Applications of porous carbon materials in the (photo)electrochemical reduction of CO_2

Research plan defense of the doctoral thesis

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Content

INTRODUCTION

- CO_2 emissions and its valorization
- CO_2 (photo)electrochemical reduction
- Catalysts based on carbonaceous materials doped with heteroatoms
- Catalyst for the (photo)electrochemical CO_2 conversion

PROBLEM STATEMENT

HYPOTHESIS

OBJECTIVES

- Overall
- Specifics

METHODOLOGY

- Nanoporous carbon materials and Electrode preparation
- Catalyst and electrode characterization
  - Physicochemical characterization
  - (Photo)electrochemical characterization
- Preparative (photo)electrolysis

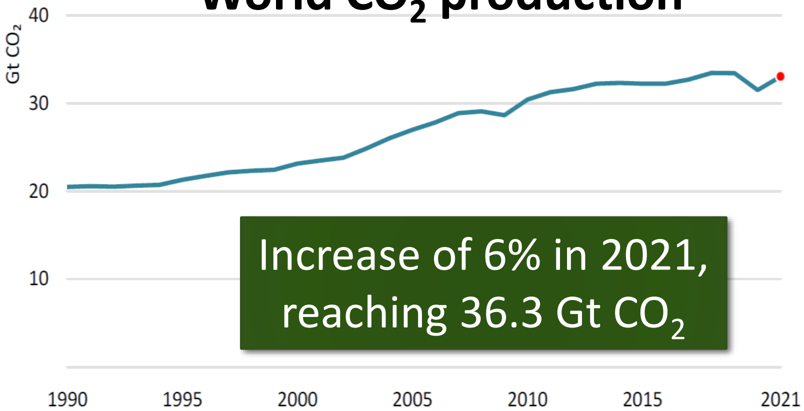
TIMELINE

EXPECTED IMPACT

INTRODUCTION

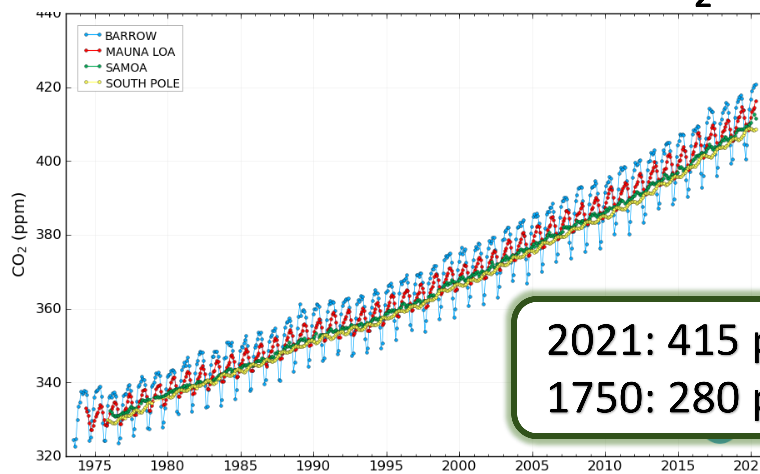
CO_2 emissions and its valorization

World CO_2 production



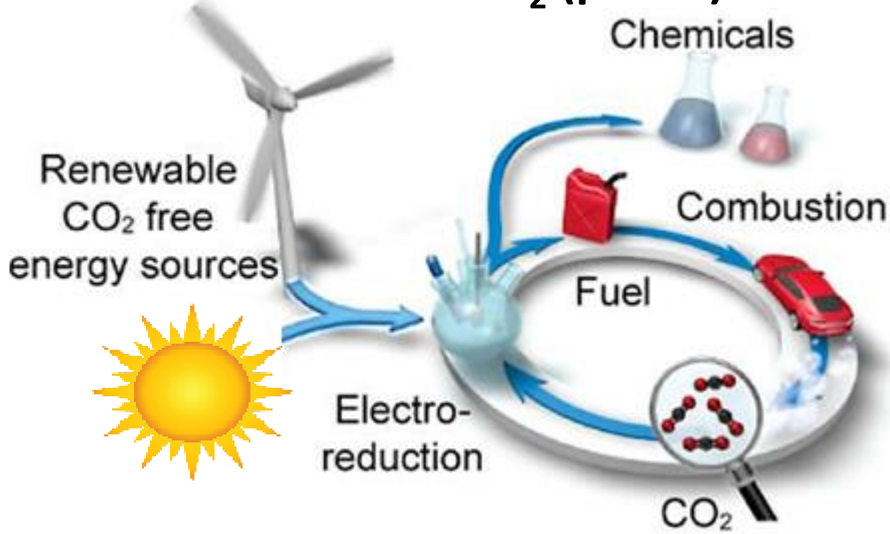
Increase of 6% in 2021, reaching 36.3 Gt CO_2

Mean of concentration CO_2



2021: 415 ppm
1750: 280 ppm

CO_2 (photo)electrochemical reduction



Mild conditions → Temperature, Pressure

Reaction products → ***Catalyst***, Electrolyte, applied voltage

CO_2 (photo)electrochemical reduction

$$^{*}+CO_2aq \rightarrow {}^{*}CO_2 + e^{-} \rightarrow CO_2^{\bullet -}$$

Reactions	$E^{\ominus}$ (V vs. RHE)
$CO_2 + e^- \rightarrow CO_2^{\bullet -}$	−1.49
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	−0.10
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	−0.12
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	−0.10
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	0.03
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	0.17
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	0.08
$2H^+ + 2e^- \rightarrow H_2$	0

Thermodynamic equilibrium potentials for CO_2RR in aqueous solution (pH = 7, T = 25°C, P = 1 atm)

Thermodynamically unfavorable

- *High overpotential*
- *Low energy conversion efficiency*
- *Slow reaction kinetics of CO2RR*

Selectivity

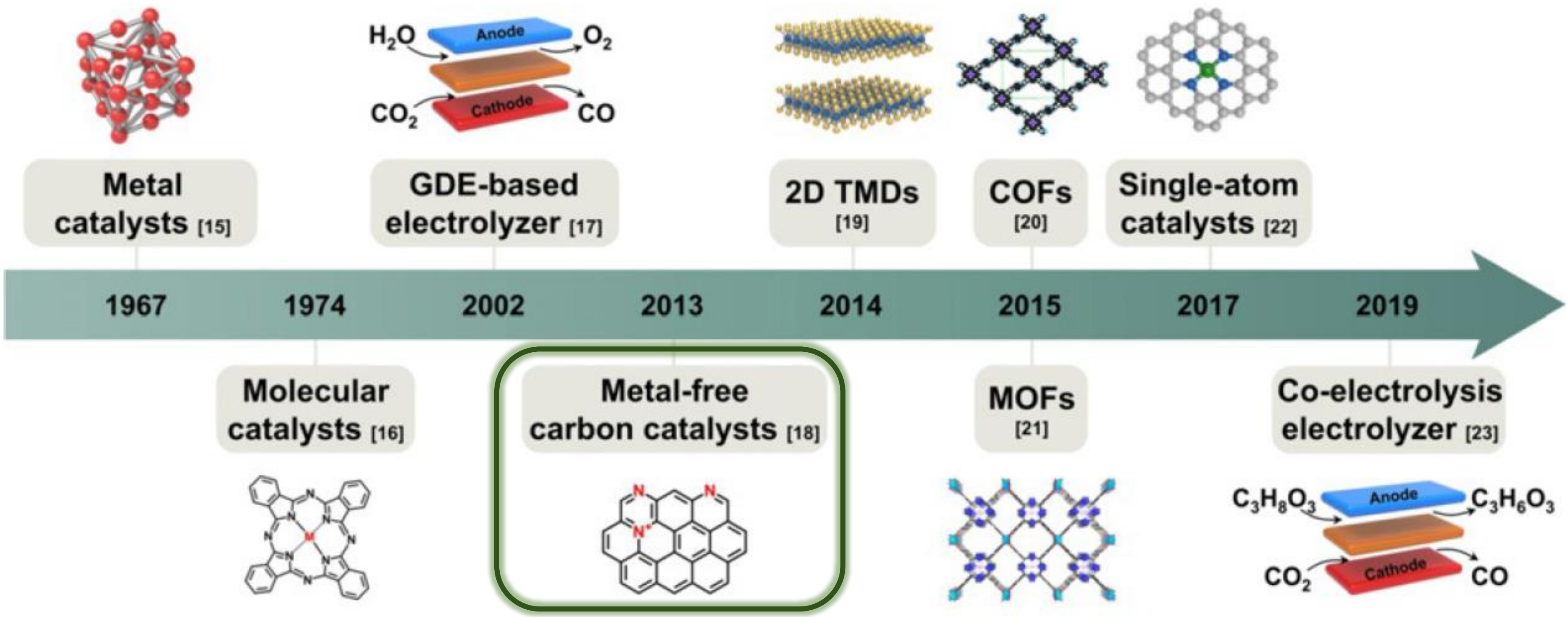
A wide range of CO2RR products can be generated due to a small difference in thermodynamic redox potential

Hydrogen Evolution Reaction (HER)

Competitive reaction of CO_2RR

Catalyst for electrochemical CO_2 conversion

Au, Pt and Hg
Electrodes



Environmental friendly

Low cost → Abundant raw materials; Chemical and physical stability

Tailored structures → Electrical properties; Textural properties

Catalysts based on carbonaceous materials doped with heteroatoms

Catalyst	Active sites	Electrolyte	Potential (V vs SHE)	Product yield	FE (%)	Reference
N-CNT	Pyridinic N	0.1 M $KHCO_3$	-0.78	CO	80.0	J. Wu, et al, ACS Nano, 2015, 9, 5364-5371
N-CNT	Graphitic N	0.5 M $NaHCO_3$	-0.90	CO	90.0	J. Xu, Y. Kan, et al, ChemSusChem, 2016, 9, 1085-1089
N-diamond	N-sp^3 C	0.5 M $NaHCO_3$	-1.00	CH_3COOH	91.8	Y. Liu, et al, J. Am. Chem. Soc., 2015, 137, 11631-11636
N-graphene	C atoms next to pyridinic N	0.5M $KHCO_3$	-0.84	HCOOH	73.0	H. Wang, et al, Green Chem., 2016,18, 3250-3256
N-3D graphene	Pyridinic N	0.1M $KHCO_3$	-0.90	CO	85.0	J. Wu, et al, Nano Lett., 2016, 16, 466-470
N-carbon	C atoms next to pyridinic N	0.1M $KHCO_3$	-0.99	CO	11.3	W. Li, et al, ChemSusChem, 2016, 9, 606-616
N-GQDs	Pyridinic N	0.1 M $KHCO_3$	-0.75	C_2H_4	31.0	J. Wu, et al, Nat. Commun., 2016, 7, 1-6
N-mesoporous carbon	Pyridinic N	0.1 M $KHCO_3$	-0.56	C_2H_5OH	77.0	Y. Song, et al, Angew. Chem. Int., 2017, 56, 10840-10844
Nanoporous carbon/CNT	C atoms next to pyridinic N	0.1M $KHCO_3$	-0.80	HCOOH	81.0	H. Wang, et al, Angew. Chem. Int., 2017, 56, 7847-7852
N-porous carbon	Pyridinic N and quaternary N	0.1 M $KHCO_3$	-0.93	CO	78.0	R. Wang, et al, ACS Appl. Mater. Interfaces, 2018, 10, 14751-14758
N,S-porous CNF	Pyridinic N and C-bonded S atoms	0.1 M $KHCO_3$	-0.70	CO	94.0	H. Yang, et al, Angew. Chem. Int., 2018, 57, 15476-15480
N,F-Holey layers carbon	Pyridinic N	0.1 M $KHCO_3$	-0.60	CO	90.0	F. Pan, et al, ACS Catal., 2019, 9, 2124-2133

Mainly N-doped

Improve electrical conductivity (carbon is less electronegative than N)

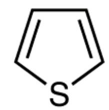
Porous carbon materials | **co-doped carbons**

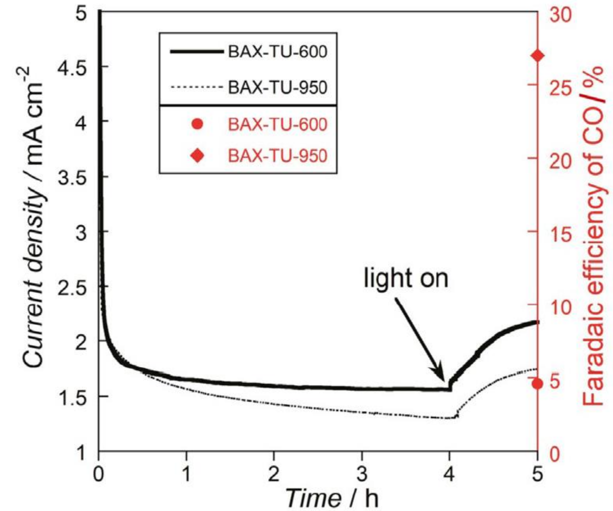
Improve activity

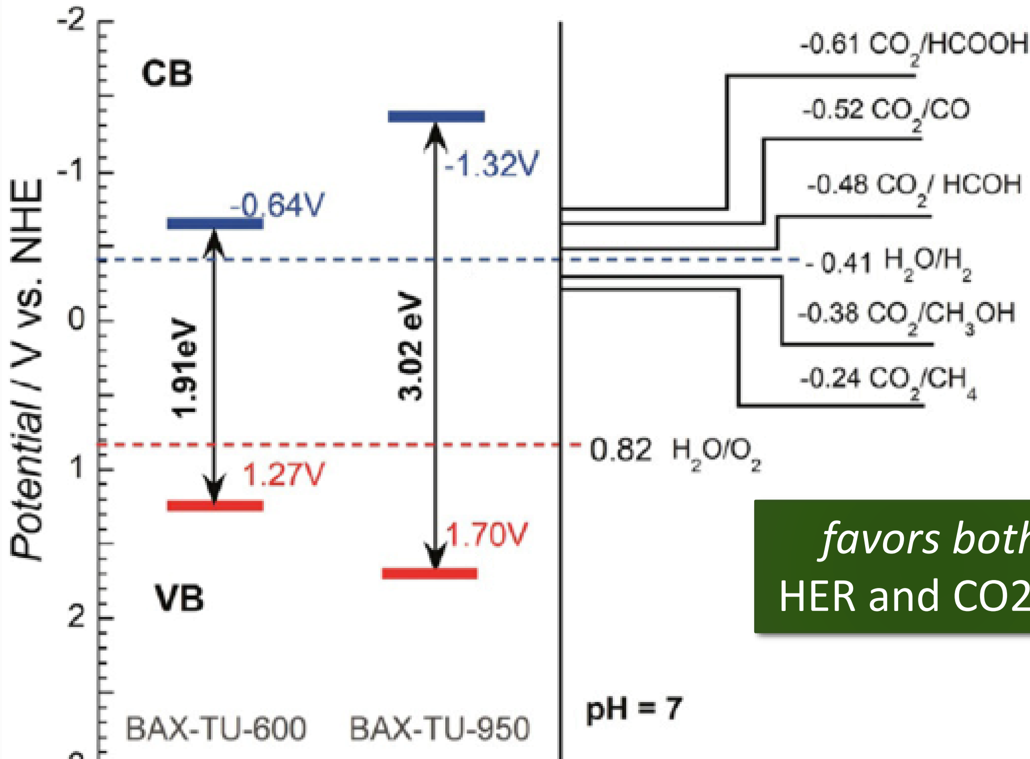
Catalyst for the (photo)electrochemical CO_2 conversion

Sample	S_{BET} [$m^2 g^{-1}$]	V_{mic}/V_t	Elemental content [at %] C	O	N	S
BAX-TU-600	1370	0.62	82.8	8.2	5.8	3.2
BAX-TU-950	1146	0.66	88.2	9.7	1.2	0.9

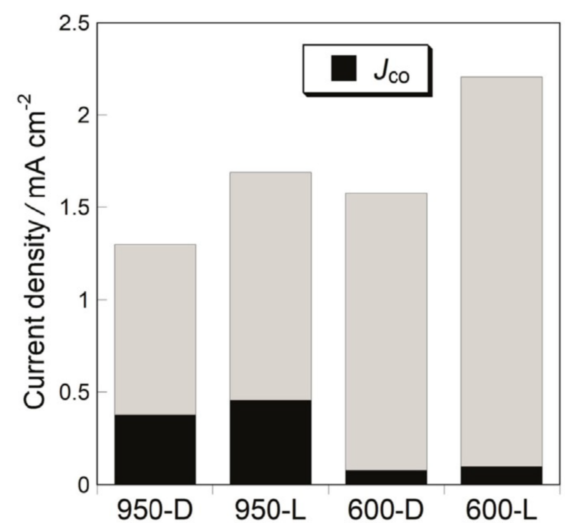
Thiophenic S
Photocurrent generation upon light irradiation







favors both
HER and CO2RR



PROBLEM STATEMENT

Textural and structural properties

How does the porosity of the carbonaceous material affect the activity and selectivity in CO_2RR?

How does the structure of the carbonaceous material affect the activity and selectivity in CO_2RR?

Catalytic activity

What is the origin of its catalytic activity or the nature of the active sites, type of heteroatoms and surface chemistry capable of reacting with the carbon dioxide molecule?

HYPOTHESIS

The 3D structure and the interconnection of the porosity in the carbon materials that lead to greater availability of active sites-nanoreactors.

The textural properties of nanoporous carbon materials (average pore size and volume), as well as the modification of the surface chemistry by the presence of heteroatoms, allow the control of the activity and selectivity of CO_2RR

Simple and easy synthesis

From benchmark to pilot plant

Preparation of (photo)electrocatalyst electrodes based on carbon materials with enhanced mass transfer.
High versatility of nanoporous carbon materials for the preparation of composites and heterojunctions with semiconductors and abundant earth metals.

OBJECTIVES

Overall

To develop catalysts based in nanoporous carbon materials, which act as sustainable and efficient (photo)electrocatalysts for the conversion of CO_2 into fuels and chemical products

Specifics

1. To correlate the porosity of the carbons with their catalytic performance.

2. To establish the relation between the (photo)electrochemical properties with the structure and composition of the electrodes/catalysts based on carbon nanoporous materials.

3. To prepare functionalized carbons materials by incorporating heteroatoms (O, N, S, P, B) and non-precious metals (e.g., Fe, Cu, Zn), and assess their catalytic activity towards CO_2RR.

4. Performance tests of the most promising materials using laboratory-scale (photo)electrochemical reactors

METHODOLOGY

Permanent search for information related to the (photo)electrochemical CO_2 reduction reactions

SciFinder
The choice for chemistry research.™

Scopus

Google scholar

Nanoporous carbon materials and Electrode preparation

Nanoporous carbon materials

Factors such as:

- Porosity control by chemical/ physical activation

- Incorporation of heteroatoms and non-precious metals

Electrode

- ***Electrode collector***: Ti foil, carbon paper, carbon cloth
- ***Casting procedures:*** Spin coating, spray coating, doctor blade, etc.
- ***Binders:*** PVDF, PTFE, cellulose, nafion
- Carbon black materials

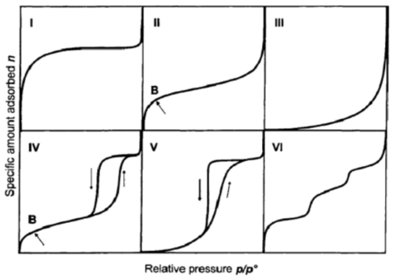
(Improvement electrical conductivity)

Catalyst and electrode characterization

Physicochemical characterization

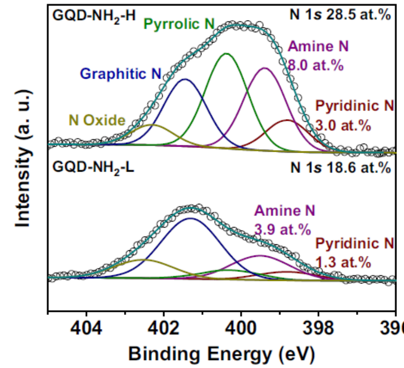
Establish the correlation between composition, textural and structural properties with their catalytic properties

N_2 Ads-Des.



- Surface area
- Pore volumes
- Pore size distributions

XPS



Heteroatoms and chemical speciation

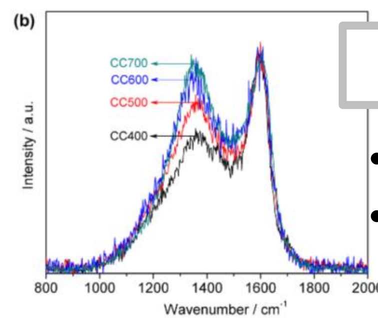
SEM

- Morphology
- Heteroatoms overall dispersion

TEM

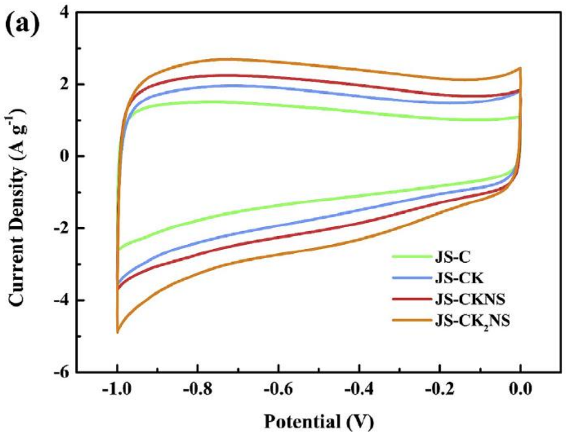
- Particle size
- Catalyst structure

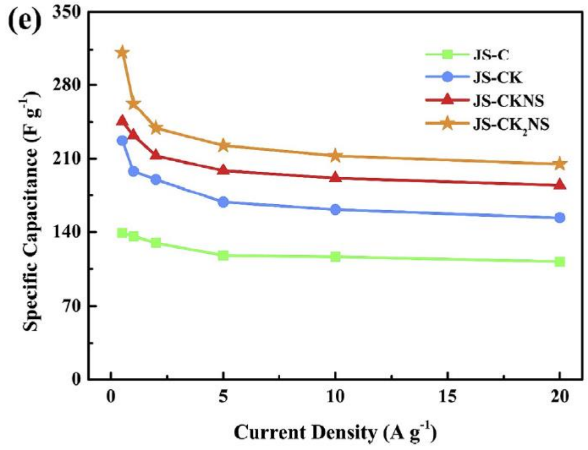
Raman spectroscopy

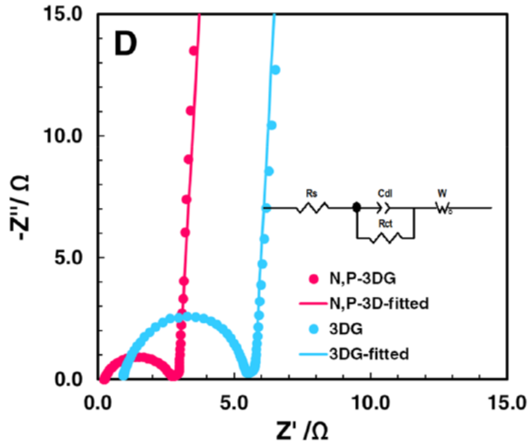


- I_D/I_G : structural defects
- Aromaticity extent

(Photo)electrochemical characterization







The (photo)electrochemical characterization will be carried out in various electrolytes by using classical electrochemical procedures such as:

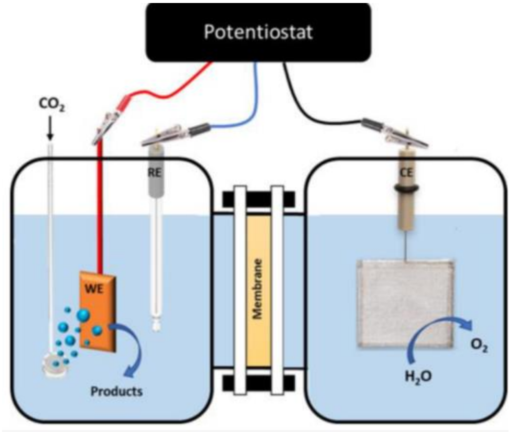
- Open-circuit potential
- Cyclic/linear sweep voltammetry
- Chronoamperometric measurements
- Electrochemical impedance, etc.

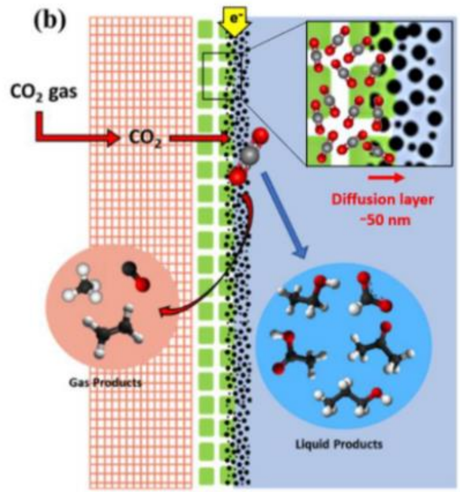
PHOTO: Solar light (150W Xe lamp)

Define parameters such as:

- Onset potential
- Overpotential
- Current density
- Tafel slope
- Photocurrent
- Tauc plot
- Mott–Schottky plots

Catalytic tests

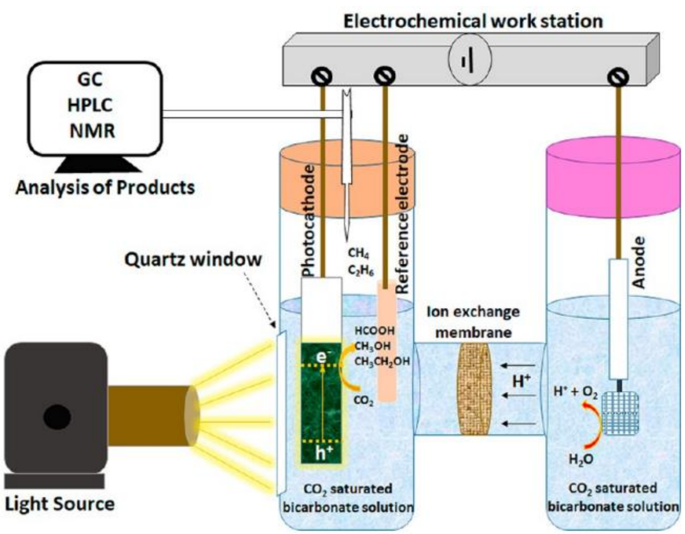




- Faradaic efficiency (FE %)
- Conversion
- Selectivity
- Yield
- Energetic efficiency

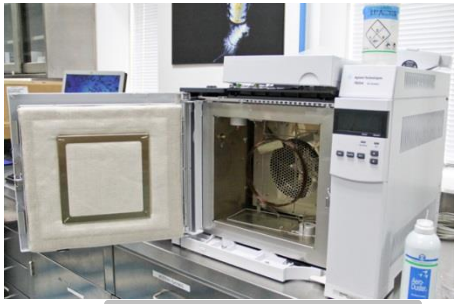
Reactor configuration

- Gas diffusion electrodes
- Membrane coated electrodes
- Membrane catalysts assembly electrodes



Determination and quantification of reaction products

HPLC-DAD



GC-TCD-FID

Timeline

ACTIVITIES	2022 unmodified	2023 Modified porosity	2024 Defined porosity and heteroatoms	2025 Stability
Bibliographic review	☑	☑	☑	☑
Catalyst and electrode synthesis	IEUA Cemhti	IEUA Cemhti	IEUA Cemhti	
Catalyst and electrode characterization	IEUA Cemhti	IEUA Cemhti	IEUA Cemhti	
Catalytic tests			IEUA	IEUA
Determination and quantification of reaction products			IEUA	IEUA
writing scientific articles	☑	☑	☑	☑
Writing doctoral thesis				☑

EXPECTED IMPACT

- To prepare electrodes based on nanoporous carbons that exhibit high performance in the conversion of carbon dioxide to chemical products of industrial interest or energy sources such as fuels **(the economical manufacture of these electrodes with the least possible environmental impact will be considered).**

- To prepare bifunctional (photo)electrocatalysts for the CO_2RR and oxygen reduction reaction (4 or 2 electrons involved).

- Generate a positive impact on the environment since this type of technology leads to the neutrality of the carbon cycle.

- Participation in seminars, courses, workshops, and other scientific events is expected, as well as dissemination in scientific papers and international conferences.


THANK
YOU
GRACIAS
ARIGATO
SHUKURIA
DANKSCHEEN
TASHAKKUR ATU
YAQHANYELAY
SUKSAMA
EKHMET
GRAZIE
MEHRBANI
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