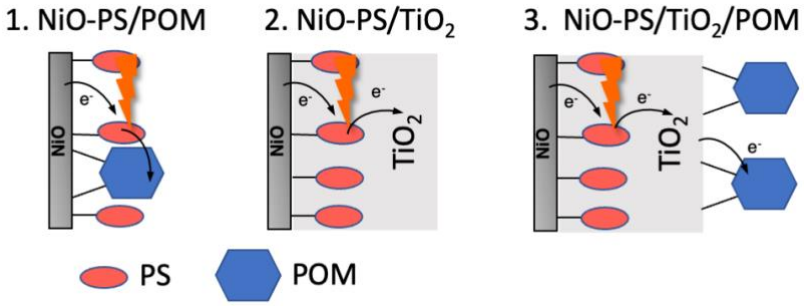
Thesis supervisors : Dr Guillaume Izzet, Pr. Anna Proust.

Development of photocathodes with improved charge extraction for efficient solar energy conversion.

The direct generation of chemical fuels from sunlight is a major scientific challenge for the development of a sustainable economy. To date, only few solar fuel-forming prototypes have been reported and solar-to-fuels energy conversion efficiencies in the 5-10% range could only be reached using high-cost materials. Some fundamental challenges especially in charge extraction need to be addressed to efficiently perform solar-to-fuels conversion. Indeed, photoinduced electron transfers occur on much shorter timescales than catalysis. Nature overcomes the problem of charge recombination processes by decoupling the light-induced charge separation from catalysis, thanks to reversible multi-electronic relays. Building on this, we intend to exploit the unique properties of polyoxometalates (POMs) as reversible multi-electron reservoirs to collect, store then deliver electrons to the catalyst.[1-3] In a complementary strategy, a thin interfacial layer of TiO_2 will be deposited on the dye-sensitized photocathode to extract and shuttle electrons toward a catalytic center, expecting to slow down charge recombination, as observed in solid-state DSSCs. Three different electrode configurations, namely NiO|PS-POM *i.e.,* POM co-immobilized with a molecular photosensitizer (PS), NiO|PS|TiO_2 and NiO|PS|TiO_2|POM, are envisioned using commercially available push-pull organic dyes. Different organic-inorganic POM-based derivatives with various redox potentials will be developed. TiO_2 thin films will be deposited by atomic deposition layer (ALD) to allow conformality and atom-level control over film thickness, under smooth deposition conditions.



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Specific techniques and skills

Inorganic synthesis, ALD, surface functionalization, spectroscopic characterization (NMR, UV-vis, IR...), electrochemistry (and spectro-electrochemistry), photo-irradiation experiments, photocatalysis tests.

Desired Profile

This is a highly multidisciplinary project with a significant component in material science and electrochemistry. The candidate should have an initial background in chemistry and an interest in working at the interface of molecular chemistry, material science, photophysics, and the development of photoelectrochemical devices. Applications (CV, motivation letter, references) should be sent to Guillaume Izzet (guillaume.izzet@sorbonne-universite.fr).

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