ETH zürich

Transition Metal Oxides as Candidates for Photoelectrochemical Water Splitting – Fundamental and Technological Challenges

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The Multimat Group

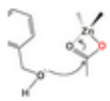
Development of efficient liquid-phase synthesis routes to inorganic materials »

- Nonaqueous sol-gel chemistry
- Nonhydrolytic thio sol-gel chemistry
- Microwave and solvothermal processing
- Liquid-phase synthesis of bulk metals



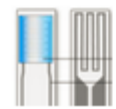
Study of chemical formation and crystallization mechanisms »

- Correlation of organic and inorganic chemistry
- Nonclassical crystallization pathways
- Oriented attachment
- In-situ reaction monitoring



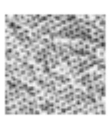
Applications »

- Visible-light driven photocatalysts
- Transparent conducting oxides
- Lithium ion batteries
- Chemoresistive CO_2 gas sensors
- Photoelectrochemical water splitting


Particle assembly and processing »

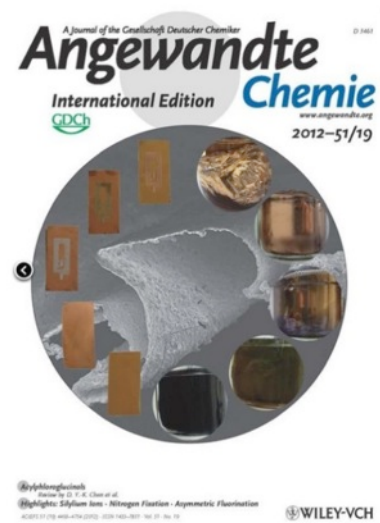
- Surface functionalization of particles
- Particle dispersions
- Thin film preparation by dip- and spin-coating
- Multicomponent powders and aerogels


Inorganic-organic hybrid materials and composites »

- Nanoparticle-polymer composites
- Oxide-based hybrid materials
- Magneto- and electrochromic materials





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Outline

- Motivation
- Introduction
- Theoretical Background
- Current Research
- Fundamental Challenges
- Technological Challenges
- Outlook
- Acknowledgement

Why photocatalytic water splitting?

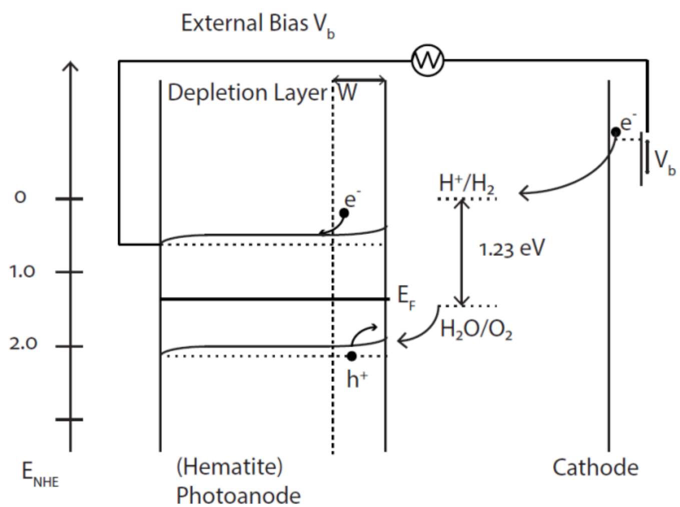
$$H_2O \rightarrow \frac{1}{2} O_2(g) + H_2;\ \Delta G = +237\ \text{kJ mol}^{-1}$$

- The energy of the sunlight reaching the surface of the earth is 4 orders of magnitudes higher than the actual need
- Storage of energy in the form of H_2
- H_2 has the highest specific energy (143 MJ/kg)
- Abundance of sunlight and water

Motivation

Aim

- The use of abundant, cheap and non-toxic semiconductors
- Enhancing the visible light response…
- Optimized morphology to compensate intrinsic properties of some semiconductors used for photocatalytic water splitting



Building blocks:

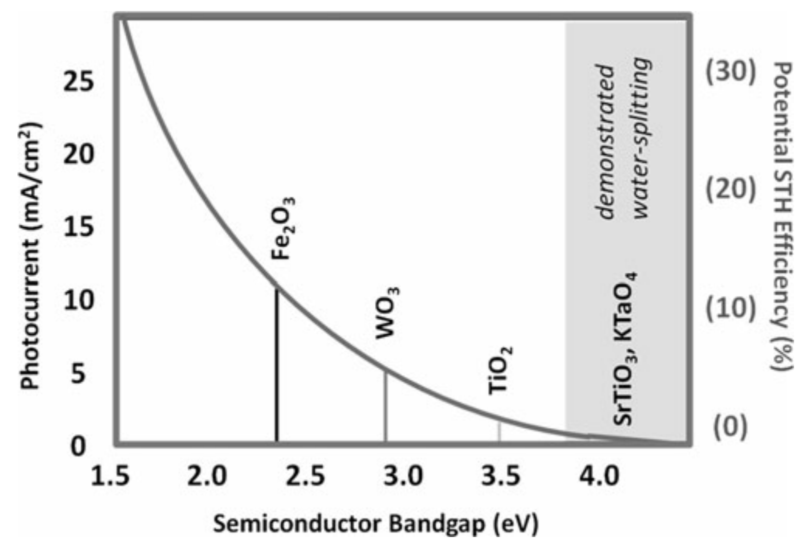
- TiO_2, Fe_2O_3, WO_3, CuO, ZnO etc. Nanoparticles

Goal

- Solar to hydrogen efficiency (n_{STH}[%]) of 5%

$$n_{STH} = \frac{J_{photo}(V_{redox} - V_{bias})}{P_{light}}$$

- Lab scale hydrogen production production rate more than 20 $lm^{-2}h^{-1}$



Van de Krol, R., Grätzel, M.: Photoelectrochemical Hydrogen Production, Springer, New York, (2012)

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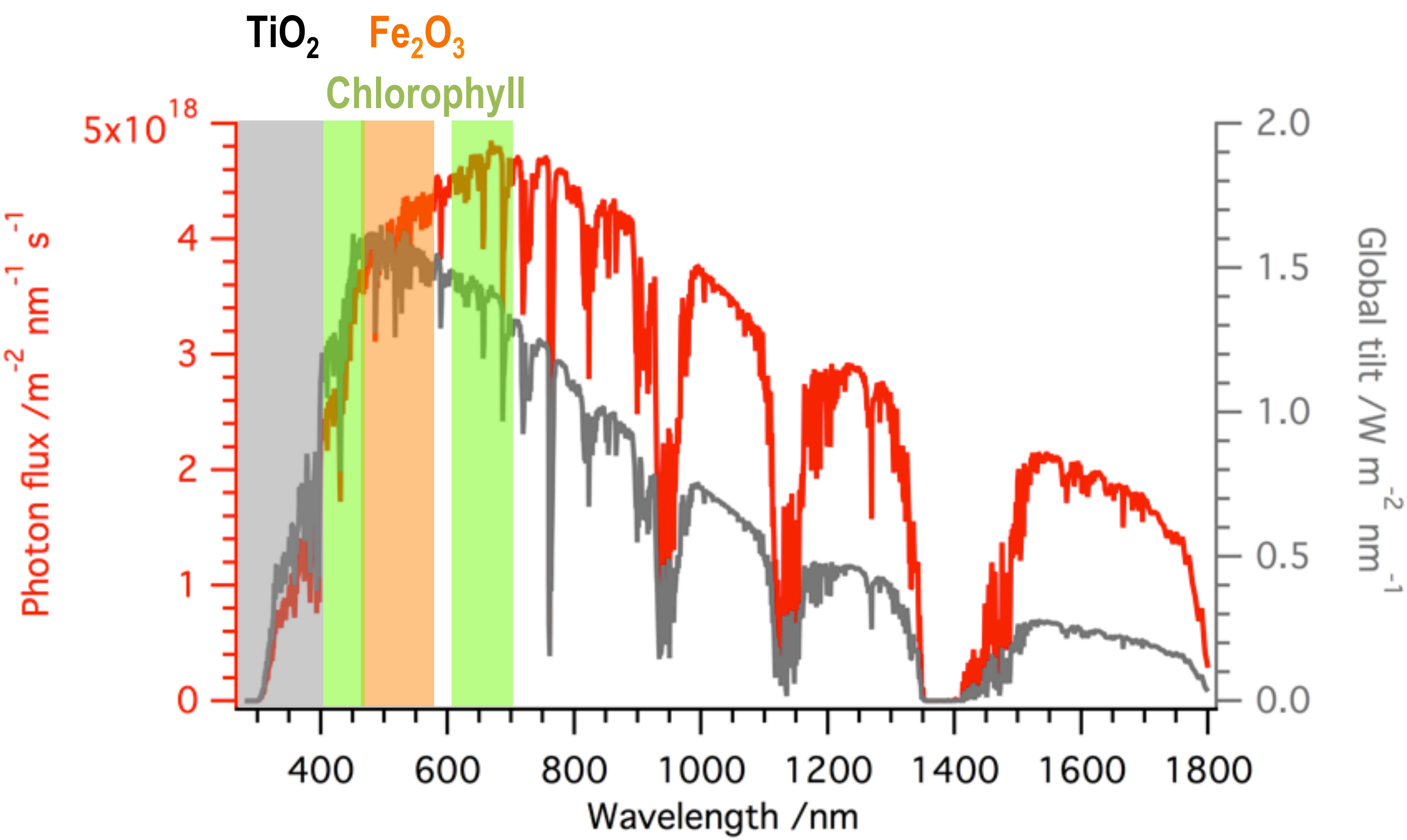
Solar spectrum



source: Thomas Fischer, Uni Köln

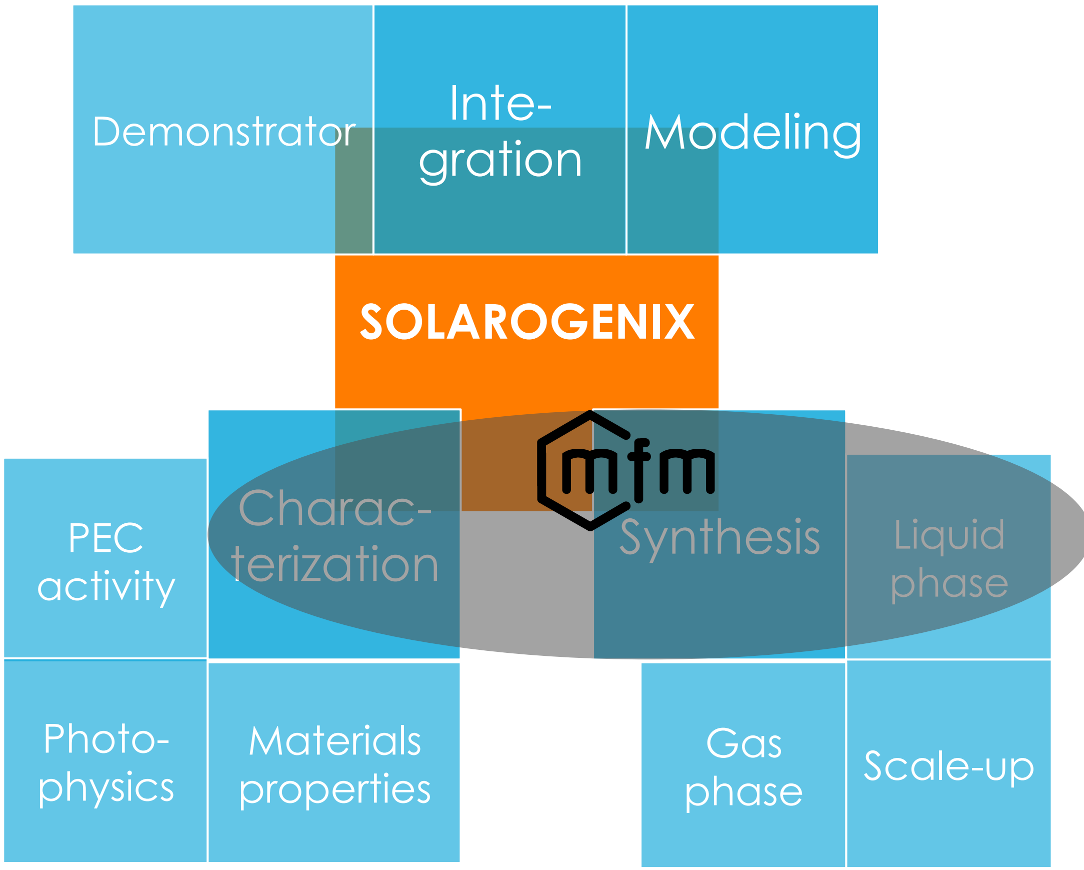
Introduction

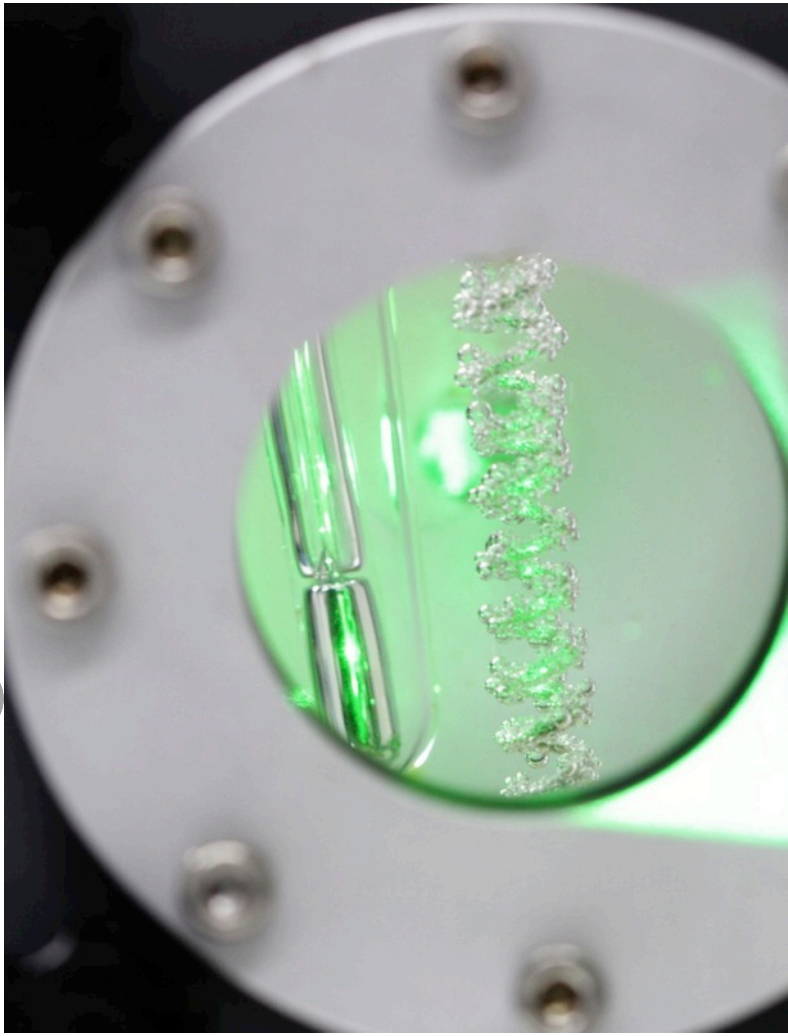
PEC effect first described by Fujishima & Honda on TiO_2 single crystals (*Nature* ***1978***, 238, 37-38)

1970	1980	1990	2000	present
	• d^0-type metal oxides for UV water splitting • Metal oxides with structural regularities	Tantalates	Other d^0 metal oxides (titantaes, niobates, etc.)	Tandem cells

K. Maeda, J. Photoch. Photobio. C: Photochemistry Reviews, 12 (**2011**), 237-268

Introduction





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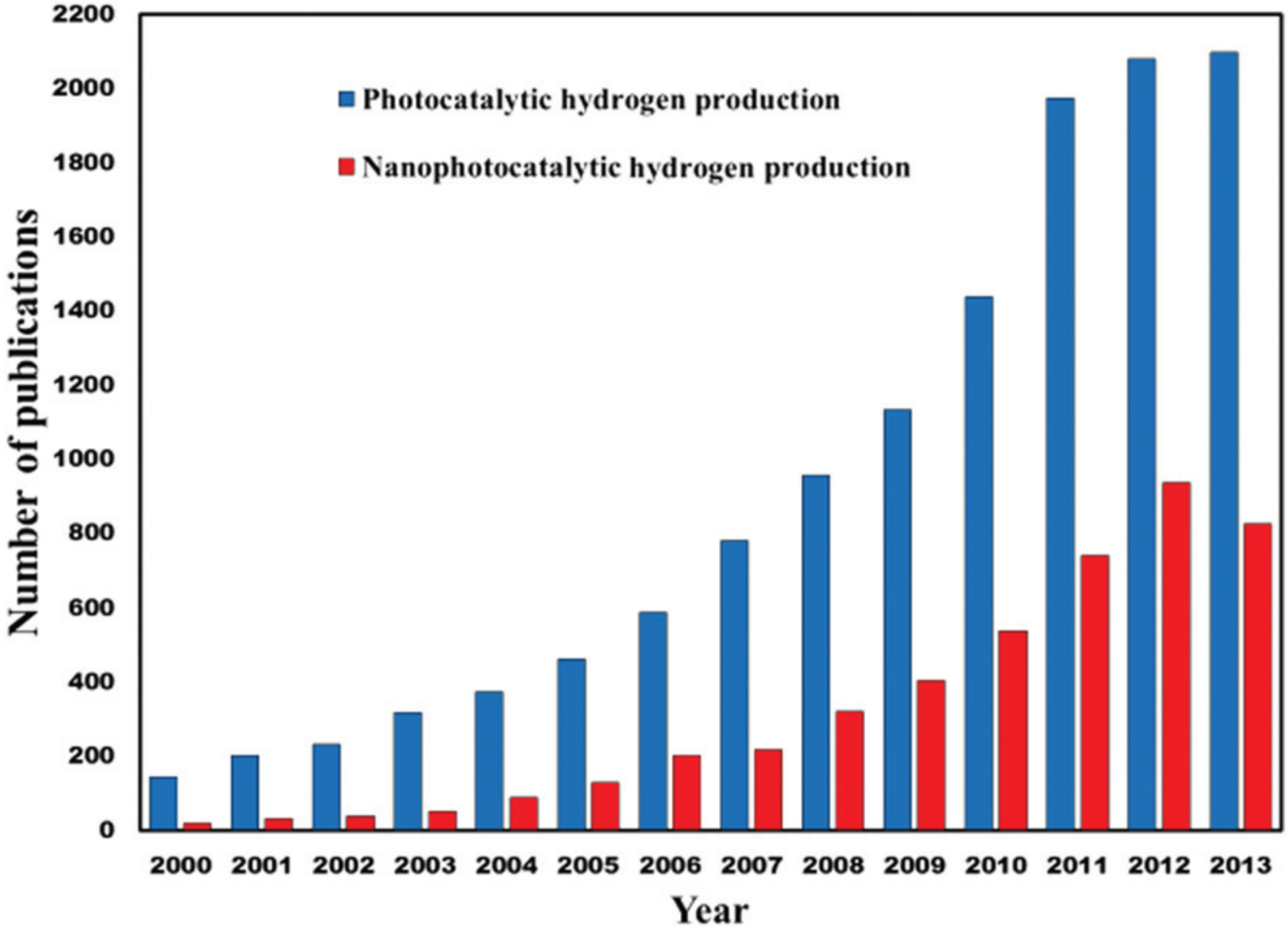
source: Thomas Fischer, Uni Köln

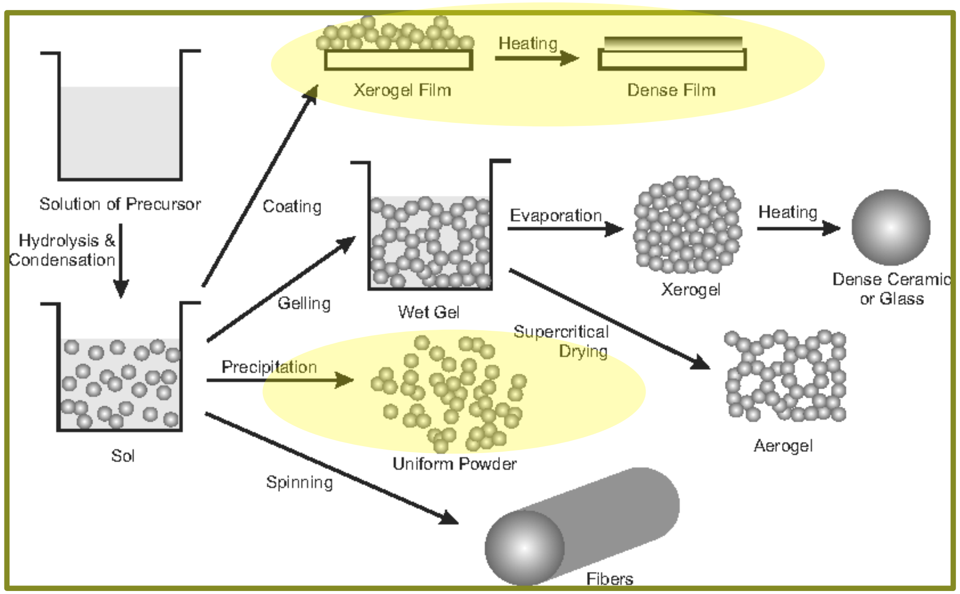
Introduction

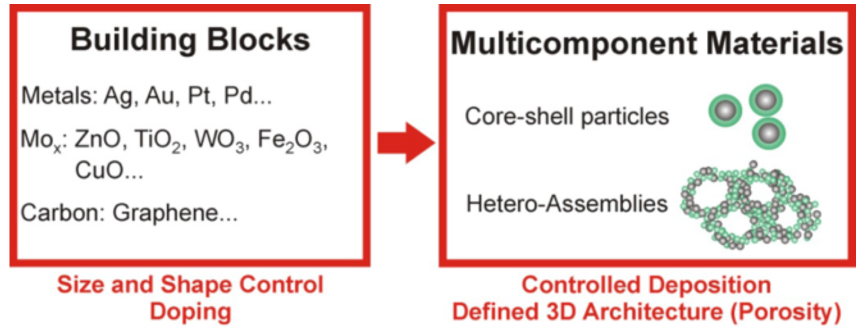
back to photoelectrochemical hydrogen production



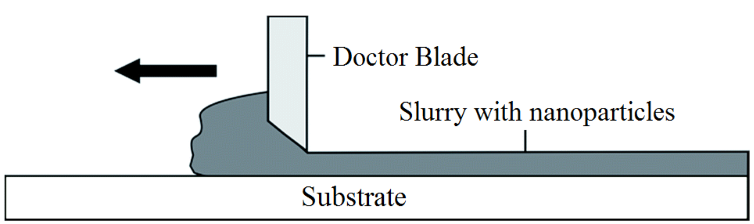
Nanoscale, 2015, **7**, 8187-8208

Synthesis Procedure and Film processing

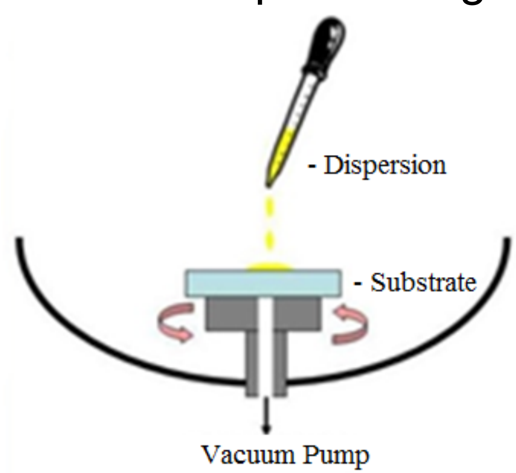




Doctor blading



Spin coating



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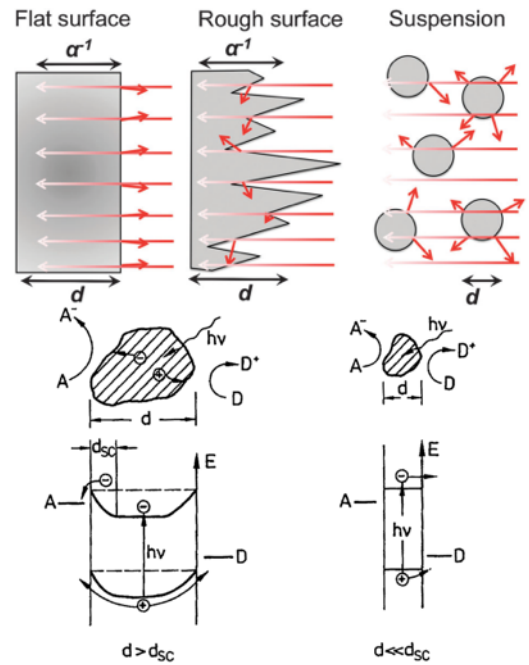
Theoretical Background

n-type semiconductors like Fe_2O_3, WO_3, TiO_2, ZnO etc.

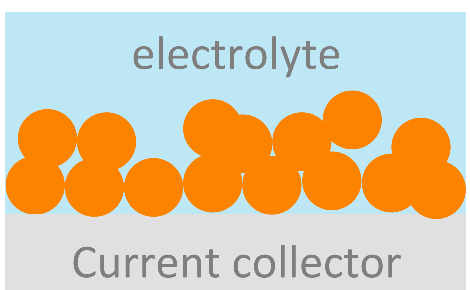
Why Nanostructuring?

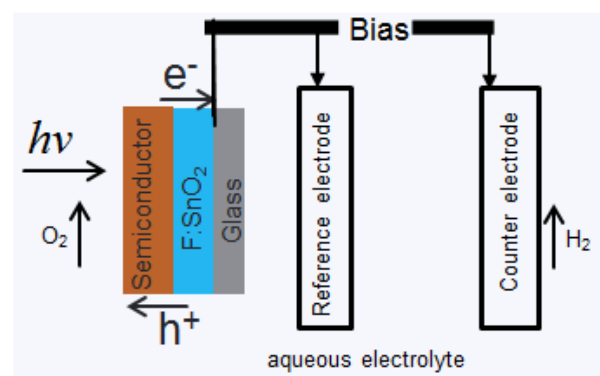
- Shortened carrier collection pathways
- Improved light distribution
- Surface area enhanced charge transfer
- (Quantum size confinement)



Drawbacks

- Increased recombination
- Lower absorbed photon flux
- (Reduced space charge layer thickness)
- (Slow interparticle charge transport)





Chem. Soc. Rev., 2013, **42**, 2294

Non-aqueous sol-gel chemistry

Metal precursors:

- Halides
- Alkoxides
- Acetates
- Acetylacetonates
- Others

Organic solvents:

- Alcohols (e.g. BnOH)
- Ketones (e.g. AcPh)
- Aldehydes
- “inert” solvents
- Amines
- Acids

Heating →

Metal oxide nanoparticles

In general:
- Good control over morphology and size

BUT: Nanoparticles are sometimes difficult to redisperse and sometimes appear to be polydisperse

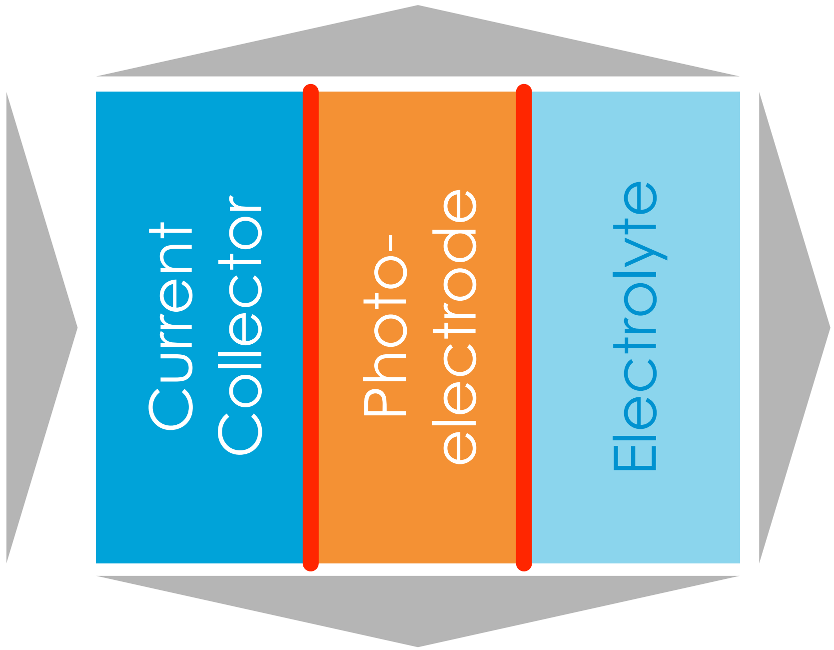
→ **Surfactant treatment prior to synthesis or postsynthetically**

Theoretical Background

Aims

- Visible light absorption
- Charge carrier transport
- Onset Potential
- Catalytic efficiency
- Stability

Bulk properties



Interface properties

Measures

- New Materials
- Optimized Morphology
- Doping
- Composite & Multilayered systems
- Tandem Cells

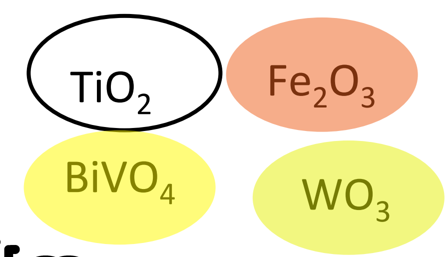
source: Thomas Fischer, Uni Köln

Current Research

…regarding *a few* simple metal oxides

n-type photoanodes

	TiO_2	Fe_2O_3	WO_3	$BiVO_4$
Vis-light absorption	none	good	medium	medium
e^- conductivity	medium	poor	good	poor
h^+ conductivity	poor	poor	medium	poor
Charge carrier lifetime	Rather poor	poor	good	poor
H_2O ox. kinetics	poor	poor	Surface passivation	poor



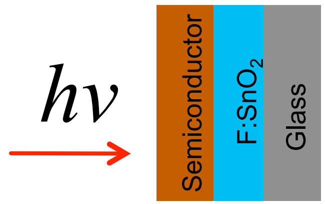
The photoelectrochemical performance of Ti doped hematite

Method	*Photocurrent [mA/cm^2 @ V vs. RHE]*
Pulsed laser deposition	0.5 mA/cm^2 @1.4 V
Hydrothermal method	1.91 mA/cm^2@ 1.23 V
Deposition annealing process	2.8 mA/cm^2@ 1.23 V
Sol-gel	**0.1 mA/cm^2@ 1.25 V**
Atomic layer deposition	0.8 mA/cm^2@ *1.8 V*
Atmospheric pressure CVD	1.0 mA/cm^2@ 1.6 V
Electrodeposition; post-growth doping	1.4 mA/cm^2@ 1.23 V
Spray pyrolysis deposition	1.98 mA/cm^2@ 1.54 V

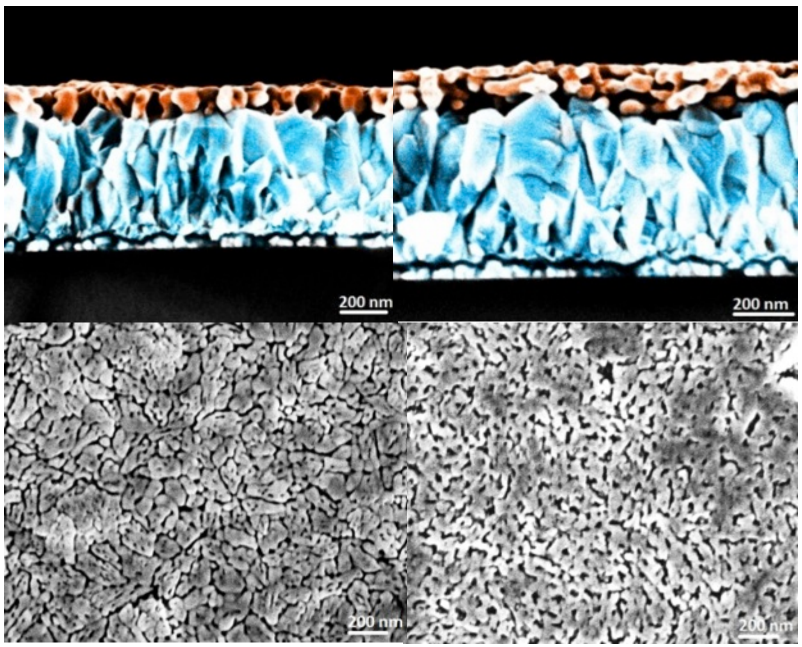
Atmospheric pressure CVD ~2 mA/cm^2@ 1.23 V
(strong preferential orientation of the [110] axis)

Fe_2O_3-TiO_2 photoanode

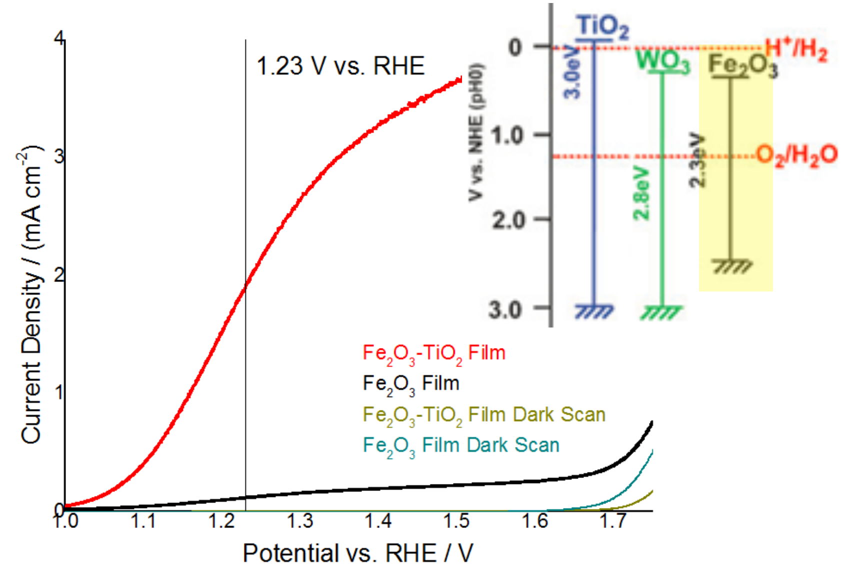
Illumination from the front

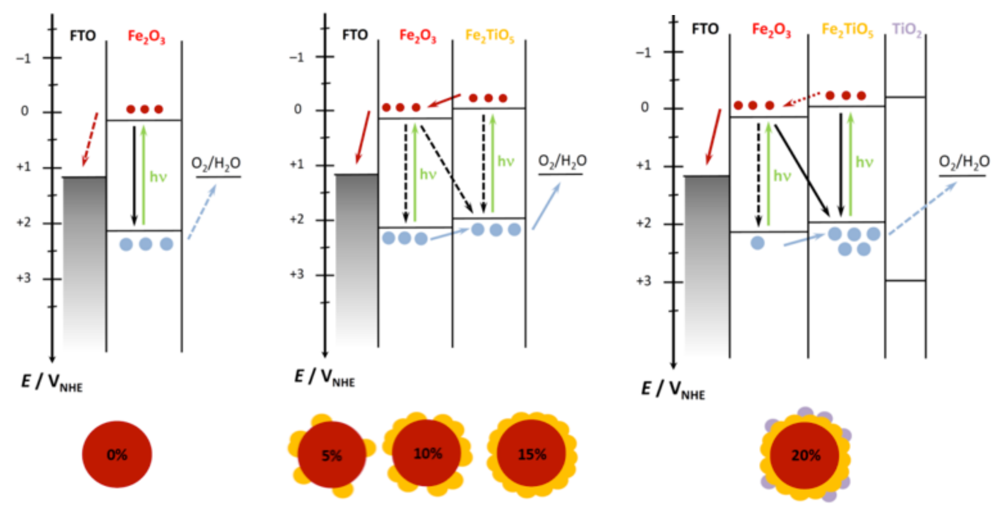


Only Fe_2O_3 | **Fe_2O_3-TiO_2**



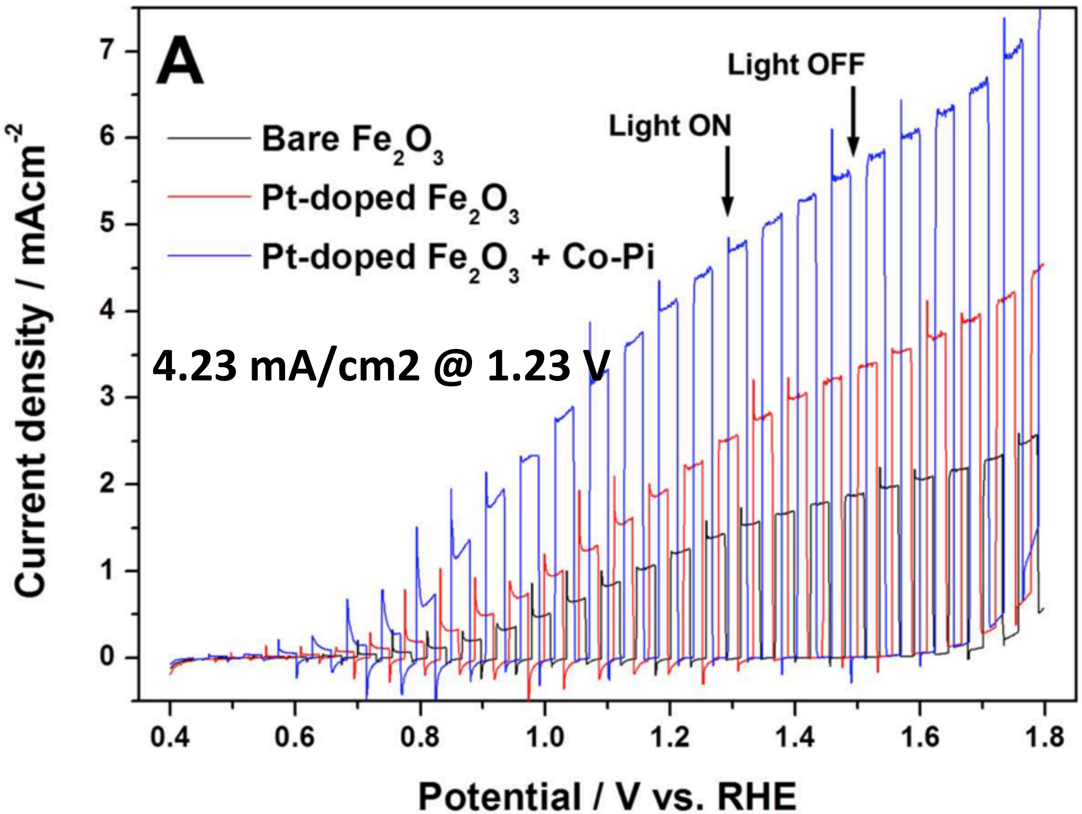
SEM analysis: cross sectional view (top) and top-view (bottom)





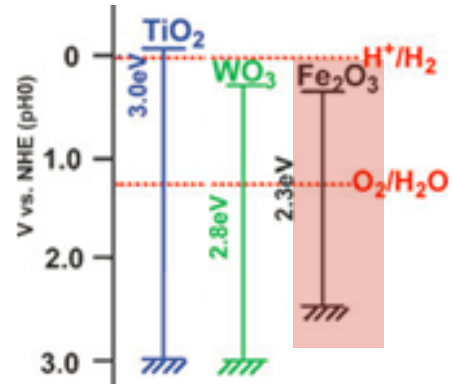
D. Monllor-Satoca and M. Bärtsch et al., **2015**, submitted

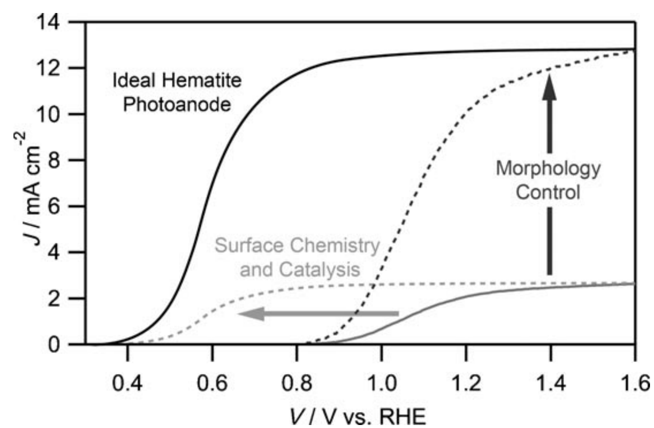
Iron oxide based photocatalyst



4.23 mA/cm2 @ 1.23 V

Chopped light J-V Scan

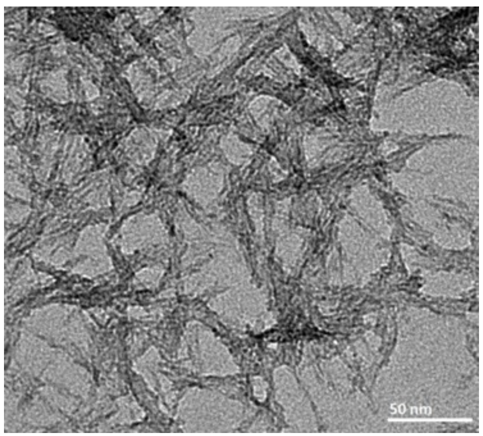




J. Y. Kim et al., *Sci Rep.* ,**2013**, 3:2681

Structurally modified TiO_2 photoanode

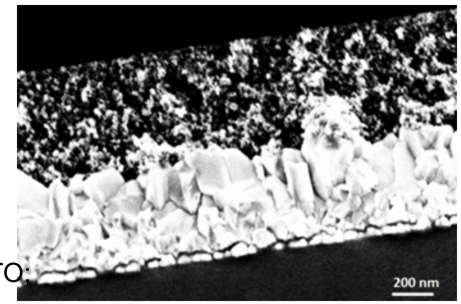
TEM of Hyper-branched TiO_2



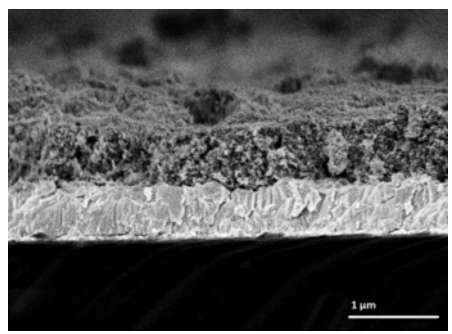
TiO_2 network structure formed after heating the particles in aq. Solution at 90 °C

Doctor blading on FTO; annealing →

Cross-sectional SEM

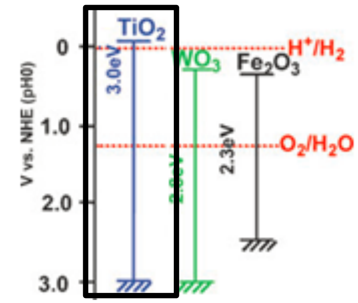


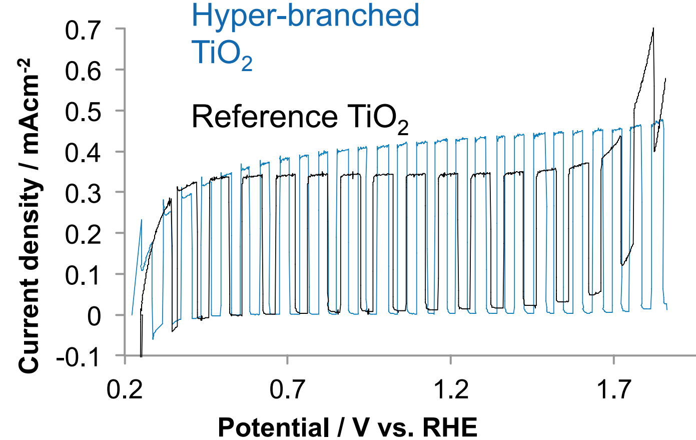
Hyperbranched TiO_2



Reference TiO_2

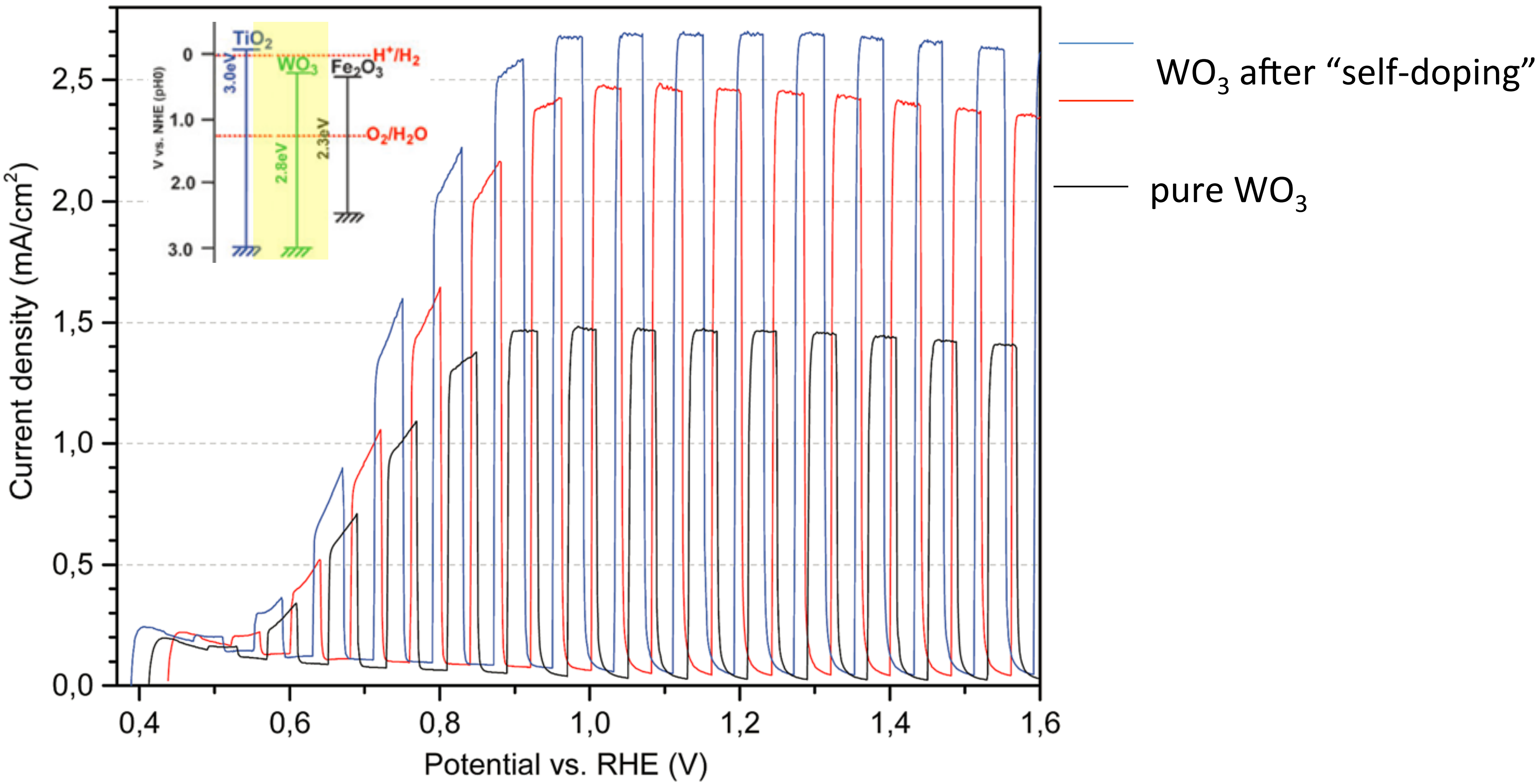
Photocurrents





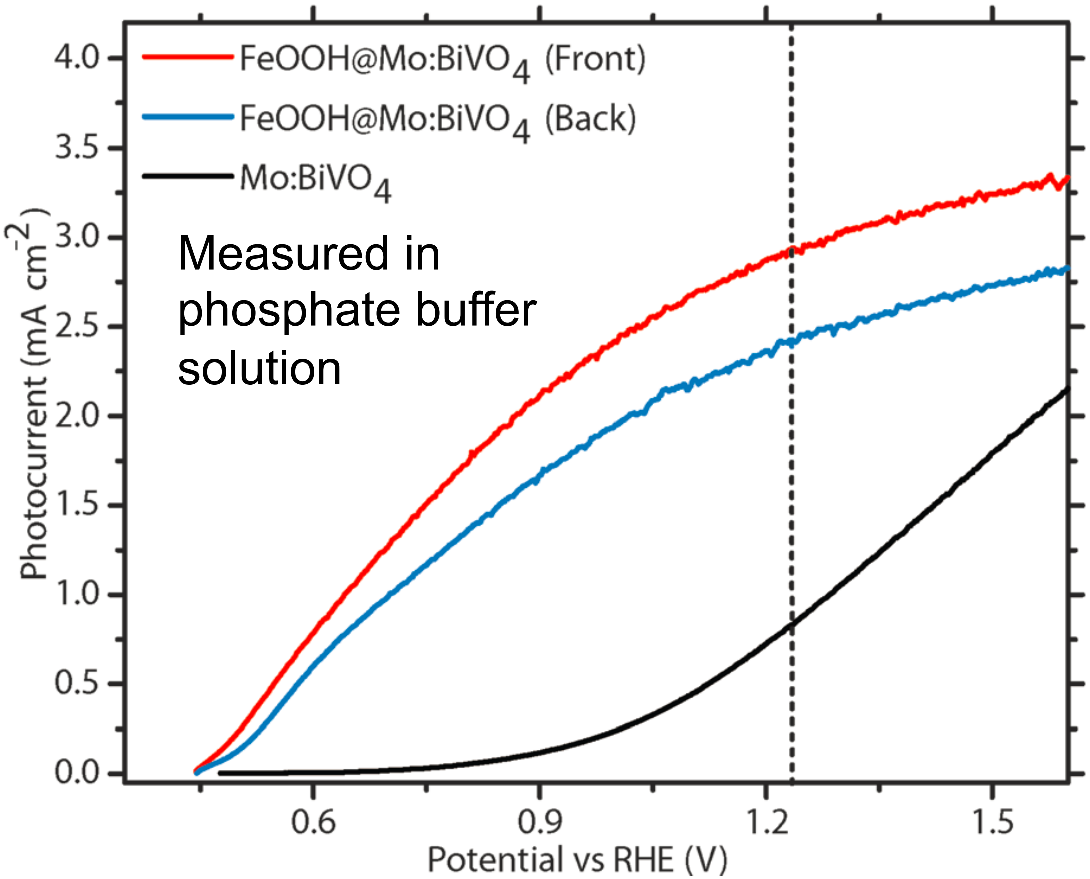
The photocurrent density of the hyper-branched photoanode is similar compared to the reference

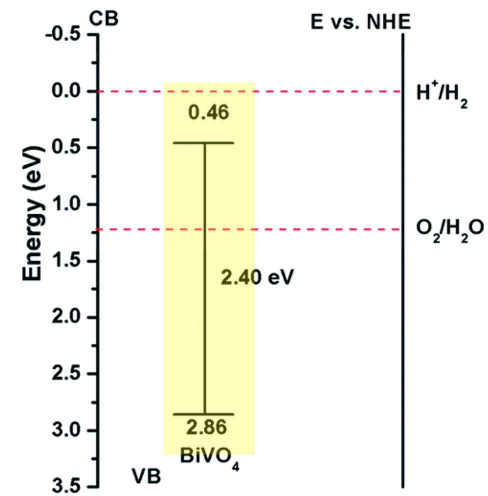
Tungsten oxide based photocatalyst



S. Hilaire, et al, *J. Mater. Chem. A*, **2014**, 2, 20530

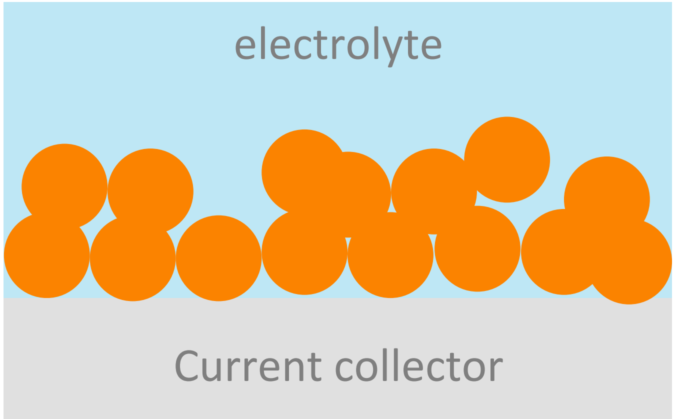
$BiVO_4$ Photoanode

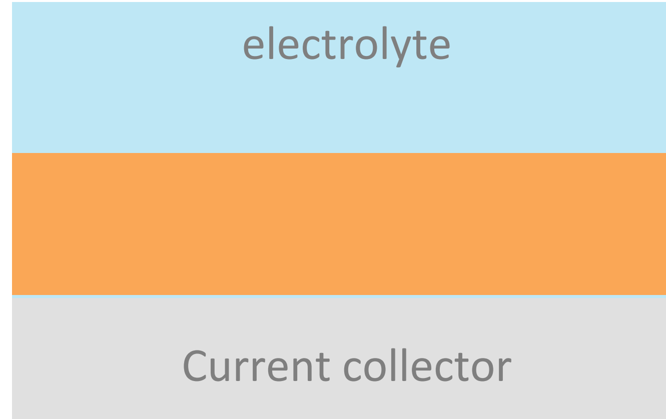




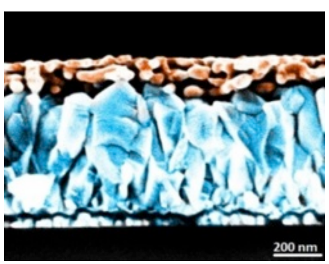
L. Chen et al., *ChemSusChem*, **2015,** 8, 1066

Fundamental Challenges

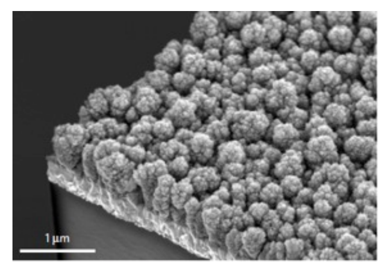




Liquid phase processing
+ Scalability
+ Electrolyte Interface
- Interface to current collector
- Grain boundaries



Gas phase processing
+ Adhesion to current collector
+ bulk quality
- Reduced electrolyte interface
- cost
- Scalability



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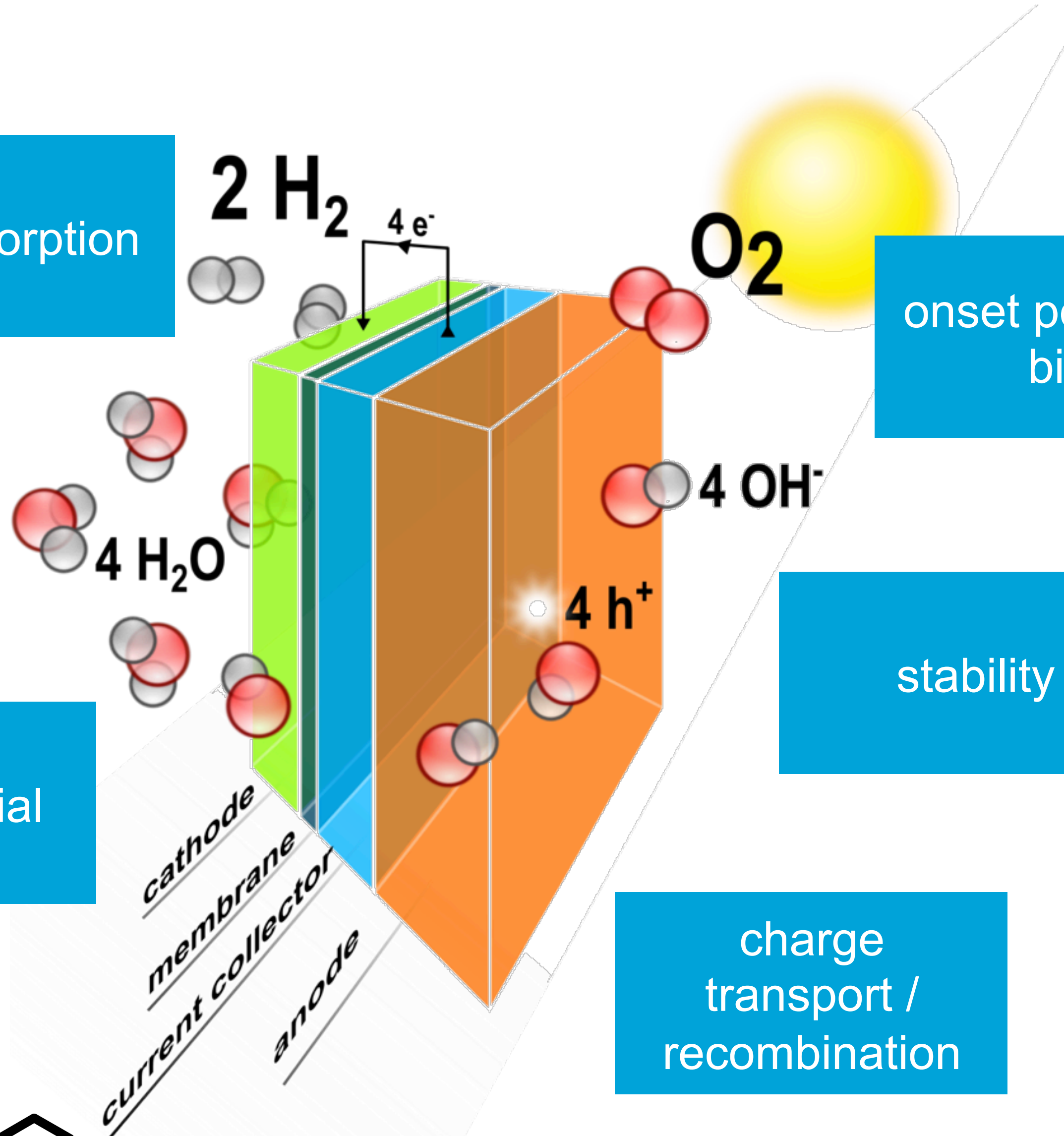
S. Warren et al., Nature Mat., **2013**, 12, 842
source: Thomas Fischer, Uni Köln

Fundamental Challenges

light absorption

over potential



onset potential / bias

stability

charge transport / recombination

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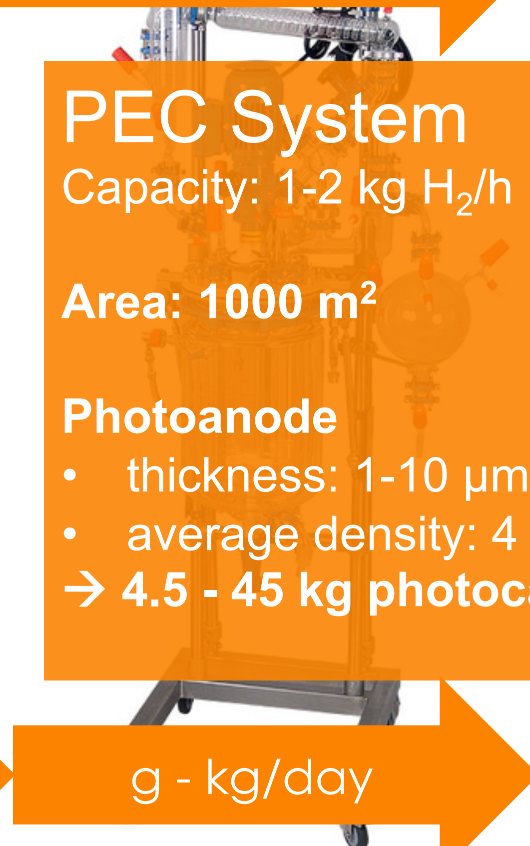
source: Thomas Fischer, Uni Köln

Materials Processing

Lab scale

Fab scale



PEC System

Capacity: 1-2 kg H_2/h

Area: 1000 m^2

Photoanode

- thickness: 1-10 µm
- average density: 4 g cm^{-3}

→ 4.5 - 45 kg photocatalyst

mg - g/day

g - kg/day

kg – t /day

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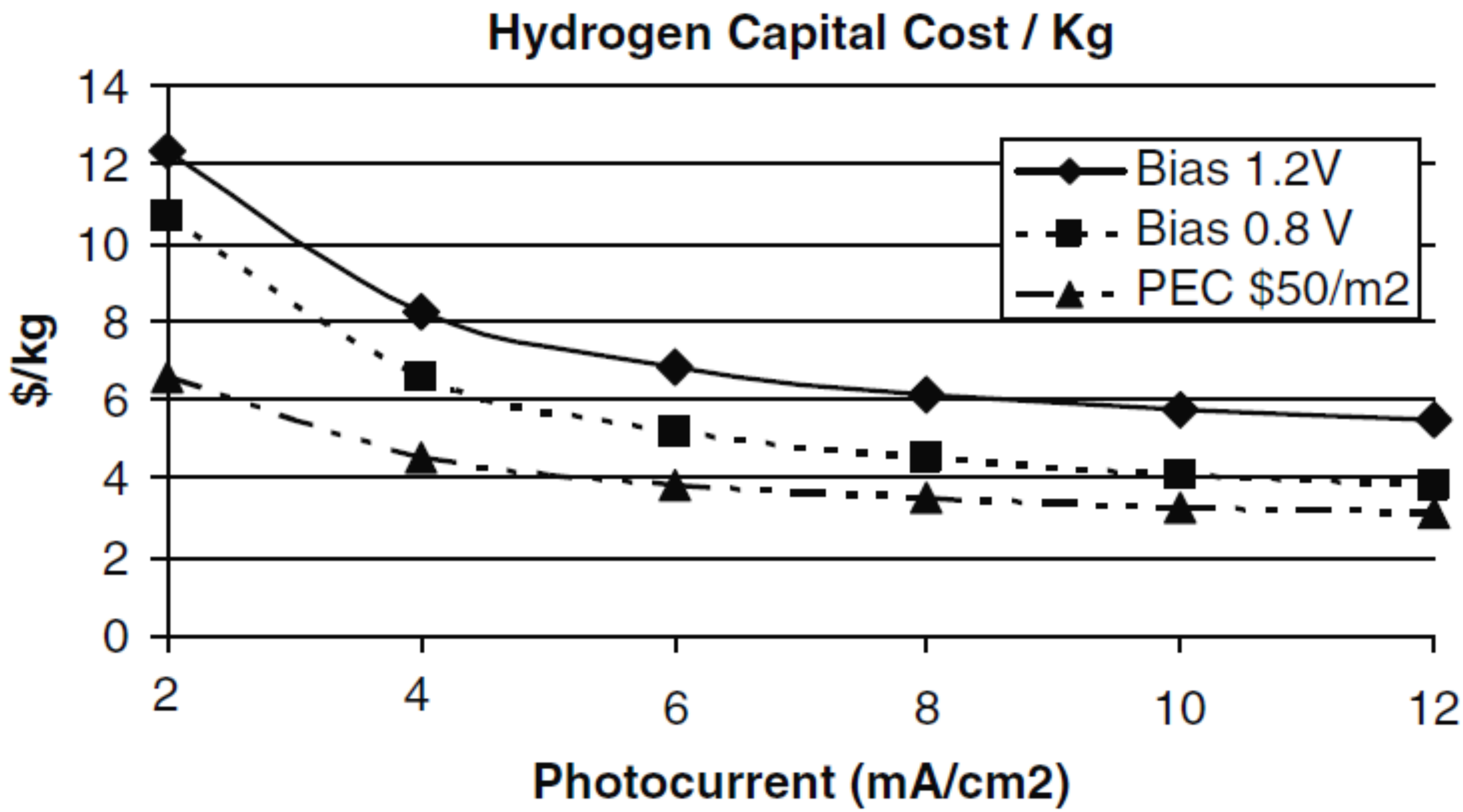
source: Thomas Fischer, Uni Köln

General Trend Regarding the Hematite Photoanode



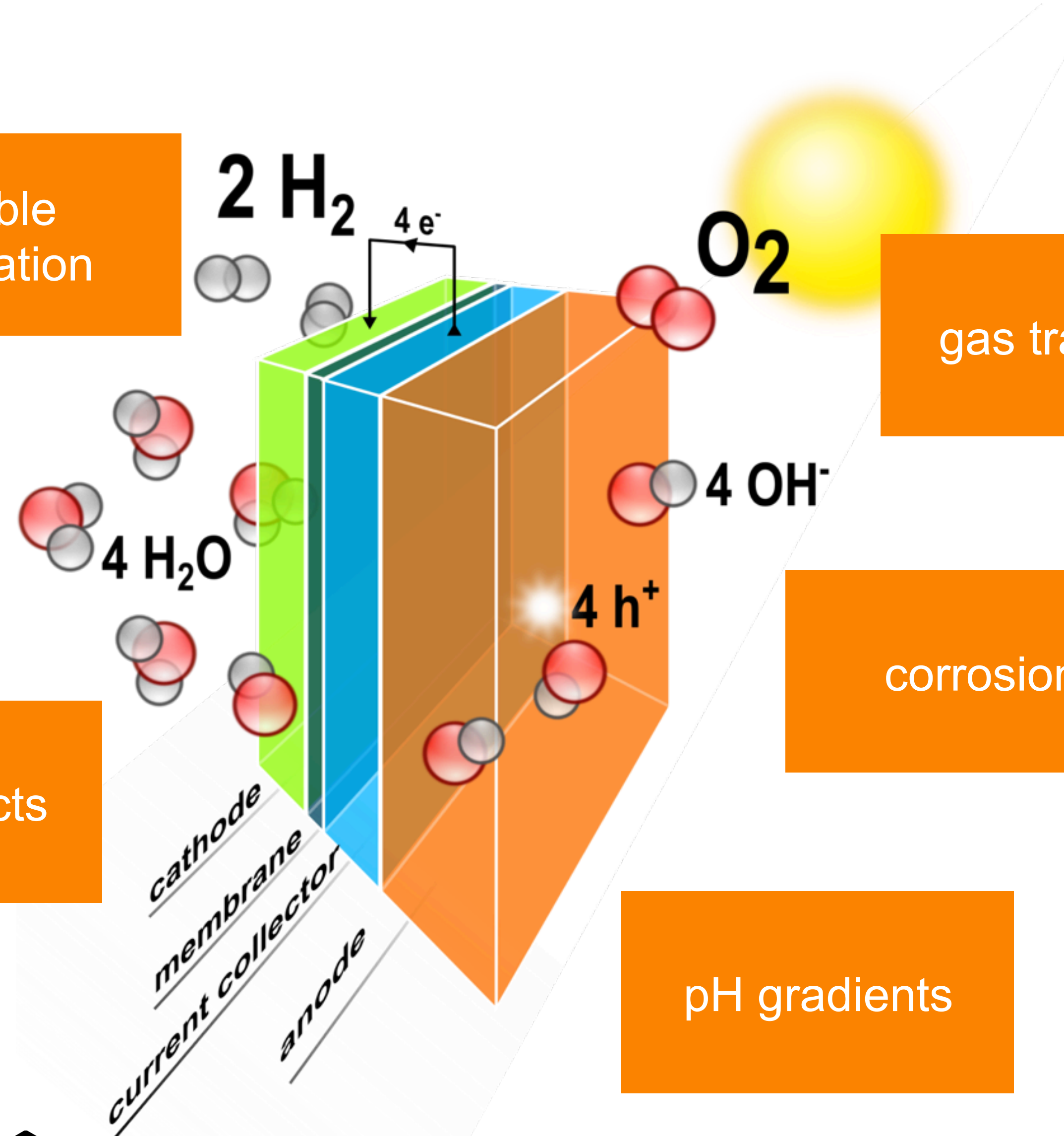
Van de Krol, R., Grätzel, M.: Photoelectrochemical Hydrogen Production, Springer, New York, (2012)

Technological Challenges

bubble nucleation

long term-stability

side products



gas transport

corrosion

pH gradients

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source: Thomas Fischer, Uni Köln

Outlook

- More efficient materials are needed, and a target of 8 mA/cm^2 is set to reach >10% efficiency
- Bias requirements must be reduced with minimal resistive voltage drops
- Durability must be increased to 15-20 years
- System costs must be reduced, and a price not exceeding \$ 160/m^2

Van de Krol, R., Grätzel, M.: Photoelectrochemical Hydrogen Production, Springer, New York, (2012)

Acknowledgement

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Thanks for your attention!!!