Molecular science for artificial photosynthesis

From bio-inspired catalyst to nanomaterials

V. Artero

Laboratoire de Chimie et Biologie des Métaux,
Université Joseph Fourier, CNRS, CEA Grenoble
www.solhycat.com

Acknowledgements

Marc Fontecave
Murielle Chavarot-Kerlidou
Jennifer Fize

PhD students
Nicolas Queyriaux
Nicolas Kaeffer
Marine Bacchi
Sigolène Canaguier
Romain Métayé
Yohan Oudart

Post-docs
Carole Baffert
Aziz Fihri
Pierre-André Jacques
Alan Le Goff
Mathieu Razavet
Phong Tran Dinh
Vincent Fourmond
Saioa Cobo
Eugen S. Andreiadis
Trevor R. Simmons
Gustav Berggren

Collaborations

IBS
Martin Field (DFT)

INAC
Colette Lebrun (ESI-MS)
Jacques Pécaut (X-Ray)

IRAMIS (surface chemistry)
Serge Palacin
Bruno Jousselme

Dalian Univ.of Technology
Licheng Sun
Mei Wang
Zhan Pan

Frei Universität Berlin
Holger Dau
Jonathan Heidkamp

NTU Singapour
Phong. D. Tran

Ibitech-S
Winfried Leibl

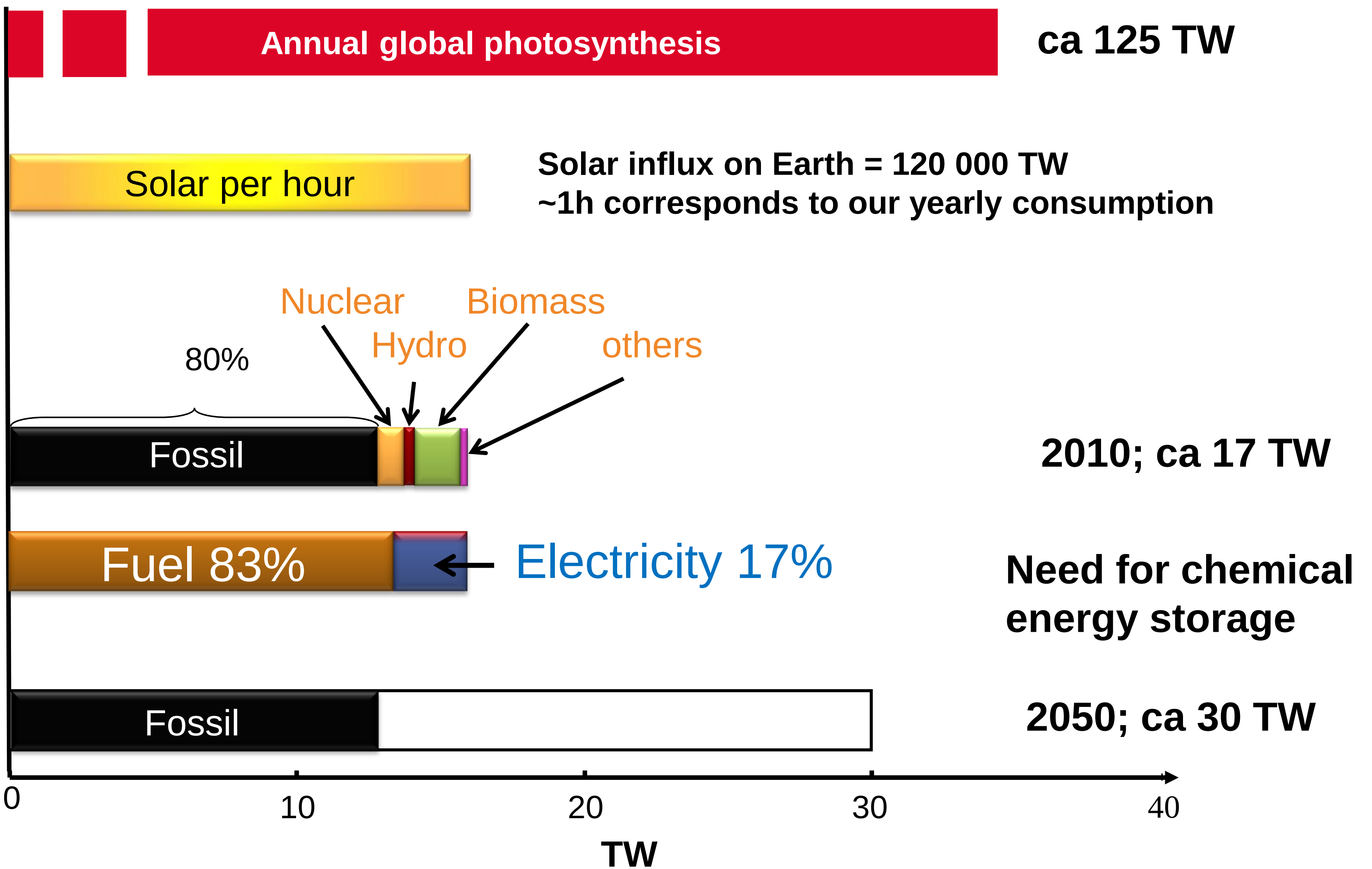
LITEN
Nicolas Guillet
Alexandre Pereira
Laure Guetaz

LETI
Murielle Matheron

IPCM- Univ. Paris 6
Anna Proust
Guillaume Izzet

LCMCP- Univ. Paris 6
Christel Laberty-Robert
Clément Sanchez

The global energy challenge



Renewable energy: Solar

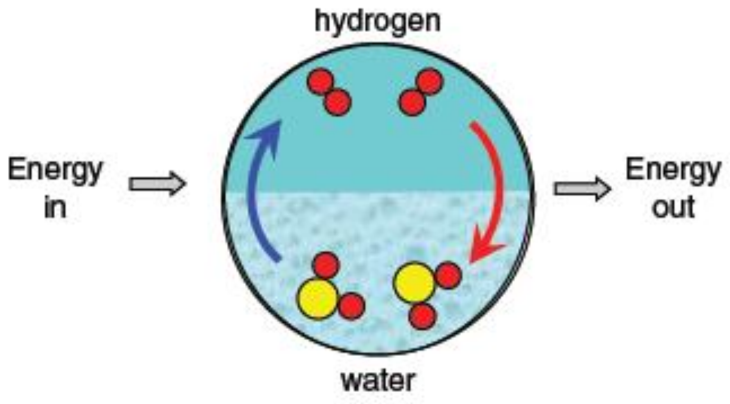
Renewable energy

- **Concentration**
- **Storage (fuels)**

Li-ion batteries:	0.46 - 0.72 $MJ.kg^{-1}$
Oil:	47 $MJ.kg^{-1}$
Hydrogen:	140 $MJ.kg^{-1}$

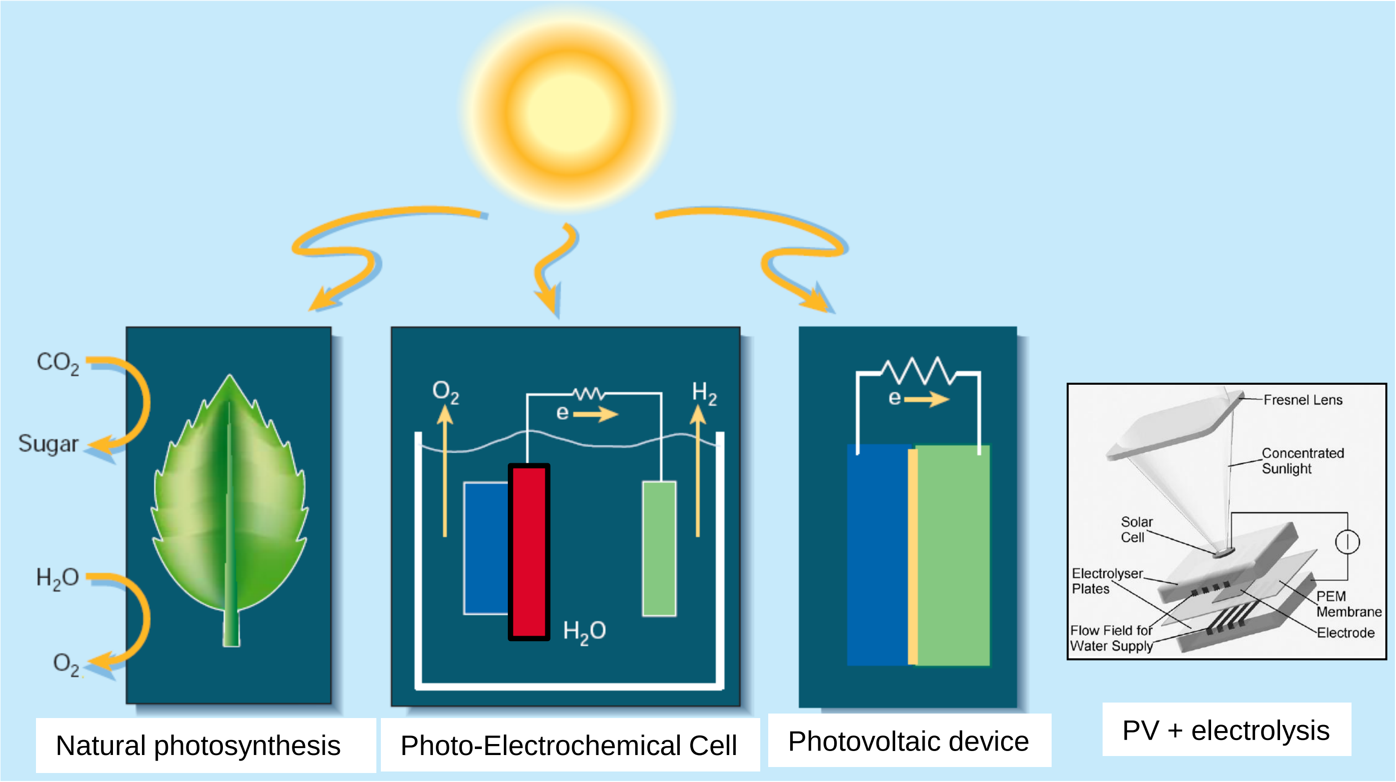
Hydrogen (H_2) **production**

CO_2 recycling and production of liquid fuels



SOLAR FUELS

Converting solar energy into chemical energy

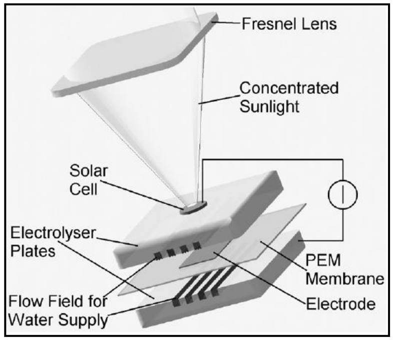


State of the art « PV + Electrolysis » technology

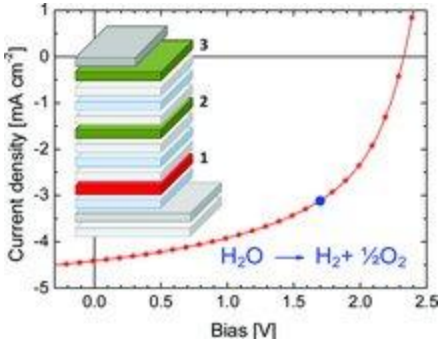
PV + electrolysis

Wired PV + Electrolysis

- Robust- Mature (>18%)
- 3 devices
  - PV
  - Electrolysis cell
  - Power management



Peharz IJHE 2007



Janssen Adv. Mater. 2013

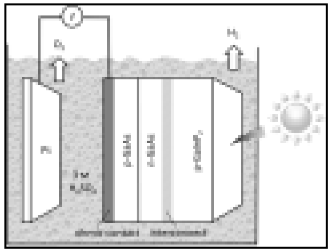
Unwired PV + Electrolysis

Energy & Fuels **1998**, *12*, 3–10

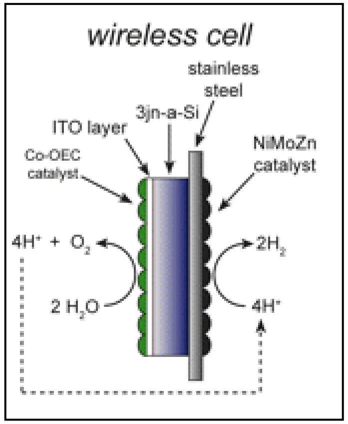
High-Efficiency Photoelectrochemical Hydrogen Production Using Multijunction Amorphous Silicon Photoelectrodes

Richard E. Rocheleau,* Eric L. Miller, and Anupam Misra

Hawaii Natural Energy Institute, School of Ocean and Earth Science and Technology, University of Hawaii at Manoa, Honolulu, Hawaii 96822

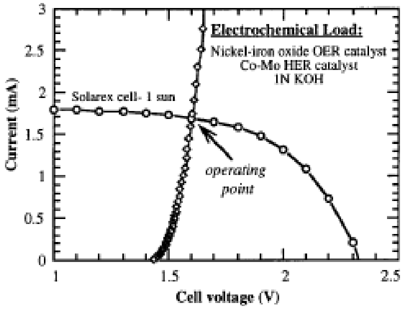


Turner Science 1998



Nocera Science 2011

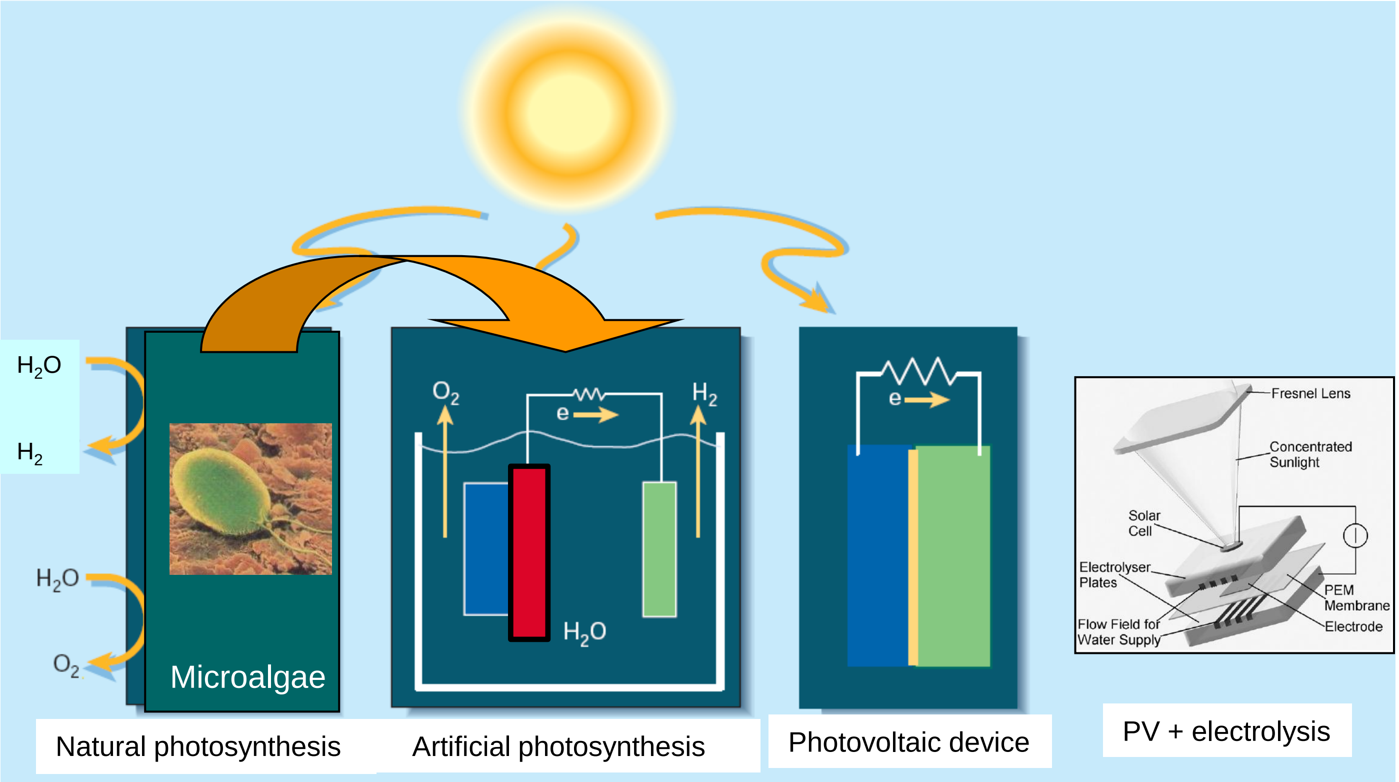
η= 7.8%
7200 h



- Single device
- Stability of PV materials into electrolyte
- One fixed operating point

SOLAR FUELS

Converting solar energy into chemical energy



Abundant and cheap materials both for light harvesting and catalysis

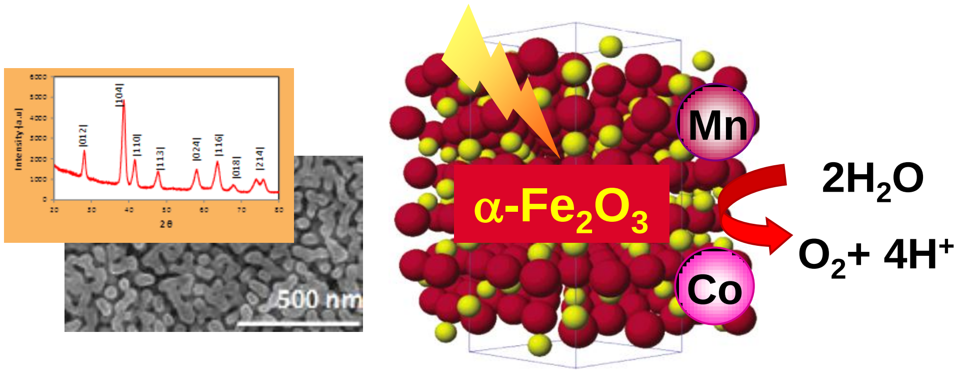
State of the art « PV + Electrolysis » technology

Sustainability
Economic viability

Fundamental research to TRL 2

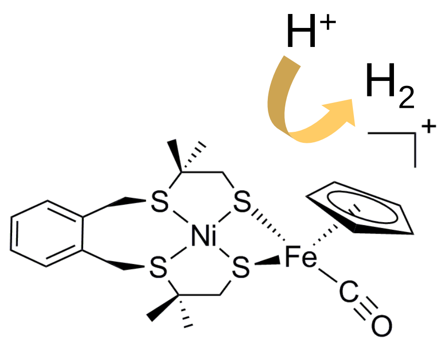
DE LA RECHERCHE À L'INDUSTRIE

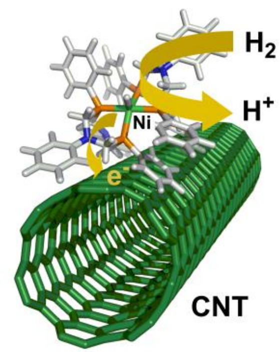
Solar Fuels: a transversal field

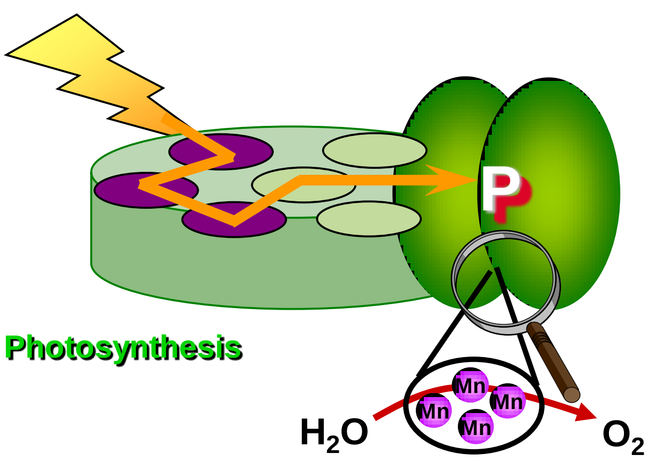


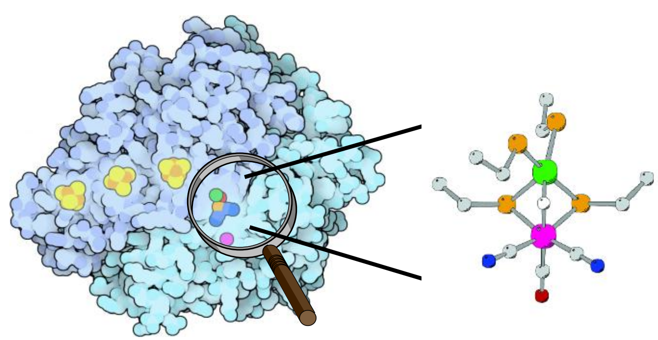
Solid-state materials

Molecular chemistry
Nanosciences









Biosciences

SOFI : an international initiative

Solar Fuels Institute

www.solar-fuels.org

The product: a solar liquid fuel

The method: being global and harness the intellectual firepower of government-funded research institutions and R&D industry


Light capture

Water splitting


CO_2 catalysis

Driven academic research will lead to simultaneous industry R&D and commercially-viable products

The tools:
- workshops
- map of knowledge
- fellow-exchange programs
- translational prize (grants)

AMPEA : a Joint program of the European Energy Research Alliance

Advanced Materials and Processes for Energy Applications

43 participant/associate institutions

14 EU countries

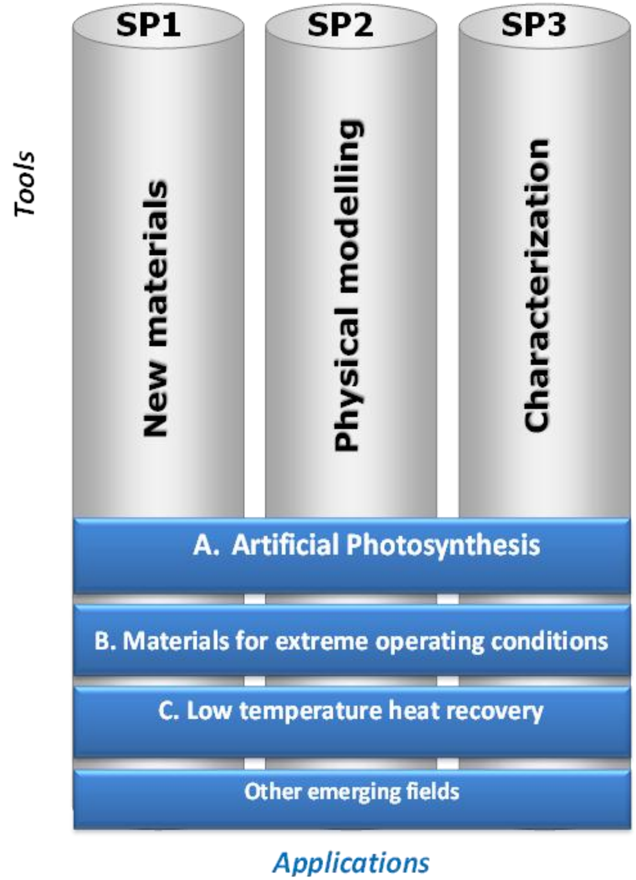
This JP is structured as a matrix with 3 “tools” sub-programmes:

SP1 : Materials Science.

SP2 : Characterization of materials and processes.

SP3 : Modelling of materials and processes

and “emerging applications,” among which
Artificial Photosynthesis appears as a first objective



Current activities in **Artificial Photosynthesis** might be grouped into three subfields:

- molecularly designed systems
- solid-state components
- nature-guided design

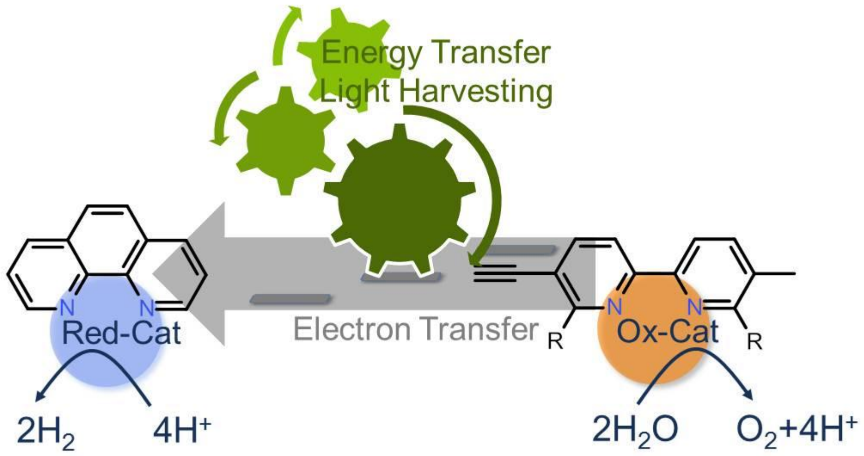
Thapper et al., *Green* ***2013****, 3, 43.*

CM 1202 “Perspect-$H_2$0”: a COST Action on Supramolecular water splitting:

www.perspect-h2o.eu

21 countries
55 research groups
Chair: Dr Benjamin Dietzek, IPHT-JENA

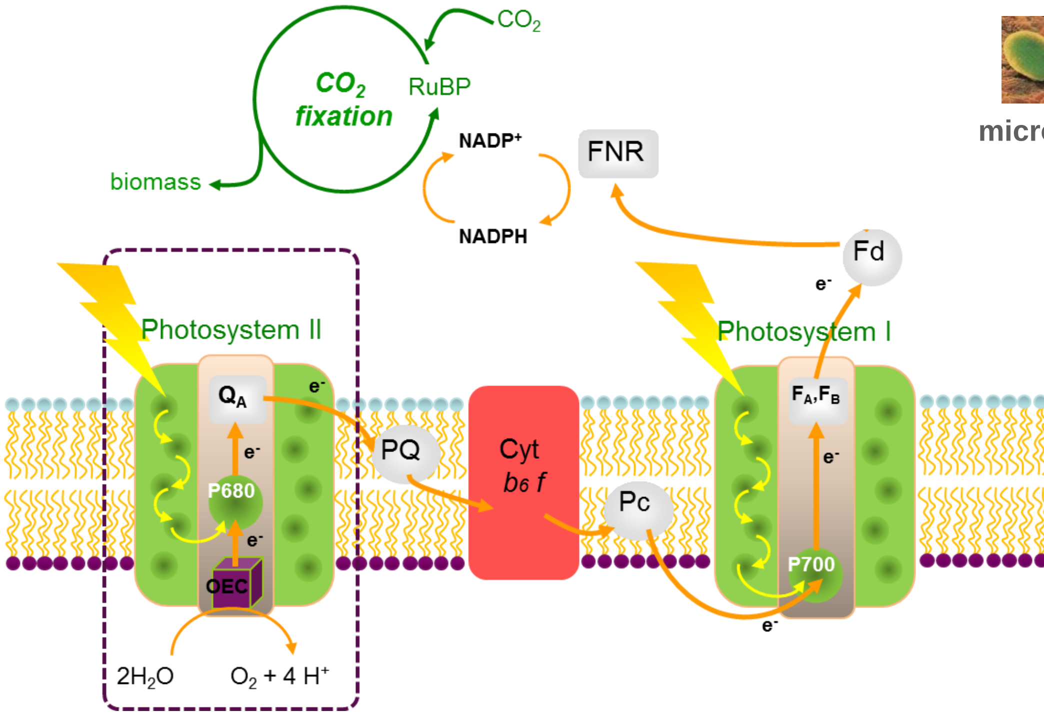
- fundamental understanding of the function determining light-induced elementary reactions in supramolecular photocatalytic water-splitting
- novel water-splitting supramolecular photocatalysts
- innovative functional systems operating in solutions, membranes or at surfaces



Working groups

1. ***Synthesis and Photocatalysis***
2. ***Device Integration***
3. ***Photoinduced Dynamics***
4. ***Intermediates & Active Species***

Photosynthesis

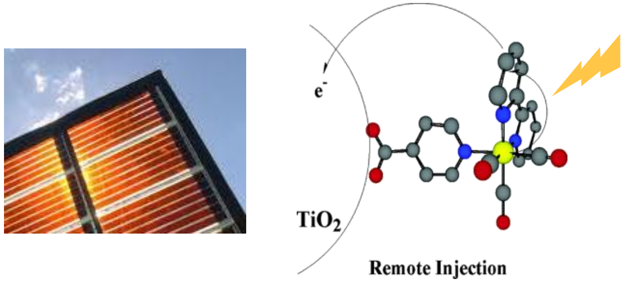


micro-algae

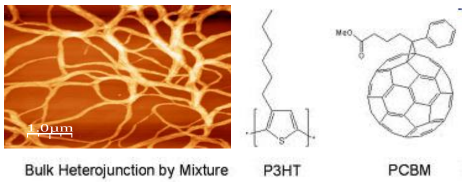
1. Conversion of light energy into electrochemical potential

Photon absorption and initial charge separation is achieved by molecular photosensitizers

Spatial charge separation through a cascade of electron transfers



Dye-sensitized solar cells (Grätzel cells)

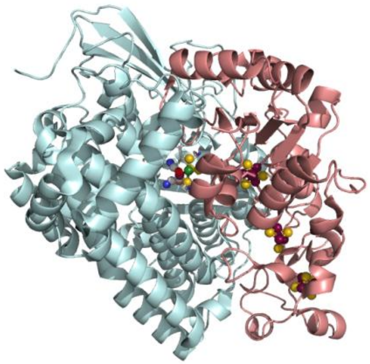


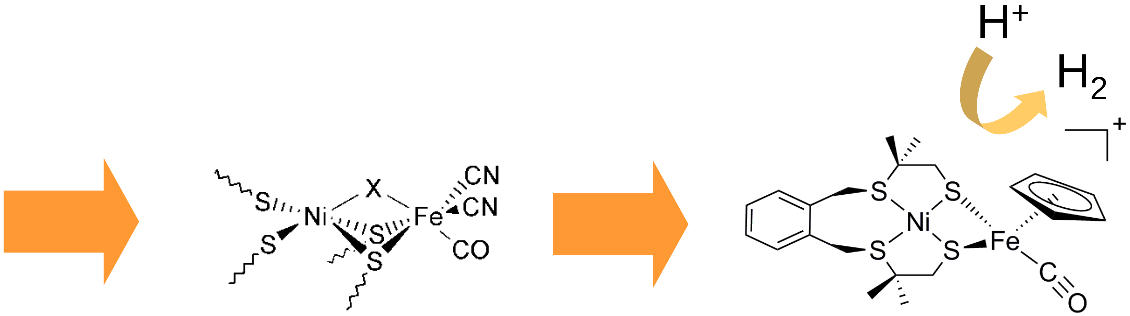
Organic photovoltaics

2. Efficient multielectron enzymatic catalysis

Fast
Close to the thermodynamic equilibrium (limited energetic loss)

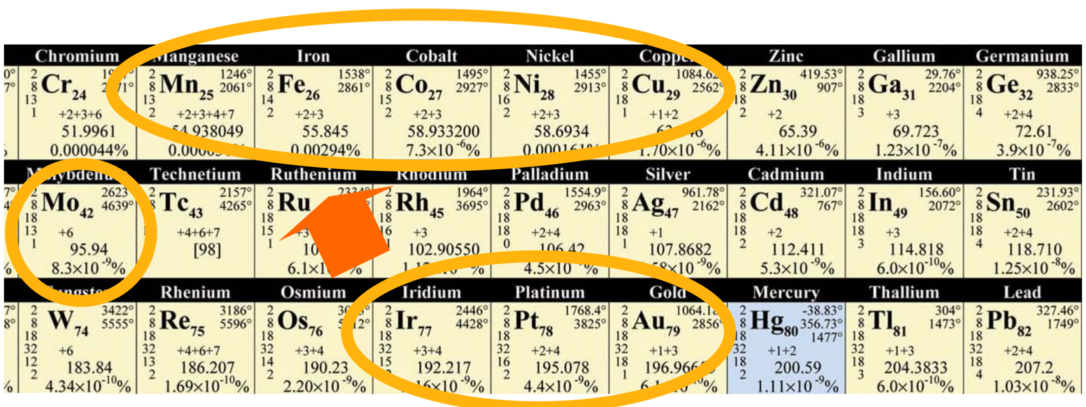
The biomimetic approach

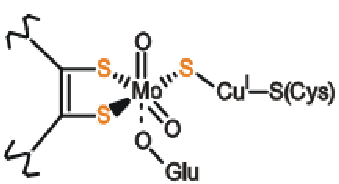


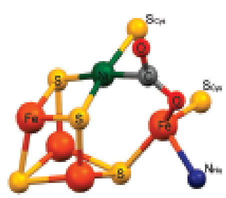


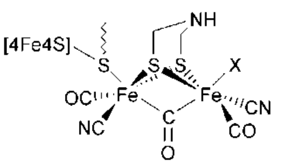
Canaguier et al. *Chem. Commun* 2010, 46, 5876

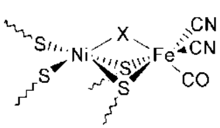
NiFe hydrogenases

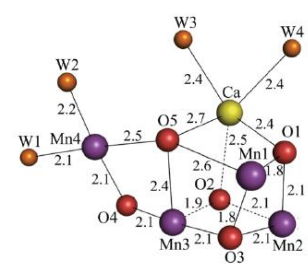










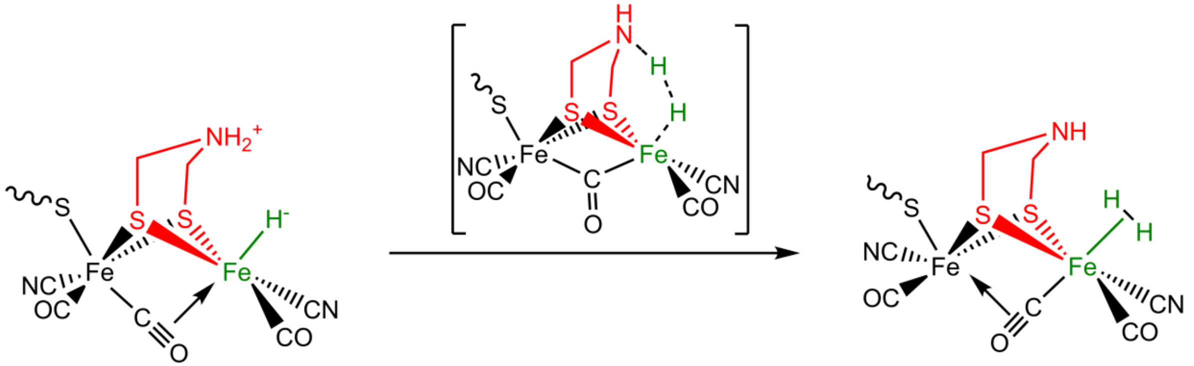


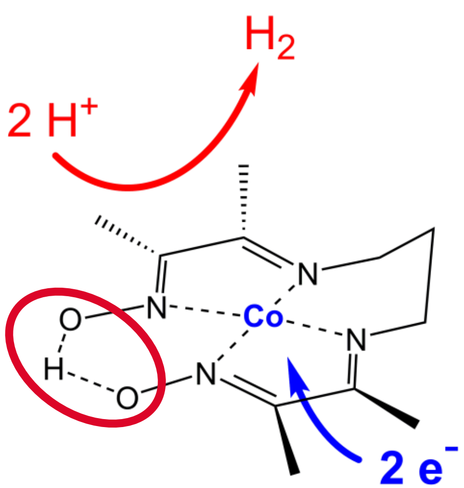
CODH and formate reductase

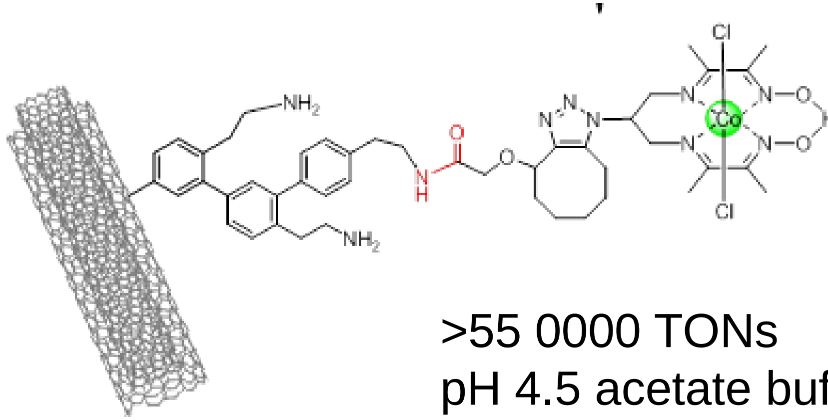
FeFe and NiFe hydrogenases

$CaMn_4$ Cluster (OEC)

Bio-inspiration: Cobaloxime and cobalt dioxime-dioxime catalysts







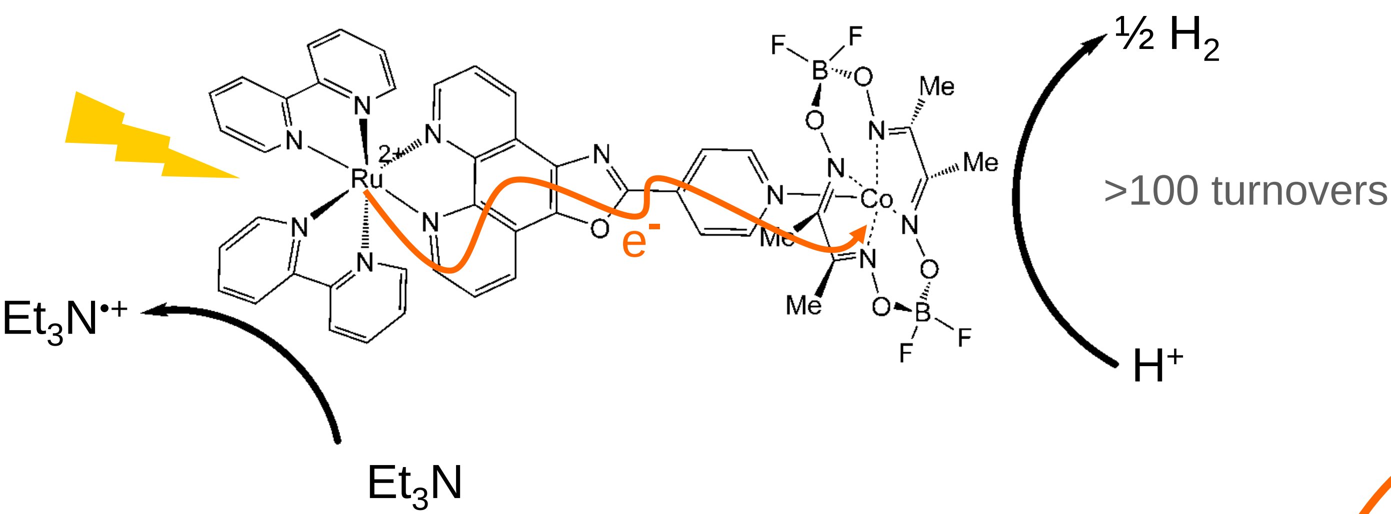
>55 0000 TONs
pH 4.5 acetate buffer
300 mV overpotential

Molecular engineering of a cobalt-based electrocatalytic nanomaterial for H_2 evolution under fully aqueous conditions

Jacques et al, *PNAS 2009*
Bhattacharjee et al. *Chem. Eur. J. 2013*

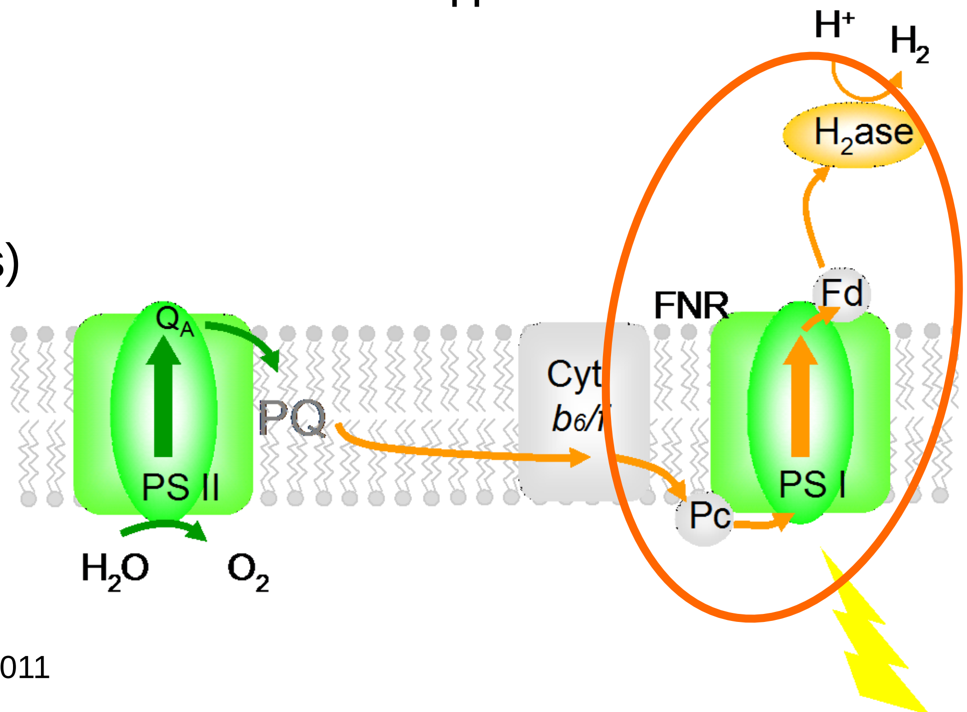
E. S. Andreiadis et al. *Nature Chemistry*, 2013
also valid for with Ni catalysts (Le Goff et al. *Science* 2009)

Cobaloxime-based supramolecular photocatalysts



Single light-driven electron transfer (ps-ns)
Bi-electronic catalysis (µs-ms)

Fihri et al. *Angew. Chem. Int. Ed. 2008*

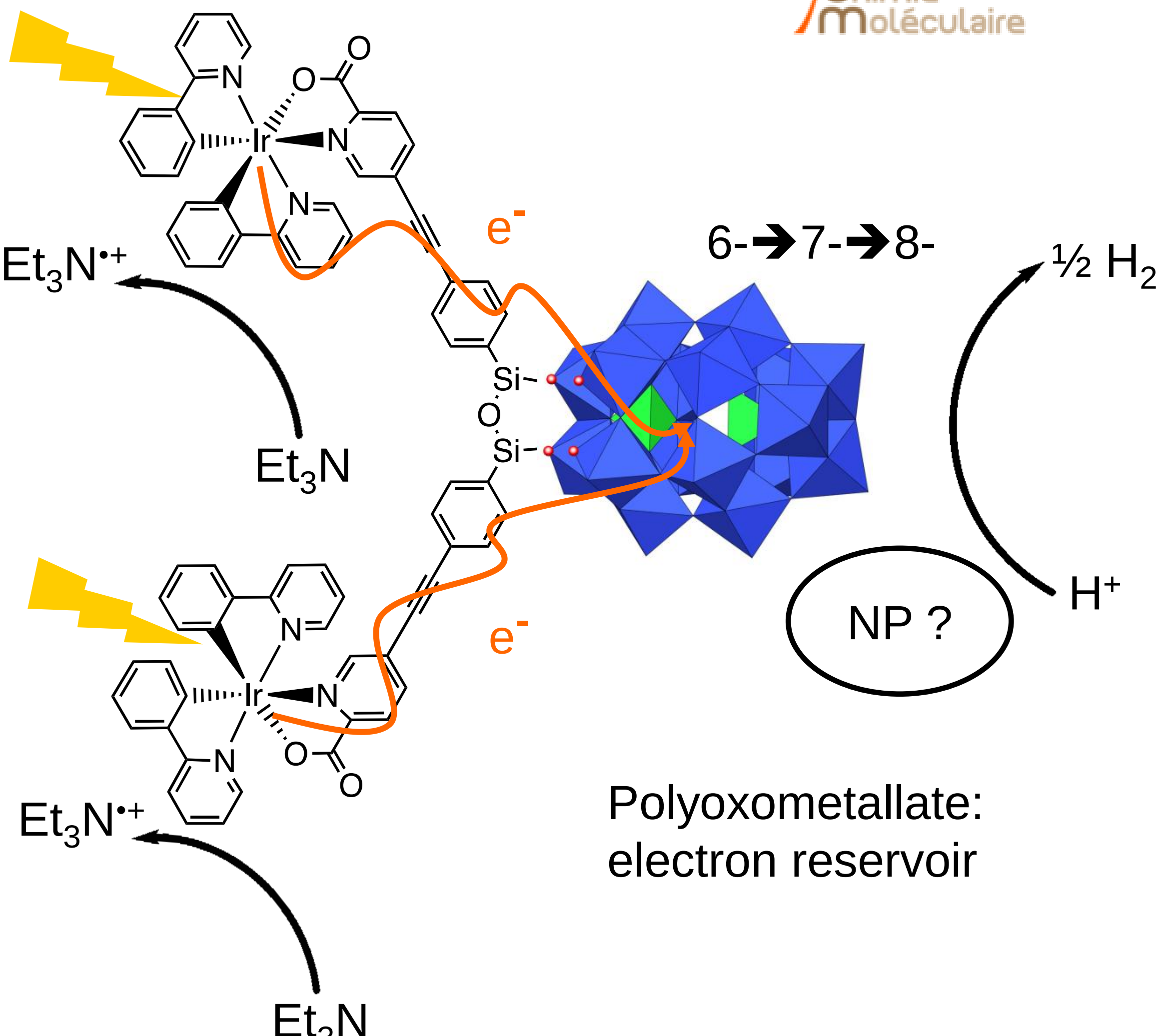


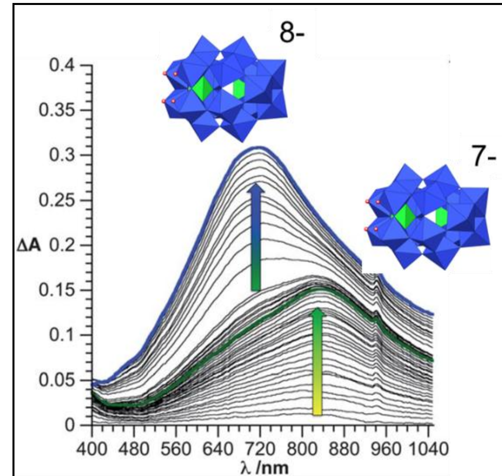
Review article
Artero, Chavarot-Kerlidou, Fontecave, Angew. Chem. Int. Ed. 2011

Charge photoaccumulation : towards improved systems

Collab. G. Izzet A. Proust, IPCM, Univ Paris 6

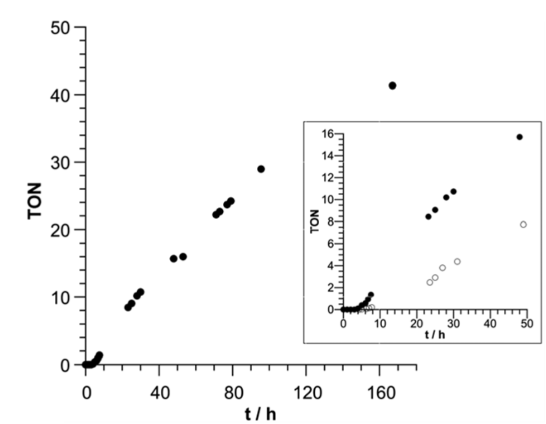
Energy Environ. Sci. **2013**, *6, 1504*





UV-Visible monitoring during continuous irradiation

H_2 evolution catalysis

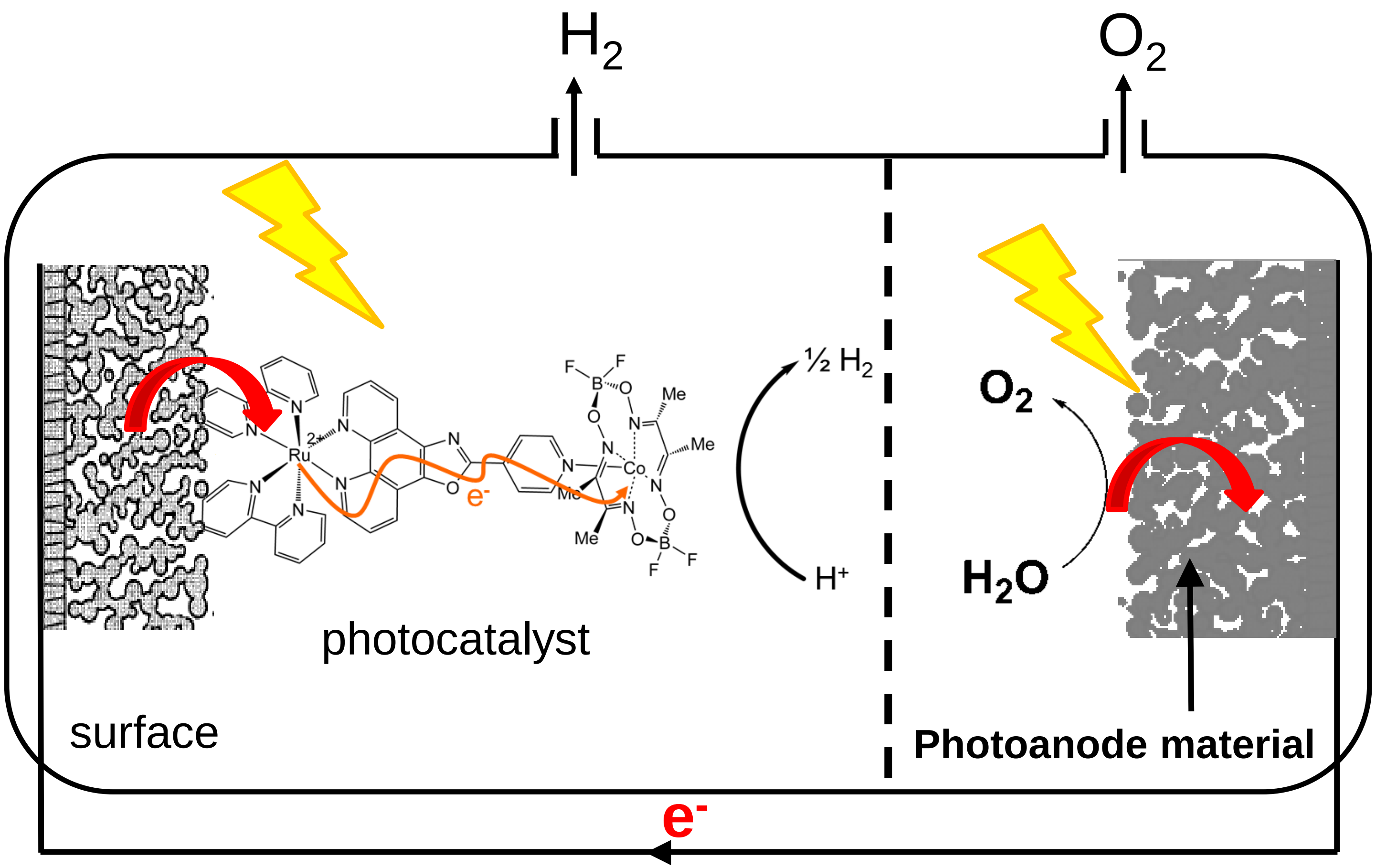


Towards Dye-Sensitized Photo-Electrosynthetic Cells (DSPEC)

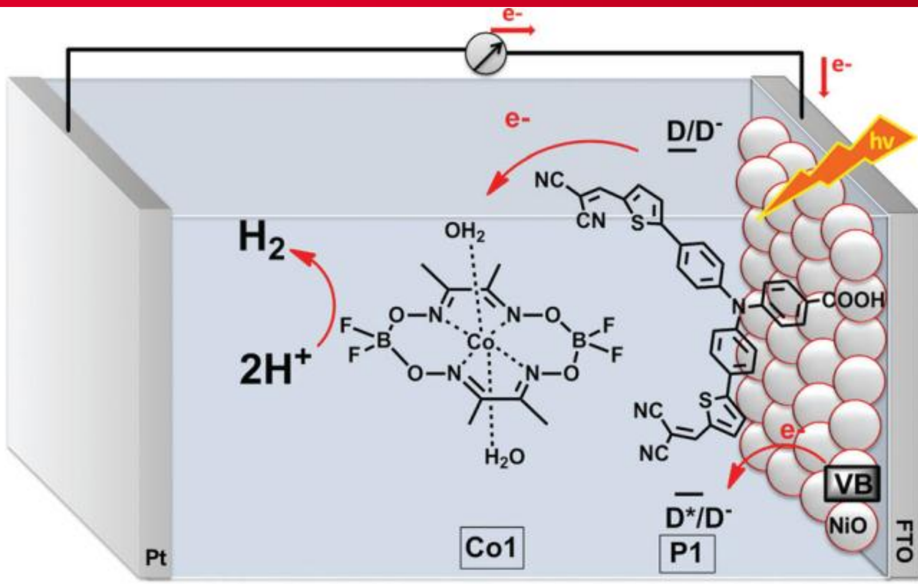
PEC cells use renewable ressources (water) to sustainably produce a fuel (H_2) and store renewable energy (sunlight)

N. Lewis, Chem. Rev 2010

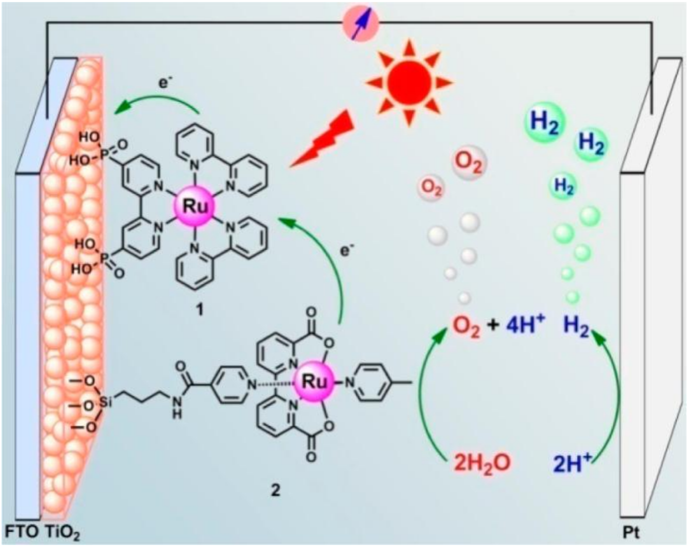
T. J. Meyer, Nature Chemistry 2011



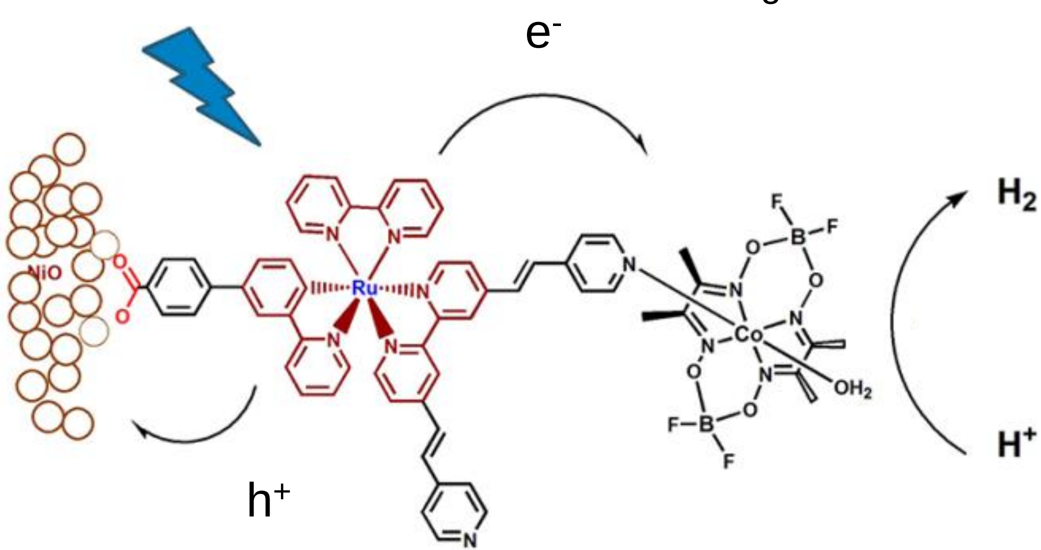
Towards Dye-Sensitized Photo-Electrosynthetic Cells (DSPEC)



Photocathode
Licheng Sun and coll. *Chem. Comm.* **2012**

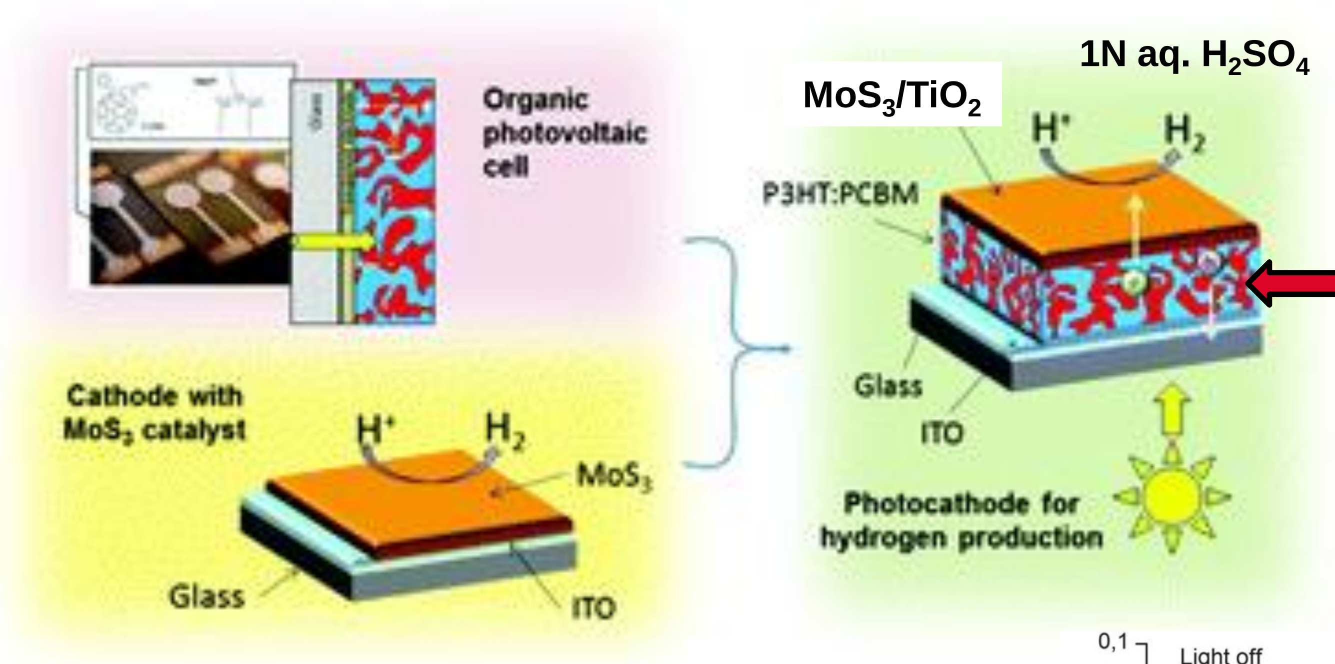


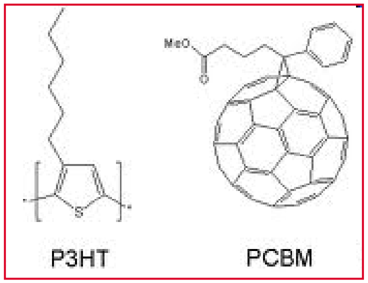
Photoanode
Licheng Sun and coll. *JACS.* **2013**

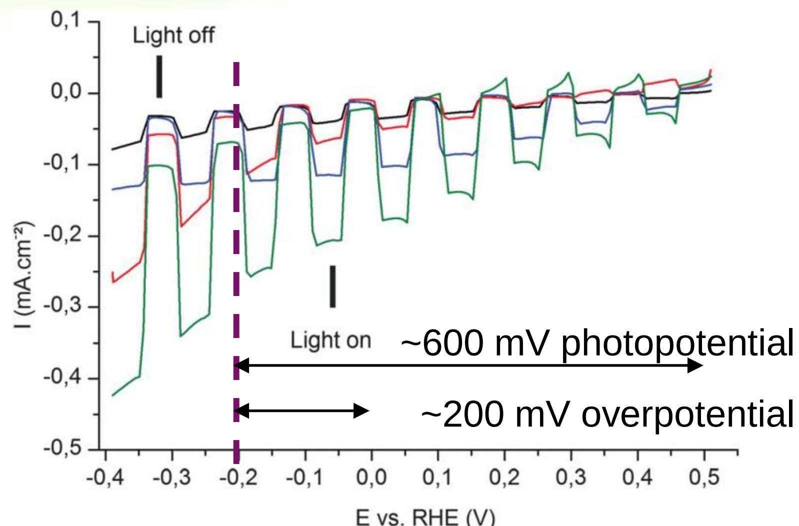


Photocathode
Yiying Wu and coll. *JACS* **2013**

Combining Organic Photovoltaics with water splitting catalysis







Collab. B. Jousselme, S. Palacin CEA-Saclay

Energy Environ. Sci. **2013**, *6, 2706*

Conclusion

Progresses towards a mature hydrogen economy depends on breakthroughs in finding new catalytic materials

Biological systems provide the synthetic chemist with both challenges and inspiration regarding the design of new and efficient catalytic systems.

One of nature's most fundamental processes – photosynthesis – holds promises for turning the sun's energy into fuels.

Combining the bio-inspired approach with nanochemical tools, new and stable energy conversion materials based on earth-abundant elements can be derived.