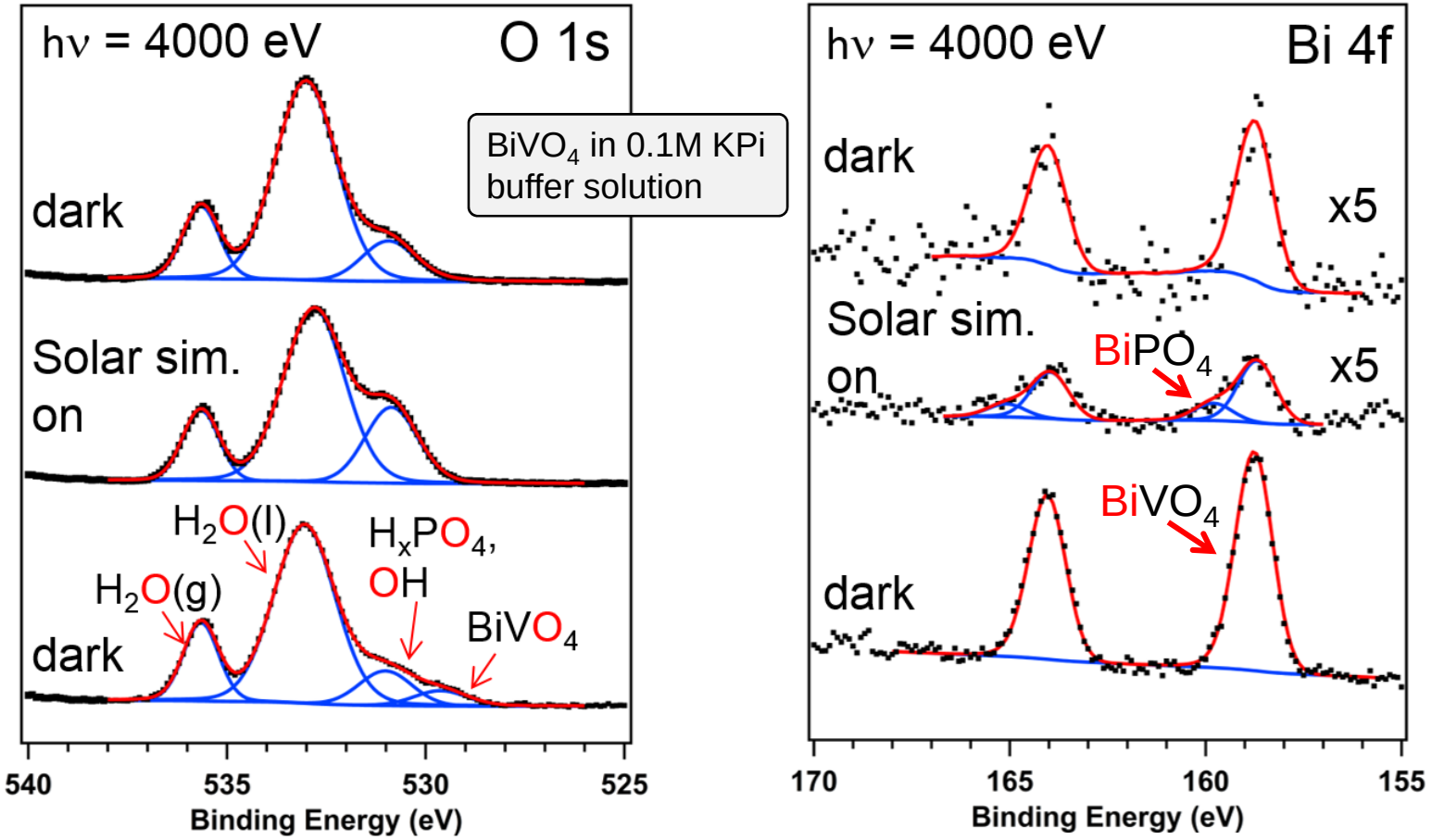
Zhi Liu, Ethan Crumlin (ALS)



Axnanda et al. *Sci. Rep.* **5**, 09788 (2015)

- Sample: spray-deposited $BiVO_4$ on FTO
- Photon energy of 4000 eV $\Rightarrow$ mean free path of photoexcited electrons through water is ~30 nm
- 0.1 M KPi solution (Debye screening length λ_D ~ 1 nm)

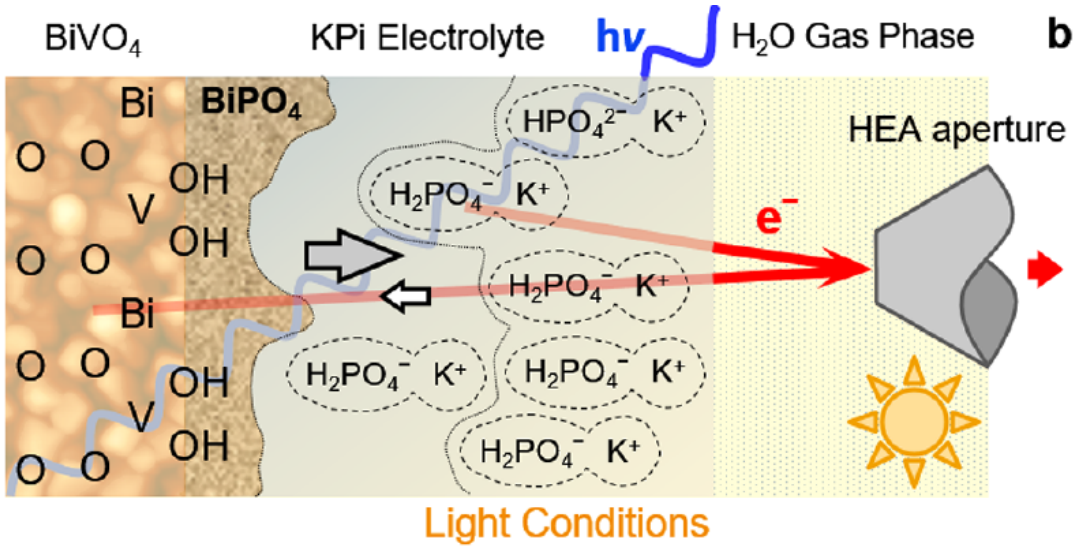
AP-HAXPES Experiments at ALS Beamline 9.3.1



- From H_2O(l)/$BiVO_4$ ratio, electrolyte layer thickness ~21 nm ⇒ bulk properties
- Illumination increases the H_xPO_4 signal and gives Bi 4f shoulder consistent with $BiPO_4$

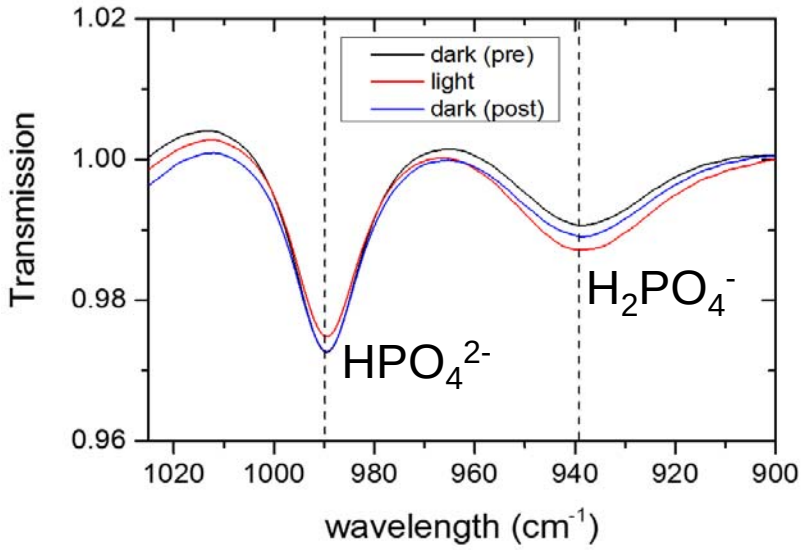
J. Electron Spectrosc. Relat. Phenom. 221, 106 (2017)

Tentative Model for $BiVO_4$ / Electrolyte Interface under Illumination



Changes are **reversible!**

Favaro et al., *J. Phys. Chem. B* 122, 801 (2018)

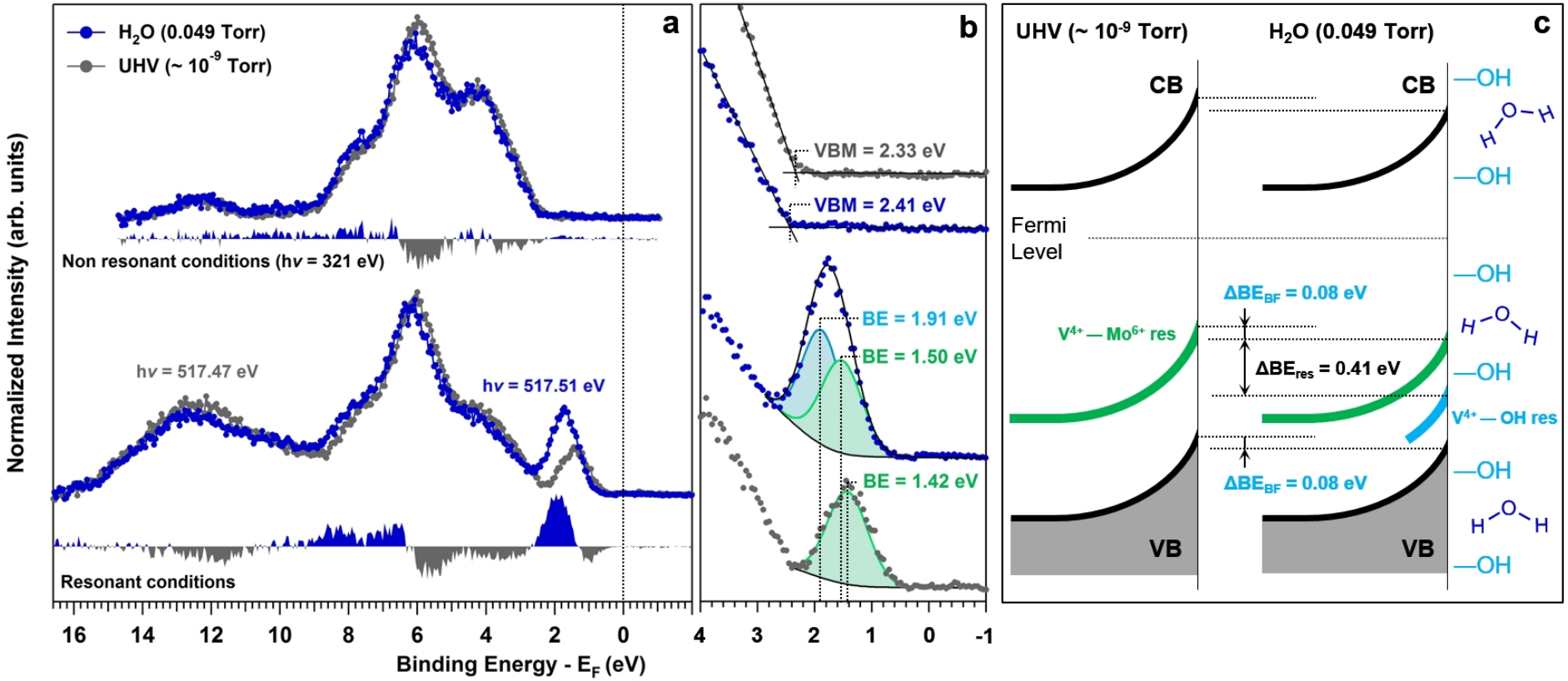


Upon illumination:

1. Protons leave the surface and are buffered by KPi ⇒ increase in $H_2PO_4^-/HPO_4^{2-}$ ratio (IR)
2. Phosphate groups adsorbs at surface ⇒ negative charging explains ΔOCP of -30 mV
3. Other phosphate groups are repelled from $BiVO_4$/electrolyte to electrolyte/vapor interface ⇒ explains increase in H_xPO_4 signal

First tentative understanding of changes at $BiVO_4$/electrolyte interface under illumination

Resonant-XPS Spectra for 1% Mo:$BiVO_4$ (010)

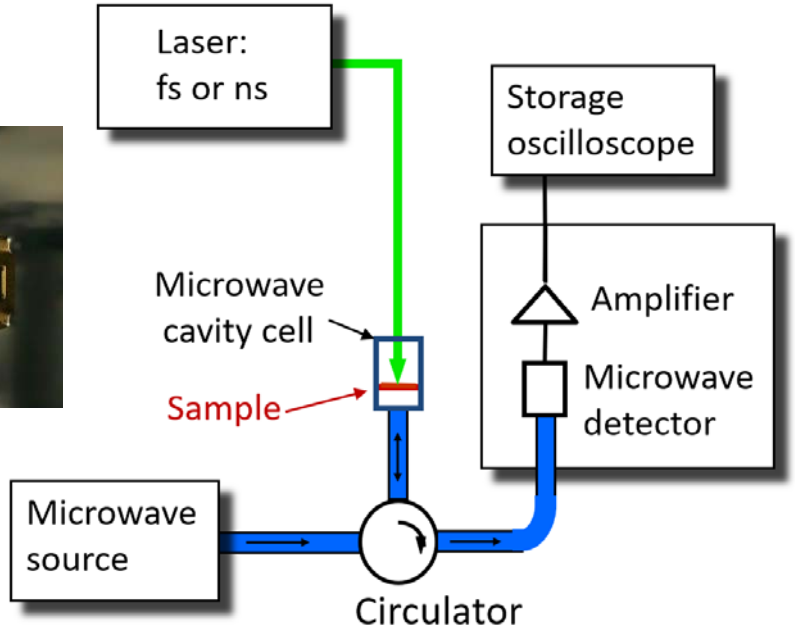


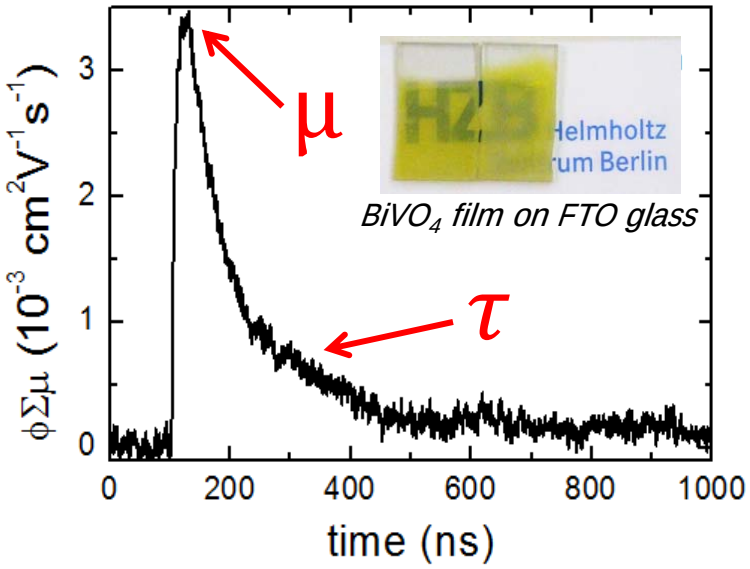
Two electronic states identified in $BiVO_4$:

- Mo-induced deep V^{4+} bulk state at 0.91 eV above VBM
- Water-induced V^{4+}-OH surface state at 0.50 eV above VBM

Time-Resolved Microwave Conductivity (TRMC)

Cavity cell





State-of-the-art TRMC setup

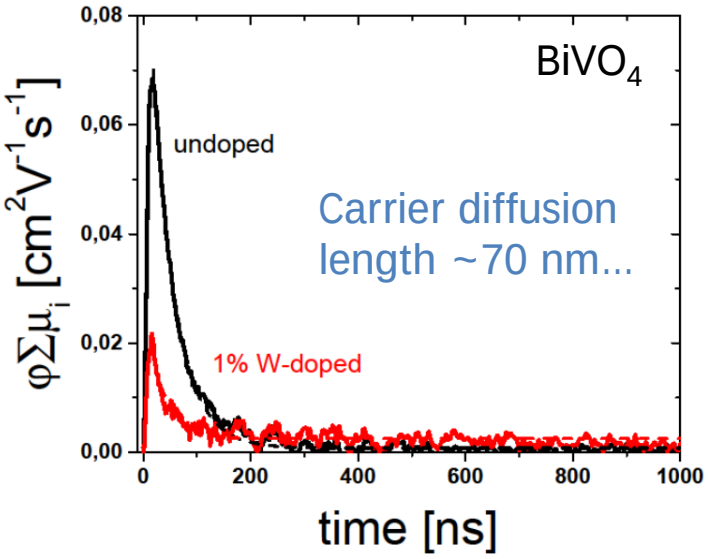
- Uses cavity cell based on design of Savenije et al., TU Delft
- Enables direct measurement of carrier lifetime (τ) and mobility (μ) with >10x higher sensitivity
- $BiVO_4$: μ = 0.044 cm^2/Vs, τ = 40 ns

Carrier diffusion length:

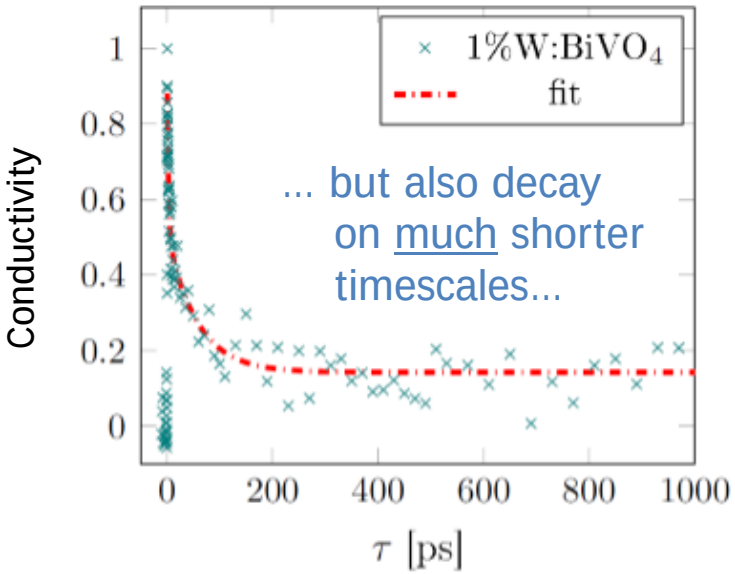
$$L_D = \sqrt{\frac{\mu k T \tau}{e}}$$

Abdi et al., *J. Phys. Chem. Lett.* 4, 2752 (2013)

Time-Resolved Spectroscopy on Absorber Materials

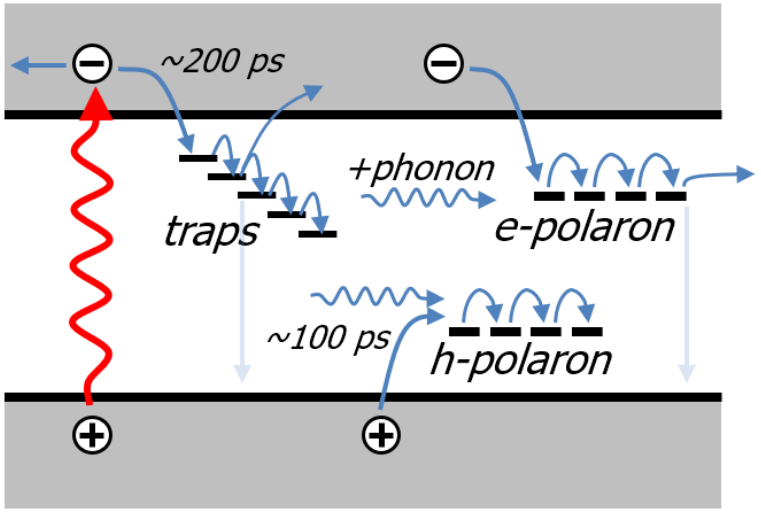


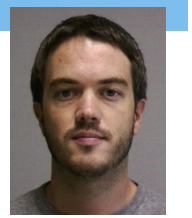
J. Phys. Chem. Lett. 4 (2013) 2752



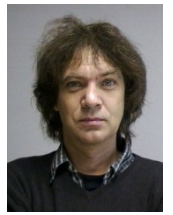
But: quantum efficiency >80%…

⇒ Decay reflects decrease in carrier mobility, not in carrier concentration!





Dennis Friedrich

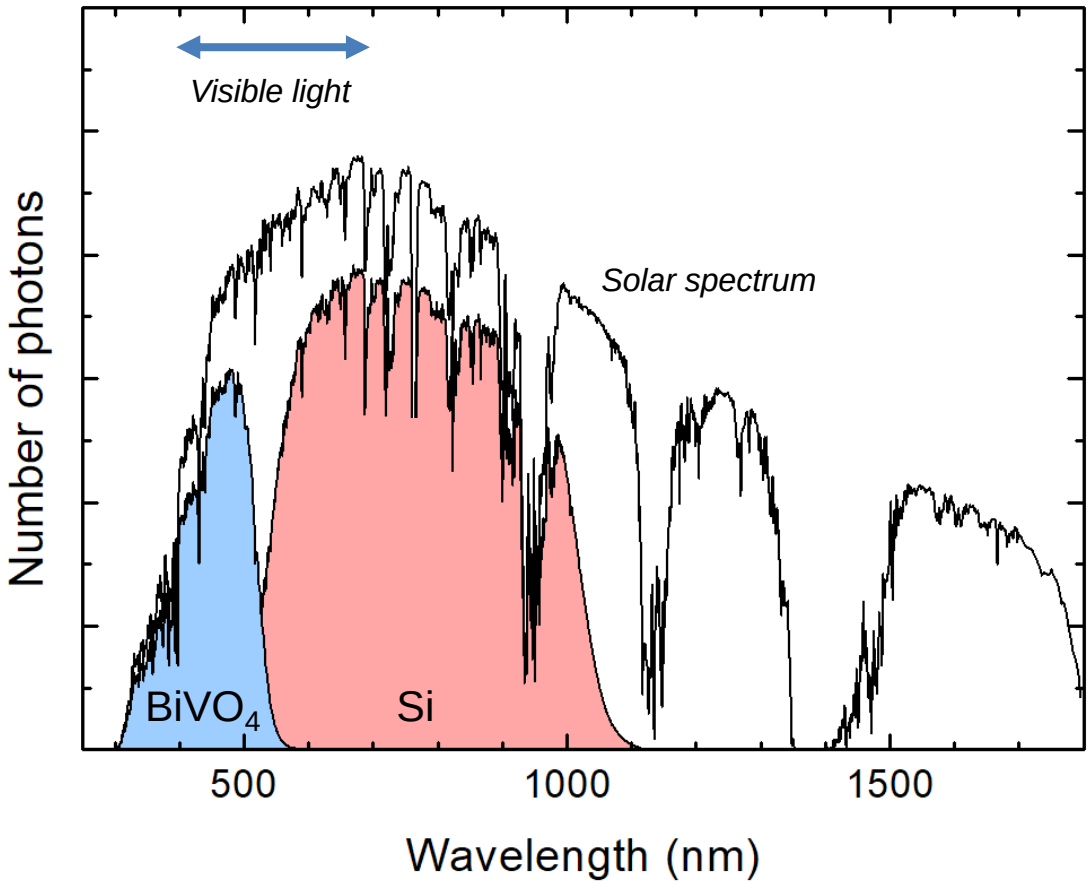


Rainer Eichberger

Evolution of photoexcited carriers in $BiVO_4$

- Free carriers → trapping & polaron formation
- Carriers slow down enormously, but are still able to reach the interface
- Carrier dynamics **very** different than in 'normal' semiconductors

The Need for Chemically-Stable Wide-Bandgap Absorbers

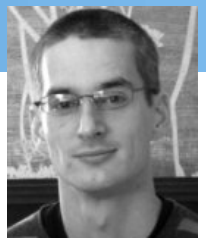


Band gaps

$BiVO_4$: 2.4 eV
Silicon: 1.1 eV

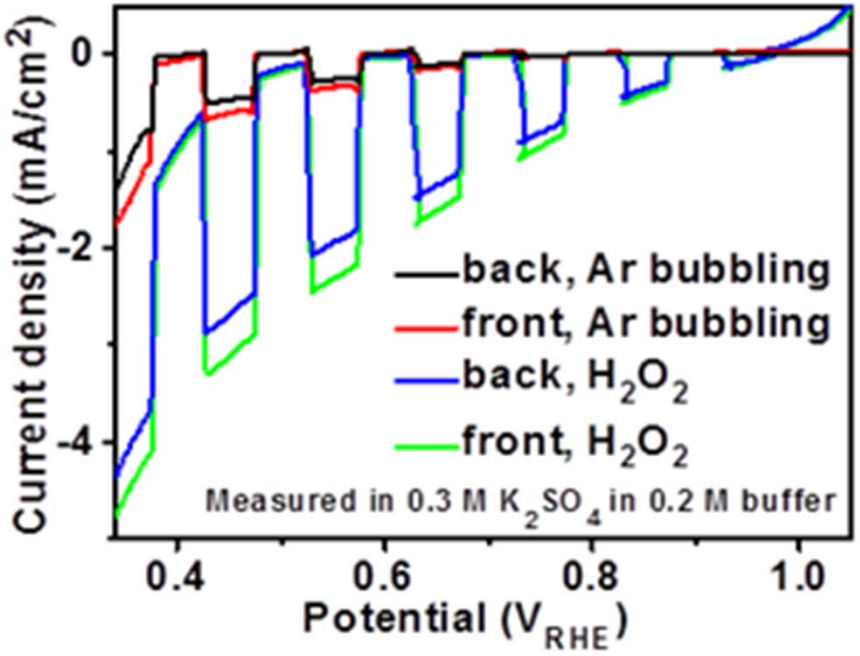
- Mismatch in photocurrent from $BiVO_4$ and silicon
- New semiconductors needed that
  - have a smaller bandgap: 1.8 eV would enable 20% efficiency
  - are chemically **stable**, **efficient**, and **cheap**

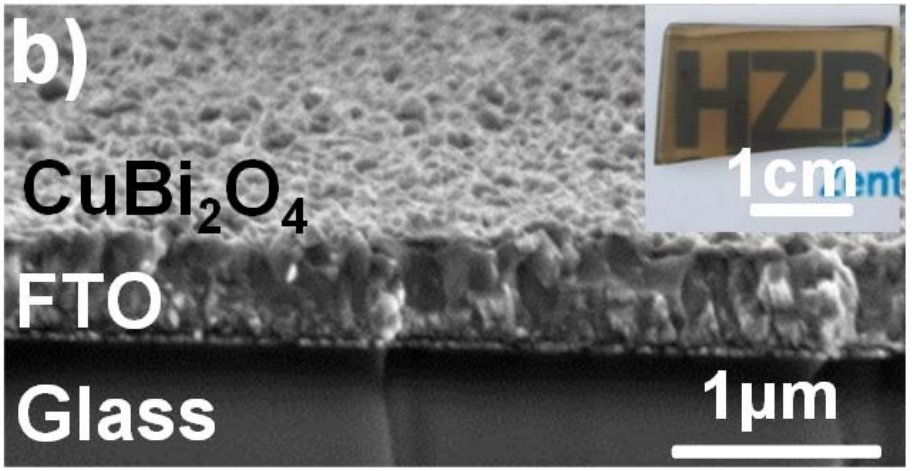
Spray-Deposited p-type $CuBi_2O_4$



Sean Berglund

Fuxian Wang

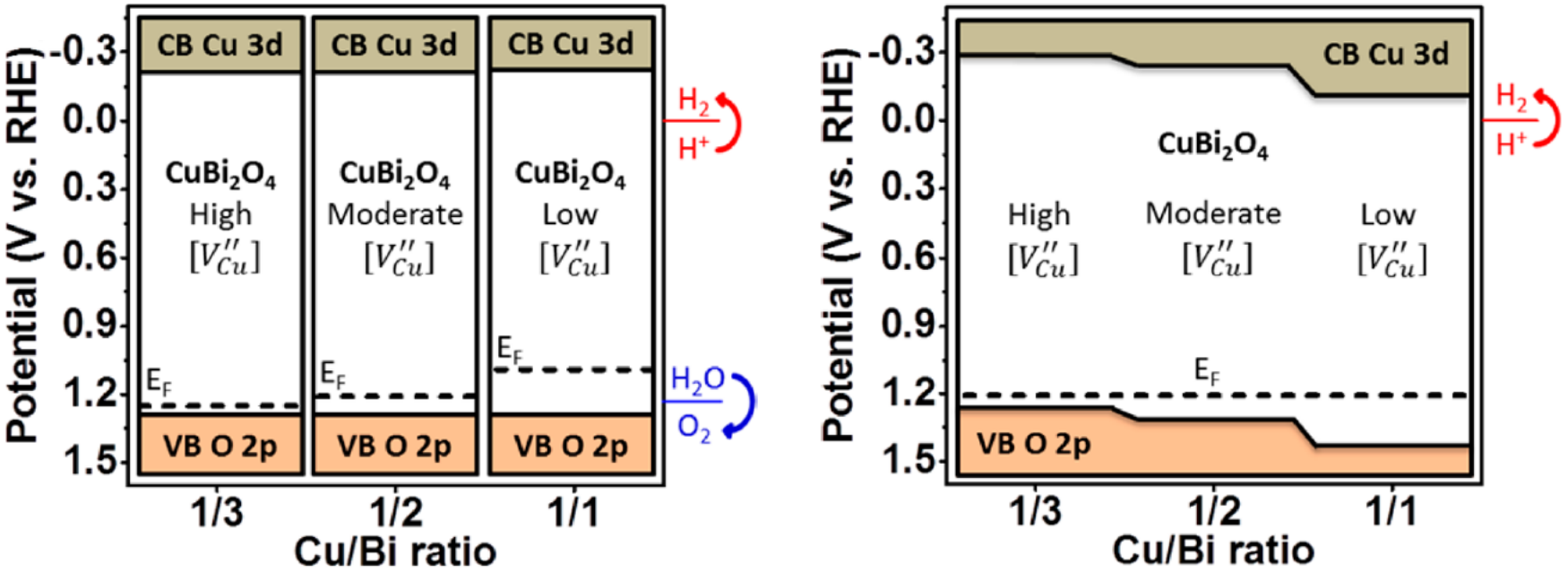




- Bandgap ~1.7 eV
- Improved spray recipe gives smooth, dense films
- Surprisingly positive photocurrent onset potential
- Challenges: **charge separation** and **stability**

Berglund et al., *Chem. Mater.* 28, 4231 (2016); Wang et al., *J. Mater. Chem. A* 5, 12838 (2017)

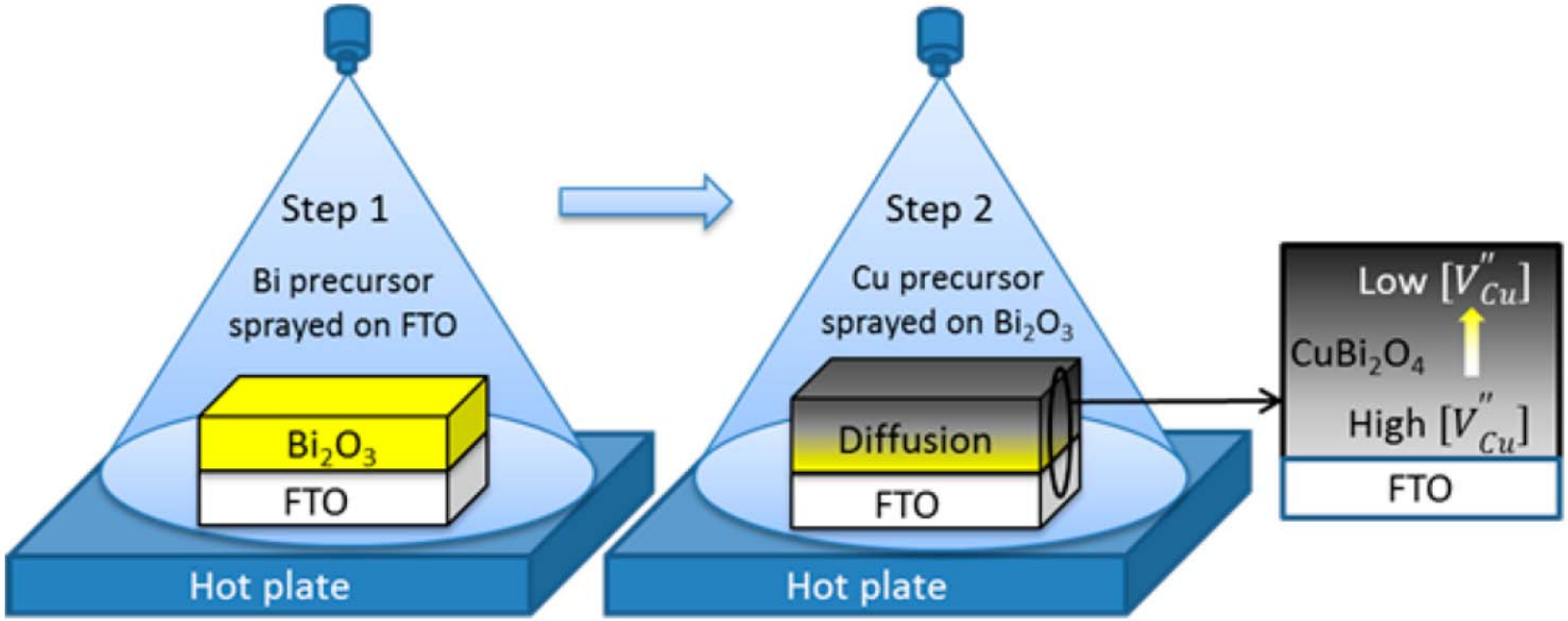
How to Improve the Charge Separation in $CuBi_2O_4$?



- Copper vacancies (V_{Cu}'') are the dominant defect in $CuBi_2O_4$
- By changing the concentration of V_{Cu}'', the Fermi level changes
- A gradient in the V_{Cu}'' concentration would then result in an electric field
- How to make a gradient in Cu vacancies?

Wang et al., *J. Am. Chem. Soc.* 139, 15094 (2017)

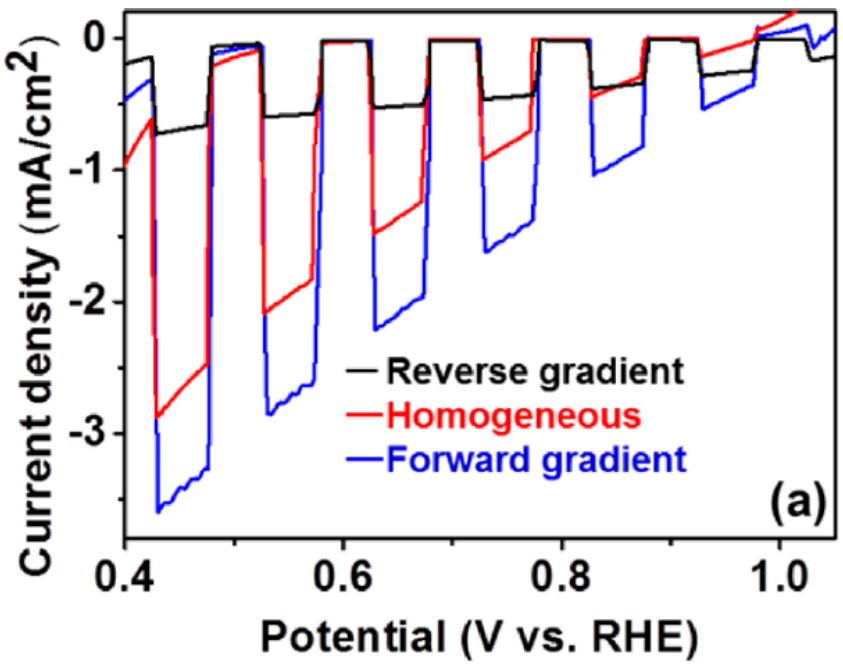
Synthesis of $CuBi_2O_4$ with Gradient of Cu Vacancies

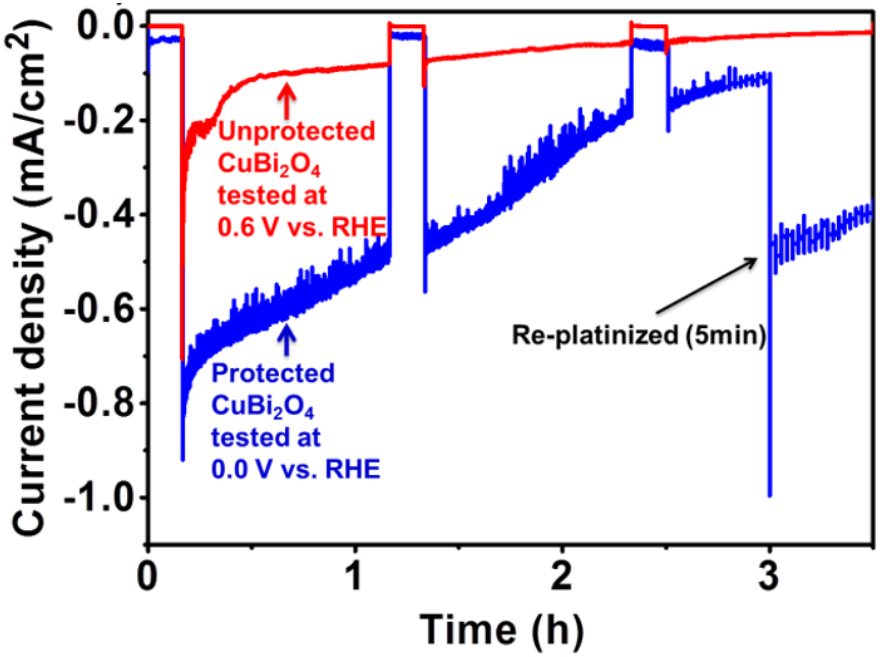


Sequential deposition of Bi_2O_3 and CuO layers by spray deposition

Wang et al., *J. Am. Chem. Soc.* 139, 15094 (2017)

Photoelectrochemical Characterization of $CuBi_2O_4$

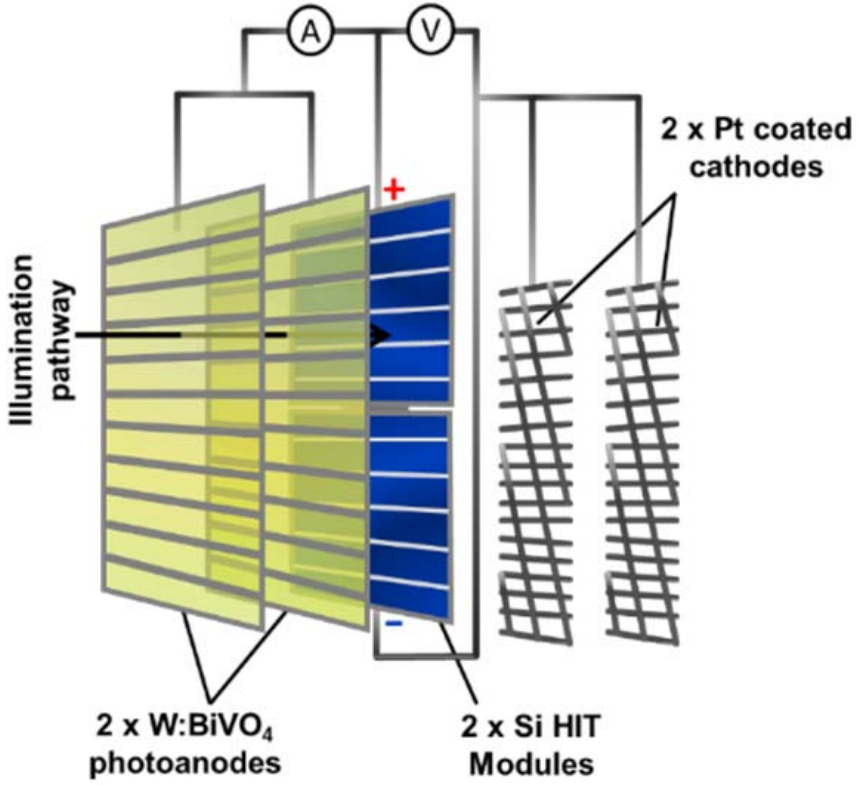


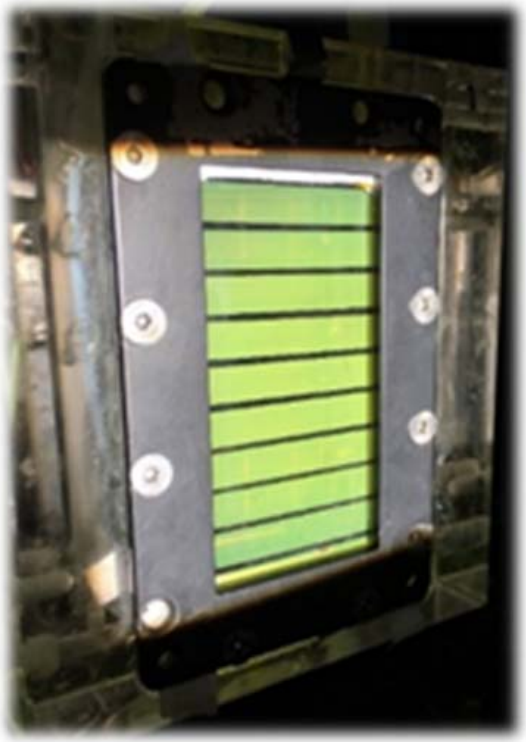


- Forward-gradient films consistently show higher photocurrent densities
- CdS / TiO_2 / Pt deposited by David Tilley's group at Uni Zürich [1]
- Dramatic improvement in lifetime (but still not good enough)
- H_2 evolution photocurrent: -1.0 mA/cm^2 at 0 V_{RHE}, Faradaic efficiency ~91%

[1] Septina et al., *Chem. Mater.* 29, 1735 (2017)
[2] Wang et al., *J. Am. Chem. Soc.* 139, 15094 (2017)

Stand-alone 50 cm² Solar Fuel Device



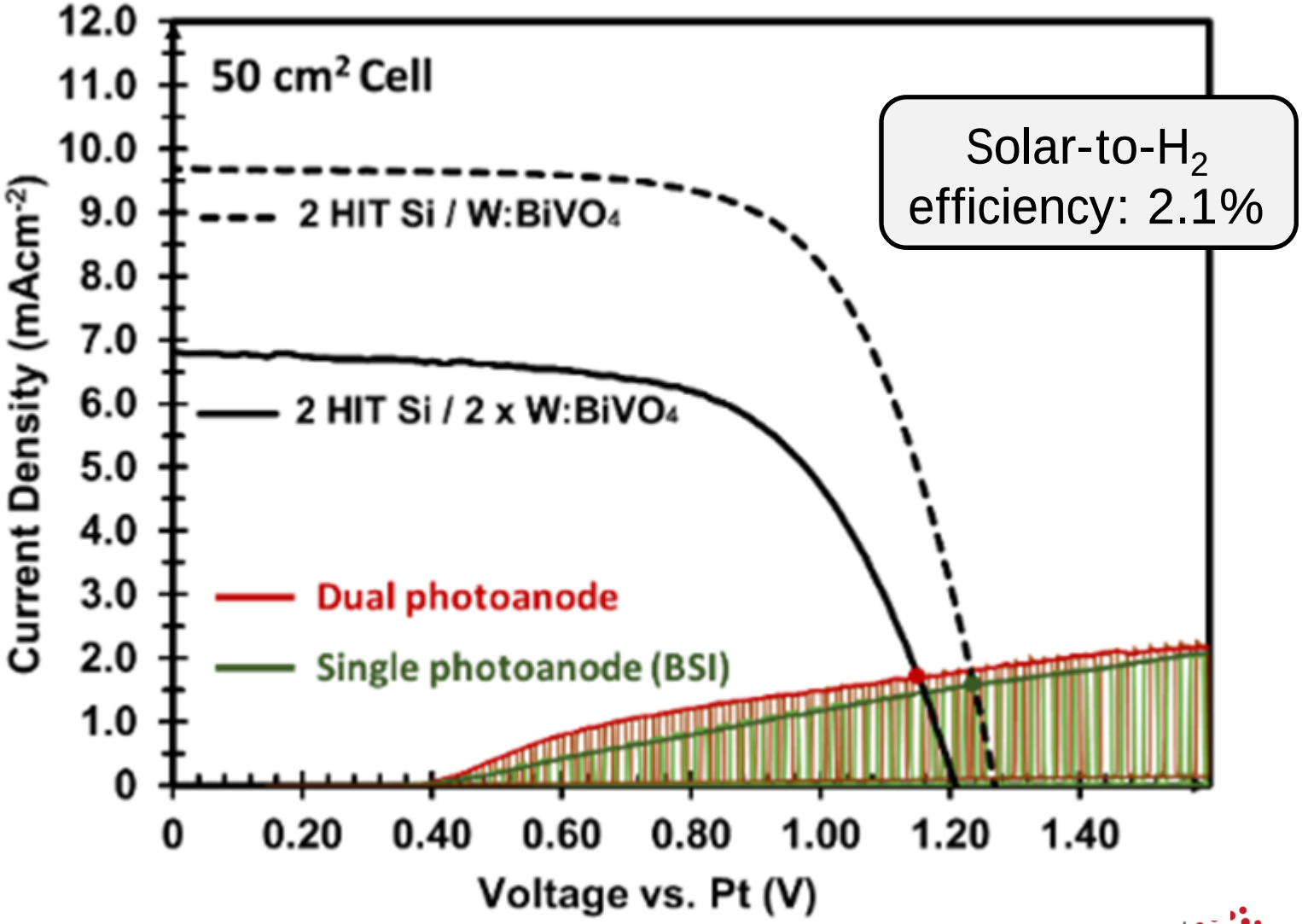


Dual photoanode concept (*) to minimize charge transport losses in $BiVO_4$

Cell provided by group of Adélio Mendes, Univ. Porto

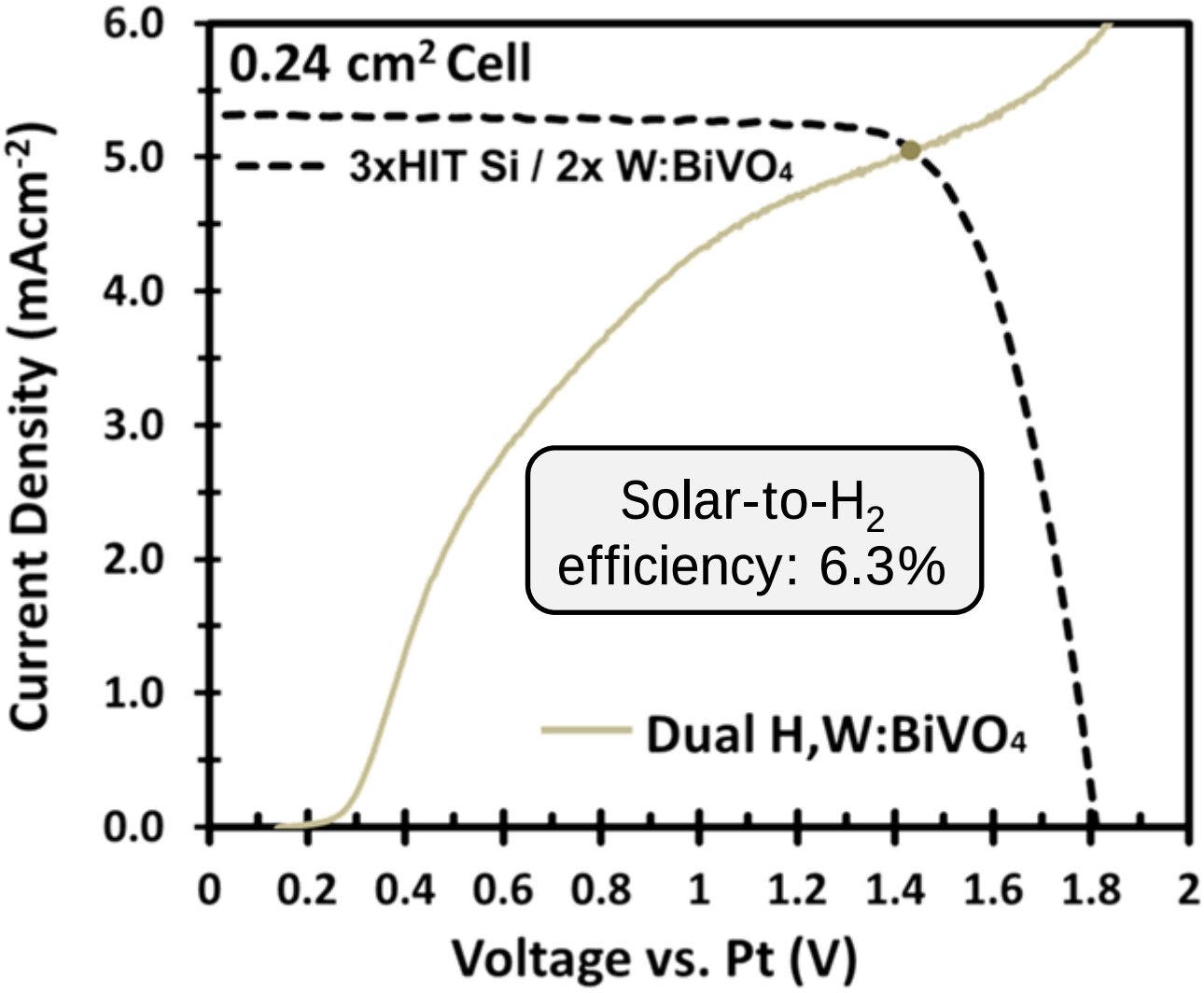
(*) Kim et al. *Nat. Commun.* 7, 13380 (2016)

Stand-alone 50 cm² Solar Fuel Device



Solar-to-H_2 efficiency: 2.1%

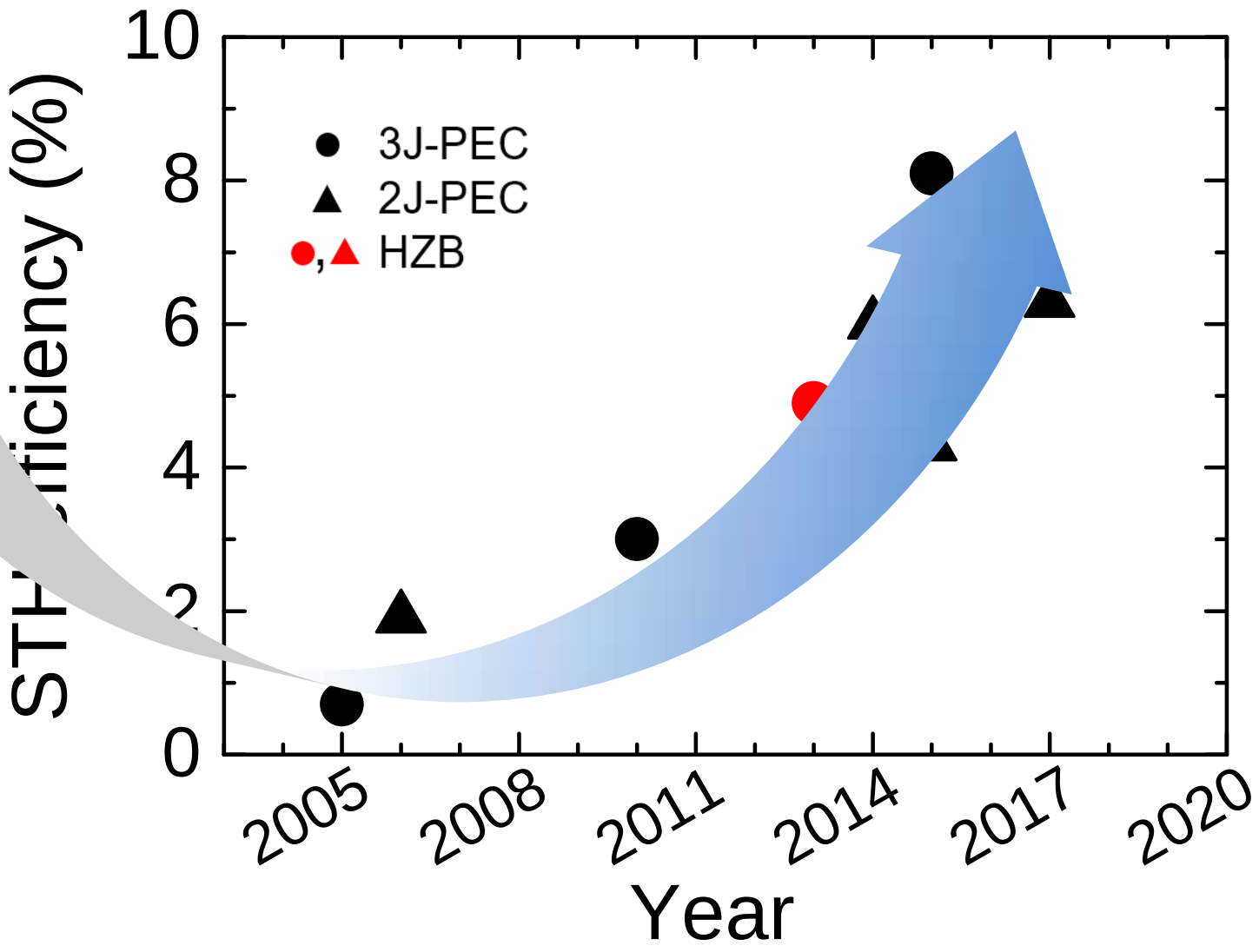
Stand-alone 0.24 cm^2 Solar Fuel Device



Summary & Conclusions

- $BiVO_4$ (2.4 eV) is a useful platform to learn about bulk and interfacial properties of oxides and scale-up challenges in PEC water splitting:
  - Surface recombination can dominate overall behavior
  - New operando X-ray methods give important new insights
  - Low mobility polaronic materials can still be efficient
- p-$CuBi_2O_4$ (1.7 eV) is a promising photocathode material
  - Gradient of intrinsic defects (Cu vacancies) helps charge separation
  - Stability needs to be improved
- Scale-up is hard, we need (electro)chemical engineers!

Progress in Oxide-Based Water Splitting Devices



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