

Mo/W containing peptides as novel catalysts for CO₂ valorization

Context

The recycling of CO₂ has become an essential challenge for our societies as it remains impossible to avoid completely the production of this greenhouse gas. Transforming CO₂ into value-added products would offer a plausible solution to this societal need. In this regard, chemists have devoted plenty of efforts to develop catalytic processes for CO₂ valorization. With this in mind, our group got interested in formate deshydrogenases (FDHs), Molybdenum (Mo) and Tungsten (W)-containing enzymes capable of catalyzing the reversible conversion of formate to carbon dioxide ($\text{HCOO}^- = \text{CO}_2 + \text{H}^+ + 2\text{e}^-$). These enzymes have their Mo/W atom coordinated by two pyranopterin-dithiolene ligands conjugated to guanine dinucleotide leading to a Mo/W-bisPGD cofactor (Moco) [2]. The coordination sphere of the metal is completed by a cysteine- or selenocysteine in the fifth position, and sulfur atom in the sixth position. FDHs have thus become a source of inspiration for the development of new catalysts for CO₂ valorization.

PhD Project

In this project, we intend to develop bio-inspired FDHs Mo/W-peptidic systems with the final goal of obtaining efficient molecular catalysts for CO₂ reduction. Different peptidic scaffolds that will contain non-natural dithiolene-like amino acids to coordinate Mo and/or W will be designed and synthesized following established protocols [3]. The Mo/W-peptides complexes will be characterized using different spectroscopic techniques (UV-Vis, Fluorescence, EPR, NMR, IR). Electrochemistry methodologies (cyclic voltammetry, bulk electrolysis) will be employed to identify the accessible redox states of the Mo/W-peptides complexes. Ultimately, their CO₂ reduction catalytic properties will be explored. Theoretical calculations will be conducted to rationalize and validate the experimental data (electronic structures, spectroscopic parameters and reactivity) in order to get a deeper understanding of the reactivities as well as a predictive tool to assist in the design of more effective catalysts.

References

1. a) R. Hille *et al.*, *Chem. Rev.*, 2014, 114, 3963; b) R. Hille, *Protein Science*, 2018, 28, 111.
2. S. Grimaldi *et al.*, *Biochim. Biophys. Acta*, 2013, 1827, 1048.
3. a) A. Frago *et al.*, *Chem. Eur. J.*, 2015, 21, 13100; b) A. Frago *et al.*, *Chem. Eur. J.*, 2013, 19, 2076.

Keywords

peptide chemistry, coordination chemistry, electrocatalysis, quantum chemistry, bioinspired complex, energy, CO₂ valorization

Required skills

Background in peptide synthesis and/or coordination chemistry.
Knowledge in electrochemistry, spectroscopy and quantum chemistry would be appreciated.

Applications

Candidates should send a CV, a motivation letter, transcripts of marks for the Master degree and contact of two referees to:

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