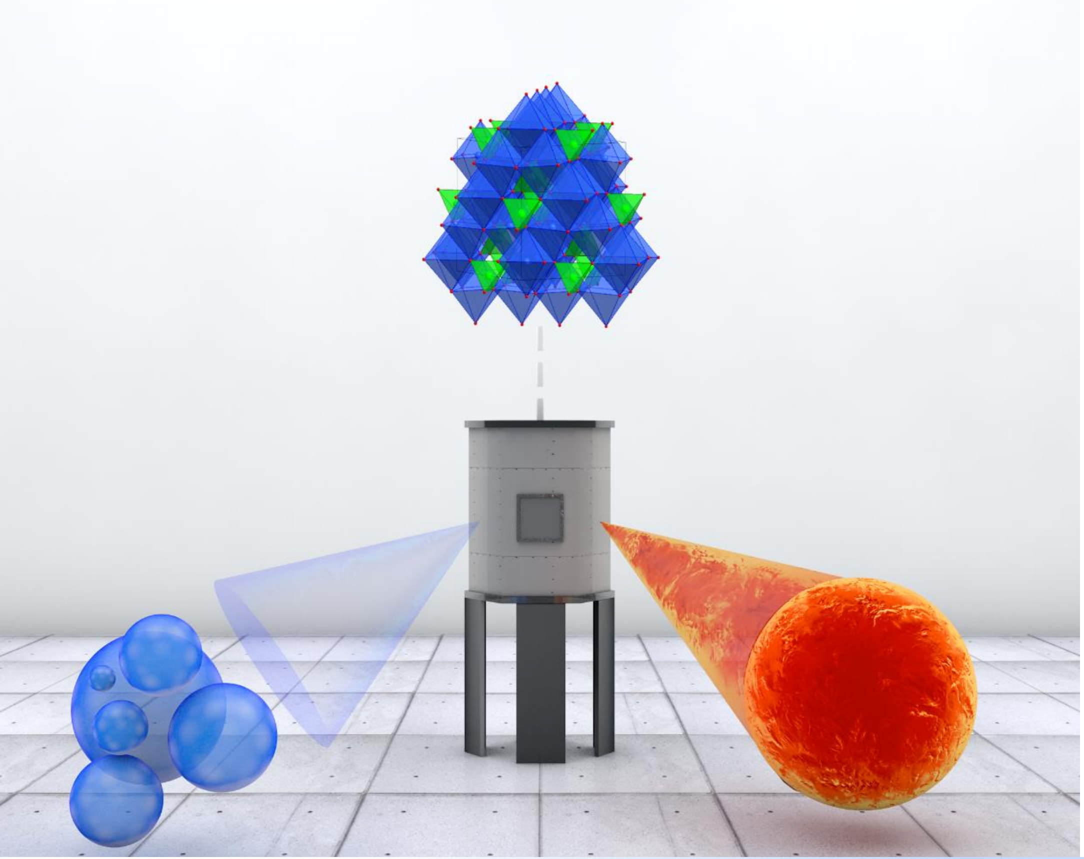
University of Zurich^UZH

SATW: Journées de Reflexion
Yverdon, 31 October 2018



Artificial Photosynthesis:

Minds

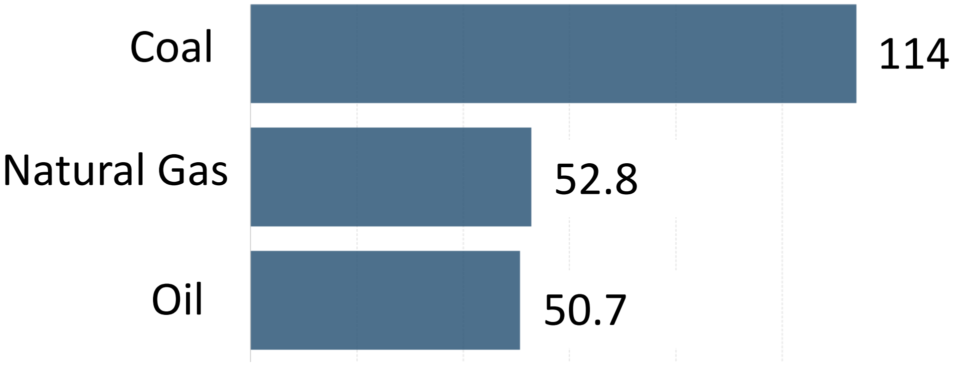
Matter

Markets

Prof. Greta R. Patzke

Department of Chemistry

How much time left?

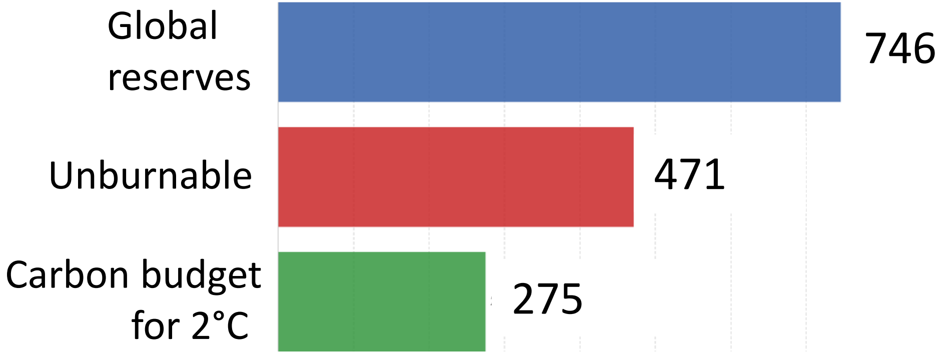


Resource analyses suggest:

Min. 100 years ?

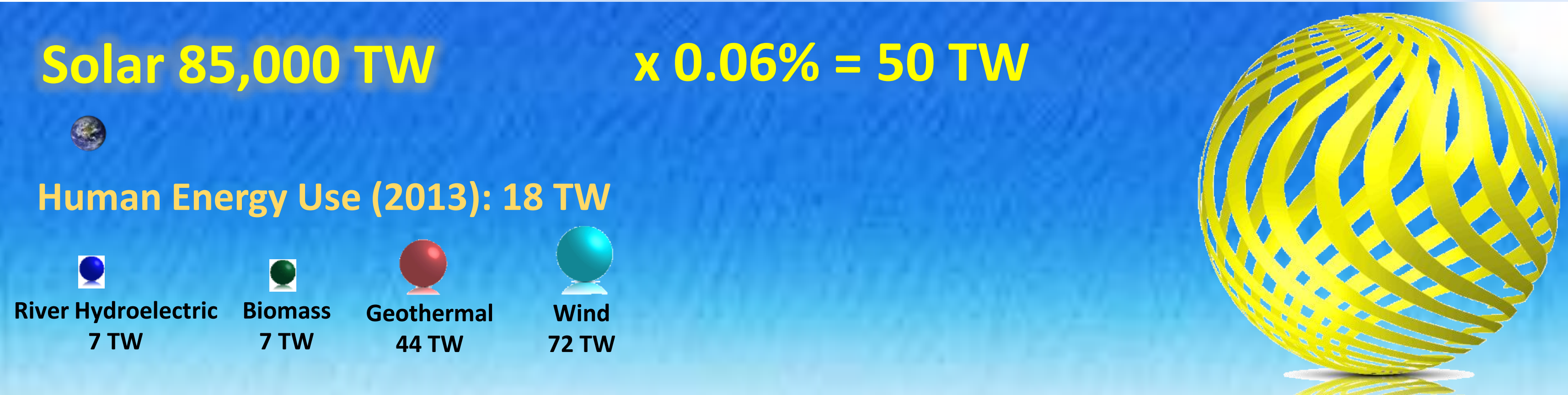
Global warming below 2 °C threshold:

65 – 80% of reserves must be left untouched (unburnable)!



tinyurl.com/ycqn7fv9

Why Solar Energy?



Solar 85,000 TW **x 0.06% = 50 TW**

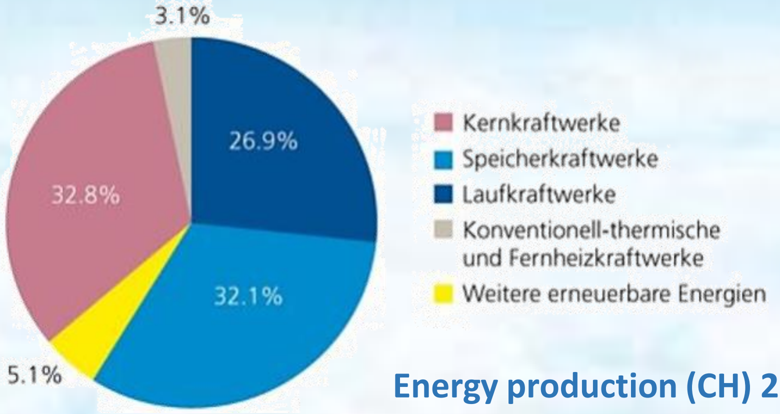
Human Energy Use (2013): 18 TW

River Hydroelectric
7 TW

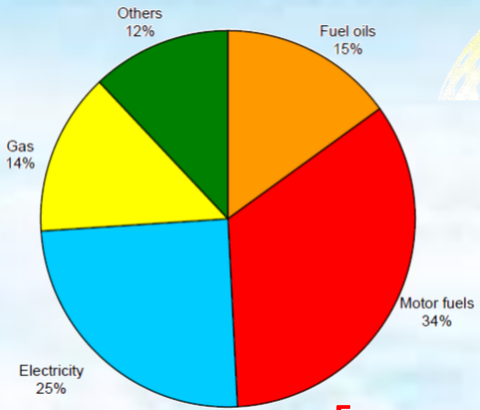
Biomass
7 TW

Geothermal
44 TW

Wind
72 TW



Energy production (CH) 2016



Energy consumption (CH) 2017

Abbott, D. *Proc. IEEE* **2010**, *98* (1), 42–66, Gesamtenergiestatistik, Tab. 24, VSE 2016, SFOE, Swiss Overall Energy Statistics 2017.

1. Nature
2. Science
3. Markets
Outlook

URPP LightChEC

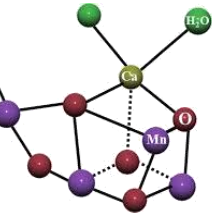
Secrets of Natural Photosynthesis

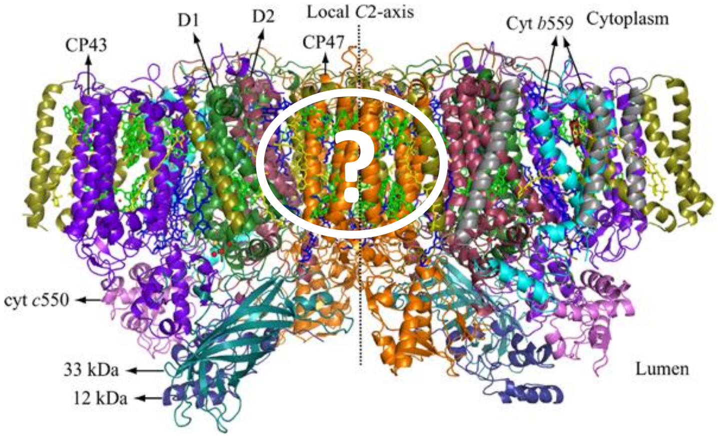
University of Zurich^UZH

Photosystem II

Protein: ca. 54'000 atoms

Inorganic core: {$CaMn_4O_5$}



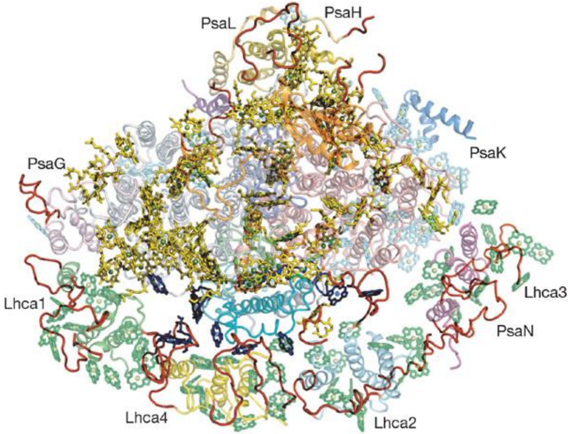


Y. Umena, K. Kawakami, J.-R. Shen, N. Kamiya, *Nature* **2011** (473) 55.

Photosystem I

Protein: ca. 36'000 atoms

Iron-sulfur clusters



I. Caspy, N. Nelson, *Biochem. Soc. Trans.* **2018** (46) 285.

$2\,H_2O \longrightarrow O_2 + 4\,e^- + 4\,H^+$

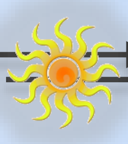
$2e^- + 2H^+ + NADP^+ \longrightarrow NADPH + H^+$

- **1. Nature**
- **2. Science**
- **3. Markets**
- ***Outlook***

A. Indra, P. W. Menezes, M. Driess *ChemSusChem* **2015**, 8, 776
Synthetic PSII mimics (examples): E. Y. Tsui, R. Tran, J. Yano, T. Agapie, *Nat. Chem.* **2013** (5) 293;
C. Zhang, C. Chen, H. Dong, J.-R. Shen, H. Dau, J. Zhao, *Science* **2015** (348) 690.

Artificial Photosynthesis (AP)

Solar energy directly to hydrogen - GW scale liquid fuels?



$$2\,H_2O \longrightarrow 2\,H_2 + O_2$$

$\Delta G° = +237.3$ kJ/mol

$E°_{rev} = 1.23$ V

Strong water oxidation catalysts (WOCs):

$$2\,H_2O \rightarrow O_2 + 4\,e^- + 4\,H^+$$

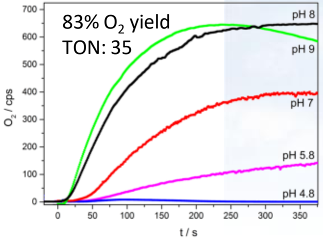
CO_2 reduction challenges:

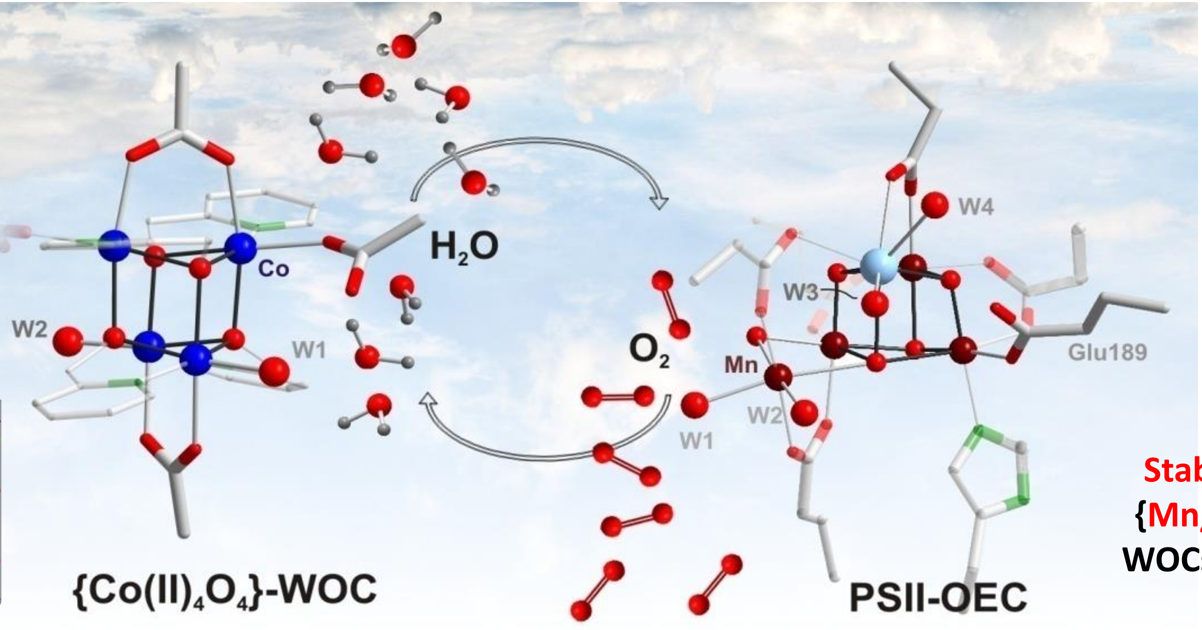
→ 6 or more proton/electron transfers limit selectivity

→ Higher BOP costs for CO_2 capture

→ Unlikely to make big dent in climate mitigation

Fundamental Research: Translating PSII





Stable & active

$\{Mn_4O_4\}$ cubane

WOCs: Challenge!

1st generation $\{Co^{II}_4O_4\}$ cubanes: Tetranuclearity & ligand environment

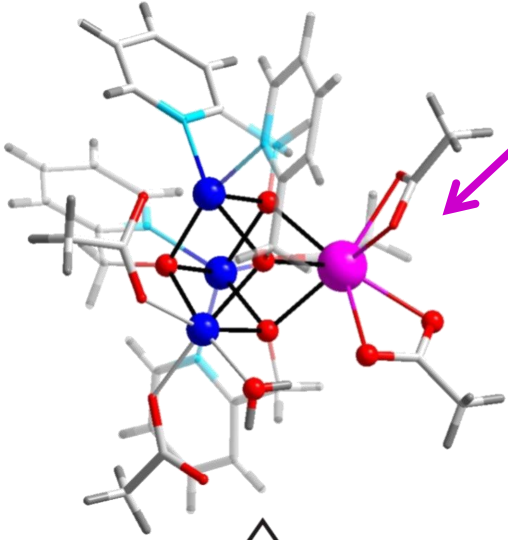
1. Nature
2. Science
3. Markets
Outlook

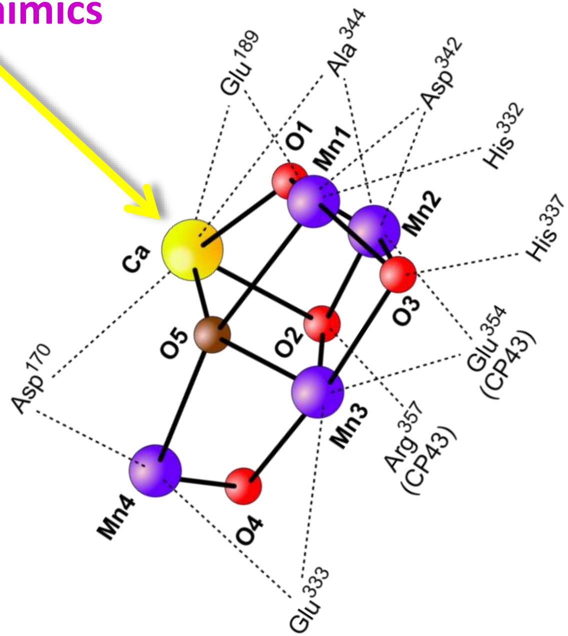
F. Evangelisti, R. Moré, F. Hodel, S. Luber, G. R. Patzke, *J. Am. Chem. Soc.* **2015** (137) 11076.

More PSI II Features in Synthetic WOCs

Why did Nature pick the redox-inert Ca^{2+}?

Ln^{3+} ions = Ca^{2+} mimics





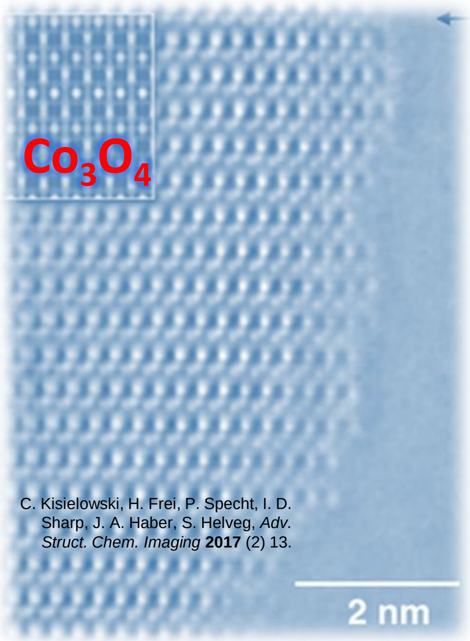
2^{nd} generation $\{Co^{II}_3O_4\}$ cubanes:

Enhanced performance & mechanistic insight

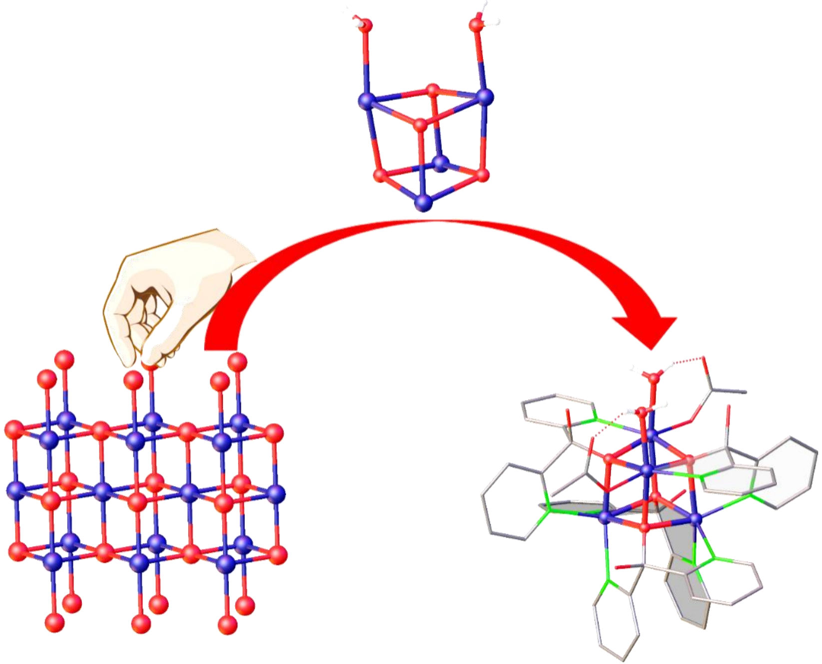
1. Nature
2. Science
3. Markets
Outlook

F. Evangelisti, R. Moré, F. Hodel, S. Luber, G. R. Patzke, *J. Am. Chem. Soc.* **2015** (137) 11076.

Bridging Molecular & Solid WOCs



C. Kisielowski, H. Frei, P. Specht, I. D. Sharp, J. A. Haber, S. Helveg, *Adv. Struct. Chem. Imaging* **2017** (2) 13.



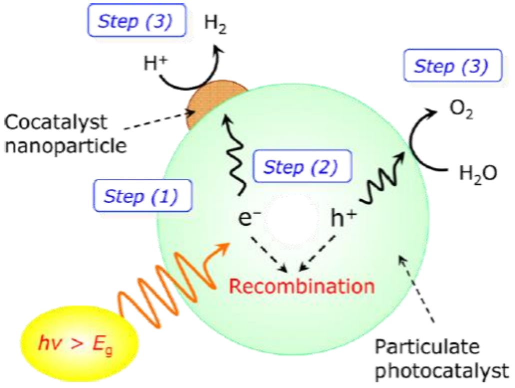
3^{rd} generation $Co^{II}_4O_4$-dpk cubane:
New molecular cut-outs of powerful solid catalysts

F. Song, R. Moré, M. Schilling, G. Smolentsev, N. Azzaroli, T. Fox, S. Luber, G. R. Patzke*, *J. Am. Chem. Soc.* **2017** (139) 14198.

1. Nature
2. Science
3. Markets

Outlook

Photocatalytic Water Splitting (off grid)



Overall water splitting: One particle (& co-catalysts)

Example: Al-doped $SrTiO_3$ loaded with $RhCrO_x$

Apparent Quantum Yield:

Improved to 69% (365 nm) with MoO_y coloading

K. Domen et al., ACS Catal. **2018** (8) 2782-2788.

Z scheme: Two catalysts

Example:

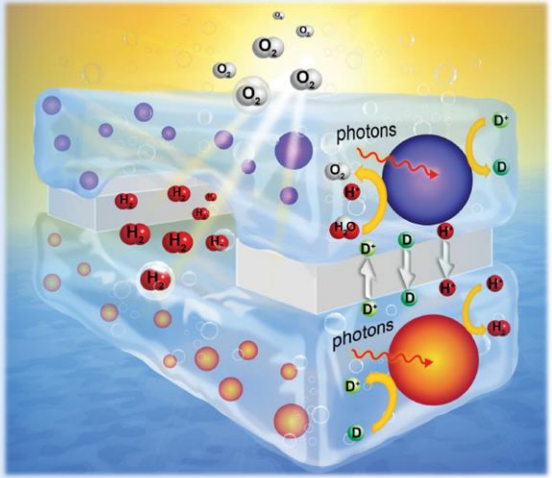
$BiVO_4$ for O_2 evolution

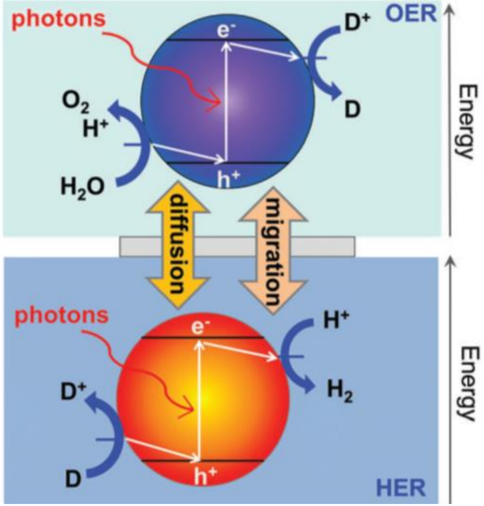
$SrTiO_3$:Rh for H_2 production

IO_3^-/I^- redox shuttle

Efficiency:

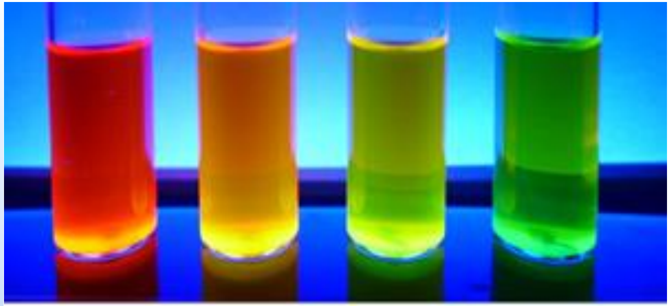
min. 1% STH efficiency

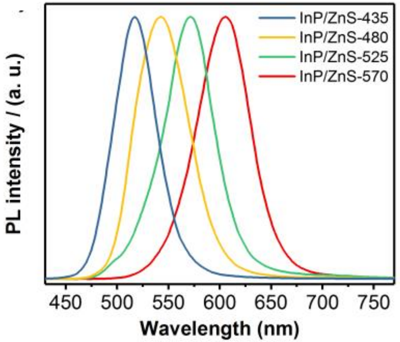


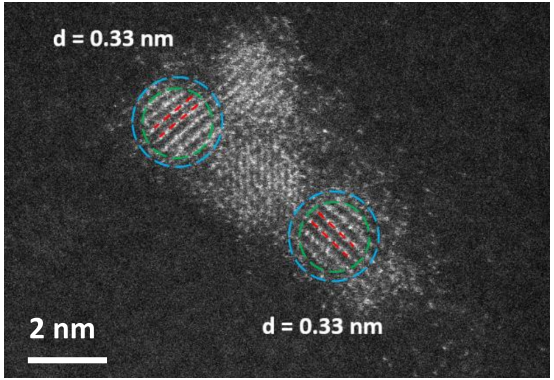


A. Z. Weber et al., Energy Environ. Sci. **2018** (11) 115.

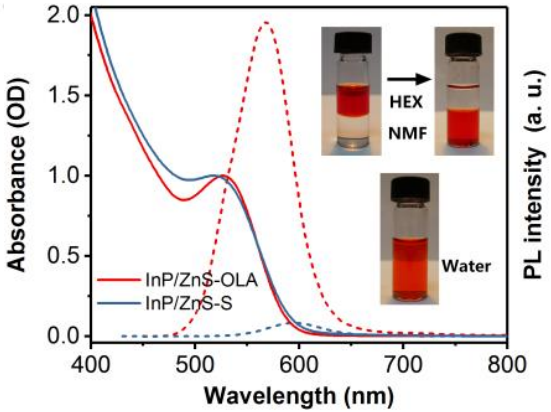
Eco-Friendly InP/ZnS Quantum Dots







We **replaced toxic Cd** in high performance QD photosensitizers!

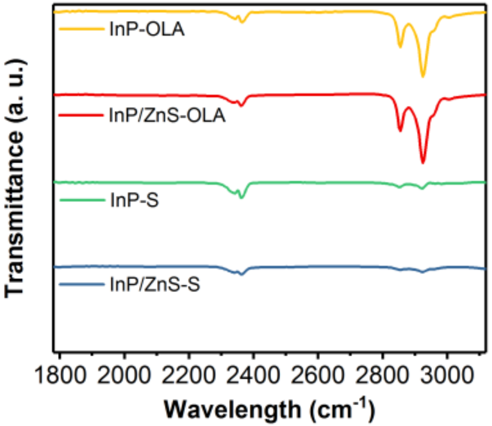


New capping with sulfide ions:

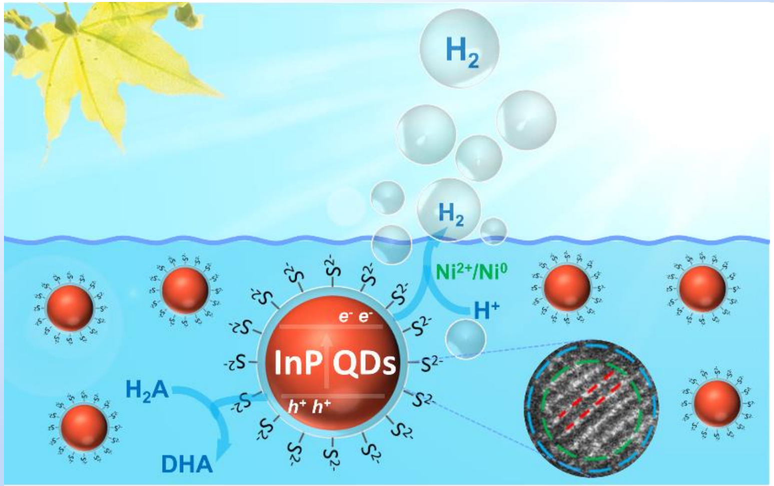
⇩

Water soluble QDs!

S. Yu, X.-B. Fan, X. Wang, J. Li, Q. Zhang, A. Xia, S. Wei, L.-Z. Wu, Y. Zhou, G. R. Patzke, *Nat. Commun.* **2018** (9) 4009.



H_2 Production with InP/ZnS-S QD Photosensitizers



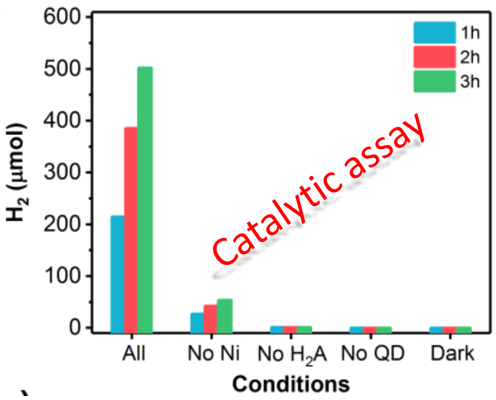
Turnover numbers **up to 128’000**

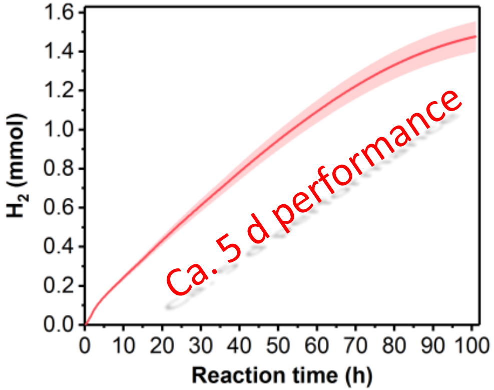
↓

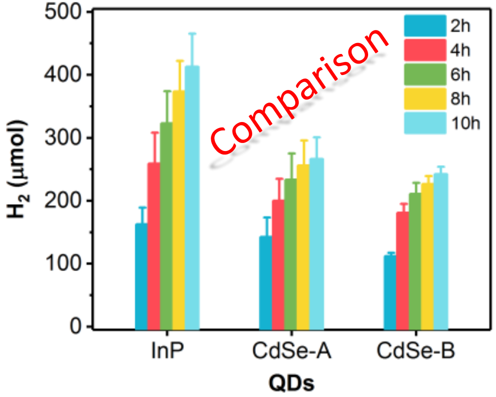
Activity for > 100 h, 31% IQY

↓

→ **Competitive** with leading Cd-QDs



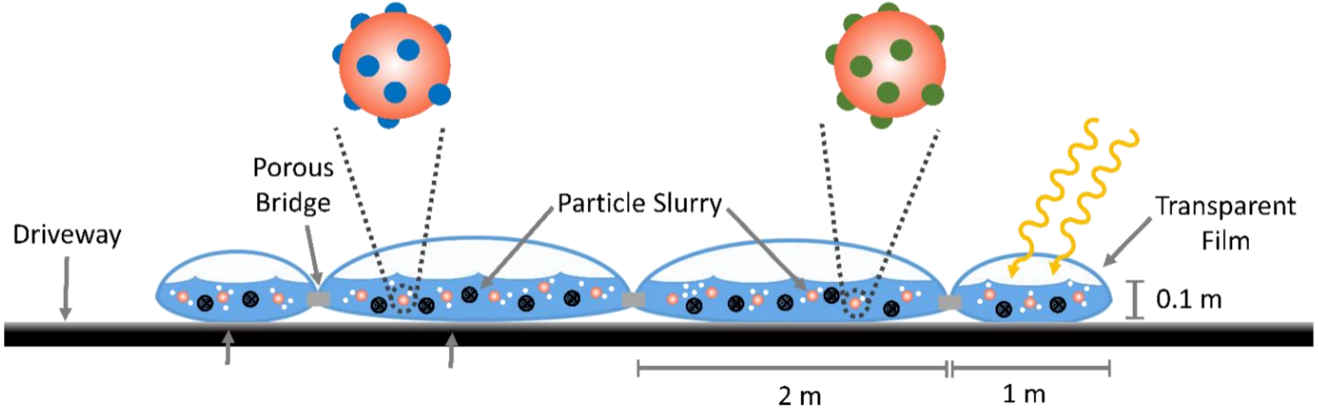




S. Yu, X.-B. Fan, X. Wang, J. Li, Q. Zhang, A. Xia, S. Wei, L.-Z. Wu, Y. Zhou, G. R. Patzke, *Nat. Commun.* **2018** (9) 4009.

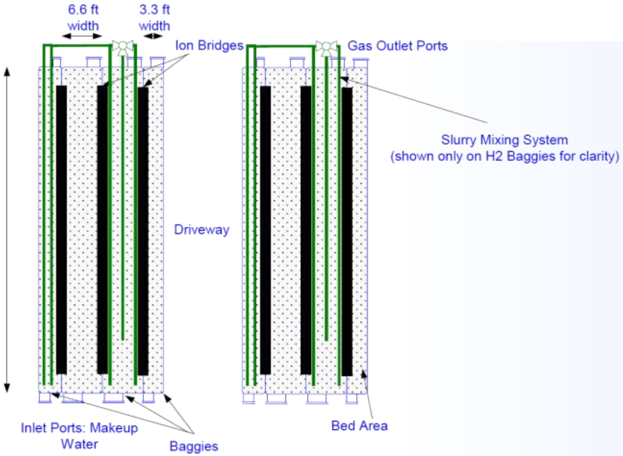
1. Nature
2. Science
3. Markets
Outlook

Photocatalytic Reactor Models



Water oxidation catalyst: O_2

Water reduction catalyst: H_2



Particle bed systems:

Low maintenance & capital costs

Levelized calculated H_2 costs:

Lower than for panel systems

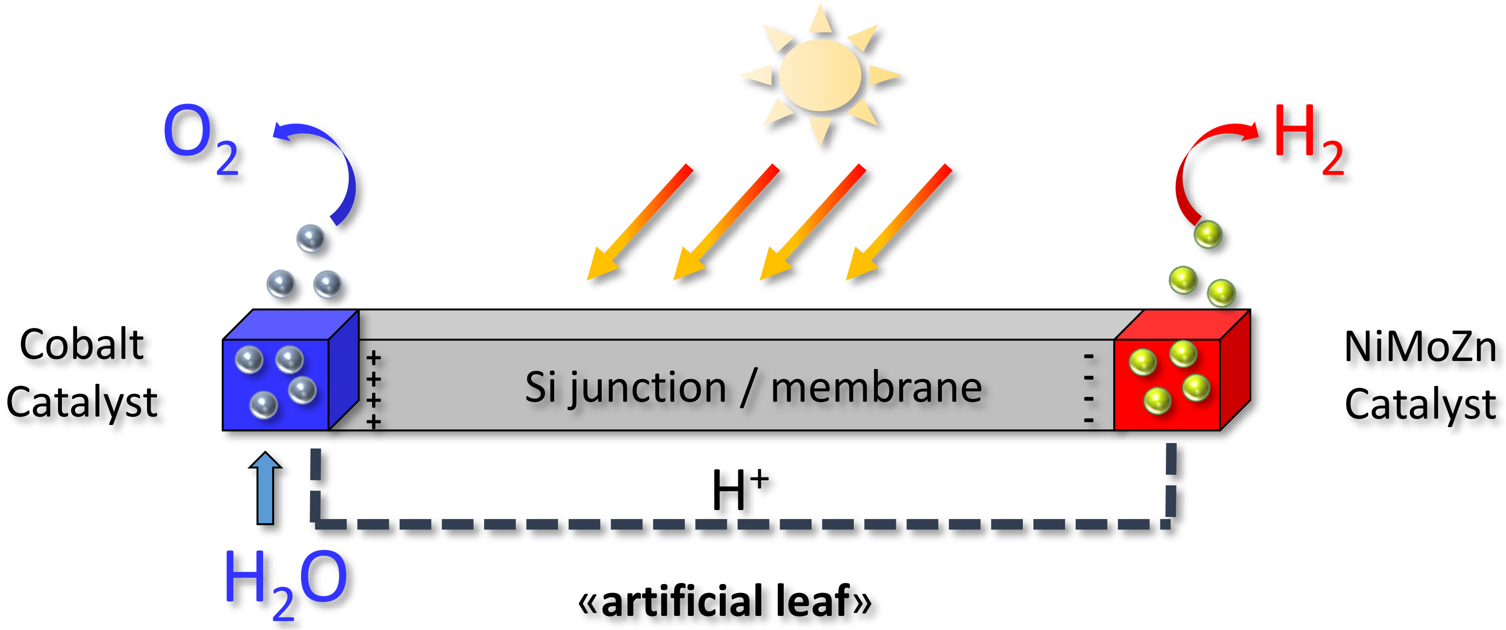
Advantage: Gas collection bags can store day's production

2009 DOE Technoeconomical Analysis of PEC Hydrogen Production.
T. F. Jaramillo et al., *Energy Environ. Sci.* **2013** (6) 1983.

1. Nature
2. Science
3. Markets

Outlook

Photoelectrochemistry: Artificial Leaf Prototype

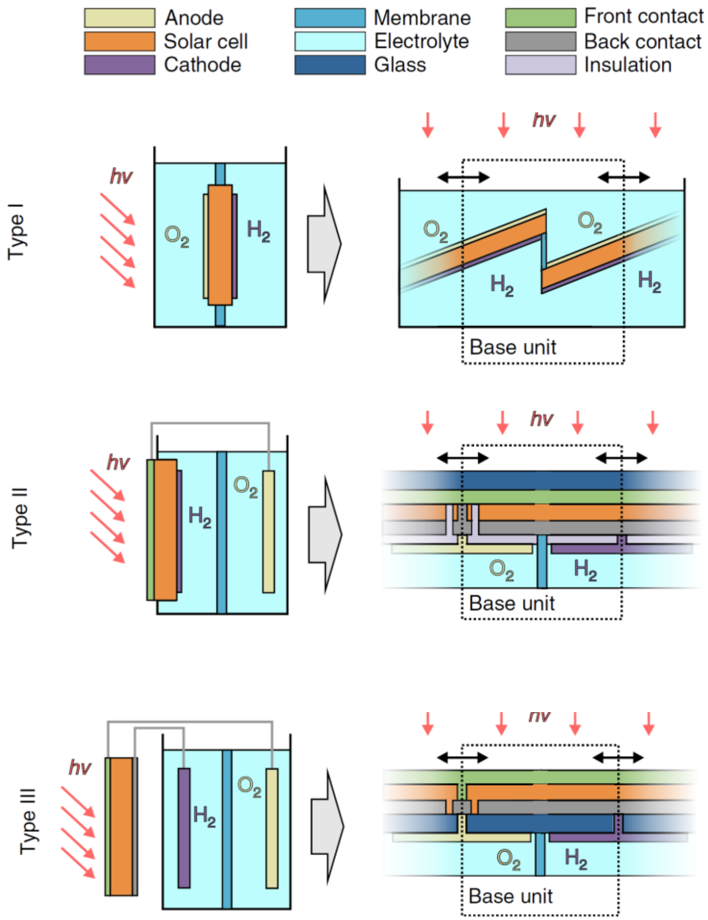


Overall solar-to-fuel efficiency 4.7%: φ(PV) · φ(WS)

φ(PV)= 7.7%, water splitting efficiency = 60%

D.G. Nocera, *Acc. Chem. Res.*, **2012**, 45, 767 & Sun Catalytix

PV-Assisted Water Splitting



Three lab prototype designs:

I. PV immersed in electrolyte with catalyst electrodes on both sides

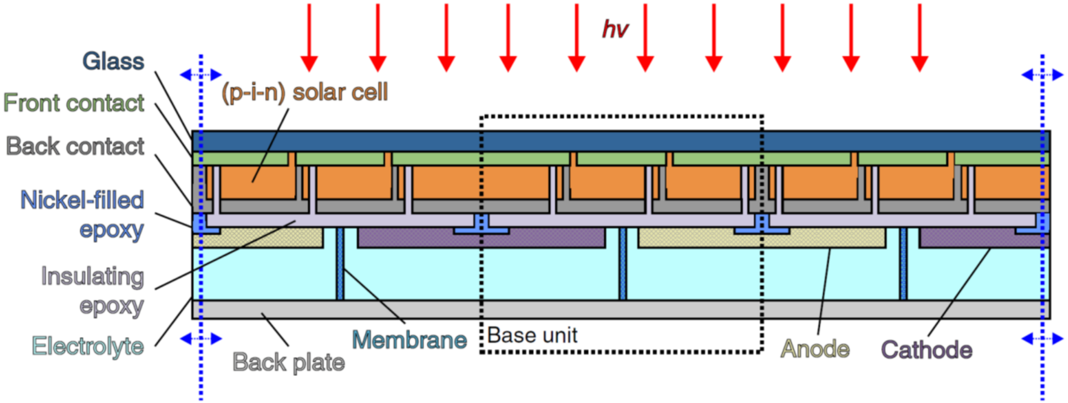
II. Only one side of PV part exposed to electrolyte (wire needed)

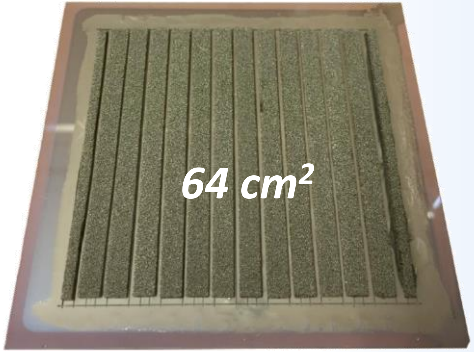
II. Complete separation of PV and electrocatalytic elements

1. Nature
2. Science
3. Markets
Outlook

B. Turan, J.-P. Becker, F. Urbain, F. Finger, U. Rau, S. Haas, *Nature Commun*. **2016** (7) 12681.

Recent Type II Upscaling





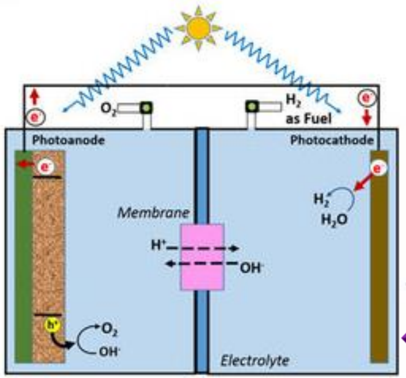
Materials: single-junction a-Si:H solar cells, Ni foam electrodes

Concept: integrated series of thin-film PV modules
& repetitive water splitting modules

Advantage: scalable, wireless, STH 3.9%, little membrane effect

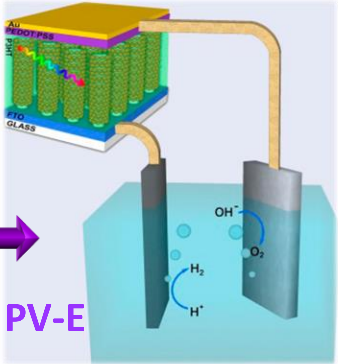
B. Turan, J.-P. Becker, F. Urbain, F. Finger, U. Rau, S. Haas, *Nature Commun*. **2016** (7) 12681.

Photoelectrochemistry (PEC) vs. PV-Electrolysis

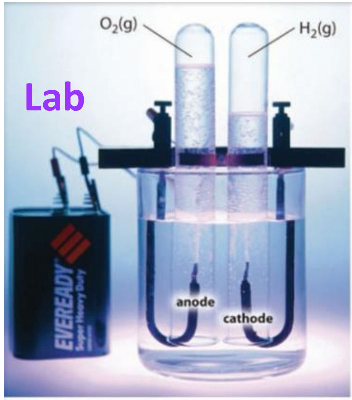


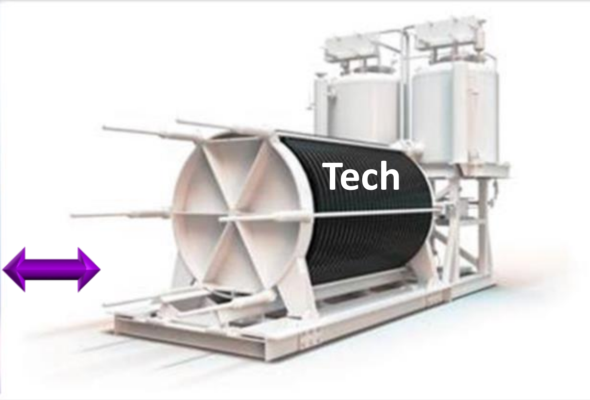
tinyurl.com/y8cfahwt

PEC



PV-E





PV-E: Immediate market option

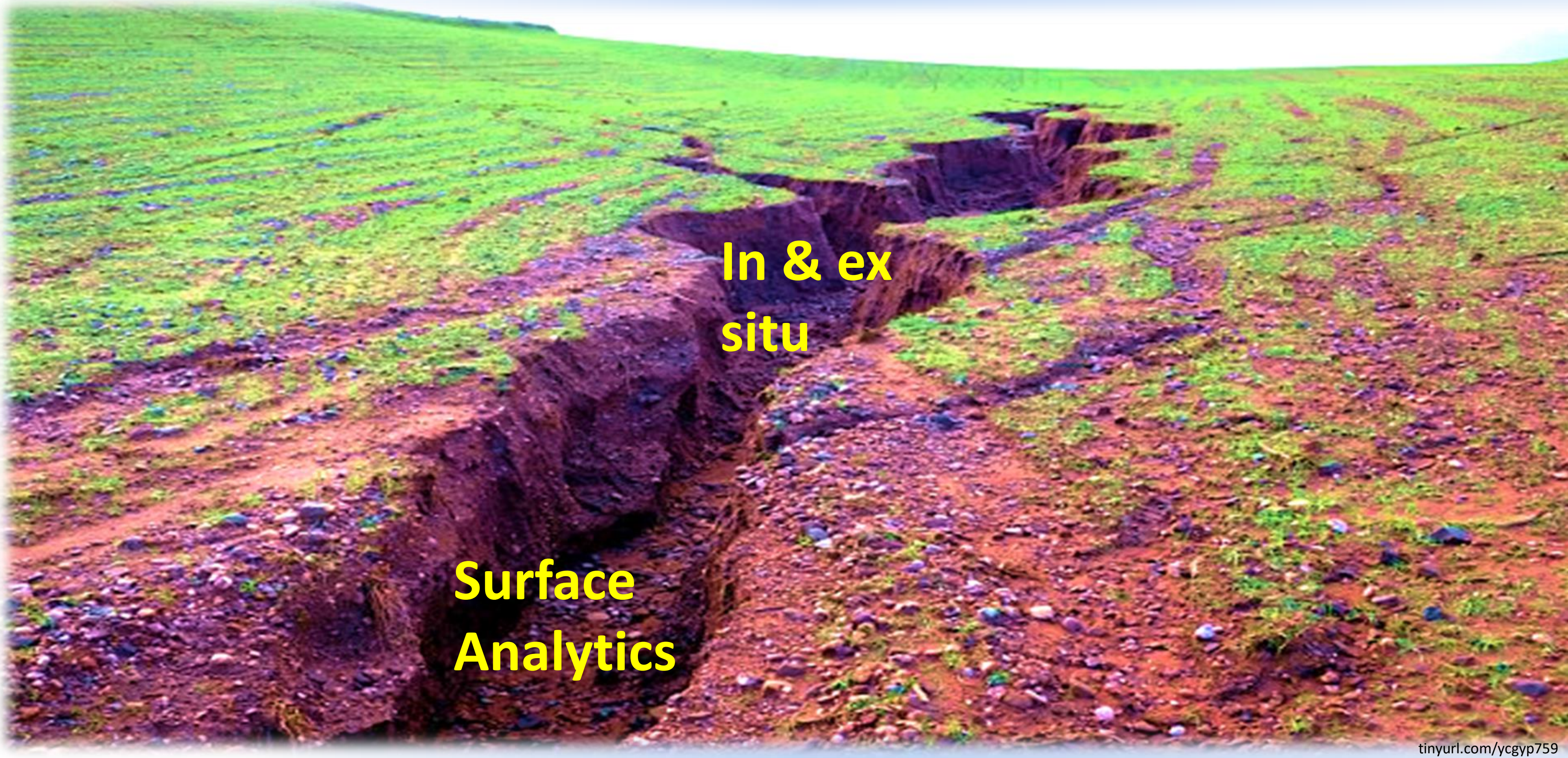
Integrated PEC device advantages: Small current densities & less gas bubbles, better heat management, no Pt/Ir required

PEC needs: Fresh materials -- Larger devices -- Clear benchmarking

1. Nature
2. Science
3. Markets
Outlook

J. Su, L. Vayssieres, *ACS Energy Lett.* **2017** (1) 121.
R. Van de Kroel, B. A. Parkinson, *MRS Energy & Sustainab.* **2017** (4) e13.

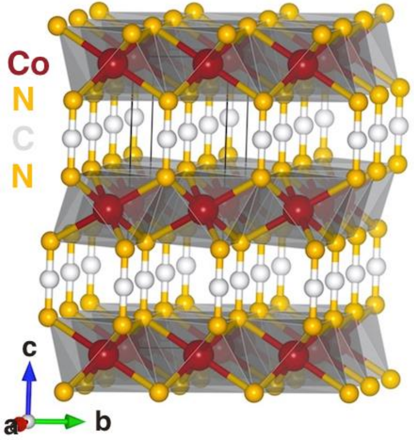
Where Do Catalysts Go?

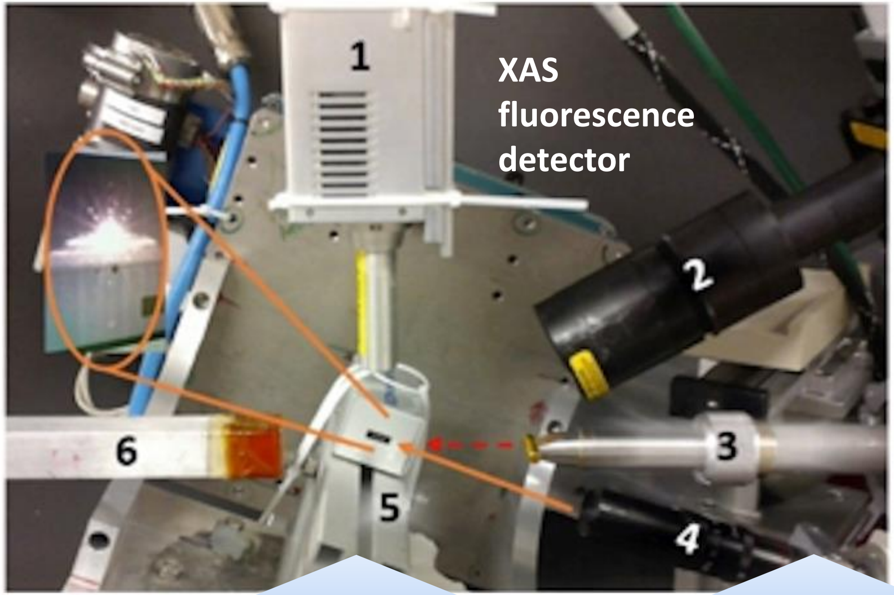


tinyurl.com/ycgyp759

Operando Raman and XAS Spectroscopy

Oxide formation?





Raman detector

X-ray source

X-ray path for transmission

SPE connector

Raman source

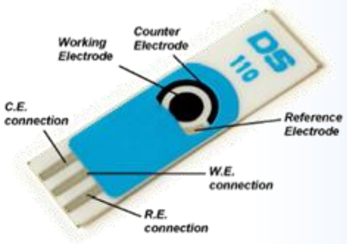
ESRF BM01 Swiss Norwegian Beamline: MNCN series

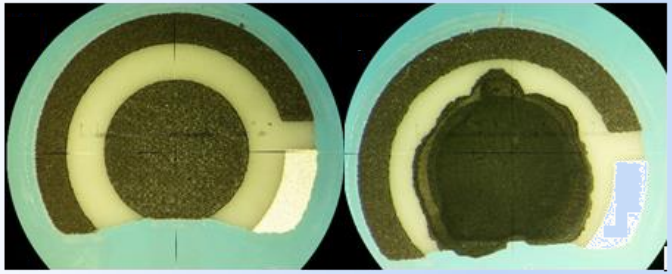
M = Co, $Co_{0.9}Ni_{0.1}$, Ni, Mn, Cu

R. J. Müller, J. Lan, K. Lienau, R. Moré, C. A. Triana, M. Iannuzzi, G. R. Patzke, *Dalton Trans*. **2018** (47) 10759.

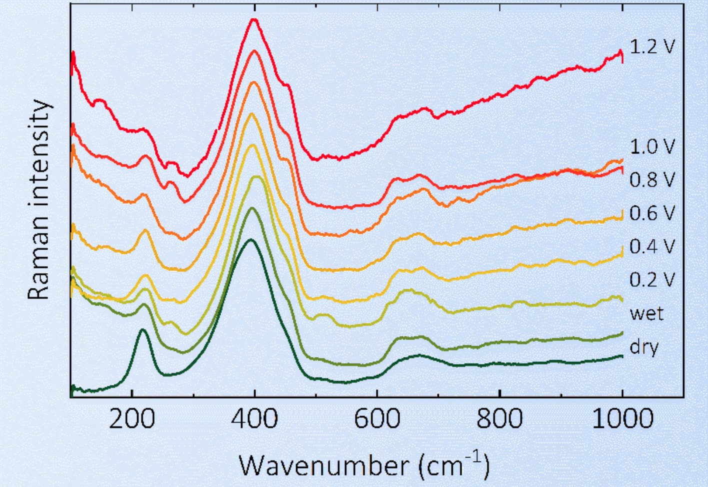
1. Nature
2. Science
3. Markets
Outlook

Ex situ & Operando Raman





Screen printed electrode (SPE):
Dropcasting of CoNCN/Nafion ink



Operando Raman spectra of CoNCN at different applied voltages:

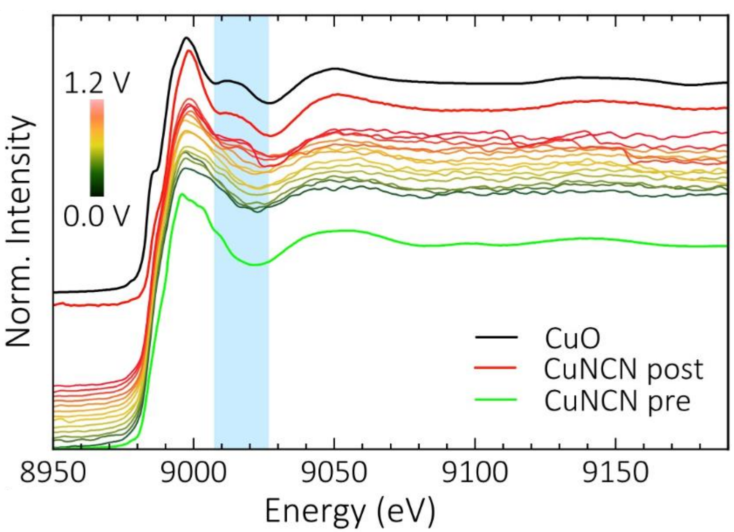
→ Oxide-related peaks absent

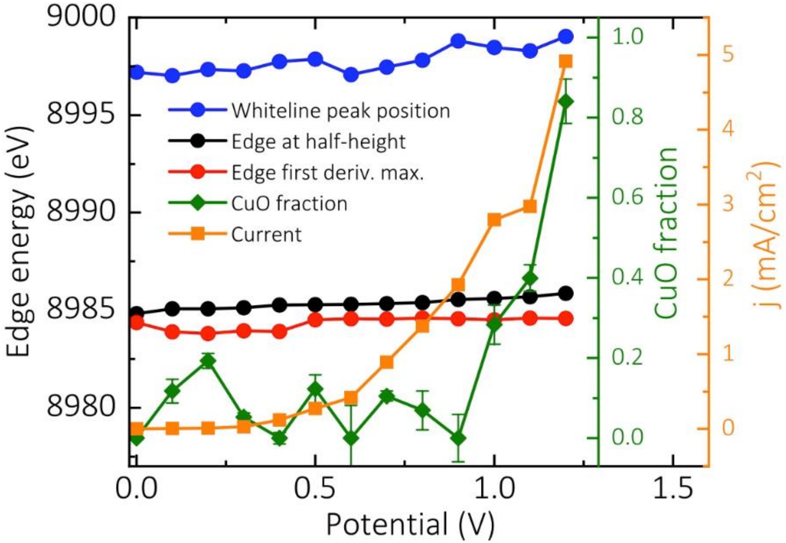
1. Nature
2. Science
3. Markets
Outlook

R. J. Müller, J. Lan, K. Lienau, R. Moré, C. A. Triana, M. Iannuzzi, G. R. Patzke, *Dalton Trans*. **2018** (47) 10759.

Operando XAS Characterization

CuNCN: XANES (fluorescence) spectra & descriptors: 80 % CuO at 1.2 V



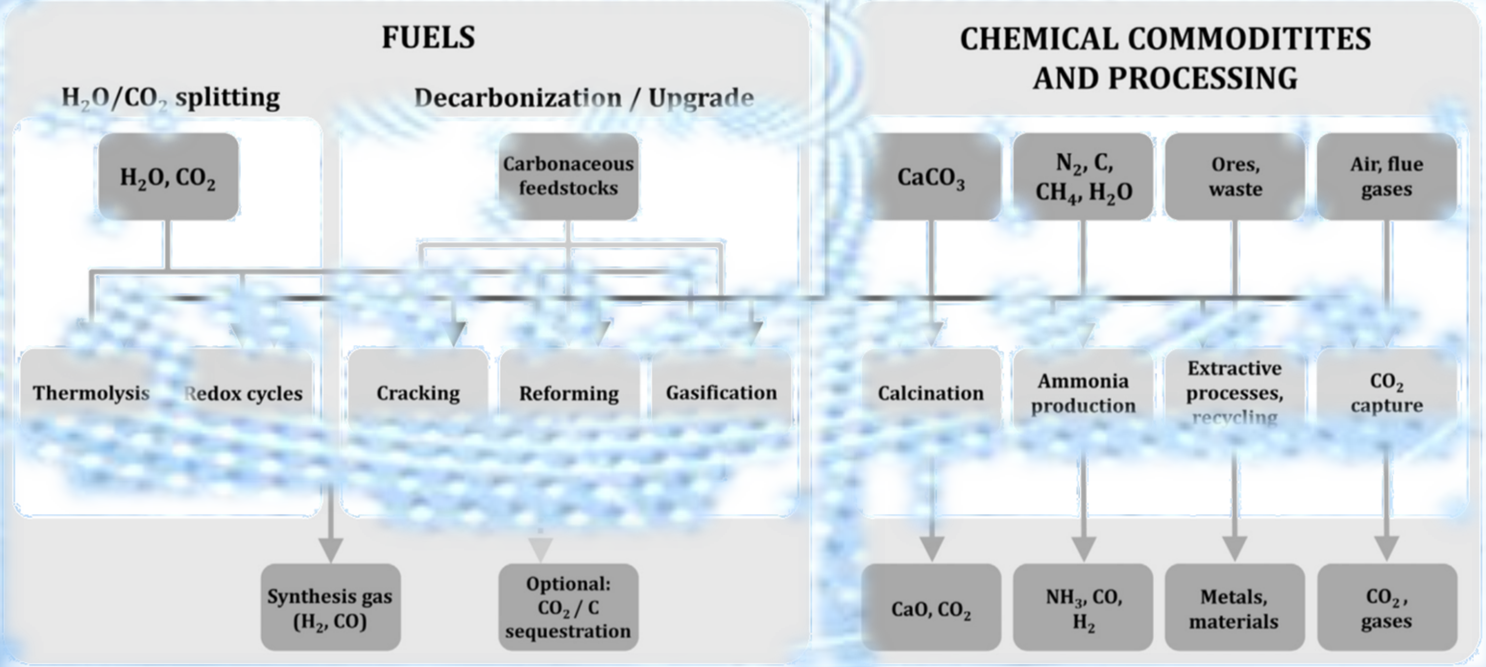


MNCN series (M = Co, $Co_{0.9}Ni_{0.1}$, Ni, Mn, **Cu**):

→ Only **CuNCN** forms oxide layer *operando*

R. J. Müller, J. Lan, K. Lienau, R. Moré, C. A. Triana, M. Iannuzzi, G. R. Patzke, *Dalton Trans*. **2018** (47) 10759.

Solar Thermochemical Routes



FUELS

H_2O/CO_2 splitting

H_2O, CO_2

Thermolysis

Redox cycles

Decarbonization / Upgrade

Carbonaceous feedstocks

Cracking

Reforming

Gasification

Synthesis gas (H_2, CO)

Optional: CO_2 / C sequestration

CHEMICAL COMMODITITES AND PROCESSING

$CaCO_3$ → **Calcination** → **CaO, CO_2**

N_2, C, CH_4, H_2O → **Ammonia production** → **NH_3, CO, H_2**

Ores, waste → **Extractive processes, recycling** → **Metals, materials**

Air, flue gases → **CO_2 capture** → **CO_2, gases**

1. Nature
2. Science
3. Markets

Outlook

E. Koepf, I. Alxneit, C. Wieckert, A. Meyer, *Appl. Energy* **2017** (188) 620.

Solar Syngas from Oxides

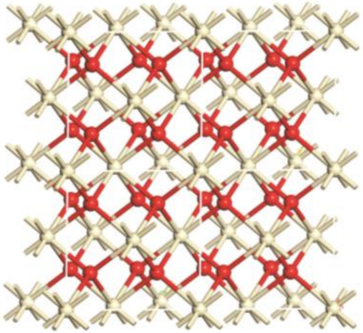
High T (1500 °C): $^{1}/_{\delta}CeO_2 \longrightarrow {}^{1}/_{\delta}CeO_{2-\delta} + 0.5\ O_2(g)$

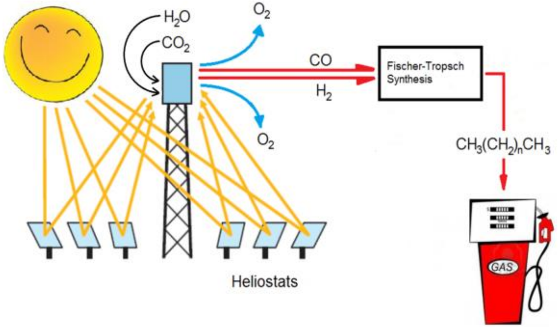
Lower T ↓ 1000 °C

$CO_2(g) + {}^{1}/_{\delta}CeO_{2-\delta} \longrightarrow {}^{1}/_{\delta}CeO_2 + CO(g)$

$H_2O(g) + {}^{1}/_{\delta}CeO_{2-\delta} \longrightarrow {}^{1}/_{\delta}CeO_2 + H_2(g)$

Best dopants for ceria?





Task: max. δ
oxygen vacancies ($V_O^{\cdot\cdot}$)

→

CO & H_2
Fischer-Tropsch fuels

1. Nature
2. Science
3. Markets
Outlook

Solar Power through Oxide Materials

- **Engineering@ETH Zurich (Prof. Aldo Steinfeld)**

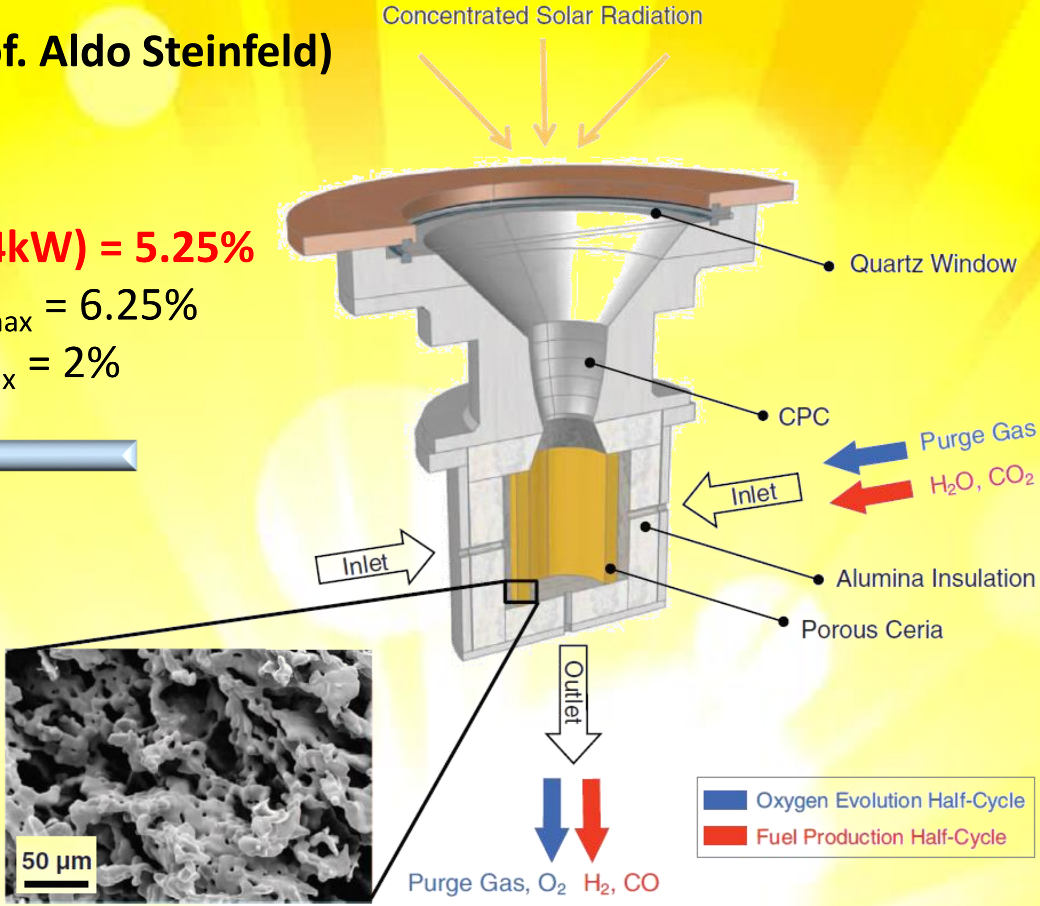
STF (4kW) = 5.25%

PV-E_{max} = 6.25%

PEC_{max} = 2%

OUR TASK:

High performance oxide reactor for present heliostat infrastructure



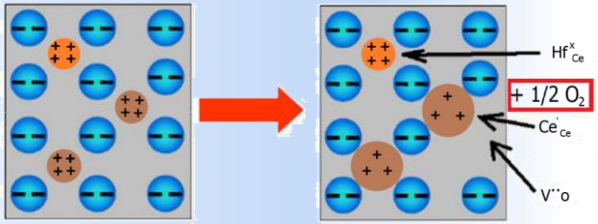
W. C. Chueh, C. Falter, M. Abbott, D. Scipio, P. Furler, S. M. Haile, A. Steinfeld, *Science* **2010** (330) 1797.
D. Marxer, P. Furler, M. Takacs, A. Steinfeld, *Energy Env. Sci.* **2017** (10) 1142.

1. Nature
2. Science
3. Markets
Outlook

Ceria: Dopant Screening

Tetravalent dopants

$2Ce^{x}_{Ce} + O^{x}_{O} \longrightarrow 2Ce'_{Ce} + V''_{O} + 1/2\ O_2$

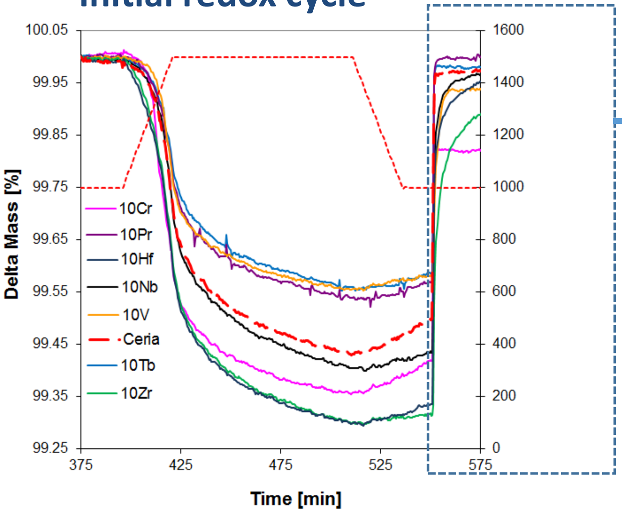


- Reversible oxygen vacancies
- Ce^{3+} is larger than Ce^{4+}

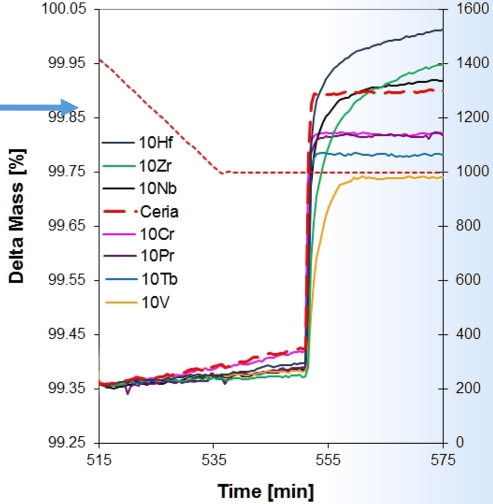
Screening of all potential tetravalent dopants in the PSE (Shannon radii)

Nb, Ta, Hf, Zr: stable & improved ceria performance

Initial redox cycle

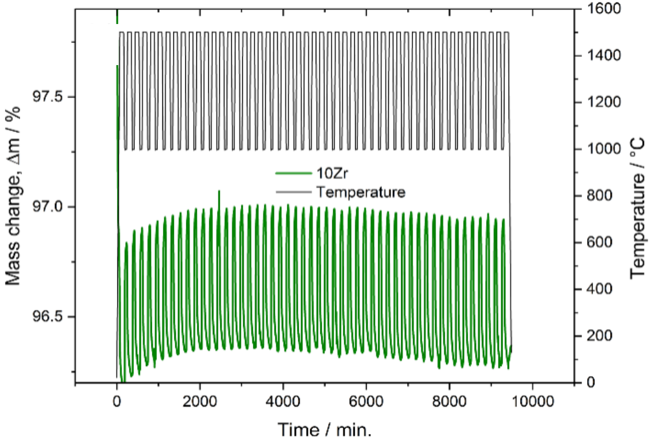


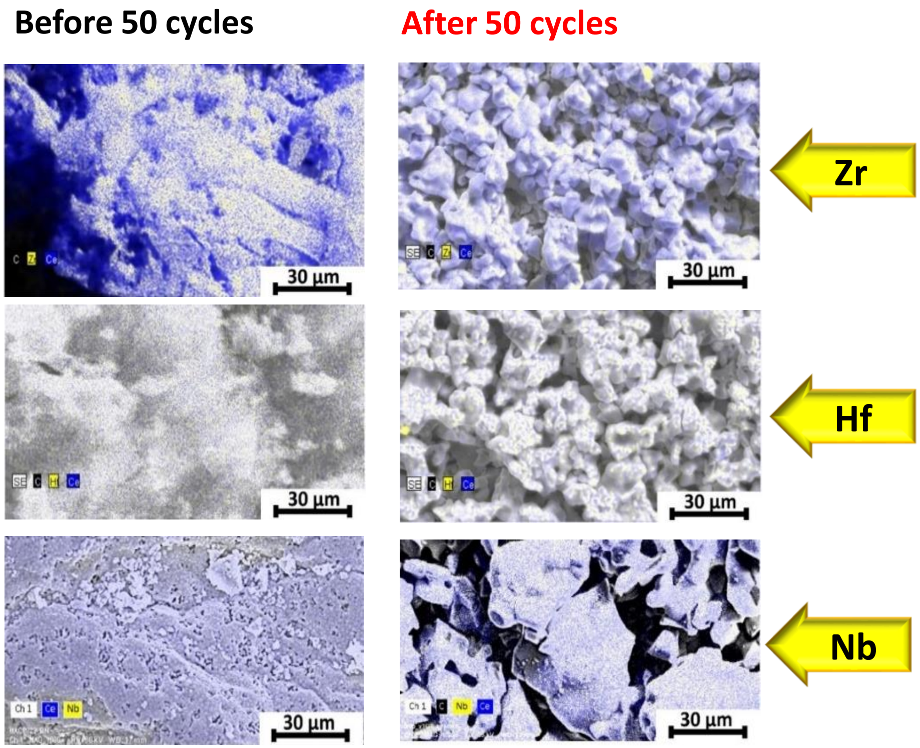
Oxidation



R. Jacot, R. Moré, R. Michalsky, A. Steinfeld, G. R. Patzke, *J. Mater. Chem A* **2017** (5) 19901.

Ceria Dopant Optimization Strategy





→ **Hf-, Zr- & Nb doped**
ceria remains stable
after prolonged TGA cycling

→ **Homogeneous dopant distribution: Key factor!**

1. Nature
2. Science
3. Markets
Outlook

R. Jacot, J. M. Naik, R. Moré, R. Michalsky, A. Steinfeld, G. R. Patzke, *J. Mater. Chem. A* **2018**, *6*, 5807.

Selected New Companies

sunfire www.sunfire.de	CO_2 & Water electrolysis (solid oxide cell stacks)
skytree www.skytree.eu **CLIMEWORKS** www.climeworks.com	CO_2 capture from air
DIMENSIONAL ENERGY www.dimensionalenergy.net	Solar thermal CO_2 conversion to methanol
opus 12 www.opus-12.com	CO_2 electrolysis to CO for on-site generation
CATALYTIC Innovations www.catalytic-innovation.com	Water oxidation for corrosion resistance

1. Nature
2. Science
3. Markets
Outlook

Techno-Economic Scenarios

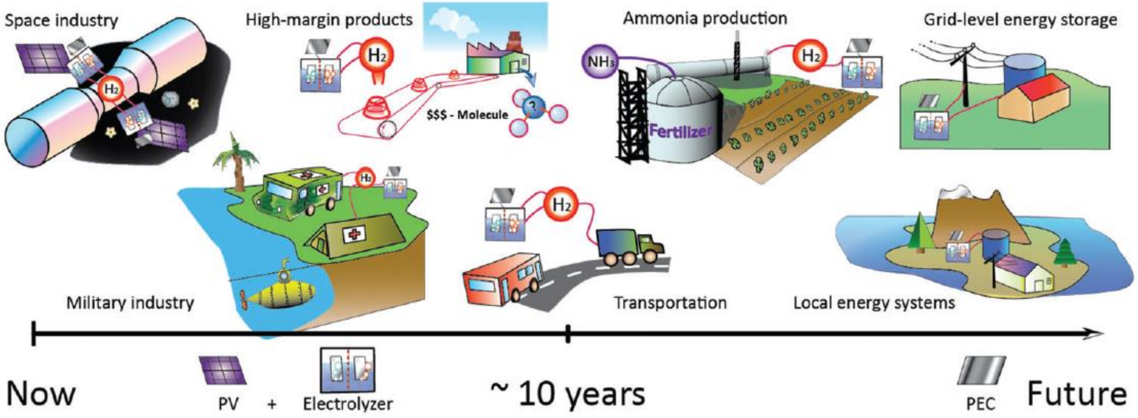
(1) Fossil H_2 prices are too low for market price as innovation driver

(2) Economic incentives through CO_2 taxes

(3) Judging new technologies without large-scale tests is premature

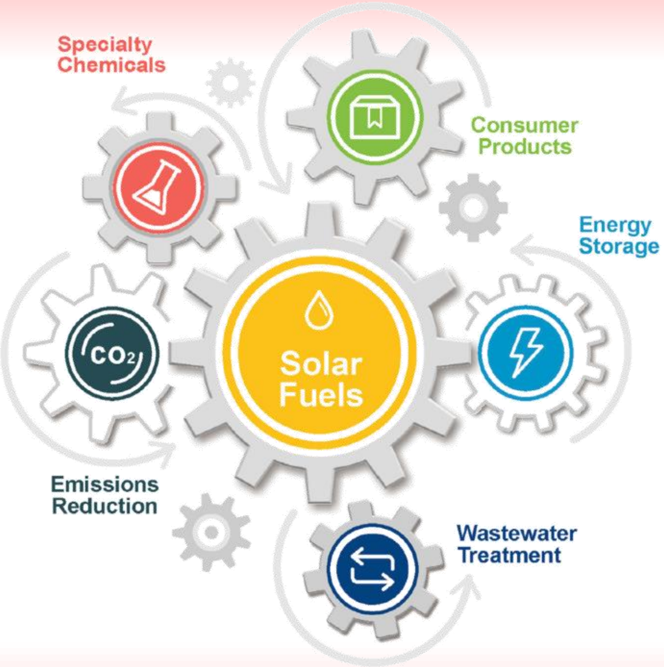
(4) Final capital investment & life cycle analysis for PV?

(5) High public acceptance level for new solar!



T. Bolsen, J. N. Druckman, F. Lomax Cook, *Chem* **2016** (1) 515.
S. Ardo et al., Energy Environ. Sci. **2018**, DOI: 10-1039/c7ee03639f.

Emergent Technology Views



Unconventional marketing ideas:

→ WOCs for corrosion inhibition

→ «Free» H_2 as water cleaning by-product

→ Electro-refinement of biomass instead of O_2 formation

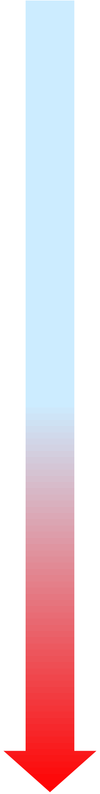
Swiss leadership through innovation:
A resource as inexhaustible as light

Entering the market evolutionarily & with public support

S. Sheehan et al., *Chem* **2018**, DOI: 10.1016/j.chempr.2017.06.003

Our Three Ways to Water Splitting

25 °C

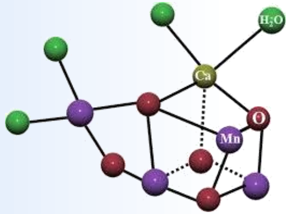


1500 °C

1. Molecular Catalysts

Principles of **Photosystem II**

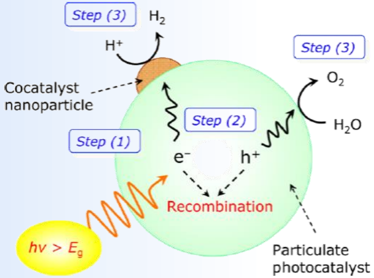
H_2 evolution with **Quantum Dots**



2. Nanoscale & Solid Catalysts

In situ formation monitoring &

Analytical **tracking**



ACS Catal. **2013** (3) 1486.

3. Concentrated Solar Power

Doped ceria vs. perovskites

Cooperation: Prof. Aldo Steinfeld, ETH Zurich

tinyurl.com/y8m27mak

University of Zurich UZH

Light to Chemical Energy Conversion: LightChEC

URPP LightChEC

Andreas Borgschulte (EMPA)

trMOKE

Advanced Analytical Technologies

Devices

Karl-Heinz Ernst (EMPA)

H_2 Formation and CO_2 Reduction

Roger Alberto

Water Reduction Catalysts & Photosensitizers

Metals in Medicine / Molecular Imaging

David Tilley

Photoelectrocatalysis

Molecular Approaches to Renewable Energies

Catalysts

Mechanisms

Greta R. Patzke

Water Oxidation Catalysts

Solids, Oxoclusters & Molecules

Peter Hamm

Ultra-fast Spectroscopy & Mechanisms

Femto Second and 2D-IR Spectroscopy

Jürg Hutter Sandra Luber

Electronic Structures and Reaction Pathways of WOC/WRC

Advanced Electronic Structure Methods

Theory

Jürg Osterwalder

Catalysts on Surfaces

Ultrafast Electron Dynamics and Scattering

UZH Priority Program: *www.lightchec.uzh.ch*

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FNSNF
Fonds national suisse
Schweizerischer Nationalfonds
Fondo nazionale svizzero
Swiss National Science Foundation

CMSZH Chemical Molecular Sciences Zurich Graduate School

University of Zurich UZH

Sino Swiss Science and Technology Cooperation

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https://tinyurl.com/y7799dc2