Title	**Molecular strategies for steering the selectivity of heterogeneous CO_2 electroreduction.**

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# months (min.3)	6 months

Project description:

Sustainable solutions for renewable energy and fuel technologies, with a focus on incorporating circular design principles represent an urgent societal and environmental need to address the impacts of climate change in the forthcoming decades. This includes a heightened emphasis on life cycle assessments across the entire value chain, including critical raw materials, and the gradual displacement of fossil fuels. Within this context, electro-induced catalytic processes are emerging as promising alternatives to traditional thermochemical technologies. These processes offer the ability to modulate reactivity across chemical, temporal, and spatial dimensions, thereby enabling the reduction of temperature and/or pressure conditions and minimizing chemical waste.[1] However, a significant challenge in implementing these innovative manufacturing methods lies in the requirement for electrocatalysts capable of promoting desired reactions with high selectivity and efficiency over prolonged periods. In this framework, the electrocatalytic reduction of CO_2 (CO2RR) into fuels[2] and chemical building blocks has garnered considerable attention due to its potential to substantially reduce emissions by replacing petrochemical production with electrosynthesis. While CO_2 electrocatalysis is progressing towards broader application and commercial viability, there remain notable hurdles that impede process efficiency and selectivity. Thus, the search for efficient, stable, and sustainable catalysts to expedite the CO2RR is of paramount importance, presenting a complex challenge for chemists today. Among pure metals, copper (Cu) stands out as uniquely capable of generating multi-carbon oxygenates and hydrocarbons (referred to as C_{2+}). Moreover, Cu is economically viable and abundant. Nonetheless, optimizing the electrocatalytic performance of Cu-based electrodes necessitates precise control over surface structures, driving numerous chemical and surface engineering endeavors in recent decades.[3]

The process of catalyst design relies on a comprehensive grasp of the underlying reaction mechanism. To gather valuable insights into reactivity descriptors for producing high-value (C_{2+}) products, careful experimental design becomes imperative. A range of surface engineering strategies, including nanostructuring, facet manipulation, alloying, defect engineering, and surface modifications such as overlayers, small molecules, and polymers, when coupled with catalyst testing, thorough operando and post-testing material characterization, and computational analysis, offer myriad avenues present numerous opportunities for probing structure-function relationships that unveil critical reactivity descriptors.

In the pursuit of advancing catalysis, there is a growing interest in leveraging synergies between heterogeneous and homogeneous approaches. Integrating organic molecules near heterogeneous active sites

introduces additional binding interactions, which finely tune the stability of intermediates, thereby augmenting catalytic performance by enhancing Faradaic efficiency, product selectivity and reducing overpotential. Molecularly enhanced heterogeneous CO2RR catalysts present an opportunity to surmount significant challenges in adjustability and stability, thereby representing a frontier in CO2RR electrocatalysis.
The proposed project aims to develop cost-effective and customized electrocatalysts based on copper and its alloys in the form of nanowires (NWs)[4,5] to harness synergy between heterogeneous and homogenous approaches. The strategy involves combining traditional surface structuring achieved through chemical and electrochemical processes with the incorporation of tailored organic molecules adsorbed onto the surface of the NWs. This approach creates a microenvironment to catalytic activity where factors such as confinement, hydrophobicity, and local electric fields work synergistically to facilitate selective multi-electron and multi-proton transfers, thereby facilitating CO_2-to-C_2 transformations. Our goal is to produce value-added products such as ethanol and ethylene, not only contributing to scientific advancement but also addressing economic and societal needs.

The project main tasks comprehend:

1. Nanowires synthesis (eventually by a design of experiments approach), deposition (on different supports and/or with different inks) and characterization (by cyclic voltammetry, SEM, TEM, XRD, etc.)
2. Electrocatalytic tests on bare NWs. CO_2 electroreduction as a function of NWs morphology, supporting material, electrolyte, electrode pretreatment.
3. Product analysis by NMR and gas chromatography.
4. Electrocatalytic tests on modified NWs. A library of tailored organic ligands will be synthetized and investigated to analyze the effect of alterations in the interfacial microenvironment between catalysts and electrolytes.
5. Operando/In-Situ investigations. The effect of the surface modifications and reconstruction during the electrocatalytic measurements will be studied by operando optical and scanning probe techniques.

Importantly, within the framework of this project, a multidisciplinary approach will be adopted that, other than including synthesis activity (supervised by DR Marco Baron) and electrocatalytic measurements (supervised by Prof. Sabrina Antonello), envisages spectro-electrochemical operando techniques (secondment at Dr Frederic Kanoufi laboratories, Department of Chemistry, Laboratoire Interfaces Traitements Organisation et Dynamique des Systèmes – ITODYS, Université Paris Cité) and high-throughput catalytic screening methods accompanied by a Design of Experiment and machine learning approach. This comprehensive approach aims to expedite the analysis of complex catalytic data and provide deeper mechanistic insights.

References

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(3) Choi, C. et al. “Highly Active and Stable Stepped Cu Surface for Enhanced Electrochemical CO_2 Reduction to C_2H_4”. *Nat Catal* **2020**, *3*, 804–812.
(4) Conte, A.; Baron, M.; Bonacchi, S.; Antonello, S.; Aliprandi, A. “Copper and Silver Nanowires for CO_2 Electroreduction”. *Nanoscale*, **2023**, 15, 3693–3703.
(5) Conte, A.; Rosati, A.; Fantin, M.; Aliprandi, A.; Baron, M.; Bonacchi, S.; Antonello, S. “Advanced Morphological Control over Cu Nanowires through a Design of Experiments Approach”. *Materials Advances*, **2024**, 5, 8836-8846.