Copper for artificial photosynthesis

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CO_2 photo-electro-reduction: solar energy storage and utilizable carbon

Half reactions:

$H_2O \rightarrow \mathbf{O_2} + 4\ H^+ + 4\ e^-$

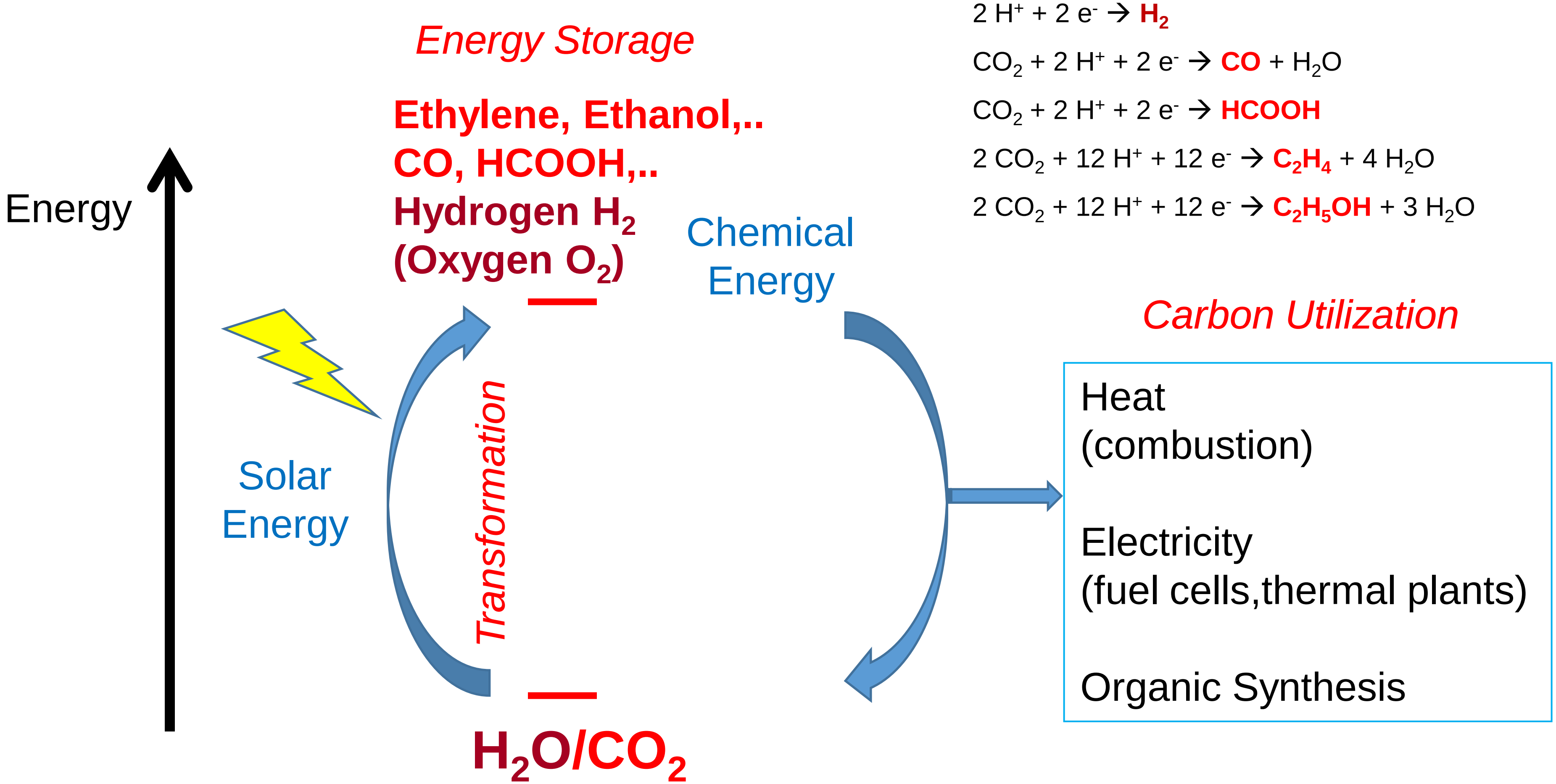
$2\ H^+ + 2\ e^- \rightarrow \mathbf{H_2}$

$CO_2 + 2\ H^+ + 2\ e^- \rightarrow \mathbf{CO} + H_2O$

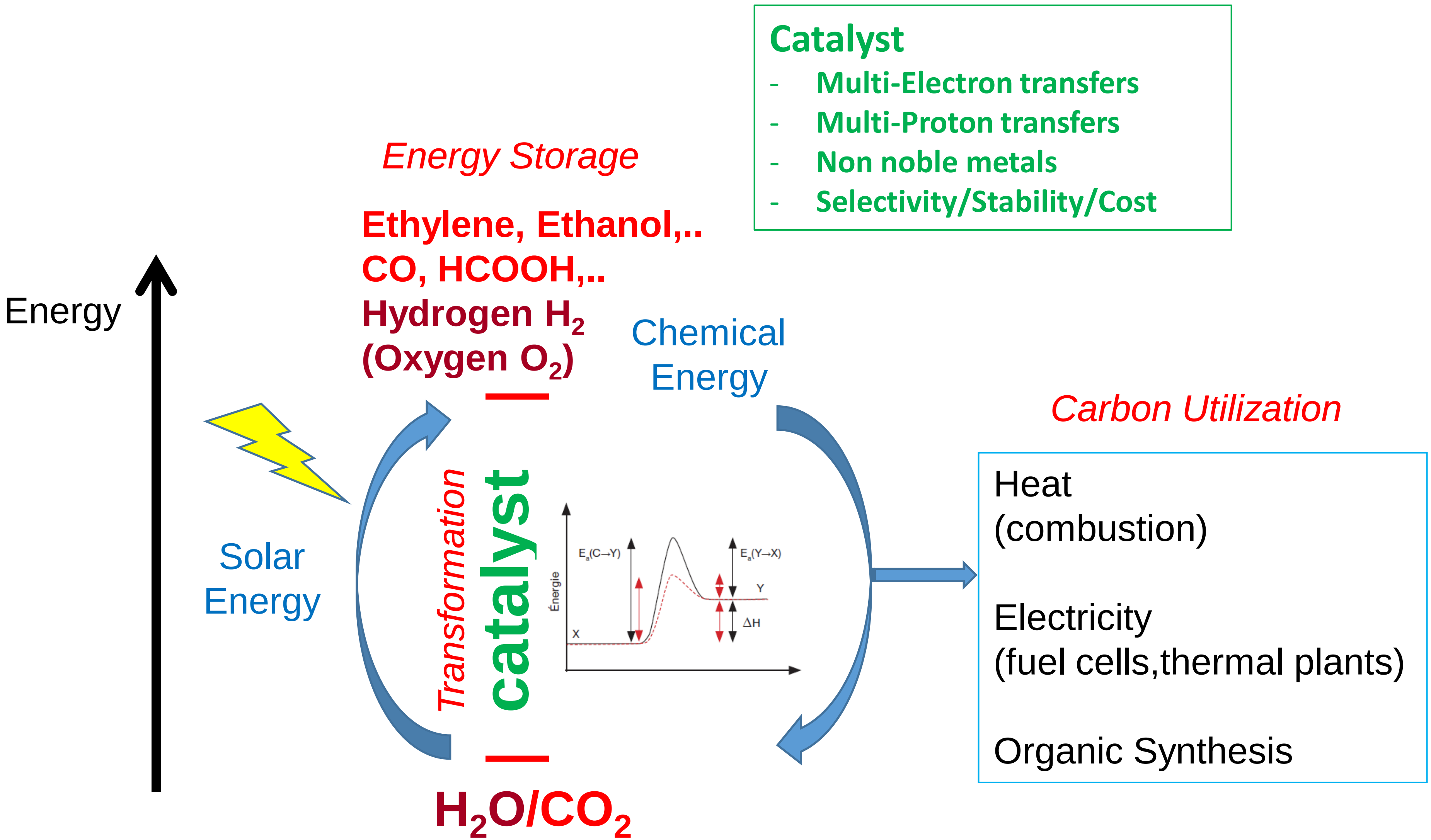
$CO_2 + 2\ H^+ + 2\ e^- \rightarrow \mathbf{HCOOH}$

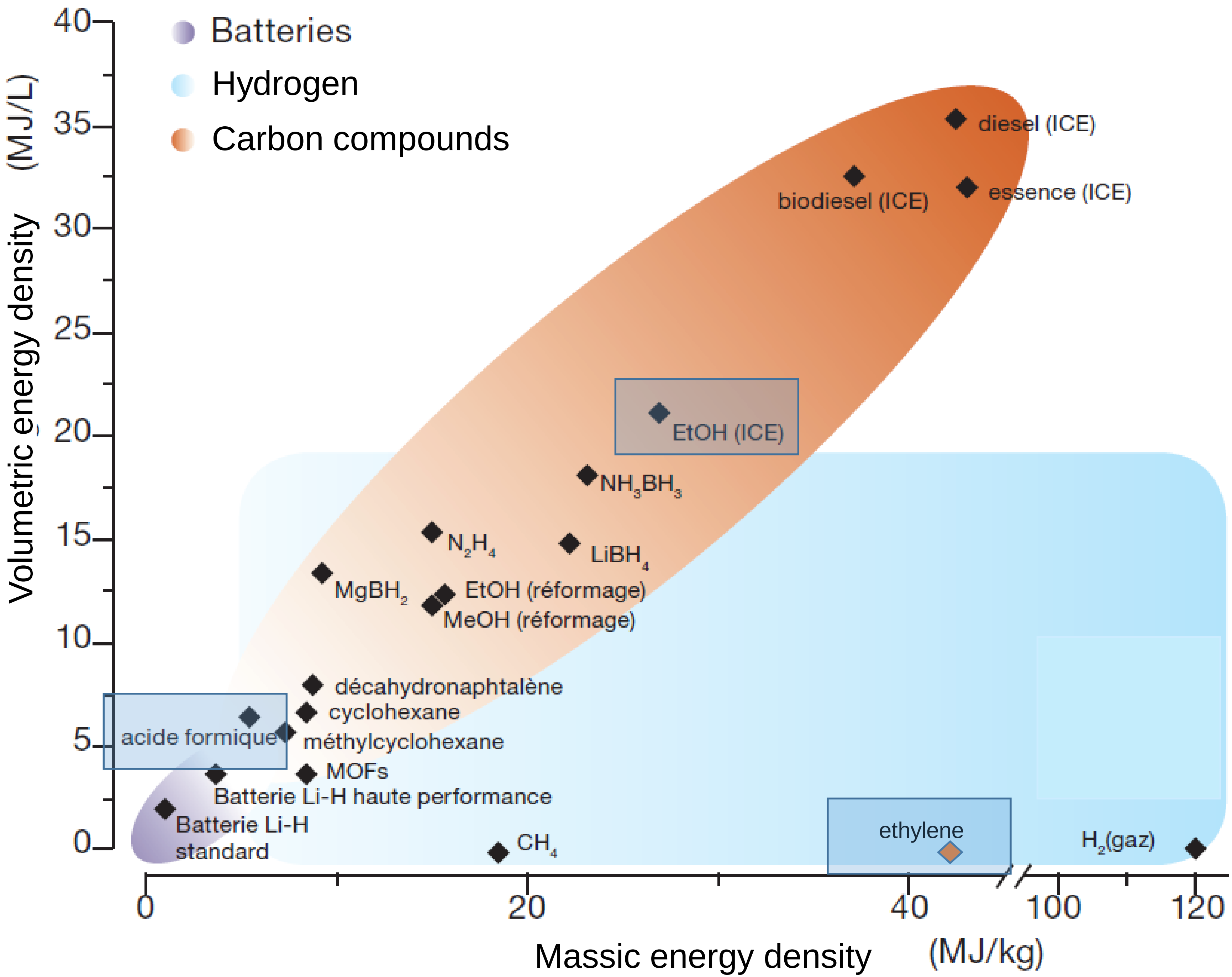
$2\ CO_2 + 12\ H^+ + 12\ e^- \rightarrow \mathbf{C_2H_4} + 4\ H_2O$

$2\ CO_2 + 12\ H^+ + 12\ e^- \rightarrow \mathbf{C_2H_5OH} + 3\ H_2O$



CO_2 photo-electro-reduction: solar energy storage and utilizable carbon





Batteries
Hydrogen
Carbon compounds
Volumetric energy density (MJ/L)
40
35
30
25
20
15
10
5
0
diesel (ICE)
biodiesel (ICE)
essence (ICE)
EtOH (ICE)
NH_3BH_3
N_2H_4
$LiBH_4$
$MgBH_2$
EtOH (réformage)
MeOH (réformage)
décahydronaphtalène
cyclohexane
acide formique
méthylcyclohexane
MOFs
Batterie Li-H haute performance
Batterie Li-H standard
CH_4
ethylene
H_2(gaz)
0
20
40
100
120
Massic energy density (MJ/kg)

ETHYLENE

47.2 MJ/kg; 0.055 MJ/L

Ethylene → Polyethylene
(polyvinyl chloride, polystyrene)

Ethylene: 200 millions tons in 2018
(the largest of any organic chemical)

Currently

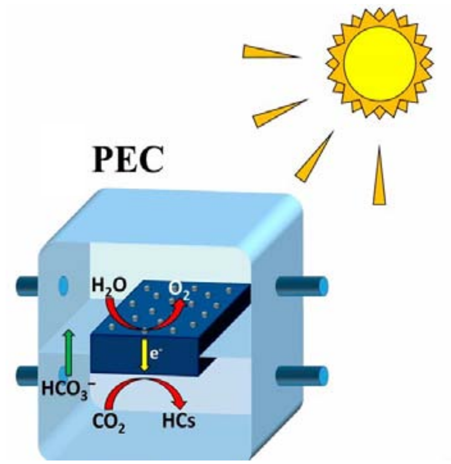
Steam cracking of naphta or saturated hydrocarbons
(750-950°C)

- ➢ Enormous energy inputs

(8% de the total primary energy consumption in chemical industry)

- ➢ Production of 2 tons CO_2 / ton ethylene)

Artificial photosynthesis: two scenarios

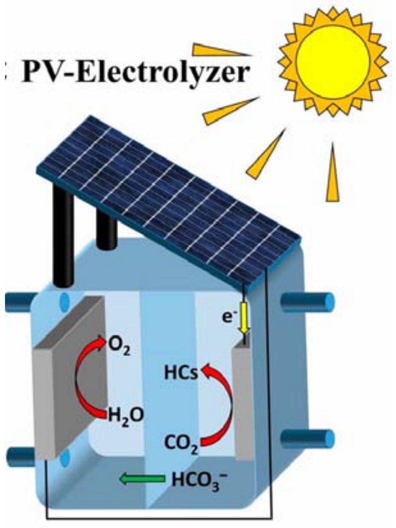


-

- Technology still immature
- Solar-To-Fuels efficiency <1%
- Low current densities (< 50 mA.cm-^{2})
- Integration > low tunability
- Light-degradation of catalysts
- Electrolyte-degradation of photoabsorber

+

- Integration > limited cost
- Mobility (free of electricity source)



+

- Mature technologies
- Closest to commmercialization
- PV-electricity price: 0.03$/kWh (↘)

(the electricity cost is the largest expense)

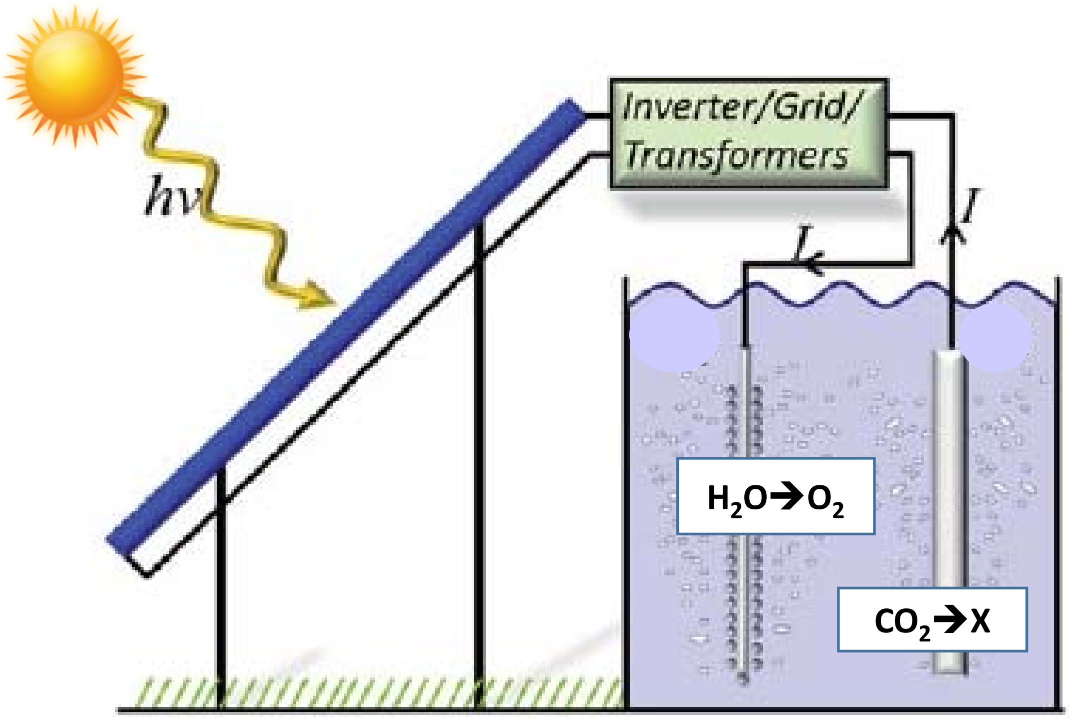
- Solar-To-Fuels yields 5-10 % (CO)
- System separation: tunable

(Independent optimization PV *vs* EC)

-

- PV to EC matching > cost

Artificial photosynthesis scenario : photovoltaics + electrolysis



MOLECULAR CATALYSTS

COPPER ?

CO_2 reduction: CHALLENGES

- **CATALYSIS**

Homogeneous/molecular catalysts ?
(which ligands? Which metal ions ?) → *Heterogeneization of molecular complexes*

Heterogeneous/solid catalysts ? → *Nanostructuration of surfaces*
Tailoring the morphology

Efficiency:
Highest current density: > 0.2 $A.cm^{-2}$

Lowest overpotential
(cathode: 0.4-1 V vs anode 0.2-0.3 V at 10-50 $mA.cm^{-2}$)

Stability (corrosion/deactivation) → *Use the same catalyst at both electrodes*
Earth-abundant materials
pH

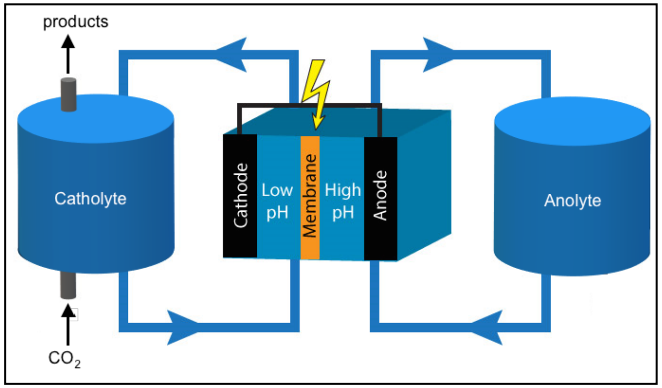
Cost
(the electricity costs are the largest contribution)

CO_2 reduction: CHALLENGES

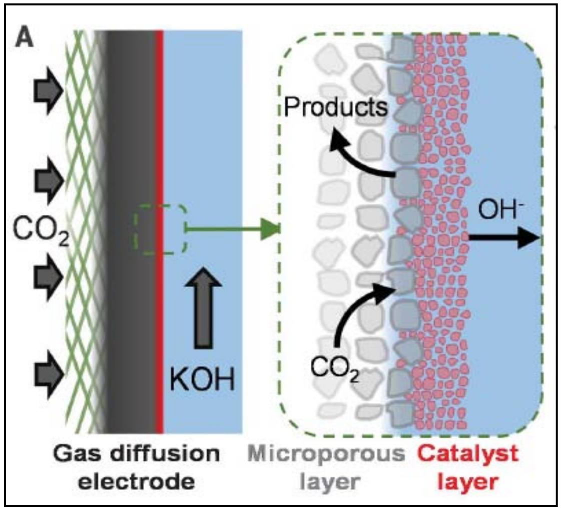
- **SOLVENT**

Water
(but low solubility of CO_2-30 mM)
Mass transport limitations

→ *Continuous flow electrochemical cell*
Gas diffusion electrodes



Liquid phase electrolyzer



Gas phase electrolyzer
(Gas diffusion electrode)

Electrolyte

→ *Optimization with ≠ cations/anions*
Ionic liquids ?

pH

→ *Alkaline electrolysis ?*
Neutral electrolysis ?

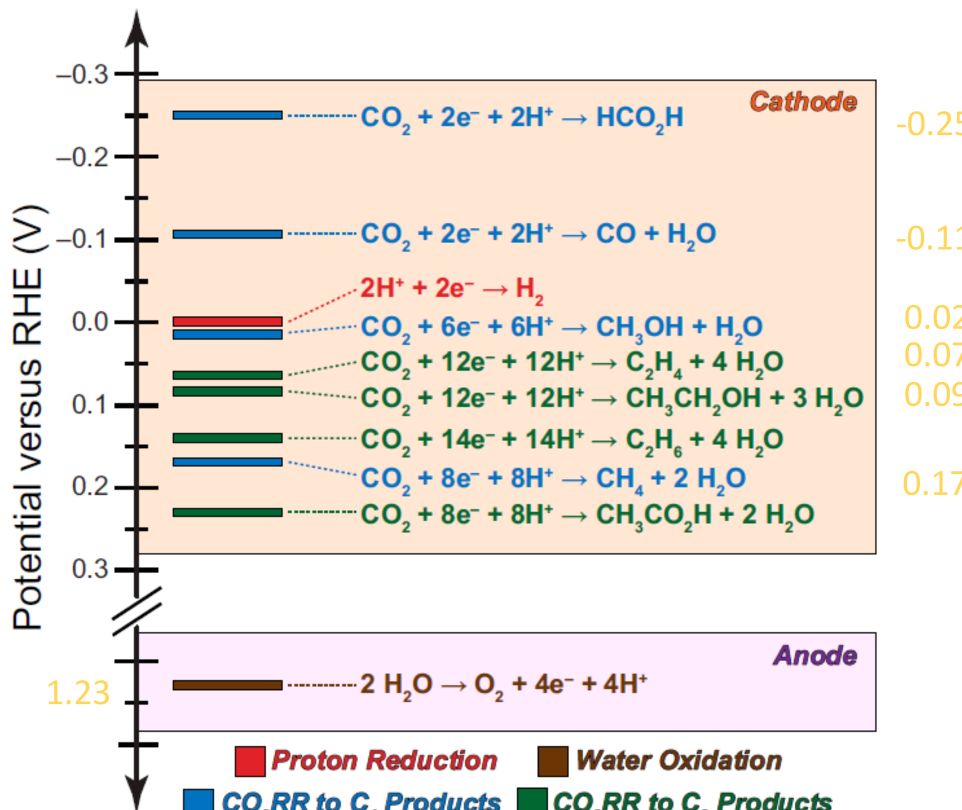
CO_2 reduction: CHALLENGES

- **SELECTIVITY**

How to avoid/control H_2 ?

How to direct the reaction towards the desired product ? (product purification)

Control by the
- *Catalyst (metal/morphology/ligand)*
- *Electrolyte*
- *Conductive support*



CO_2 reduction: CHALLENGES

- **PRODUCTS**

Liquid ? (ethanol, formic acid)

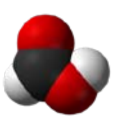
Gas ? (CO, CH_4,..)

2 e^- (CO,..) or ne^- (CH_4, C_2H_4..) products?

Fischer-Tropsch

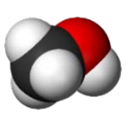
CO ($3B)

Economically unviable
(high CAPEX)+ CO_2 emissions



New markets ?

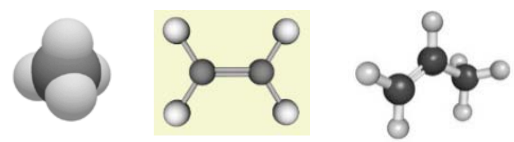
HCO_2H ($0.6B)



Fuel

CH_3OH

Rarely observed in CO2RR



Hydrocarbons

CH_4 too cheap
Ethylene interesting ($220B)
but currently cheap (shale ethane cracking)
Propylene very interesting

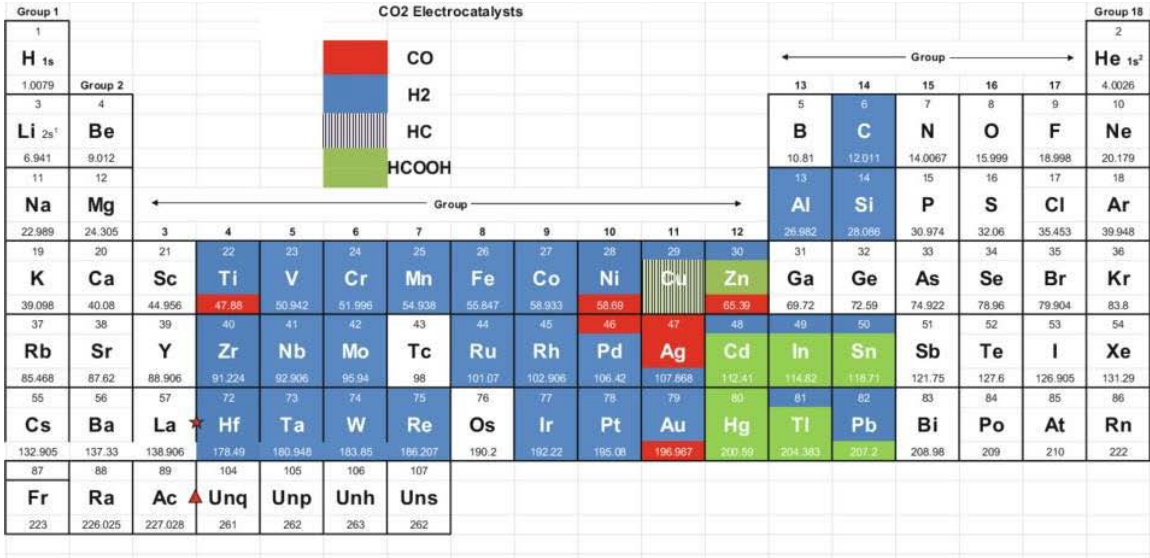
Alcohols

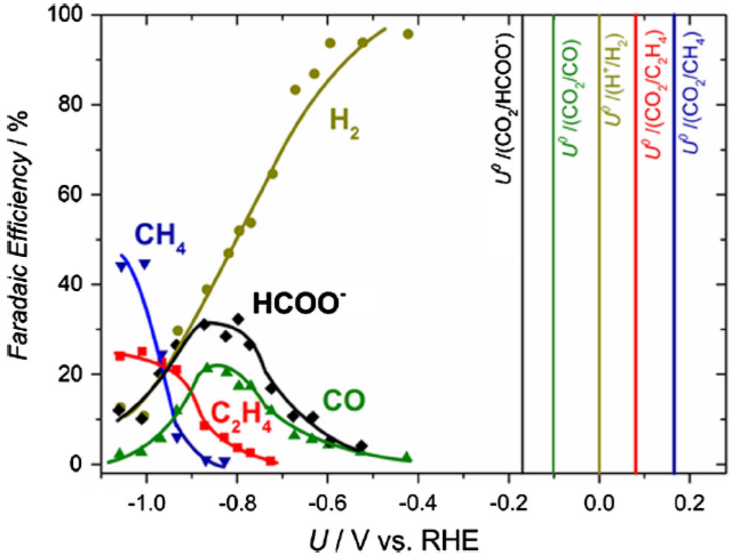
Ethanol very interesting ($75B)
+ propanol + ethylene glycol

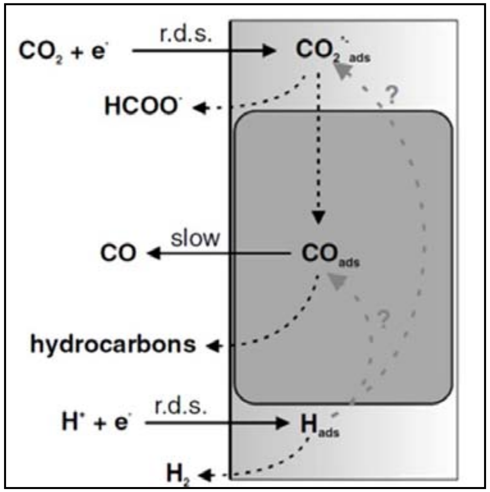
CO_2 reduction catalysis: Why Copper ?

- **METALS**

Pt, Fe, Co	**H_2**
Ag, Au, Pd, Zn, Ni	**CO**
Pb, Sn, Sn	**HCO_2H**
Cu	**Hydrocarbons**
	Alcohols

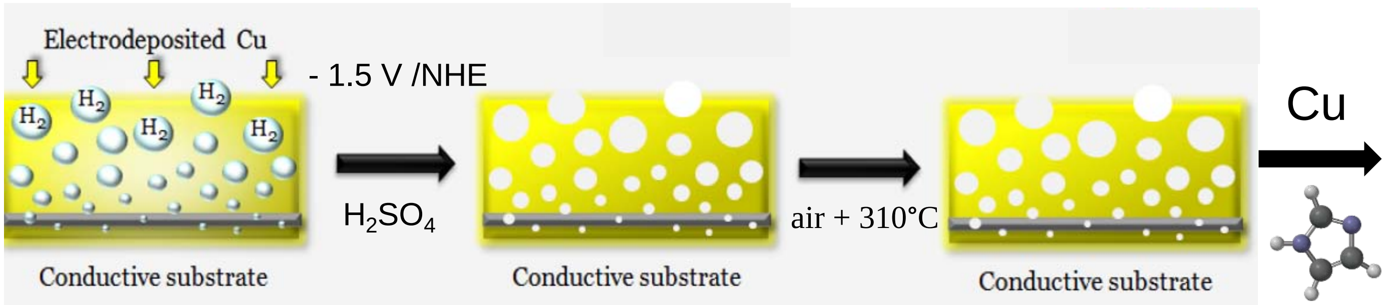


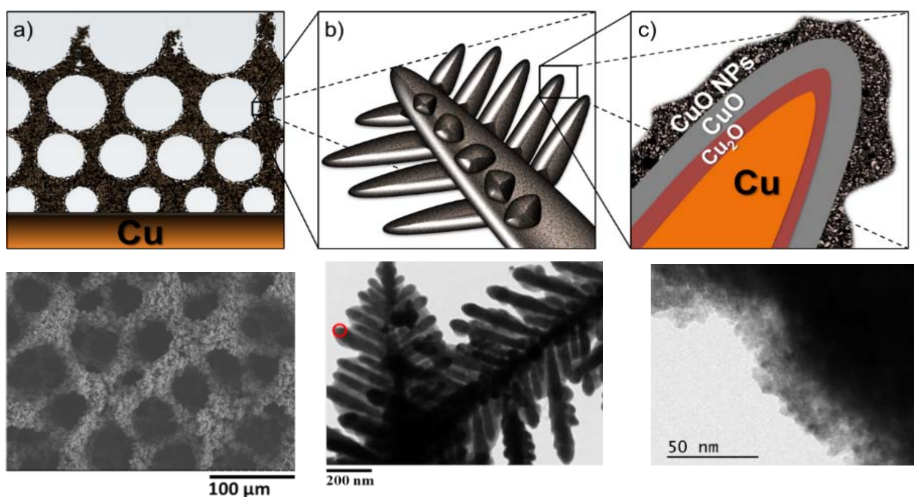




Porous dendritic Cu-based material

Nanostructuring surfaces
Tailoring the morphology





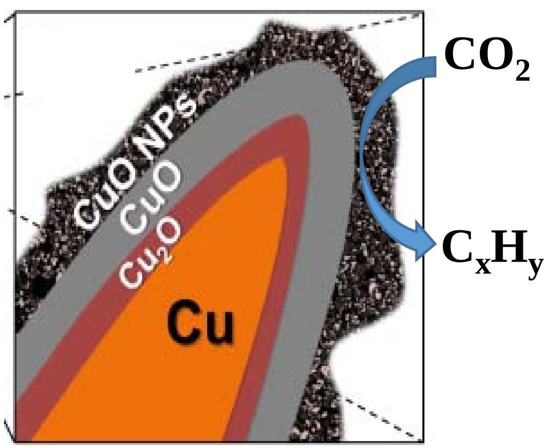
- ✓ *macro/micro-porous structure (efficient mass transfer)*
- ✓ *high (electrochemical) surface area*

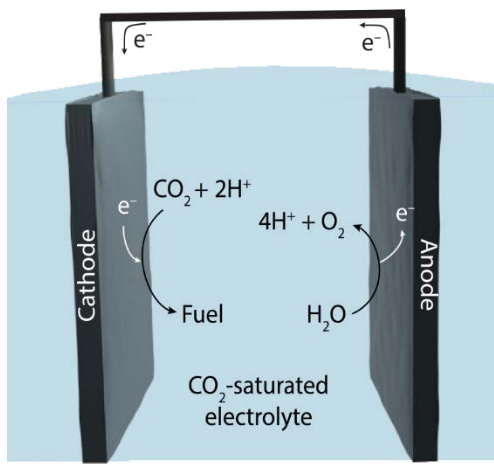
Angew. Chem. 2017, 56, 4792

Porous dendritic Cu-based material

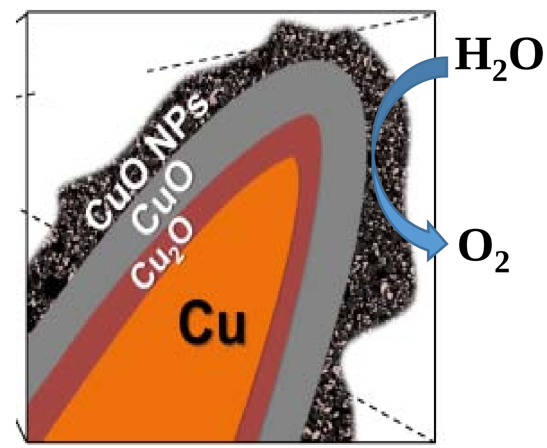
The same catalyst for the **anode** and the **cathode**

Dendritic porous Cu oxide Cathode





Dendritic porous Cu oxide Anode



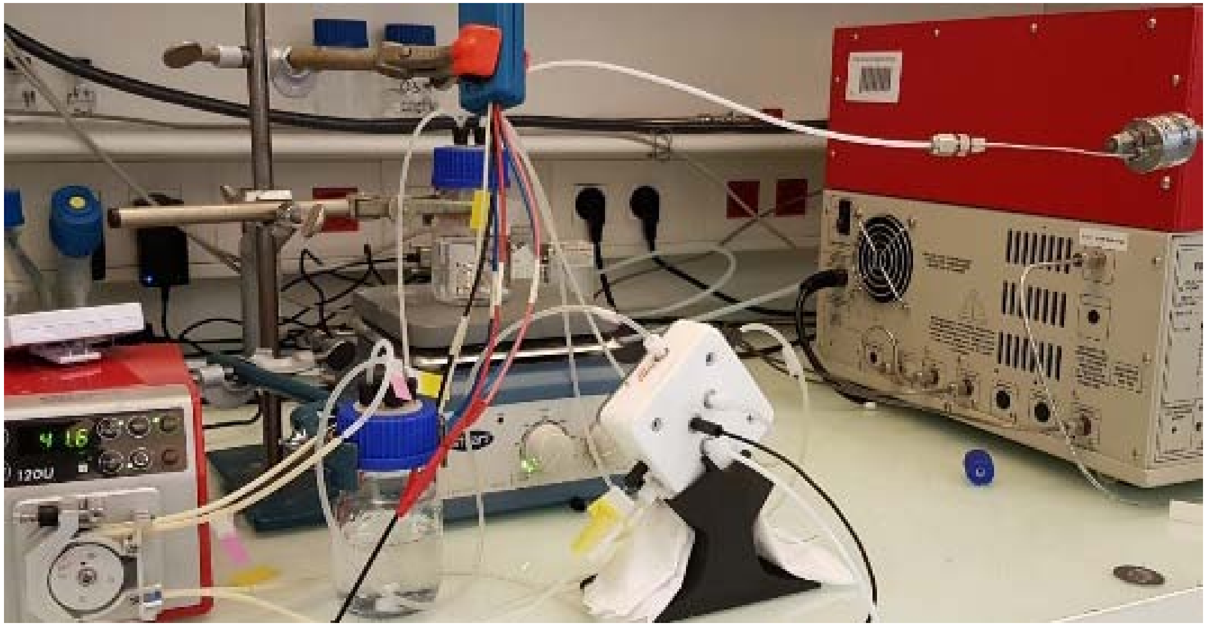
A stable and efficient CO_2 reduction catalyst :
Selective for **ethylene** formation

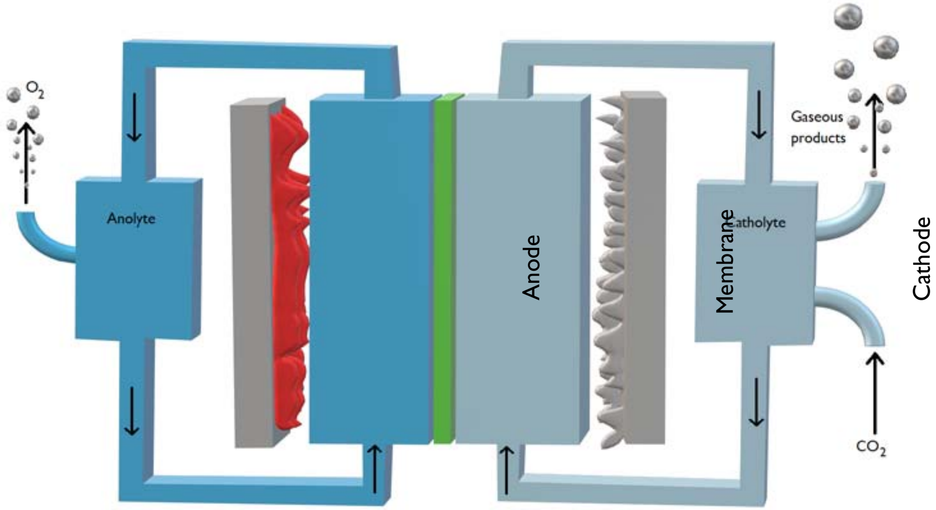
A stable and efficient O_2 evolution catalyst :
10 mA.cm^{-2} **at 280 mV overpotential** (1M NaOH)

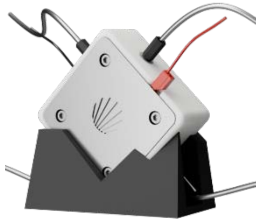
Proc. Natl. Acad. Sci. 2019, 116, 9735

Angew. Chem. 2017, 56, 4792

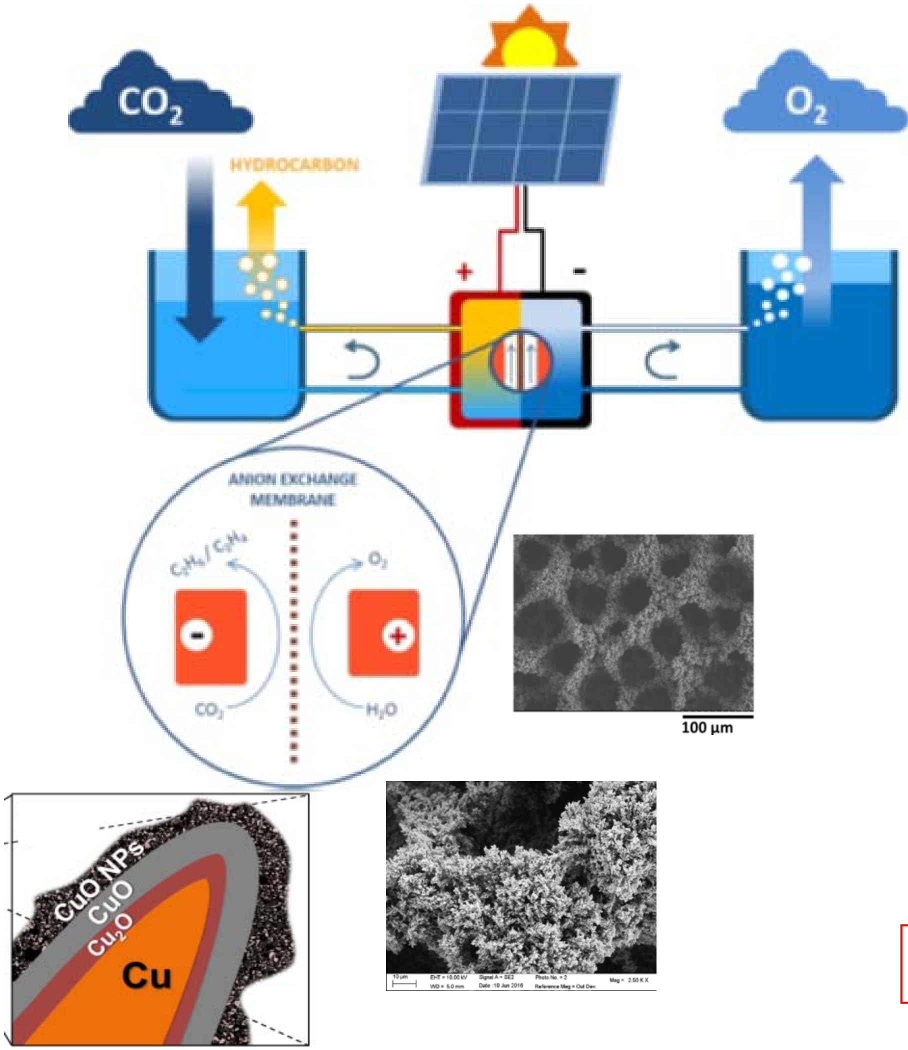
A flow electrochemical cell







From sun to hydrocarbons: photovoltaic + electrolyzer



PV coupled to Electrolyzer

F. Bella

perovskite solar cells
yield: 16.7%
delivering 2.8 V

Ethylene C_2H_4 (35%)
Ethane C_2H_6 (8%)
H_2 42%; HCOOH 6%; CO 5%

Current density 18 mA.cm^{-2}

$$2\ CO_2 + 2\ H_2O \rightarrow C_2H_4 + 3\ O_2$$

Solar-to-hydrocarbon efficiency : 2.3 %

Proc. Natl. Acad. Sci. 2019, 116, 9735-9740

From sun to hydrocarbons: photovoltaic + electrolyzer

photovoltaics	cathode	anode	electrolyte	product	solar to fuel efficiency (%)	partial current density (mA/cm^2)[a]
Si	Cu_2O-derived Cu	IrO_x	0.2 M $KHCO_3$	C_2H_4	1.5	6.5
Si	In	IrO_x	1 M $KHCO_3$	HCOOH	1.4–1.8	N.R.[b]
Si + InGaN	In	Ni–O	3 M $KHCO_3$	HCOOH	0.97	~ 0.4
SiGe	Ru-based polymer	IrO_x	0.1 M phosphate buffer (K_2HPO_4:KH_2PO_4 = 1:1)	HCOOH	4.6	~ 0.1
GaAs/InGaP	Pd/C	Ni	2.8 M $KHCO_3$/BPM/1.0 M KOH	HCOOH	10	~ 8
Si	Au	CoO_x	0.5 M $KHCO_3$	CO	2.0	~ 1.5
$Cu(In_xGa_{1-x})(S_ySe_{1-y})_2$	Au	Co_3O_4	0.5 M $KHCO_3$	CO	4.23	N.R.
perovskite	Au	IrO_2	0.5 M $NaHCO_3$	CO	6.5	~1.4
Si	WSe_2	Co–O/OH	50% EMIM-BF_4 in water (cathode)/potassium phosphate buffer (anode)	CO	4.6	N.R.

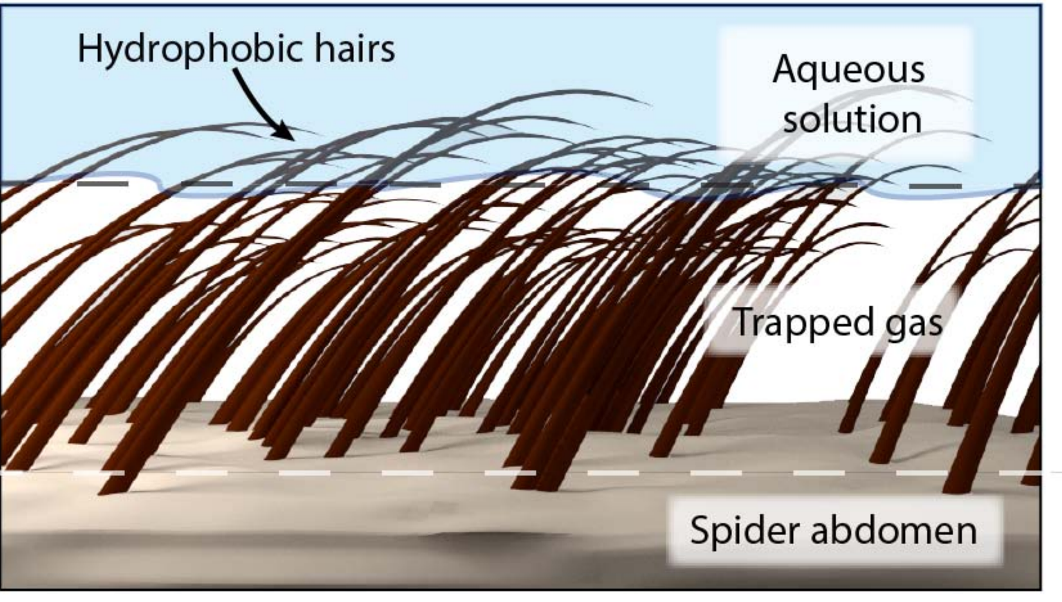
ACS Sustainable Chem. Eng. 2017, 5, 9191

Hydrophobicity and Nature

Nature has special mechanisms to keep gas trapped at a surface when submerged

Diving bell spider

Plastron

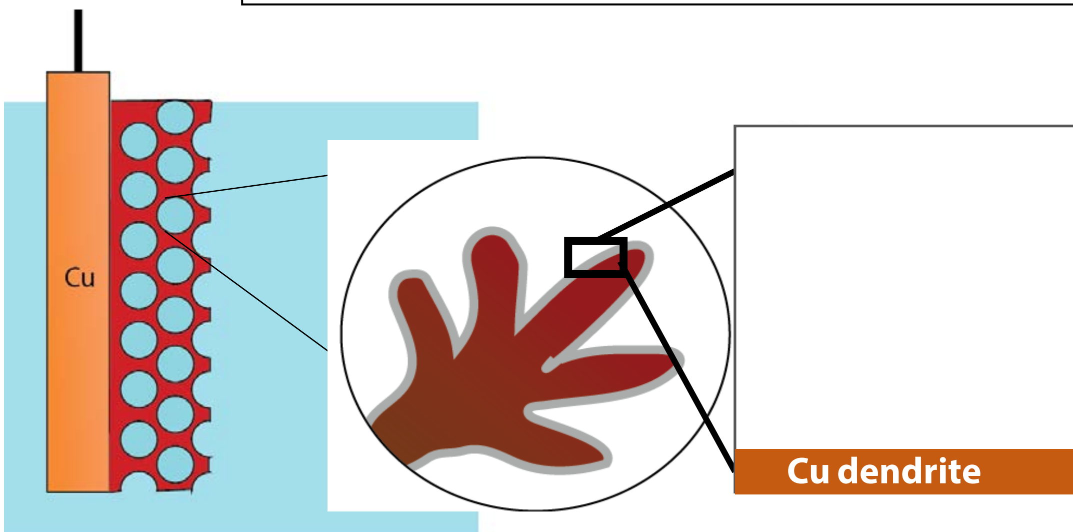


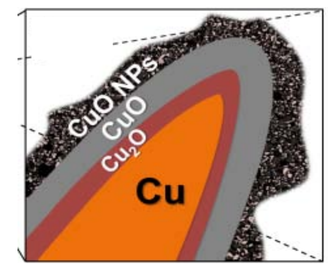
Gas trapping is controlled by hydrophobic hairs called 'a plastron'

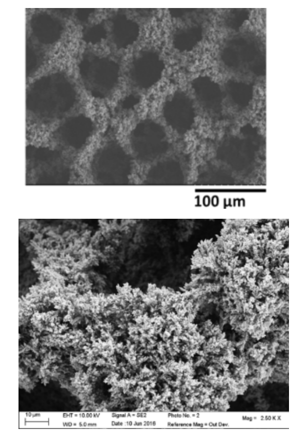
This allows the spider continue to breathe underwater

Can a similar effect be exploited for CO_2 reduction using hydrophobicity?

Towards more selective CO_2 reduction: Hydrophobic surface modification

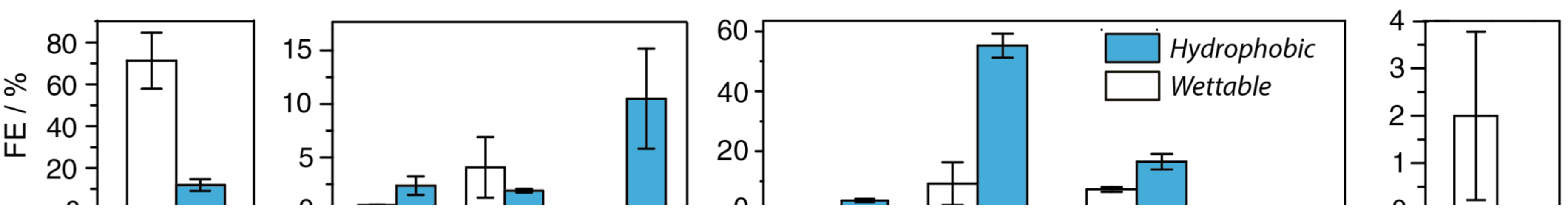






Controlled current electrolysis (*30 mA.cm*$^{-2}$)

in 0.1 M $CsHCO_3$ *with* CO_2 *at flow rate of 5 ml min*$^{-1}$.

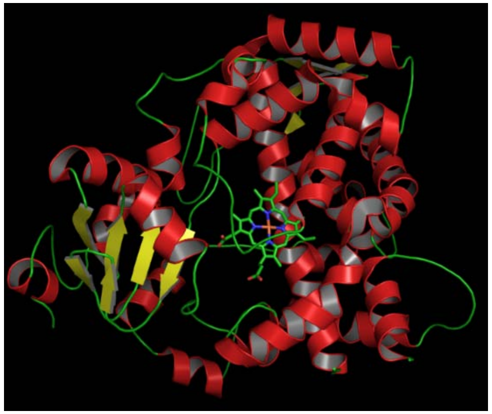


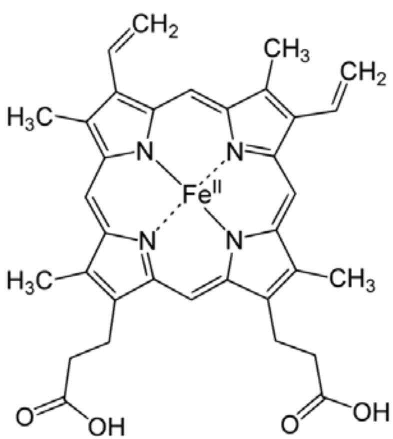
Wettable dendrite requires –1.1 V *vs.* RHE
Hydrophobic dendrite requires –1.5 V *vs.* RHE

Nature Materials 2019, 18, 1222-1227

Flow of CO_2 on the hydrophobic dendrite

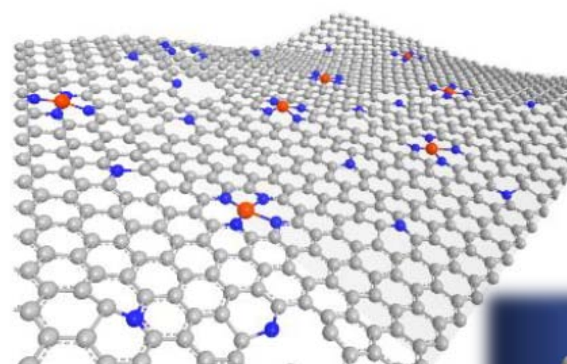
Bioinspired heterogeneous catalysts
Cu for the conversion of CO_2 into Ethanol

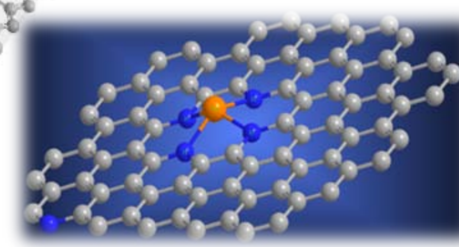




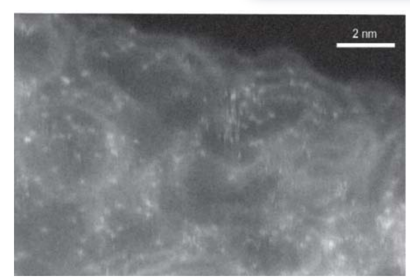
ZIF-8
Cu(II)Cl_2
Phen

1050 °C
Ar





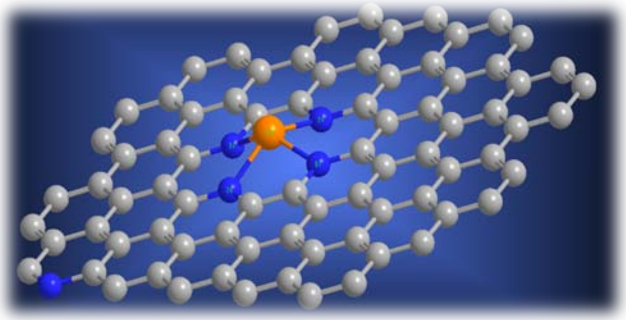
N,Cu-doped carbon materials

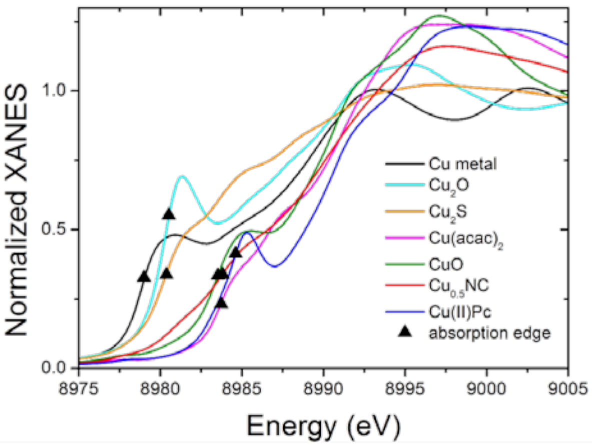


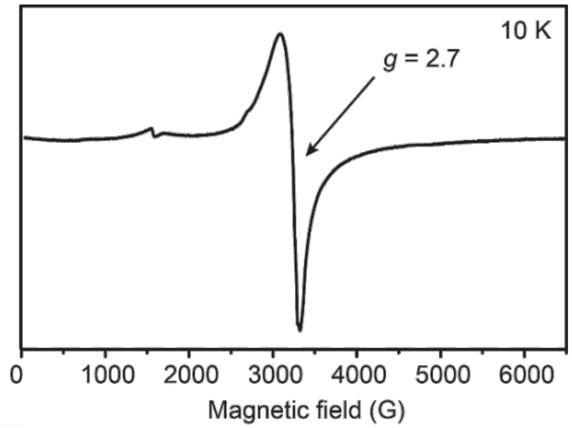
Angew. Chem. 2019, <u>58</u>, 15098-15103

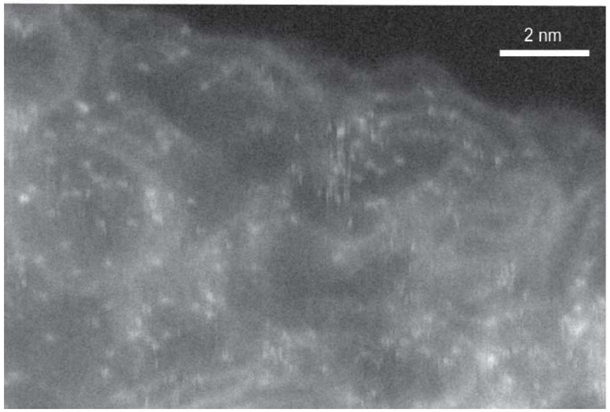
Dilan Karapinar

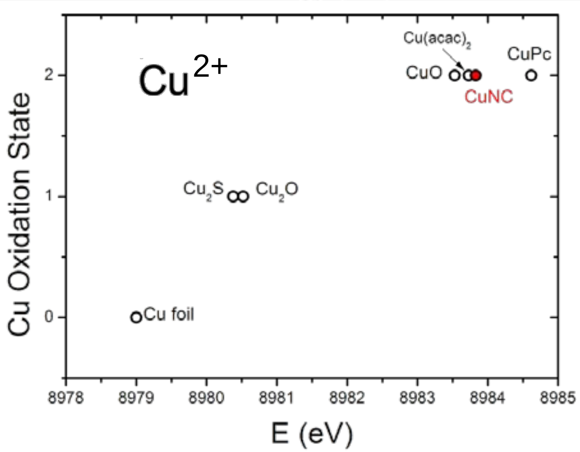
Cu for conversion de CO_2 into Ethanol !!

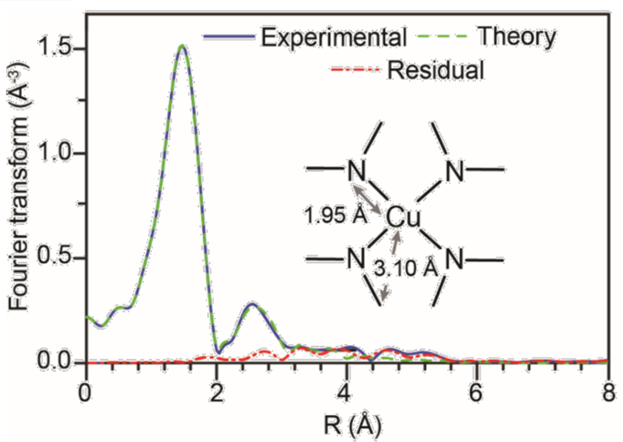








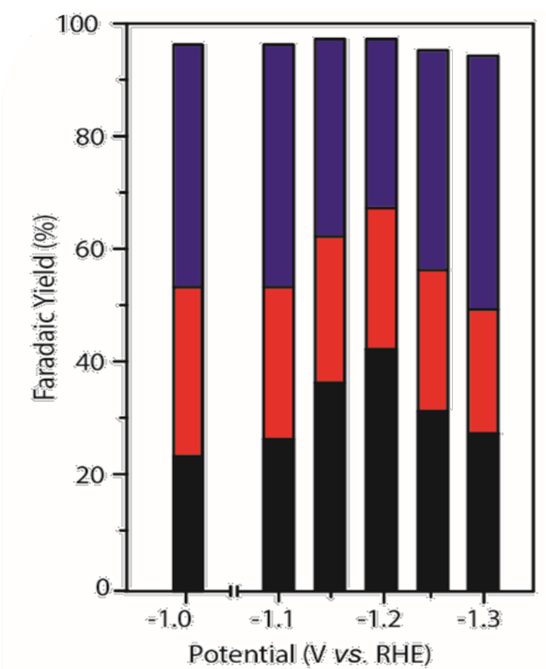


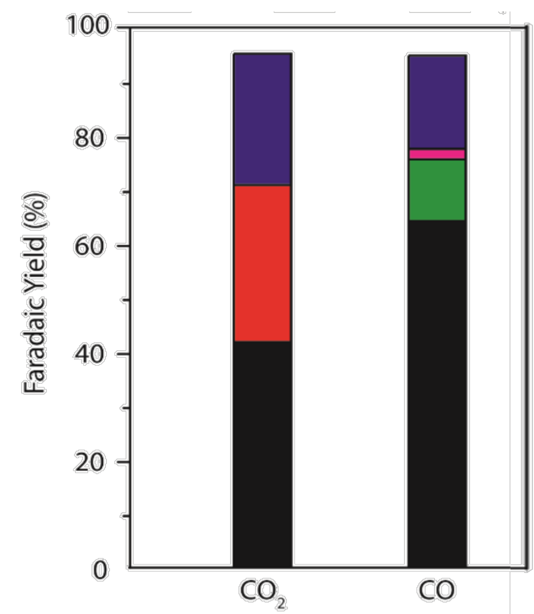


Cu for conversion de CO_2 into Ethanol !!

CO_2 reduction

CO reduction



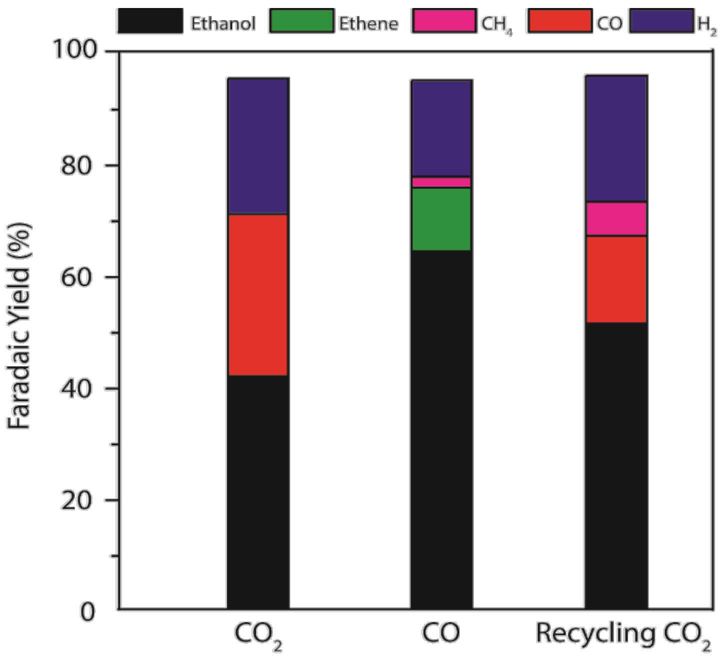


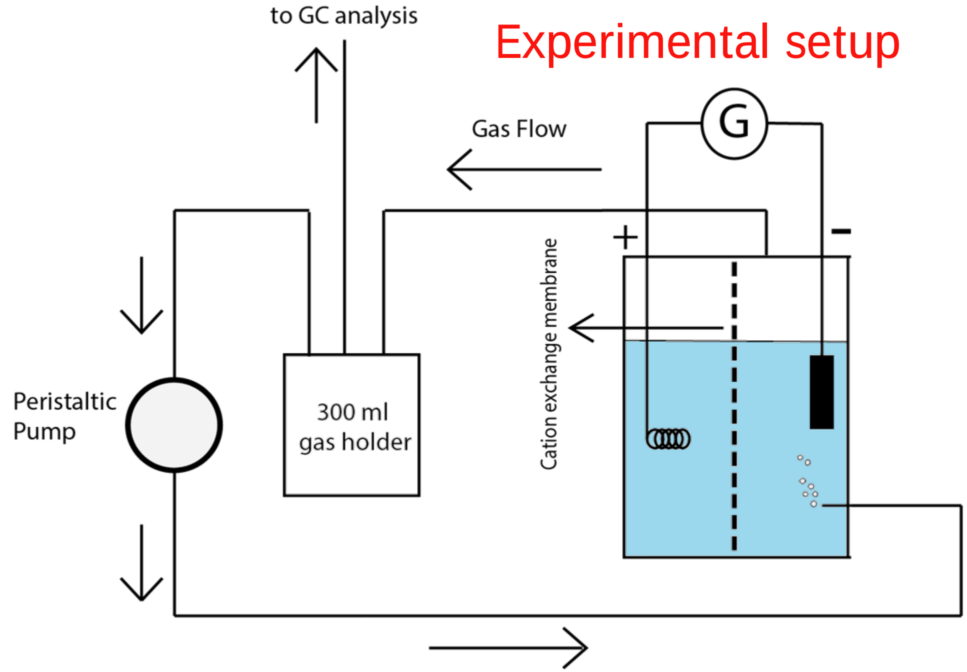
Ethanol (45%):
the only product in liquid phase

0.1 M $CsHCO_3$ (pH 6.8)
AEM membrane
2.5 mL_{CO2}/min

Ethanol (66%):
C_2 products (75%)

Cu for conversion de CO_2 into Ethanol !!





> 55% FY ethanol from CO_2 electroreduction

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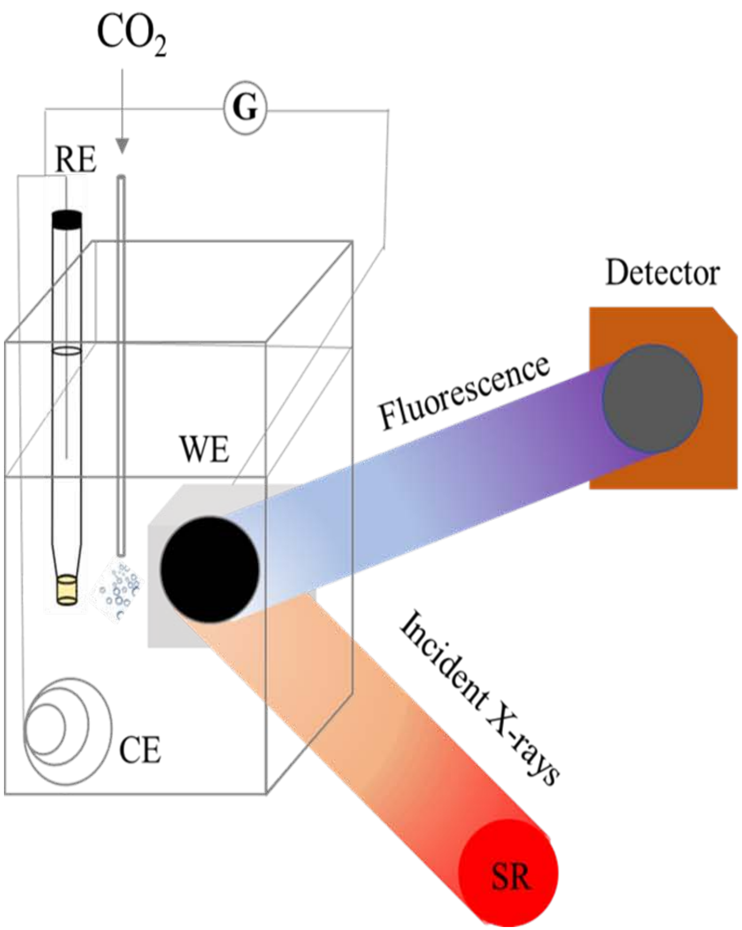
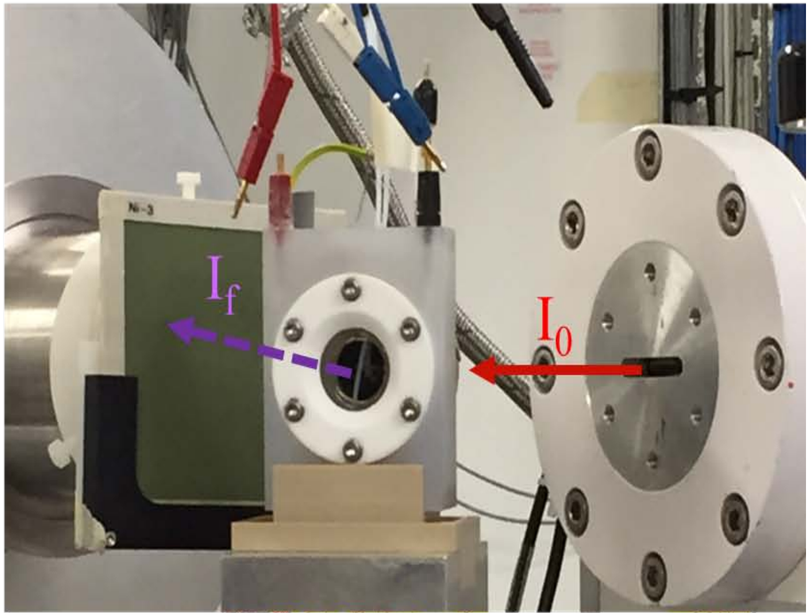
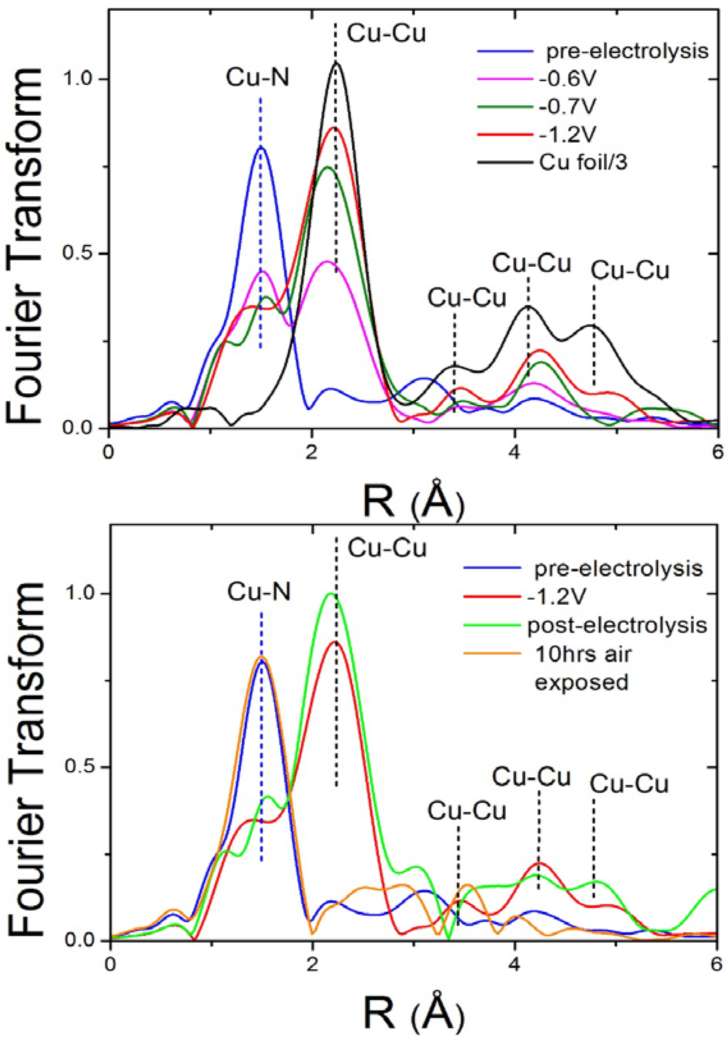
Operando in situ EXAFS



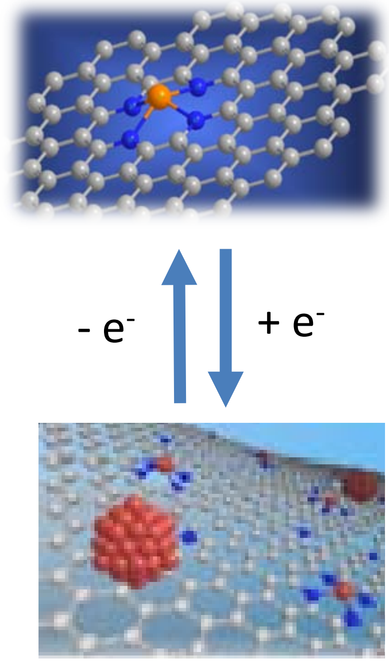


X-ray spectroelectrochemical setup used at the SAMBA beamline. RE, CE and WE stand for reference, counter and working electrode. SR stands for synchrotron radiation

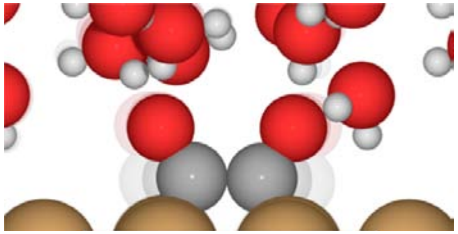
Active sites: transient Cu nanoparticles ?



Operando XAS characterization of Cu-NC



Coupling CO*/CO*:
formation of C-C bonds



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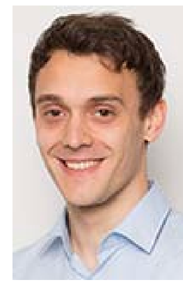
Victor Mougel

Tran Ngoc Huan

Sarah Lamaison

Dilan Karapinar



David Wakerley

Acknowledgments

Collège de France

Dr Victor Mougel

Dr. Huan Ngoc Tran

Dilan Karapinar

Dr. David Wakerley

Sarah Lamaison

Dr. Gwenaëlle Rousse

ICGM

Dr. Frédéric Jaouen

Dr. Nastaran Ranjbar

Soleil

Dr. Andrea Zitolo

UPMC

Prof. Nicolas Menguy

Dr. Dario Taverna

Chimie Paristech

Dr. Sandrine Zanna

University of Torino

Dr Federico Bella

Copper for artificial photosynthesis

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