EUROPEAN SYNCHROTRON RADIATION FACILITY

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Experiment Report Form

ESRF	**Experiment title:** Understanding Charge Transfer and Redox Cascade Phenomena in Photoelectrode Architectures by in-operando XAS: a BAG proposal. ROUND 3	**Experiment number**: 08-01-1004
Beamline:	**Date of experiment**: from: 16/04/2018 to: 24/05/2018	**Date of report**: 16/05/2018
Shifts: 18	**Local contact(s)**: Francesco d'Acapito	*Received at ESRF:*

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Report:

The project for the fourth round of the BAG proposal was focused on the study of W-based photoanodes for photoelectrochemical water splitting. These are intensively studied (as witnessed by the literature). Aim of the experiment is the direct observation of the 5*d* band of W, that is the main contributor to the conduction band of the semiconductor. This is possible thanks to the easy accessibility of the L_{III} edge of 5*d* elements.

In fact, the main aim of the present experiment was to direct observe possible structural modifications occurring in WO_3 during illumination with visible light, that are accompanied by possible modifications in the electronic structure under operative conditions.

WO_3 is a semiconductor which absorbs visible light and shows interesting performances as a photoelectrode, such as high photocurrents and stability. The latter, in particular, is needed for time consuming X-ray absorption experiments, such as recording differential spectra, where X-ray energy E is fixed, μ measured in the dark and under visible illumination, then again to the next value of E. This allow to record two full XAS spectra in parallel, whose subtraction ($\Delta\mu$) gives the effect of visible light on local structure and oxidation state of the absorbing atom. The (photo-) electrochemical cell coincides with the one adopted in rounds 1-to-3 experiments and was filled of Na_2SO_4 0.1M. A Pt wire and a AgCl/Ag (in 1M KCl) were used as the counter and reference electrode. The visible light source was a 400 nm LED.

All experiments were carried out in the fluorescent mode using a 13-elements detector.

The materials under investigation were WO_3 photoanodes prepared at the Dipatimento di Scienze Chimiche e Farmaceutiche, Università di Ferrara, by Prof. Stefano Caramori and Dr. Vito Cristino, the latter invited to participate to the experiment.

A few photoelectrodes were pre-tested in Università degli Studi di Milano in conventional laboratory cella and in the XAS spectroelectrochemical cell, in all cases illuminating with a 400 nm LED. The results showed

interesting activities that suggested the need of limiting the formation of oxygen bubbles during XAS experiments. In addition, electrodes showed a rather high reproducibility (approx. 5%), that is particularly suitable in case of the need of using several samples during 18 shifts, for examples, when the use of a "fresh" one is desired for the sake of comparison between different acquisitions.

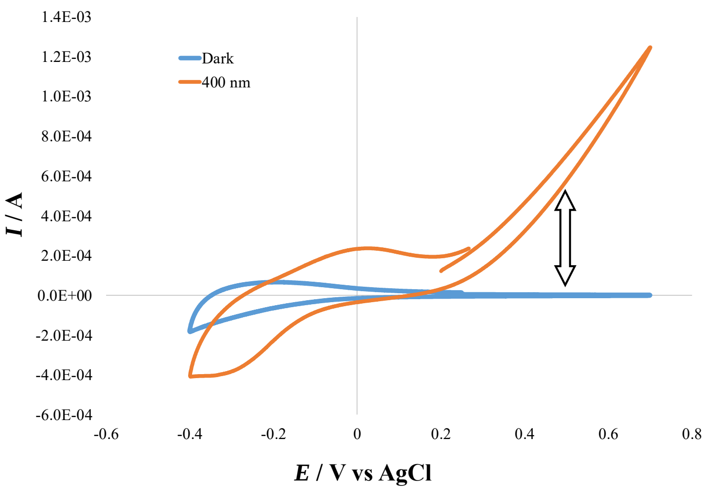

Figure 1. *CVs of WO_3 in the dark (blu) and under 400 nm (orange) recorded in Na_2SO_4 at 10 mV s^{-1}*

Figure 1 represents an example of cyclic voltammetry of a WO_3 photoanode in the dark and under 400 nm illumination. It is evident that the main feature appearing under visible illumination is a dramatic increase of current at $E > 0.2$V, corresponding to oxygen evolution. The other interesting aspect of these CVs is the series of oxidation/reduction peaks between -0.4 and 0 V, representing the W^{6+}/W^{5+} redox couple, also responsible for a change of the material's colour (blue in the reduced form, light yellow in the oxidized one).

Both phenomena were studied by XAS.

The best approach would have been by recording full XAS $\Delta\mu$ spectra. Unfortunately, the recent renewal of LISA and of its relevant control software did not allow it. Any attempt of recording subsequent dark→light spectra lead to unreproducible results. We then focused on fixed energy measurements as a function of time, switching on and off the light. Different energies and applied potential values have been tried. In this experimental report we will focus on the results at the two energies shown as grey and blue lines in Fig. 2. These energies correspond to the excitation from the W 2*p* states to the crystal field split W 5*d* states having t_{2g} (grey line) and e_g symmetry (blue line), and therefore are the most relevant for detecting variations in the local electronic structure of W. In addition, we will report only on the results obtained at 0.5 V, that is when the photocurrent is well apparent (see the arrow in Fig. 1).

The results are shown in Fig. 3. It is readily seen that, at both the energies taken into account in this report, an increase of the absorption coefficient is observed under illumination. This is in contrast with what is expected. In fact, the absorption of an UV-vis photon with promotion of an electron to the conduction band, which is mainly made up by W 5*d* states, should decrease the White Line amplitude and therefore the X-ray absorption coefficient. This rationale is also in agreement with the spectrum of reduced WO_3 shown in Fig. 2, where the expected decrease in μ is readily observed. Possible explanations of this phenomenon, that was observed also for different values of the applied potential, reside in structural modifications of WO_3 under UV-vis illumination, but this requires further experimental investigations.

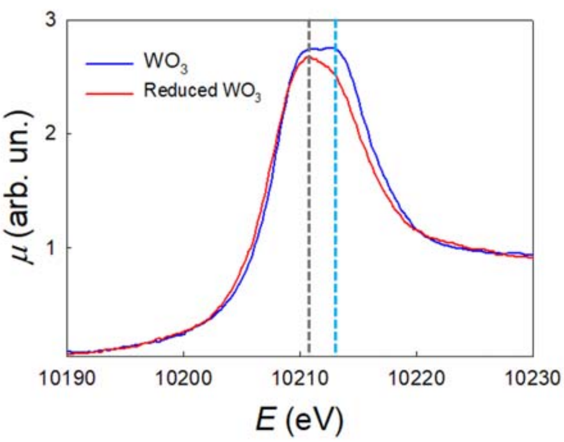

Figure 2. *W L_{III}-edge XANES spectra of WO_3 and reduced WO_3. The grey and blue lines highlight the energies for the fixed energy experiments described in this experimental report.*

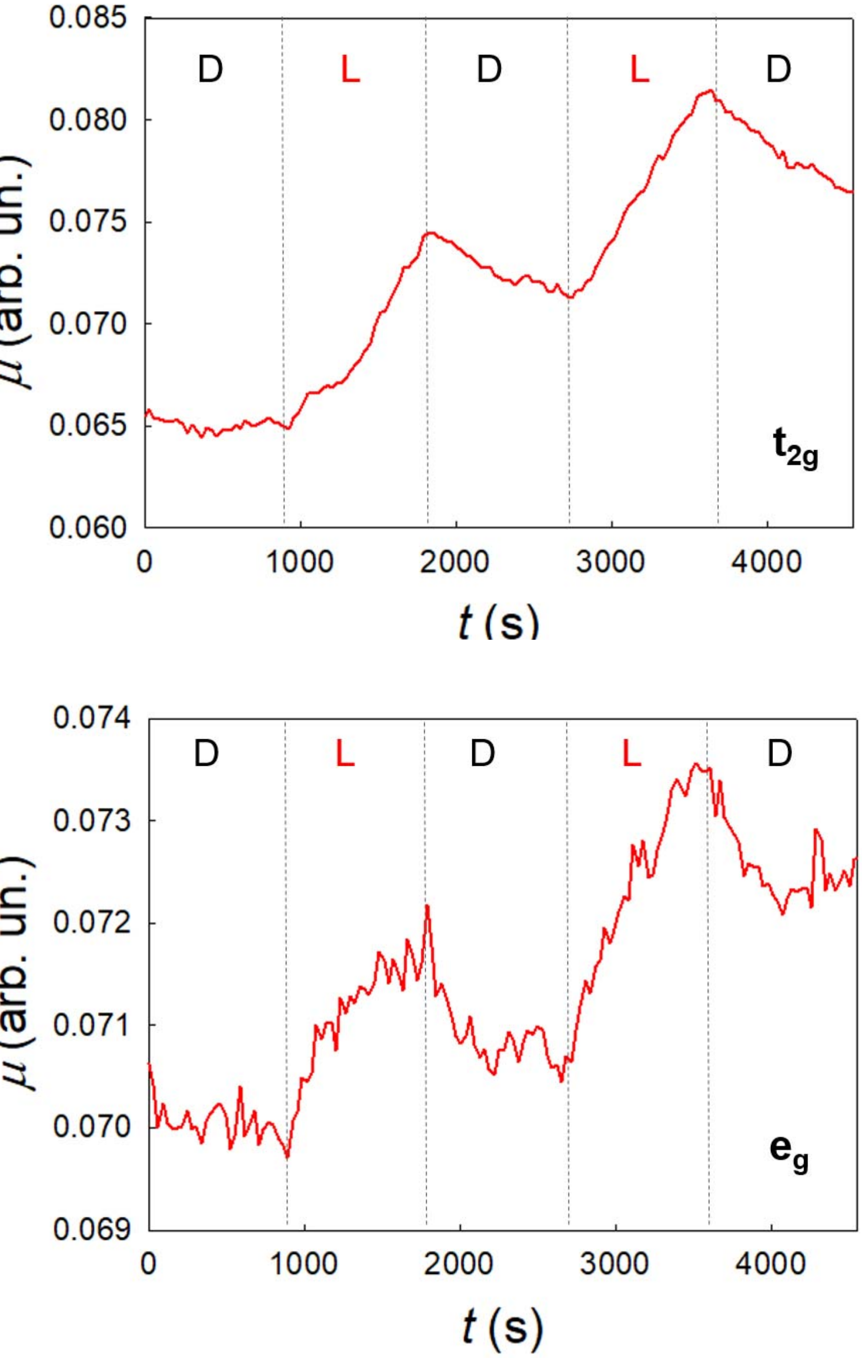

Figure 3. *Variation of the X-ray absorption coefficient at the energies corresponding to t_{2g} (upper panel) and e_g (lower panel) W 5d orbitals, upon switching on (L) and off (D) the UV-vis illumination.*