Operando XAS: probing dynamic processes during photocatalysis

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Independence from the reliance of fossil and nuclear fuels requires the sustainable production of green energy and chemicals. As an alternative, utilisation of solar energy from the sun is possible by several means: solar thermal applications[1], the direct conversion to electricity (photovoltaic)[2] or storage in the form of chemical energy as solar fuels[3]. One promising clean energy carrier and renewable fuel source is hydrogen harvested from photoelectrochemical (PEC) water splitting[4-6].

The perovskite oxynitrides ($LaTiO_2N$, $BaTaO_2N$, $SrTaO_2N$) are well known materials for visible light driven water splitting, due to the size and energy position of the band gap[7, 8]. Polycrystalline powder oxynitrides are extensively studied as photoelectrodes, and their performances enhanced by using various co-catalysts[9]. However, powder samples do not provide well-defined surfaces allowing detailed investigation of the solid–liquid interface, which is where the electrochemical reaction takes place. Thin films are ideal model systems for such investigations of the surface and interfaces properties, due to the specific arrangement at the atomic level of the constituent elements along surfaces.

Pulsed reactive crossed-beam laser ablation (PRCLA)[10] is the unique approach of the **Thin Films and Interfaces group** (TFI) at the Paul Scherrer Institute. This modified pulsed laser deposition (PLD) technique allows the fabrication of oxynitrides thin films with tuneable compositions (e.g. nitrogen content) and different crystalline properties, such as amorphous, polycrystalline and epitaxially oriented films, with tuneable crystallographic orientations.

However, the surface catalytic activity of oxynitrides (AO terminated perovskites in general) and the understanding of the oxygen evolution reaction (OER) mechanism on an atomistic level remain open questions. X-ray absorption spectroscopy (XAS) provides the means to probe the solid-liquid interface and elucidate structural and electronic properties *in-situ* and *operando*. Where surface sensitivity can be realised with grazing incidence XAS (GIXAS) geometries[11]. Enabling the following of the surface evolution/dynamic surface reconstruction that occurs in oxynitrides, which effect the overall long term performance of these photocatalyst materials.

The driving force are typically due to applied external stimuli such as a bias (voltage) or exposure to light. These external stimuli can be modulated (using a potentiostat and chopped illumination, respectively) in combination with *operando* modulated excitation XAS (MEXAS) and phase sensitive detection (PSD)[12-14]. As MEXAS-PSD is looking at the changes occurring due to the photocatalytic reactions at the surface, this makes it indirectly surface sensitive. Surface sensitivity is enhanced further by coupling GIXAS geometries with MEXAS-PSD[15].

In this talk, I will overview some of the research highlights and applications of my group, with respect to thin films grown by PLD. Followed by a more specific example looking at ex situ and operando XAS measurements on oxynitrides thin film photocatalysts for visible light water splitting.

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