

Short Term Mobility program

Final Report

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Using sunlight to convert H_2O and CO_2 into chemical fuels is an appealing solution to the problems posed by the intermittency of solar energy. Photoelectrochemical reactions are currently being pursued as a means for this conversion. Among the promising photoanodes for solar water splitting, in particular for oxygen evolution reaction (OER), BiVO_4 has recently drawn significant attention due to its high chemical stability and catalytic activity. The VB maximum of BiVO_4 , an n-type semiconductor, is lower than the OER (+1.23 V vs. NHE at pH 0), allowing holes to be transferred to the electrolyte and subsequently oxidize water. However, charge carrier recombination at surface states limits the efficiency of BiVO_4 -based devices by eliminating VB holes before water oxidation occurs. In this light, a better comprehension of the surface properties of BiVO_4 is essential to advance device performances.

The performed research is the continuation of a project started by *M. Favaro* (previously at the ALS, Berkeley, USA and currently at the HZB, Germany) and *E. Magnano* and *S. Nappini* (IOM-CNR). The project (and related ongoing collaboration) is focused on well-defined systems (i.e. single crystals and compact conformal films) that allow to reduce the complexity of applied materials but, at the same time, aid to draw significant conclusions on their electronic and surface properties. In particular, due to the unique characteristics of Bach beamline (IOM-CNR) driven by the aforementioned scientists, we focused on performing *soft X-ray resonant spectroscopies*. The latter are the most promising evolution of synchrotron-based techniques to probe the electronic density of complex materials. The joint efforts of HZB and IOM-CNR to tackle this challenge will greatly advance our knowledge on the electronic density at the surfaces,

with a significant impact on the whole scientific community. The knowledge gained through these investigations enhances material comprehension and boost the optimization of novel complex energy-related materials.

The experimental activity started with the investigation of Mo-doped BiVO_4 single crystals (prepared by the Leibniz Institute in Berlin), which constitute a valid playground to apply surface science techniques aiming at the understanding of the unique electronic properties of doped BiVO_4 . The activity involved a systematic investigation performed at beamline Bach. High resolution photoelectron spectroscopy was performed acquiring the V 2p, O 1s, Mo 3d, and Bi 4f core levels (taken at 200 eV photoelectron kinetic energy), the valence band (VB) and the V $L_3M_{4,5}M_{4,5}$ Auger transition. In the case of the core levels and VB, being the photoelectron kinetic energy of 200 eV, the first 2 unit cells of $\text{BiVO}_4(010)$ were probed ($\sim 22.5 \text{ \AA}$). Then, the V $L_{2,3}$ and the O K edge, centered in the soft X-rays (SX) regime (510-550 eV), were investigated via the near edge X-ray absorption fine structure (NEXAFS) spectroscopy. The photon energy range at which the V L_3 edge was scanned was used to perform resonant angle resolved photoemission spectroscopy (ARPES). As shown in Figure 1, we took two different energies within the resonance state of V L_3 edge to enhance different features in the VB, comprising the localized resonance above the valence band maximum. The measurements in Figure 1 show that although a weak dispersion with the azimuthal angle is present on VB, the resonance centered at about 1.4 eV does not modulate. This is a strong evidence for the localization of the resonance within the energy band gap of the material. Following research needs now to be performed in order to understand the role of such localized state in the photoelectrochemical performance of the material (e.g. charge shuttling vs. recombination center).

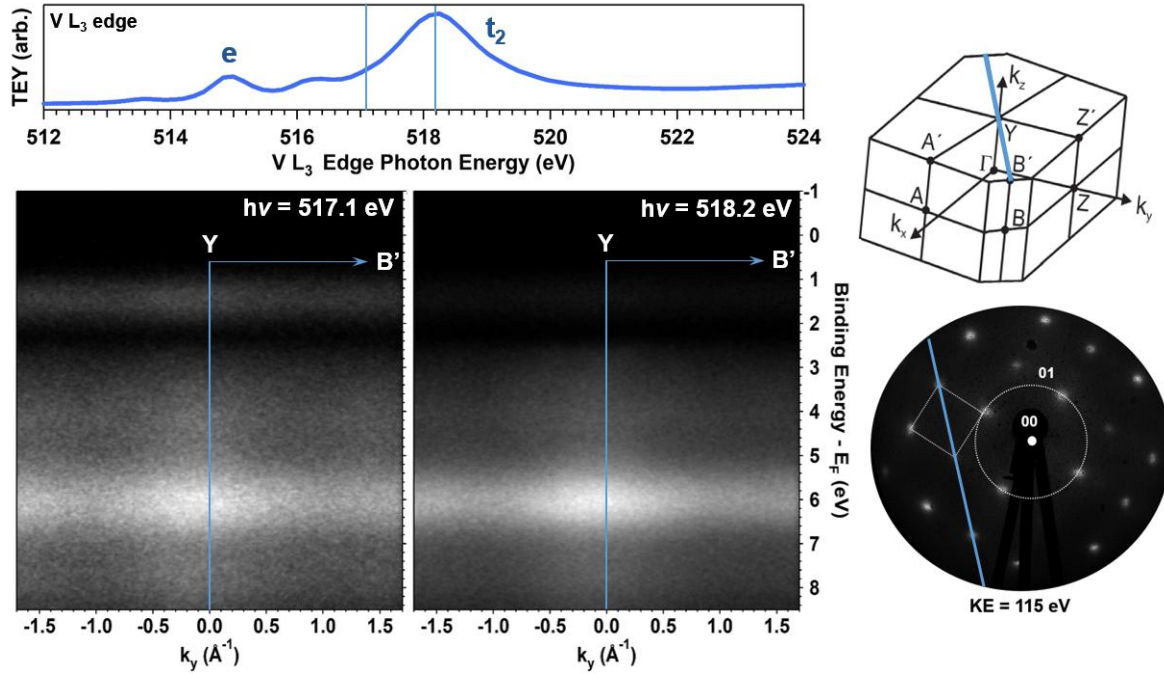


Figure 1. Left: V L₃ edge and resonant ARPES spectra taken on BiVO₄(010) surface. The two photon energies used to perform resonant ARPES are indicated in the V L₃ edge. Right: LEED pattern of the BiVO₄(010) surface and first Brillouin zone. The resonant ARPES measurements were performed along the Y→B' direction.

Aside the measurements on BiVO₄ single crystals, we have fully characterized a novel material for hydrogen evolution reaction (HER), namely copper bismuth oxide (CuBi₂O₄). The material, prepared at the Institute for solar fuels at HZB, was in form of a compact conformal polycrystalline film deposited on fluorine-doped tin oxide (FTO). We performed core level analysis at a photoelectron kinetic energy of 200 eV. Moreover, we performed depth profiling using both Cu 2p and Bi 4f spectra to investigate the eventual presence of a surface/induced band bending. Finally, we performed NEXAFS in TEY mode scanning over the Cu L_{2,3}, Cu M_{4,5} and O K edge. In order to understand the electronic structure of the material, we performed then ResPES on the Cu L₃ edge (we performed the same study using the Cu M_{4,5} resonance, but with scarce results due to the low brightness of the aforementioned edge). The results are reported in Figure 2. The main conclusion is that, also in this case, a localized resonance is present above the valence band maximum (centered at a photon energy of 931.4 eV and at a binding energy of about 2 eV). We advance the hypothesis that the presence of such localized

in-gap state could be then taken as a descriptor of complex oxides based on transition metals. The work is still in progress and will lead to a joint publication in a peer-review journal.

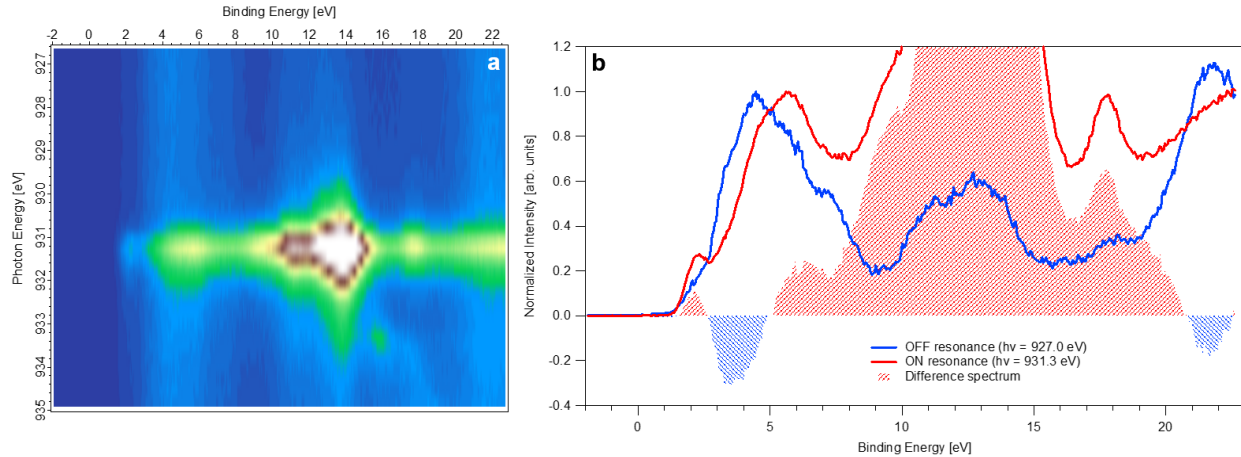


Figure 2. a: Resonant PES (along the Cu L_3 edge) performed on a conformal polycrystalline CuBi_2O_4 films; b: in and off resonance VB profiles taken from the bi-dimensional map reported in Figure a. The difference spectrum evidences the modulation of the overall VB with the increase of the photon energy, passing from off-resonance to on-resonance conditions. In particular, it is possible to observe the localized state above the VB maximum centered at a binding energy of about 2 eV.