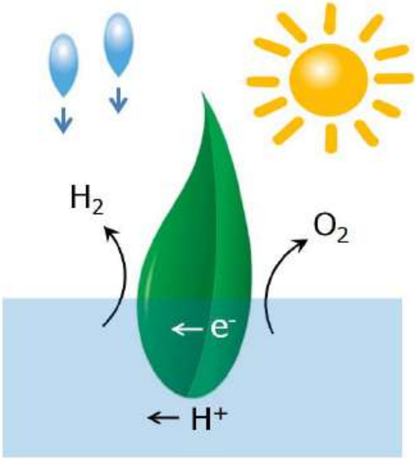

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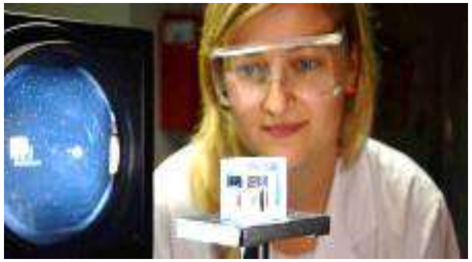

Towards Efficient Solar Fuels Production

from materials to large-area devices

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Berlin, Germany
E-Mail: fatwa.abdi@helmholtz-berlin.de

IKATAN ILMUWAN INDONESIA INTERNASIONAL

Helmholtz-Zentrum Berlin für Materialien und Energie GmbH

HZB Helmholtz Zentrum Berlin

Wannsee – Lise-Meitner Campus

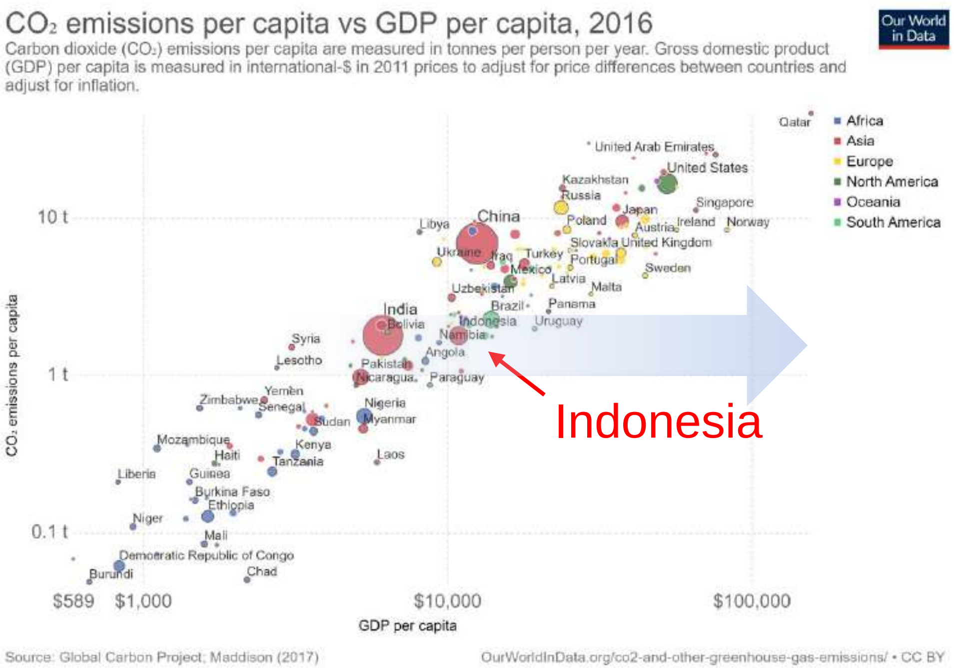
- BER-II Nuclear Research Reactor
- Compound semiconductor photovoltaics
- Solar Fuels
- Electrochemical energy storage (battery)
- Soft matter & functional materials
- Magnetic materials

Adlershof – Wilhelm-Conrad-Röntgen Campus

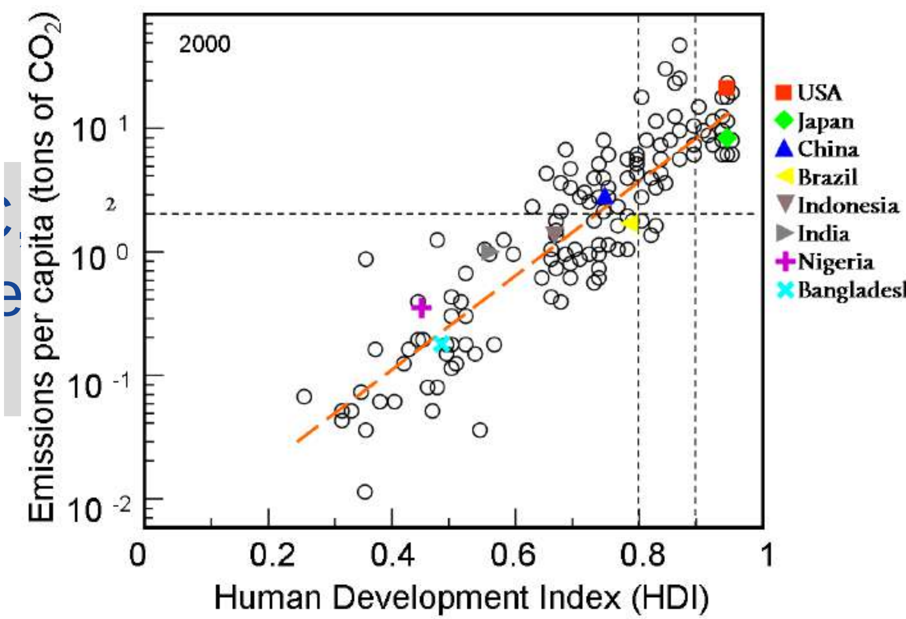
- BESSY-II Synchrotron
- Silicon & perovskite photovoltaics
- Energy Materials In-situ Laboratory
- Nano-architectures for Energy
- PV Competence Center Berlin (PVcomB)

Why Renewable Energy? Reducing CO_2 emission

$$CO_{2,total} = population \times \frac{GDP}{population} \times \frac{CO_2}{GDP}$$



Costa et al. PLOS One 6 2011 e29262



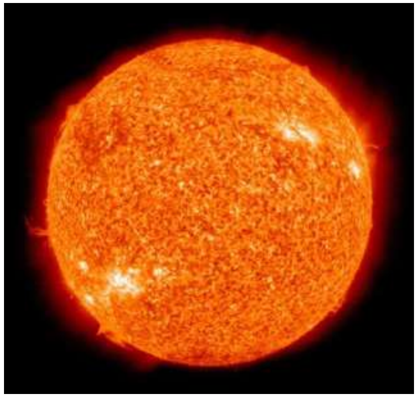
How to break the relationship?

$$\frac{CO_2}{GDP} = \frac{E_{cons.}}{GDP} \times \frac{CO_2}{E_{cons.}}$$

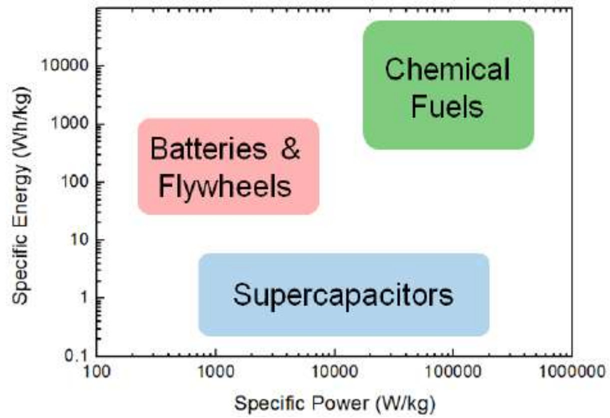
more efficient use of energy

low/zero-carbon energy source

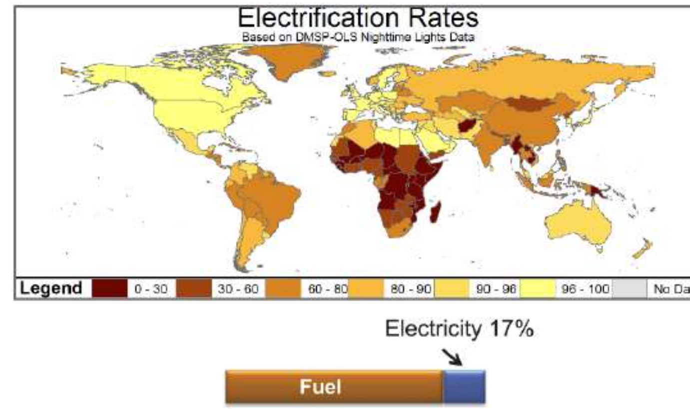
Hard Facts on Renewable Energy



Sunlight is the most abundant source of energy
120,000 TW vs. 30 TW (2050)



Energy- and power-densities of chemical fuels are off the chart



Our energy use: 17% electricity, 83% fuels
Large infrastructure for fuels

Fuels from sunlight

Is this possible?

$$6\ CO_2 + 6\ H_2O \rightarrow C_6H_{12}O_6 + 6\ O_2$$

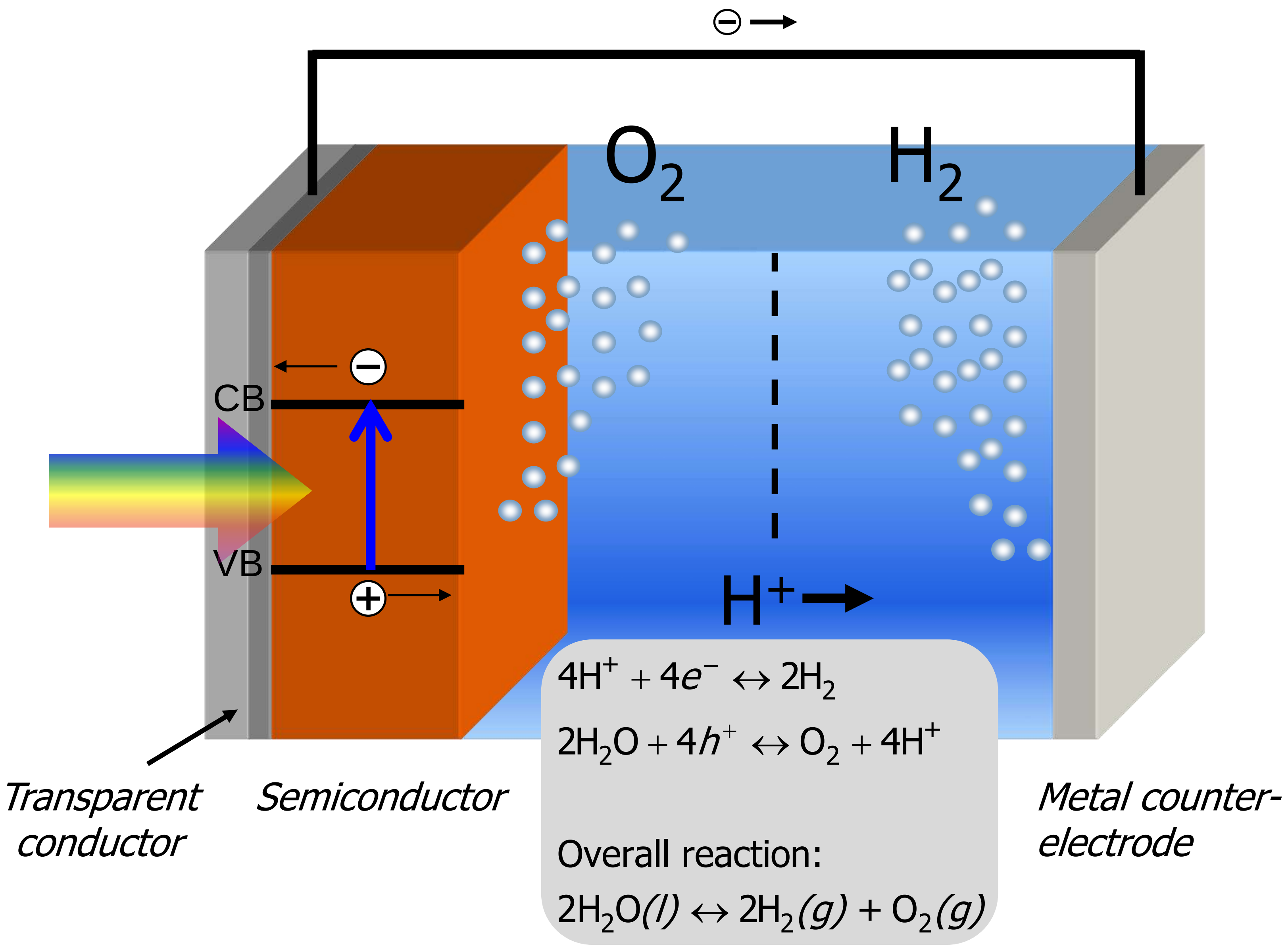
$$2\ H_2O \rightarrow 2\ H_2 + O_2$$

fuels

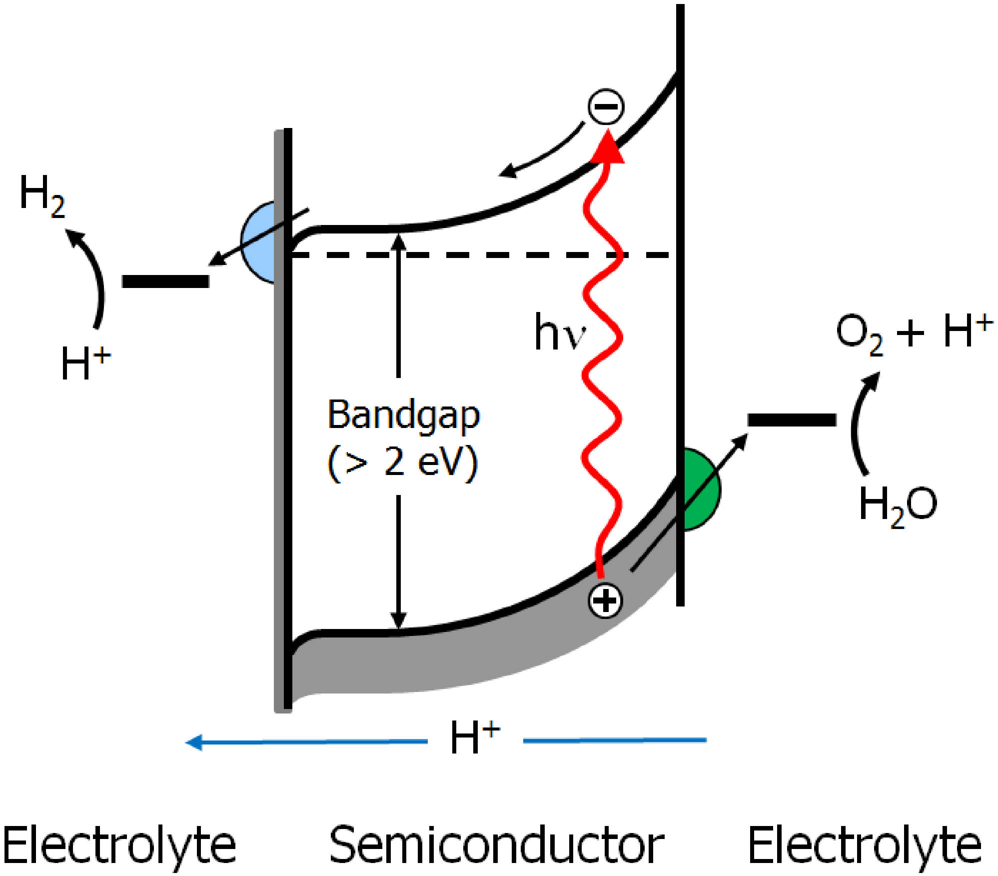
Haber Bosch → ammonia

chemical feedstock for Fischer-Tropsch → methanol, diesel, etc.

Photoelectrochemical Cell



The „Holy Grail“ : Direct Photoelectrolysis



Requirements

- Good visible light absorption
- Suitable band edge positions
- Efficient O_2/H_2 evolution (catalysis)
- Efficient carrier transport
- High (photo)chemical stability
- Low cost

We are interested at complex metal oxide semiconductors

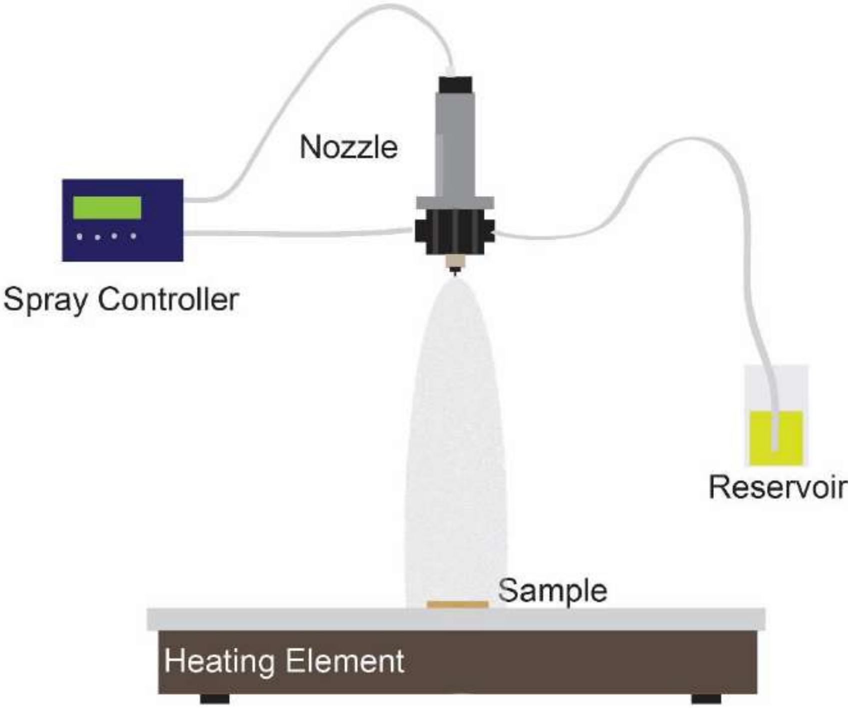
A Success Story: Bismuth Vanadate ($BiVO_4$)

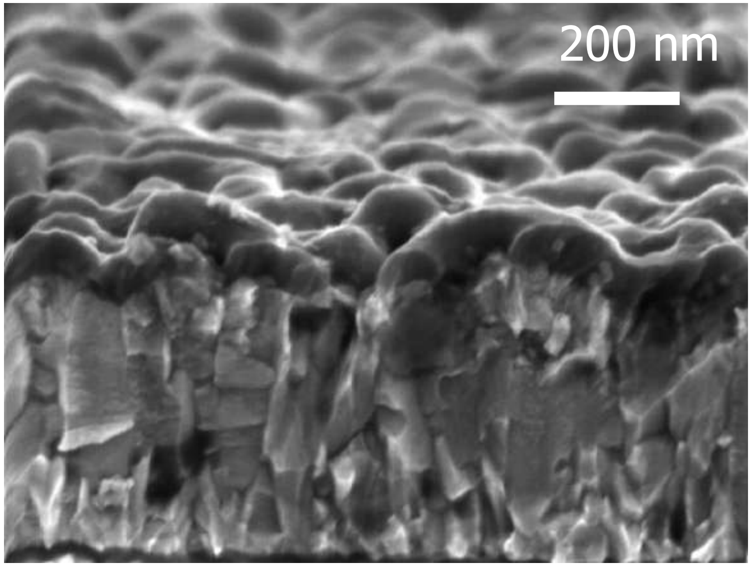
- Yellow pigment (paint, printing ink)
- Photocatalytically active: first reported by Kudo et al. in 1998
- Photoactive phase: monoclinic scheelite
- n-type, bandgap is 2.4 eV

Spray Deposition of $BiVO_4$ Thin FIlms

Precursor & Spray Parameters

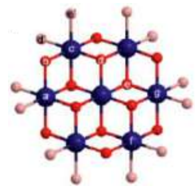
- Solvent: ethanol + acetic acid
- 0.02 M $Bi(NO_3)_3{\bullet}5H_2O$
- 0.02 M $VO(AcAc)_2$
- Substrate temperature: 450°C





Overcoming the Performance Limiting Factors

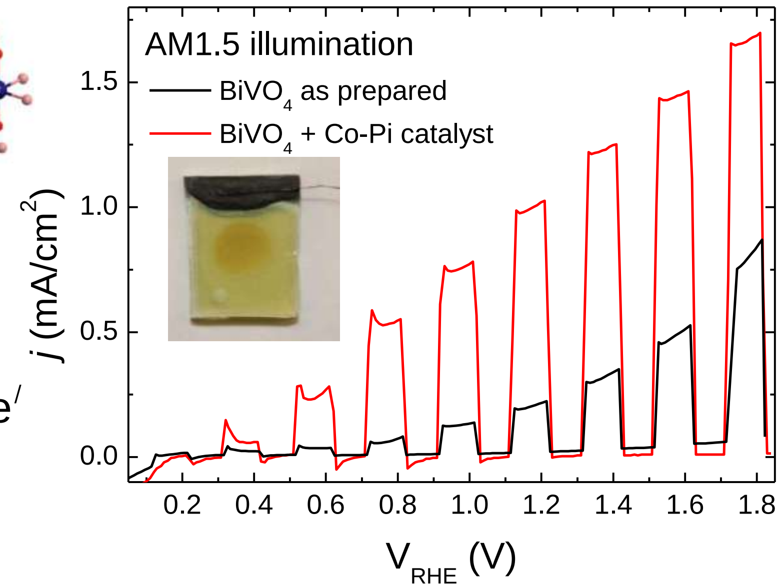
Performance limitations due to:



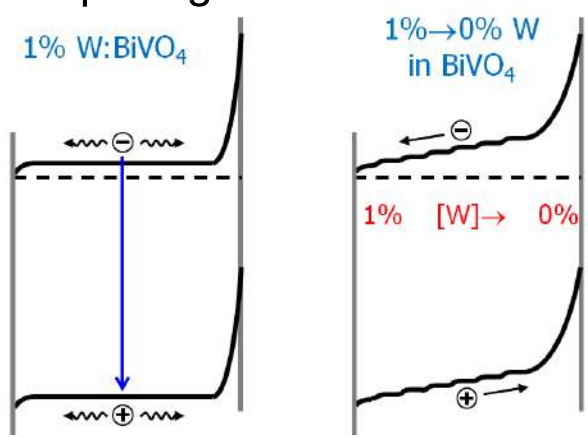
- **Slow water oxidation kinetics**
  - → deposit CoPi OEC [1]
- **Poor carrier transport**
  - → doping with W [2] ; H insertion [3]

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

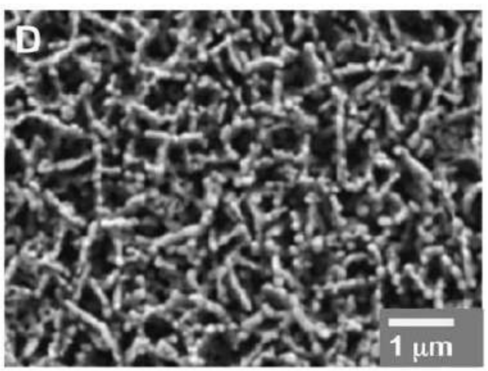
$$H_2(g) \rightarrow 2H_i^{\bullet} + 2e^{/}$$

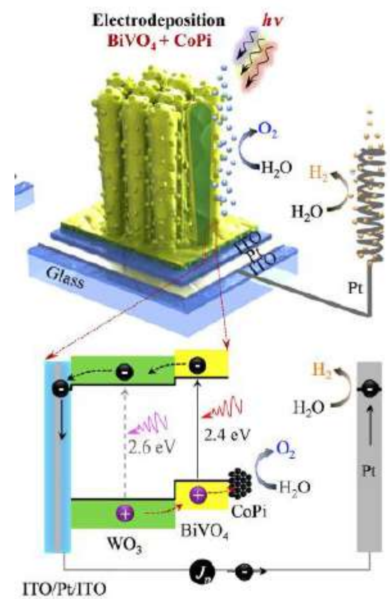


- **Poor charge carrier separation**
  - → dopant gradient [4]



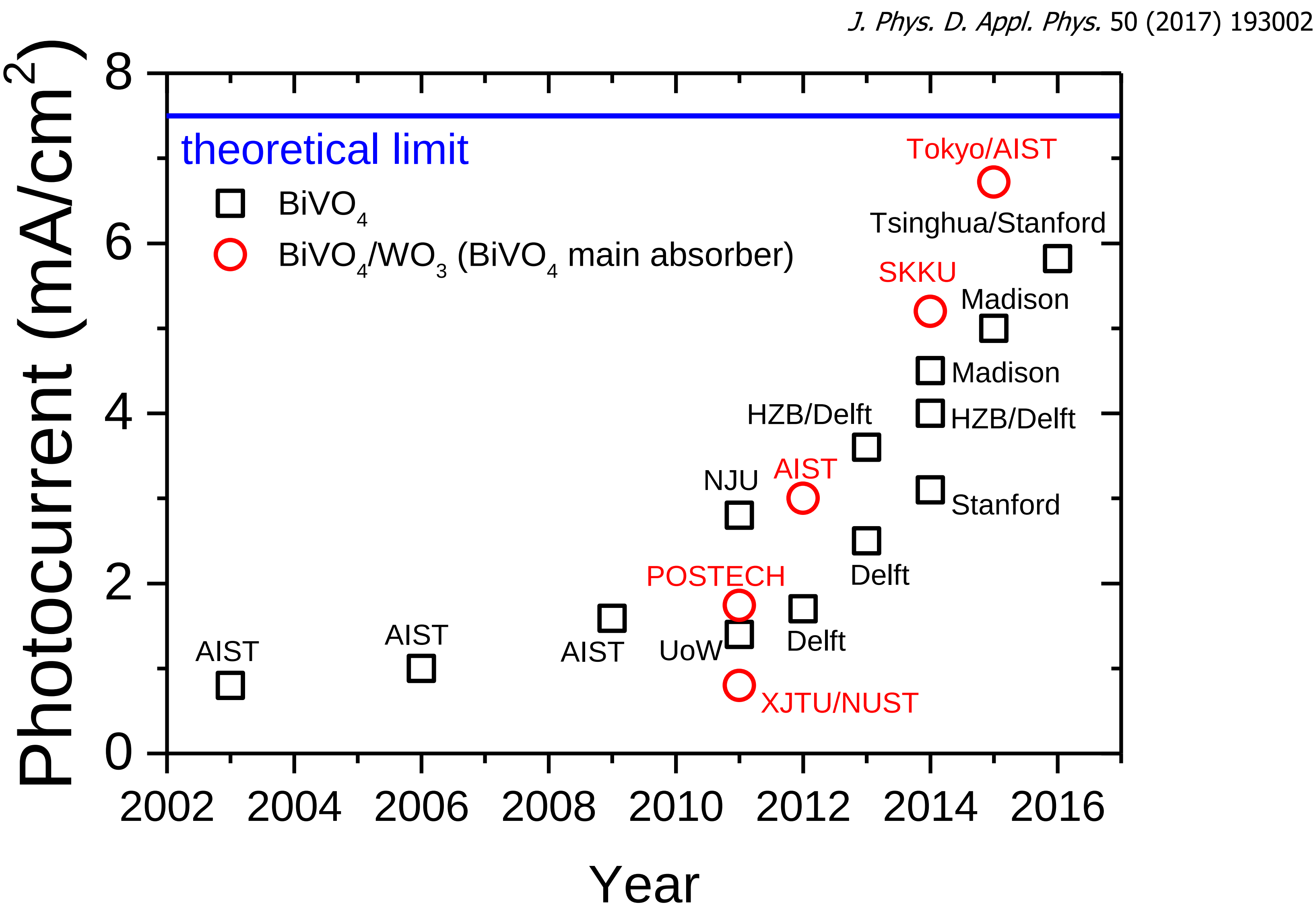
→ nanostructuring [5,6]





[1] *J. Phys. Chem. C* 116 (2012) 9398
[2] *ChemCatChem* 5 (2013) 490
[3] *Adv. Energy Mater.* 7 (2017) 1701536
[4] *Nat. Commun.* 4:2195 (2013)
[5] Kim et al. *Science* 343 (2014) 990
[6] Pihosh et al. *Sci. Rep.* 5 (2015) 11141

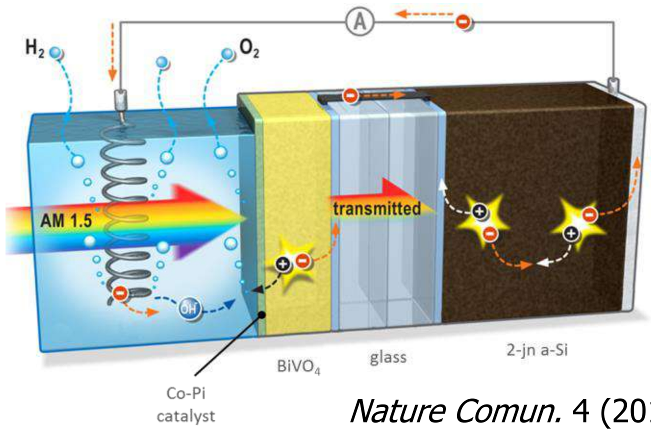
Progress in $BiVO_4$



Highest reported photocurrent already very close to the theoretical maximum

Oxide ($BiVO_4$)-based devices show increasing efficiencies

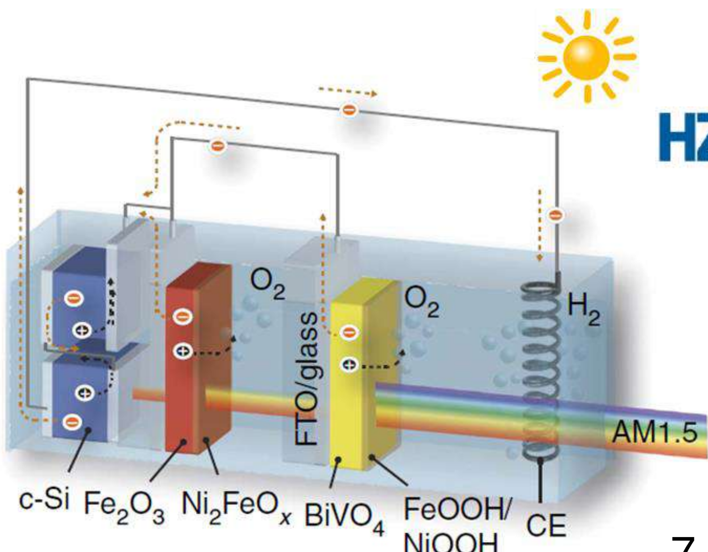
Reported solar-to-H_2 (STH) efficiencies
for water splitting devices based on oxide absorbers



5.2% STH efficiency

TU Delft
HZB Helmholtz Zentrum Berlin

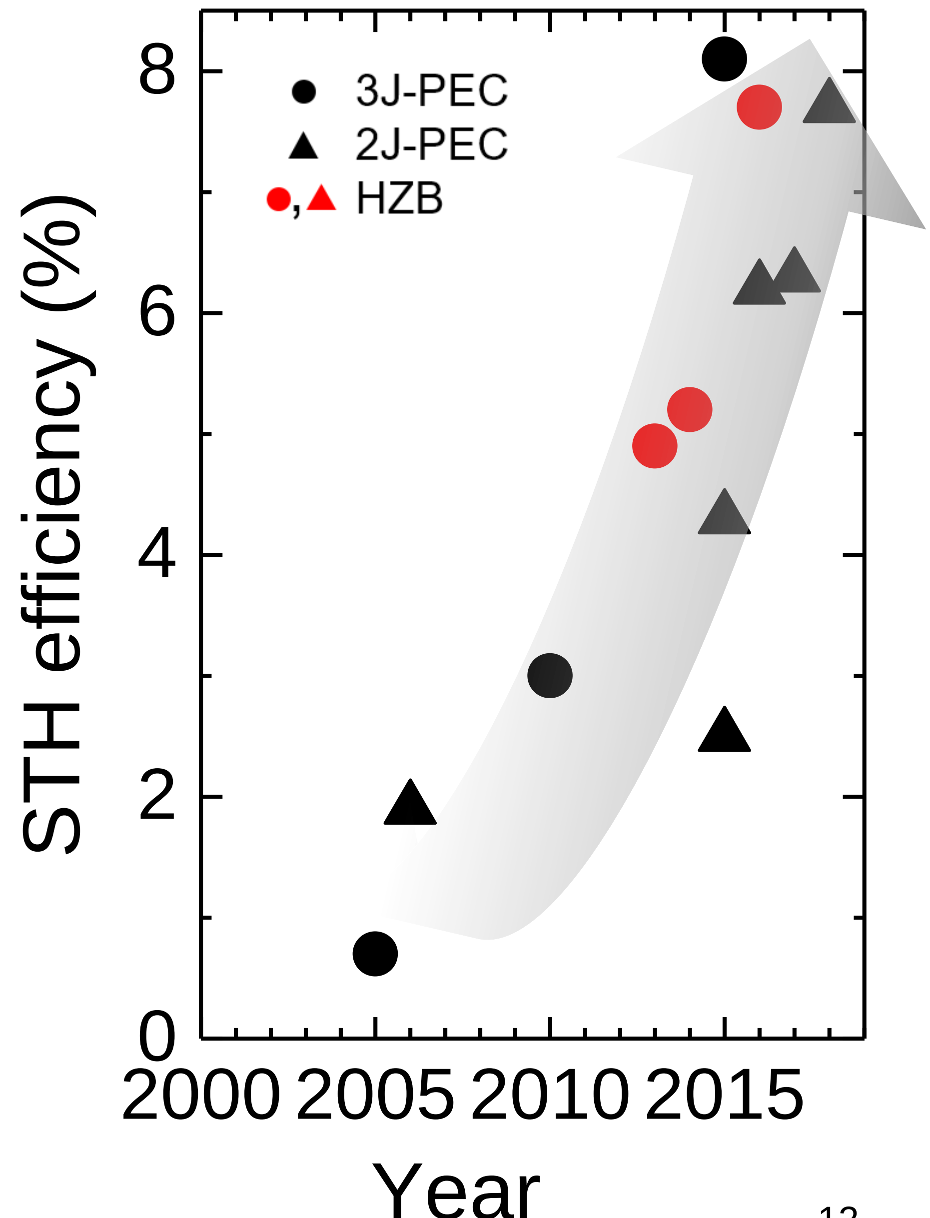
Nature Comun. 4 (2013) 2195



HZB Helmholtz Zentrum Berlin

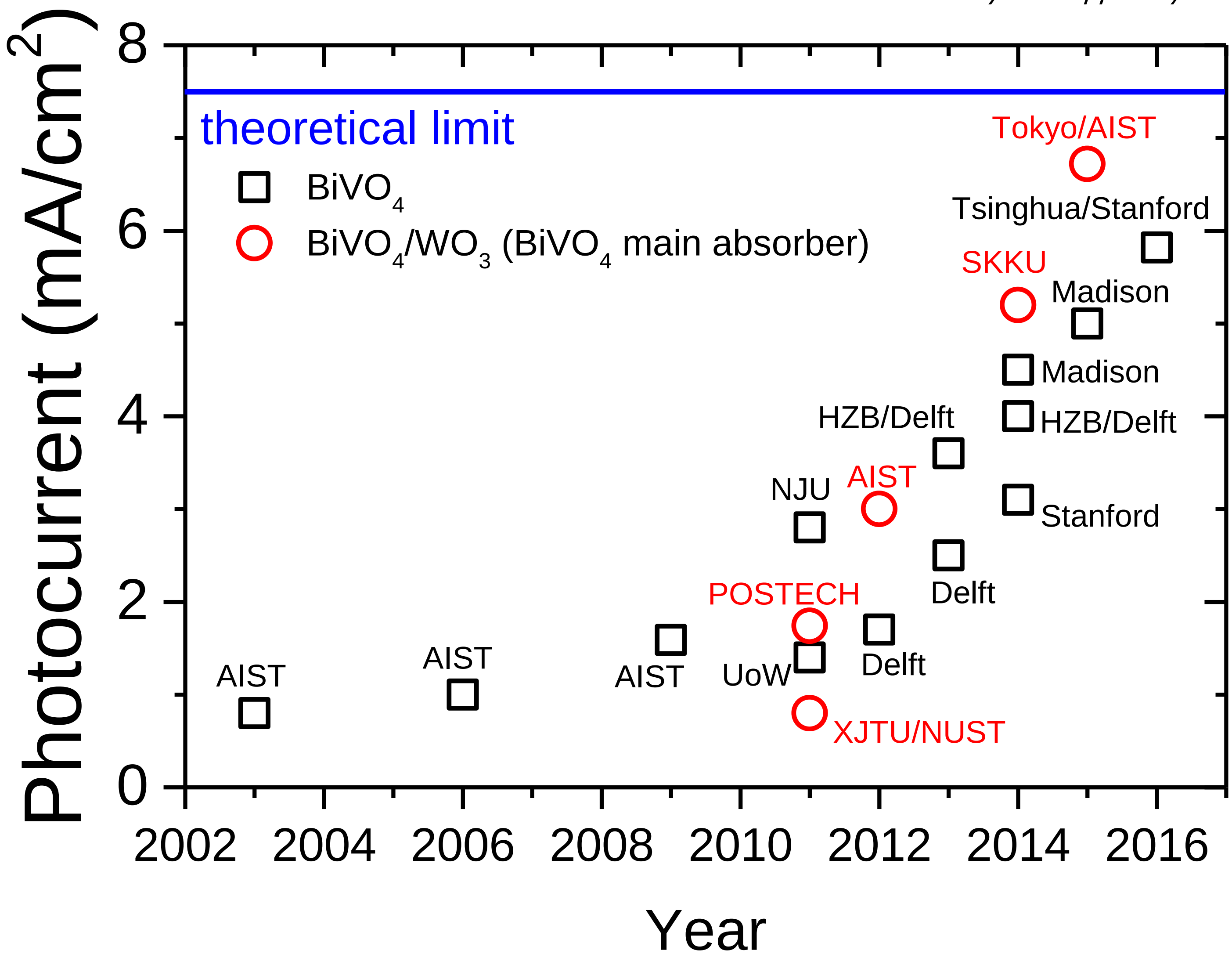
Nature Comun. 7 (2016) 13380

7.7% STH efficiency



Progress in $BiVO_4$

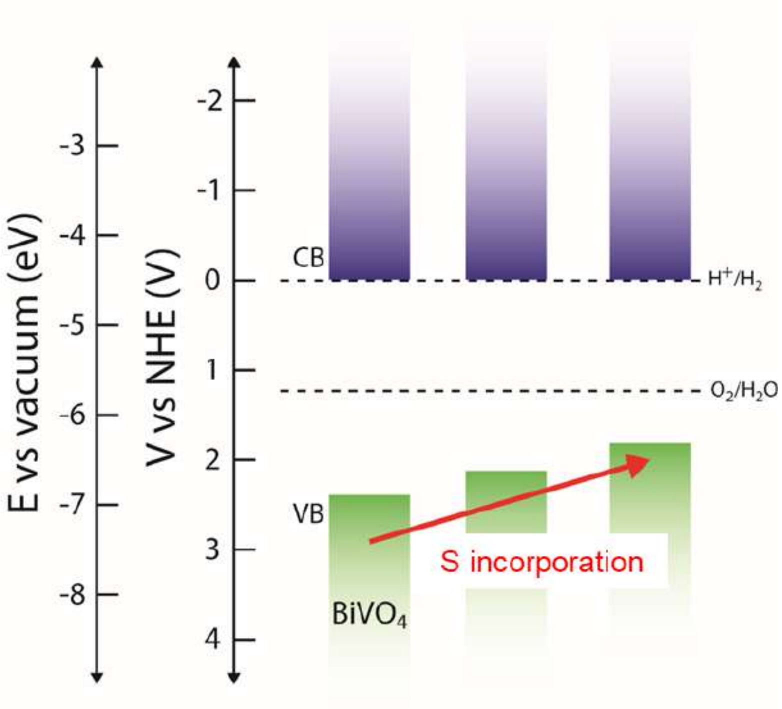
J. Phys. D. Appl. Phys. 50 (2017) 193002

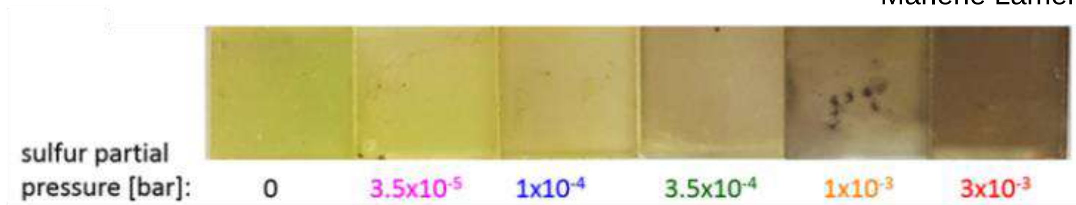


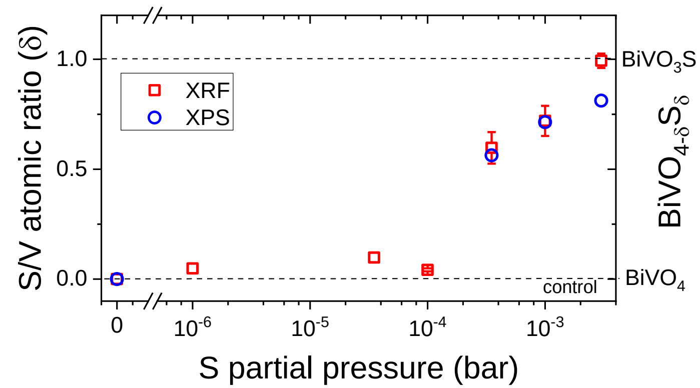
How can we go beyond the theoretical limit?

Sulfur incorporation to reduce the bandgap of $BiVO_4$

Marlene Lamers

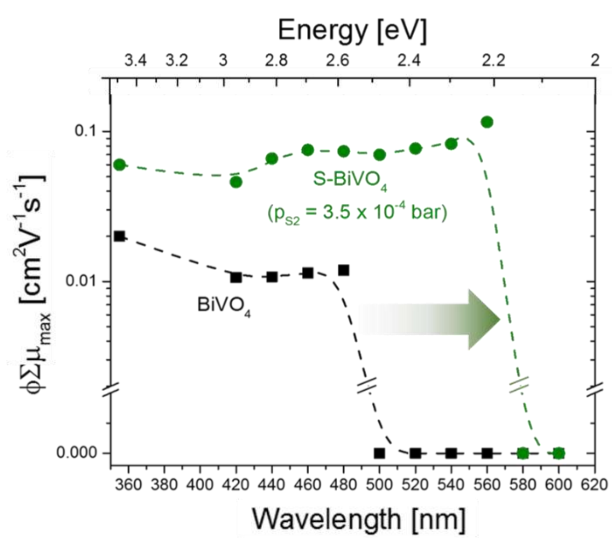






- Bandgap shifted by ~0.3 eV, which increases the STH_{max} to 12%
- N-incorporation has also been reported, but not successful for our $BiVO_4$

Solar RRL 4 (2020) 1900290

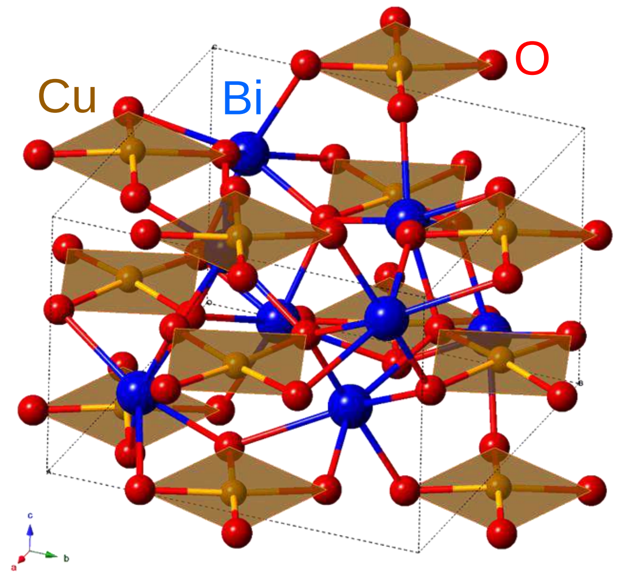


NANYANG TECHNOLOGICAL UNIVERSITY SINGAPORE

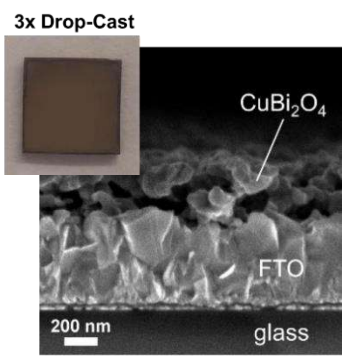
KAUST

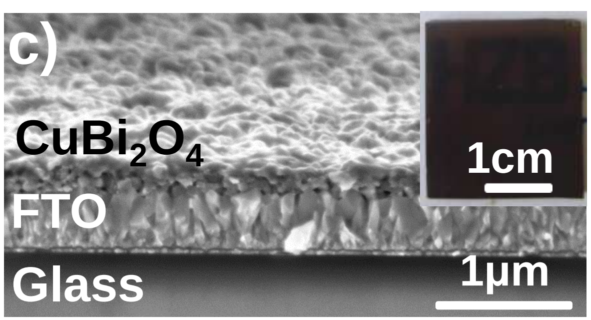
Chem. Mater. 30 (2018) 8630

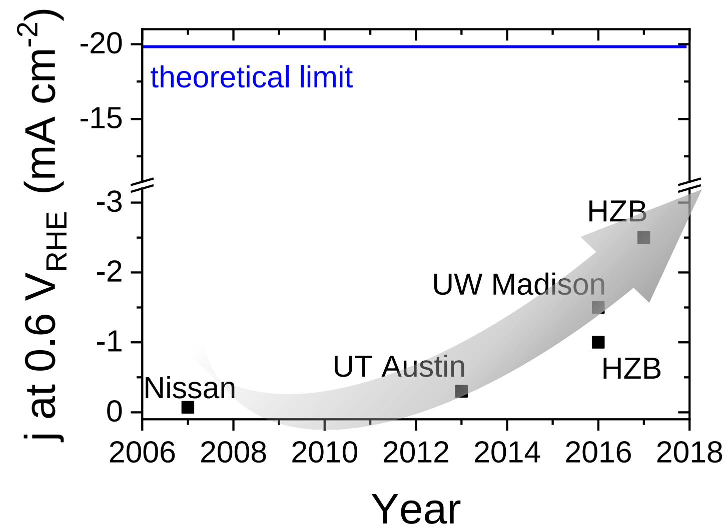
$CuBi_2O_4$ – a novel complex metal oxide



- Bandgap ~1.8 eV
- Mobility and diffusion length comparable to $BiVO_4$
- Band edges straddle the H_2 and O_2 evolution potential
- Large photovoltage ~1.0 V
- Stability is an issue – protection layer





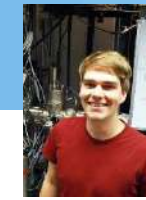


Chem. Mater. 28 (2016) 4231
J Mater. Chem. A 5 (2017) 12838
JACS 139 (2017) 15094
J Mater. Chem. A 7 (2019) 9183
APL Mater. 8 (2020) 061101

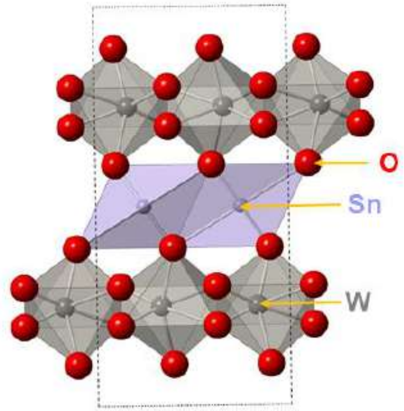
<u>Ongoing collaboration with UI (Dr. M. Khalil)</u>
$CuBi_2O_4$/Bi NPs for photoelectrochemical CO_2 reduction to HCOOH

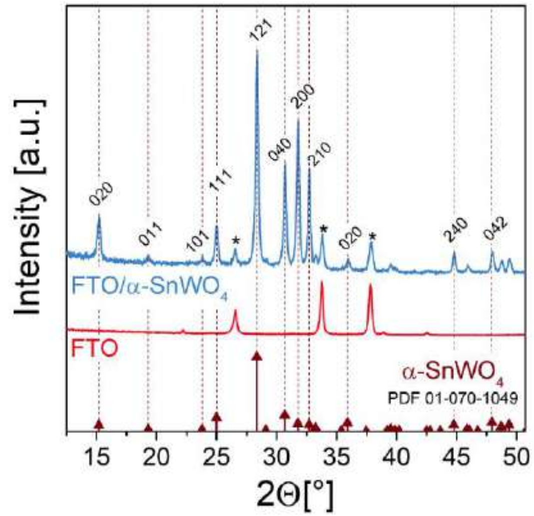
UNIVERSITAS INDONESIA

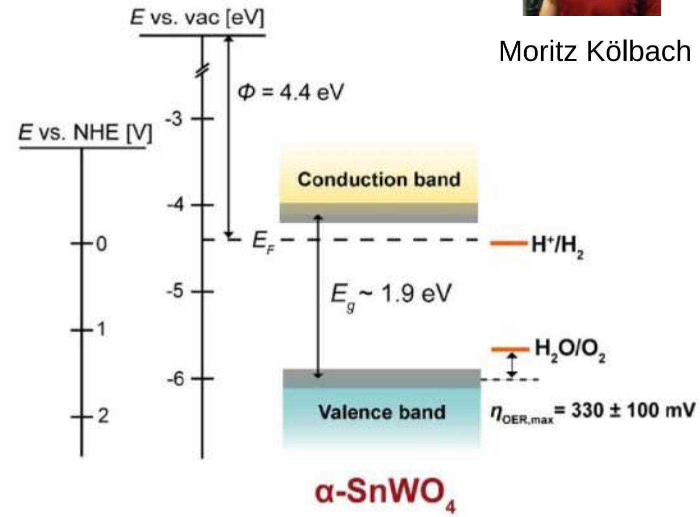
α-$SnWO_4$ – a novel complex metal oxide



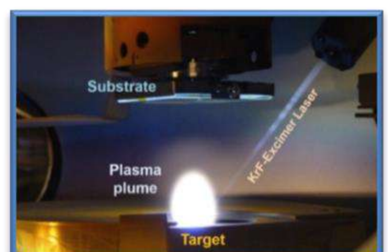
Moritz Kölbach

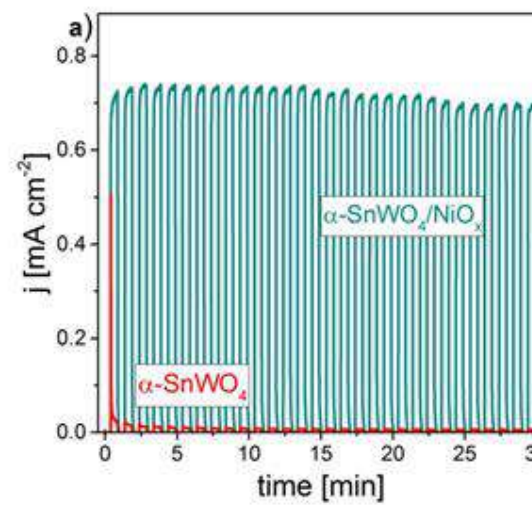






- E_g ~ 1.9 eV; **STH_{max} > 20 %**
- Orthorhombic crystal structure
- E_{FB} ~ 0 V vs. RHE

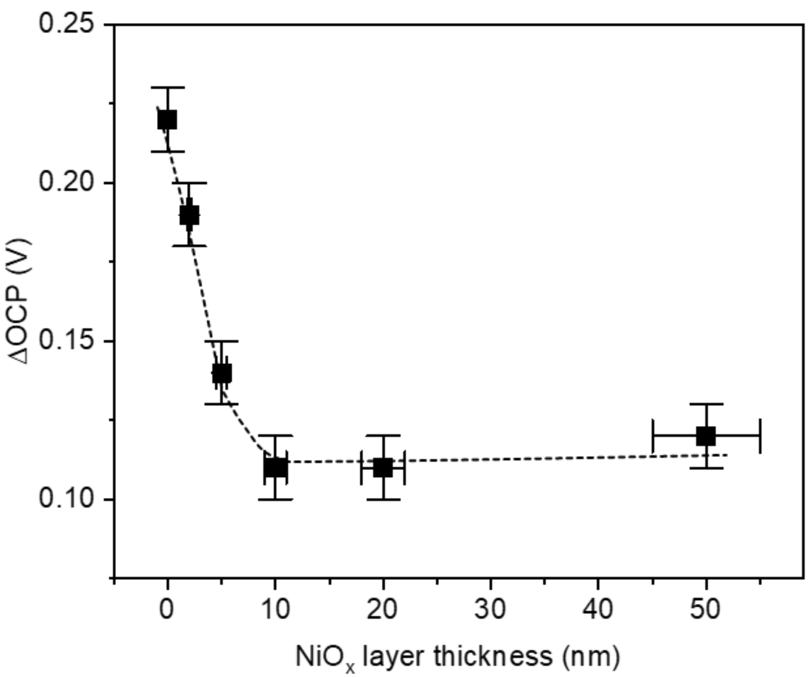


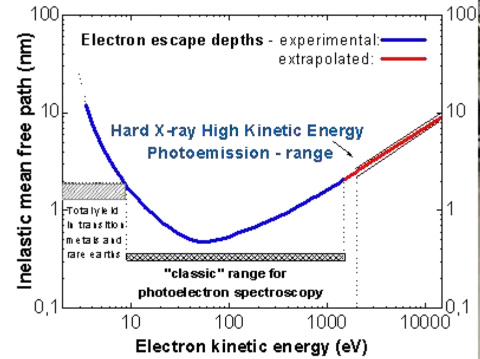


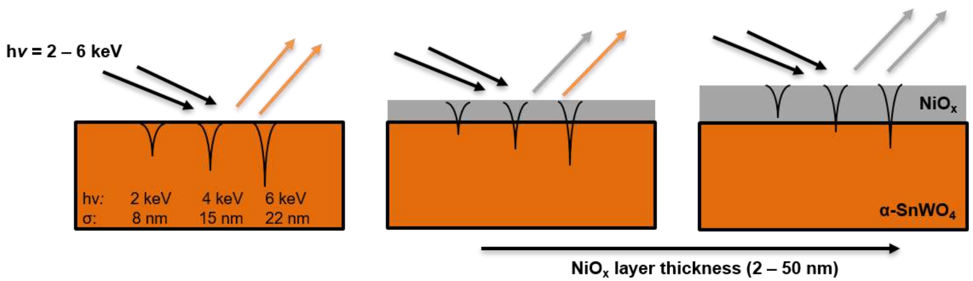
- Thin films deposited using pulsed laser deposition (PLD)
- Bare film is unstable due to self-oxidation: Sn^{2+} oxidizes to Sn^{4+}
- NiO_x deposition extends the photoelectrochemical stability and we obtained record photocurrent of ~0.75 mA/cm^2

Chem. Mater. 30 (2018) 8322

Understanding the limitations of α-$SnWO_4$/NiO_x

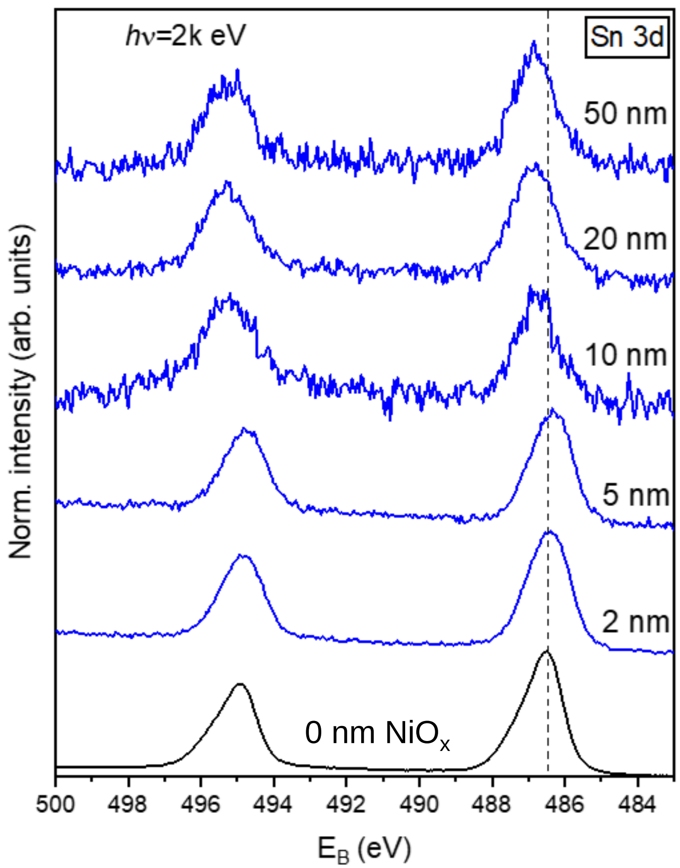


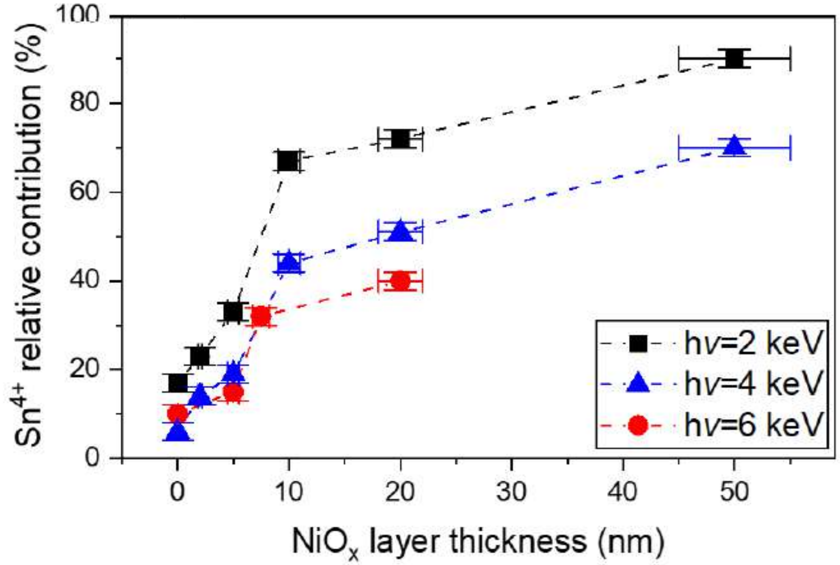


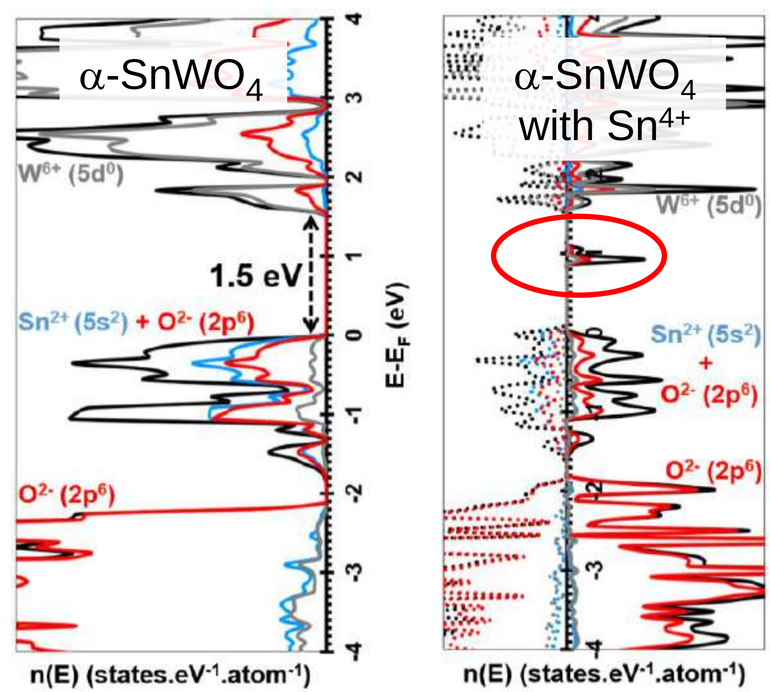


- Photovoltage (OCP) decreases with NiO_x deposition
- Hard X-ray Photoemission Spectroscopy (HAXPES) was performed at the BESSY-II synchrotron
- Films with different thicknesses of NiO_x were investigated with varying photon energies (i.e., different information depth)

Understanding the limitations of α-$SnWO_4/NiO_x$







Patrick Schnell

The presence of Sn^{4+} at the α-$SnWO_4/NiO_x$ interface (as defects or SnO_2 phase) causes the limited photovoltage

KAUST

Schnell et al. *submitted*

Next step: Scale-up!

Only a handful of reports (out of more than 100) demonstrated active area > 1 cm^2

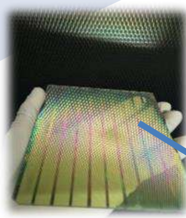
Efforts at HZB

PEC DEMO

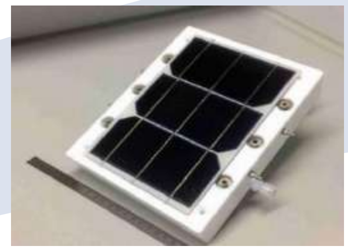
<1 cm^2 device

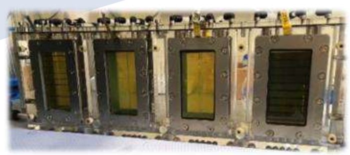
STH efficiency 6.3%

50 cm^2 electrode



200-250 cm^2 modules





Sust. Energy Fuels 3 (2019) 2366

STH efficiency 2.1%

10 m^2 modules

PECSYS

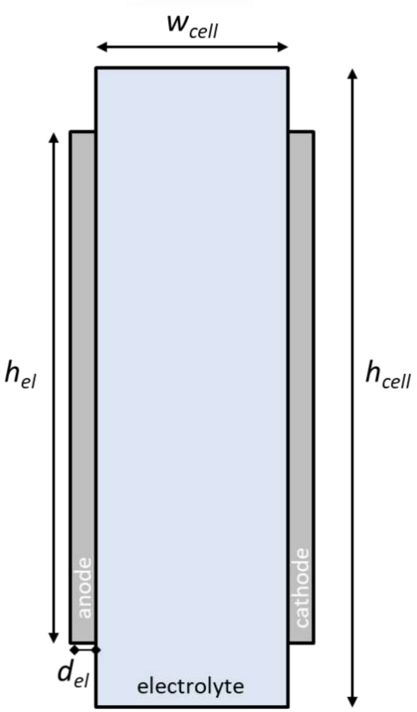
Dr. Sonya Calnan

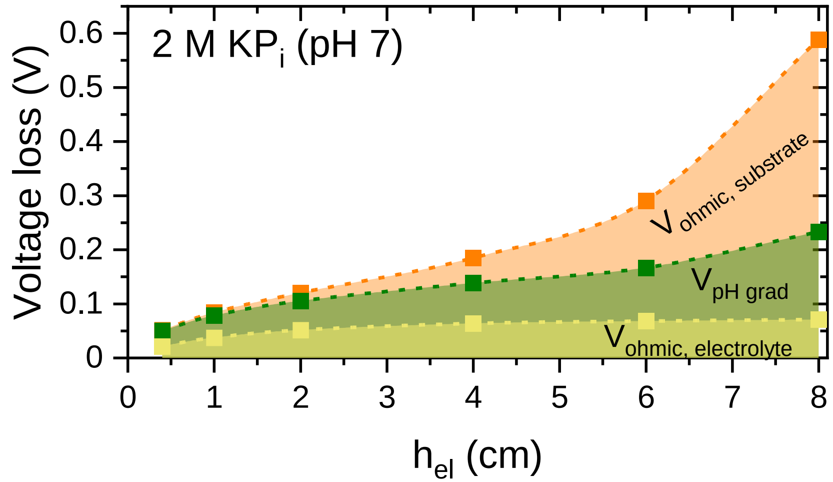
PVcomB

Efficiency limited by potential drop in the electrolyte due to proton conductivity

→ Electrochemical engineering

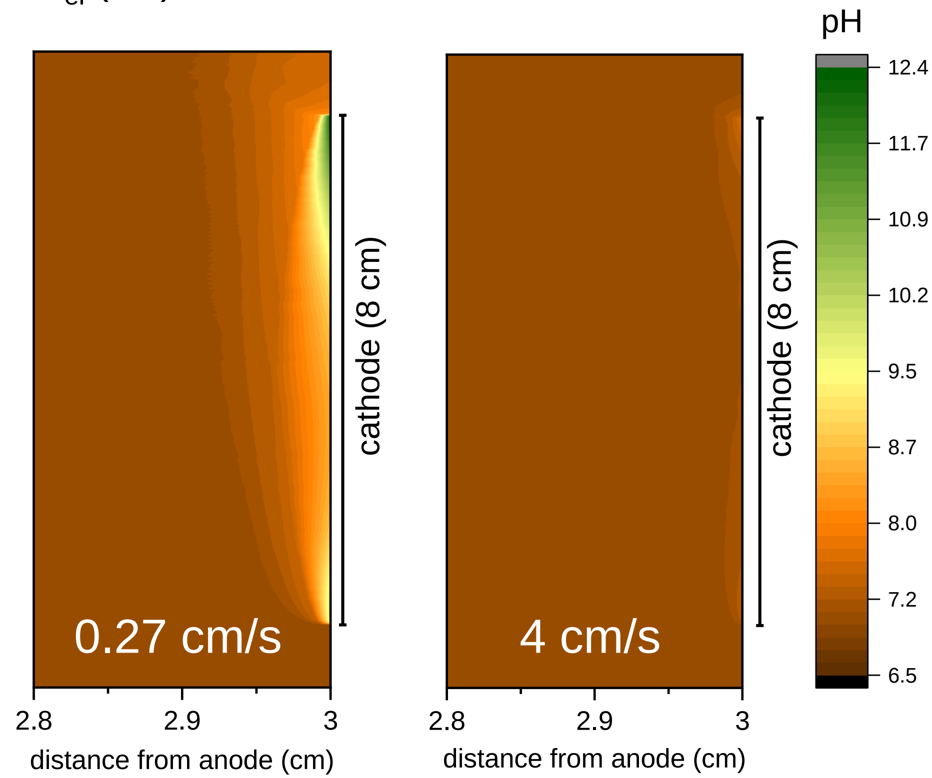
Multiphysics simulations are important in identifying losses





- V_{loss} increases for larger electrode area; (8 cm) :
  - ~330 mV substrate
  - ~200 mV pH grad.
  - ~70 mV ionic drop

pH gradient can be alleviated by increasing the flow rate

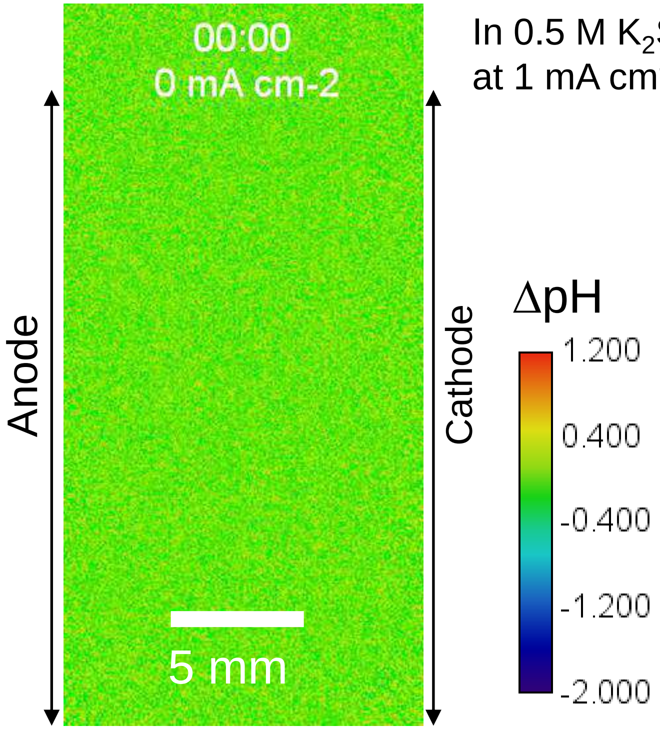


Sustainable Energy Fuels 4 (2020) 2734

Experimental validation is needed to support the simulation

Keisuke Obata

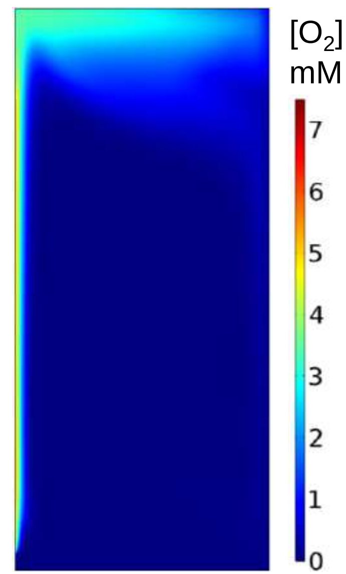
In-situ pH measurement



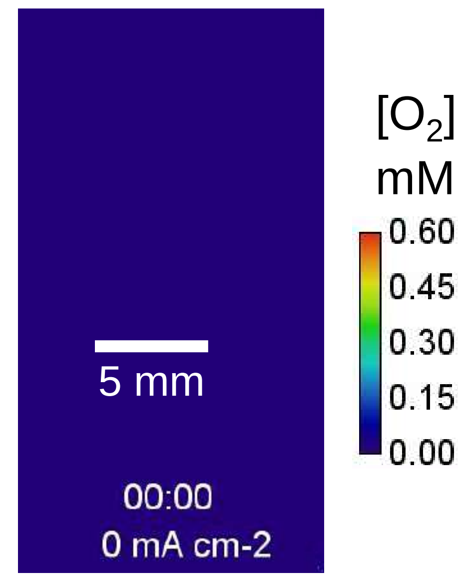
In 0.5 M K_2SO_4 (pH 7) at 1 mA cm^{-2}

Bulk pH change throughout the entire water splitting cell

O_2 cross-over and separation



Simulation

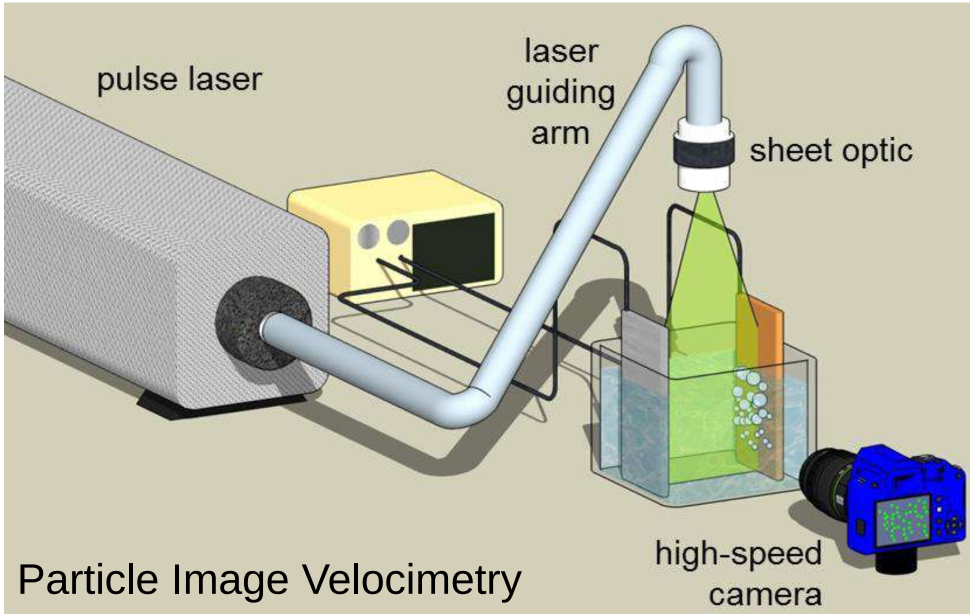


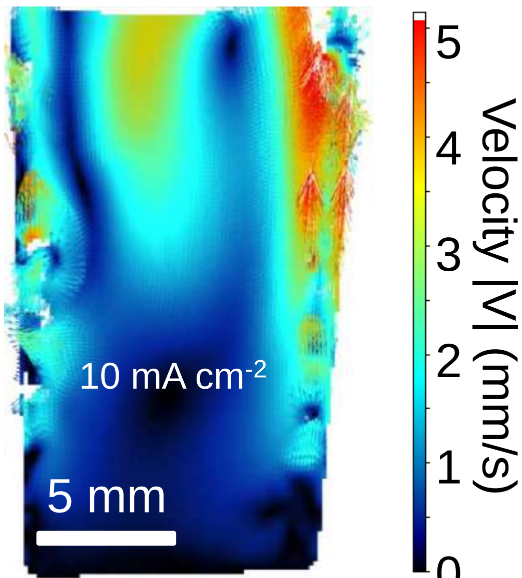
Measurement by O_2 sensitive fluorescence film

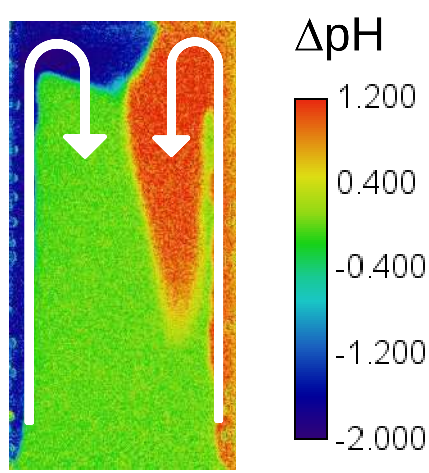
Obata et al. *in revision*

Further experimental validation approach in our group

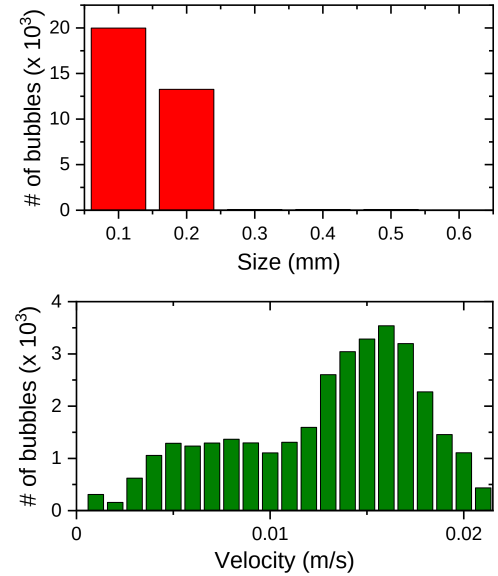
Electrolyte velocity and pressure measurement







Bubble dynamics using Shadowgraphy



HEMF

Helmholtz Energy Materials Foundry – Solar Fuels Devices Facility

All capabilities available to external users

Take-home messages

- Solar energy is the way to go
  - We just need to store it!! → Solar Fuels
- Materials development is key in order to enable breakthroughs in photoelectrochemical water splitting
  - Progress in $BiVO_4$ has overcome many of the materials limitations; the bandgap now limits the achievable photocurrent
  - Sulfur incorporation shifts the bandgap by 0.3 eV (STH max. 12%)
  - $CuBi_2O_4$ or α-$SnWO_4$ is a promising novel oxide with 1.8-1.9 eV bandgap
- Scale-up is challenging; important to develop ‘feeling’ for this
  - The combination of modeling and experimental validation is powerful to fully unravel the limitations in electrochemical cells

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