



Université Claude Bernard



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Chemical band modulation of oxide semiconductors: a spectroscopic and photoelectrocatalytic study

Modulation chimique de la structure de bandes des oxydes semiconducteurs : une étude spectroscopique et photoélectrocatalytique

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Over the last century, photoelectrochemical water splitting has gained increasing attention for the direct, carbon-free storage of sunlight energy into chemical bonds through the conversion of water into H_2 . It can be achieved by a photoelectrochemical (PEC) tandem cell composed of a photocathode (p-type semiconductor), for hydrogen production and a photoanode (n-type semiconductor), for oxygen production connected in series¹. A semiconductor-liquid junction, associated with a built-in electric field is developed at the surface of the photoanode and the photocathode resulting respectively in an upward and downward band bending, such that photogenerated minority carriers (holes and electrons respectively) are spontaneously driven towards and injected into the liquid phase under illumination, thereby limiting charge recombination². Finally, electrocatalysts are deposited on the surface of each photoelectrode to improve the kinetics of the electrochemical reactions involving photogenerated charges (namely water oxidation and reduction). Despite many attempts to develop efficient photoelectrocatalytic systems, developing photoelectrodes combining, high (photo)chemical stability, low fabrication costs, and good optoelectronic (light absorption and charge transport) properties remains a challenge³. In particular, combining good charge transport and charge separation properties is difficult, as improving conductivity typically reduces the width of the band bending and impairs charge separation.

An intriguing solution to this trade-off is the use of ferroelectric transition metals oxides (FE-TMOS, in which a local breaking of the centrosymmetry point group of the crystal unit cell occurs, leading to spontaneous electric polarisation. This polarisation allows for enhanced band-bending and improved charge separation. Moreover, it is possible to tune the bandgap values of some FE-TMOS by acting on their metal-oxygen bond length, thereby modifying coulombic repulsion and orbital hybridization in the material without affecting their ferroelectric properties. This should generate photoelectrode absorbers exhibiting good light absorption (a bandgap in the 1.5-2.5 eV range) and outstanding charge separation properties, leading to improved PEC performances. For instance, the band bending magnitude and bandgap energy of n-type Bi_2FeCrO_6 (BFCO) (2.6 eV) photoanodes can be tuned by modifying the Fe/Cr cation ratio in their composition. Indeed, *Cardenas et al.*⁴ highlighted the relationship between the degree of cationic ordering in BFCO double perovskite and their chemical states. Cationic long-range order was achieved by distorting the cation from octahedral (Fe^{3+} , Cr^{3+}) to tetragonal (Fe^{2+} , Cr^{4+}) bond distances, thus reducing the bandgap from 2.6 to 1.43 eV. Therefore, this tetragonal cationic order Fe/Cr may be tuned to influence the magnitude of the band bending and to produce photoanodes with enhanced collection depth (i.e., the distance over which photogenerated

charges can be harvested and utilized) and ultimately improved kinetics for the photoelectrocatalytic process. Importantly, charge recombination can also be significant at the surface of metal oxide photoelectrodes due to high densities of surface states, resulting in Fermi level pinning and, therefore, drastically lowering the photovoltage of the system. We propose that the use of ferroelectric materials and appropriate chemical surface treatments, such as the deposition of a protective thin layer of defect-free metal oxide thin film (TiO_2 , Al_2O_3 , NiO ...) on the surface of the absorber, will limit the occurrence and influence of these deleterious surface states³.

In recent years, UPS has been a useful tool to measure surface crystallography, chemistry, and stoichiometry on the magnitude of this band bending^{4,5,6}. To further understand the development of band bending at the semiconductor surface, **we propose for this Ph.D. thesis an in-depth study of electronic properties of BFCO thin films under an external voltage source and probe the magnitude of the band bending as a function of dopant density (Fe) and applied voltage**. This methodology will make it possible to manipulate the position of the Fermi level and directly map the evolution of band edges from the so-called "flat-band" configuration where the applied voltage compensates the band bending to the point where the Fermi level enters one of the bands. Besides, coupling an applied voltage and an external light source will allow to characterize the influence of charge carrier generation on the electronic structure and understand the distribution of the density of states of photogenerated carriers. Finally, the influence of the aforementioned protective surface layer on the potential surface state densities will be studied. These spectroscopic studies will be complemented by PEC measurements, in which photovoltage, photocurrent, and solar-to-chemical efficiencies will be measured. These PEC measurements will be performed in a typical three-electrode configuration with white light illumination of the working photoelectrode. Finally, incident wavelength-dependent studies and electrochemical impedance spectroscopies will be employed to draw up a very precise picture of the band structure at the semiconductor-liquid junction of the proposed materials. Combining UPS and PEC experiments will allow us to explore in-depth the physical and chemical aspects of the photoelectrocatalytic process and provide a crucial insight into the optimization of the band structure of TMOS absorbers.

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

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