

PhD position available in Bio-Inorganic Chemistry

A CEA-funded PhD position is available at the **Laboratoire de Chimie des Métaux de Transition** (UMR 5249, CEA-CNRS-Université Grenoble Alpes; Grenoble, France). **The position will open in October 2017**, in the SolHyCat group (www.solhycat.fr), for a 3-year PhD research-project dedicated to the synthesis and study of bio-inspired metal-sulfides clusters for the activation of small molecules (N₂, HCN, CO₂).

Reference: SL-DRF-17-0234.

Applications must be sent to matthieu.koepf@cea.fr before the 15th of May 2017.

Expected candidate background: We are looking for a self-motivated candidate with a strong interest in molecular chemistry and electrochemistry. The candidate should have a solid background in coordination chemistry and synthetic chemistry (organic/inorganic). He/she must demonstrate a good knowledge of usual spectroscopic and electrochemical analytical methods.

Bioinspired Polymetallic Chalcogenide Clusters for Advanced Electrocatalysis

Topic : Bioinorganic chemistry and electrocatalysis

Affiliation : Ecole Doctorale de Chimie et Sciences du Vivant (EDCSV), Université Grenoble Alpes, France

Supervision: *PhD supervisor* Vincent ARTERO

Mentor Matthieu KOEPF

Expected starting date: October 2017

Project summary:

The development of sustainable alternatives to energy-intensive industrial processes represents a major challenge for the coming decades. In that context, exploring solar-driven approaches for the production of basic chemicals and fuels is particularly appealing.¹ It will require to shift paradigm from thermally- to electro-driven processes, which are directly relevant to solar-driven approaches, and thus, must be associated with the development of innovative catalytic materials. Over the past years, the SolHyCat group has built a strong expertise in the design, synthesis and study of bioinspired protons²⁻⁵ and carbon dioxide^{6, 7} reduction electrocatalysts. Some of which could successfully be integrated into functional photocatalytic devices.⁸ We are now seeking to expand the scope of active electrocatalysts for multielectronic reactions. **This PhD will be dedicated to the exploration of the reactivity of discrete synthetic chalcogenides clusters towards simple species (H⁺, CO₂, N₂). The main goal will be to probe the ability of bioinspired polymetallic sulfides assemblies to activate dinitrogen under ambient conditions.**

Electro-reduction of dinitrogen to ammonia is a highly demanding process requiring the transfer of 6 electrons and 6 protons to dinitrogen. Few catalysts are known for this reaction, most of which are based on noble metals (Pt, Pd, Ru) or mixed samarium oxides, and require high temperature and pressure to be effective.⁹ In stark contrast, naturally occurring nitrogenases catalyze the reduction of dinitrogen to ammonia, under physiological conditions, using discrete organometallic cofactors based on earth-abundant transition metal chalcogenides such as Fe₇S₉CX clusters, with X = Mo, V, or Fe.¹⁰

The activity of these iron-based enzymes for dinitrogen reduction is remarkable, but is not exclusive. Under specific conditions, the reductive coupling of CO, CO₂ and HCN is observed as well.¹¹⁻¹³ The catalytic activity of the Fe₇S₉CX cofactor, thus, appears to be quite intriguing. Remarkably, the inclusion of related synthetic Fe₄S₄ and Fe₆S₇Mo₂ motifs within tin-sulfide matrices led to gels able to catalyze the reduction of N₂ and related substrates.¹⁴ In the latter gels, the active sites were confirmed to be the discrete iron-sulfide clusters stabilized within the structure.¹⁵ Due to the amorphous nature of the materials, however, the rationalization and fine tuning of the reactivity of the system remains challenging.

With this project, **we will prepare well-defined ligand-supported iron- and molybdenum-sulfide clusters inspired from the active site of the nitrogenases. We will study their reactivity towards dinitrogen and related species.** The use of **polypyrrole-based ligands will be introduced as versatile synthetic platforms to design a new class of thiolated cavitands.** The successful synthesis of discrete ligand-supported chalcogenides clusters will offer an unprecedented opportunity to study subtle structure-activity relationships in a new class bioinspired molecular materials and rationally tailor the catalysts for nitrogen reduction.

Project organization:

Ligands synthesis and characterization (year 1). The first objective will be to synthesize ligands possessing thiolated cavities (cavitands) around polypyrrolic platforms. Thiolated substituents will be grafted at the periphery of adequately substituted porphyrins (or related) macrocycles via *a*) classical peptide coupling strategy to introduce di- or oligo-peptides featuring cysteines, or *b*) 1,3-dipolar cycloaddition to build rigid thiolated substituents. The versatility of these two approaches will allow the introduction of a variety of substituents to form the cavity, and will offer the unique possibility to fine-tune both the first and second coordination sphere of the clusters.

Assembly of the chalcogenides clusters (year 1+2). The stabilization of chalcogenides clusters within the cavitands will be the second objective of this project. First we will investigate the stabilization of preformed iron- and molybdenum- sulfur clusters and within the cavities of the ligands, by direct thiol exchange. In a second approach, the ligand-assisted assembly of iron-sulfur clusters, from molecular precursors, will be investigated. In this case, the organic scaffold is expected to template the assembly of the clusters and control their nuclearity.

Electrochemical activation of the supported clusters (Year 1-3). The final objective of this PhD will be to explore the potential of the obtained clusters for driving the electrocatalytic reduction of selected substrates. The reactivity of the isolated cavitands-supported chalcogenides clusters will be investigated in the presence of potential substrates (H⁺, CN⁻, CO₂, N₂), after chemical and electrochemical reduction. The systems will be tested in homogeneous conditions, or after immobilization of the supported clusters on Multiwall Carbon Nanotube (MWCNTs) electrodes.

References:

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Additional information:

Funding:

This position will be funded by the Commissariat à l'Énergie Nucléaire et aux Énergies Alternatives (CEA) for 3 years, starting in october 2017. The gross monthly salary will be *ca.* 2000 euros for the first two years and *ca.* 2100 euros the third year. The student will benefit of a total of 51 days of vacation per year.

Research unit:

The Laboratoire de Chimie et Biologie des Métaux is part of the Biosciences and Biotechnology Institute of Grenoble (BIG) which is affiliated to the Direction de la Recherche Fondamentale of the CEA. The student will join the newly created SolHyCat team (team leader Vincent Artero), which will offer a stimulating international working environment. Please visit our website for further information:

<https://www.solhycat.com>

<http://big.cea.fr/drf/big/Pages/CBM/Accueil>

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This project will kick off a brand new line of research in our lab!

Reference: SL-DRF-17-0234.