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Synthesis and *in situ/operando* photoelectrochemical characterization of photoelectrodes of titanium oxysulfides doped rare-earth for solar energy conversion
Synthèse et caractérisation photoélectrochimique *in situ/operando* de photoélectrodes à base d'oxysulfures de titane dopés aux terres-rares pour la conversion de l'énergie solaire

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Context. Photoelectrochemistry has been proposed as a promising approach for converting and storing solar energy under the form of chemical energy in solar fuels, such as H_2. In particular, D4 photoelectrochemical (PEC) cells, consisting of an n-type photoanode connected to a p-type photocathode in series, have the potential to exceed 20% in direct solar-to-hydrogen conversion efficiency (η_{STH}) when applied to solar water splitting.[1] However, actually achieving high conversion efficiencies supposes the development of photoelectrodes combining several characteristics: (i) optimal sunlight absorption, (ii) good charge transport and charge transfer properties, (iii) long-term chemical stability under operating conditions. Unfortunately, discovering semiconductor materials hitting these criteria has proven to be a very complex challenge, with only a handful of reported materials approaching the target performance for commercial viability (typically set at η_{STH} > 10%) and no convincing complete and efficient D4 PEC cell reported to date. As of today, there is still a strong need for PEC material optimisation in terms of optical properties and stability under operating conditions. **This project proposes expanding the library of photoelectrode materials by investigating oxysulfide materials under relevant photoelectrochemical conditions, in which bandgap and chemical composition can easily be tuned through controlled solution-based synthesis. Furthermore, the use of advanced *in situ* and *operando* tools will lead to the precise understanding of the structure-electronic properties relationships exhibited by these new PEC materials.**

Objectives. The project aims at advancing the research field of photoelectrochemical solar fuel through the following research objectives:

- Developing innovative oxysulfide photoelectrode semiconductors.
- Deciphering photoelectrochemical mechanisms with *in situ* and *operando* tools, mainly through Ultra-violet Photoelectron Spectroscopy (UPS) in voltammetric and NAP XPS/UPS mode.
- Implementation of the proposed photoelectrodes in a photoelectrochemical cell.

Project details. Regarding absorption properties, calculations show that photoelectrode materials with bandgaps (E_g) in the 1.5 – 2.2 eV range are required to achieve η_{STH}>10%. Recently, two oxysulfide materials have been proposed as photocatalysts: $Sm_2Ti_2S_2O_5$ (E_g = 2 eV)[2] and $Y_2Ti_2S_2O_5$ (E_g = 1.9 eV).[3,4] These materials show promising stability in mildly acidic solution, with no substantial degradation after 20 hours of operation. Furthermore, bandgap engineering has been demonstrated on the oxysulfides doped rare-earth $(Gd,Ce)_2O_2S$ systems: we demonstrated that it was possible to modify the bandgap from 4.7 eV for Gd_2O_2S to 2.1 eV for $Gd_{0.6}Ce_{1.4}O_2S$ by tuning the stoichiometry of the material.[5] For this project, and following our previous bandgap engineering studies, **we propose to synthesize titanium oxysulfides doped rare-earth semiconductors and probe their electronic structure by UPS under external light irradiation and an adjustable voltage source (voltammetric mode). *Quasi-operando* Electrochemistry Near Ambient Pressure (EC-NAP) UPS/XPS measurements performed by "dip and pull" methodology will also be planned at the HIPPIE beamline (MAX-LAB synchrotron Sweden) facility to monitor the evolution of the electronic make-up of the photocathode at the solid-liquid interface under operating bias.**

The materials will be synthesized by means of solution-based techniques: colloidal synthesis, solvothermal synthesis, sol-gel synthesis, electrodeposition, and so on. The photochemical bandgap modulation will be investigated by employing advanced *in situ* and *operando techniques*. First, electrochemical impedance

spectroscopy and UPS will be used to measure surface state electron density and interfacial charge transfer/recombination under illumination. Then, *operando* Raman will be employed to investigate the changes undergone by the electrocatalyst upon charge transfer from the absorbing layer and electrochemical hydrogen production at its surface. The Raman spectrometer will also be employed to perform fluorescence lifetime measurements, which can inform on the charge separation efficiency in the photocathode. Moreover, X-Ray absorption experiments will be planned to monitor metal oxidation states in the absorbing layer and at the electrocatalytic site under operating conditions.
Finally, the best performing photoelectrodes will be integrated into a complete PEC cell, studied in a standard two-electrode photoelectrochemical setup, where H_2 and O_2 production will be measured as a function of light intensity and temperature. Finally, stability measurements under illumination will be performed, monitoring H_2 and O_2 production over time and chemical degradation of the material(s) with *operando* tools.

Profile of the candidate: For this project, the candidate must have knowledge in materials science, characterization, and strong skills in chemistry and photoelectrochemistry with a master (M2) or engineering school degree.

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