Supersonic cluster beam synthesis of innovative transition metal oxides photoelectrodes for hydrogen production

Background and motivation
The need for efficient devices converting renewable energies to fuels such as H\textsubscript{2} may be tackled by photoelectrochemical water splitting: electron/hole pairs generated at two photoelectrodes (PE) drive the half-reactions producing H\textsubscript{2} and O\textsubscript{2}. The state of the art PE built with ternary metal oxides (TMOs) like CuFe\textsubscript{2}O\textsubscript{4} face major limitations like scant efficiency, photocorrosion and instability. They are ascribed to the low charge transfer induced by the small polarons due to the TMO hybrid valence band orbitals, and to the high recombination rate of charge carriers at the TMO surface and bulk states. Moreover, current PE lacks a comprehensive investigation of different TMO phases, stoichiometries and transport properties for sizes below 50 nm. The project strategy is to overcome the current limits by: 1) reducing the TMO sizes by producing PE of ZnFe\textsubscript{2}O\textsubscript{4}, CuFe\textsubscript{2}O\textsubscript{4} and BiFeO\textsubscript{3} with a nanogranular morphology (NG-TMO) at scales below 50 nm by supersonic cluster beam deposition (SCBD); 2) determining the PE morphological, optical and electrochemical behavior for three different NG-TMO compounds; 3) determining the PE transport behavior from the reaction kinetic constants (k\textsubscript{h} for the hopping process and k\textsubscript{r} for recombination process), as a function of TMO selected stoichiometries, phases and sizes.

The expected project breakthroughs are: 1) a new class of nanostructured PE for electrochemistry, NG-TMOs; 2) morphological, optical and stoichiometric properties correlation with PE thickness and annealing temperature; 3) Electrochemical properties correlation with the PE thickness and annealing temperature; 4) charge transport correlation with morphology, optical response, stoichiometry; 5) reveal the role of small polarons and surface recombination in NG-TMOs at scales below 50 nm.

The student will be tutored by three experienced tutors at the Università Cattolica (UCSC) for the PE synthesis and physical properties characterization, at the university of Padova (UPD) and university of Notre Dame (ND) for the PE electrochemical characterizations.

Profile
• Master’s degree or comparable qualification in Physics, Chemistry, Material Science or adjacent fields. The title must be obtained before OCTOBER 31ST 2022.
• Previous experience in characterization or synthesis of nanostructured materials is a plus.
• Good knowledge of the English language, both spoken and written, is essential.
• Strong commitment, ability to work in a team, and eagerness for international mobility is desired.

Opportunities
• Experimental research participating to the international collaboration between UCSC, ND (USA) and UPD, with at least one year spent in Notre Dame.
• Double degree opportunity.

Supervisors
• Prof. Luca Gavioli, UCSC, Italy luca.gavioli@unicatt.it
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