Hierarchical porous catalysts based on carbon materials for the production of green fuels: valorization of CO_2 and NH_3 production

Research Plan Defense_Doctoral Thesis

Ali FAYAD

PhD Student in Electrochemistry. Science and Technology

Thesis Directors: Dr. Conchi ANIA, Dr. Jesus INIESTA

CEMHTI, CNRS (UPR 3079), Université d'Orléans, 45071 Orléans, France

Instituto Universitario de Electroquímica, Universidad de Alicante, 03080 Alicante, Spain

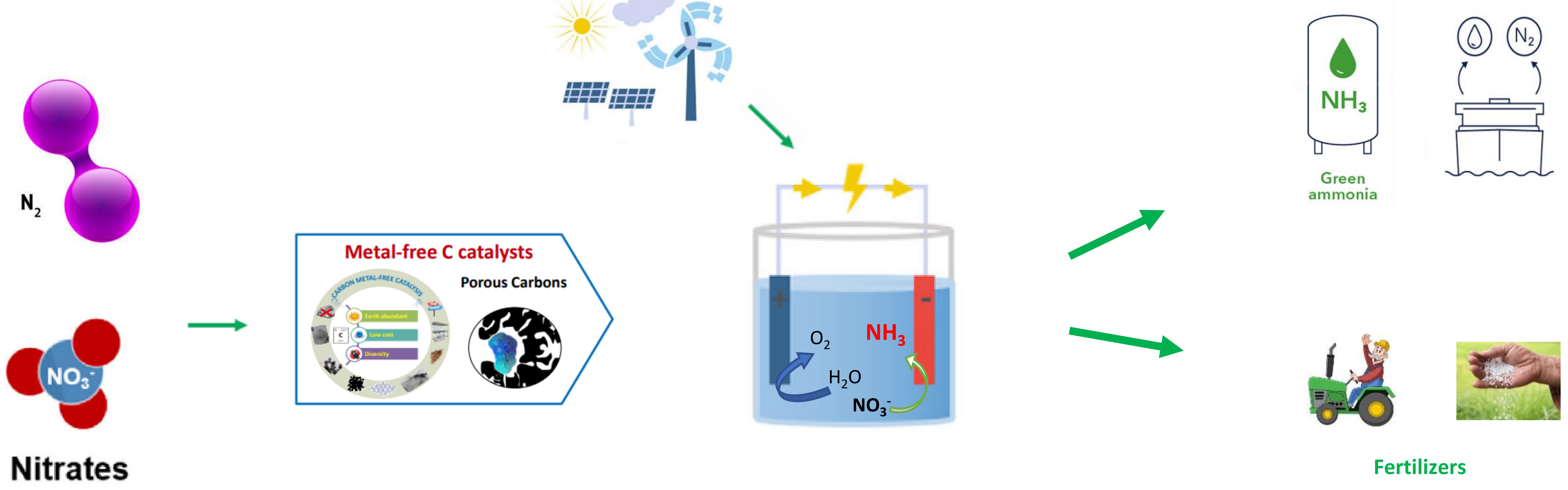
Outline

- **Introduction and State of the Art**:
  - -NH_3 production
  - -Valorization of CO_2
- **Problem and hypothesis**:
  - - Problem statement:
    - -Nanoporous Carbons characteristics
    - -Catalytic activity
  - -Hypothesis
- **Objectives**: -general and specific objectives
- **Methodology:**
  1- Literature Survey
  2- Synthesis of catalysts: nanoporous carbons
  3- Electrodes prepation
  4- Characterization Techniques
  5- Photo(electro)chemical characterization
  6- Catalytic Assays
- **Time Line**
- **Expected Impacts**

Introduction and State of the Art:

NH_3 production

- The conventional Haber-Bosch process for Ammonia production is responsible for 1.8% of the global CO_2 emissions and nearly 2% of global energy consumption due to its operating extreme conditions (500°C, 300 bars) and the fossil fuel dependence.
- The electrochemical reduction of N-Compounds is one of the most promising technologies to replace the Haber-Bosch process for the production of NH_3 as a green H_2 energy vector at ambient conditions (room T, atm pressure).
- Metal-free carbon materials are excellent candidates for this reaction due to their versatility of structure, abundance and conductivity.



Introduction and State of the Art:

NH_3 production

NO3RR: 8-electron transfer reaction:

$NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^-$

NRR: 6-electron transfer reaction:

$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$

$NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^-$ (1)

$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$ (2)

$NO_3^- + e^- \rightarrow NO_3^{2-}$ ($E_0 = -0.89 \pm 0.02$ V (vs. SHE)) (3)

$NO_3^{2-} + H_2O \rightarrow {}^*NO_2 + 2OH^-$ ($k = 5.5 \times 10^4\ s^{-1}$) (4)

${}^*NO_2 + e^- \rightarrow NO_2^-$ ($E = 1.04$ (vs. SHE)) (5)

${}^*NO_2^- + e^- \rightarrow {}^*NO_2^{2-}$ ($E = -0.47$ (vs. SHE)) (6)

${}^*NO_2^{2-} + H_2O \rightarrow {}^*NO + 2OH^-$ ($k = 1.0 \times 10^5\ s^{-1}$) (7)

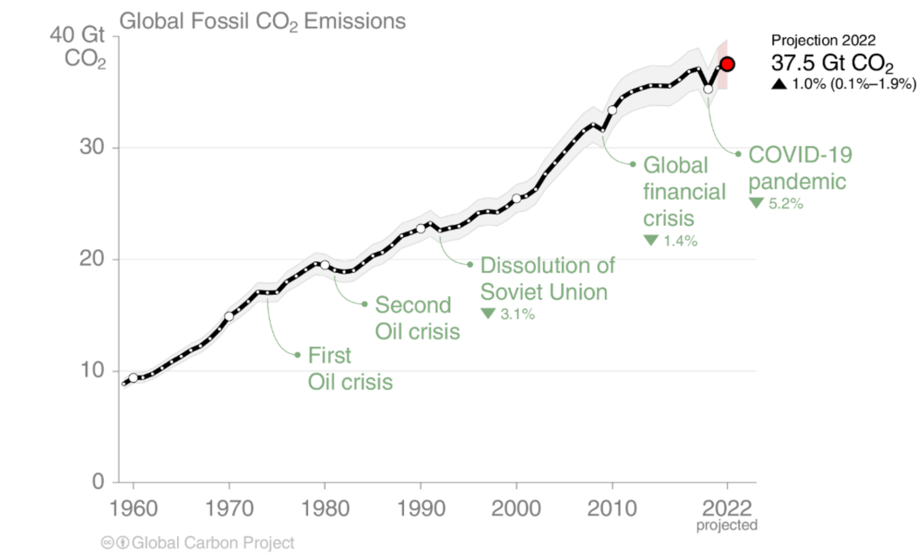
TABLE 1: Redox potentials of reducing N_2 to NH_3 [10–12].

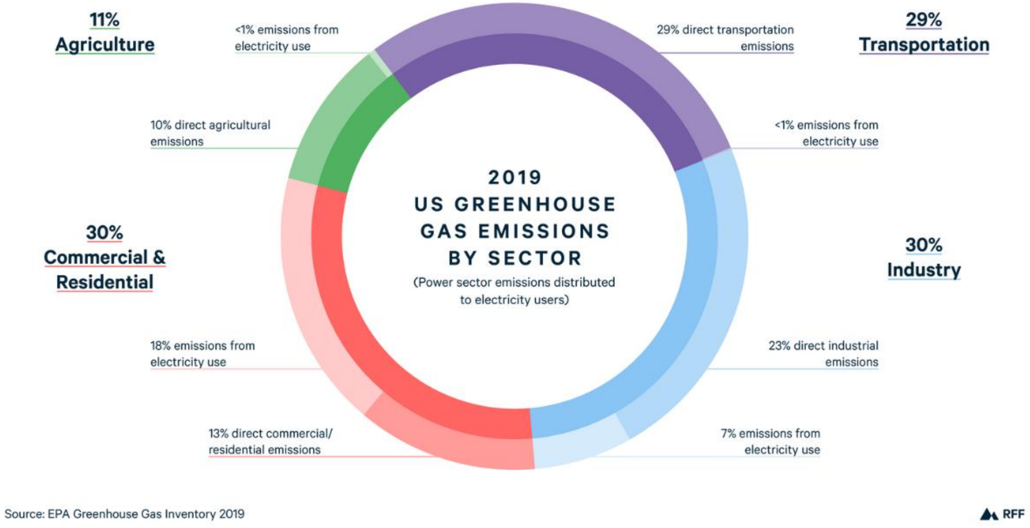
No.	Reaction	E^0 (V)
1	$H_2O + 2h^+ \longrightarrow 0.5O_2 + 2H^+$	1.33^b
2	$H^+ + e^- \longrightarrow 0.5H_2$	-0.42^a
3	$N_2 + e^- \longrightarrow N_2^-$	-4.16^b
4	$N_2 + H^+ + e^- \longrightarrow N_2H$	-3.2^b
5	$N_2 + 6H^+ + 6e^- \longrightarrow 2NH_3$	0.55^b

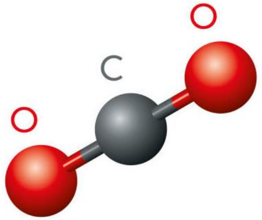
$^aE^0$ vs. NHE at pH 7; $^bE^0$ vs. NHE at pH 0.

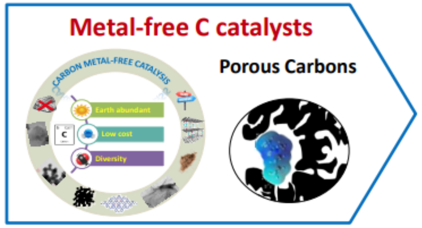
Hydrogen Evolution Reaction (HER) main competitive reaction

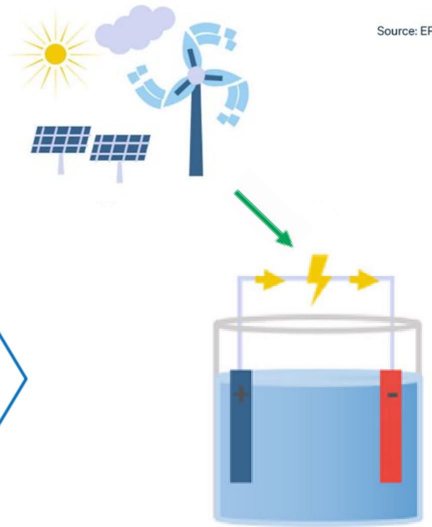
Introduction and State of the Art: valorization of CO_2











Renewable fuels

Chemicals

Introduction and State of the Art: valorization of CO_2

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

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 conditions

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

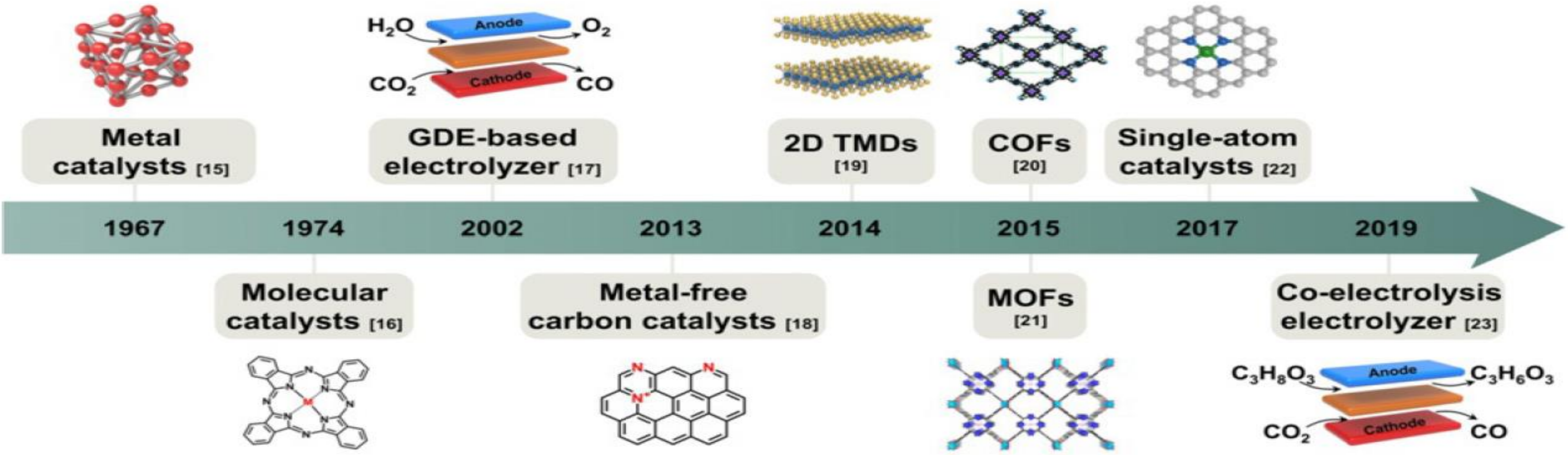
Selectivity

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

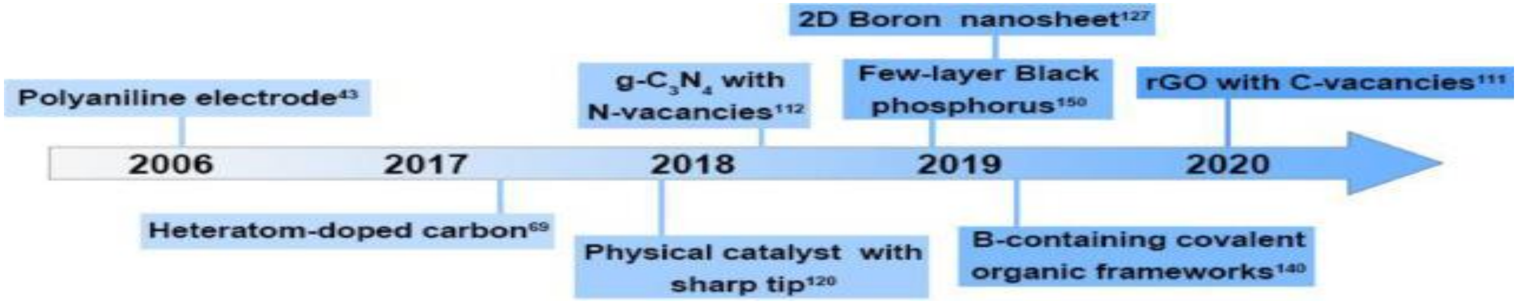
Hydrogen Evolution Reaction (HER)

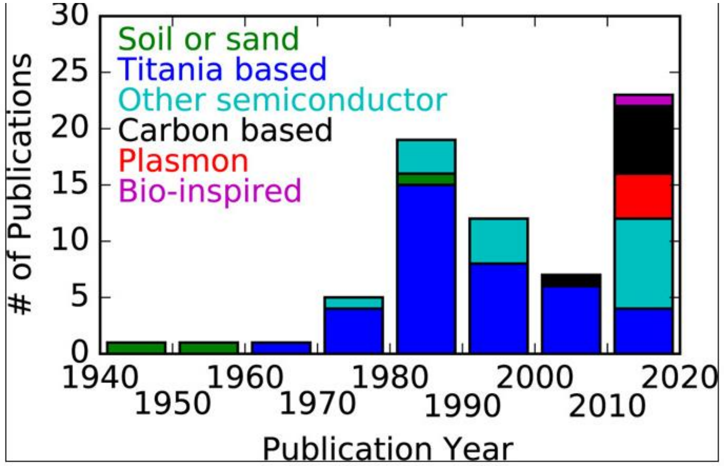
Competitive reaction of CO_2RR

Catalyst for photo(electro)chemical CO2 conversion



Catalyst for photo(electro)chemical NH3 conversion





Photo(electro)catalysts based on CARBON materials

	Catalyst	Electrolyte	Potential	Product yield	FE (%)	Reference
CO2	**N-CNT**	0.1 M $KHCO_3$	-0.78v vs SHE	CO	80.0	J. Wu, et al, ACS Nano, 2015, 9, 5364-5371
CO2	**N-3D graphene**	0.1M $KHCO_3$	-0.90v vs SHE	CO	85.0	J. Wu, et al, Nano Lett., 2016, 16, 466-470
CO2	**N-mesoporous carbon**	0.1 M $KHCO_3$	-0.56v vs SHE	C_2H_5OH	77.0	Y. Song, et al, Angew. Chem. Int., 2017, 56, 10840-10844
CO2	**N-porous carbon**	0.1 M $KHCO_3$	-0.93v vs SHE	CO	78.0	R. Wang, et al, ACS Appl. Mater. Interfaces, 2018, 10, 14751-14758
CO2	**N,S-porous CNF**	0.1 M $KHCO_3$	-0.70v vs SHE	CO	94.0	H. Yang, et al, Angew. Chem. Int., 2018, 57, 15476-15480
CO2	**N,F-Holey layers carbon**	0.1 M $KHCO_3$	-0.60v vs SHE	CO	90.0	F. Pan, et al, ACS Catal., 2019, 9, 2124-2133
NH3	**Black phosphorus (BP)**	0.1 M HCl	−0.4 v vs RHE	NH3	23.3%	Liu D, Wang J, Bian S, Liu Q, Gao Y, Wang X, Chu PK, Yu XF. Advanced Functional Materials. 2020 Jun;30(24):2002731.
NH3	**N-doped porous carbons (NPC)**	0.05 m H2SO4	-0.9v vs RHE	NH3	10.2%	Zhao S, Lu X, Wang L, Gale J, Amal R. Advanced Materials. 2019 Mar;31(13):1805367.
NH3	**F-doped porous carbons**		-0.3v vs RHE		54.8%	Zhao S, Lu X, Wang L, Gale J, Amal R. Advanced Materials. 2019 Mar;31(13):1805367.
NH3	**B-doped porous carbons**		-0.5v vs RHE		10.8%	Zhao S, Lu X, Wang L, Gale J, Amal R. Advanced Materials. 2019 Mar;31(13):1805367.

Challenges: scarce results; lack of consensus on origin of catalytic activity….

Problem and hypothesis:

Problem statement:

Nanoporous Carbons characteristics:

Role of the porosity of a carbon catalyst…
and
Role of the structural features and composition of the carbon catalyst in the performance and selectivity in CO_2RR and N-compounds RR ?
What is nature of the photo(electro)active sites in SC/C hybrid catalysts?

Catalytic activity:

Photo(electro) catalytic activity towards CO_2RR and N-compounds RR
Selectivity of products (role of catalysts properties)
Optimization of activity (production rates) and experimental set-up (cell configuration, illumination…)
Stability of the catalysts (long term)

Problem and hypothesis:

Hypothesis:

- The 3D structure and the interconnection of the nanoporosity in the carbon materials may lead to greater availability of active sites.

- The nanoporosity of the carbon catalysts (average pore size and volume), and their surface chemistry (composition, conductivity, photoactivity) may lead to tune the activity and/or selectivity towards CO2RR, NO3RR and NRR.

- The low cost, versatility of materials and abundance may make carbon materials that allows the preparation of composites and heterojunctions with semiconductors and hetero.atoms.

Objectives:

General objective:

To demonstrate the ability of carbon materials with hierarchical porosity and hybrid SC/C catalysts for the photo(electro)catalytic activity for CO_2 conversion and NH_3 production.

Specific objectives:

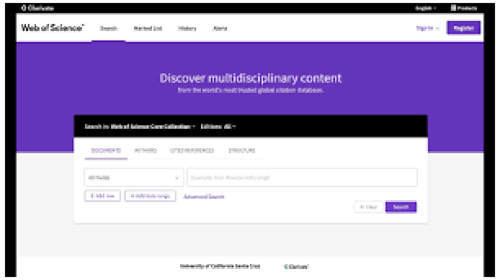
1. Synthesizing carbon materials and hybrid SC/C mixtures with photo(electro)catalytic activity for the target reactions.

2. Establishing the correlation between the nanoporosity and the chemical composition of the carbon materials with their catalytic activity towards N-compounds RR and CO_2RR, for the production of molecules of interest such as CO, methanol, ethanol, ammonia or formic acid.

3. Identifying the nature of the active sites in C-based and hybrid SC/C catalysts and the impact on reactiviy and stability.

5. Optimizing the operating conditions (e.g., cell configuration, electrodes morphology, illumination conditions, etc) to obtain high production rates (and improved selectivities) for CO_2 conversion and NH_3 production.

Methodology:



1- Literature Survey :

Continuous on the valorization of CO_2 and NH_3 via (photo)electrochemical processes; more specifically, on the studies related to the use of metal free carbon-based materials for both the N-compound RR and the CO_2RR.

Methodology:

2- Synthesis of catalysts: nanoporous carbons
3- Electrodes preparation

Nanoporous carbons:

- Synthesis from various precursors (coal, biomass, polymers...)
- Controlled porosity through activation processes (e.g., physical/chemical)
- Functionalization via heteroatom (e.g., N,O,S,F…) or metal dopoing (e.g., Cu, Fe)

Hybrid C/SC catalysts:

- Selection of SC (e.g., Ti-, Bi-, W- based) with visible light activity.

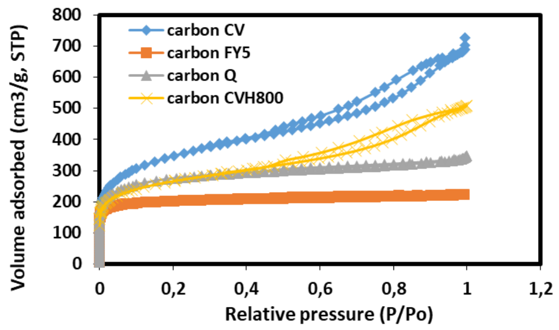
Electrodes Preparation:

- **Supports:** Ti foil, Toray paper, glassy carbons...
- **Binders:** Nafion, PVDF, PTFE, Cellulose
- **Casting Procedures:** spin and spray coating, doctor blade…

Methodology:

4- Characterization Techniques

Gas adsorption/desorption isotherms

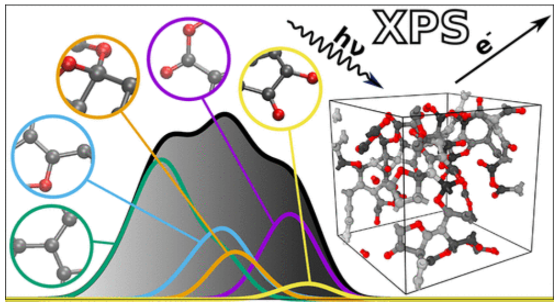


- Specific surface area (S_{BET})
- Pore volume ($V_{micropores}$, $V_{mesopores}$)
- Pore size distributions

SEM

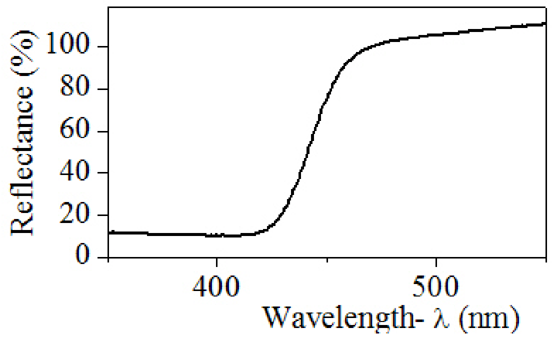
- Morphology and hetero-atom dispersion

X-ray photoelectron spectroscopy



- Material surface chemistry and hetero-atom identification.

Difuse reflectance UV-Vis spectrophotometry



- Optical properties (band gap).

Raman

- Structural properties

Elemental Analysis

- Quantitative determination of C,H,N,O,S content in the carbon materials.

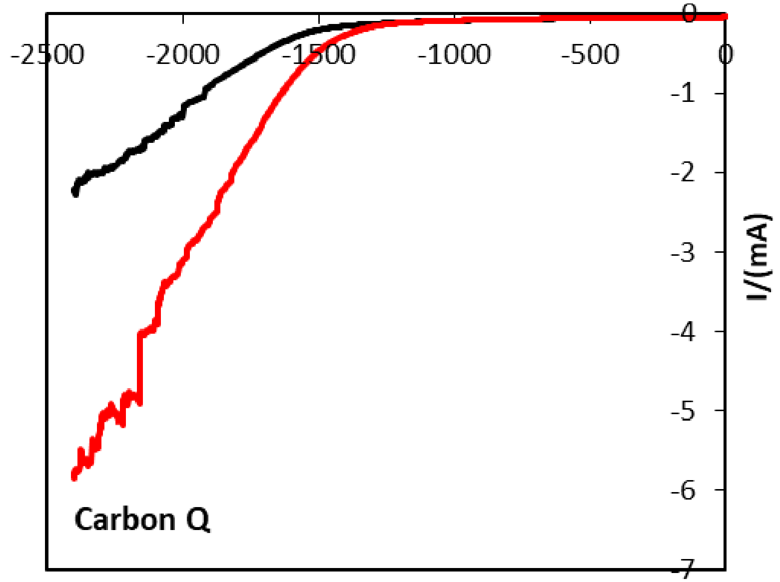
Methodology:

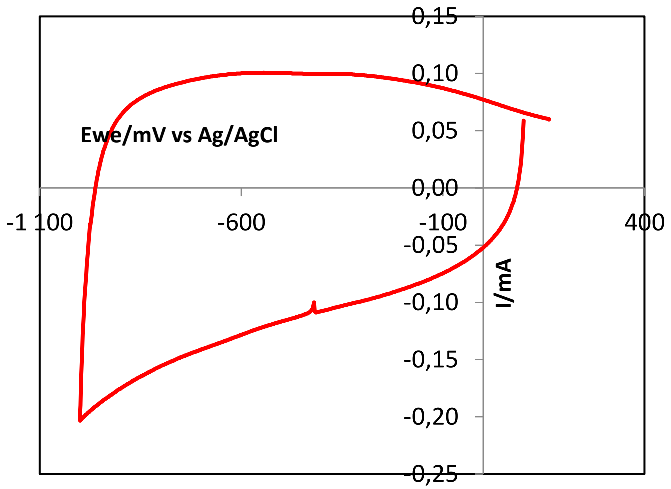
5- Photo(electro)chemical characterization

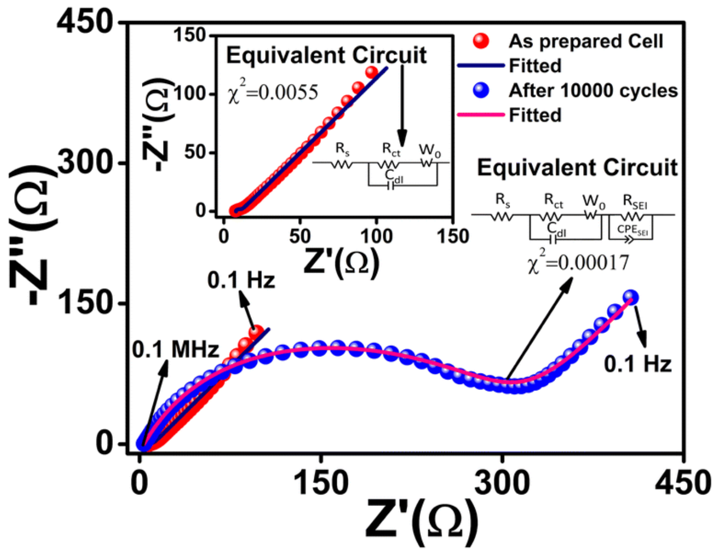
The photo(electro)chemical characterization will be carried out in various electrolytes, illumination sources and using classical procedures:

- Open-circuit potential
- Cyclic/linear sweep voltametry
- Rotating Ring Disk Electrode (RRDE)
- Chronoamperometric measurements
- Electrochemical impedance

LED Lamp





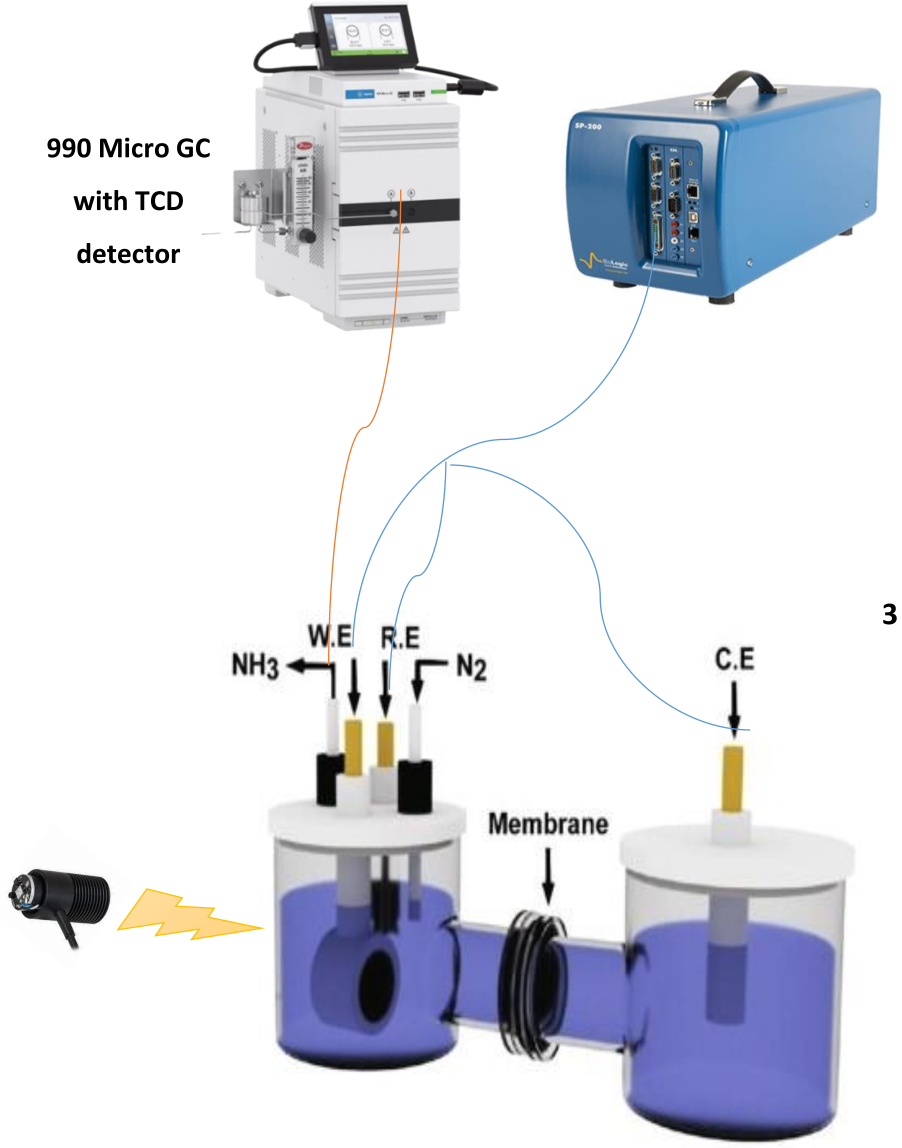


With different parameters to be identified:

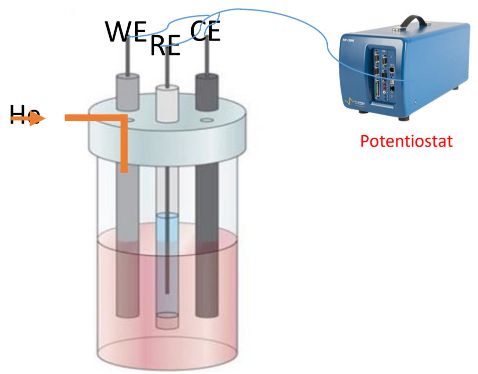
- Current density
- Onset potential
- Electrochemical window
- Over potential
- Tafel slope

Methodology:

6- Catalytic Assays



3 electrode cell : examples for NRR



3 electrode electrochemical cell for preliminary electrochemical tests

Catalytic performance evaluation will be considering:

- Faradaic efficiency (FE %)
- Production Yield
- Conversion
- Selectivity towards the desired reaction

Product and intermediates quantification and identification:

- Analytical methods and adsorption in UV-Vis range for liquid phase products.
- Online connected micro-GC for quantification of gas phase products.

Time Line

	Year 1 (2022-2023)	Year 2 (2023-2024)	Year 2 (2024-2025)
Bibliographic review	☑	☑	☑
Catalyst and electrode synthesis	☑	☑	☐
Catalyst and electrode characterization	☑	☑	☑
Catalytic tests	☐	☑	☑
Determination and quantification of reaction intermediates and products	☐	☑	☑
writing scientific articles		☑	☑
Participating in seminars, courses, conferences and scientific events	☑	☑	☑
Writing doctoral thesis			☑

Cemhti

INSTITUTO DE ELECTROQUÍMICA UNIVERSIDAD DE ALICANTE

Cotutelle agreement between Univ. Orleans and Univ. Alicante

Expected Impacts

• To prepare multifunctional nanoporous carbon-based metal-free (photo)electrocatalysts for the simultaneous conversion of N-compounds and CO_2 into chemical products of industrial interest at moderate conditions: ammonia, methanol, carbon monoxide, ethanol, urea, etc.

• To demonstrate the feasibility of photocatalytic and/or electrochemical procedures for the conversion of N-compound and CO_2, using non noble metal materials.

• To participate in the dissemination and communication of the outcome of the thesis, through the participation in seminars, courses, workshops, and other scientific events, as well as the publication of scientific papers.

Carbon 12.011

Thank you for your attention

Acknowledgements