Bio-inspired systems for solar energy storage

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Living organisms: a source of inspiration?

ORIGINS

≈ 4 billions years of evolution

-Molecules and macromolecules
-Materials
-Processes
-Catalysis

-Replication
-Regulation/Adaptation
-Repair

A « living » machinery with exceptional performances (?)

Living organisms: a source of inspiration?

ORIGINS

≈ 4 billions years of evolution

A « living » machinery with exceptional performances (?)

However…drastic limitations

-Temperature, Pressure

-Solvent, water

-Requirement for non toxic products

-Limited availability of chemical elements (metals…)

-Limited availability of stable precursors (H_2O, CO_2, N_2, O_2,..)

-….

Living organisms: a source of inspiration?

ORIGINS

≈ 4 billions years of evolution

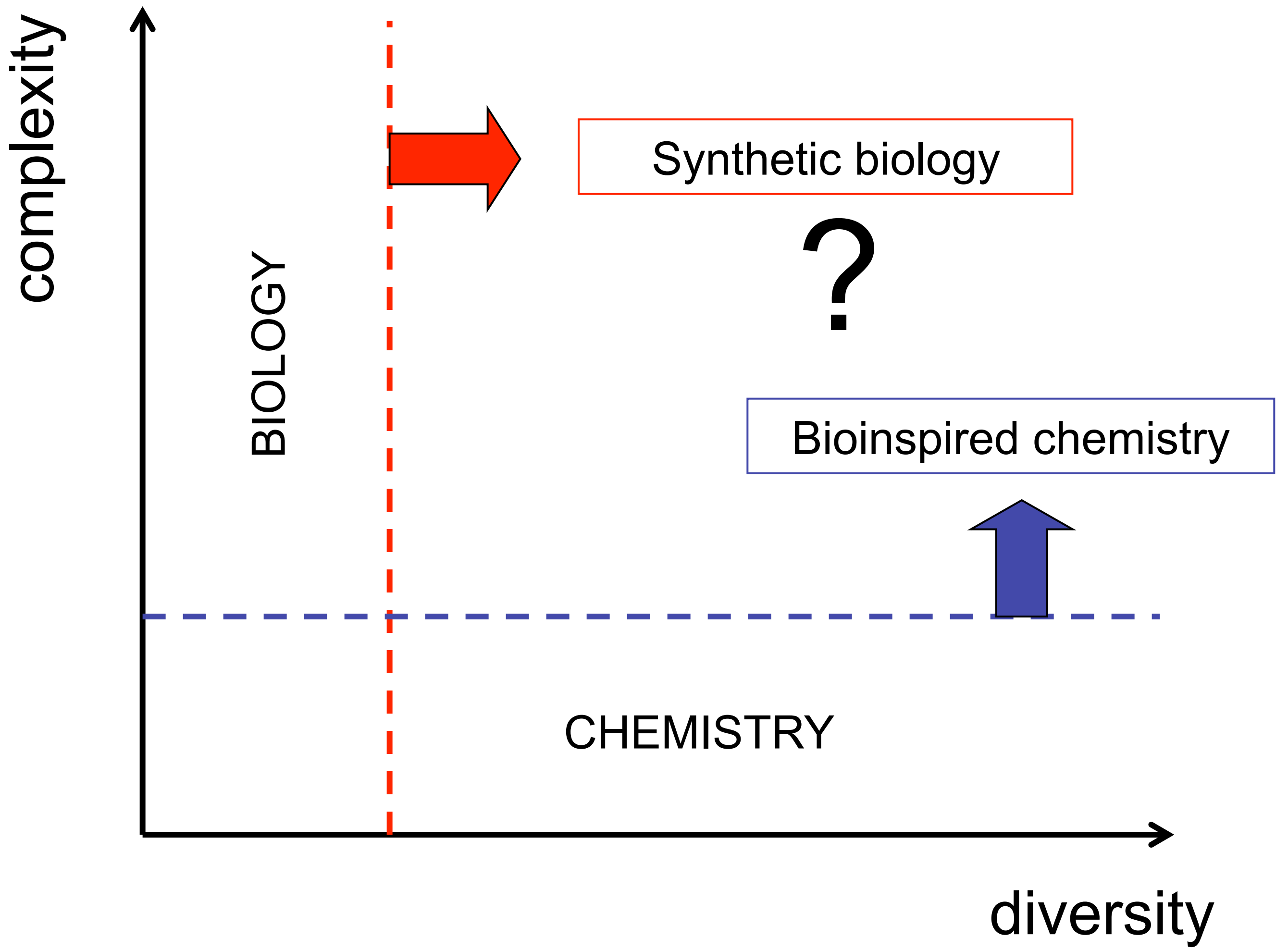
-Molecules and macromolecules
-Materials
-Processes
-Catalysis

-Replication
-Regulation/Adaptation
-Repair

Understand

A « living » machinery with exceptional performances (?)

« Copy » (from biomimetism to bioinspiration)
In order to « invent » new materials/molecules/processes


complexity
BIOLOGY
Synthetic biology
?
Bioinspired chemistry
CHEMISTRY
diversity

From JM Lehn

Bioinspired chemistry

« Exceed the limits of life »?

Principles for biological organization

Combinations of natural and non natural atoms and molecules → Bioinspired systems

Principles for biological function

Bioinspired chemistry
« Exceed the limits of life »?

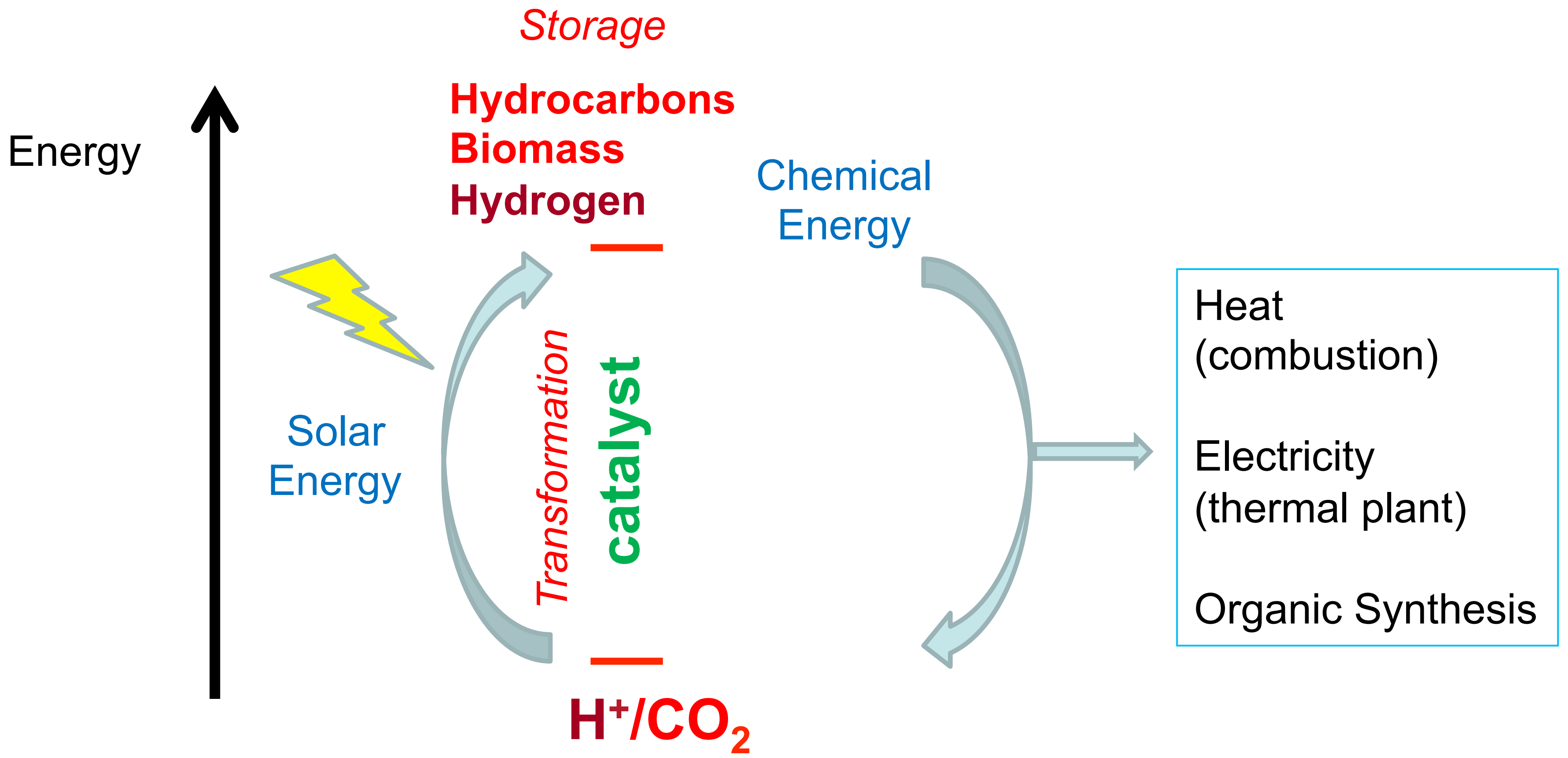
Principles for biological organization

Combinations of natural and non natural atoms and molecules → Bioinspired systems

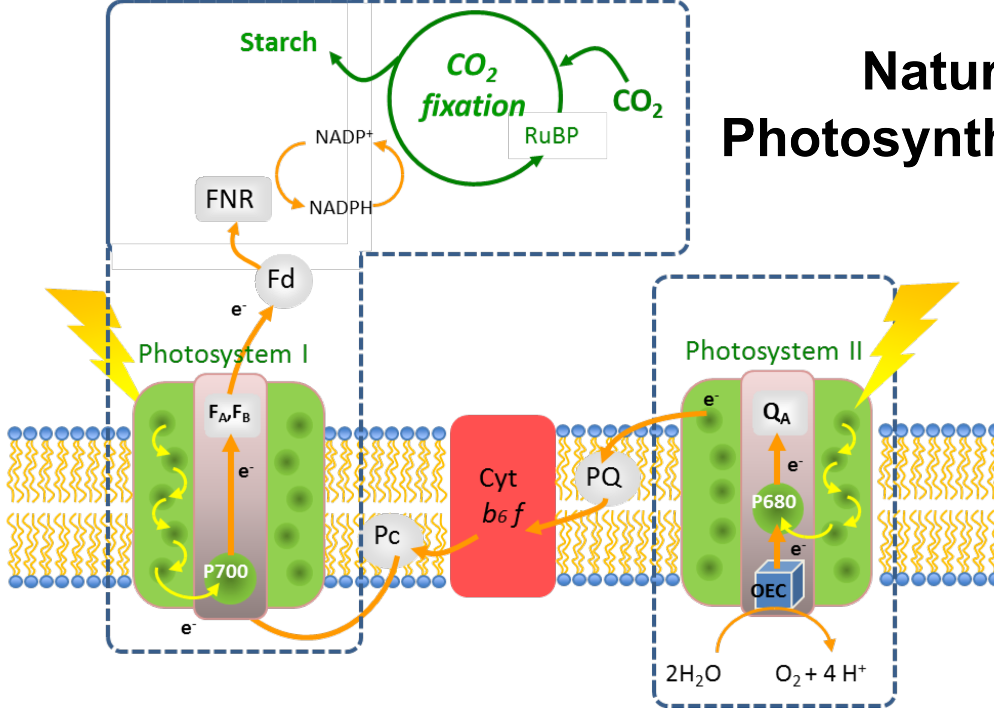
Principles for biological function

Biology: Molecules → Chemistry: Molecules and **Solids**

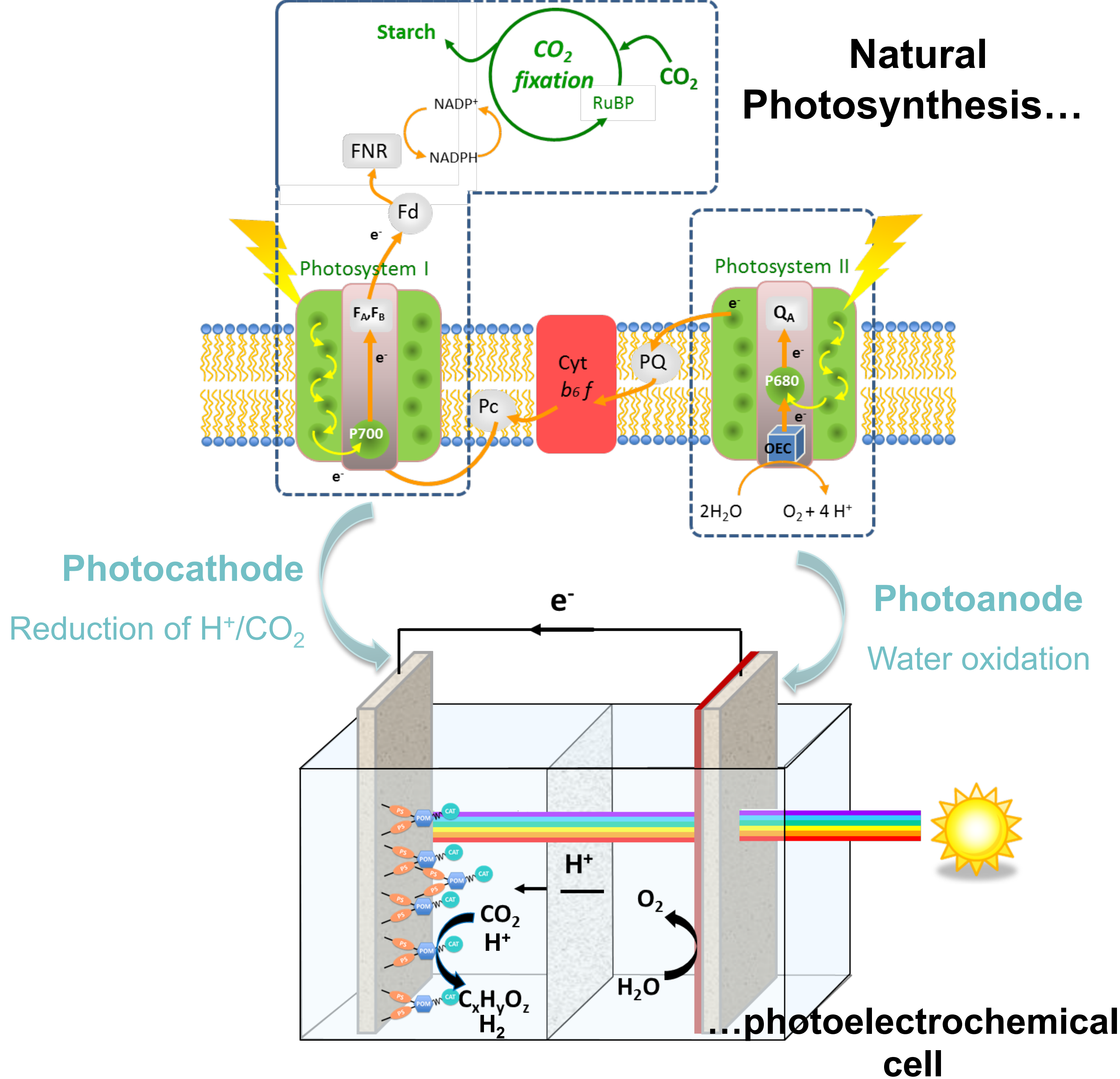
Solar energy chemical storage



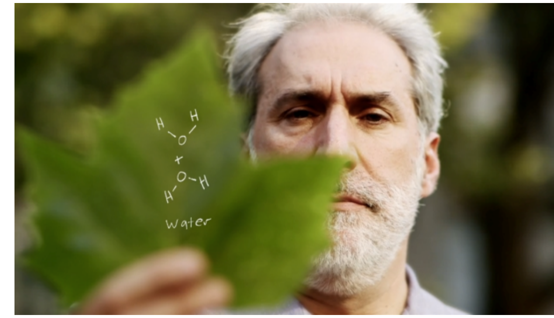
Natural Photosynthesis…



Scenario 1: a photoelectrochemical cell

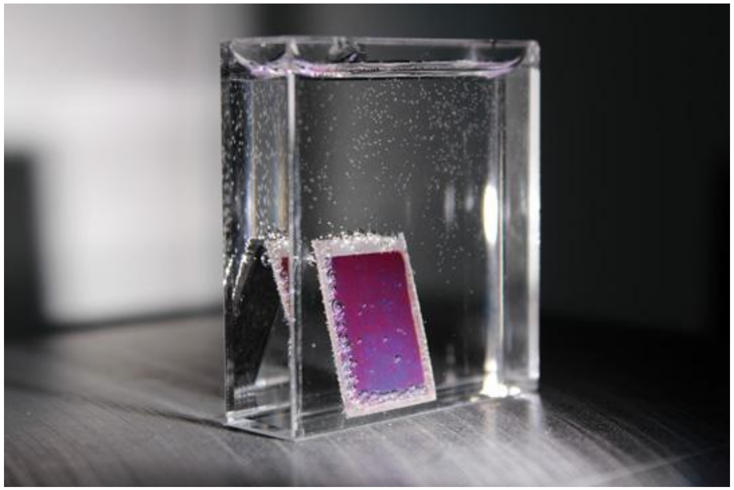


« The artificial leaf »

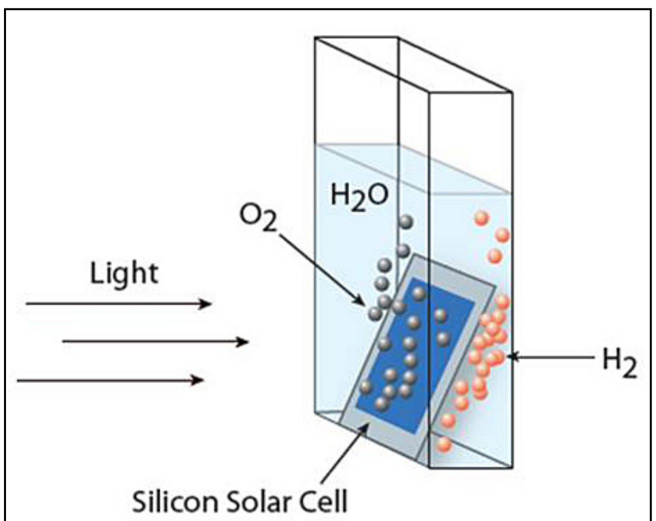


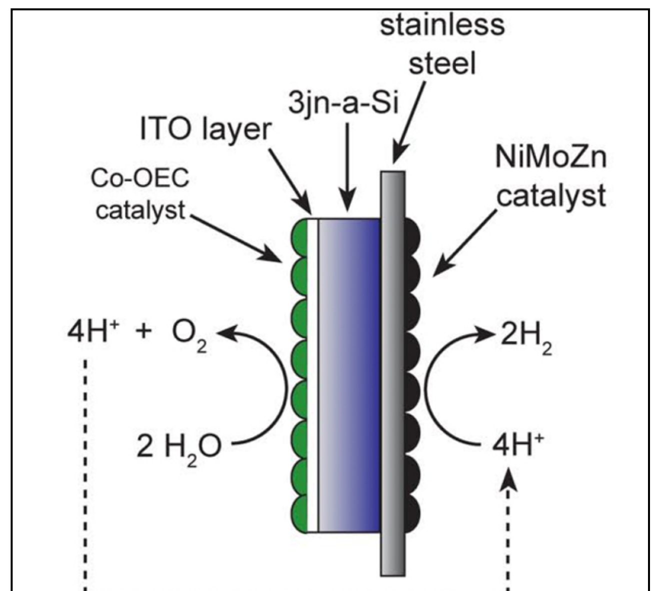
D. NOCERA, Harvard

D. Nocera. *Science*, 2011, 334, 645.

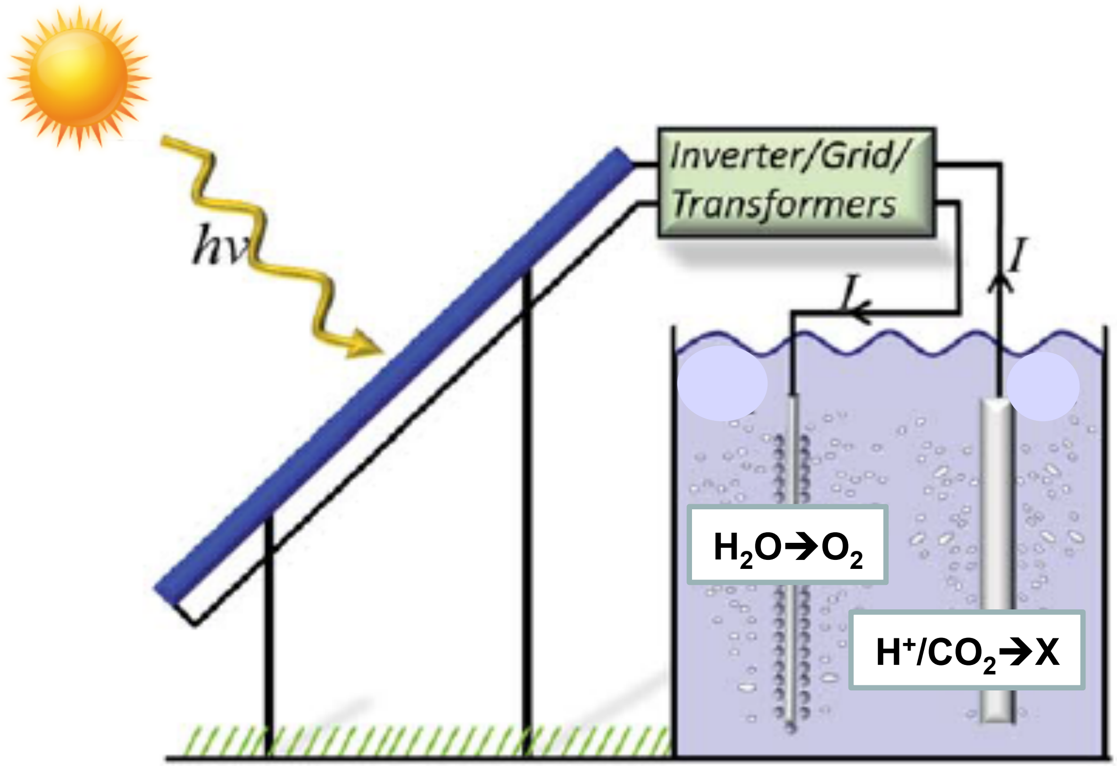


Solar-to-H_2 = 4.7 %
(PV 7%)
1.5 $mA.cm^{-2}$





Scenario 2: PhotoVoltaic + electrolysis



Solar cells:
Towards artificial photosynthesis

WATER SPLITTING

Water photolysis at 12.3% efficiency via perovskite photovoltaics and Earth-abundant catalysts

Jingshan Luo,[1,2] Jeong-Hyeok Im,[1,3] Matthew T. Mayer,[1] Marcel Schreier,[1] Mohammad Khaja Nazeeruddin,[1] Nam-Gyu Park,[3] S. David Tilley,[1] Hong Jin Fan,[2] Michael Grätzel[1]*

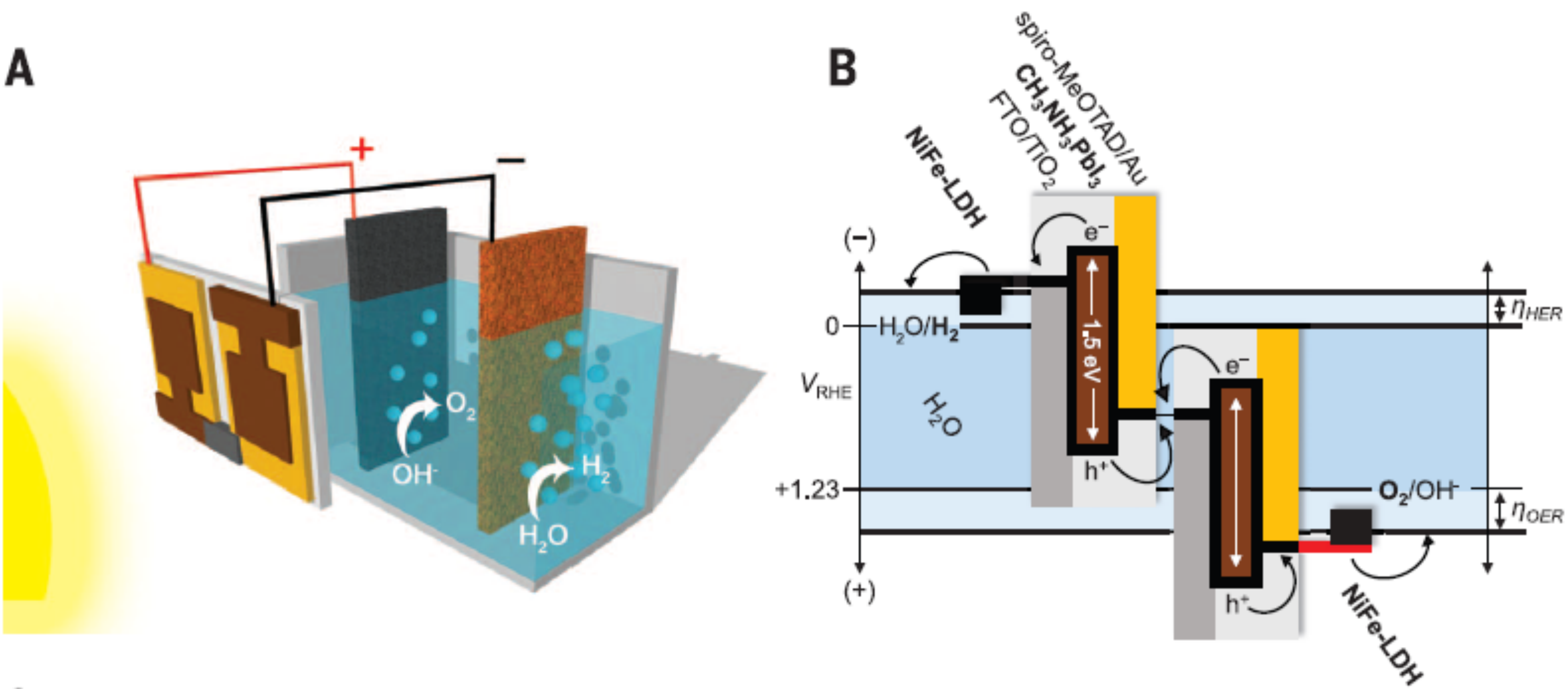
- semi-conductors: perovskite

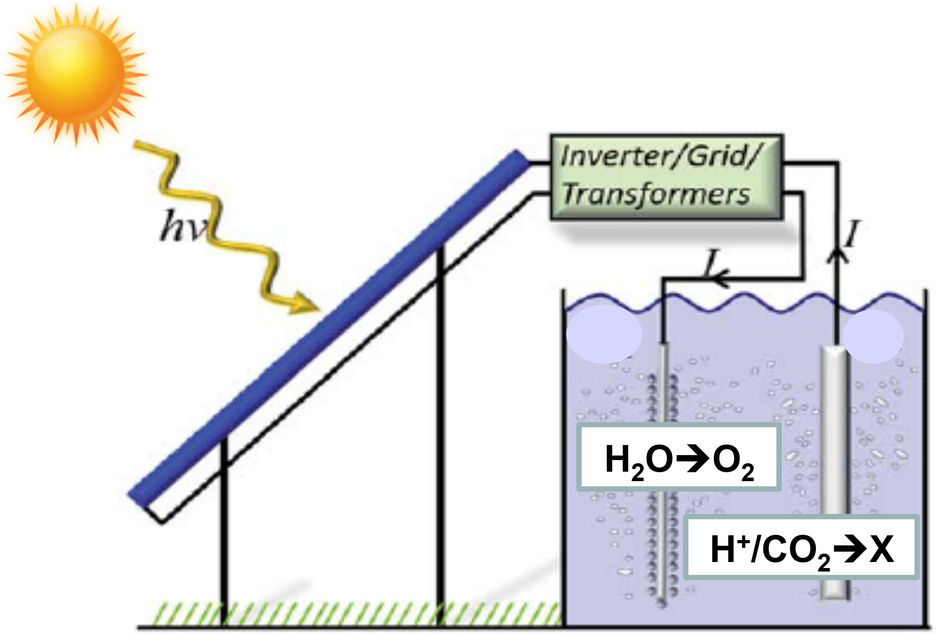
($CH_3NH_3PbI_3$) phototensions > 2V.

- Catalysts: Ni, Fe hydroxides

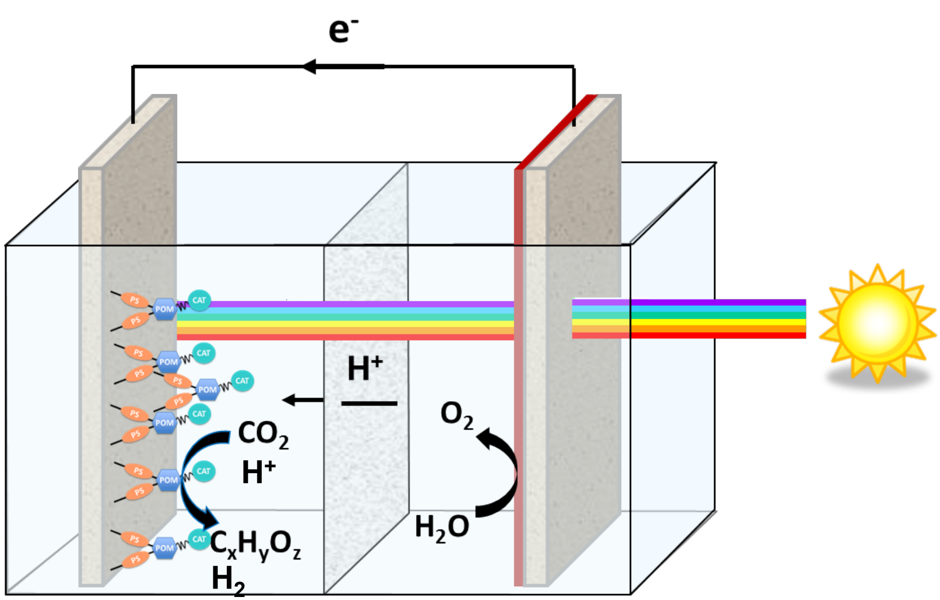
For both oxidation and reduction of water

Small overvoltages (0.2V)





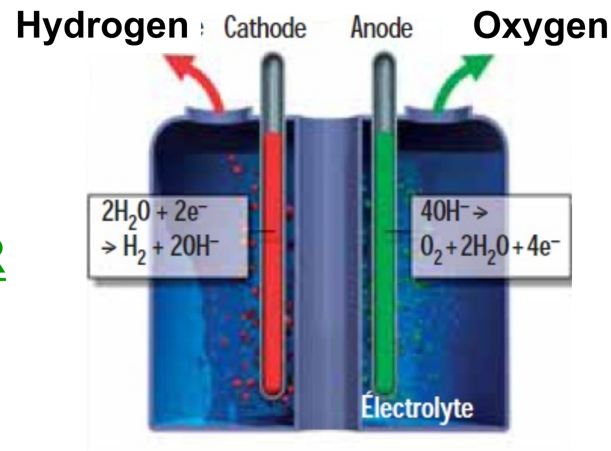
Mature technologies
High cost
(low capacity factor of PV)



Target:15-25 % ?
(energy conversion
efficiency)

Immature technologies
Low cost
(integration)

Storage into hydrogen: catalysis



ELECTROLYZER

PHOTOELECTROLYZER

Energy input (solar electricity..)

Production H_2

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$$

$$4H^+ + 4e^- \rightleftharpoons 2H_2$$

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

H_2O **H_2**

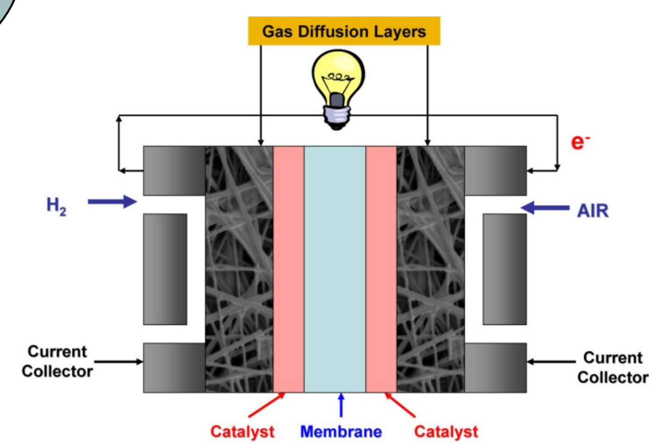
Energy output (electricity, heat..)

Oxidation H_2

FUEL CELL

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

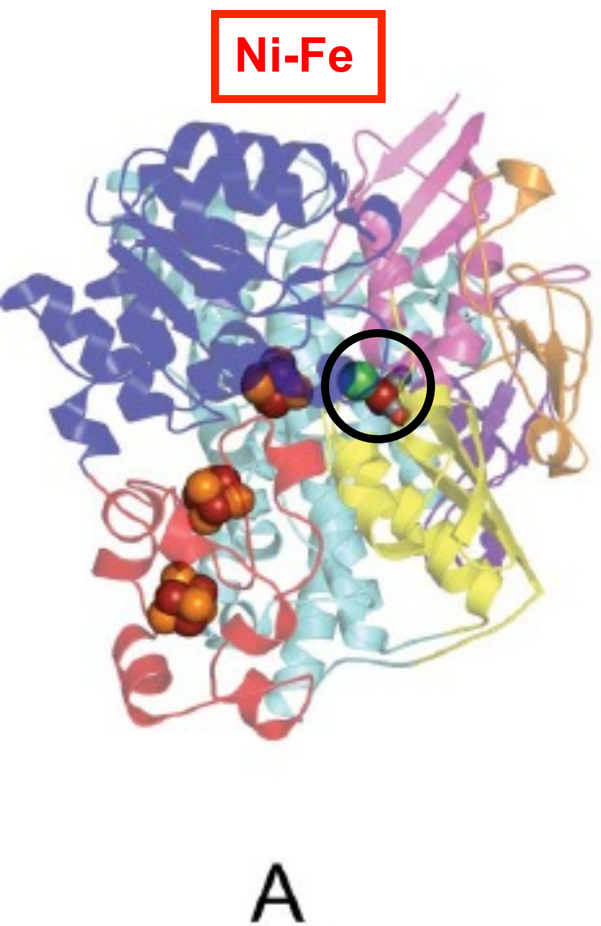
$$\Delta H = -\,570\ kJ.mol^{-1}$$

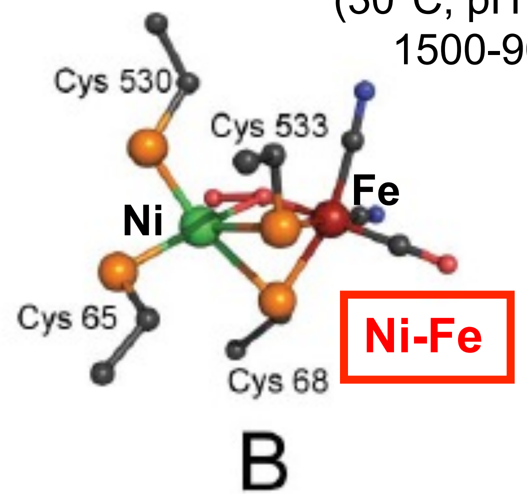


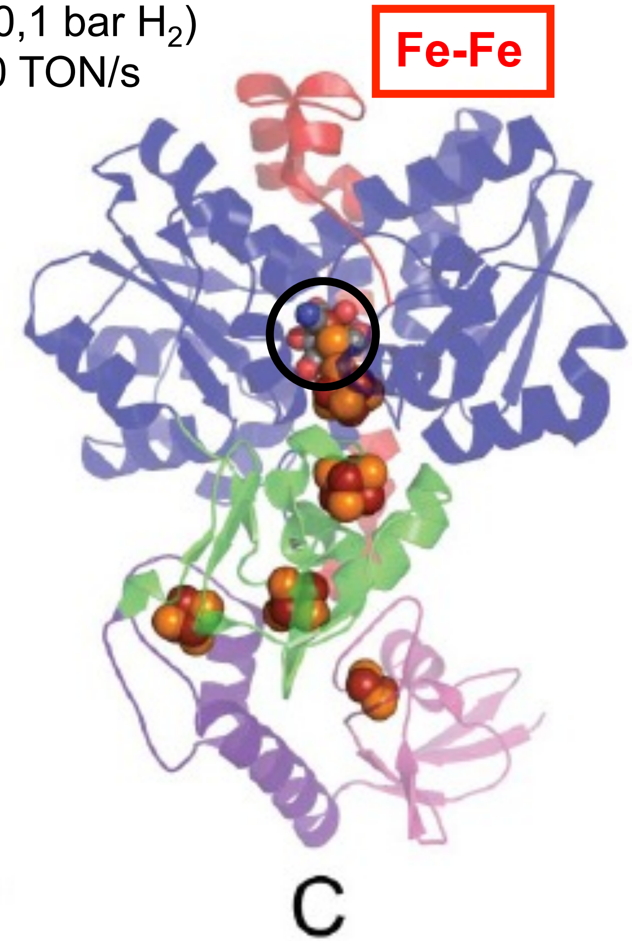
Hydrogenases

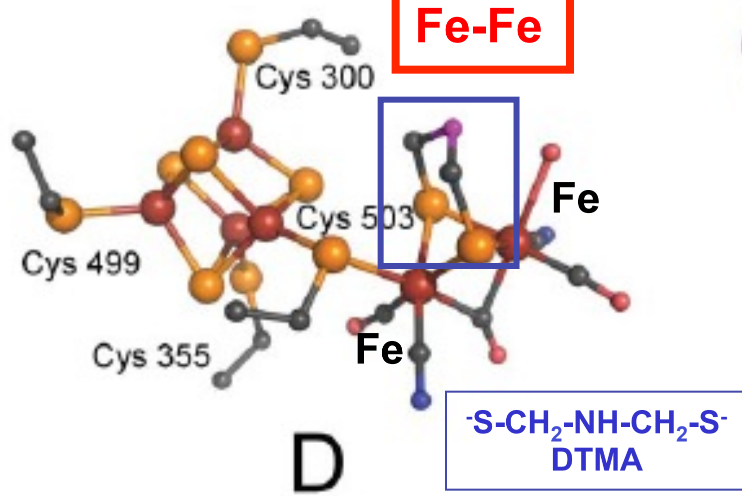
$$2\,H^+ + 2\,e^- \rightleftharpoons H_2$$

E = -400 mV vs SHE
(30°C; pH 7; 0,1 bar H_2)
1500-9000 TON/s





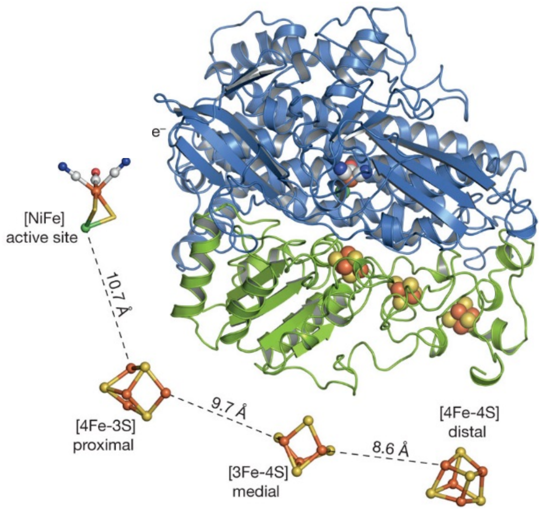


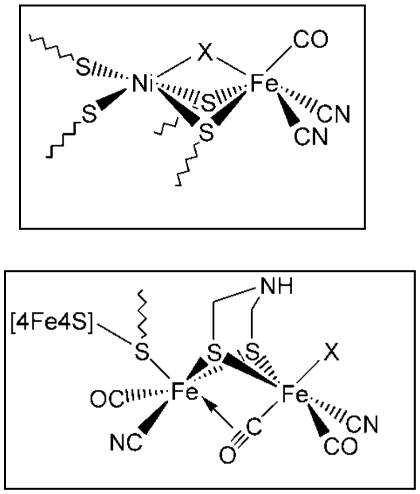


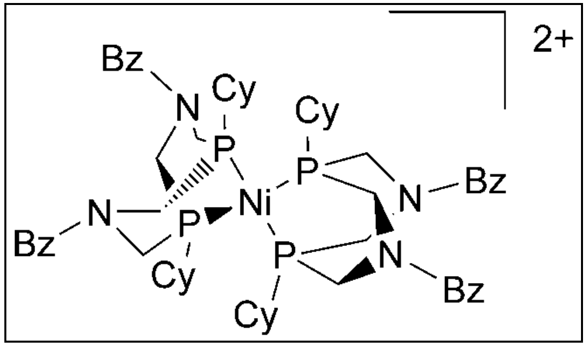
Volbeda, A. et al., *Nature* (1995), **373**, 580-587.
Volbeda, A. et al., *J. Am. Chem. Soc.* (1996), **118**, 12989-12996.

JW Peters et al *Science* (1998) 282, 1853
Y Nicolet et al *Structure* (1999) 7, 13

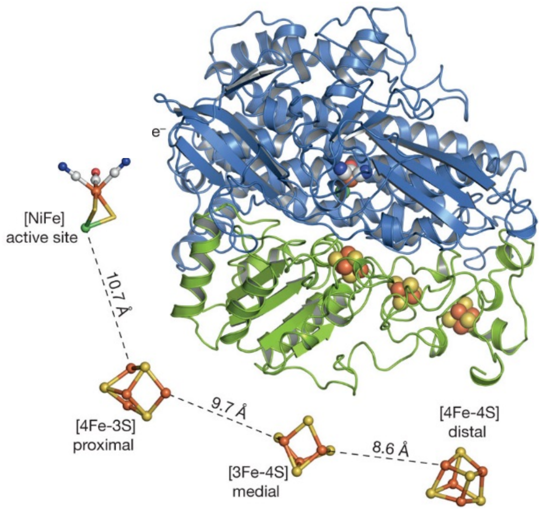
From hydrogenases to bio-inspired nanocatalysts

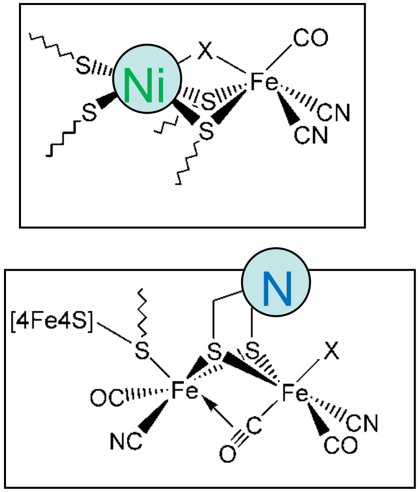


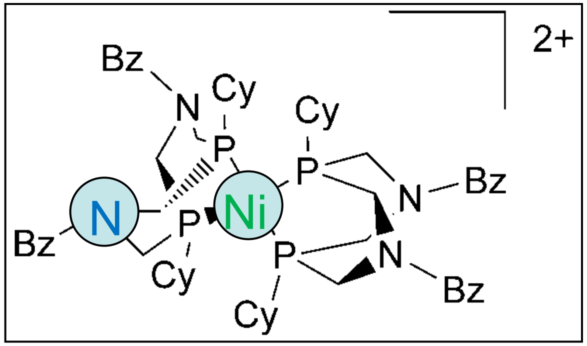




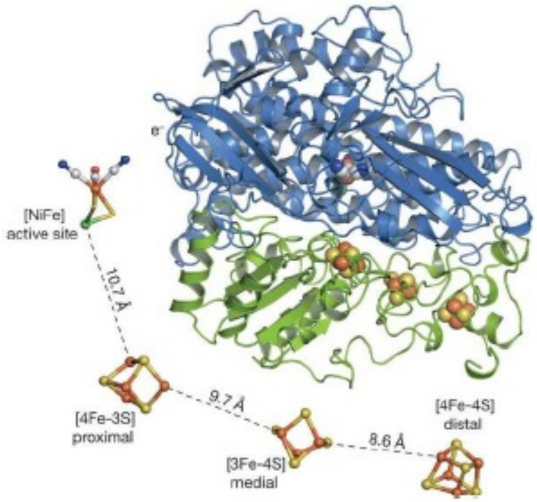
From hydrogenases to bio-inspired nanocatalysts

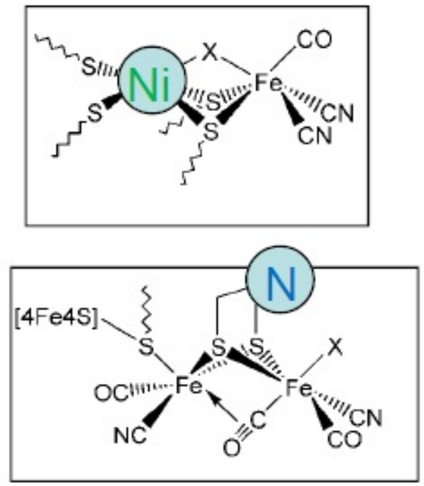


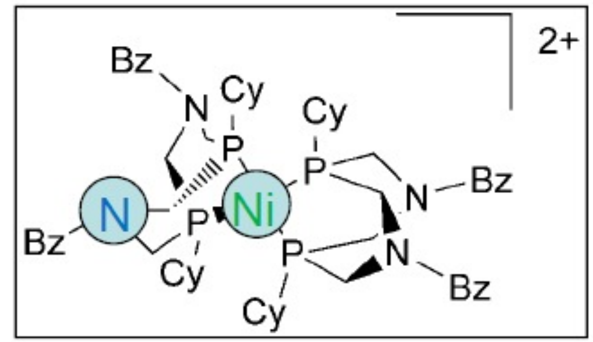


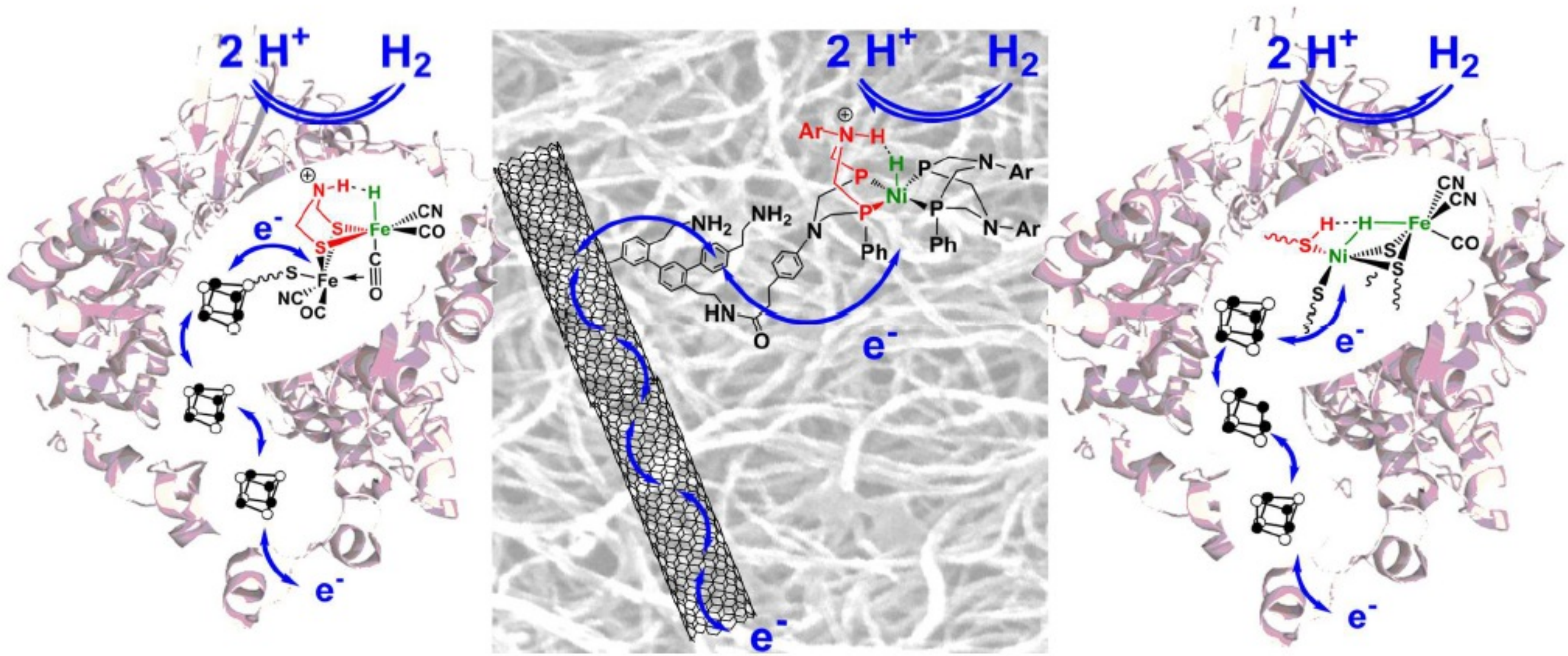


From hydrogenases to bio-inspired nanocatalysts





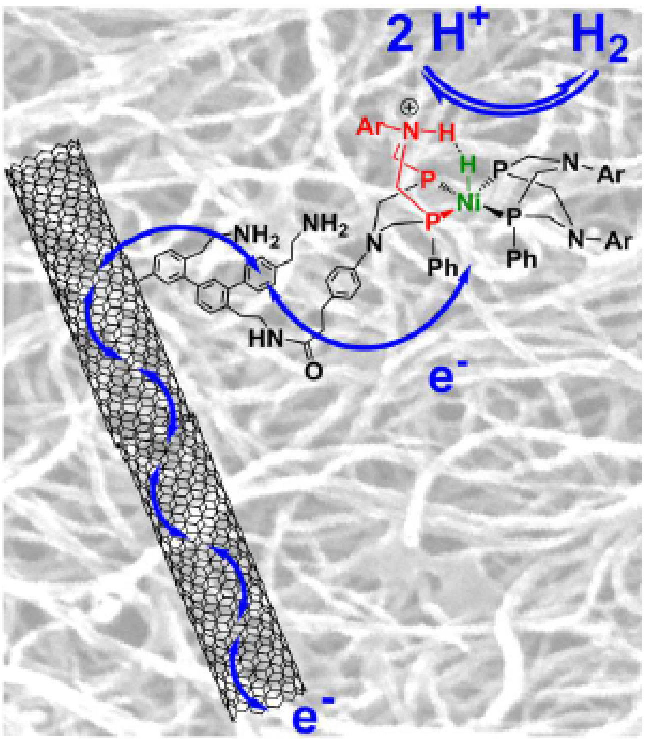




From hydrogenases to bio-inspired nanocatalysts

From Hydrogenase Mimics to Noble-Metal Free Hydrogen-Evolving Electrocatalytic Nanomaterials
A. Le Goff, V. Artero, B. Jousselme, N. Guillet, R. Métayé, A. Fihri, S. Palacin, M. Fontecave
Science 2009, 326, 1384-1387

Noncovalent Modification of Carbon Nanotubes with Pyrene-functionalized Ni complexes: Carbon Monoxide Tolerant Catalysts for H2 Evolution and Uptake
P. D. Tran, A. Le Goff, J. Heidkamp, B. Jousselme, N. Guillet, S. Palacin, H. Dau, M. Fontecave, V. Artero
Angew. Chem. 2011, 50, 1371 –1374



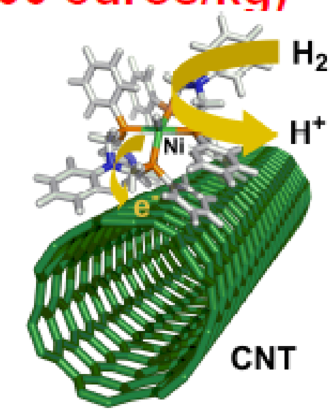
A bioinspired Ni complex grafted on NTCs deposited on an electrode

+++

A catalyst for oxidation and production of H_2
>100.000 cat cycles !!
Stability
Compatible with PEM technology (acid pH)
Overvoltage= 20 mV !!
Resistance to CO
Cost: Ni 20 euros/kg (Pt: 20000 euros/kg)

- - -

Weak current densities
~5-20 mA.cm^{-2}
(1/100 vs Pt)
Acidic pH

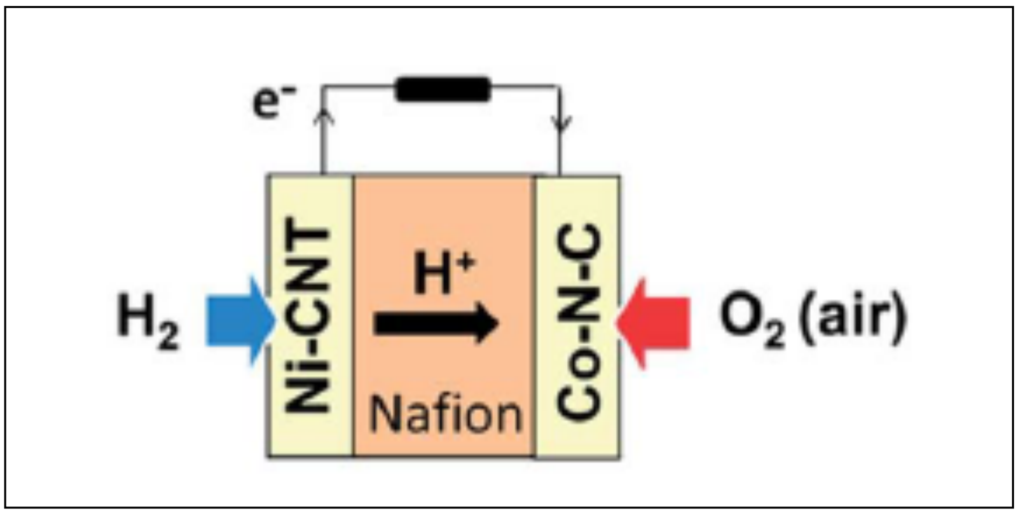


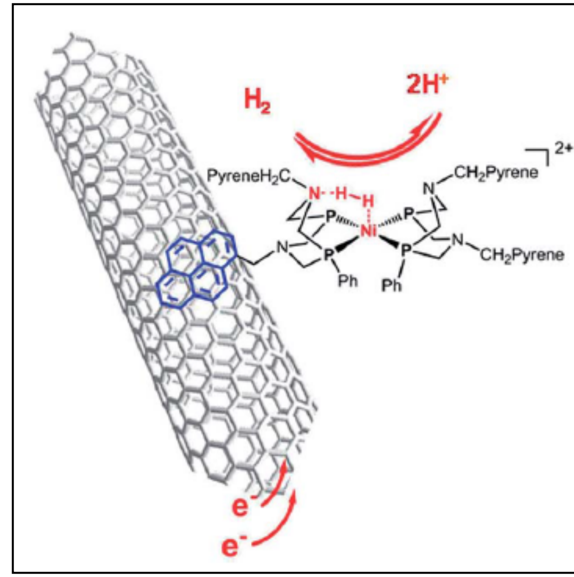
Cite this: *Chem. Sci.*, 2015, **6**, 2050

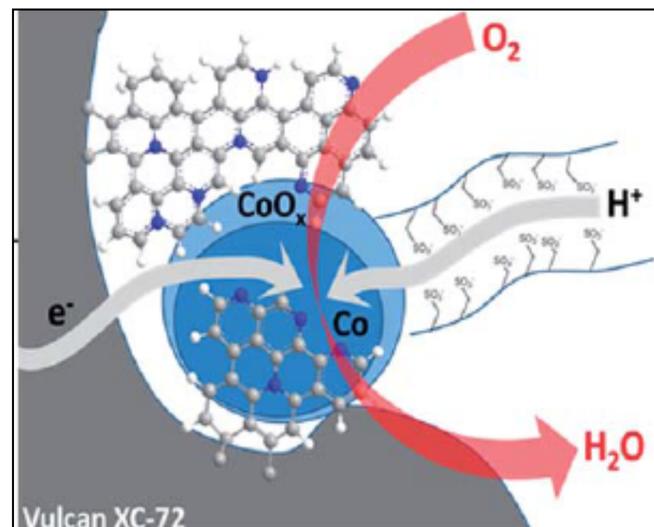
A noble metal-free proton-exchange membrane fuel cell based on bio-inspired molecular catalysts†

P. D. Tran,‡[a] A. Morozan,‡[b] S. Archambault,‡[c] J. Heidkamp,‡[d] P. Chenevier,[e] H. Dau,[d] M. Fontecave,[af] A. Martinent,*[c] B. Jousselme*[b] and V. Artero*[a]

The first fuel cell (PEM) without noble metals !!





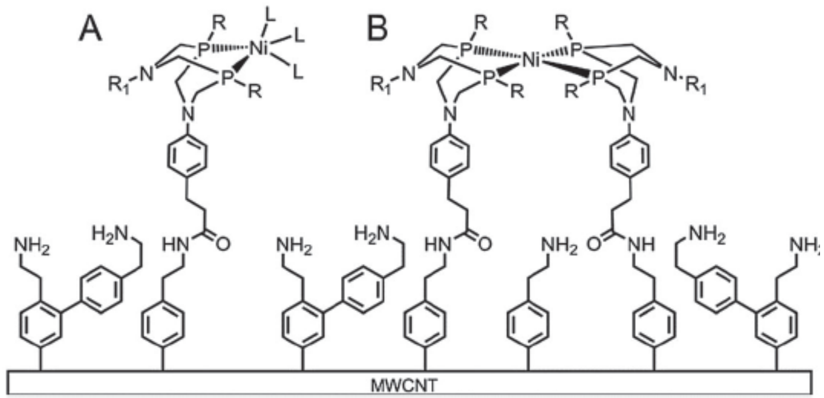


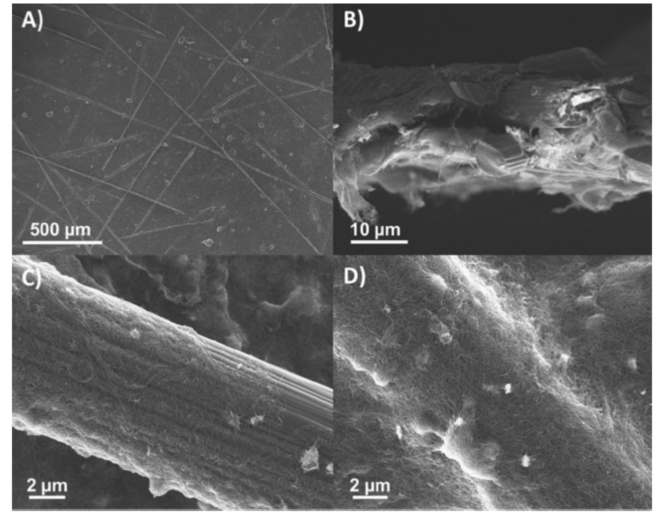
N-heterocyclic polymer
$Co^{2+/3+}$; metallic Co

Further optimization…

Three-dimensional structuration of the electrode (carbon microfibers)

V. Artero et al *En. Env. Sci.* 2016





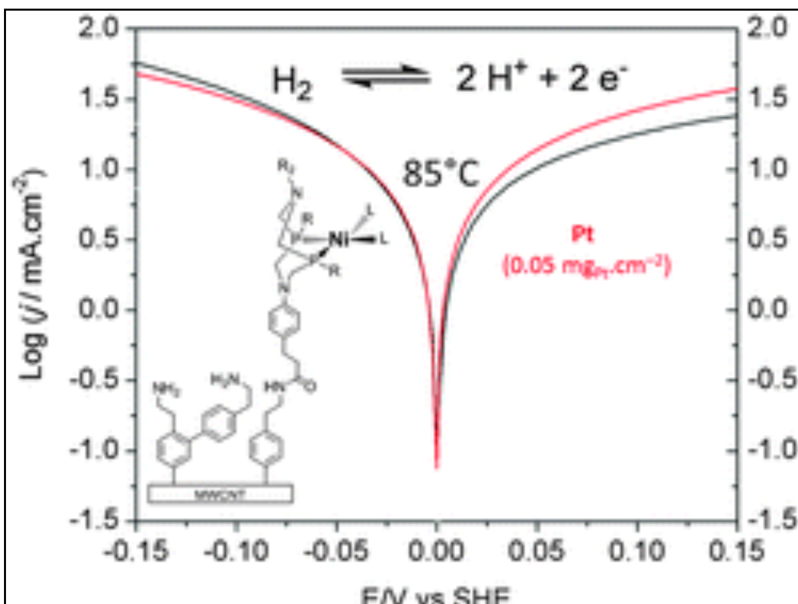


Table 1 Current obtained for hydrogen oxidation at 100 mV and 300 mV overpotential, and for hydrogen evolution at 100 mV overpotential with the $NiP^{Cy}{}_2$-functionalized MWCNT + carbon microfiber (2.5×10^{-8} mol_{Ni} cm^{-2}) and Pt/C (2.5×10^{-7} mol_{Pt} cm^{-2}) electrodes at 25 °C and 85 °C

	E vs. SHE	$NiP^{Cy}{}_2$ (2.5×10^{-8} mol_{Ni} cm^{-2})	Pt/C (2.5×10^{-7} mol_{Pt} cm^{-2})
25 °C	+100 mV (H_2 ox)	6.1 mA cm^{-2}	14.0 mA cm^{-2}
	+300 mV (H_2 ox)	11.67 mA cm^{-2}	36.4 mA cm^{-2}
	−100 mV (H_2 prod)	7.1 mA cm^{-2}	18.4 mA cm^{-2}
85 °C	+100 mV (H_2 ox)	16.8 mA cm^{-2}	26.6 mA cm^{-2}
	+300 mV (H_2 ox)	40.1 mA cm^{-2}	60.9 mA cm^{-2}
	−100 mV (H_2 prod)	38.3 mA cm^{-2}	32.2 mA cm^{-2}

Solar energy storage into carbon

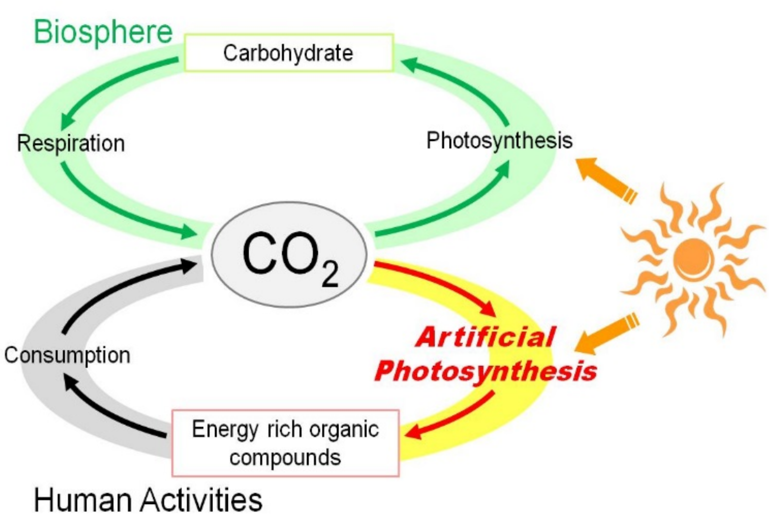
Solar energy

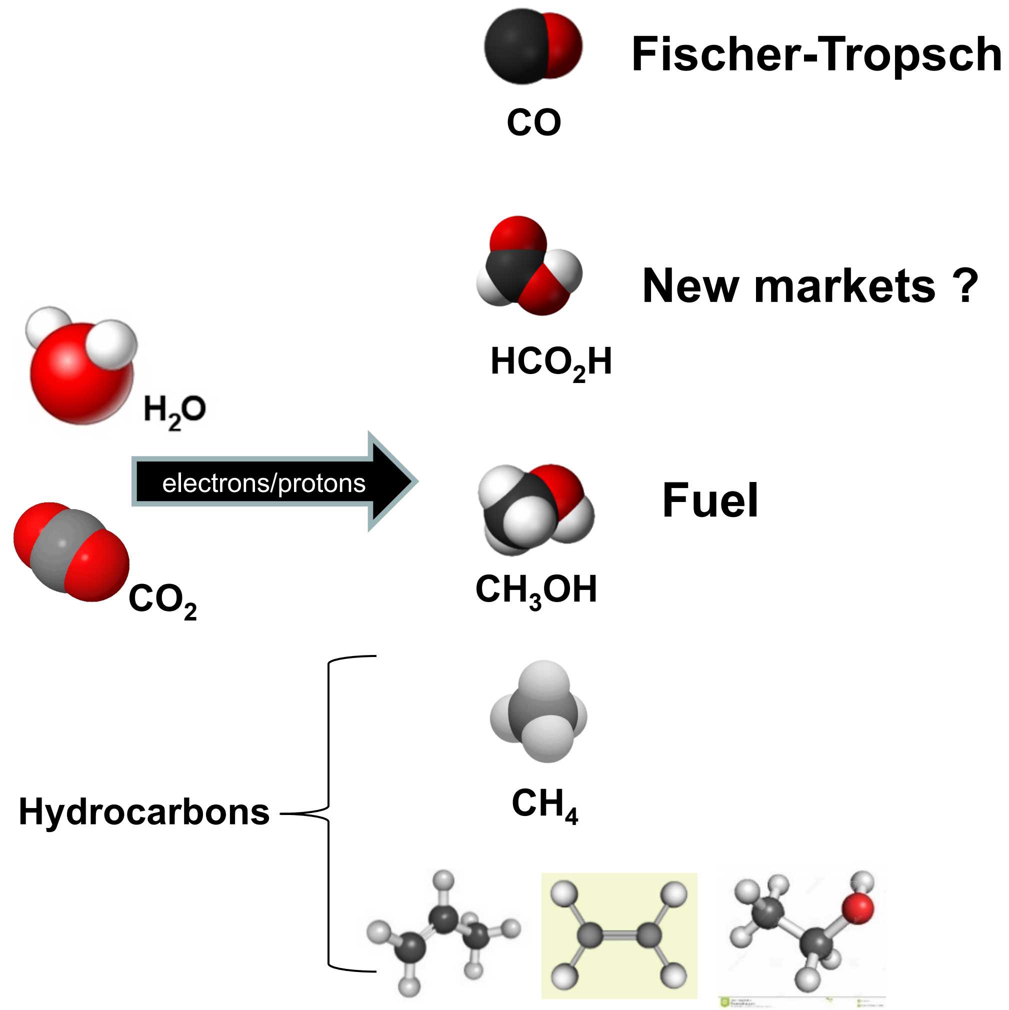
⬇

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

⬇

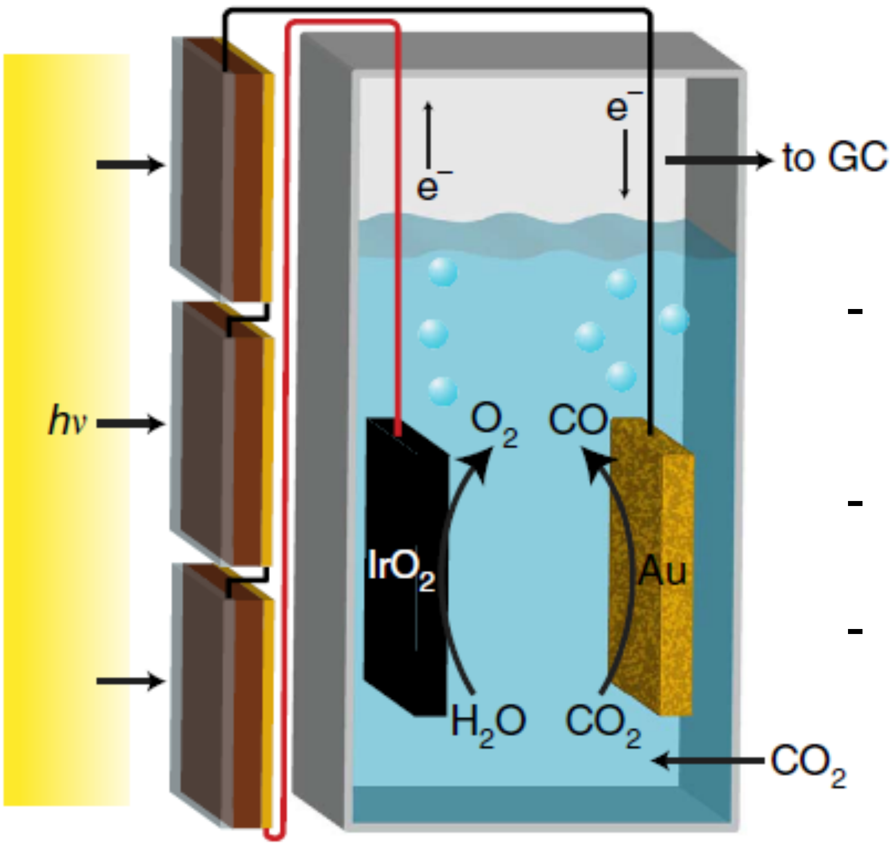
CO_2 valorization





2015: from CO_2 to carbon monoxide

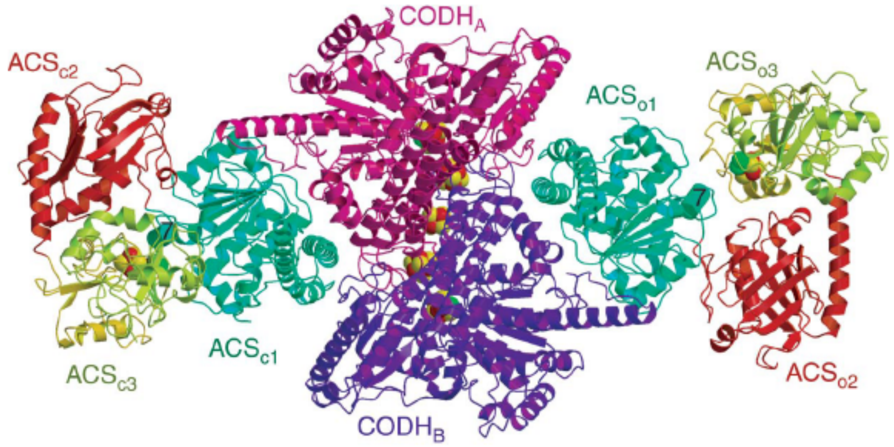
M. Grätzel and coll. *Nature Communications* 2015

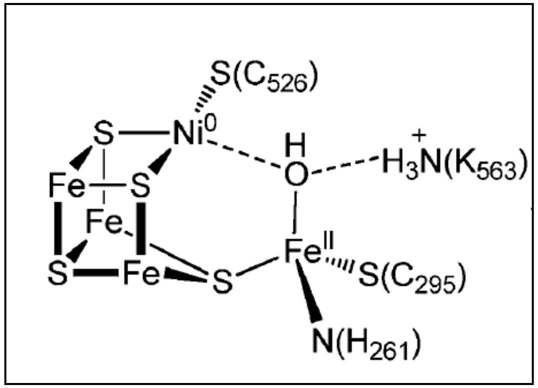


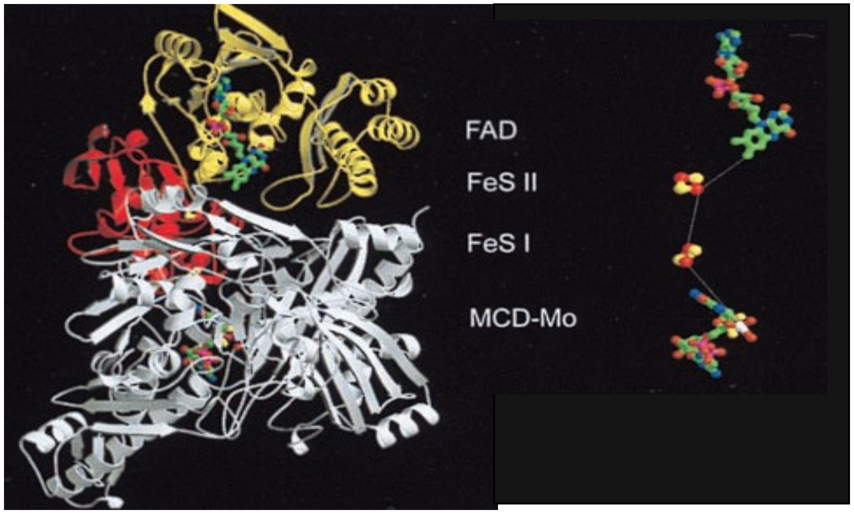
- semiconductor: perovskite $CH_3NH_3PbI_3$
- Catalysts « noble »: Au; IrO_2
- Yield (CO/sun): 6.5 %

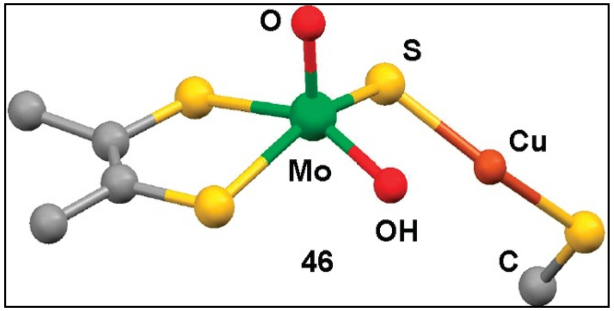
Enzymes: « CO_2 reductases »

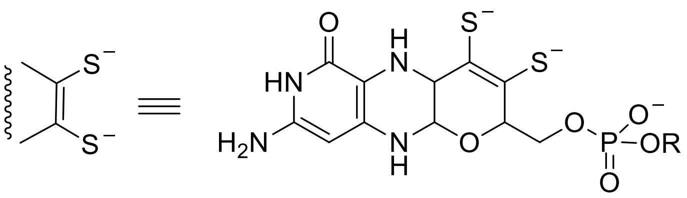
CO dehydrogenases $CO + H_2O \rightleftharpoons CO_2 + 2e^- + 2H^+$







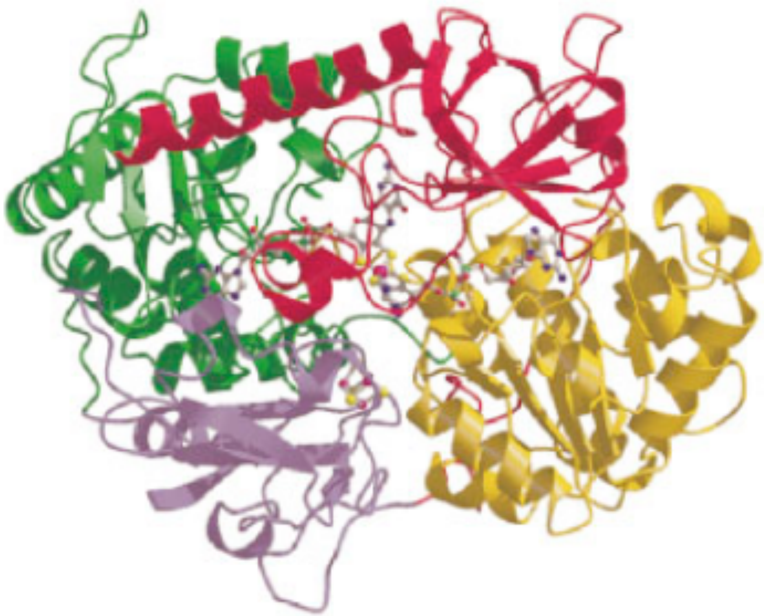


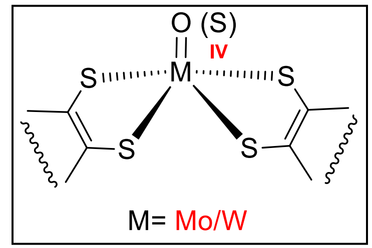


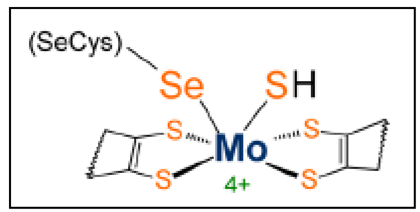
Enzymes: « CO_2 reductases »

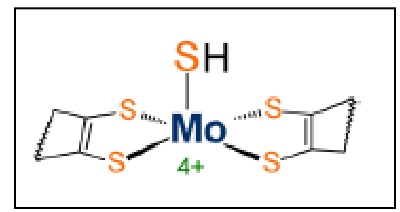
Formate dehydrogenases

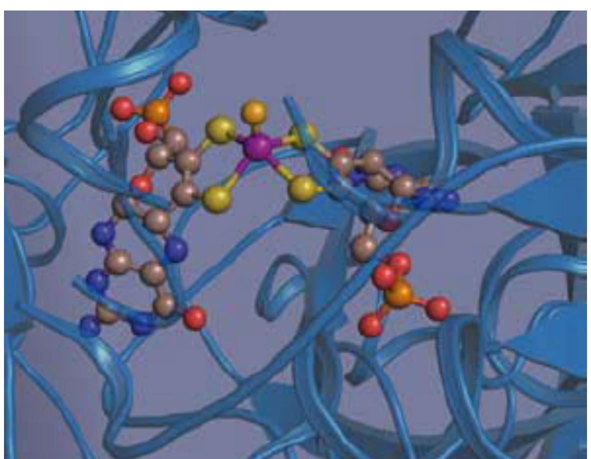
$$HCOO^- \rightleftharpoons CO_2 + H^+ + 2e^-$$

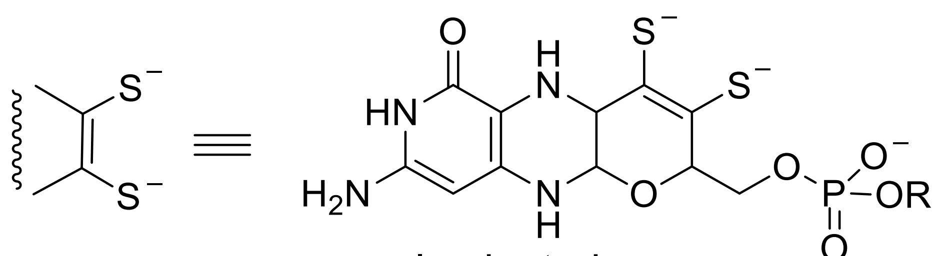






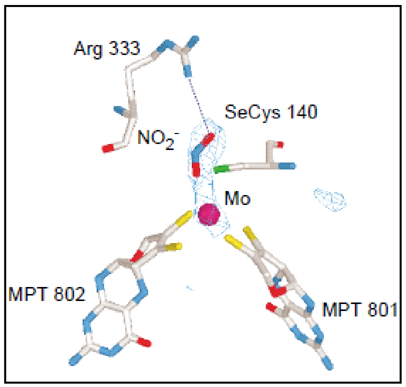


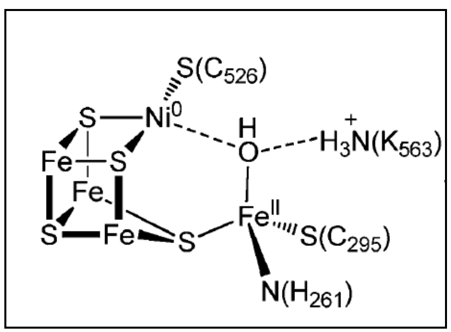


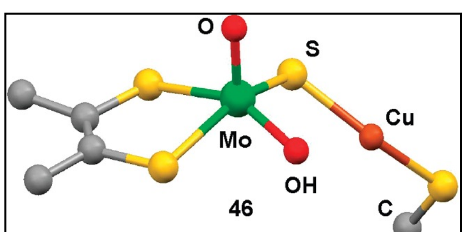


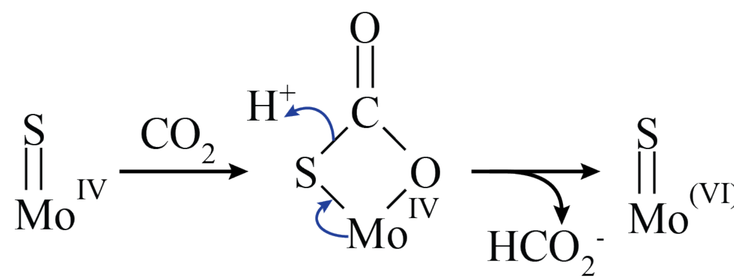
molypdopterin

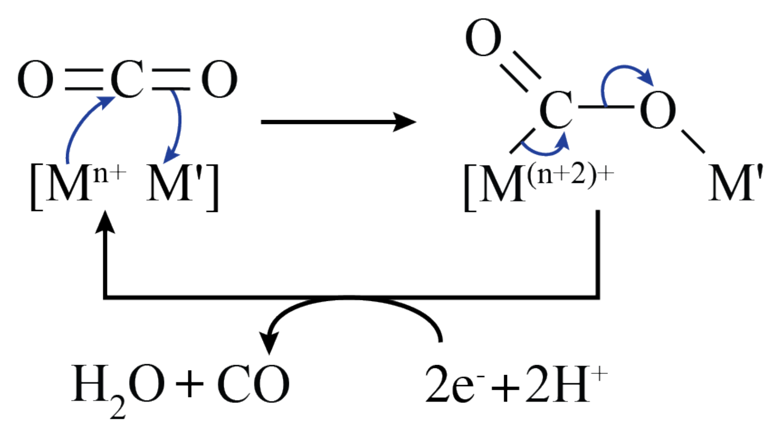
Enzymes: « CO_2 reductases »



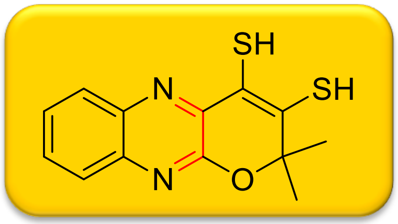




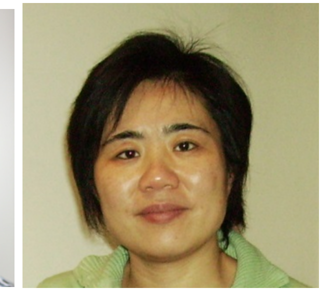


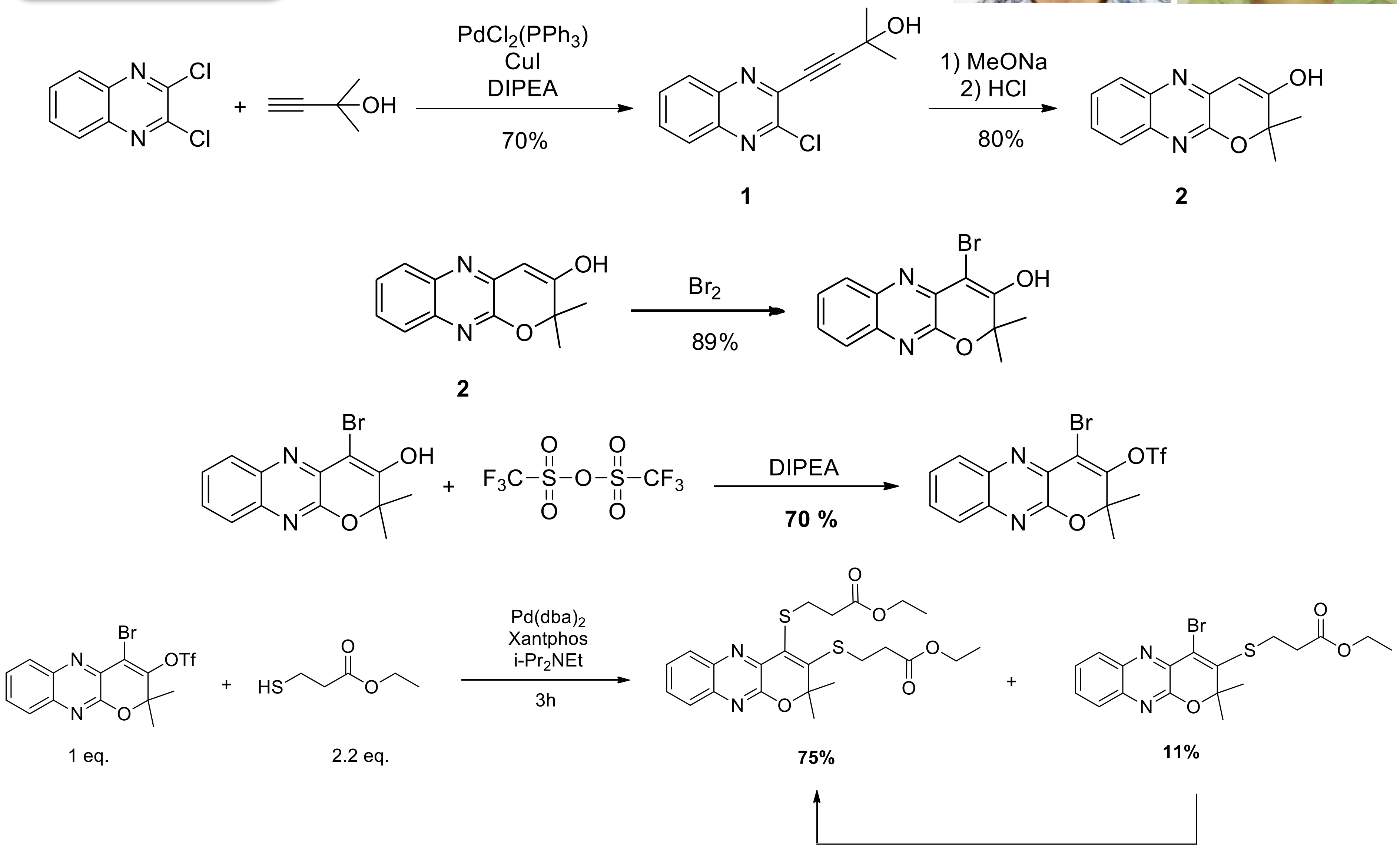


[M = Ni , M' = Fe] ou [M = Mo , M' = Cu]



Ligand mimick: dithiolene

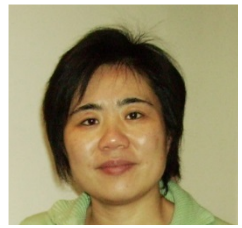


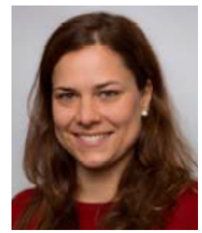


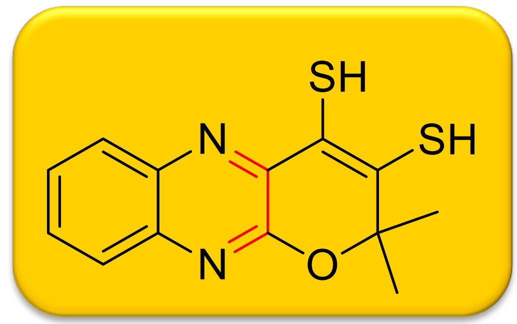
Biomimetic catalyst

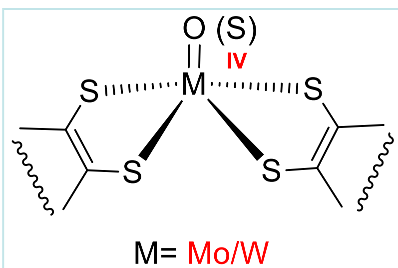
J.P. Porcher, Y. Xu-Li, T. Fogeron, M. Gomez-Mingot, E. Derat, M. Fontecave

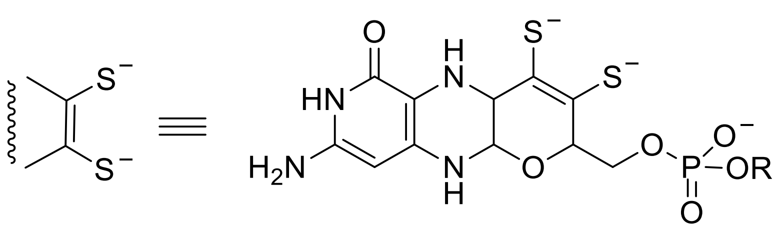
Angew Chem 2015 54 14090

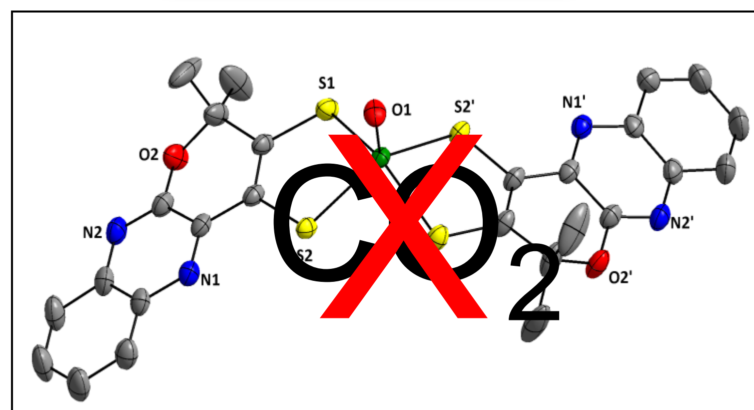




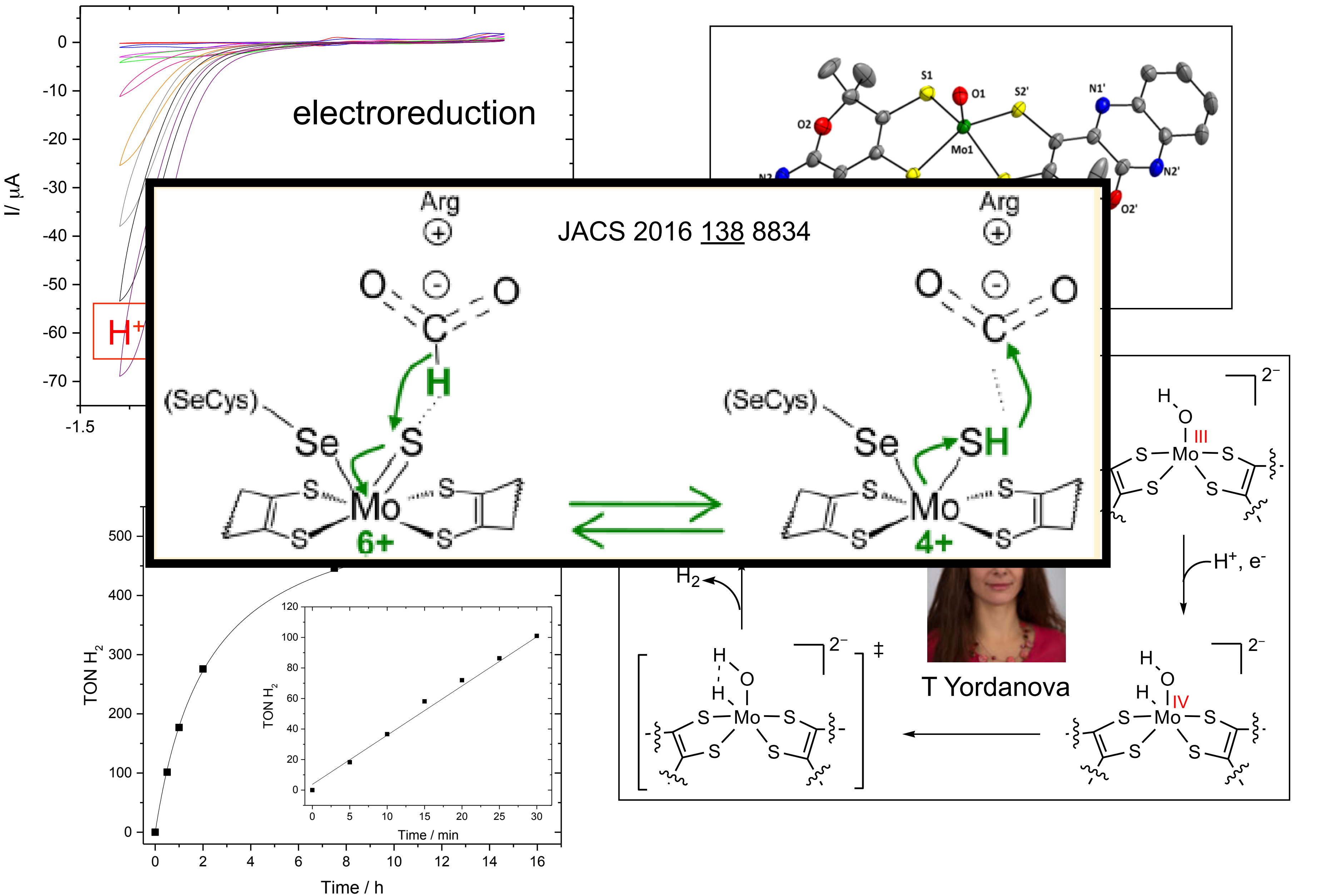




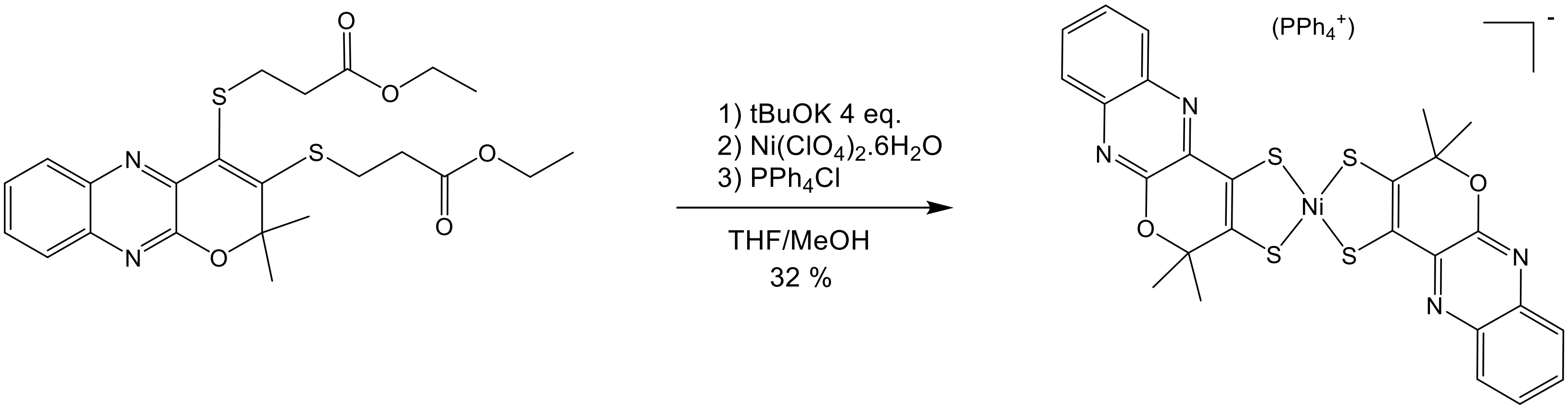


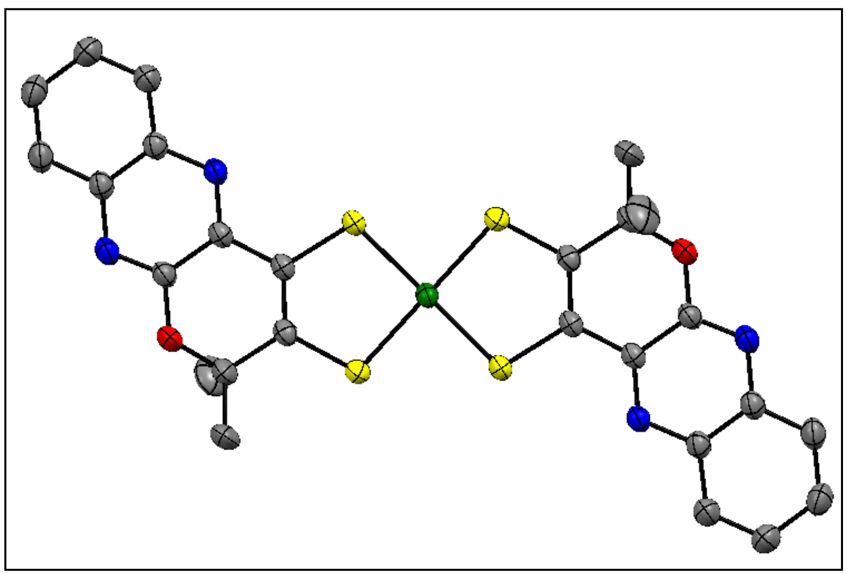


An excellent catalyst for H_2 production



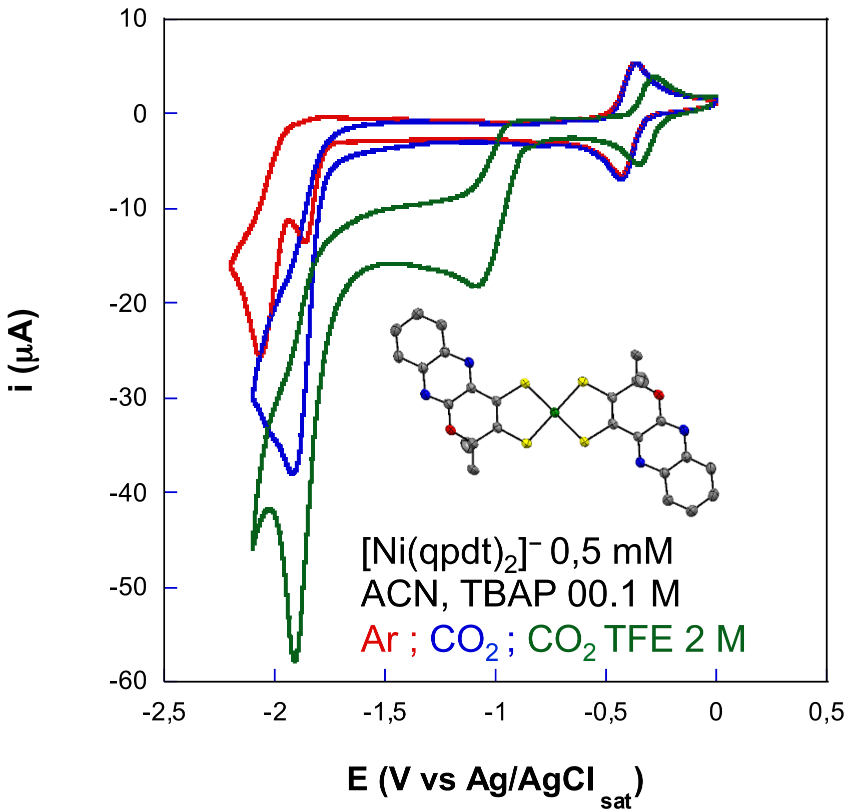
A Ni-dithiolene catalyst for CO_2 reduction

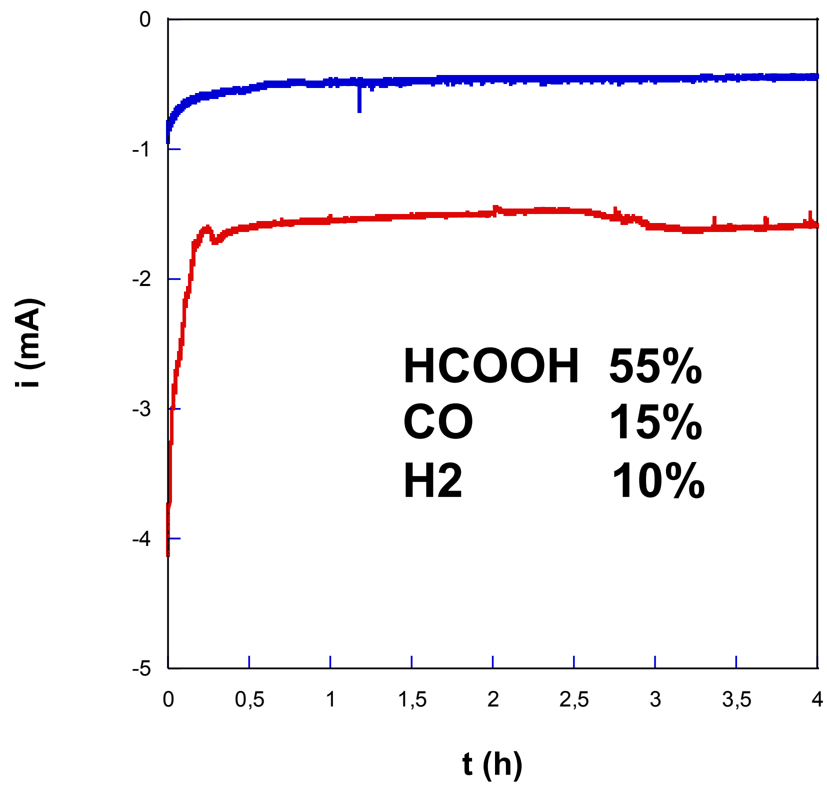




T. Fogeron

A Ni-dithiolene catalyst for CO_2 reduction





Electrolysis in ACN TBAP 0,1 M, TFE 2M, CO2 atm at -1,9 V vs $Ag/AgCl_{sat}$

No complex, $[Ni(qpdt)_2]^-$ 0,5 mM

Bioinspired heterogenous chemistry

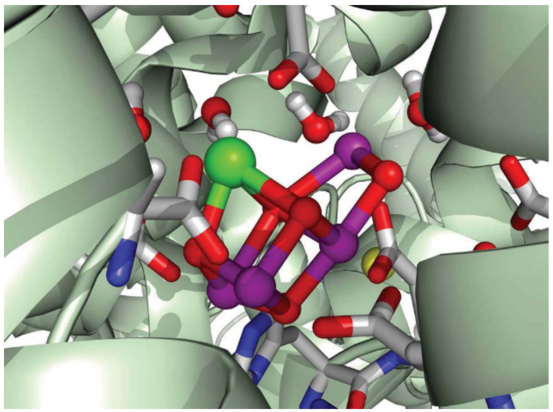
Biology: Molecules

→

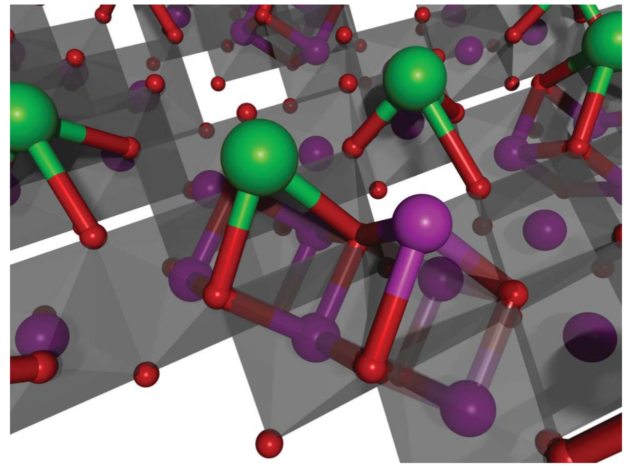
Chemistry: Molecules and **Solids**

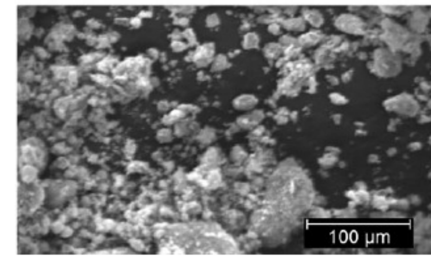
Bioinspired heterogenous chemistry

From PSII to $CaMn_2O_4,xH_2O$



Photosystem II

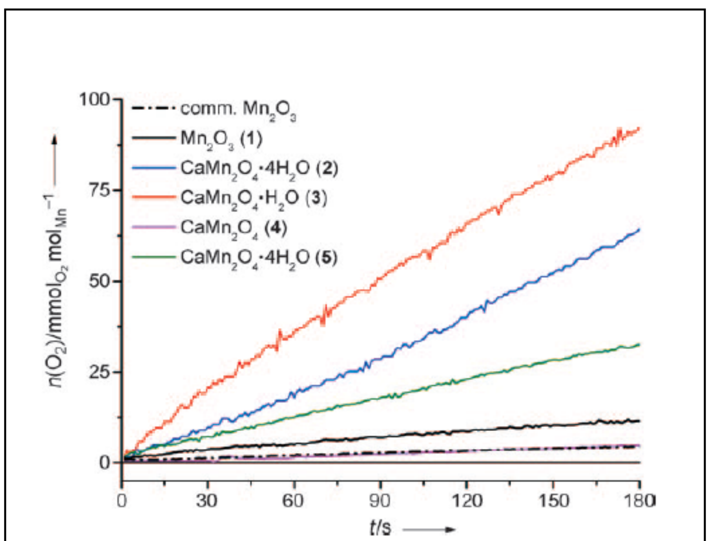




$CaMn_2O_4$

Water oxidation

Particles, Ce(IV)



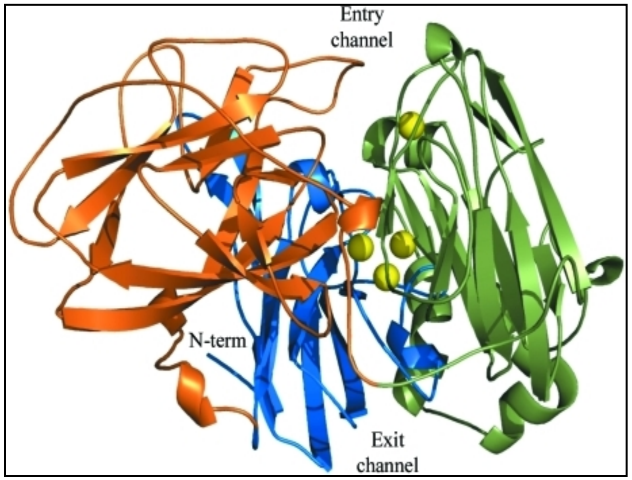
$CaMn^{IV}_{1.6}Mn^{III}_{0.4}O_{4.5}(OH)_{0.5}\cdot zH2O$

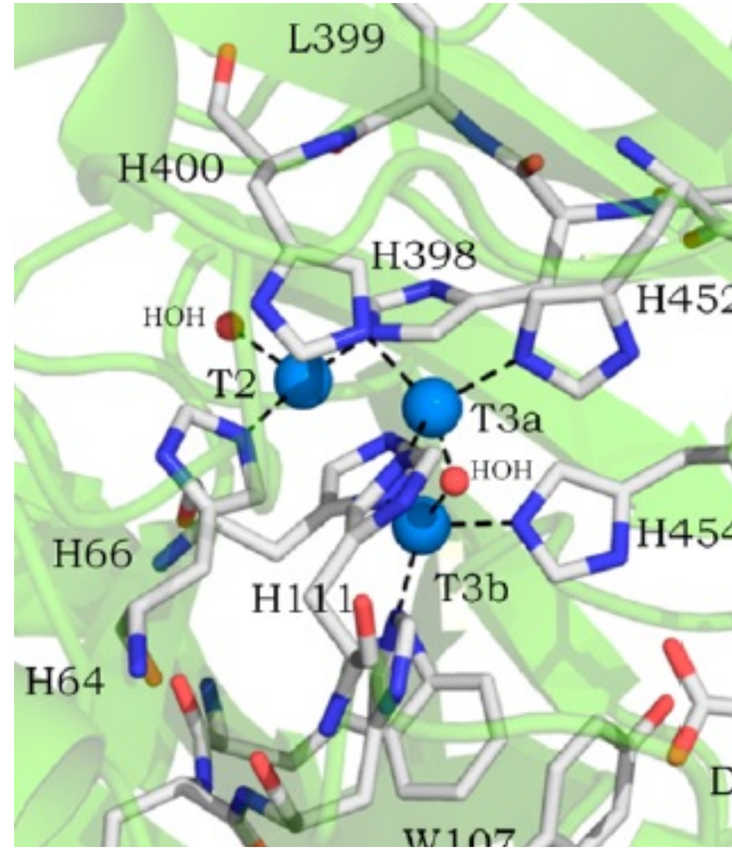
- Mn(III) and Mn(IV)
- Mn and Ca
- Free coordination sites

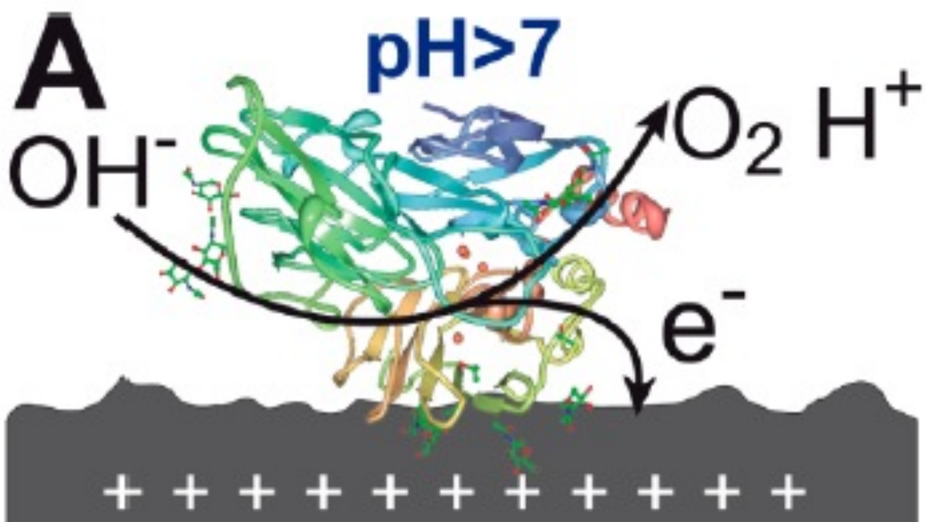
Angew Chem 2010 49 2233, Dalton trans 2012 41 21

Why not Copper ?

Laccase, a copper enzyme

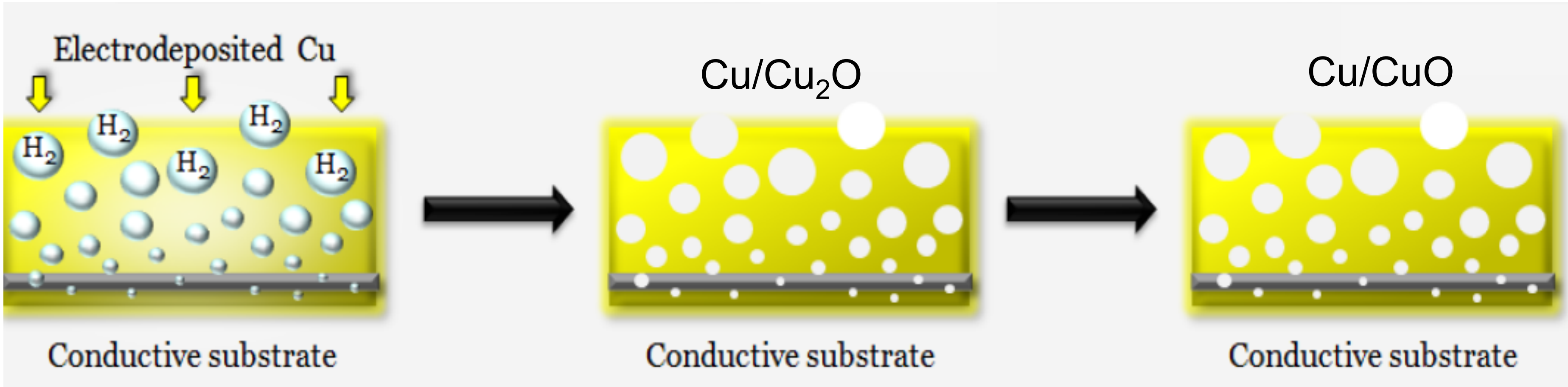






J. Am. Chem. Soc. 2014, 136, 5892−5895

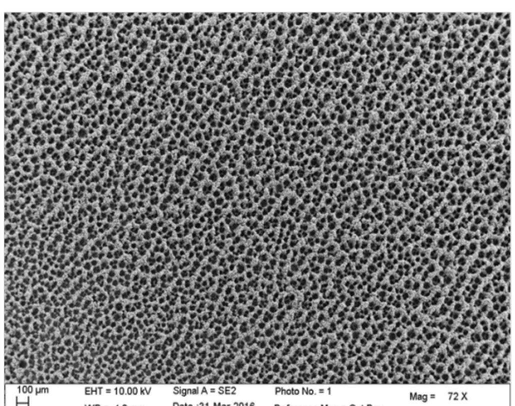
Porous dendritic CuO material

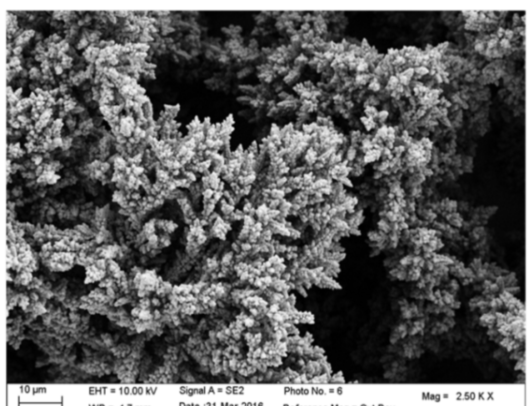


- - 1.5 V vs NHE; H_2SO_4
- Annealing: air + 310°C

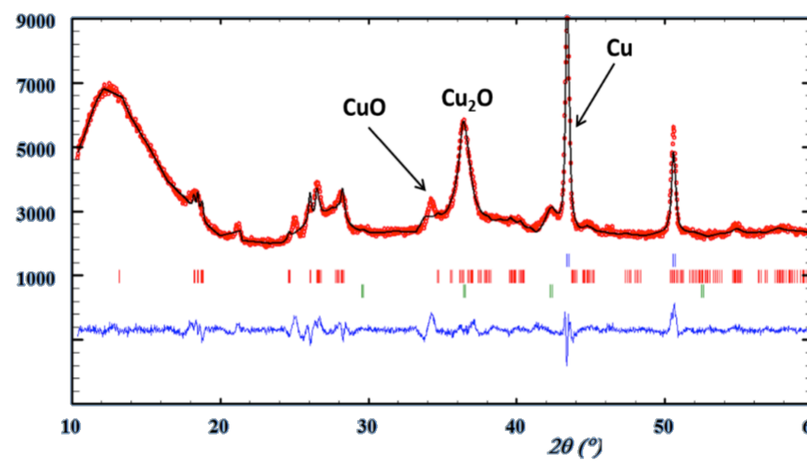
-micro-porous nanostructures
-high surface area of the material.

SEM images of CuO porous nanodendrite electrode



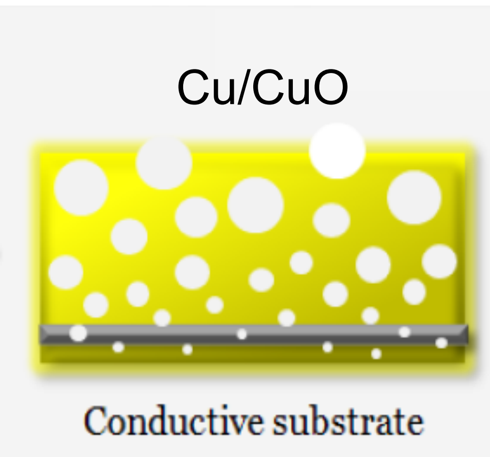


Powder XRD pattern : Cu, Cu_2O and CuO.

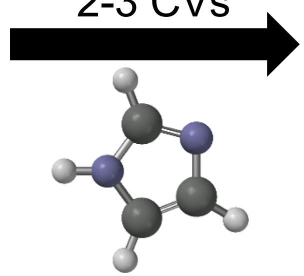


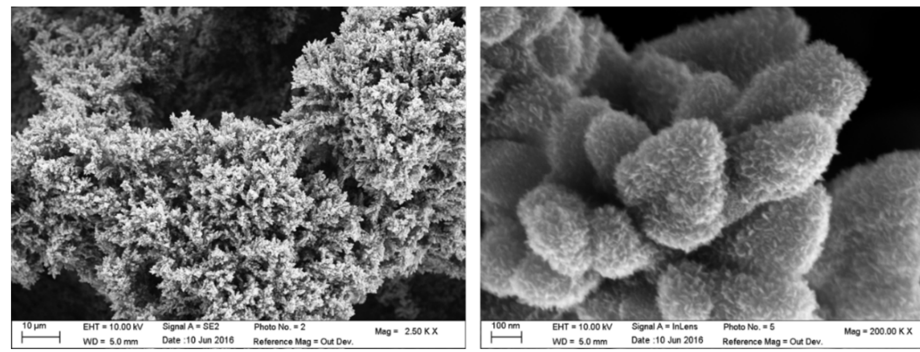
Porous dendritic CuO material

Towards a bioinspired water oxidation solid catalyst

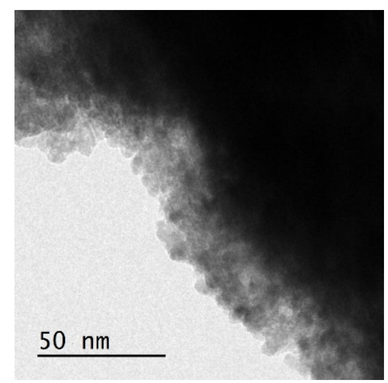


Electropolymerization
Imidazole or Cu(Im)
2-3 CVs

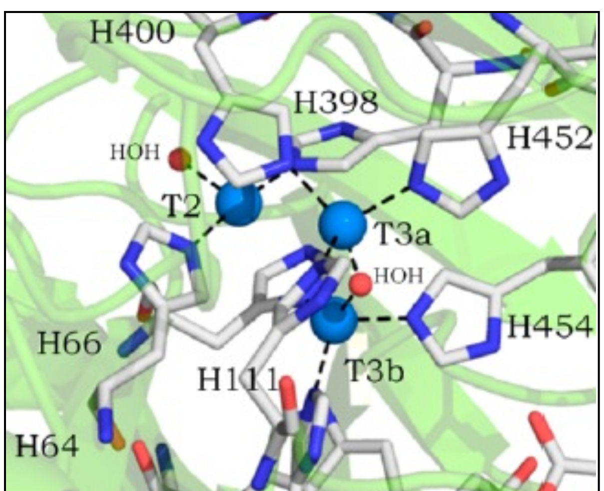




SEM/TEM



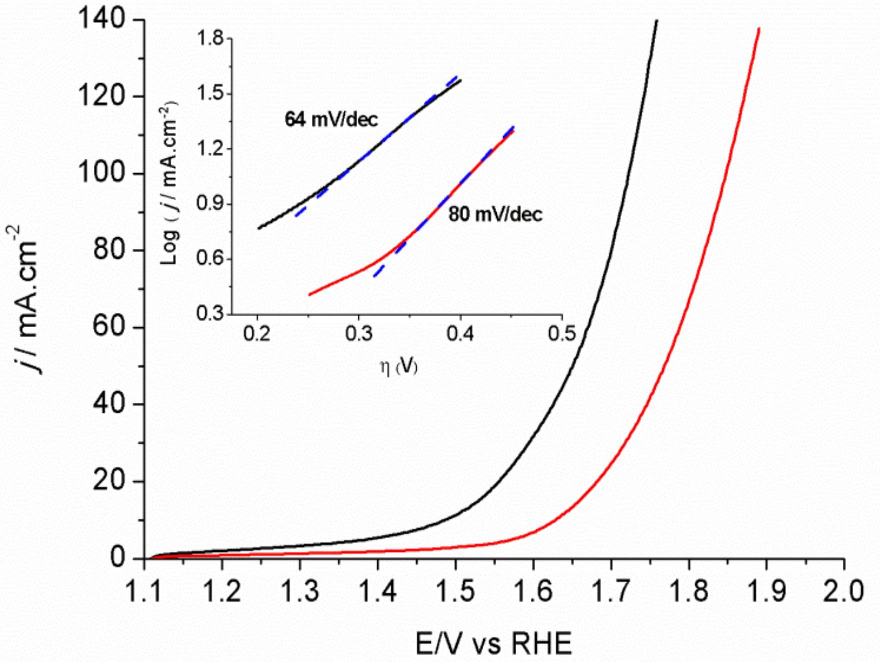
Laccase
Cu-Histidine

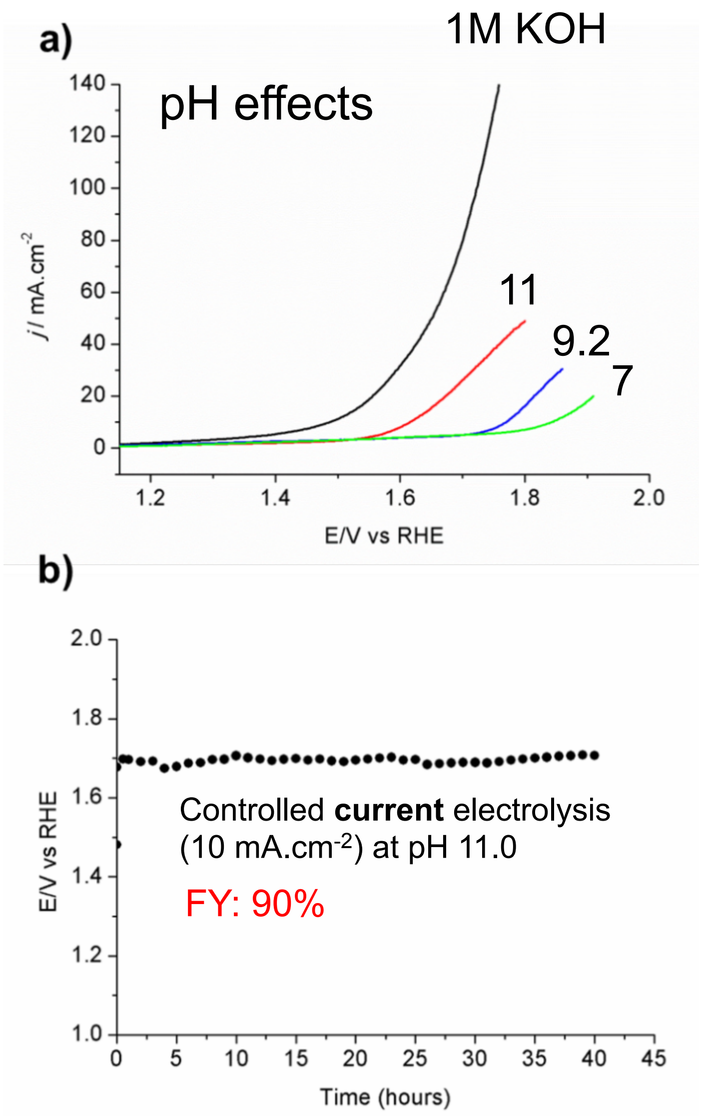


Porous dendritic CuO material

Towards a bioinspired water oxidation solid catalyst

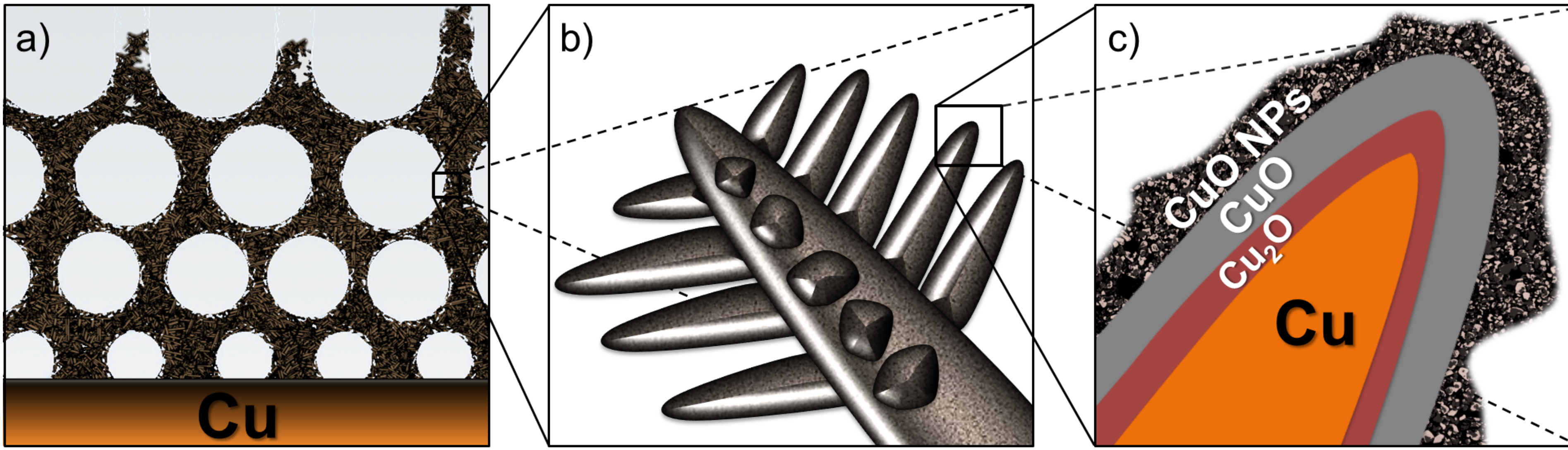
Cu/CuOx (red)
Cu/CuOx/Cu(imidazole) (black)
1.0 M NaOH, 10 mV.s^{-1}

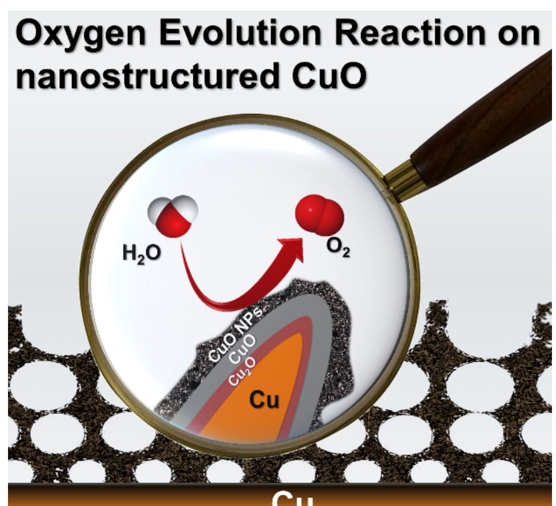




A current density of 10 mA.cm^{-2}
for O_2 evolution
at 270 mV overpotential!

Conductive material | High surface area | Structuration





Angew. Chem. 2017, under revision

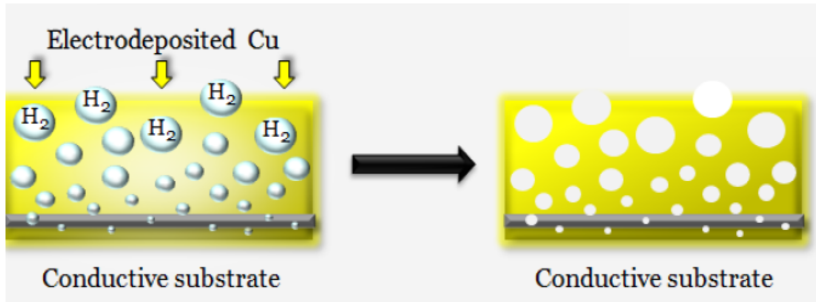
Victor Mougel

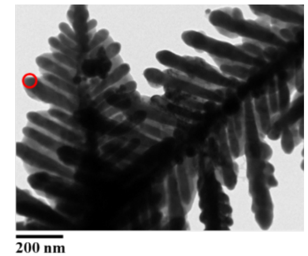
Tran Ngoc Huan

Tran Ngoc Huan

Porous dendritic Cu material

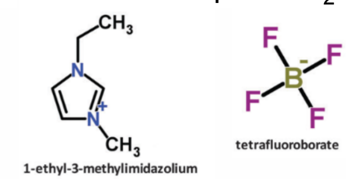
Towards a CO_2 reduction catalyst

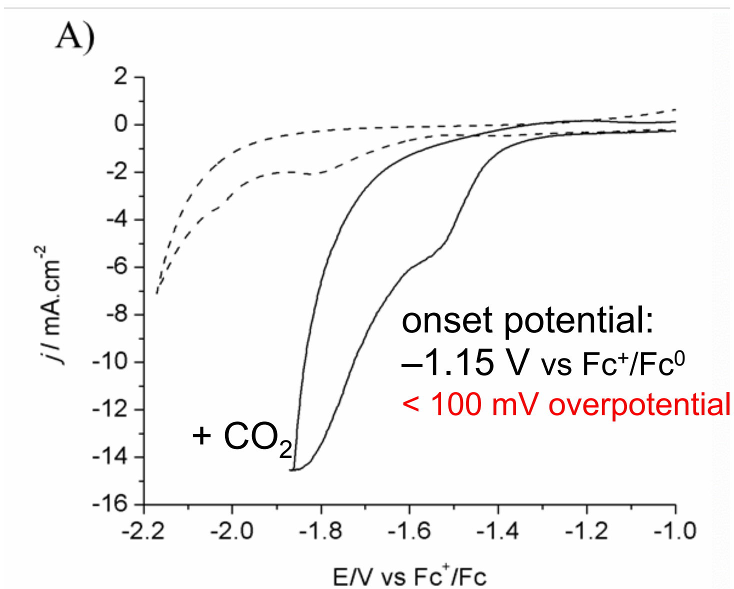




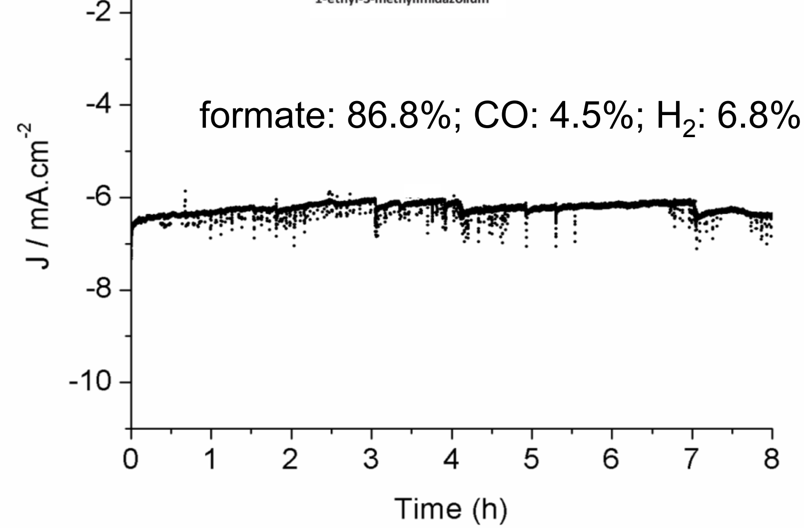
$$CO_2 + 2\,e^- + 2H^+ \rightarrow HCOOH$$

Solvent: ionic liquid + H_2O (8%)





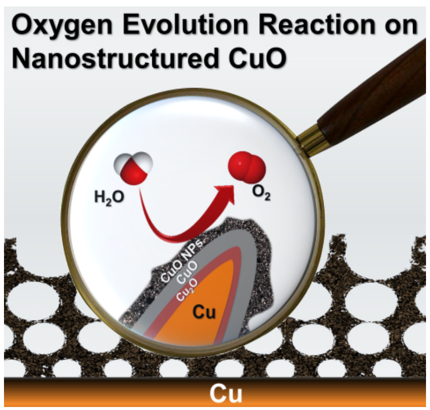
CVs on a modified Cu electrode in EMIM/H_2O (92/8 v/v): N_2 and CO_2.



CPE of CO_2 at –1.55 V vs Fc^+/Fc^0 in EMIM-BF_4/H_2O (92/8% v/v)

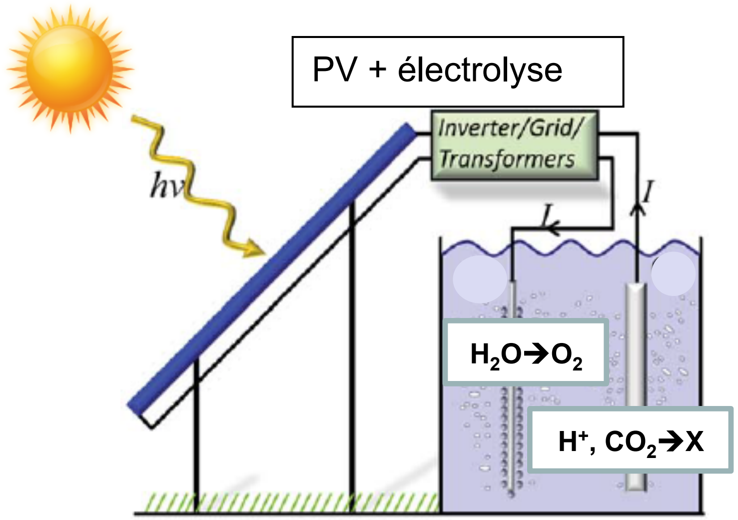
Chem. Sci. 2017 8, 742-747

Copper for an electrolytic cell



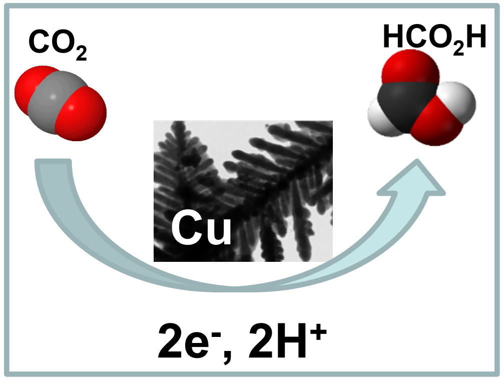
Angew. Chem. 2016

Tran Ngoc Huan



Issues to address:

- Water at the cathode
- Cathode selectivity (H2)
- More reduced species at the cathode (CH_4, C_2H_2,..)
- Long-term stability



Chem Sci 2016

Victor Mougel

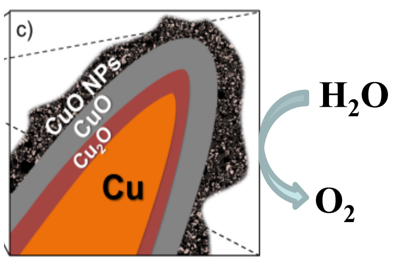
Towards an electrolytic cell

Issues to address:
- Solvent: Water
- Cathode selectivity (H_2)
- More reduced species at the cathode (CH_4, C_2H_2,..)
- Long-term stability
- Cell design

membrane

Anode

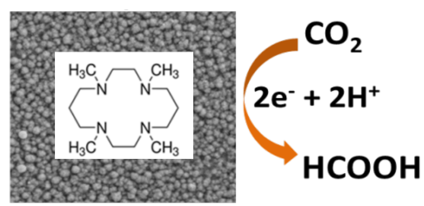
Water oxidation



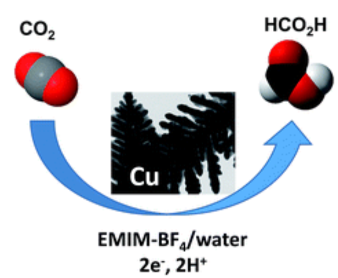
Submitted to Angewandte Chemie

Cathode

CO_2 ➢ HCOOH

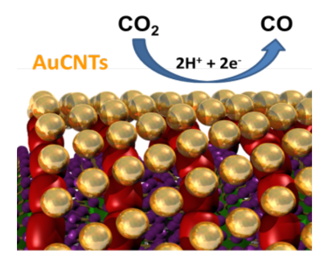


Chem. A Eur. J. 22(**2016**) 14029-14035

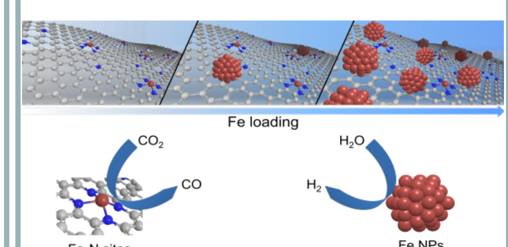


Chemical Science, **2017**, 8, 742-747

CO_2 ➢ CO

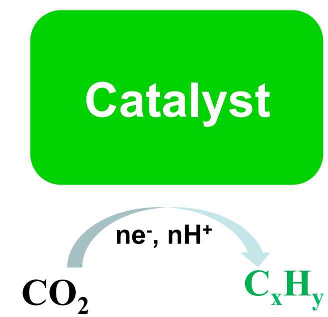


ChemSusChem 8,(**2016**) 2317 -2323



Accepted in ACS Catalysis

CO_2 ➢ C_xH_y

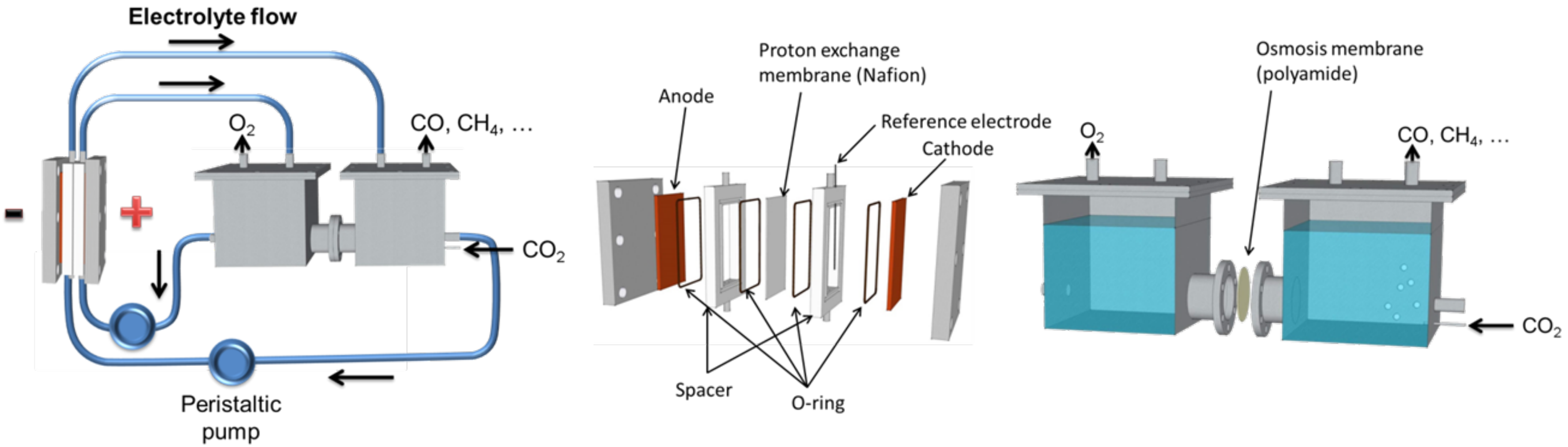


C_xH_y: CH_4, C_2H_4, C_2H_6, C_3H_6
FY of H_2: 43%

Under Investigation

Flow electrolytic cell

- Low CO_2 solubility: constant bubbling
- Efficient release of reaction byproducts
- Highly versatile

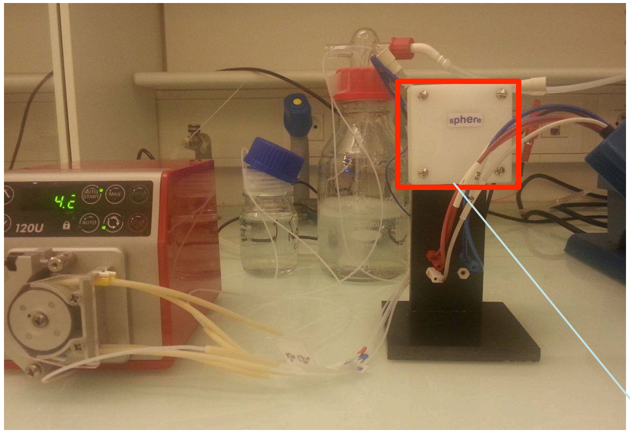


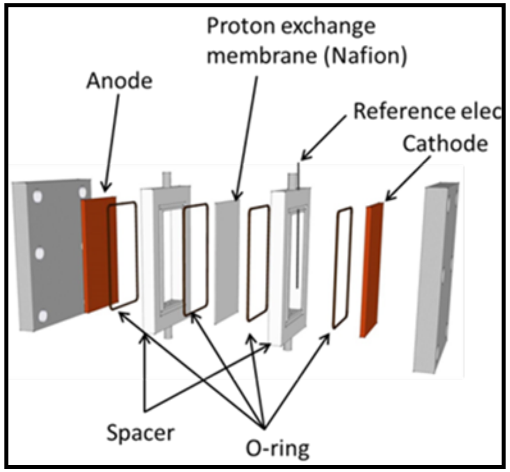
Small interelectrode d

Electrolyte circulation

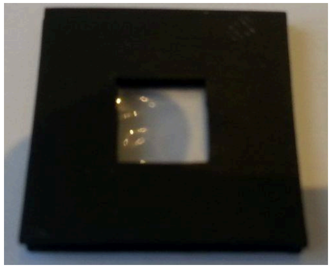
Conducting membrane

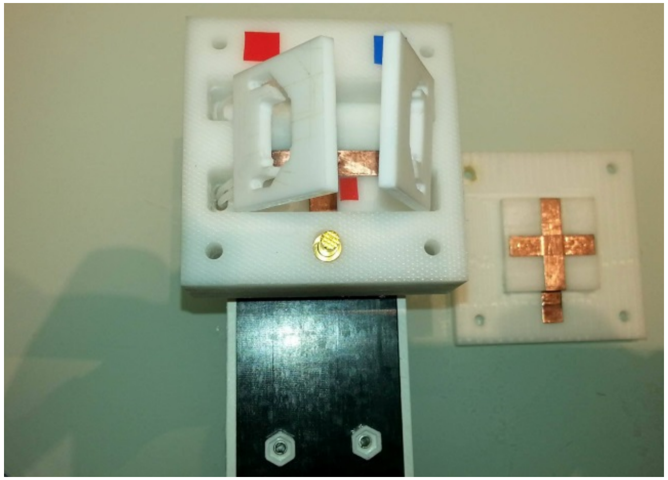
Flow electrolytic cell



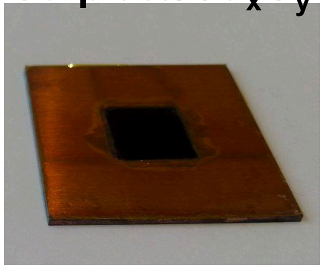


Nafion memb





Cu plate/Cu_xO_y



http://sphere-energy.eu/

Small interelectrode d

Electrolyte circulation

Conducting membrane

Bio-inspired systems for solar energy storage

Marc Fontecave

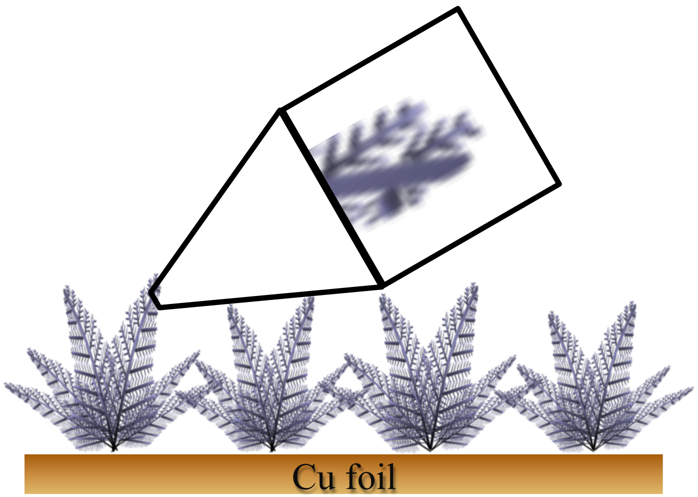
Laboratoire de Chimie des Processus Biologiques, UMR 8229 CDF/CNRS/UPMC
Collège de France, 11 Place Marcelin Berthelot, 75231 Paris Cedex 05
marc.fontecave@college-de-france.fr; Phone: (0033)144271360

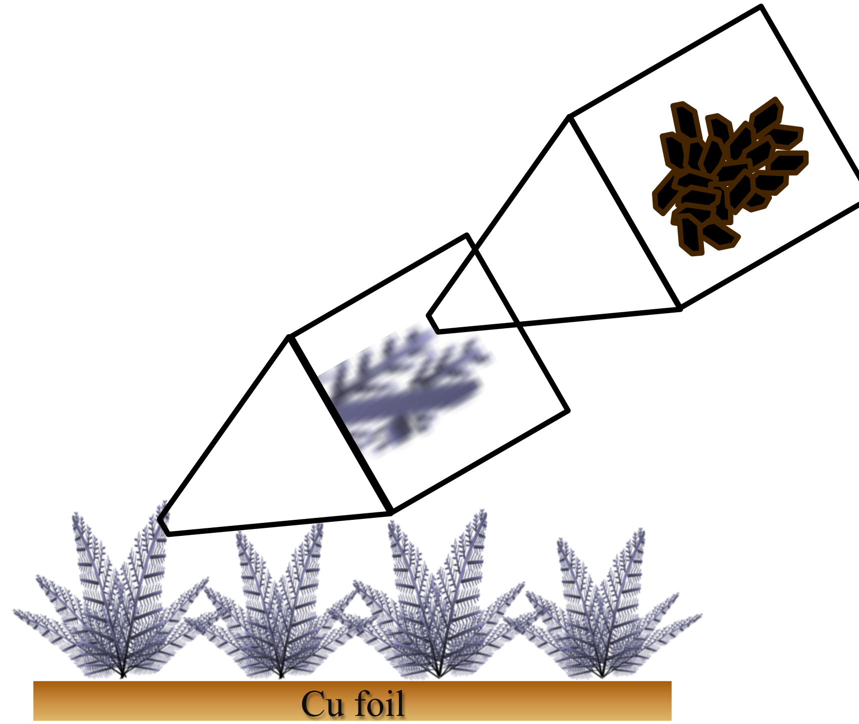
Conclusion: Rational design of a solid electrocatalyst

Conductive material

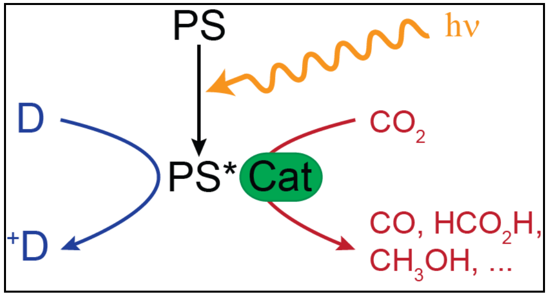
High surface area

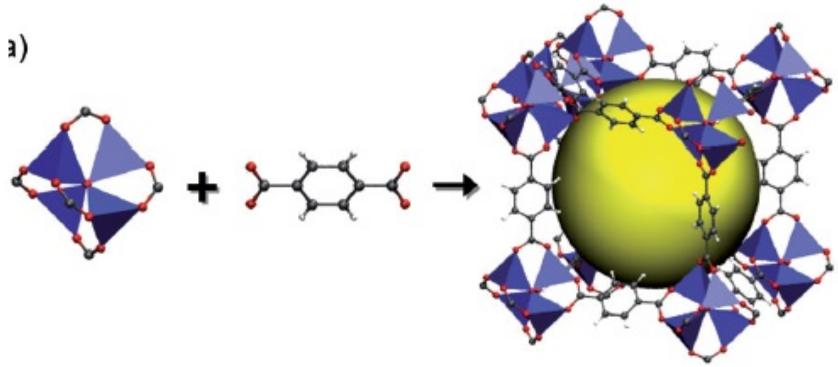
Structuration





Metal-Organic Frameworks (MOF)

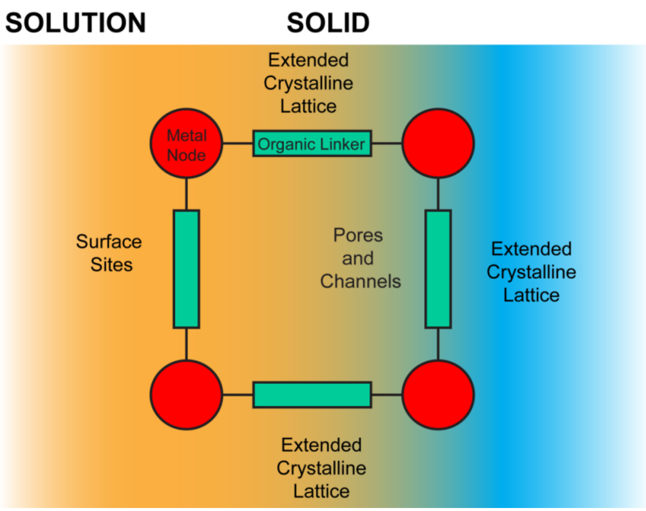


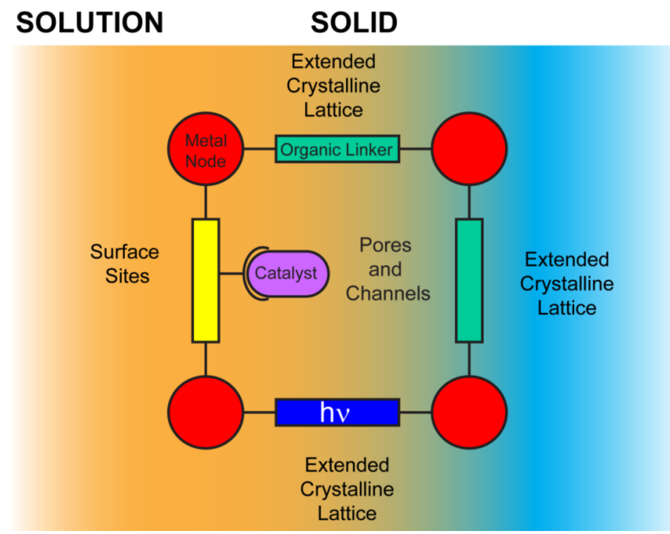



M. Chambers


C. Mellot-Draznieks


X. Wang



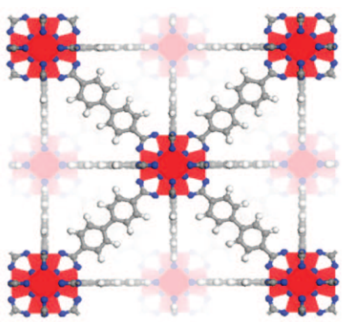


Metal-Organic Frameworks: metal nodes and organic linkers forming a crystalline coordination polymer with pores, channels and surface sites

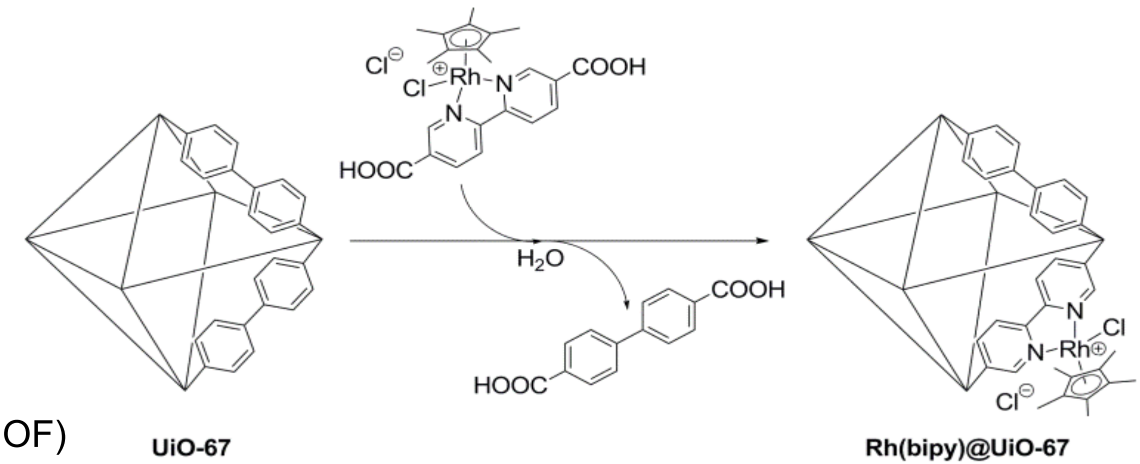
An artificial photosystem: template a light absorber close to a catalyst within a MOF

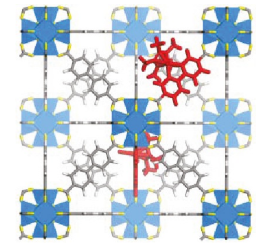
Using MOF as….a catalyst

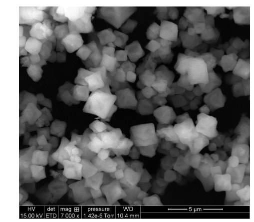
1. Rhodium complex heterogenization in UiO-67 through post-synthetic ligand exchange.



UiO-67 (Zr-based MOF)







Using MOF as….a catalyst

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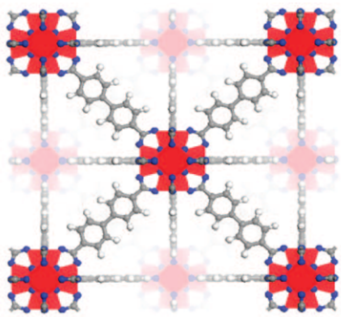
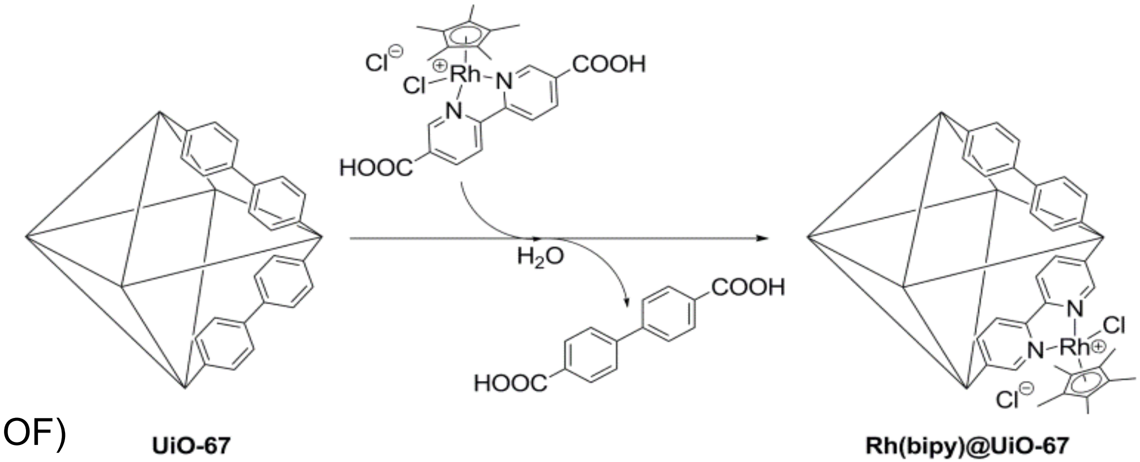
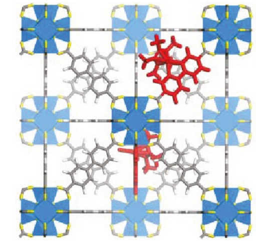
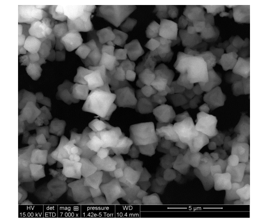


UiO-67 (Zr-based MOF)

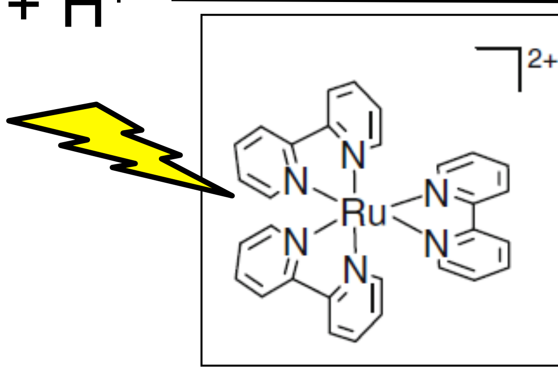


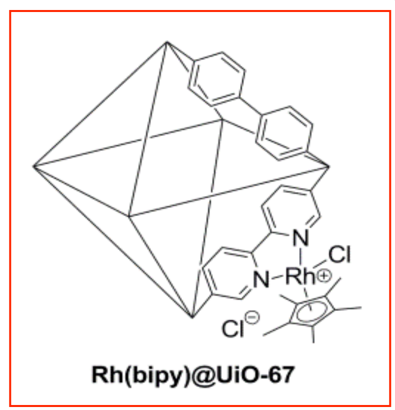




2. Using Rh@UiO-67 (10% incorporation) as a catalyst **for CO_2 reduction**.

$CO_2 + H^+ \longrightarrow HCOOH + H_2$





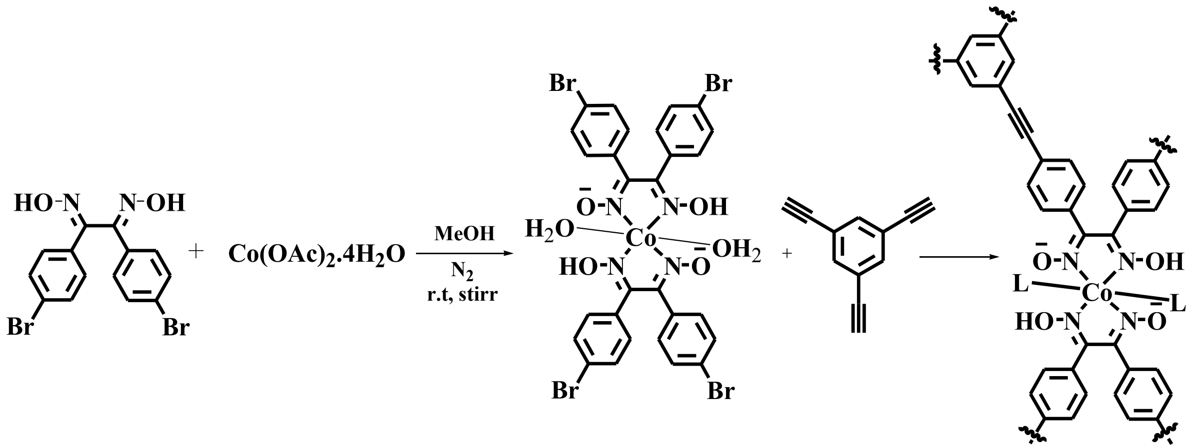
TON = 47 36
(7 h)

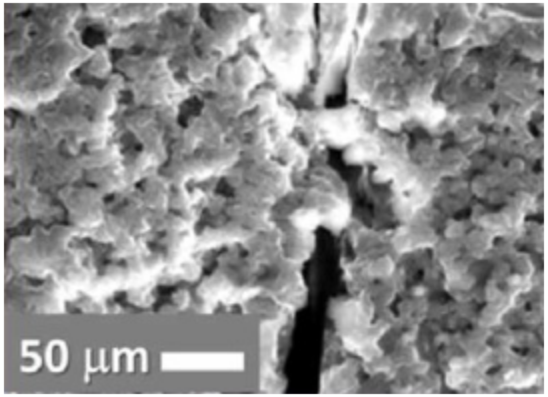
- Active
- Stable (4 days)
- Recyclable

M.B. Chambers et al, *ChemSusChem* 2015, 8, 603

Using a polymer as….a catalyst

ACS Appl Mater Interfaces. 2016 8 19994





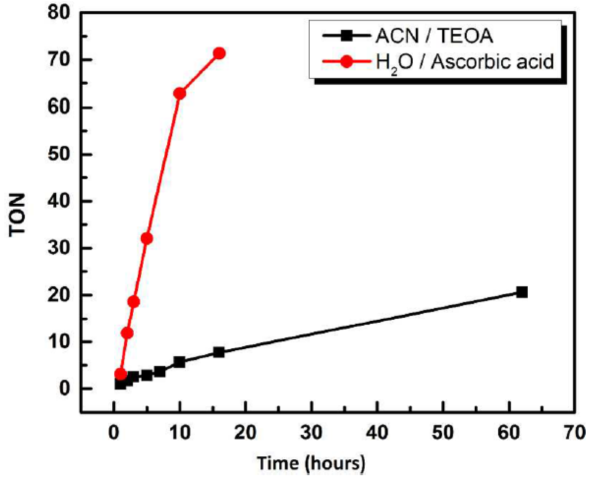
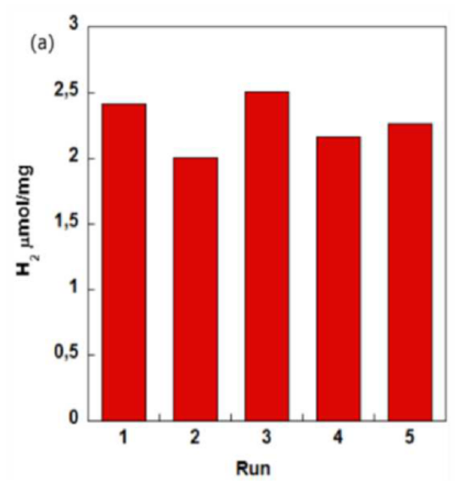
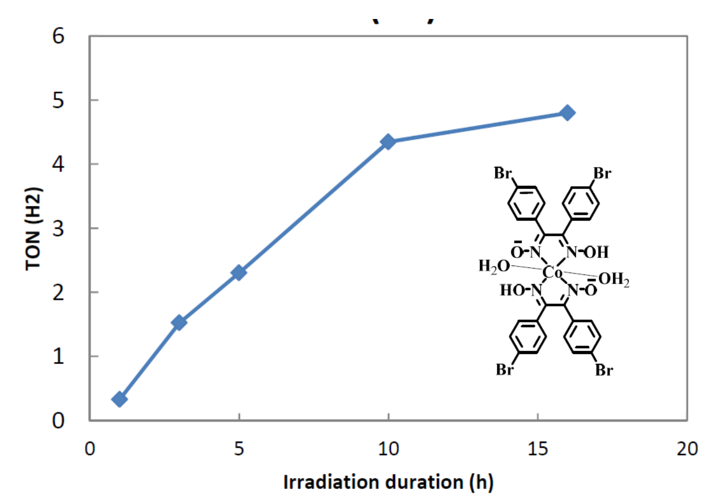


Figure 5. Catalytic activity for the PCoP toward H_2 production in the two systems reported. Conditions: $Ru(bpy)_3Cl_2$, 10 mM; filter, >415 nm. Symbols: black squares, H_2 evolution in a 5:1 (v:v) ACN/TEOA solvent system under N_2 saturated conditions; red circles, H_2 evolution in an H_2O/ascorbic acid (0.1 M) pH 4 solvent system under N_2 saturated conditions.



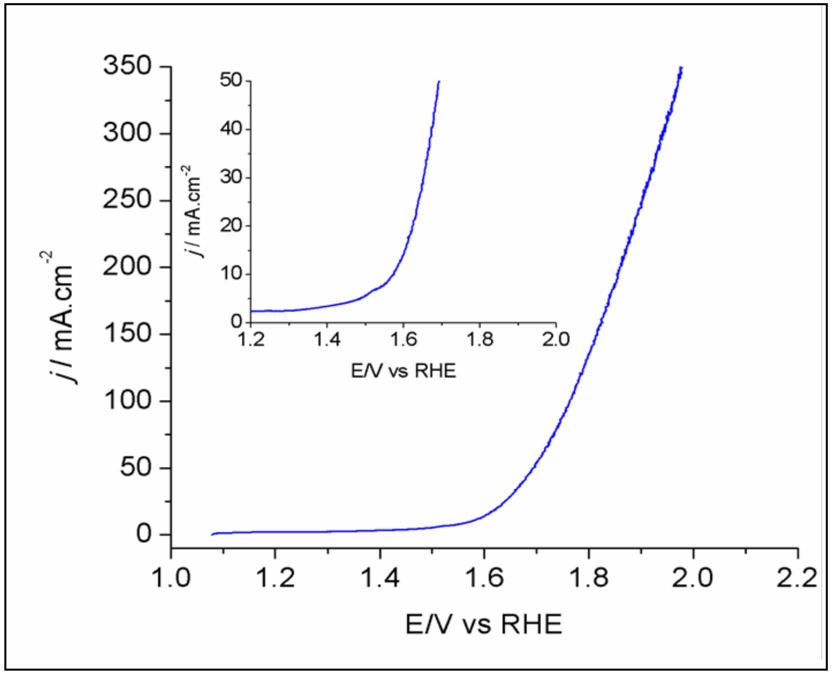


Porous dendritic CuO material

Towards a water oxidation catalyst

Tran Ngoc Huan

Victor Mougel



Linear sweep voltammetry in 1.0 M NaOH
scan rate : 10mV/s

Electrolysis (4hours)
Stable current
FY: 90%

A current density of 10 $mA.cm^{-2}$
for O_2 evolution
at 340mV overpotential!