ELECTROCATALYTIC REDUCTION OF CO_2 INTO FUELS AND VALUE CHEMICALS USING METAL PORPHYRINS AND NANOPARTICLES

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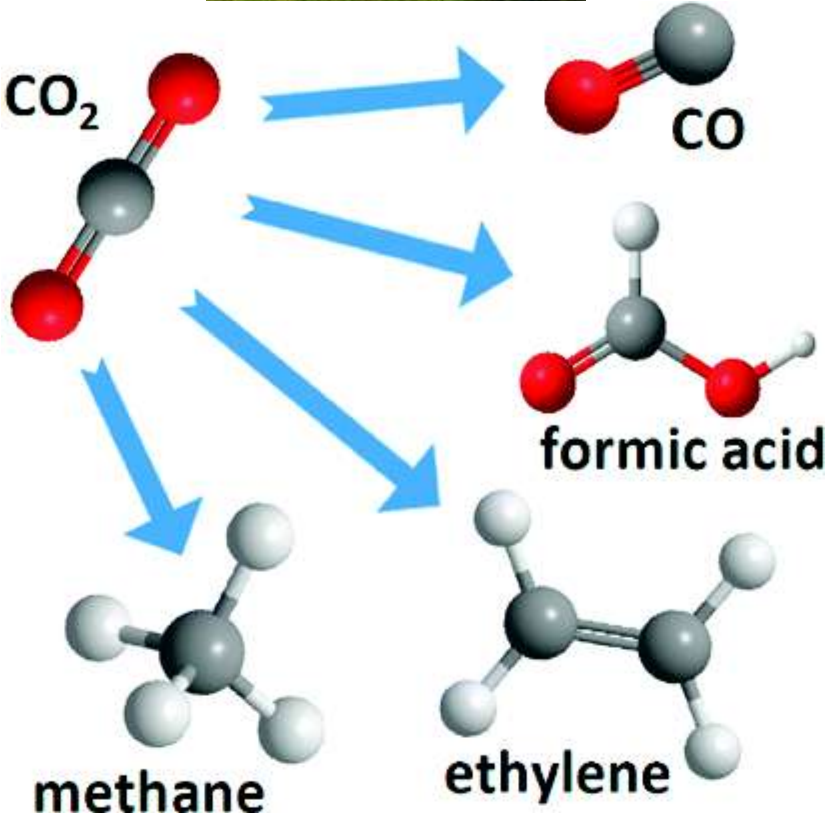
CO_2 Electroreduction

- CO_2 can be converted to fuels and value chemicals by electrochemical reduction.
- By using excess electricity from photovoltaics, wind or water the products of CO_2RR (CO_2 Reduction Reaction) are concidered as non-fossil
- The approach is sometimes called artificial photosythesis



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CO_2
Waste or wealth?

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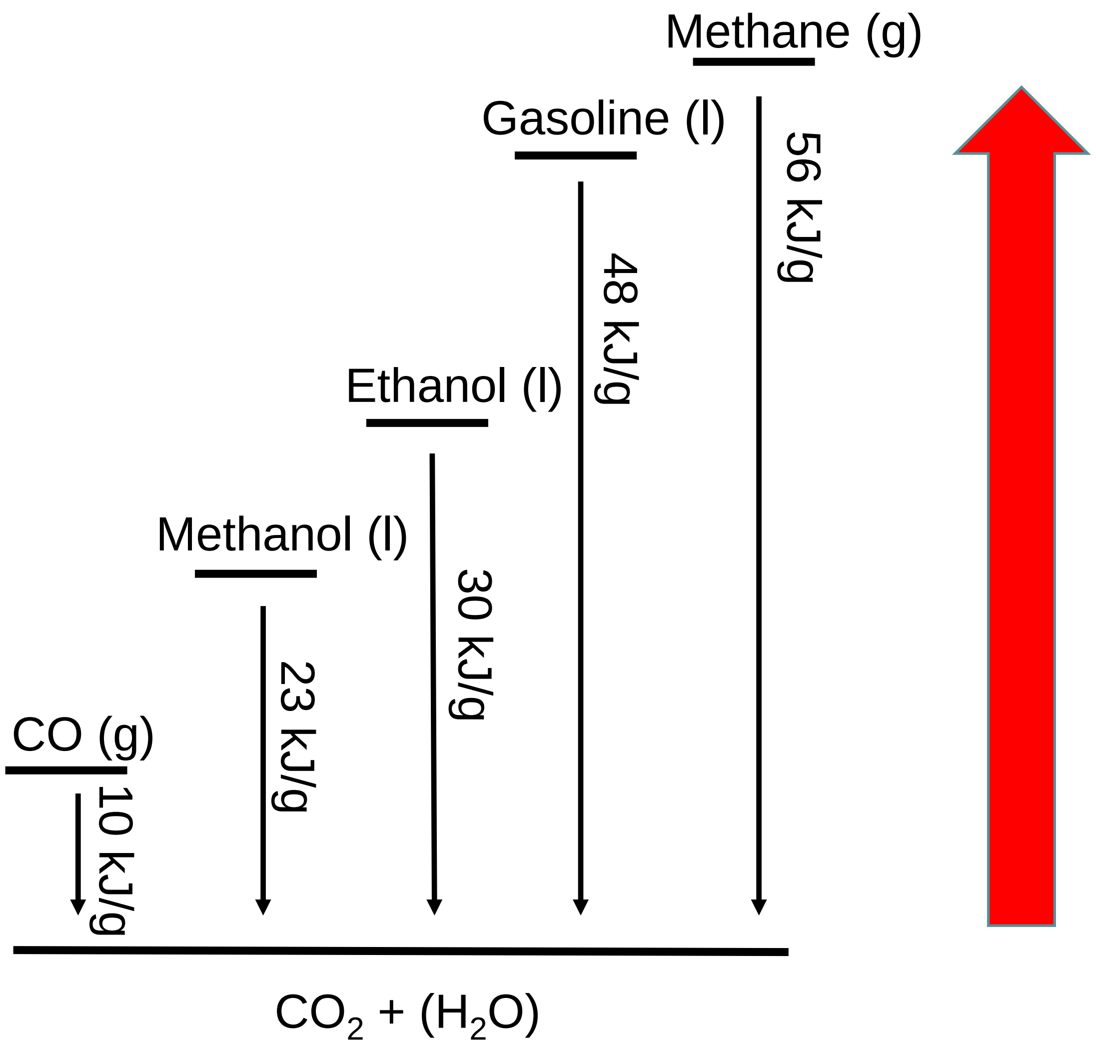
Energy of combustion vs. energy of conversion



- By the laws of thermodynamics, at least the same amount of energy has to be put in the system to convert CO_2 into value products.
- Currently five times more energy is needed in liquid fuel synthesis

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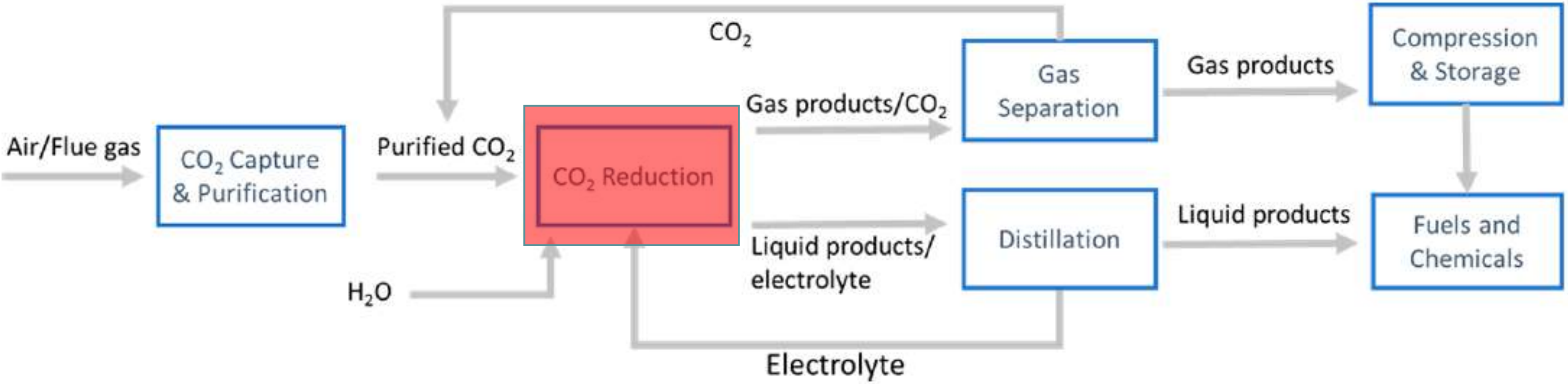
Full CO_2 conversion process



Electrochemical reduction of CO_2

Half reactions

Cathode reaction: $2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$

Anode reaction:

Products	**Reaction**	**E°(V vs. RHE)**
CO	$CO_2 + 2e^- + 2H^+ \rightarrow CO + H_2O$	-0.11
HCOOH	$CO_2 + 2e^- + 2H^+ \rightarrow HCOOH$	-0.25
HCOH	$CO_2 + 4e^- + 4H^+ \rightarrow HCOH + H_2O$	-0.07
CH_3OH	$CO_2 + 4e^- + 4H^+ \rightarrow CH_3OH + 2H_2O$	0.02
CH_4	$CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O$	0.17
C_2H_6	$CO_2 + 12e^- + 12H^+ \rightarrow C_2H_4 + 4H_2O$	0.06
$CO_2^{\bullet -}$	$CO_2 + e^- \rightarrow CO_2^{\bullet -}$	-1.5
H_2	$2H^+ + 2e^- \rightarrow H_2$	0.0

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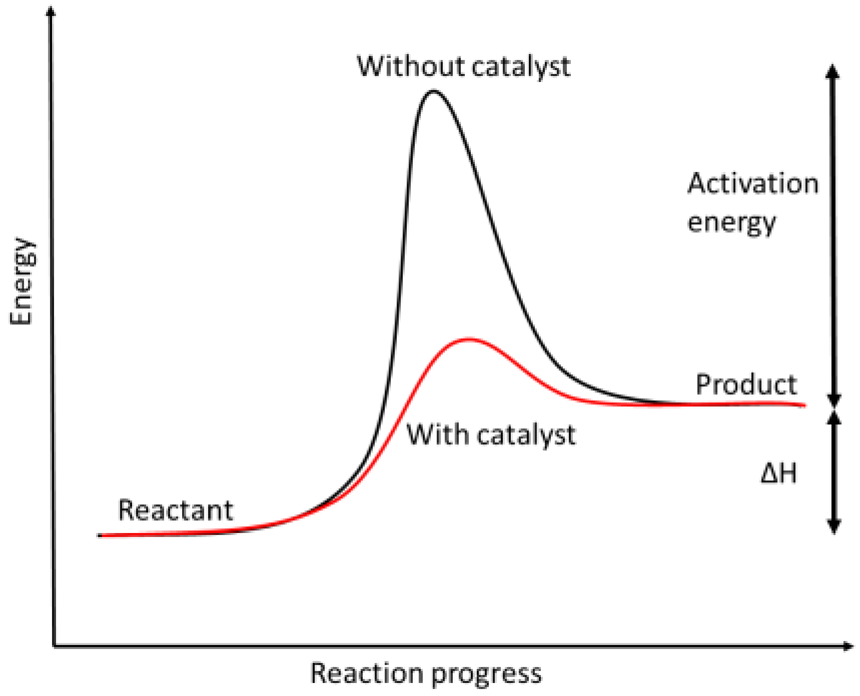
Challenges of CO_2RR

- Carbon dioxide is stable molecule and as such activation and utilization of CO_2 as a chemical feed stock is difficult

  - Actual potential for CO_2 reduction to known products is much higher than standard potential
  - High potentials lead to favor hydrogen evolution reaction (HER)
  - Low current density (< 100 $mAcm^{-2}$)
  - Side reactions lead to low faradic efficiency



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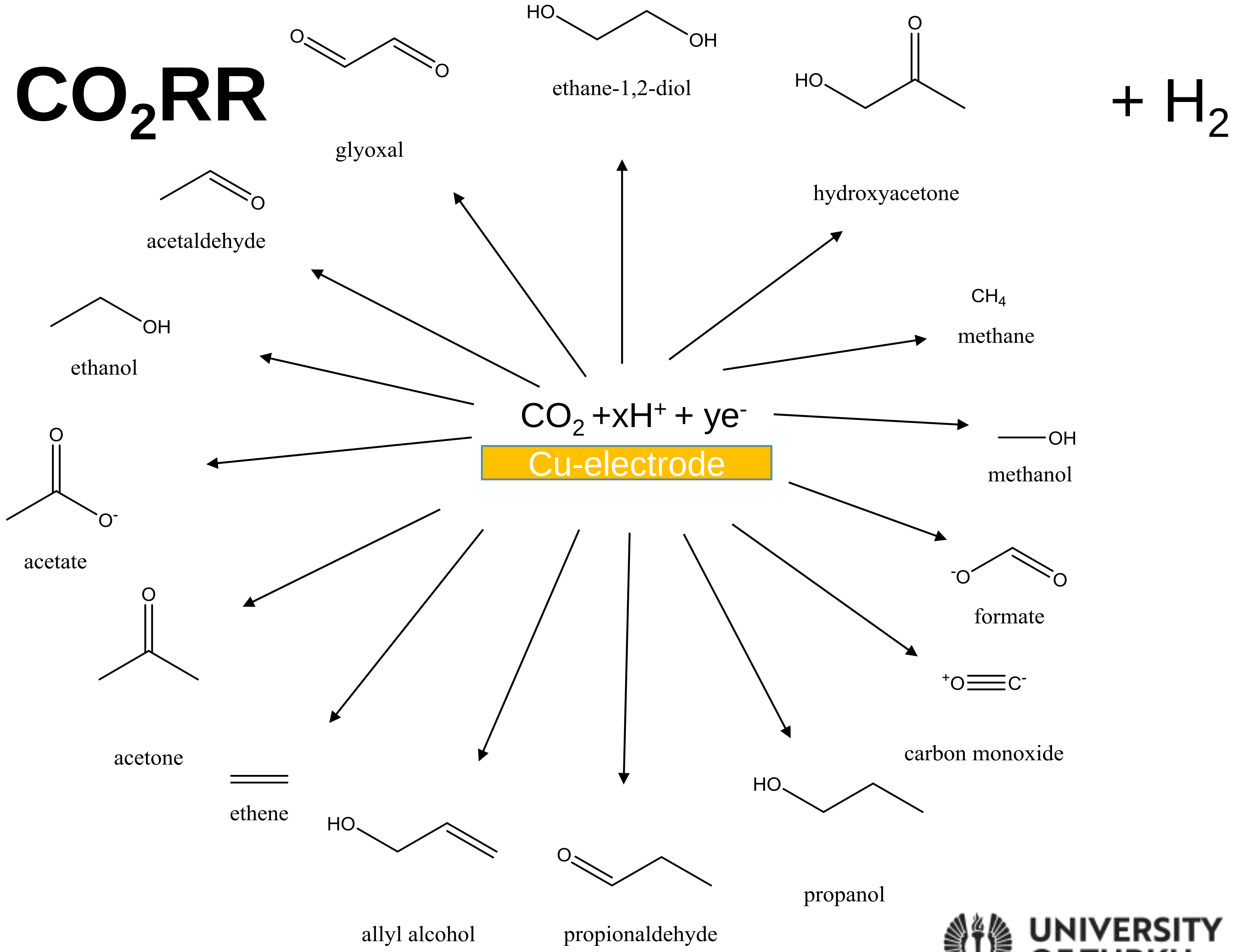
Challenges of CO_2RR

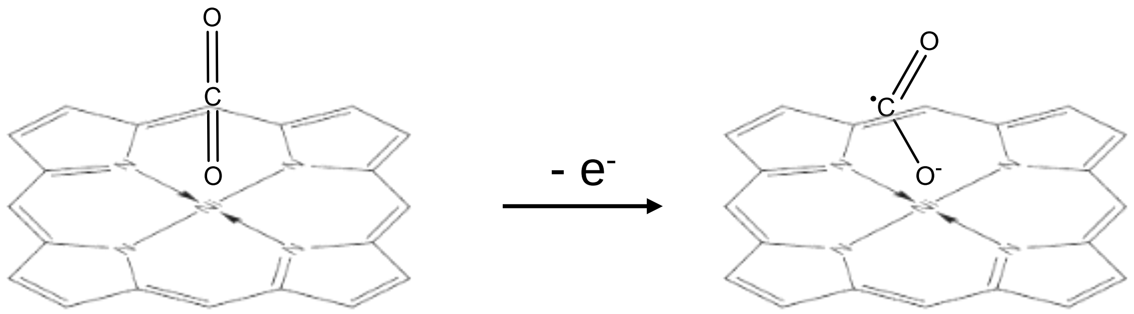
- Electrochemical reduction of CO_2 leads into multiple products
- Unwanted reaction products lower the faradic effieciency thus can be concidered as ”parasitic” reactions
- Need for selctive catalyst materials



Kuhl, K.P. et al *Energy Environ. Sci*. **2012**, *5*, 7050

Activation of CO_2RR using metal porphyrins

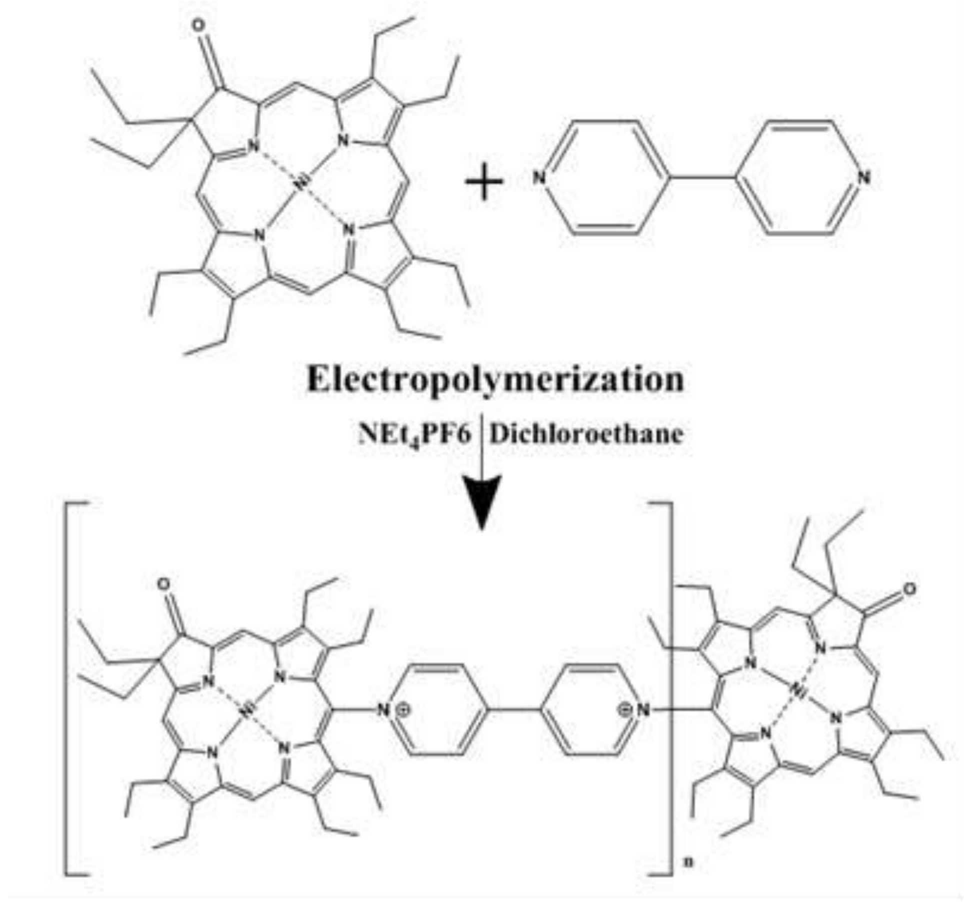
- CO_2RR occurs in multiple steps. The rate limiting step is the first step one-electron transfer to CO_2 to form radical intermediate $CO_2^{\bullet-}$, which requires an enormous amount of energy.
- We have studied this activation step using metal-centered porphyrin polymers
- Parasitic reactions are disabled by using aprotic solvent (MeCN)

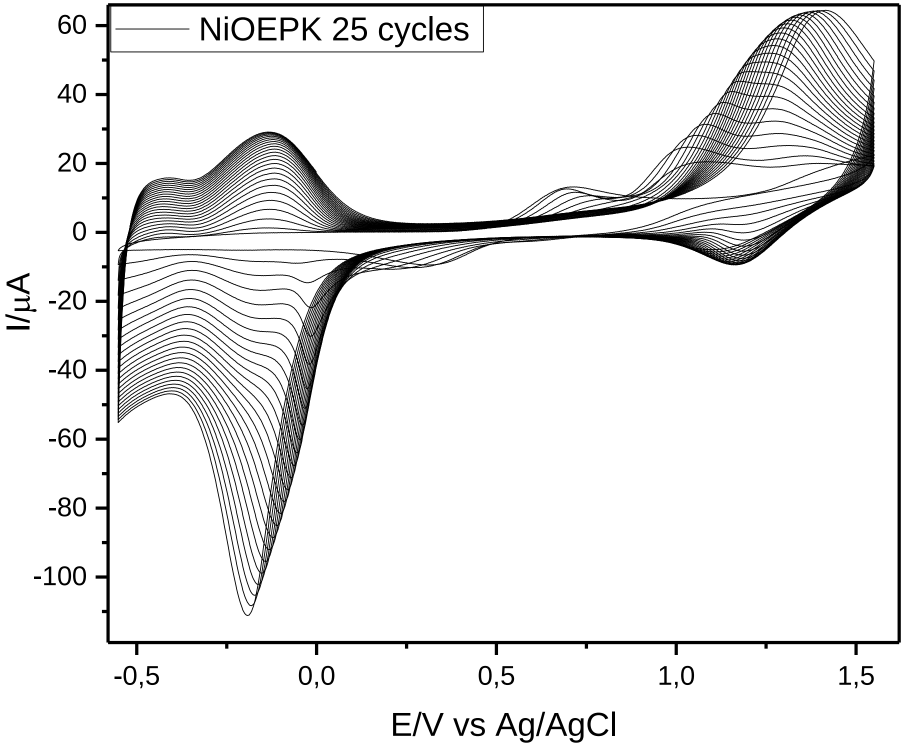


Kochrekar, S., Kalekar, A., Damlin, P., Salomäki, M., Meltola, N., Kvarnström, C., **2019** *manuscript to be submitted*

Metal porphyrin polymers

Preparation of conjugated polymer catalyst





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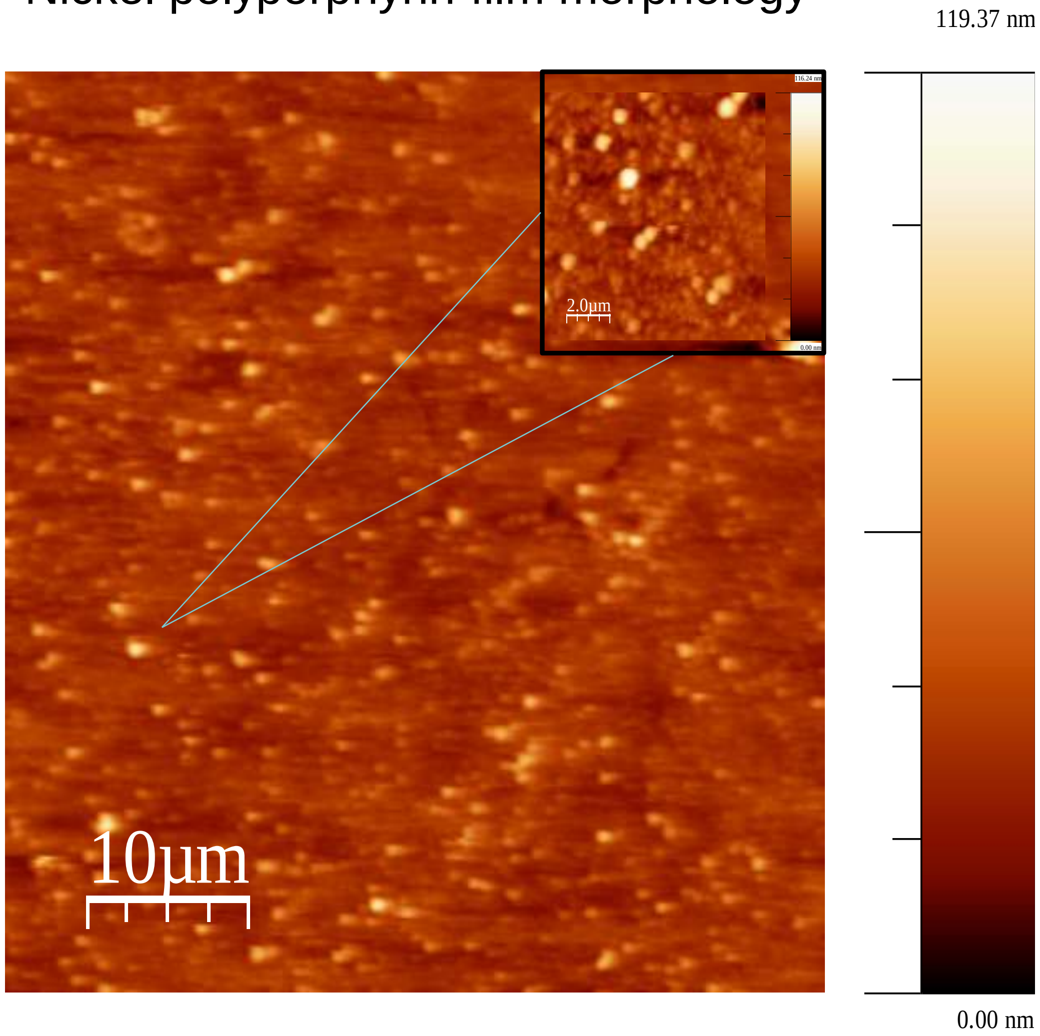
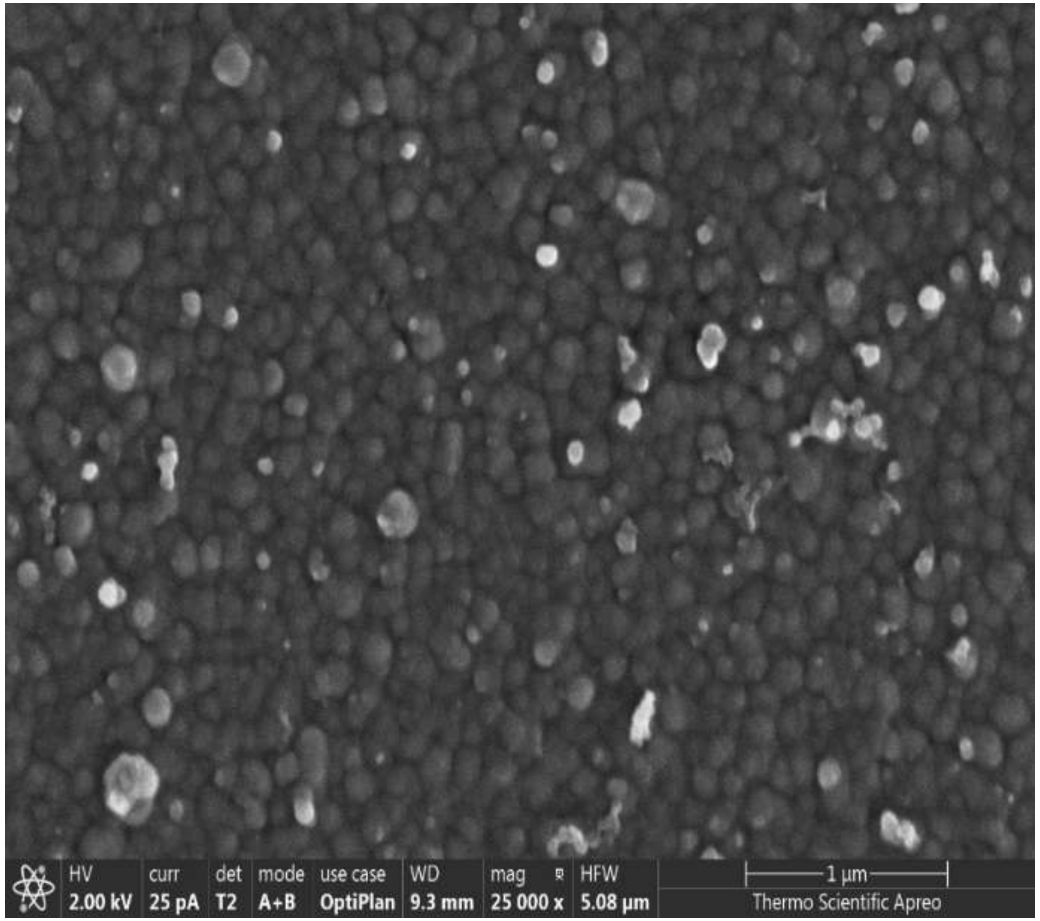
Metal porphyrin polymers

Nickel polyporphyrin film morphology



Atomic force microscopy



Scanning electron microscopy

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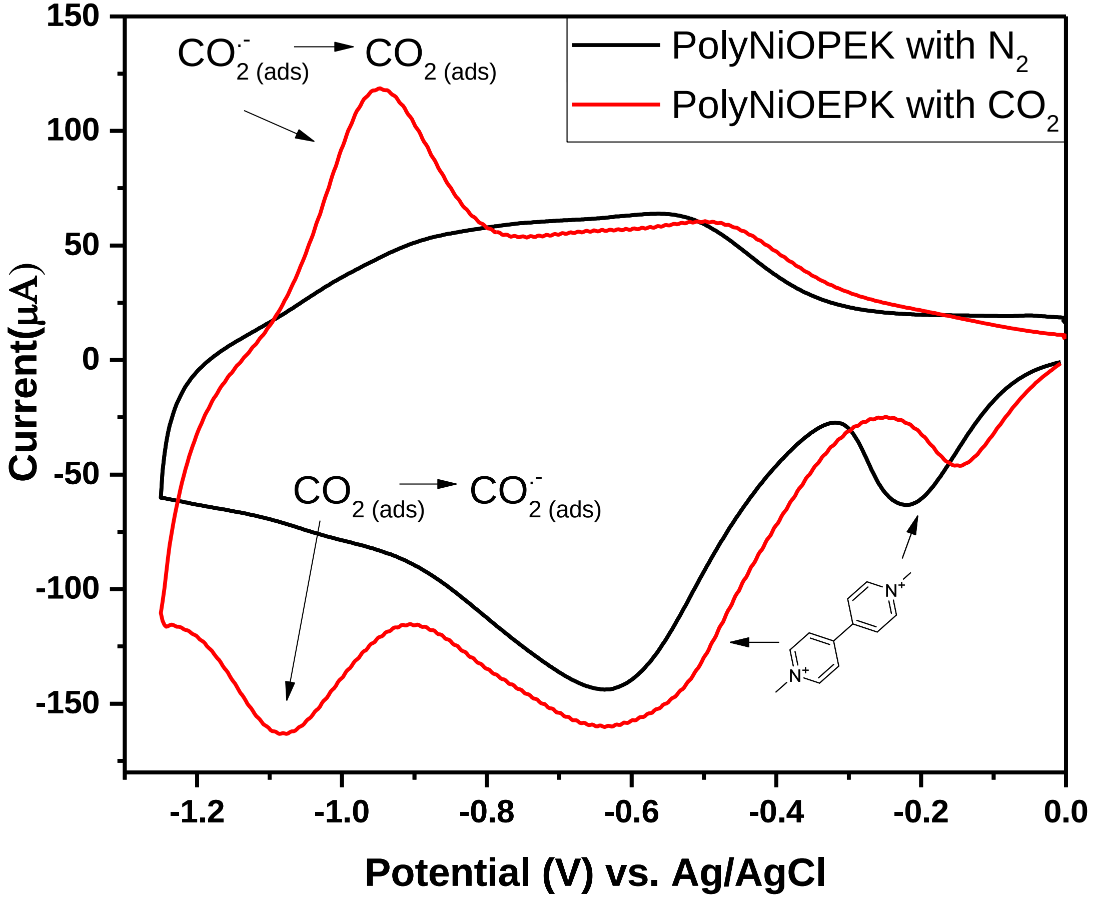
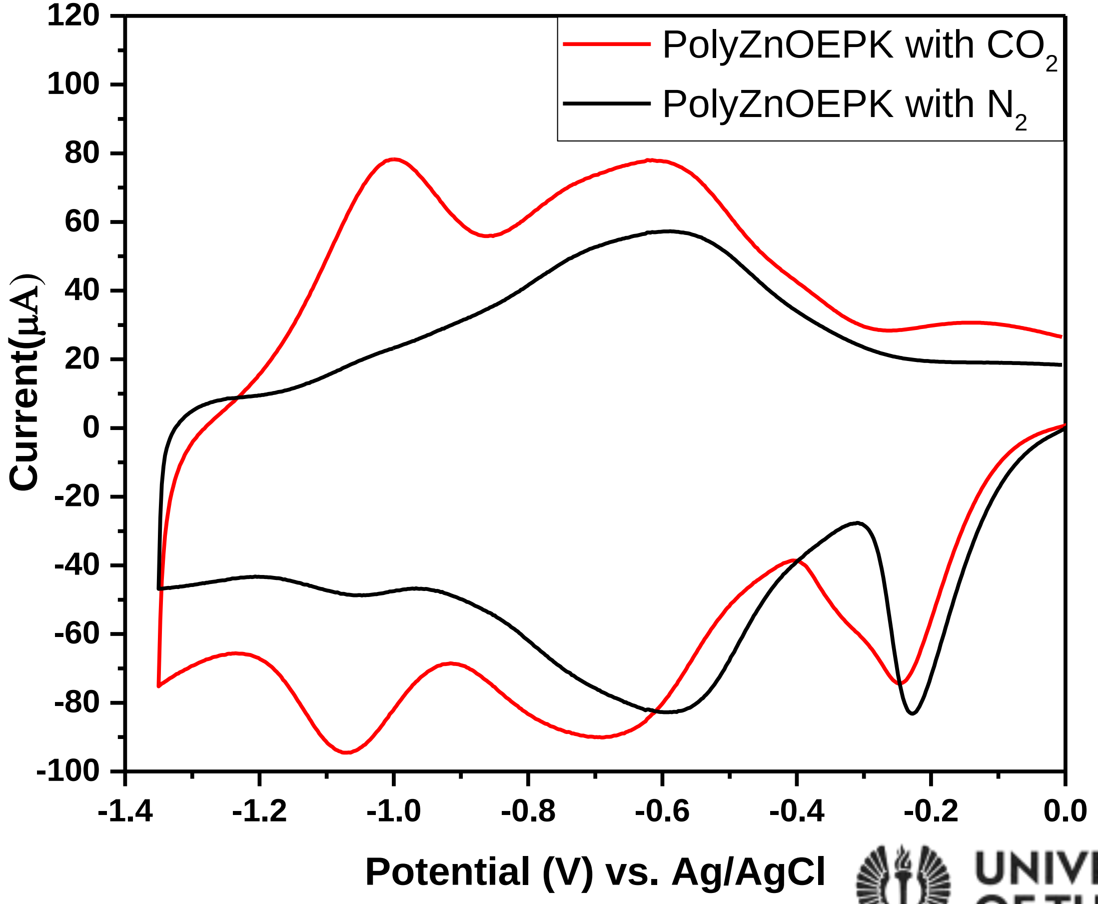
Electroreduction of CO_2

Nickel-centered porphyrin polymer



Zinc-centered porphyrin polymer



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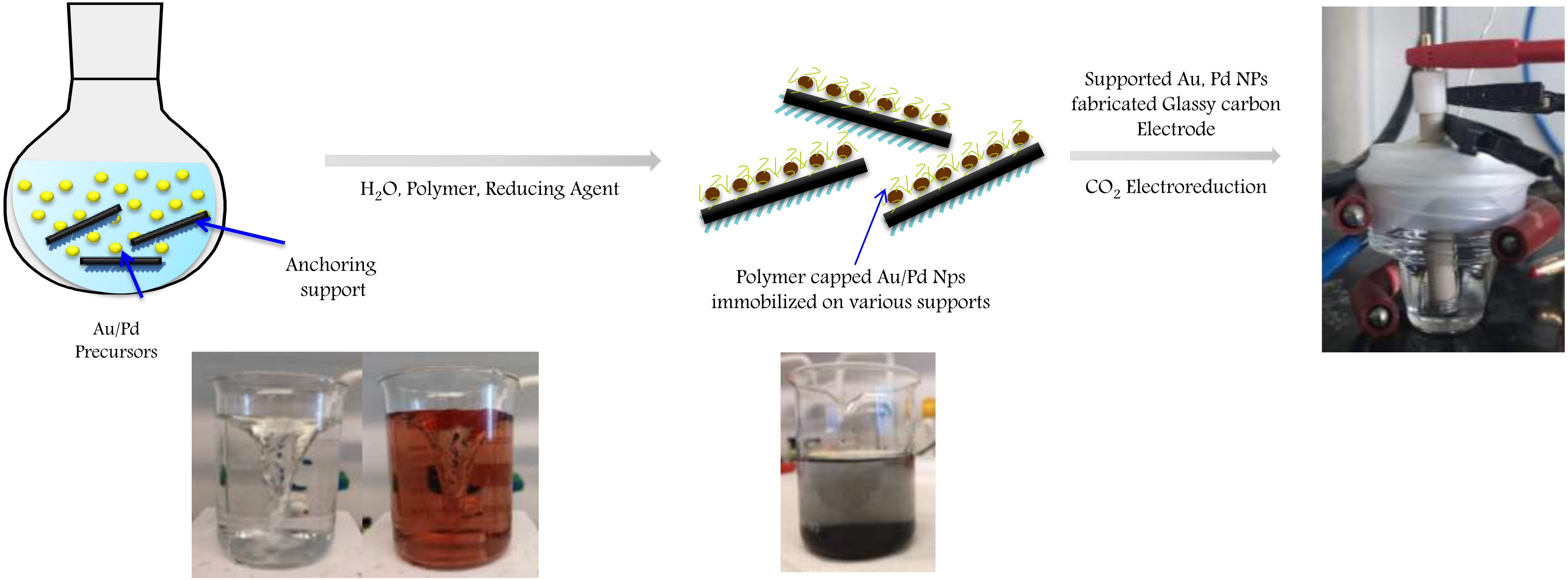
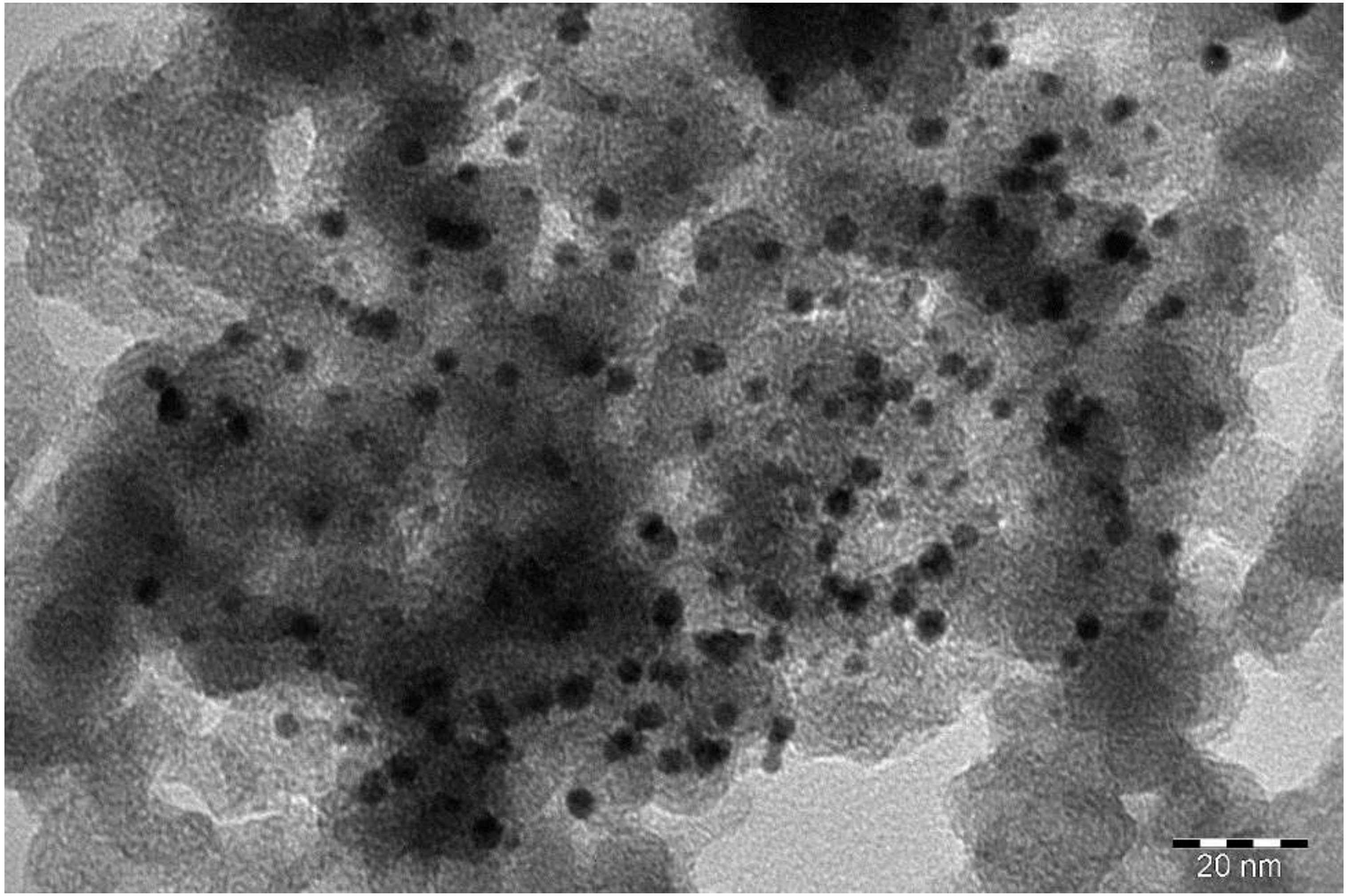
Supported Au, Pd Nanoparticles for CO_2 Electroreduction

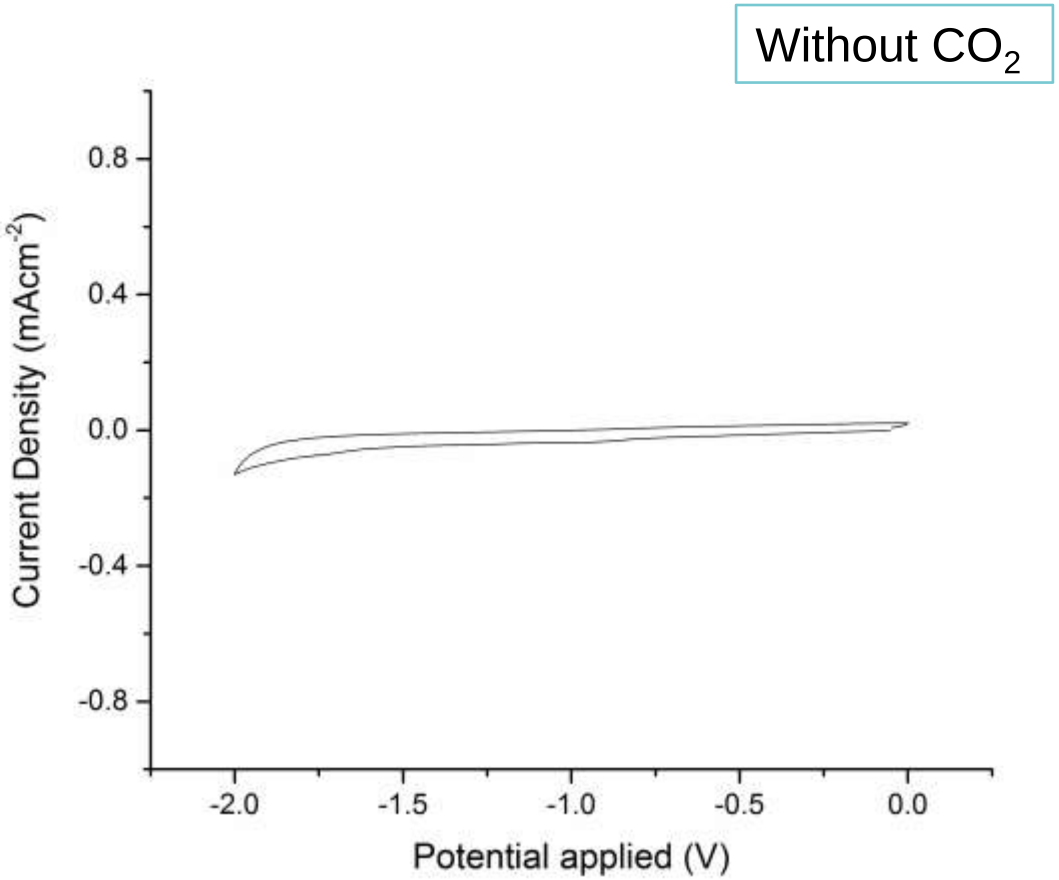


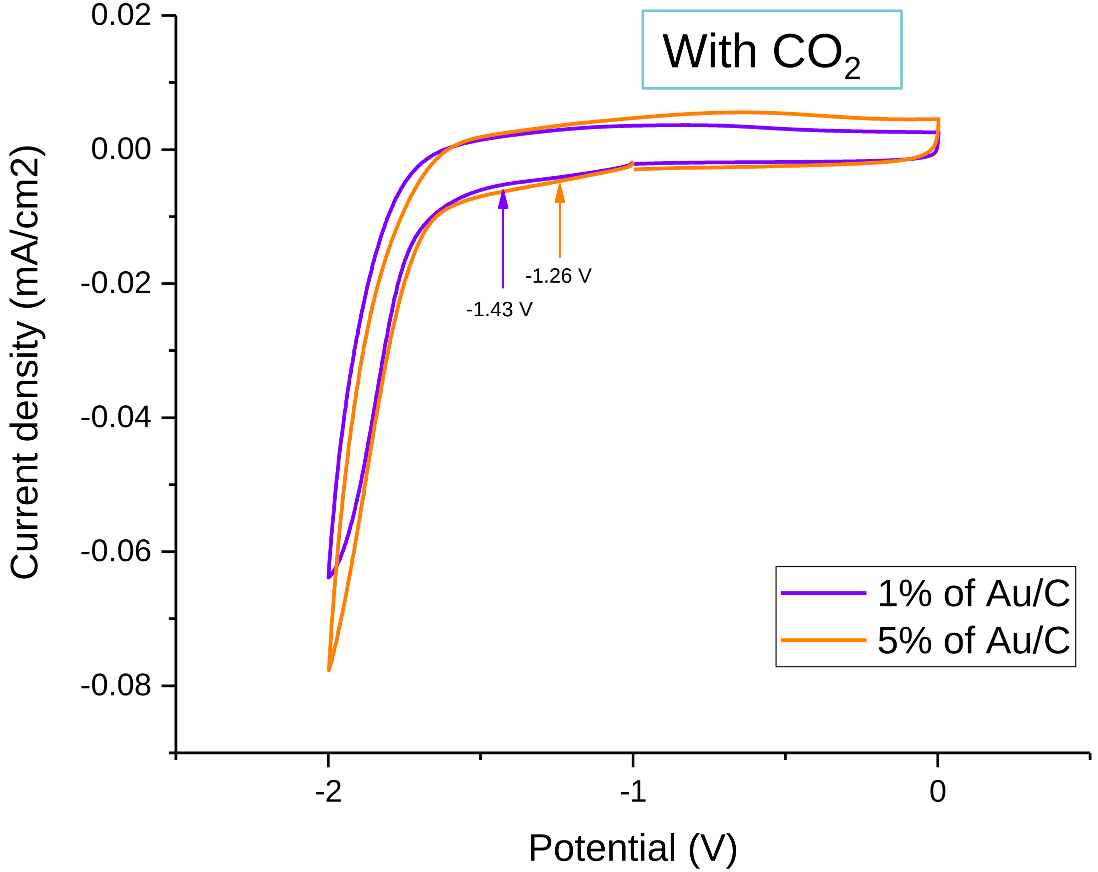
Transmission Electron Micrograph: 1%Au/C



~3 nm Au nanoparticles

Electroreduction of CO_2 on nanoparticle surface





Kesavan, L. et al *manuscript*

Conclusions and future aspects of CO_2RR

- Electrochemical reduction of CO_2 has a great potential of becoming a major contributor to sustainable production of fuels and chemicals
- In our group, we have focused on catalysis materials and design of nanostructure and morphology of substrates, all aiming towards a better performance what comes to selectivity, long-term stability, efficiency and economic competitiveness of CO_2 converter systems.
- The rate limiting step is the first step one-electron transfer to CO_2 to form radical intermediate $CO_2^{\bullet-}$, which requires an enormous amount of energy
- The current densities and turnover of catalysts must be greatly improved in order to produce economically viable systems
- Key scientific issues to be solved:
    - The development of inexpensive and stable catalysts
    - The catalyst must be highly selective for a specific product
    - Operation of catalyst at minimal or no over potential

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