PLA DE RECERCA / PLAN DE INVESTIGACIÓN
CURS / CURSO 2022-23

Candidat o candidata a doctor / Doctorando o doctoranda Ali FAYAD	
DNI, Passaport, NIE / DNI, Pasaporte, NIE LR0985292 / AU5PSMZ5X	**Correu electrònic / Correo electrónico** ali.fayad@cnrs-orleans.fr
Programa de doctorat / Programa de doctorado Electroquimica, Ciencia y Tecnología	
Línea de recerca / Línea de investigación Electrocatálisis fundamental y aplicada	
Títol de la tesi / Título de la tesis Hierarchical porous catalysts based on carbon materials for the production of green fuels: valorization of CO2 and NH3 production / Catalyseurs à porosité hiérarchisée à base de matériaux carbonés pour la valorisation de CO2 et de la production de NH3	

MEMÒRIA DEL PLA DE RECERCA
MEMORIA DEL PLAN DE INVESTIGACIÓN

1. Antecedents i estat actual del tema / Antecedentes y estado actual del tema

Ammonia production plays a significant and irreplaceable role in providing the nutritious food security for 7.7 billion people all over the world. That is due to its fundamental involvement in the production of fertilizers (90% of produced NH3 goes consumed in the fertilizers industry). This vast production of NH3 relies on the conventional Haber-Bosch fossil dependent process, which requires fossil dependent extreme T and P conditions (~ 500°C, 300 bars), severely revealing a high cost environmental impact. Today's Haber-Bosch produced NH3 is responsible for around 2% of the global energy consumption and nearly 1.6% of the world's CO2 emissions due to its reliance on the fossil energy [1, 2]. This poses the necessity of exploring efficient new sustainable strategies of producing ammonia under mild conditions. As a green alternative, the electrochemical reduction of N-compounds under mild conditions could be a feasible way to manipulate renewable energy in producing ammonia as a promising green hydrogen energy vector, aiming to replace the conventional Haber-Bosch process [3-6]. Similarly, the (photo)electrochemical reduction of CO2 (CO2RR) has become an alternative to mitigate the environmental impact generated since the fuels produced would reduce the demand for fossil fuels [7]. The main challenges are related to the search for sustainable catalysts with high activity and controlled selectivity towards C2 products over C1 compounds, due to their higher energy storage power.

To date, the catalysts with the best performance in these reactions are those based on noble metals, metallic phases, or transition metal oxides (Cu, Fe, Pt), which have shown relatively high Faradaic efficiency (85 - 95%). However, the challenge is to find efficient catalysts for reaching high conversions and suppressing competitive reactions (e.g., hydrogen evolution). Triggered by the multiple disadvantages of metal-based catalysts (cost, scarcity, durability), the research on metal-free abundant catalysts has become a priority. In this regard, metal-free carbon catalysts are excellent candidates due to their versatility of structure, abundance and conductivity [3-6]. Although not much explored for these reactions, the improved performance (described in terms of conversion, Faradaic efficiency, selectivity) has been mainly attributed to the effect of heteroatom doping on the electronic properties of the carbon material, and/or creating specific electrocatalytic active sites [7-9]. The role of porosity has been less studied and remains not yet clear [6 and references therein]. In addition, two main challenges of carbon-based (photo)electrocatalysts are their still rather low production rates and that selectivity to form C2 compound.

Considering this, the aim of this thesis is to anayse the use of carbon materials as (photo)electrocatalysts for the reduction of N-compouds and CO2. The study will emphasize on the understanding of

the roles of nanoporosity and surface chemistry to rationalize the electrocatalytic activity of nanoporous carbons in terms of Faradaic efficiency of products and the selectivity of the reaction.

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2. Bibliografia més rellevant / Bibliografía más relevante

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3. Objectius de la investigació / Objetivos de la investigación

This doctoral thesis explores the use of mixed catalysts based on nanoporous carbonaceous materials with controlled porosity for the electroreduction of CO2 under solar irradiation (and its valorization to fuels and chemical consumables of added value) and the electrosynthesis of NH3 from through low pressure processes. The goal is to: i) synthesize hybrid catalysts with hierarchical porosity based on carbonaceous materials and their coupling with semiconductors, and ii) show that these hybrid catalysts are efficient in CO2 conversion and NH3 production reactions.

Although the use of carbon materials for the reduction of CO2 has become a hot topic, there are still many important aspects that need to be further investigated: the role of the nanoporous texture, and the structure of the carbon materials in the overall photoelectrochemical parameters; the nature of the active sites; the impact of composition on conductivity, reactiviy and stability. Thus, the thesis proposes to explore the impact of the nanopore/CO2 interfaces and the electronic conductivity on the selectivity for the production of molecules of interest such as CO, methanol, ethanol, or formic acid.

In contrast, the use of metal-free carbon catalysts has been much less explored in the photo(electro)chemical synthesis of NH3. Hence, in this thesis we will explore different nitrogen sources (e.g., N2, NO3-) under moderate reaction conditions. For the most efficient materials, the operating conditions will be optimized (e.g., morphology of the electrodes, gaseous or liquid route). On the other hand, synthesizing compounds with C-N bonds from the co-reduction of N-sources and CO2 electrocatalytic offers advantages for the production of urea (fertilizer) or acetamides (chemical used in plasticizers and solvents). CO2 is used as the C source in these reactions, and for the nitrogen source, N2 and nitrates/nitrites are of interest, as they are abundant sources.

4. Metodologia, hipòtesi i planificació temporal / Metodología, hipótesis y planificación temporal

To attain the objectives, the following tasks and methodoloby will be carried out:

Task 1. Literature survey on the valorization of CO2 and NH3 via photo(electro)chemical processes. A special focus will be settled on porous carbon-based catalysts (electrocatalysts and photocatalyst), the conditions of the reactions, the reactors used, and the identification methods (analytical detection of reactants and byproducts). The literature survey aims to have a vision on the current state of the art of the materials used for this application and specifically on the family of carbon materials.

Task 2. Synthesis and functionalization of the catalysts.
SubTask 2.1. Nanoporous carbon-based catalysts. Following the experience of the group, the synthesis of carbon materials with controlled porous, physicochemical, structural, optical and electrochemical properties will be performed following various processes: thermo-oxidative methods from various precursors (polymers, biomass); sol-gel methods; hydro/solvothermal approaches, etc. The method will be chosen upon the outcome of the literature survey. Particular emphasis will be paid to C3N4, activated carbon, graphene derivatives and their mixtures.

SubTask 2.2. Hybrid catalysts. Modification of the properties of the carbons prepared in Task 2.1 will be performed (e.g., doping with heteroatoms, loading of abundant metals as Fe, Cu) when necessary using various techniques (thermal, wet impregnation, etc.). The incorporation of transition metal

oxides (semiconductors) to improve the photocatalytic activity of the materials will be considered (e.g., TiO2, WO3, Bi2WO6), based on the experience of the team.

SubTask 2.3 Functionalization of selected materials by the incorporation of heteroatoms (O, F, N, S) and non-precious metals with catalytic activity (e.g., Fe, Cu). The incorporation of surface functionalities will be carried out using wet oxidation procedures, infiltration, thermal treatments, etc.

Task 3. Characterization techniques.
SubTask 3.1 Physicochemical characterization of the materials: The prepared materials from Task 2 will be characterized from different techniques to evaluate composition, porosity, structural properties, morphology, conductivity, etc. Several complementary techniques will be used such as: elemental analysis, FTIR, Raman spectroscopy, XPS, thermogravimetric analysis, TPD/MS, TEM/SEM, among most representatives. The optical properties of the obtained materials will be characterized by difusse reflectance UV-Vis spectrophotometry.

SubTask 3.2 (Photo)electrochemical characterization of the electrodes/catalysts. Several casting procedures (e.g., spin coating, spray coating, film deposit by doctor blade), electrode collectors (e.g., Ti foil, graphite, Toray paper, glassy carbon) and binders (e.g., PVDF, PTFE, cellulose, nafion) will be explored for the preparation of the supported catalysts and electrodes. The photoelectrochemical characterization will be carried out in various electrolytes and using classical electrochemical procedures such as open-circuit potential, cyclic/linear sweep voltametry, chronoamperometric measurements, electrochemical impedance, etc.

Task 4. Catalytic assays.
The catalysts prepared in Task 2 will be tested for activity, selectivity, stability and response to transient illumination. Target reactions will be the electroreduction of CO2 and N-compounds, both independently and simultaneously.
SubTask 4.1. N-compounds conversion. The catalysts will be tested for N-compounds (e.g., N2, NO3-, NO2-) conversion into NH3/HNO3/urea. Divided and undivided (H-cell) cells will be used, using sacrificial cationic proton donors and aqueous electrolyte (e.g., KNO3) at various pH conditions. A carbon anode will be used to prevent cross-over of metal from the anode to the cathode. The targeted products will be quantified using UV-vis, NMR, HPLC and GC. Other evolving gaseous products such as (CO, CH4, H2, etc.) as well as CO2, N2, or NOx mixtures will be also determined. Samples will be first tested in dark, and then under polarization and/or irradiation, evaluating the effect of light intensity, wavelength, external bias potential, etc. Operation conditions will be optimized for cells showing the best performance. The studies will be performed with classical photoelectrochemical techniques (cyclic voltammetry, chronoamperometry, etc.).

SubTask 4.2. CO2 conversion. In parallel with Task 4.1, catalytic tests will be performed using CO2 streams as feed in available catalytic setups at room temperature and low pressure (ca. 1-2 bar). Benchmark catalysts will be tested for comparison purposes. A similar methodology described in Task 4.1 will be used. Preparative reduction of CO2 using electrochemical and photocatalytic approaches and their combinations will be carried out using various reactor configurations. The stability of the best performing materials will also be explored under long polarization and/or illumination conditions, as well as by the assessment of any likely deactivation.

SubTask 4.3. Simultaneous conversion of N-compounds and CO2. Based on the outcome of the previous reactions, multifunctional catalysts with dual properties for both reactions will be tested. Best performing materials will be tested in a flow single reactor cell, optimizing the connections of the cell (control of gas/liquid flow, pressure, voltage, illumination), the analytical procedures to determine conversion and selectivity of the reduction of nitrate/dinitrogen to hydrogen and ammonia, the liquid phase analysis, etc. The final performance of the cell will be based on productivity, and power to product efficiency.

Task 5. To participate in seminars, courses, workshops and other scientific events organized at the host institutions, as well as dissemination in scientific papers and international conferences (e.g., International Carbon Conference, Reuniones del Grupo Especializado de Electroquímica, meeting of the French Carbon Society, International Society of Electrochemistry, among most representative).

5. Impacte esperat/ Impacto esperado

• To prepare multifunctional nanoporous carbon-based metal-free (photo)electrocatalysts for the simultaneous conversion of N-compounds and CO2 into chemical products of industrial interest at moderate conditions: ammonia, methanol, carbon monoxide, ethanol, urea, etc.
• To demonstrate the feasibilyt of photocatalytic and/or electrochemical procedures for the conversion of N-compound and CO2, 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 publicaiton of scientific papers.

6. Implicacions ètiques o de bioseguretat/ Implicaciones éticas o de bioseguridad.

Indique si la memòria contempla algun dels següents aspectes que puguen tenir implicacions ètiques o relatives a la bioseguretat:

Indique si la memoria contempla alguno de los siguientes aspectos que puedan tener implicaciones éticas o relativas a la bioseguridad:

A. Recerca en humans o utilització de mostres biològiques d'origen humà
Investigación en humanos o utilización de muestras biológicas de origen humano
Si ☐ No ☒

B. Utilització de cèl·lules troncals embrionàries humanes, o línies derivades d'elles
Utilización de células troncales embrionarias humanas, o líneas derivadas de ellas
Si ☐ No ☒

C. Assaigs clínics
Ensayos clínicos
Si ☐ No ☒

D. Ús de dades personals, informació genètica, uns altres
Uso de datos personales, información genética, otros
Si ☐ No ☒

E. Experimentació animal
Experimentación animal
Si ☐ No ☐

F. Utilització d'agents biològics de risc per a la salut humana, animal o per al medi ambient
Utilización de agentes biológicos de riesgo para la salud humana, animal o para el medioambiente
Si ☐ No ☒

G. Ús confinat d'organismes modificats genèticament (OMG)
Uso confinado de organismos modificados genéticamente (OMG)
Si ☐ No ☒

H. Alliberament d'OMG
Liberación de OMG
Si ☐ No ☒

Si ha contestat afirmativament en alguna de les qüestions anteriors, explique els aspectes ètics referits a la recerca que es proposa, les consideracions, procediments o protocols a aplicar en compliment de la normativa vigent. En tot cas, la recerca en aquestes àrees requerirà de l'autorització del comitè d'ètica de la UA i/o dels organismes preceptius (més informació). Aquesta autorització, que ha de ser prèvia a l'inici dels treballs experimentals, serà exigible per al dipòsit de la tesi.

Si ha contestado afirmativamente en alguna de las cuestiones anteriores, explique los aspectos éticos referidos a la investigación que se propone, las consideraciones, procedimientos o protocolos a aplicar en cumplimiento de la normativa vigente. En todo caso, la investigación en estas áreas requerirá de la autorización del comité de ética de la UA y/o de los organismos preceptivos (más información). Esta autorización, que tiene que ser previa al inicio de los trabajos experimentales, será exigible para el depósito de la tesis.