# *Low-cost nanocatalysts for the electrochemical $CO_2$ reduction to valuable products*


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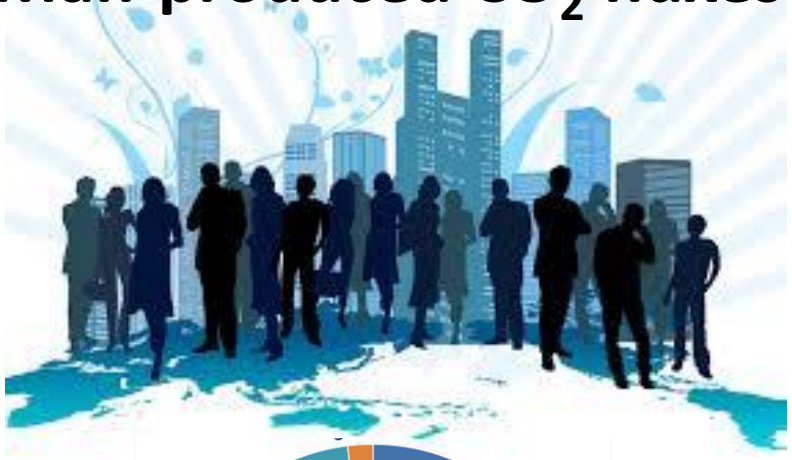
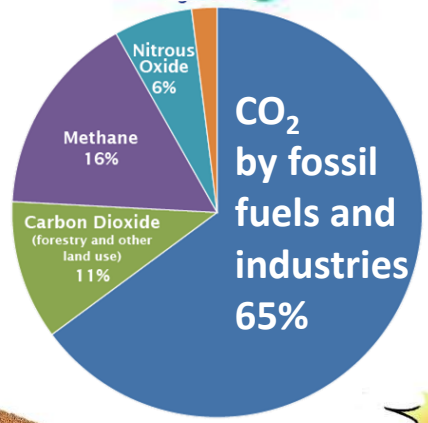
# Man-produced $CO_2$ fluxes



## Food

## GHG emissions:




## Combustion

## Wastes (residues)

**0,3 Gton di C/y**

Source: FAO (2016)

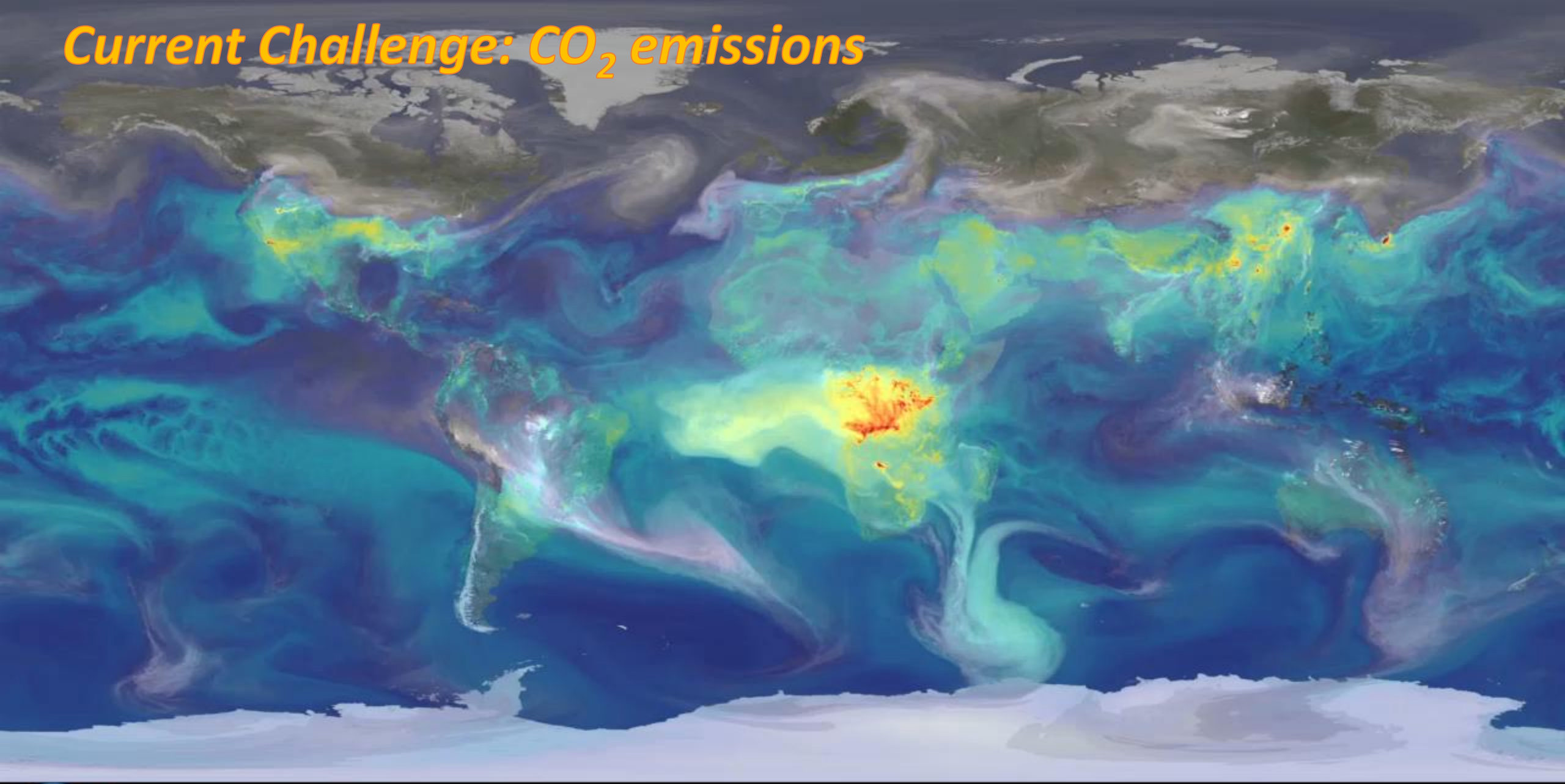
**2,6 Gton/y**

## $CO_2$ in flue gases

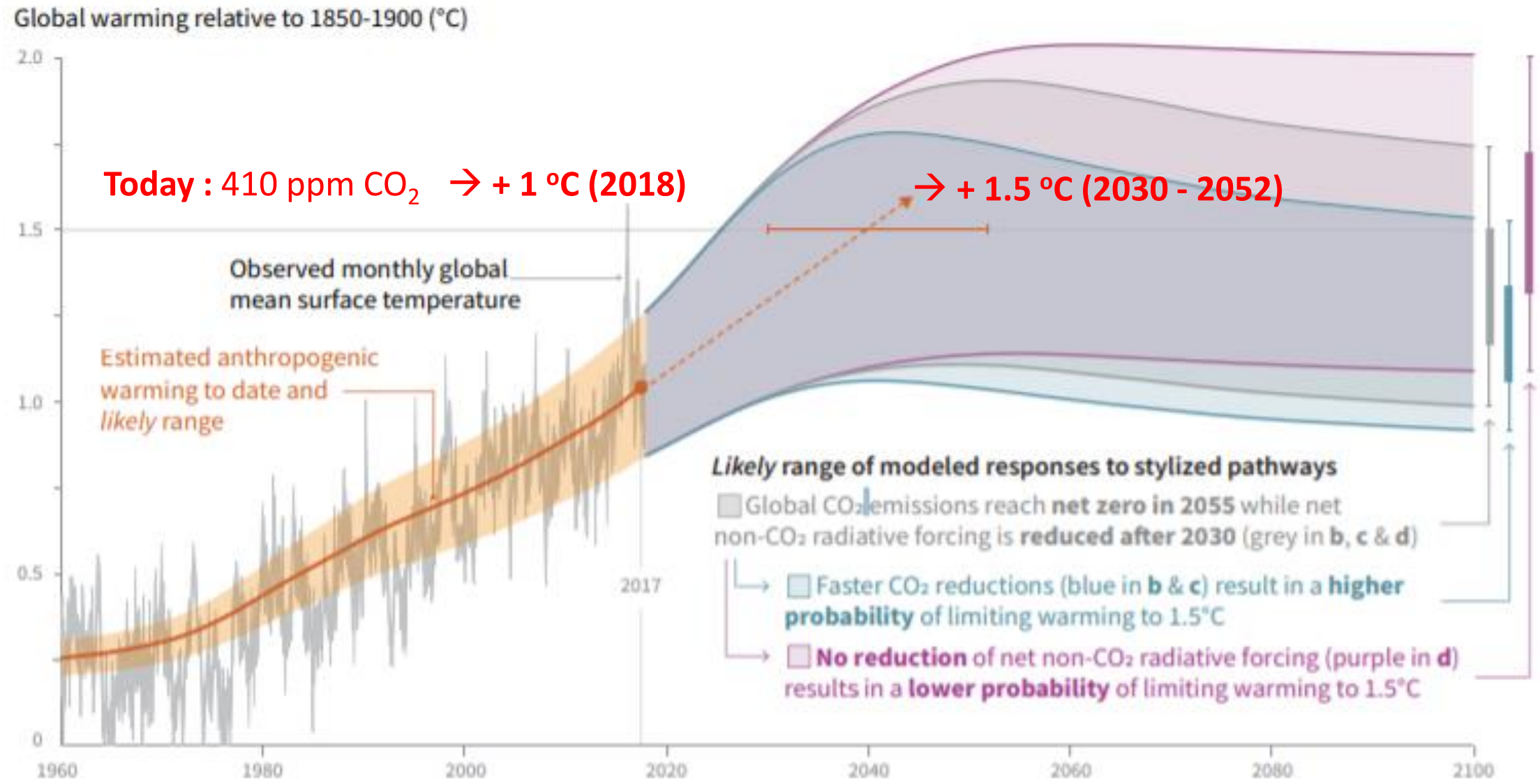
**9,7 Gton di C/y**

Source: NATURE CLIMATE CHANGE | JAN 2016 |

# Current Challenge: $CO_2$ emissions

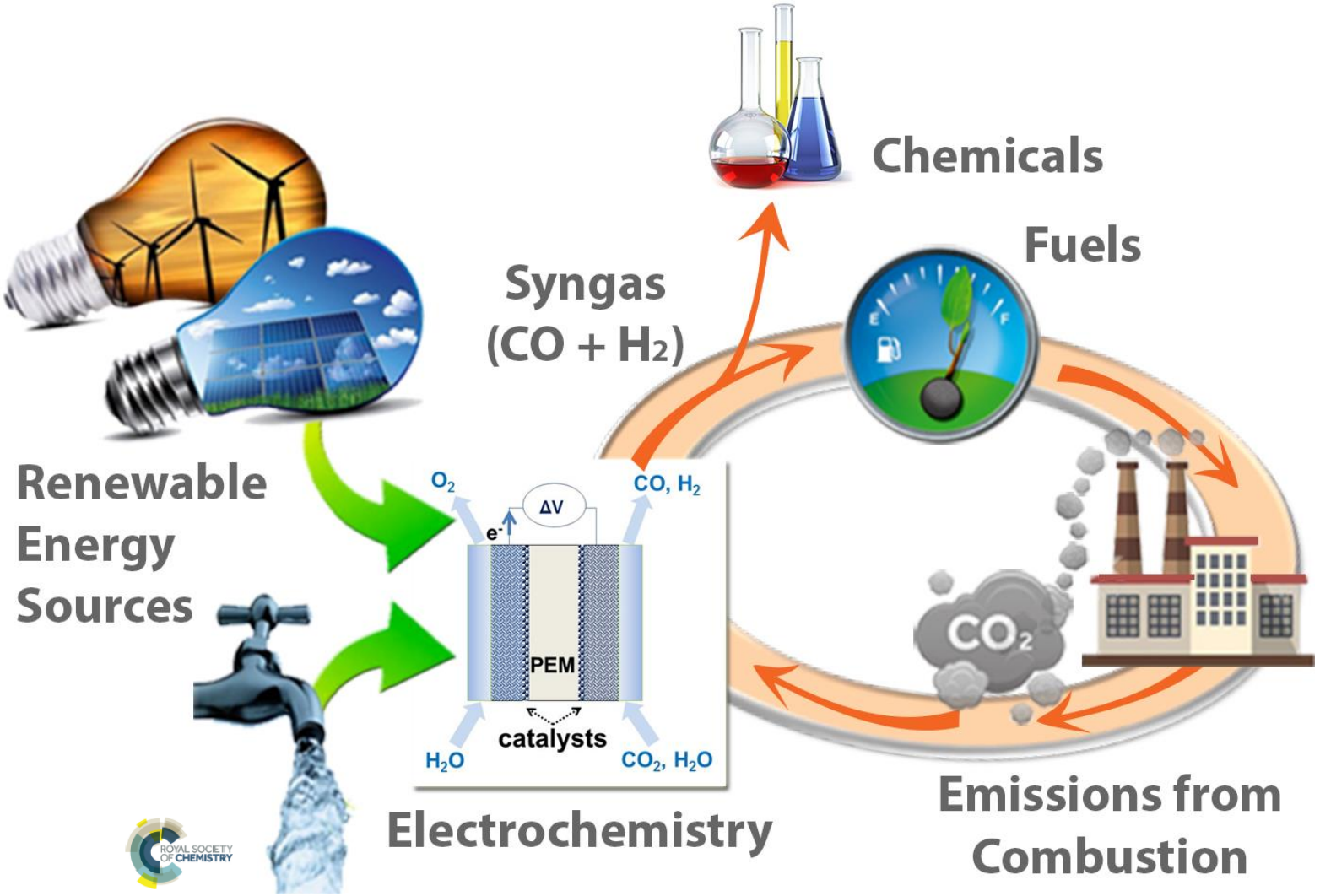


# Variation of the mean global temperature & predictive models *vs. future global $CO_2$ emissions*




**Source:** IPCC Special Report 2018, Global Warming of 1.5°C, Figure SPM.1

# $CO_2$ recycling by electrochemistry




Green Chemistry

CRITICAL REVIEW

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Cite this: *Green Chem.*, 2017, **19**, 2326

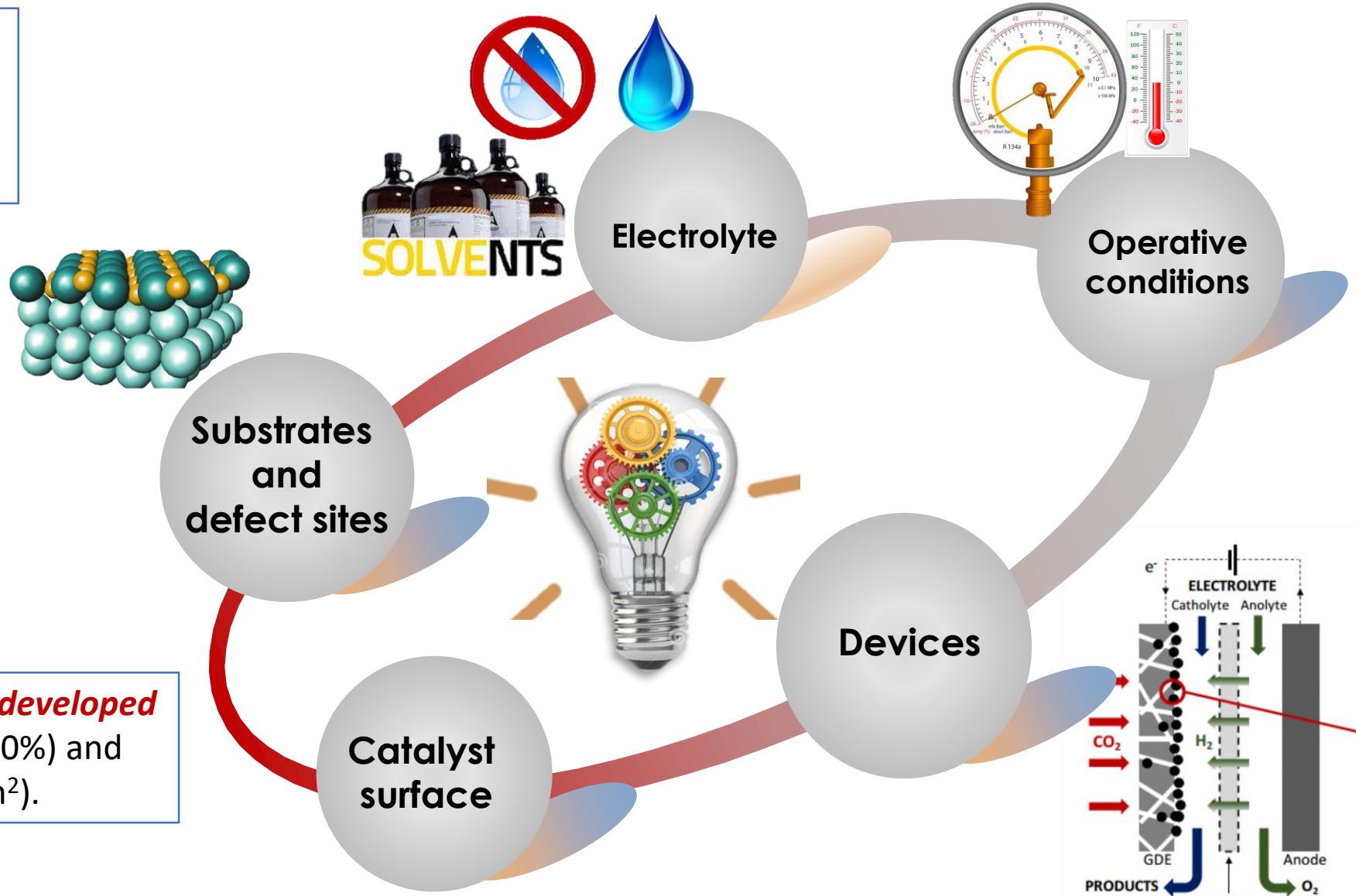
Syngas production from electrochemical reduction of $CO_2$: current status and prospective implementation†

Simelys Hernández,[*a,b] M. Amin Farkhondehfal,[a] Francesc Sastre,[c] Michiel Makkee,[c] Guido Saracco[b] and Nunzio Russo[a]

Hernández S., *et. al.* ***Green Chem., 2017, 19, 2326–2346***.

# *Challenges of Photo/Electrocatalytic $CO_2$ reduction to Fuels*

***A Multidisclipinary approach is necessary*** **for engineering** of catalysts, electrocatalytic reactor and process conditions.




***Novel low-cost catalysts has to be developed*** to achieve high selectivity (FE > 90%) and productivity ($j$ > 200 mA/cm$^2$).

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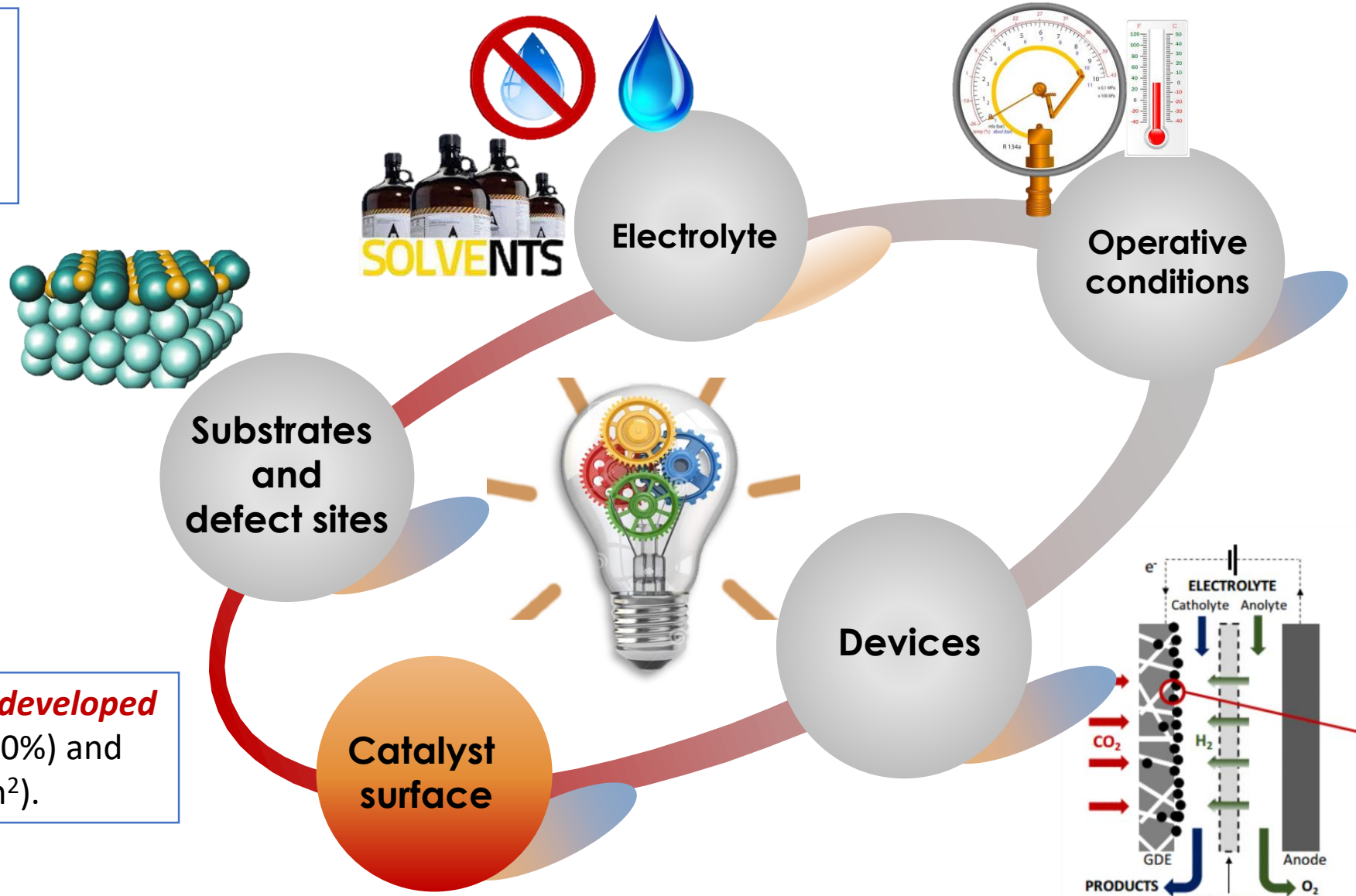
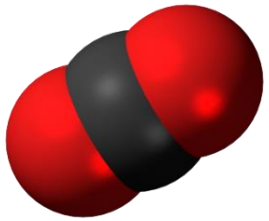
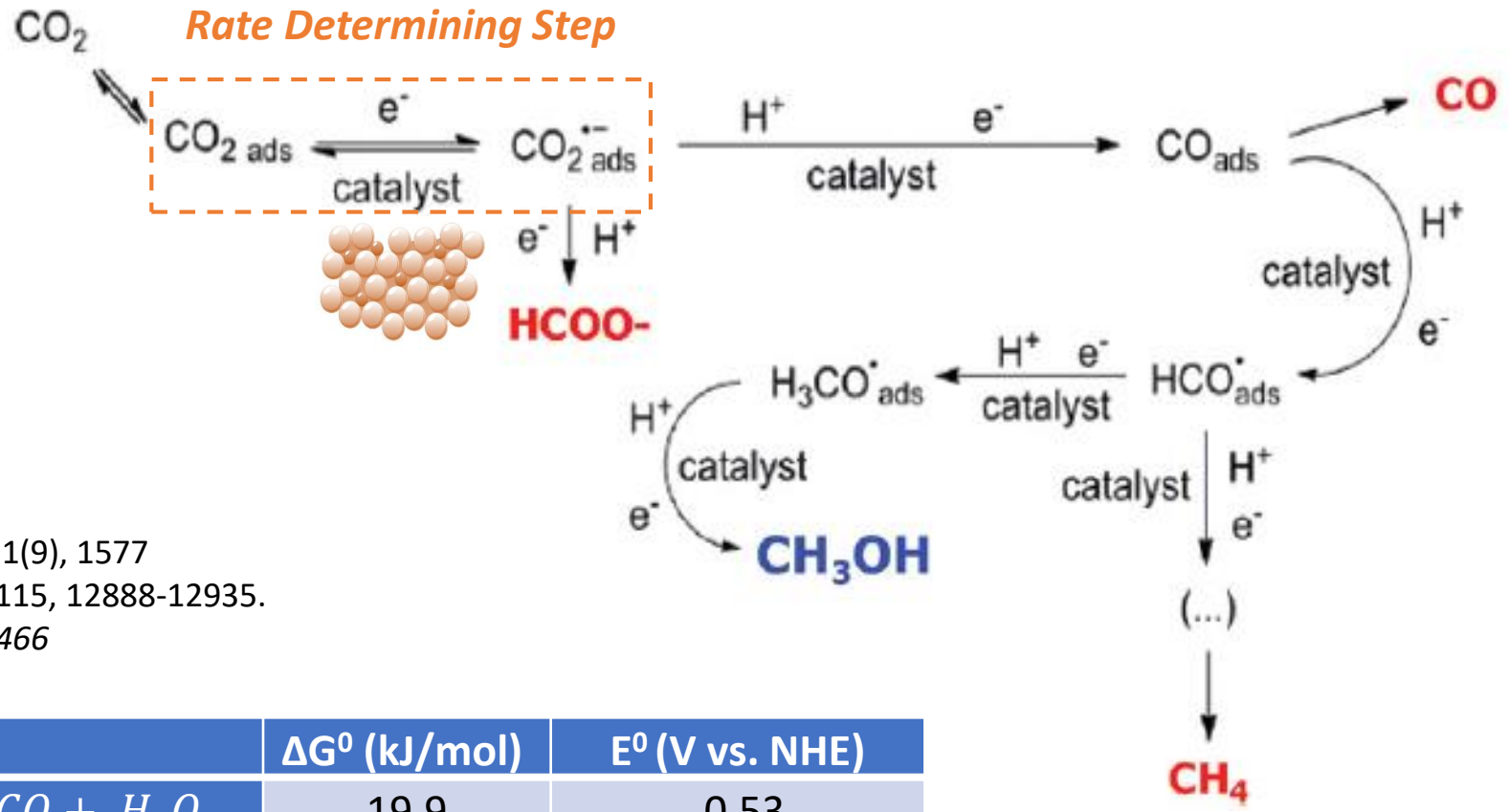



***Novel low-cost catalysts has to be developed*** to achieve high selectivity (FE > 90%) and productivity ($j$ > 200 mA/cm$^2$).

# *Electrochemical Reduction of $CO_2$: a multiple-steps reaction*

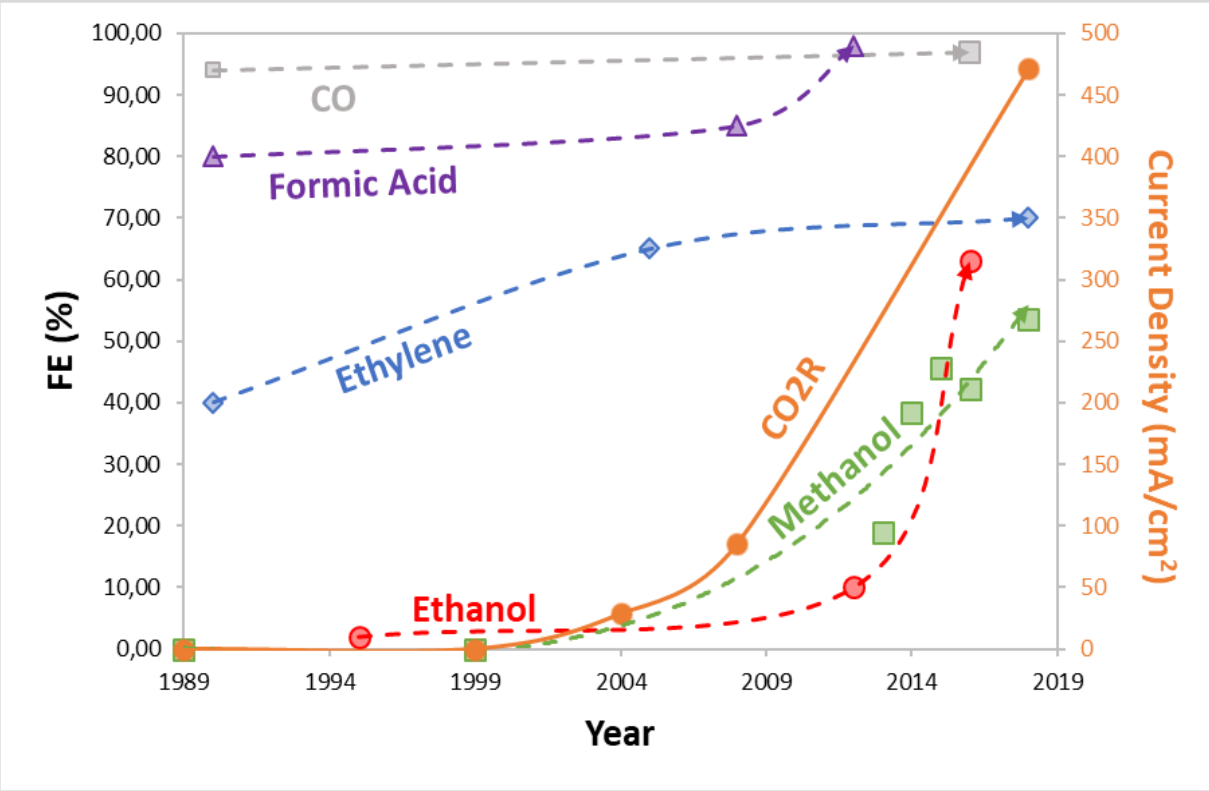





- Y. Lan, *et. al.* Int. J. Electrochem. Sci., 2014, 1(9), 1577
- J. L. White, *et. al.* Chemical Reviews, 2015, 115, 12888-12935.
- *Jones et. al. Isr. J. Chem. 2014, 54, 1451 – 1466*

| Reaction | $\Delta G^0$ (kJ/mol) | $E^0$ (V vs. NHE) |
|---|---|---|
| $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$ | 19.9 | -0.53 |
| $CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$ | 38.4 | -0.61 |
| $CO_2 + 4H^+ + 4e^- \rightarrow H_2CO + H_2O$ | 27.5 | -0.48 |
| $CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$ | -130.8 | -0.38 |
| $CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$ | -17.3 | -0.24 |
| $CO_2 + e^- \rightarrow CO_2^{\circ -}$ | 183.32 | -1.9 |

# State-of-the-art
## Electrocatalytic $CO_2$ reduction to Fuels




Adapted from: De Luna et al., Science 364, eaav3506 (2019).

**State-of-the-art:**

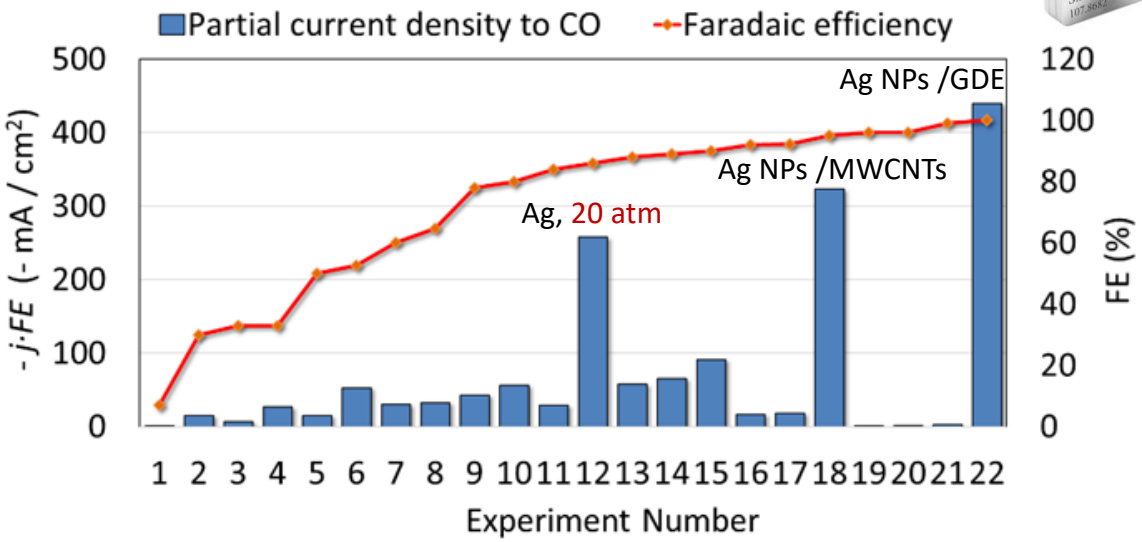
- *Currently, only CO and formic acid (HCOOH) and ethylene have been obtained with a relevant productivity to be scaled up.*

- ***Higher energy density products*** *(ethanol, methanol, propanol, etc) have not reached high selectivity & conversion efficiencies*

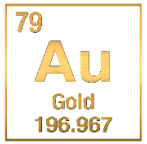
*H. Guzmán,…, S. Hernández et. al. Photo/electrocatalytic hydrogen exploitation for solar fuels production, Chapter 11 in: Handbook of Hydrogen Production from Solar Energy, Elsevier.*

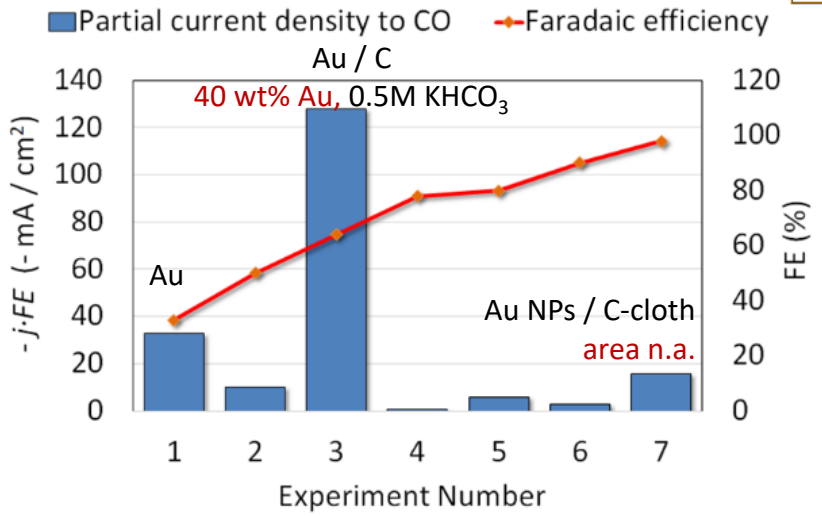
# Electrocatalysts for the $CO_2$ reduction to CO

## Ag-based catalysts

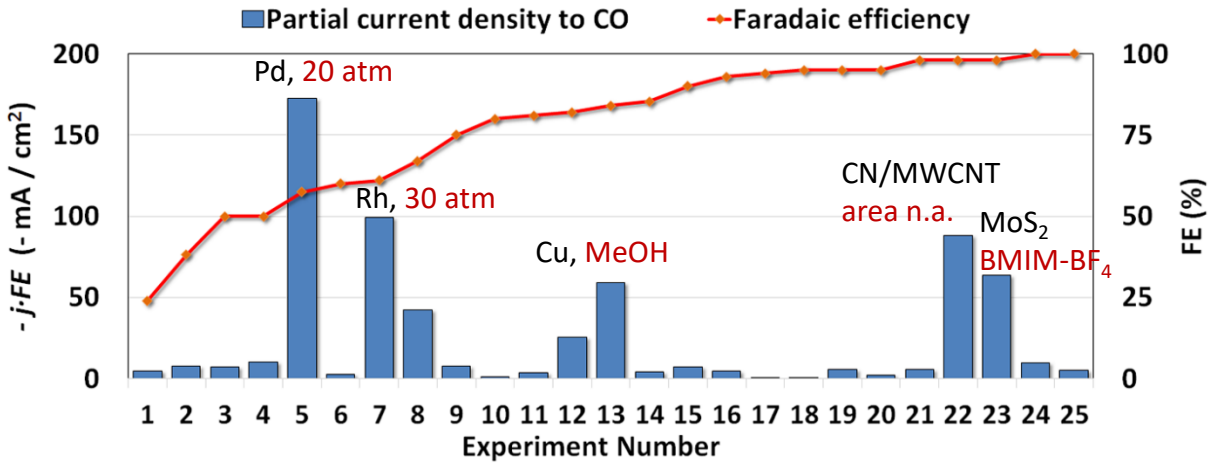




## Au-based catalysts



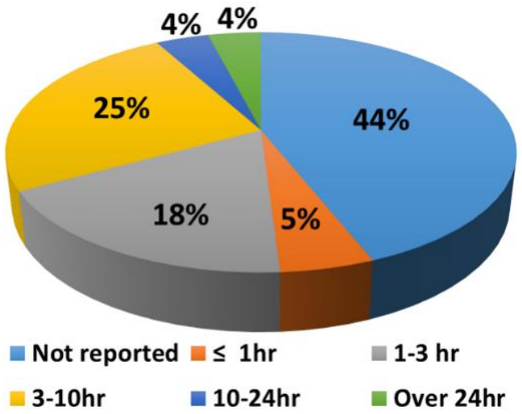

## Others




***Appropriate current densities have been achieved but..***

***Criticisms for scale up:***

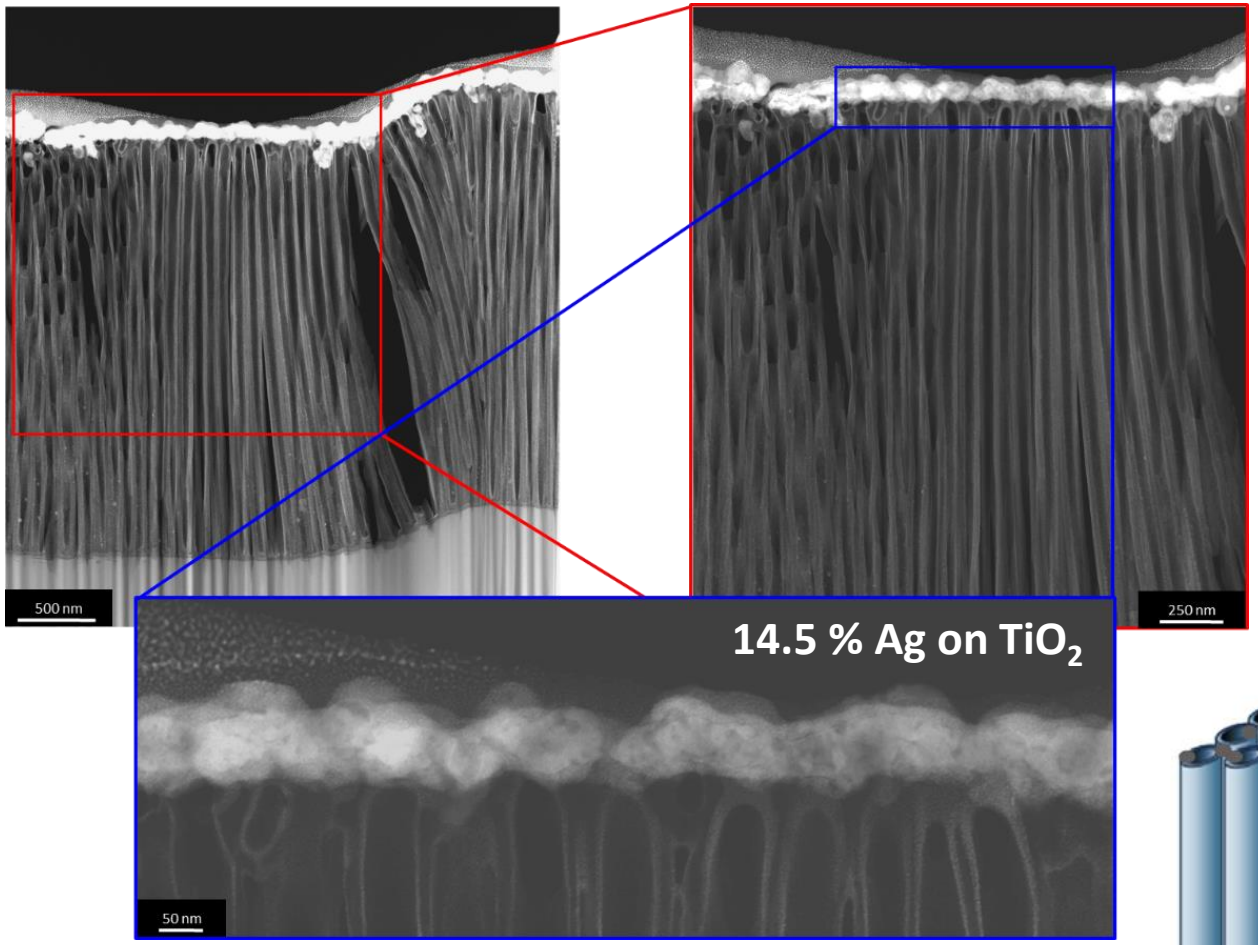
- Small electrode areas (low productivities)
- Use of harsh electrolytes
- Few hours of proved stability




Hernández S., *et. al. Green Chem., 2017, 19, 2326–2346*

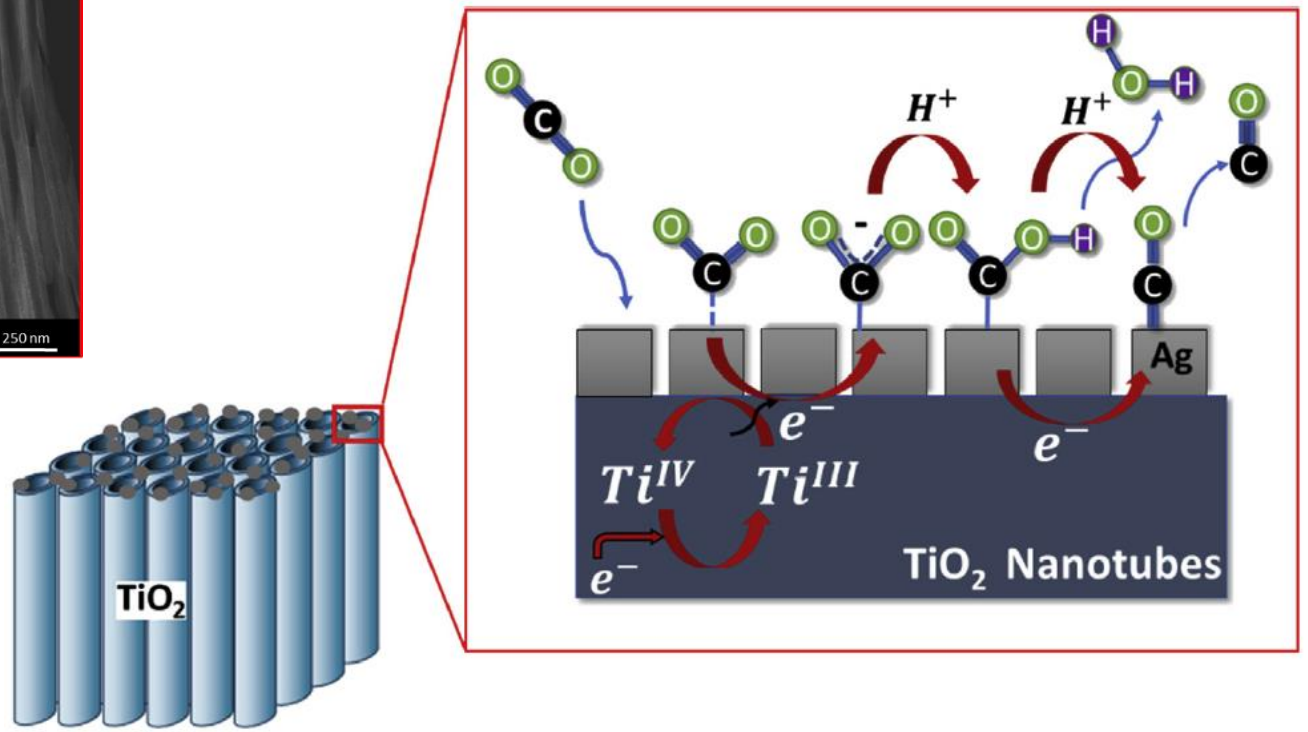
# *Electrochemical reduction of $CO_2$ for Syngas production on Ag/$TiO_2$ NTs*

**↓ Ag amount ⇒ ↓ cost**




**Role of $TiO_2$ Substrate on $CO_2$ reduction**

Titania **enhance the stability of key $CO_2^{\cdot-}$ intermediate** decreasing the $CO_2$ electroreduction overpotential




M. Amin Farkhondehfal, S. Hernandez, et. Al. Int. J. Hydrogen Energy, 2019, in press, DOI: 10.1016/j.ijhydene.2019.04.180

# *Electrochemical reduction of $CO_2$ for Syngas production on Ag/$TiO_2$ NTs*

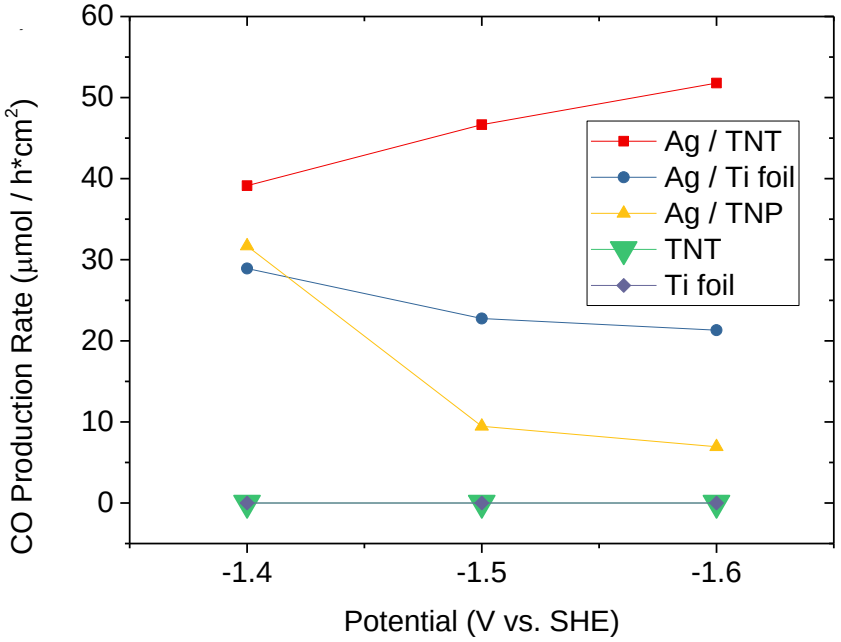
## Role of $TiO_2$ Substrate on $CO_2$ reduction

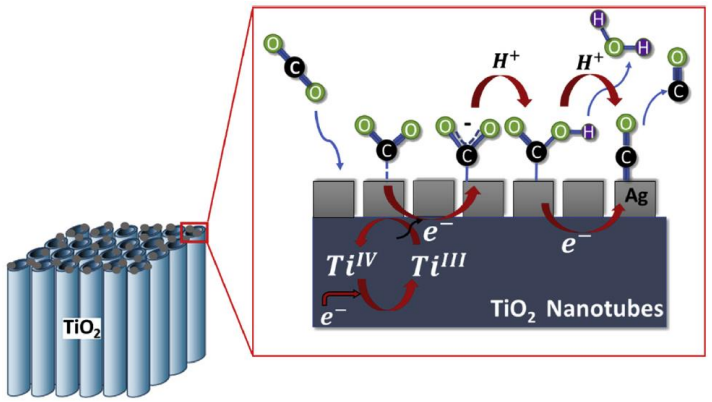
↑ electrochemical surface area (ECSA) &

↑ e- transport due to 1D structure

⇩

**↑ catalytic activity**

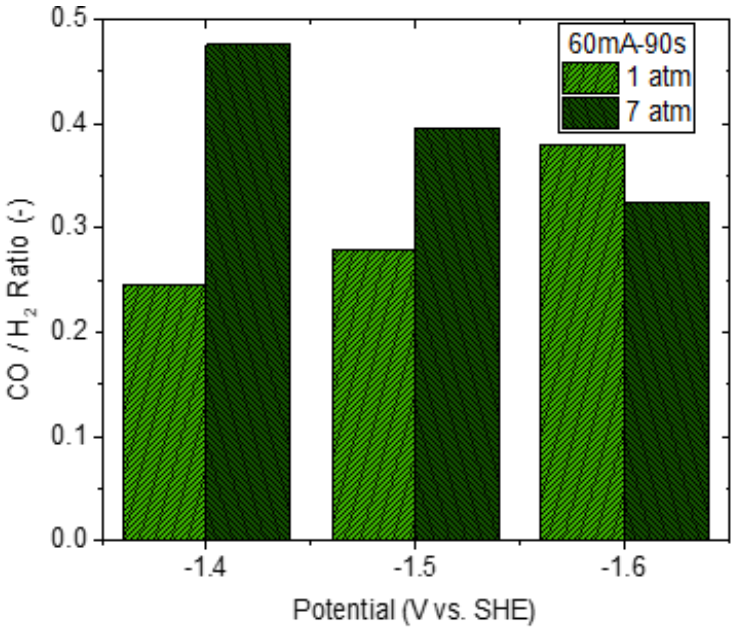



**Tunable $CO/H_2$ ratio** at dif. potentials and $CO_2$ pressures, e.g. 1:2 ratio (at 1.4 $V_{SHE}$ and 7 bar)

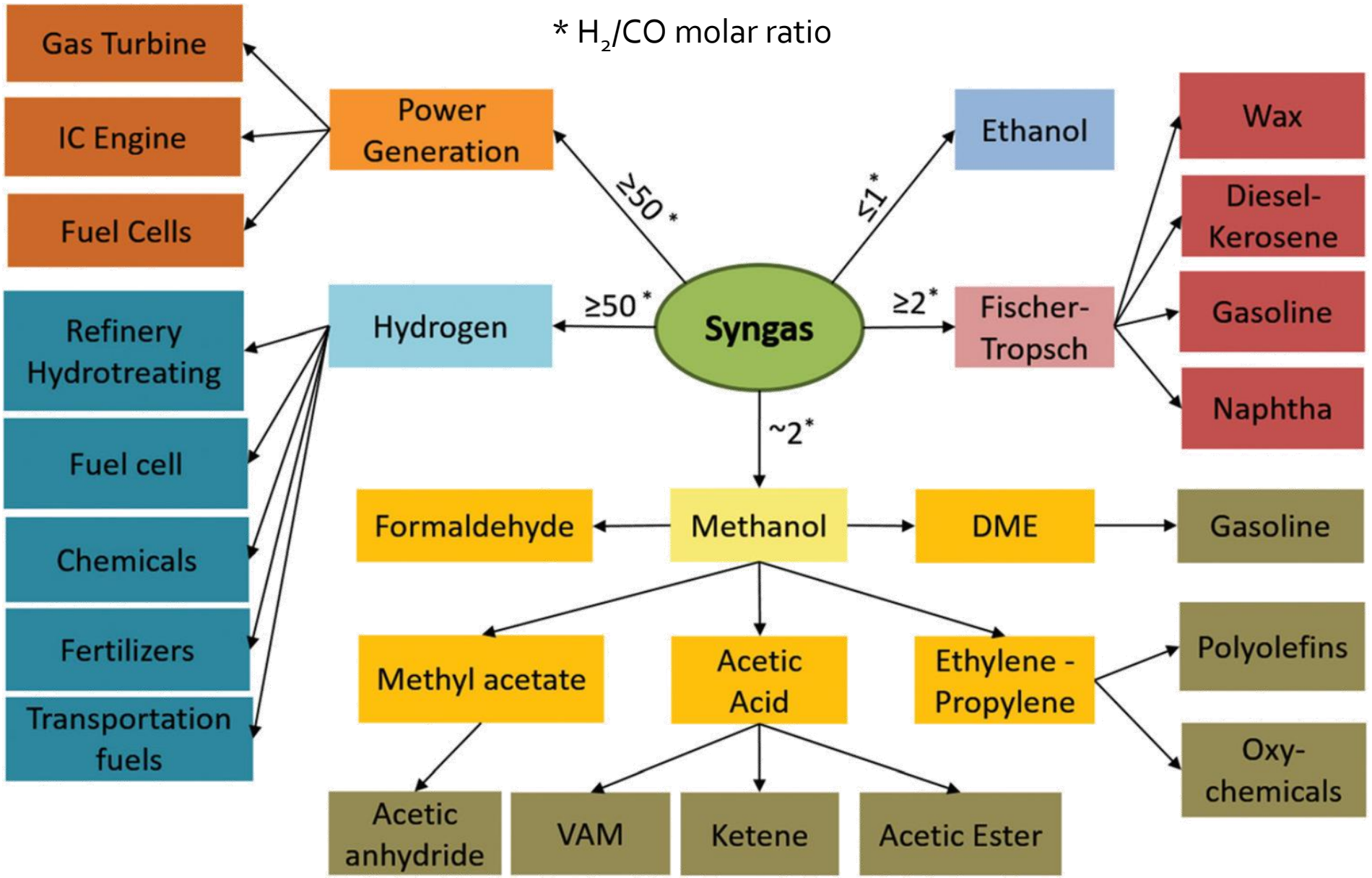
⇩

ideal for methanol production




A. Farkhondehfal, Hernández S., et. al. *Int. J. Hydrogen Energy* **2019**, DOI: 10.1016/j.ijhydene.2019.04.180.

# *Syngas from $CO_2$ : An opportunity*

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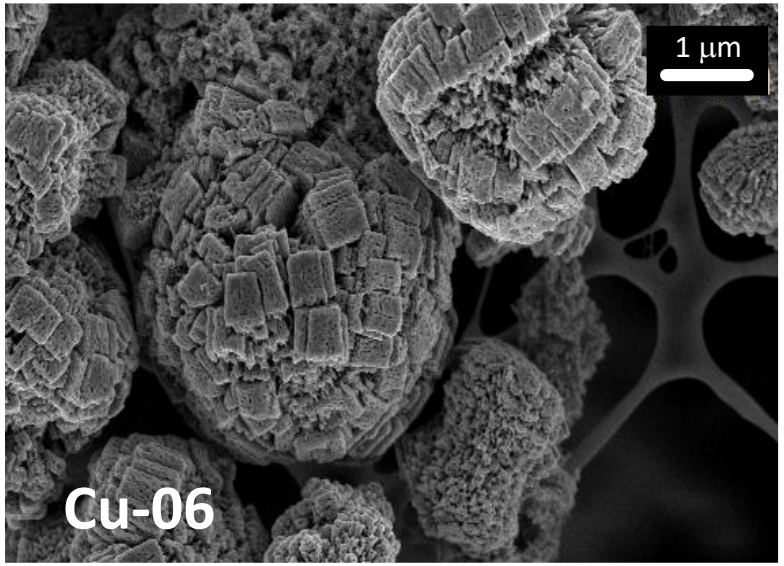
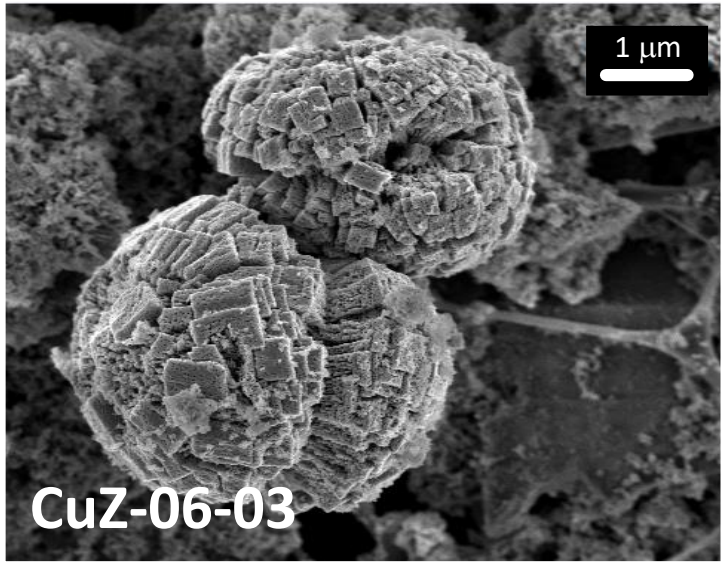
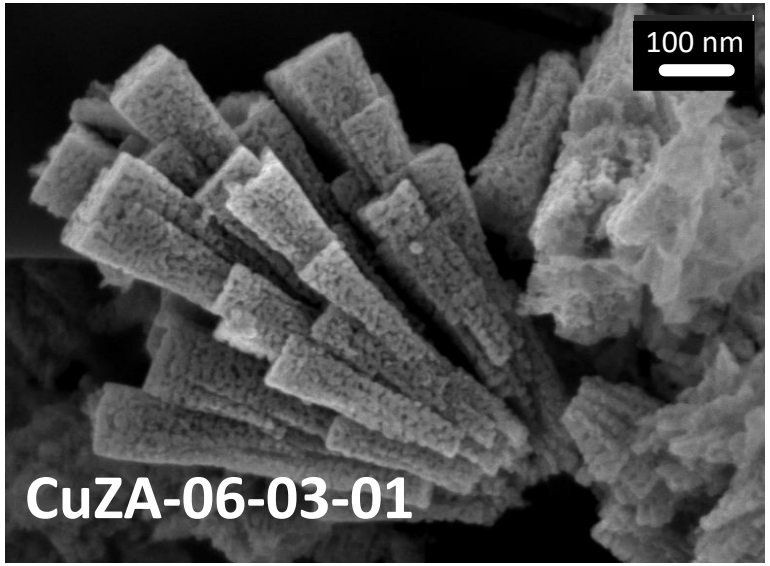


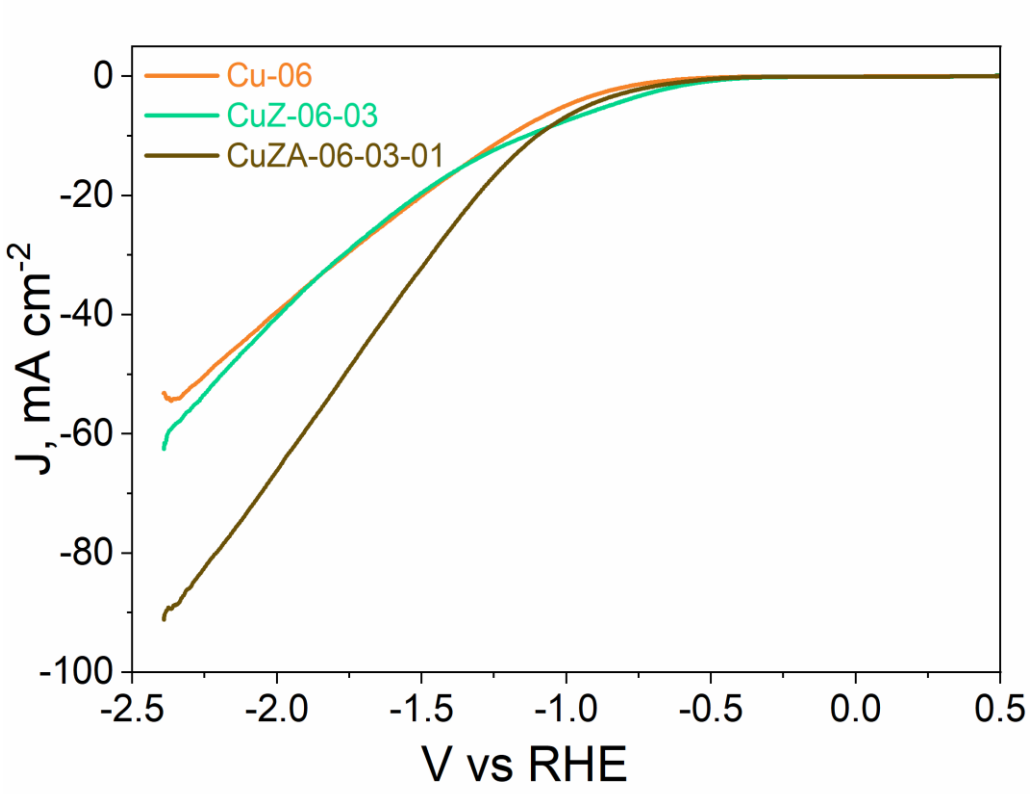

| Catalyst | BET surface area, $m^2\ g^{-1}$ | Total pore volume, $cm^3\ g^{-1}$ | EDS, atomic ratio | Crystallite size, nm (11-1) CuO | Superficial $Cu^0$+$Cu^{1+}$ (rest is $Cu^{2+}$) |
|---|---|---|---|---|---|
| **Cu-06** | 18.4 | 0.11 | Cu/O 1:1 | 16.98 | 22% |
| **CuZ-06-03** | 55.16 | 0.23 | Cu/Zn 60:40 | 7.08 | 8% |
| **CuZA-06-03-01** | **101.65** | **0.37** | **Cu/Zn/Al 60:30:10** | **8.49** | **5%** |

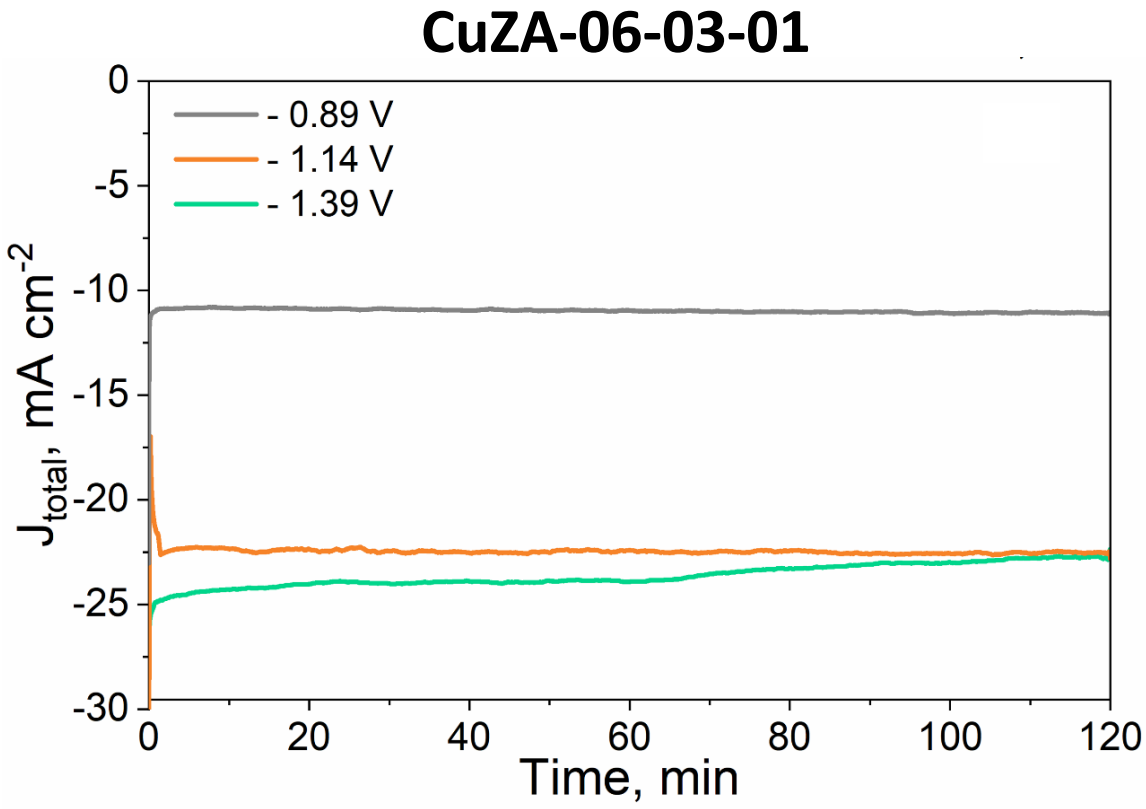
Guzman H., Hernández S., et. al. *paper under preparation;* ***Reproduction of the information of images herein cannot be done without the written consent of the authors.***

# *Electrochemical reduction of $CO_2$ with Cu-Zn-Al-based catalysts to syngas and oxygenated products*

## Role of ZnO & $Al_2O_3$ on $CO_2$ electro-reduction

- ↑ catalytic activity & ↑ stability
- Industrially relevant current densities (up to 90 mA/cm$^2$)

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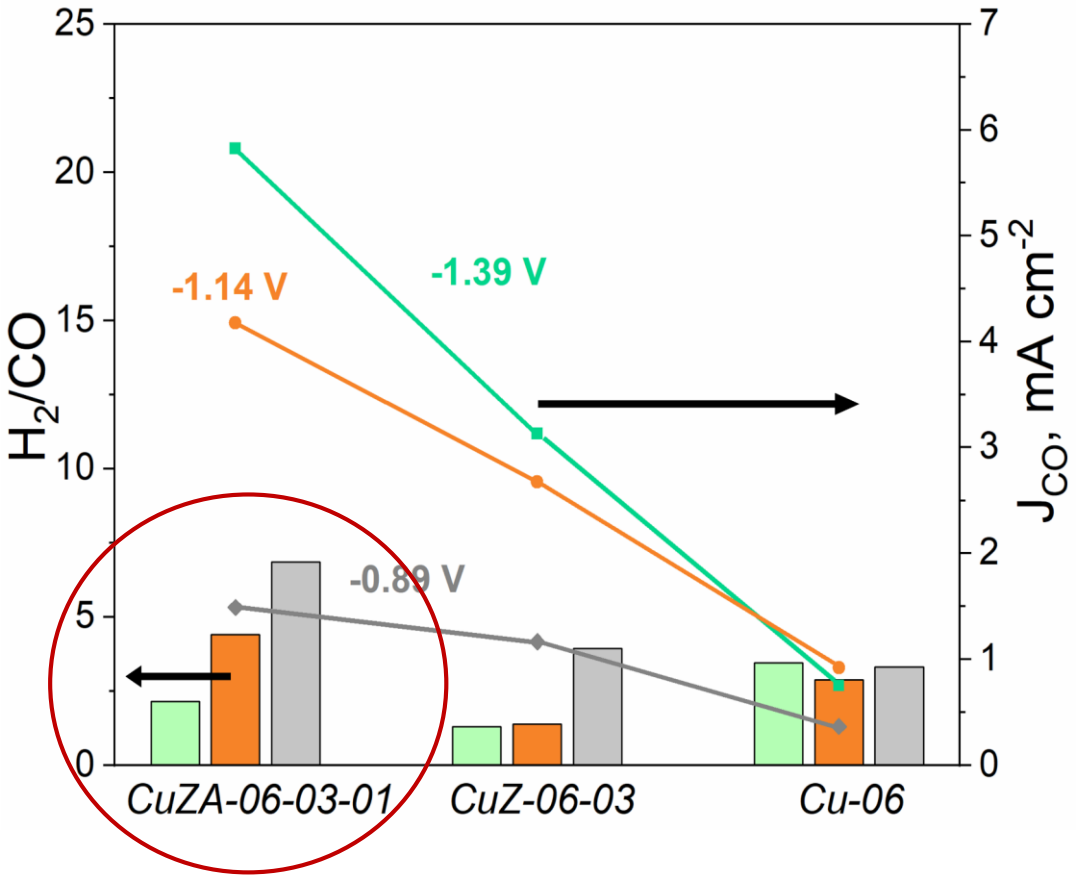
## Role of ZnO & $Al_2O_3$ on $CO_2$ electro-reduction

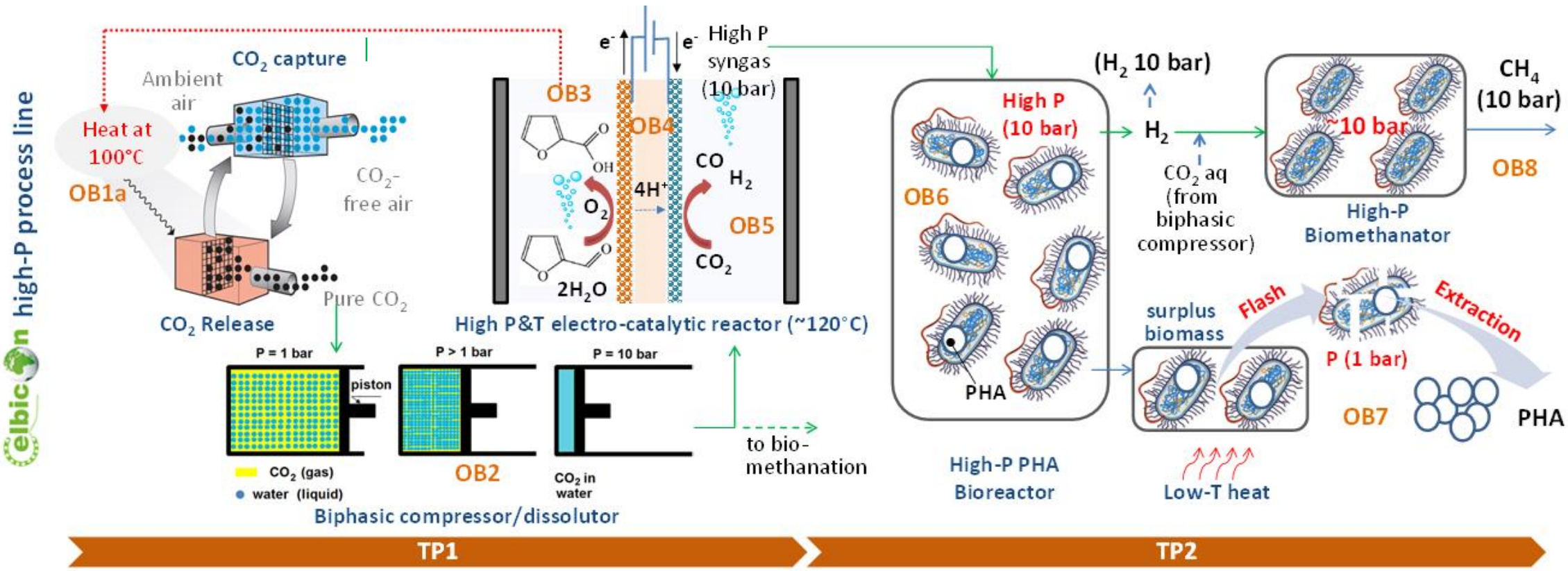
- ↑ selectivity towards syngas ($H_2$ and CO) formation than bare Cu
- Tuneable $H_2$/CO ratio (with CuZA-06-03-01) by changing the applied potentials




Guzman H., Hernández S., et. al. *paper under preparation;* 

# EU projects in Electrochemistry

## (2016 – 2019)




www.celbicon.org

See the demo plant at: https://www.youtube.com/watch?v=kotXejzcj0w&t=9s

# EU projects in Electrochemistry

(2017 – 2021)

ISTITUTO ITALIANO DI TECNOLOGIA

European Commission

HORIZON 2020

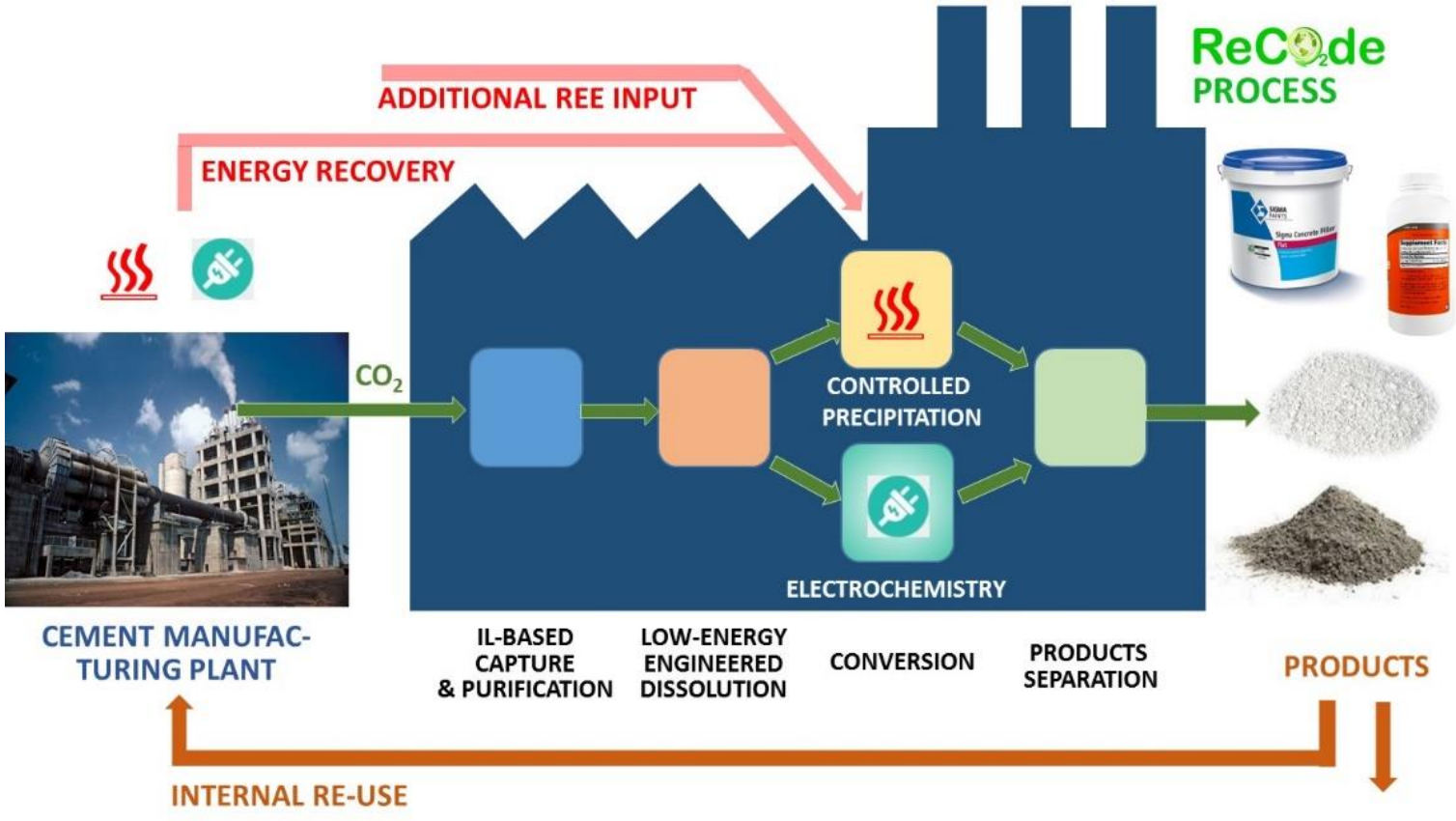
POLITECNICO DI TORINO

DiSAT chimica fisica materiali scienza e ingegneria

CREST Catalytic Reaction Engineering for Sustainable Technologies

## ReCO2DE

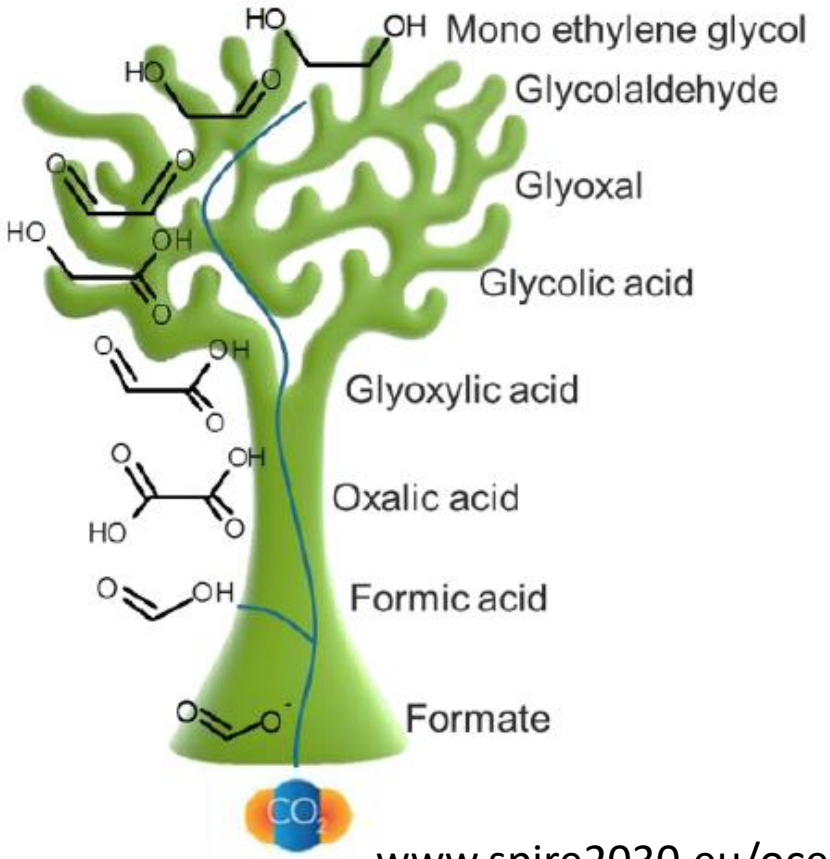
**Recycling carbon dioxide in the cement industry to produce added-value additives: a step towards a $CO_2$ circular economy**




www.recodeh2020.eu

## ocean

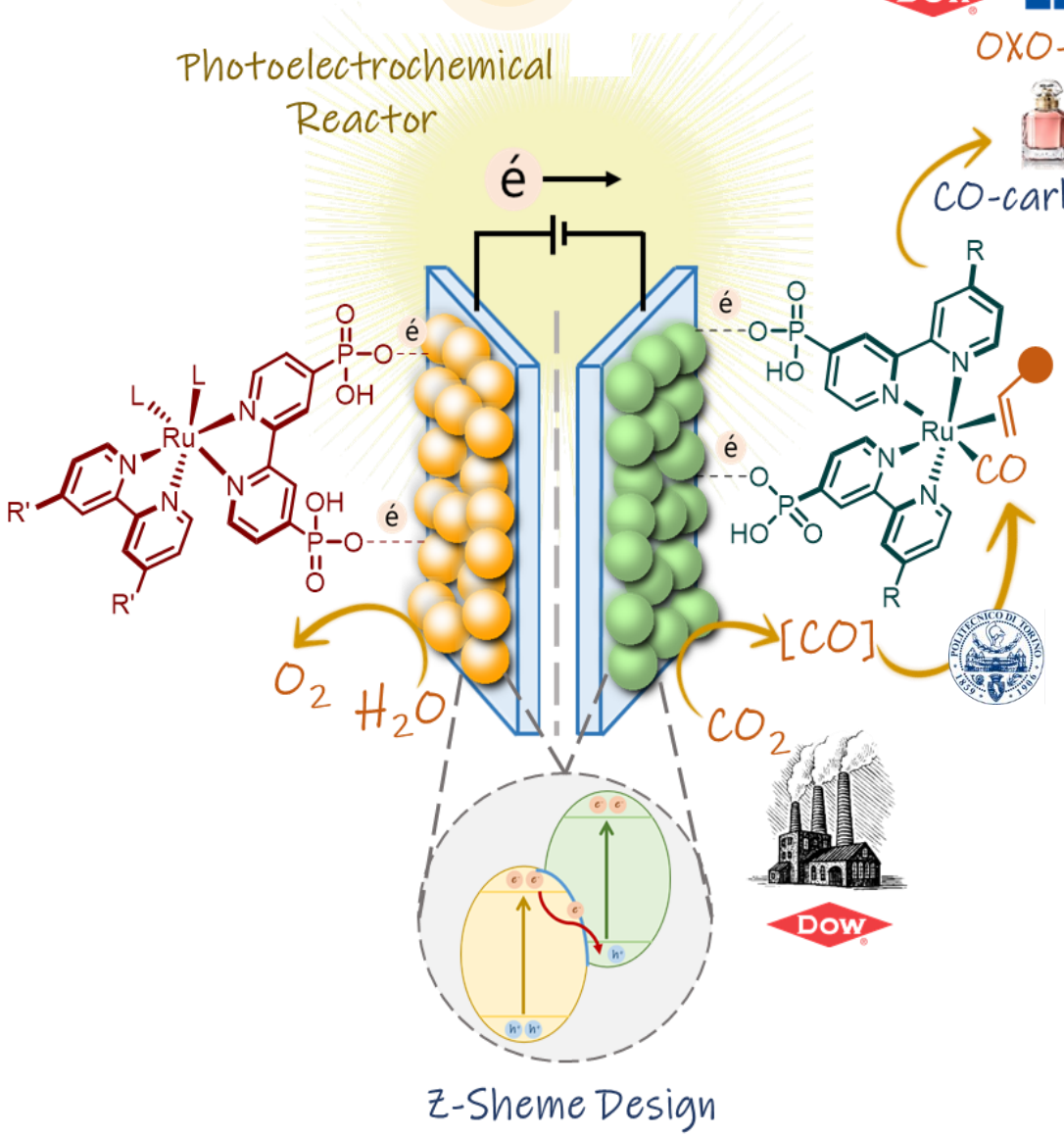
**Oxalic acid from $CO_2$ using Electrochemistry At demonstratioN scale**




www.spire2030.eu/ocean

# $CO_2$ conversion to commodity chemicals

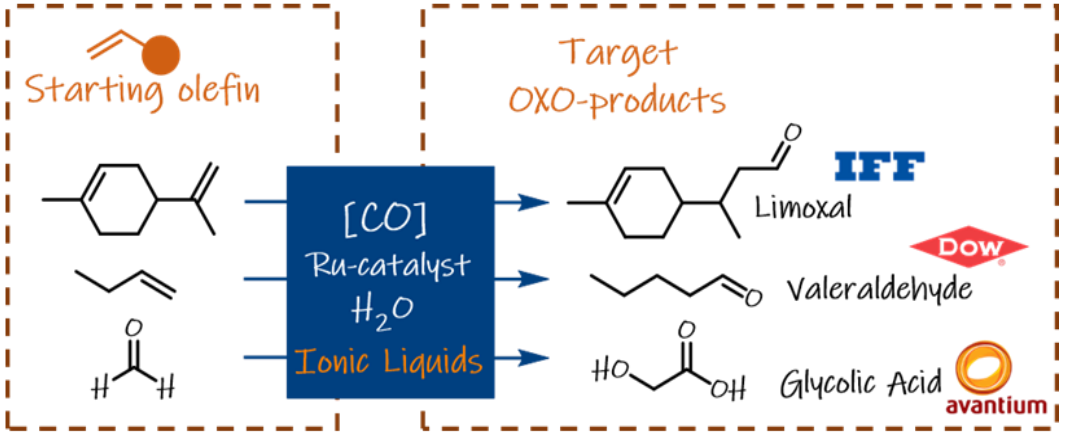
SunCO$_2$Chem




DOW IFF avantium

OXO-Products

CO-carbonylation

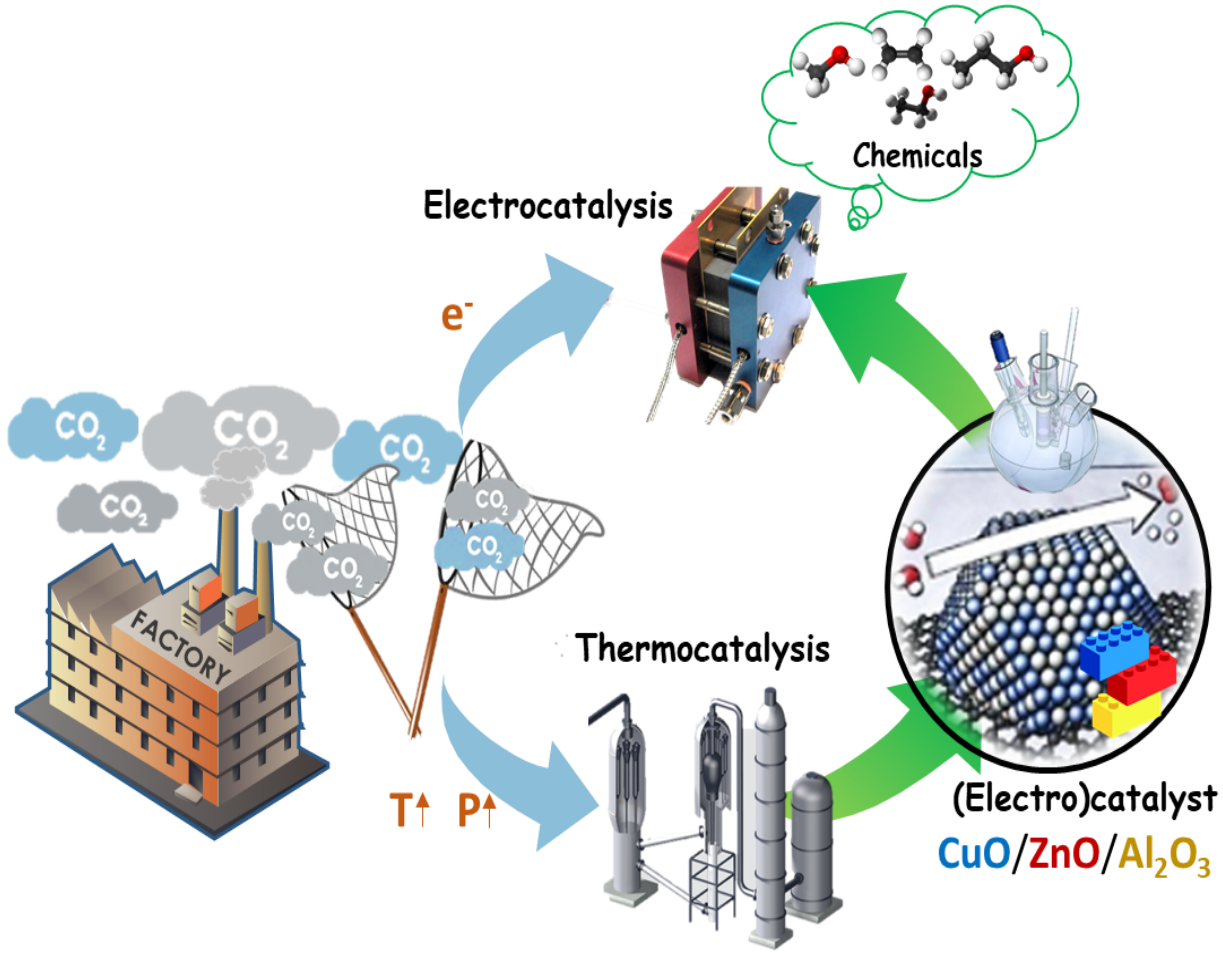



European Commission

https://cordis.europa.eu/project/id/862192/it

# Future Prospective

The basic knowledge of thermochemical catalysis can be exploited to understand the synergies between electro and thermo catalysis to make further progresses in the development of $CO_2$ reduction electrocatalyst materials.



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## Thank you for your attention

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