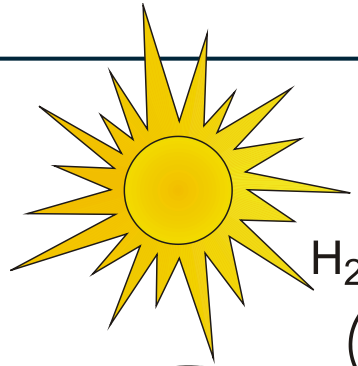
# Photochemical Systems for Artificial Leafs

DOE/BMBF Workshop, 29.06.2021

Matthias Beller


*Nature Catalysis* 2018, *1*, 332–338; *Nature Commun.* 2015, *6*, 5933; *Nature Commun.* 2014, *5*, 3091; *Nature* 2013, *495*, 85-89; *Science* 2011, *339*, 1733-1736.



Energy

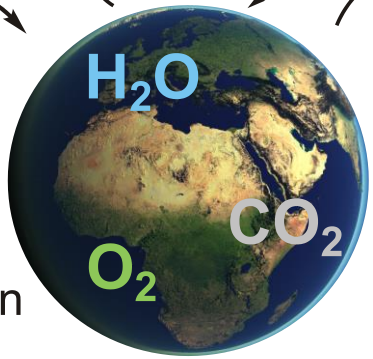
$H_2$

$H_2$ Generation

$H_2O$ $O_2$

$H_2O$

$CO_2$



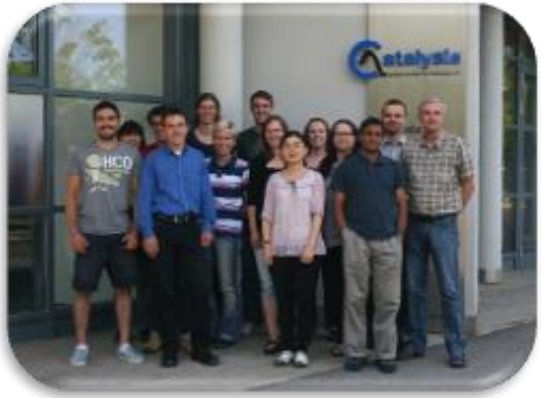

Fuel Cells

$H_2$ Combustion

MeOH, $CH_4$
$HCO_2H$

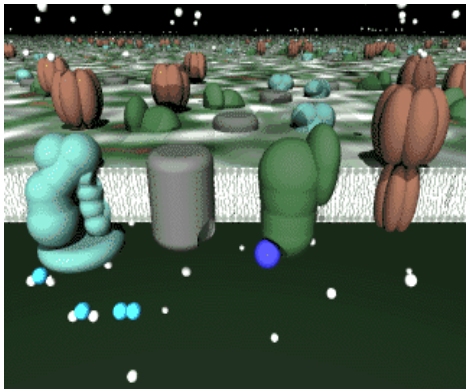
$H_2$ Storage

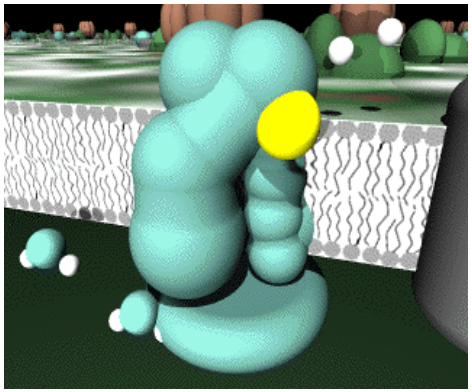
$O_2$ $CO_2$

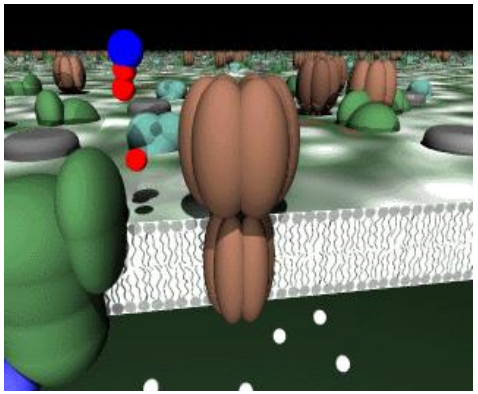


***Can this and related concepts be price competetive?***

# The „weak“ Point of Photosynthesis





- Only visible light is used (400 – 700nm): 50% loss
- Reflection, absorption and transmission by leaves: 20% loss
- Limited light reaction efficiency (8-10 photons per $CO_2$): 72-77% loss
- Respiration required for translocation and biosynthesis: 40% loss

Total theoretical efficiency is not more than 5.5-6.6% (reality: <0.6%)

# $H_2$ Prices for Different Production Technologies

Hydrogen from methane:
**1,40 $/kg**

Detz et al., Energy Environ. Sci., **2018**.

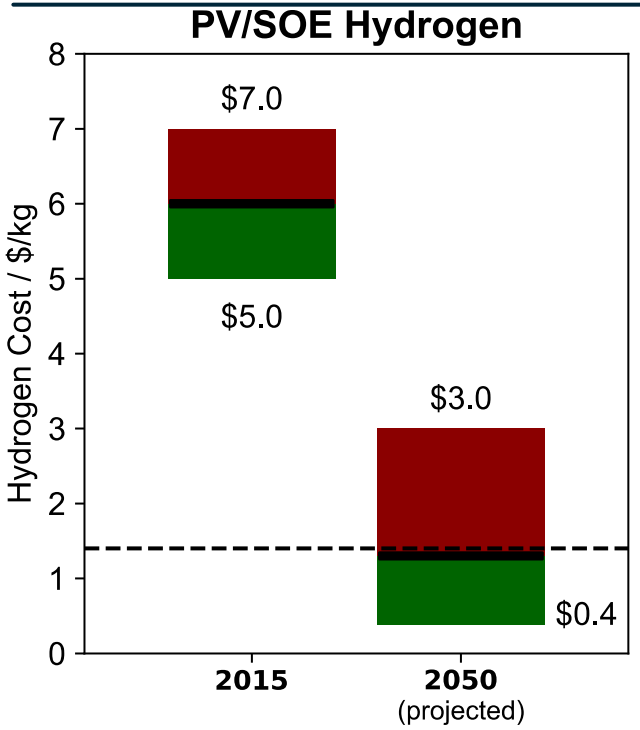
Hydrogen from water splitting (photovoltaic + electrolysis):
**5,60 $/kg**

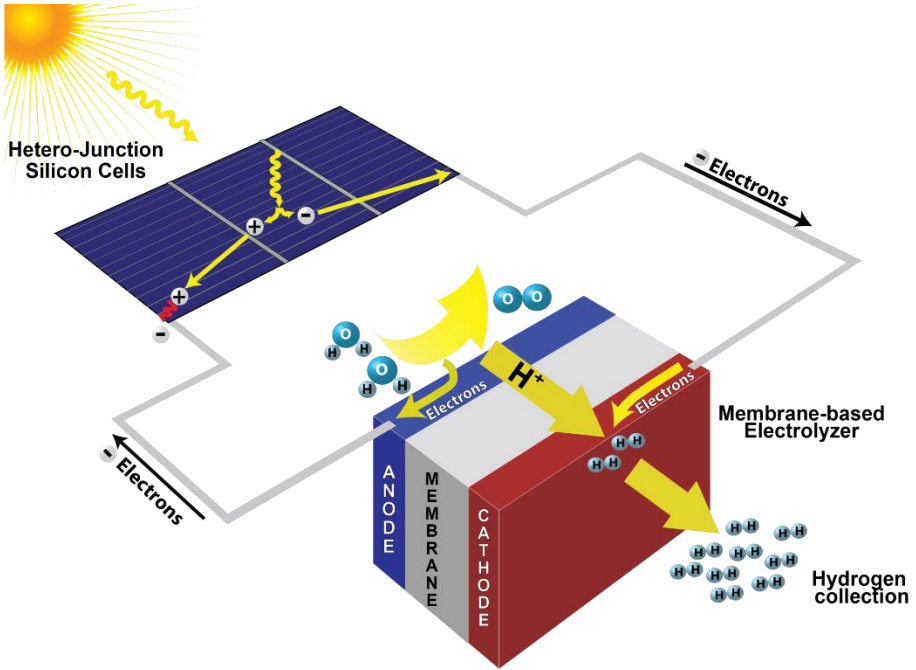
Detz et al., Energy Environ. Sci., **2018**.

Hydrogen from photocatalytic water splitting (single bed particle suspension):
**1,60 $/kg**

Jaramillo et al., Energy Environ. Sci., **2013**.

# Electrocatalytic hydrogen production




**Left: Cost range of green hydrogen produced using photovoltaic (PV)/solid oxide electrolysis (SOE), upper and lower bounds of confidence intervals are shown above and below bars, respectively. Values for 2015 estimate (average cost ca. $6/kg) and 2050 projection (average cost ca. $1.3/kg) are shown. Dotted line shows current price of fossil fuel derived hydrogen ($1.4/kg). Data source: Detz *et al., Energy Environ. Sci.* 2018, 11, 1653 – 1669.**
**Right: Schematic of PV/electrolysis assembly.**

**Solar-to-hydrogen efficiency:** 2%, **catalyst cost:** 3000 $/kg, **catalyst lifetime:** 0.5 years

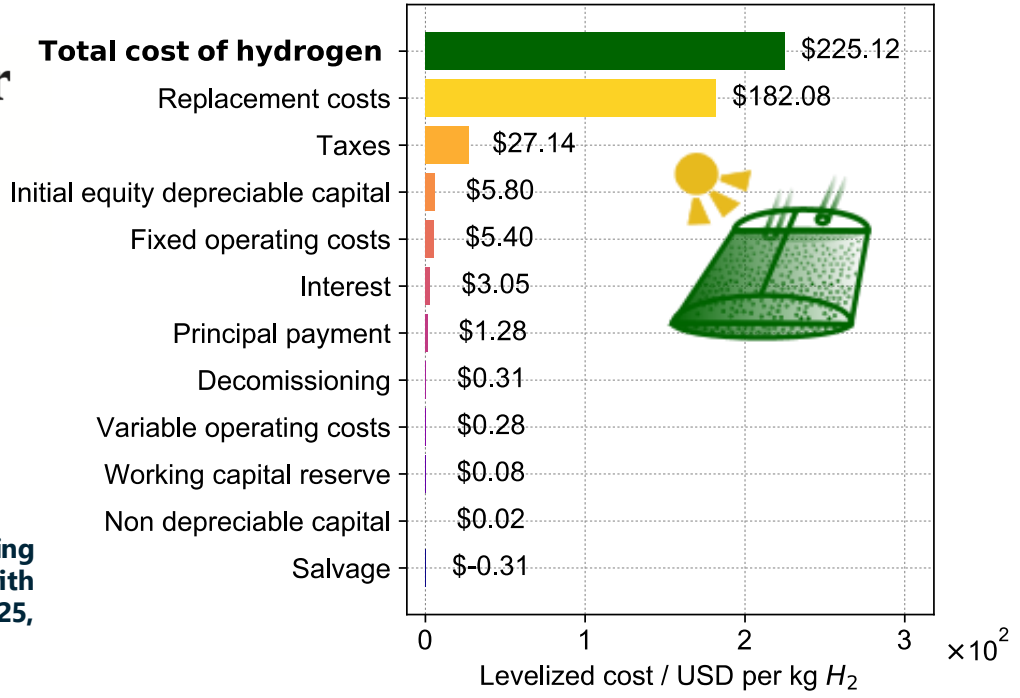
WATER SPLITTING

# Metal-free efficient photocatalyst for stable visible water splitting via a two-electron pathway

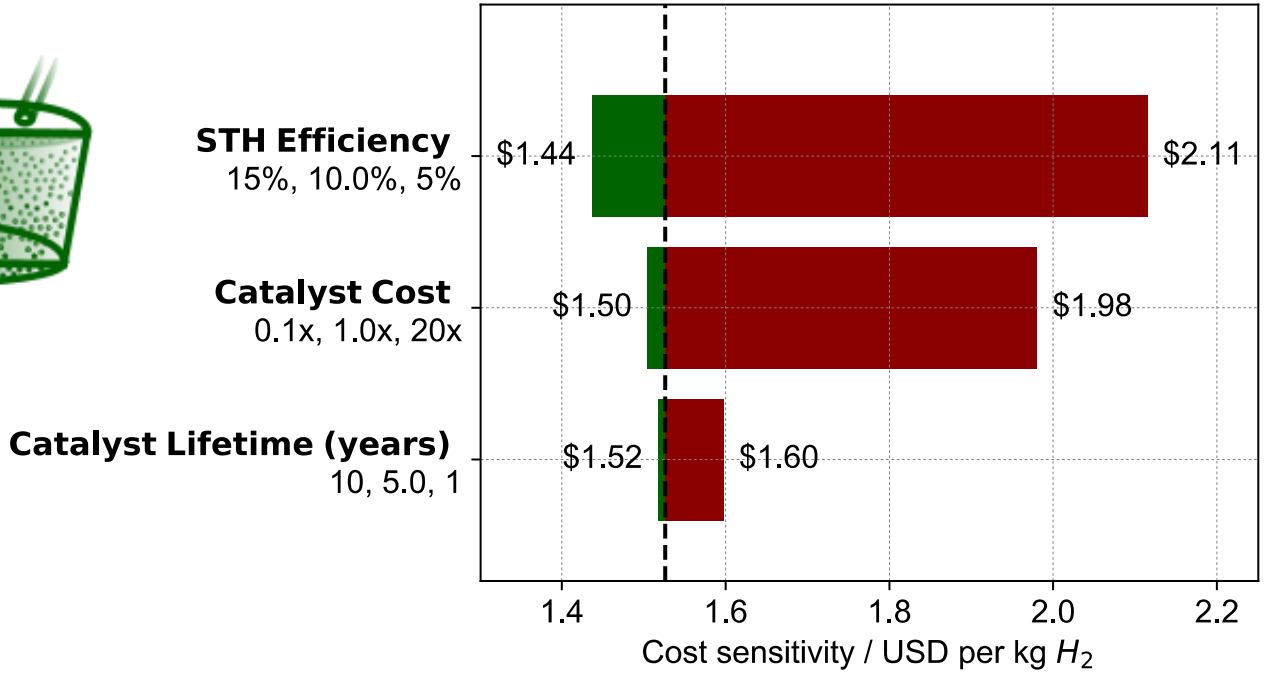
Juan Liu,[1] Yang Liu,[1] Naiyun Liu,[1] Yuzhi Han,[1] Xing Zhang,[1] Hui Huang,[1] Yeshayahu Lifshitz,[1,2]* Shuit-Tong Lee,[1]* Jun Zhong,[1] Zhenhui Kang[1]*

Kang *et al.*, *Science* **2015**, 347, 6225, 970 – 975

**Breakdown of levelized green hydrogen cost produced using photocatalysis in single bed, suspended particle reactor with catalyst parameters taken from Kang *et al.*, *Science* 2015, 347, 6225, 970 – 975.**



# Photocatalytic Hydrogen Production – Future




**Sensitivity analysis for green hydrogen produced using photocatalysis in single bed, suspended particle reactor Average cost (solar-to-hydrogen efficiency: 10%, particle cost multiplier: 1x, lifetime: 5 years) is $1.54/kg. Sensitivity of estimated price to variations of efficiency, particle cost multiplier and lifetime is shown.**

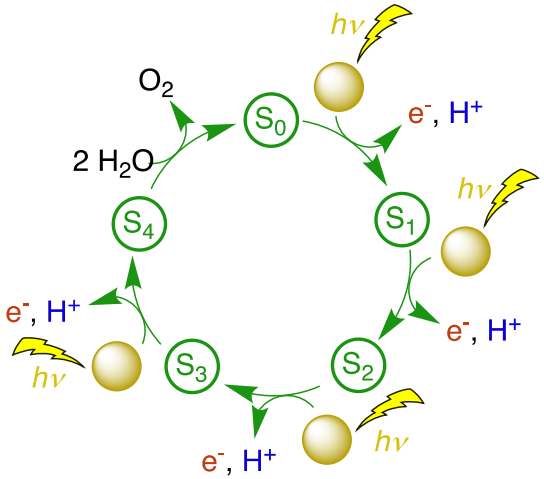
**Techno-economic model made by J. Schneidewind according to: Pinaud *et al.*, *Energy Environ. Sci.* 2013, 6, 1983 – 2002.**

# How to develop more efficient Photochemical Systems?


You have to kiss many
frogs to find your prince!

Arthur Frey, 3M,
Inventor of Post IT

# Key challenges in photocatalytic water splitting




shorter — Usable wavelengths — longer

Decreasing kinetic complexity

**$TiO_2$, $SrTiO_3$, …**

$2\ H_2O \xrightarrow{4\ h\nu} O_2 + 2\ H_2$

**Natural photosynthesis**

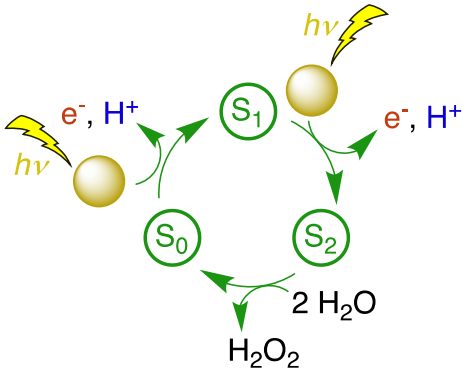
$2\ H_2O \xrightarrow{4\ h\nu} O_2 + 4\ H^+ + 4\ e^-$

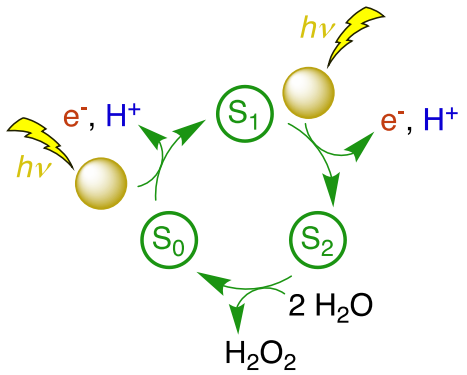
**$C_3N_4$/CDot**

$2\ H_2O \xrightarrow{2\ h\nu} H_2O_2 + H_2$

$2\ H_2O_2 \rightarrow O_2 + 2\ H_2O$

⊖ Energy loss due to $H_2O_2$ formation/disproportionation




$O_2 + 2\ H_2O$

LIKAT Rostock

**Centre: Overview of approaches to light-driven water splitting, arranged by usable wavelength range (top scale) and kinetic complexity (side scale). Note that wavelength ranges are only approximate.**
**Left: Generic reaction cycle for photosynthesis inspired systems.**
**Right: Generic reaction cycle for $H_2O_2$ pathway.**

# Problems, Opportunities, and Risks


- To achieve this goal, different communities have to work together in a real interdisciplinary manner (whi is in the drivers seat?); sometimes the language is different; molecular versus materials approach, …
- To improve the performance of the photocatalyst, e.g. CDot/C3N4, RhCrOx/SrTiO3:Al, CoO, …
- Heterogeneous vs. homogeneous photochemical systems; key parameters are: stabilitiy/lifetime; catalyst production, cost, upscaling, catalyst regeneration, light absorption, catalyst concentration, reproducability, …

- How to achieve a real catalyst design?
- …
- …..

# What´s next? The only limitation is our imagination!

Supports ?

?

? Metals

?

Different Mechanism

?

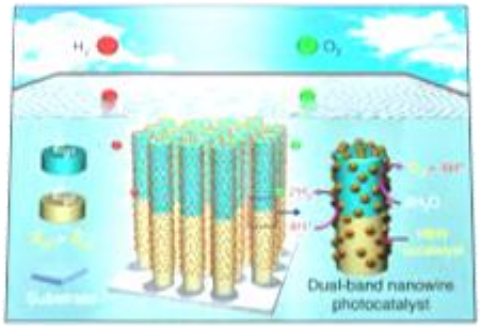
New Reactions

# Recent Examples Photocatalytic Systems for Water Splitting

**Reviews: a) Reaction systems for solar hydrogen production via water splitting with particulate semiconductor photocatalysts** T. Hisatomi, K. Domen, *Nature Catalysis*, 2, 387-399 (2019); b**) Achieving solar overall water splitting with hybrid photosystems of photosystem II and artificial photocatalysts** W. Wang, J. Chen, C. li, W. Tian, Nature Communications 5, Article number: 4647 (2014).

**Development of a photoelectrochemically self-improving Si/GaN photocathode for efficient and durable $H_2$ production** G. Zheng et al. Nature Materials 2021, https://doi.org/10.1038/s41563-021-00965-w

A photoelectrochemically self-improving behaviour of a silicon-gallium nitride photocathode active for hydrogen production with a Faradaic efficiency approaching ~100% is shown.



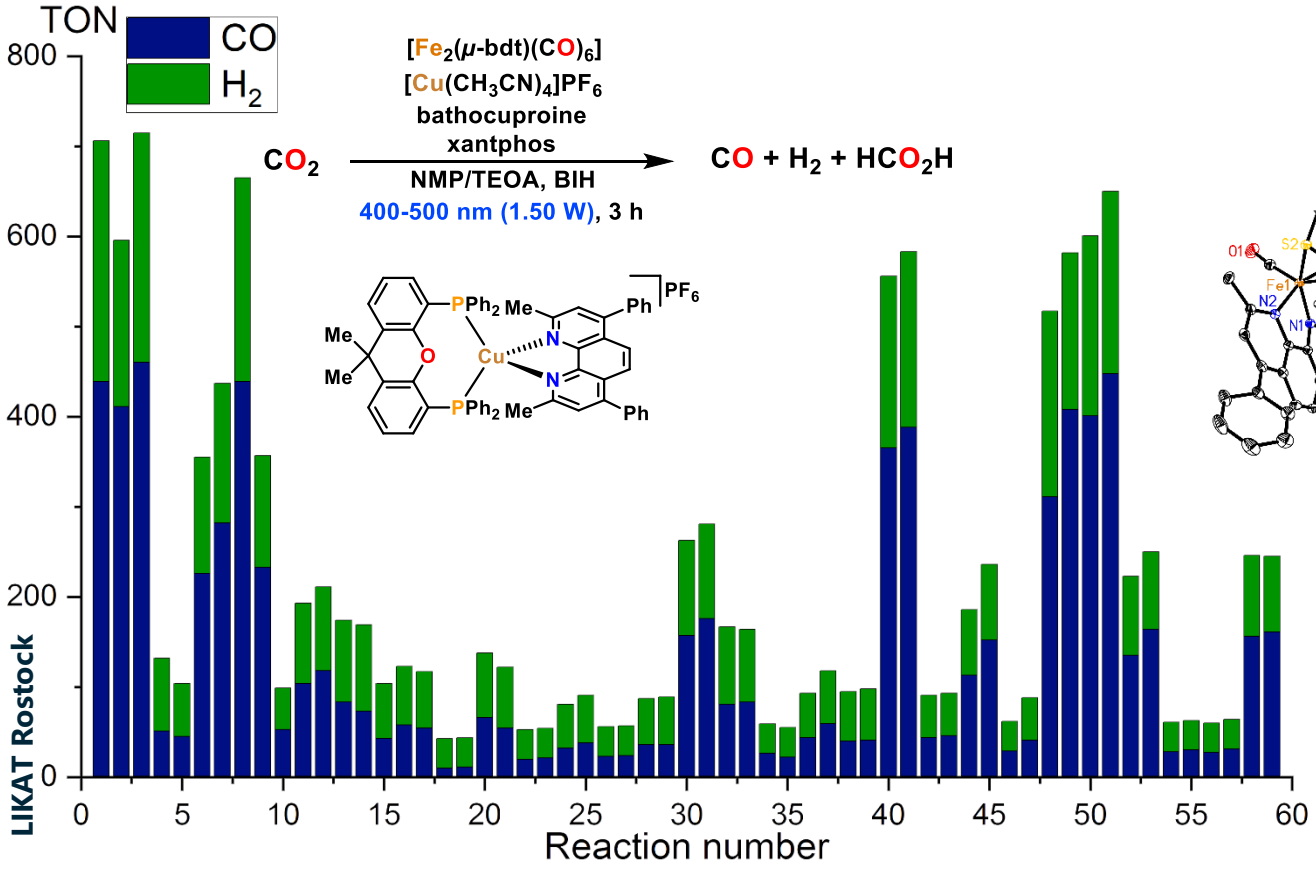

**A photochemical diode artificial photosynthesis system for unassisted high efficiency overall pure water splitting**
F. Chowdhury et al., Nature Communications, 9, Article number: 1707 (2018)

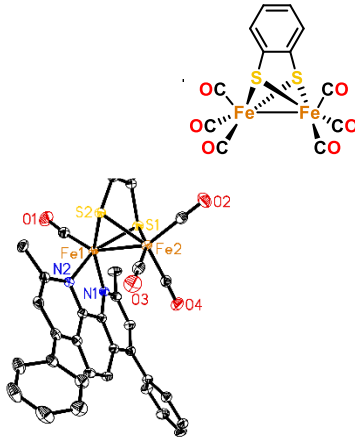
Using multi-band InGaN nanosheet photochemical diode (PCD) structures in wafer-level photochemical diode arrays exhibited solar-to-hydrogen efficiency ~3.3% in neutral (pH ~ 7.0) overall water splitting reaction. In part of the visible spectrum (400–485 nm), the energy conversion efficiency and apparent quantum yield reaches ~8.75% and ~20%.

**Two-photon, visible light water splitting at a molecular ruthenium complex** J. Schneidewind et al. Energy Environ. Sci. 2021, DOI: 10.1039/D1EE01053K

A new mechanistic paradigm for water splitting, which requires only two photons and offers a new method to extend the range of usable wavelengths far into the visible region is presented. Two-photon water splitting is enabled by absorption of a shorter wavelength photon, which produces an intermediate capable of absorbing a second longer wavelength photon (up to 630 nm). The second absorption causes O–O bond formation and liberation of $O_2$.

# Reproducibility in Photocatalytic $CO_2$ Reduction




Marx *et al.*, *ChemCatChem* 2020, *12*, 1603.

# To start a “provocative” Discussion:

- Innovations in better (with respect to STH efficiency) materials needed.
- Real life problems (upscaling, stability, etc) have to be addressed by demonstration units.
- Less „model“ studies with SR of SO (in high impact) journals.
- A holistic approach is needed.
- No real path to commercial viability for PEC; path to commercial viability for PV + E requires significant CAPEX reductions for PV & electrolyzers; in general commercial viability for photocatalytic approach.

# A Vision for Sustainability

sunlight/
renewable energy

water/ seawater

catalyst

catalyst

pure oxygen

pure hydrogen

$CO_2$
from industry

catalyst

biowaste

clean drinking water

pharmaceuticals

convenience goods

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**Thank you !**