PhD subject

Design of new heptazine based catalysts for carbon circular economy

In the sustainable energy field, research intensifies on new catalysts able to synthesize fuels or valuable chemicals in a greener way. In this area, the heptazine polymers (g-C3N4) are more and more popular. These **organic materials are low-cost and easy to synthesize.** They also present the **advantage of having photochemical activities** that allow, by exposing them to light, to **decrease the quantity of energy needed for several electrochemical reactions of interest in the field of sustainable energy, like H_2 formation (HER), O_2 formation (OER) and CO_2 reduction.** Moreover, some derivatives show some particularities like the ability to store photochemically induced charges (allowing time-delayed catalysis). Unfortunately, **the catalytic activities of these compounds alone remains too weak and addition of co-catalysts are needed to obtain a satisfaying efficiency.** The co-catalysts are usually metallic nanoparticles or metallic complexes. The g-C3N4 materials are obtained by simple, but difficult to control, pyrolytic syntheses. The obtained bulk are **highly insoluble rendering their physico-chemical characterization difficult**. That is why, **their photo-electrocatalytic activities are still not fully understood and poorly rationalized.** Recent publications show that **some polymer properties are retained at molecular scale.** The project consists in applying a molecular approach to **develop ligand based heptazine complexes and to study their electrocatalytic, eventually, photo-electrocatalytic, in order to better understand the materials.** The heptazine platform (C3N4) is among the rare ligands able **to stabilize low oxidation degrees of metals.** This is a strategic property to obtain efficient reduction catalysts with lower overpotentials, and better catalyst durability avoiding nanoparticle formation. Paradoxically, the **heptazine chemistry is poorly referenced in the literature**. This is mainly due to difficulties to control the derivative's reactivity. **The CAMPE Laboratory is specialized in the chemistry of these derivatives and designed many original methods to functionalize them.**

This PhD thesis will include **new heptazine ligand syntheses, complexation of these ligands** with first row transition metals, **physico-chemical characterization of the obtained catalysts,** and finally **catalytic CO_2 reduction studies**.

The PhD student will work at the CAMPE laboratory in the "CEA Grenoble". CAMPE is a laboratory for fundamental research combining chemists specializing in synthesis, theoreticians specializing in molecular modeling, spectroscopists and specialists of instrumentation. The laboratory undertakes research in chemistry and molecular physical chemistry, focusing on the CEA's major programs: new technologies for energy, the nanosciences, and chemistry for health and the environment. **Missions with collaborators**, notably in an **ETH Zürich group, could be organized in order to test the most promising catalysts on systems close to application**.

Profile : The candidate should hold a master degree (or engineer school diploma) in chemistry. He/she must have a background and practice of organic and/or coordination chemistry including purification and classical characterization methods (chromatography, NMR, GC, Mass…). Interest and/or experience in catalysis or electrochemistry would be beneficial. A good knowledge of English is recommended.

To apply, thanks to send a résumé and a cover letter to julie.andrez@cea.fr