

Bio-inspired Molecules and Materials: CO₂ Reduction as a Case Study

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Abstract: This account reviews our recent research activities in the field of CO₂ reduction. We discuss here the potential of the bio-inspired approach for the design of electrocatalytic systems for small molecule transformation. Exploiting the billion years of evolution of natural systems, we illustrate the potential of bio-inspired strategies across multiple scales to design catalytic systems. We demonstrate in particular how the shape of biological systems as well as enzymatic active sites and their environment can constitute effective sources of inspiration for the design of electrocatalysts with improved performances.

Keywords: Bio-inspired chemistry · Catalysis · CO₂ reduction · Electrochemistry · Interface engineering



Victor Mougel has been a tenure track assistant professor of Inorganic Chemistry in the Department of Chemistry and Applied Biosciences at ETH Zurich since December 2018. He completed his Bachelor's and Master's degree in Chemistry at the ENS of Lyon, and carried out his PhD at the University of Grenoble under the supervision of Prof. Marinella Mazzanti. He then joined ETH Zurich as an ETH Fellow before starting his independent career as a CNRS associate researcher at Collège de France in Paris in 2016. His present scientific focus is on the electrochemical activation of small molecules notably following a bio-inspired approach. An ultimate goal of his research group is to establish a practical system for the electroreduction of N₂ to ammonia inspired by the nitrogenase enzyme, for which he recently received support *via* an ERC starting grant.

1. Introduction

Biological systems vastly overperform artificial ones for a broad number of applications, ranging from catalyzing complex transformations selectively or performing extremely complex chemical reactions. As such, they constitute a unique source of inspiration for the design of artificial systems, and for the chemists to design new functional molecules and materials. This is particularly true in the context of small molecule (N₂, CO₂, H₂O, *etc.*) transformations, as these constitute the raw materials for all living organisms to develop. Natural systems have developed over 3.8 billion years to master these transformations with high efficiency and selectivity, utilizing – by definition – earth-abundant elements to mediate these reactions. Our laboratory utilizes this source of inspiration in a broad sense in an attempt to mimic some of the functions of natural systems to design new catalysts for the transformation of small molecules utilizing electrical energy sources. In this account, we will showcase a selection of recent results from our group illustrating the application of bio-inspired strategies to the transformation of CO₂ into value-added products by electrochemical means.

2. Bio-inspired Chemistry

Nature has inspired a very large number of human inventions, fulfilling the wish to fly like a bird, see in the night like a cat,

fabricate materials as strong as silk, among many others. The man-made substitutes can be realized following two approaches, called bio-inspired or bio-mimetic strategies. The two concepts designate two different ways of utilizing natural systems as sources of inspiration to figure out the problems that they originally solve. The concept of bio-inspiration indicates that the function of the natural system is reproduced, without necessarily reproducing its exact structure or organization, while biomimicry targets the replication of its exact structure. These two concepts are often easily illustrated by taking a plane as an example: a plane is bio-inspired, as it reproduces the function to fly of many natural systems. Yet, it does not utilize the same strategy or structure to execute this function, and the early attempts of designing planes with flapping wings were not particularly successful. Modern planes often also possess a bio-mimetic feature: the curved tip of the wings implemented to save fuel were directly inspired by the shape of bird wingtips.^[1] In recent years, such approaches have also been followed in chemistry for the design of new functional systems and materials.^[2–4]

The bio-inspired approach is indeed a particularly suitable tool to tackle small molecule transformations: some organisms have evolved over billion years to efficiently metabolize small molecules in photosynthesis, utilizing the energy from sunlight to convert carbon dioxide and water into complex organic molecules (sugars) and dioxygen. In addition a large number of microorganisms have been identified as being effective to mediate selectively other very challenging reactions involving small molecules, such as the transformation of dinitrogen to ammonia, the partial oxidation of methane to methanol, the reduction of protons to H₂, to cite the most prominent ones.

The bio-inspired approach to the catalytic transformation of small molecules necessitates a strong interplay between biochemistry and synthetic chemistry. A good knowledge of the structure of enzyme active sites is the cornerstone of the bio-inspired approach, and the chemical understanding gained on small bio-inspired models is key to better understand the more complex enzymatic systems.

3. CO₂ Reduction

Among all the reactions involving small molecules listed above, one of the most important with respect to our current societal and environmental challenge is the transformation of CO₂ into

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value-added organic molecules. The Paris 2021 agreement has set goals to reduce CO₂ emissions by 95% by the year 2050.^[5,6] The use of CO₂ as a feedstock for chemical synthesis was proposed as a way to contribute to decreasing anthropogenic CO₂ emissions by *ca.* 10%.^[7] However, the low cost of the final products combined with the cost associated with CO₂ capture and purification currently restricts the switch to using CO₂ as a C1 building block. There is hence a critical need for both reducing the cost of CO₂ reduction and increasing the value of the chemicals produced. Many prominent research groups in Switzerland and in the world have devoted significant research efforts to CO₂ reduction, but despite significant advances the efficiency of the processes and the complexity of the products obtained are still not competing with natural systems.

Our laboratory has also attempted in the recent years to tackle this challenge following bio-inspired and bio-mimetic approaches across multiple scales, from the microstructures of living organisms to the active sites of enzymatic systems (Fig. 1). The overall goal from a bio-inspired point of view is to design a system replicating the function of natural photosynthetic systems (*e.g.* utilizing an energy source to transform CO₂ and H₂O into complex organic molecules). Choosing the source of energy to mediate these reactions is key: we opted to use electricity, as it can be conveniently generated from sustainable means such as photovoltaics. Electricity can then be converted into chemical bonds in an electrolyzer, catalyzing the CO₂ reduction reaction (CO₂RR) at the cathode and water oxidation (or oxygen evolution reaction, OER) at the anode. The design of the catalysts used at the anode and cathode is derived from the bio-inspired or bio-mimetic analysis of natural systems, with the aim to tackle the three major challenges in CO₂ reduction:

- CO₂ has a very low solubility in water, which strongly limits the kinetics of the CO₂ reduction reaction. Electroreduction of CO₂ hence require efficient management of the gaseous reactant mass transport.
- Saturating an aqueous solution with CO₂ determines the pH of the solution, as the formed bicarbonate acts as a pH buffer. The catalysts developed have to be efficient in such a neutral media.
- CO₂ reduction to value-added products typically involves multi electron and proton transfers, requiring the catalysts to be selective *vs.* the kinetically and thermodynamically more facile competitive formation of hydrogen.

4. Reactant Management at the Macroscale

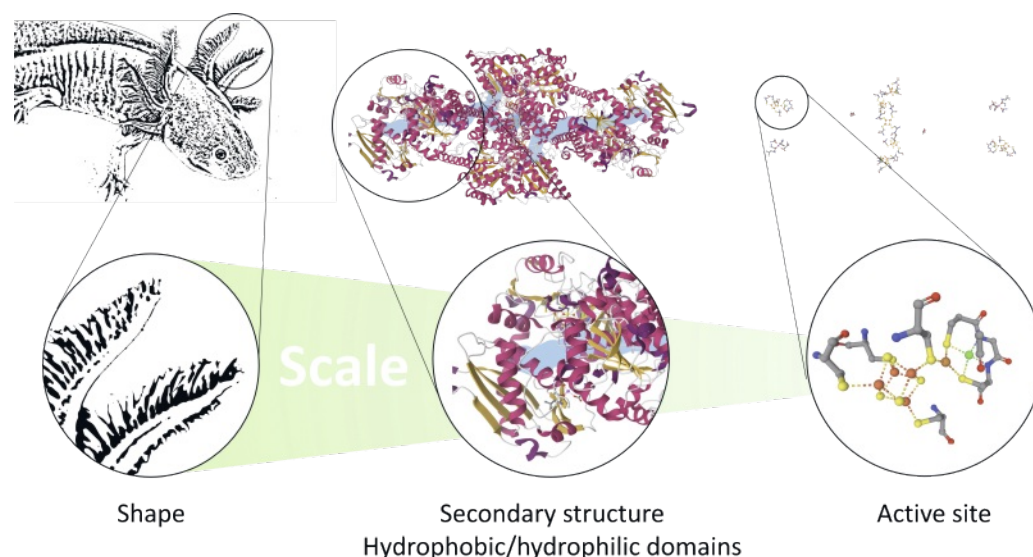
One key aspect to mediate CO₂ reduction efficiently is to use the right interface, having the ability to solve the mass transfer issues originating from low solubility of the reactant, CO₂, and to

limit the energy losses to a minimum. We have hence developed a flow electrolyzer in collaboration with the startup, Sphere Energy, which is now commercially available.^[8,9] The cell aims at lowering the resistive losses while favoring an efficient CO₂ saturation of the solution. Such a system ensures the constant saturation of CO₂ in water by flowing a CO₂-saturated electrolyte solution through the cathodic compartment. However, this electrolyte flow is not sufficient to compensate for the extremely low kinetics of the reaction resulting from the intrinsic low solubility of CO₂ in water. In such an electrochemical reaction, the reaction only occurs in the vicinity of the electrode. The fast consumption of the CO₂ contained in the solution situated at the proximity of the electrode favors a loss of selectivity *via* the competitive reduction of protons to hydrogen.

In nature, a significant number of organisms have evolved to harvest efficiently poorly soluble gases (in particular O₂) in aqueous media. This typically occurs for animals having the necessity to breathe under water, using high surface area structures called gills. Inspired by the dendrite shape of newt gills (Fig. 1, left), we have been addressing mass-transport limitations by using high surface area metallic dendritic electrodes, generated by a hydrogen-evolution-assisted electrodeposition approach.^[10,11] We have exploited this strategy to synthesize several metal and metal alloy electrodes, notably using Cu, Zn, and Ag metals and alloys.^[12–14] The choice of the metal or alloy used allowed the selectivity of the electrocatalysts to be modulated for the reduction of CO₂ to CO, C₂H₄ or syngas mixtures.

This strategy was extended to design new electrocatalysts to efficiently promote water oxidation in the conditions imposed by CO₂ electroreduction at the cathode (moderate pH, concentrated bicarbonate/carbonate solution). Only a small number of moderately efficient artificial water oxidation reactions were reported under such conditions, as most OER catalysts were developed to show maximum efficiency in the context of alkaline or polymer electrolyte membrane (PEM) electrolyzers for water splitting, *e.g.* in highly acidic or highly basic media. Since most enzymes are efficient at moderate pH, we took inspiration from an enzyme known to reversibly mediate the oxygen reduction reaction, the Laccase. Inspired by its copper oxo/hydroxo active site, we identified CuO-coated Cu dendrites as very efficient catalysts to mediate the OER in the conditions imposed by CO₂ reduction at the cathode (Fig. 2, left compartment).^[15] Utilizing the same material at both the anode and the cathode and a fully optimized electrolyzer cell, we were able to obtain an electrolyzer system with over 21% energy efficiency for the conversion of CO₂ to hydrocarbons (C₂H₄ + C₂H₆) (Fig. 2, right compartment).^[14] In addition, the high energy efficiency of the system allowed us to explore the coupling to in-

Fig. 1. Multi-scale bio-inspired approach mimicking the shape, secondary structure, and active sites of living and enzymatic systems.



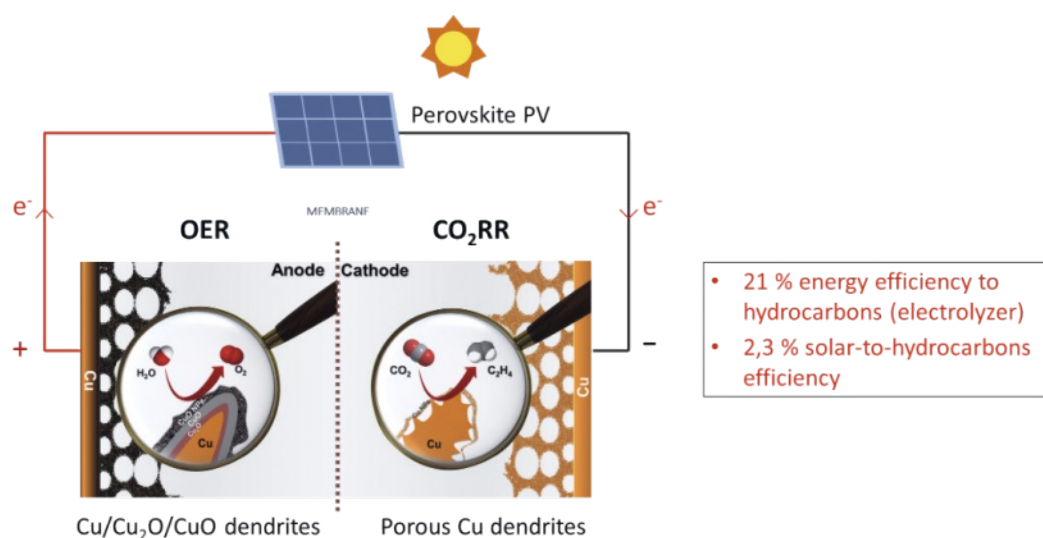


Fig. 2. Schematic representation of the PV-coupled electrolyzer setup using Cu-based dendritic electrodes at both anode and cathodes for the overall CO_2 reduction.

expensive perovskite photovoltaic cells, in collaboration with the teams of Profs. Bella and Hagfeldt. A benchmark 2.3% solar to hydrocarbons efficiency was hence obtained using a system based only on earth-abundant elements.^[14]

5. Bio-inspiration at the Molecular Level: Replicating Enzyme Active Sites

While efficient, such heterogeneous catalysts based on metal or metal oxide surfaces often present a lack of selectivity, notably due to the multiple reaction sites at the surface of the catalysts. On the contrary, enzymatic systems often constitute the quintessence of selective catalysts, being able to mediate complex transformations with selectivity close to unity. In the context of CO_2 reduction, metalloenzymes promoting CO_2 transformation constitute a great source of inspiration to prepare non-noble metal catalysts.^[16] Metal complexes replicating features of the active sites of such enzymes can be prepared and investigated. A variety of molecular catalysts mimicking the active site of the formate dehydrogenase (FDH) enzymes have been reported^[17,18] but none catalyzed CO_2 reduction in electrochemical conditions.

In that context, we investigated the electrocatalytic properties of a molecular complex mimicking the active site of another enzyme mediating CO_2 transformation, the Mo-Cu CO-dehydrogenase enzyme (CODH2). CODH2 is known to catalyze the CO oxidation to CO_2 and not the reverse reaction, but reasons for this irreversibility are still unclear.^[16] The active site of CODH2 is constituted of a heterobimetallic Mo-Cu center in which the two ions are bridged by a sulfide ion, the Mo ion also being coordinated by a molybdenopterin ligand and an oxo/hydroxo moiety.^[19] We showed that the bimetallic complex $[(\text{bdt})\text{Mo}^{\text{VI}}(\text{O})$

$\text{S}_2\text{Cu}^{\text{I}}\text{CN}]^{2-}$ (bdt = benzenedithiolate) (Fig. 3), mimicking its active site, was electrocatalytically active for the selective reduction of CO_2 to formic acid. The different product selectivity observed with respect to the enzyme it models (formate vs. CO) appeared particularly surprising. Thanks to the simplicity of this small molecular model of the enzyme active site, we demonstrated, using a combination of infrared spectroelectrochemical studies coupled with density functional theory, that the complex is only a pre-catalyst, while the active catalyst is generated upon reduction in the presence of CO_2 . We found that the two-electron reduction of $[(\text{bdt})\text{Mo}^{\text{VI}}(\text{O})\text{S}_2\text{Cu}^{\text{I}}\text{CN}]^{2-}$ triggers the transfer of the oxo moiety to CO_2 forming CO_3^{2-} and the complex $[(\text{bdt})\text{Mo}^{\text{IV}}\text{S}_2\text{Cu}^{\text{I}}\text{CN}]^{2-}$ and that a further one-electron reduction is needed to generate the active catalyst. Its protonation yields a reactive $\text{Mo}^{\text{V}}\text{H}$ hydride intermediate which reacts with CO_2 to produce formate as the main reduction product from CO_2 reduction (Fig. 3).^[20]

Beyond the identification of a new selective catalyst for CO_2 reduction, this study allowed an unknown activation pathway of the bio-inspired active site to be identified. It highlights that such studies also have the potential to provide feedback to the investigation of the enzymatic system *via* the study of simple models of their active site. The different selectivity of the CODH2 enzyme and this mimic may indicate that the secondary enzymatic structure plays a key role in determining the enzyme selectivity. It highlights the interest to also consider the environment of the active site to design active bio-inspired catalysts, as discussed below in section 6.

In addition, this work illustrated the potential of thiolate ligands for the generation of active catalysts for the electroreduction of CO_2 to formate. Thiolate ligands, being soft Lewis bases

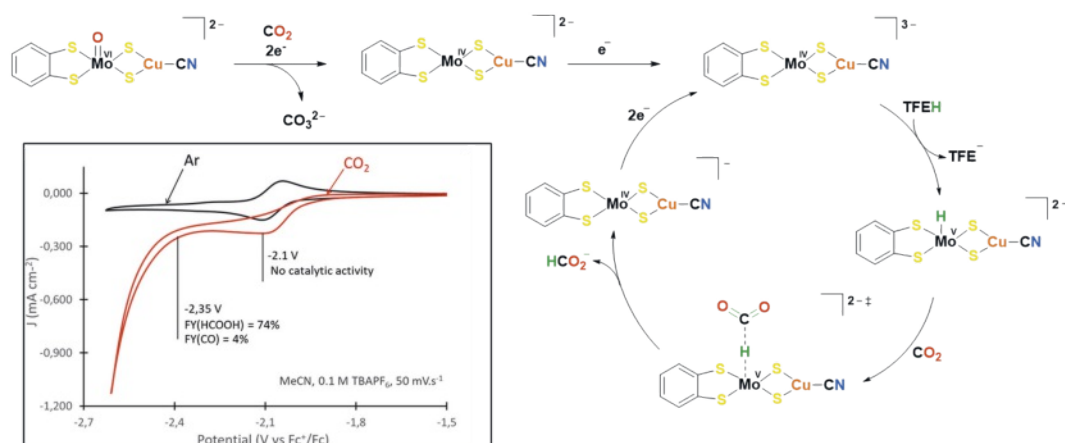


Fig. 3. Proposed reaction mechanism for the electrochemical CO_2 reduction using $[(\text{bdt})\text{Mo}^{\text{VI}}(\text{O})\text{S}_2\text{Cu}^{\text{I}}\text{CN}]^{2-}$ and associated CV studies in the absence and presence of CO_2 (inset).

with σ - and π -donation properties, have the potential to allow for an easy generation of metal hydride species by providing increased electron density on reduced metals while maintaining strong metal–ligand covalency. However, despite being ubiquitous in the enzymatic systems competent for CO_2 transformation (CODHs^[19,21–24] and FDHs^[25,26]), thiolate ligands had not been used for the design of CO_2 reduction catalysts until very recently.^[27–29] We hence explored the synthesis and catalytic activity for electrocatalytic CO_2 reduction of a series of cobalt(III) pyridinethiolate complexes. We demonstrated that [bipyridine-bis-(2-pyridinethiolato)-cobalt(III)-hexafluoro-phosphate] (Fig. 4) was a highly selective catalyst for formate production operating at a very low overpotential of 110 mV to achieve a TOF of 10 s^{-1} . Density functional theory studies coupled to electrokinetic analysis allowed a reaction mechanism to be proposed for the reaction and highlighted the key role of electronic tuning of the complex by its ligand properties on generating a coordinatively unsaturated intermediate and stabilizing the formed hydride species (Fig. 4).^[30] Such a molecular understanding of the key parameters required to generate a highly active catalyst is of prime importance for the design of functional materials.

The preparation of catalysts inspired by enzyme active sites is indeed not limited to molecular complexes but can also be used as a strategy for the preparation of bio-inspired materials. Porphyrins and porphyrinoids are ubiquitous as enzymatic active sites, being found in a very broad range of enzymes involved in small molecule activation and transformation.^[31] We hence explored the use of site-isolated materials containing porphyrin-like M-N4 sites for CO_2 reduction (Fig. 5).^[32–36] Such materials could combine the robustness and ability to be operated in flow conditions of heterogeneous catalysts with the selectivity of molecular systems.

We investigated the use of Fe-N-doped carbon materials (Fe-NC) presenting isolated Fe sites in a porphyrin like Fe-N4 environment. These materials, inspired by the active sites of heme-containing

monooxygenases and peroxidases, had been identified as ideal materials to mediate the oxygen reduction reaction in fuel cells.^[37,38] We identified that these materials are highly selective for promoting the electroreduction of CO_2 to CO and optimized their catalytic activity by modulating the catalyst–electrode interface.^[33,36]

However, CO or formate have much less added value than the multi-carbon compounds observed when reducing CO_2 at bulk metallic copper electrodes, yet with a low selectivity. Aiming at combining the ability of copper electrodes to promote multi-carbon product formation and the high selectivity of single-site materials, we explored the use of Cu-NC materials for CO_2 RR.^[34] These materials turned out to be highly selective for the electroreduction of CO_2 to ethanol, with over 55% FY for ethanol. Yet, *in situ* X-ray absorption spectroscopy (XAS) studies revealed a reversible restructuring of the material in operando conditions, the application of a negative potential resulting in the disappearance of the single-sites and the formation of small Cu nanoparticles (Fig. 6). Interestingly, we identified that this behavior was also occurring in a second type of well-defined single site Cu materials bearing phthalocyanine active sites.^[32]

6. Mimicking Secondary Enzyme Features

The restructuring behavior observed for these copper materials and the different selectivity observed with the Mo-Cu CODH active site mimics highlight a key feature in bio-inspired chemistry: replicating the enzyme active site does not ensure that it will stay intact under catalytic conditions. Such restructuring is typically prevented in enzymatic systems thanks to the encapsulation of the active sites into the protein framework. In addition to stabilizing the active sites *via* secondary interactions with the protein structure, the protein is key to control the reactant and products income and outcome to the active site of the enzyme. In particular, the hydrophobic/hydrophilic domains of the proteins ensure a fine control of the availability of the

Fig. 4. Proposed reaction mechanism for the generation of HCOOH, H_2 and CO. The relative Gibbs free energies (ΔG , kcal mol⁻¹) and transition state barriers (ΔG^\ddagger , kcal mol⁻¹) are given relative to the preceding intermediate.

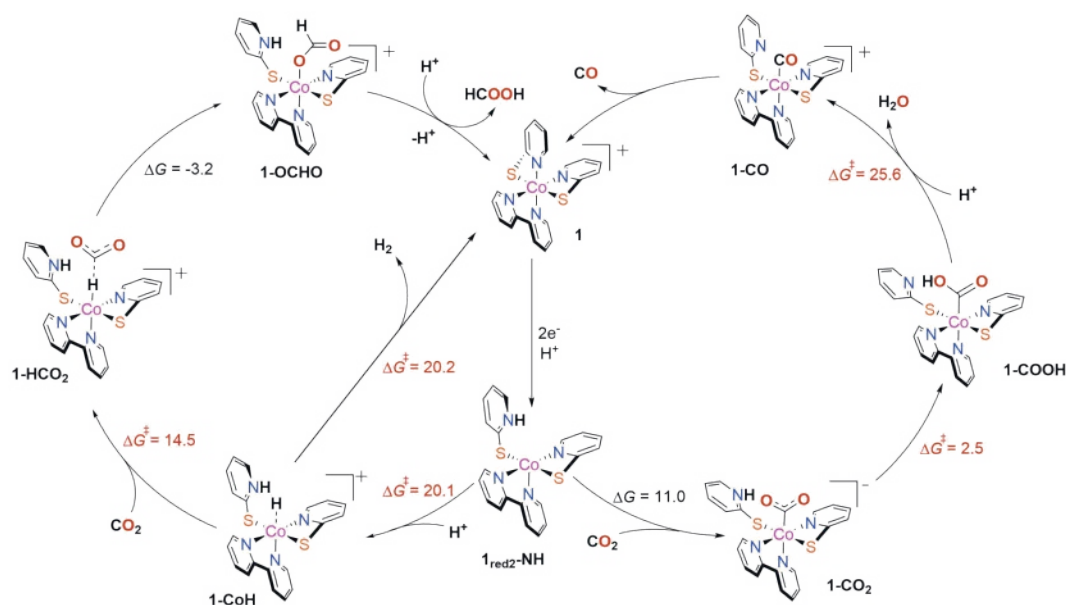
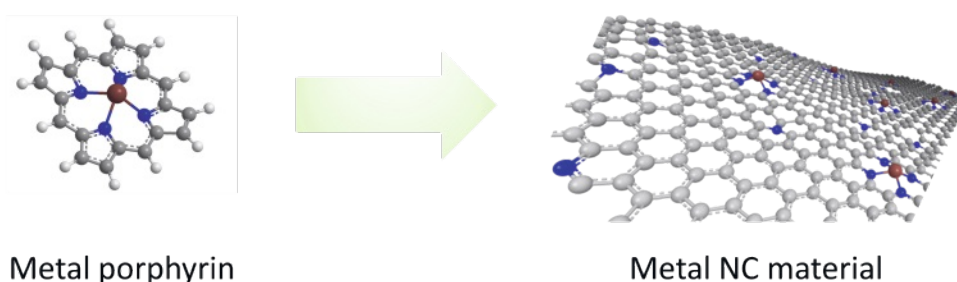


Fig. 5. M-NC materials: heterogeneous porphyrins analogues.



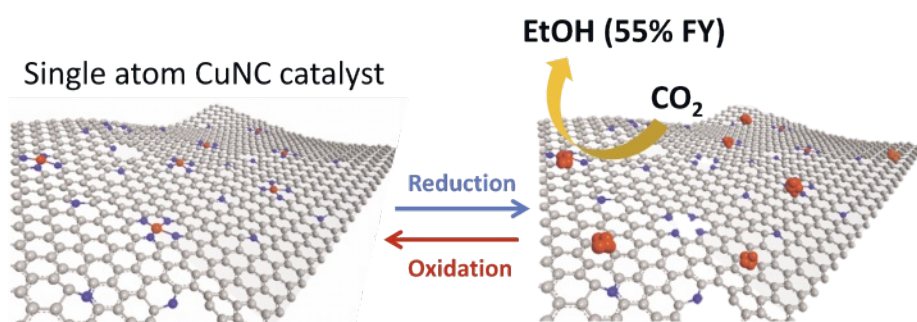


Fig. 6. Reversible restructuring of single atom CuNC materials in CO_2 RR conditions, generating in situ Cu^0 nanoparticles promoting the selective reduction of CO_2 to ethanol in 55% FY.

reactants at the active site as well as allowing the confinement of reactive intermediates. Such a reactant and product management is, for example, key for the CODH/Acetyl-CoA Synthase (ACS) enzymes. These two enzymes, found as a heterotetramer containing two units of each enzymatic site, catalyze in anaerobic microorganisms the reduction of CO_2 to CO at the CODH enzyme and its further coupling to a methyl synthon to form acetate in the ACS unit, in a similar reaction to that occurring in the Monsanto process.

In this system, the protein framework is essential for driving the reaction: selectivity of the CODH active site is provided by its position at the end of a hydrophobic channel, ensuring a high concentration of CO_2 at the active site, required for a high selectivity for CO_2 reduction vs. the direct reduction of H^+ to H_2 .^[39] Furthermore, hydrophobic channels also connect the active sites of both enzymes, ensuring that the produced CO is efficiently transported to the ACS active site. Such a management of the produced CO avoids releasing toxic CO into the organisms and ensures a high concentration of CO at the ACS active site *via* its confinement into these hydrophobic channels.

Based on this analysis, we targeted the replication of hydrophobic environments at the active site combined with the capability to maintain high CO concentration in the vicinity of the catalysts, in order to mediate multi-carbon product formation (resulting from the coupling of C1 products).

Post analysis of the dendritic Cu catalyst presented above in section 4 allowed us to identify that one of the key parameters for the formation of multi-carbon products in that system was of similar origin. We observed the formation of nano-Kirkendall voids in the electrode structure upon conversion of the initial CuO surface to porous Cu dendrites, increasing the contact time of the CO generated upon $2 e^- \text{CO}_2$ reduction and increasing the faradaic yield for multi-carbon products (Fig. 2, right magnifier). Building upon this experimental observation, we envisioned further modifying this catalyst to increase its selectivity for CO_2 reduction to multi-carbon products and to lower the formation of H_2 resulting from direct H^+ reduction. We targeted a system allowing for an increased CO_2/H^+ ratio at the active site and for a longer contact time of CO, the primary product of CO_2 reduction, in order to allow for an enhanced multi-carbon product formation. By analogy of the CODH/ACS enzymes, we explored the potential of the hydrophobic environment at the active site.

For that purpose, we prepared superhydrophobic Cu electrodes inspired by the diving bell spider strategy to harvest gas bubbles. The diving bell spiders indeed utilize a two-scale strategy to retain an air bubble around their body, *via* the use of hydrophobic hairs on their plastrons. This two-scale strategy, using hydrophobicity at the nanoscale on a micro-structured support (the hairs), allows a superhydrophobic surface to be generated, where a gas layer is trapped in the space between the spider

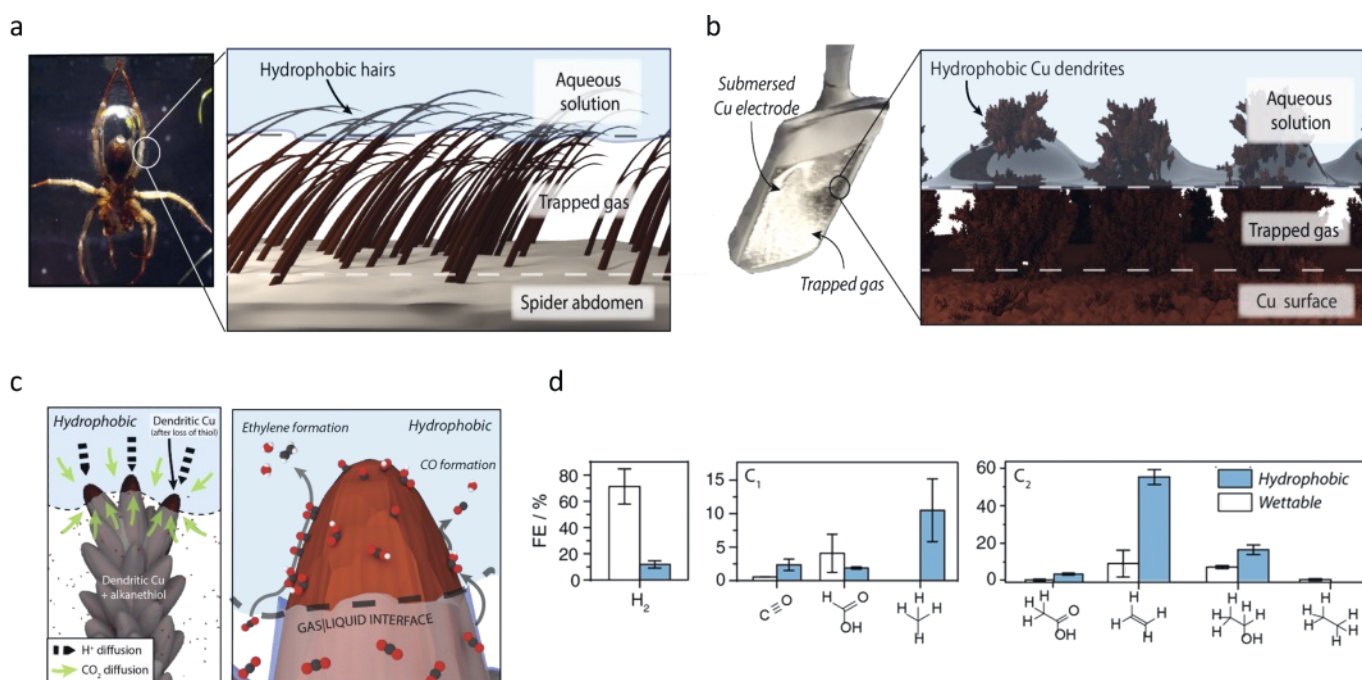


Fig. 7: (a) Diving bell spider superhydrophobic strategy for subaquatic breathing and (b), schematic representation of the analogous superhydrophobic strategy applied at the electrode/electrolyte interface of a Cu-dendrite electrode, (c) illustration of the gaseous layer trapped beneath the solution and the formation of key products on the surface and (d) Product formation at the hydrophobic vs. wettable Cu dendrite surface when passing an overall current density of -30 mA cm^{-2} . Figure adapted from ref. [40].

plastron and the top of the hairs acting as micro-structured pillars (Fig. 7a).

Following a similar two-scale approach to superhydrophilicity, we applied a hydrophobic treatment to the previously described Cu dendrites. Thiolation of the Cu dendrites hence led to a superhydrophobic surface (Fig. 7b), thereby allowing for an increase of the relative CO_2/H^+ ratio at the triple phase interface while increasing the contact time of the electrogenerated CO with the surface of the electrode (Fig. 7c).^[40] While detrimental to the overall overpotential, this strategy allowed a 6-fold increase of the selectivity of the Cu dendrite to multi-carbon products (Fig. 7d). Such a strategy highlighted that the sole modification of environment for the reaction to take place, without modification of the active site itself is sufficient to induce major change in the selectivity and efficiency of the catalysts.

7. Conclusion and Outlook

The examples developed here on CO_2 reduction highlight that bio-inspiration is a key tool for the design of catalytic systems utilizing only earth-abundant metals for the transformation of small molecules, mastered by biological systems.

This approach provided effective results at multiple scales, attempting to replicate the active site of the enzymes, their environment, and larger scale microstructures of living systems. To complement these approaches, we are currently exploring the replication of another key feature of enzymatic system: their ability to master efficient coupled proton and electron transfers. A better understanding and mimicking of these steps should increase the efficiency of catalytic systems by minimizing the losses associated with the electron transfer to the active site and allow for a better control of product selectivity.

The design of further improved catalytic systems will necessitate combining all these different approaches, to be able to prepare catalysts reproducing not only the enzyme active site but also their secondary environment and reactant management framework and to integrate them at micro-structured interfaces reproducing structures optimized over billions of years of evolution.

These requirements highlight the need for our research to be largely interdisciplinary, spanning from the design of molecular enzyme active sites mimics to micro-structured materials and *via* the design of electrochemical devices allowing their properties to be tested. We will continue to exploit these tools in the coming years to investigate our next grand challenge, the electrochemical N_2 reduction to ammonia, having the potential to provide a delocalized and CO_2 -neutral alternative to the Haber-Bosch process.

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