EUROPEAN SYNCHROTRON RADIATION FACILITY
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ESRF

Experiment Report Form

ESRF	**Experiment title:** Understanding Charge Transfer and Redox Cascade Phenomena in Photoelectrode Architectures by in-operando XAS: a BAG proposal. ROUND 1	**Experiment number**: 08-01-1004
Beamline:	**Date of experiment**: from: 09/11/2015 to: 16/11/2015	**Date of report**: 10/12/2015
Shifts: 18	**Local contact(s)**: Francesco d’Acapito	*Received at ESRF:*

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Report:

As proposed in the BAG project and after the encouraging results obtained in previous experiments on Fe_2O_3/IrO_x photoanodes (CH-4209), we underwent a deeper spetro-photoelectrochemical investigation of photoelectrodes made of one or more components (architectures). The aim of the BAG proposal is the study under operative conditions of the semiconductor alone and its interactions (charge transfers) with overlayers, the latter added to improve the performances by optimizing its density of states distribution, limiting charge recombination and improving the interface reaction kinetics. The 2-year project focuses on both photoanodes and photocatodes. In the present (first) round, we studied the *in-operando* behavior of Cu-based photocatodes, namely electrodeposited Cu_2O and a Cu_xO composite prepared from CuI nanoparticles by a facile synthesis. In both cases, the material is synthetized directly onto a conductive tin oxide electrode doped with fluorine (FTO) that, for the electrodeposited material, can be previously covered by a thin layer of Cu or Au to enhance the adhesion of the semiconductor layer and charge collection. Cu-based oxides represent indeed one of the most studied classes of phocathodes for their good absorption of visible light, relative low cost and simple preparation. On the other hand, the main drawback coincides with their low stability, particularly in the case of Cu(I) oxides. This also explains the need of a protective overlayer. Round 3 and 4 will be devoted to study the same semiconductors in the presence of overlayers.

In the present experimental setup, the photoelectrode is mounted in a cell properly designed to be highly transparent to both UV-Vis and X-ray photons. The cell, reproduced in Figure 1, is made of a mylar film and is strenghten by a silicon frame. As highlighted in the picture, the cell allows the lodging of a Pt counter electrode and a glass tube that hosts a Ag/AgCl reference electrode. The electrolyte solution was aqueous 0.1 M K_2HPO_4 (pH 9.1) or 0.5 M NaH_2PO_4 + 0.5 M NaOH (pH=11.1).

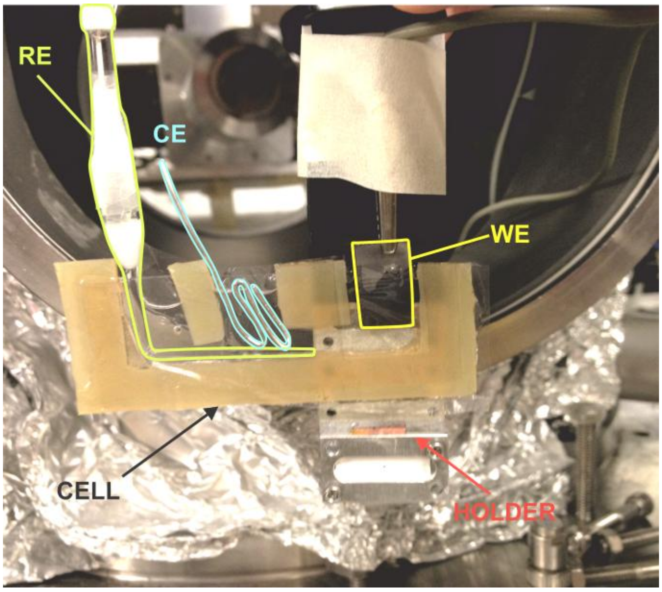

Figure 1. *Picture of the spectro-photoelectrochemical cell attached to a BM-08 beamline sample holder. WE-working electrode (i.e. the photoelectrode under investigation), CE- counter electrode, RE – reference electrode. The picture was collected during the experiment.*

The visible light source was a 400 nm LED that can be controlled through the beamline software for precise timing and synchronization with the X-ray absorption acquisition system.

As done in the CH-4209 experiment, this allows to record in parallel spectra under visible light and in the dark: for each point (for each X-Ray energy value), the absorption coefficient was measured both in the presence and in the absence of visible light. The great advantage of this system is that errors associated to possible different instrumental conditions can be avoided. In this way it is possible to subtract the two spectra without preliminary treatment. All experiments (except for standard materials prepared as pellets) were carried out in the fluorescent mode using a 13-elements detector.

For both types of electrodes we adopted the following techniques:

1 - FEXRAV (Fixed Energy X-Ray Absorption Voltammetry), which consists in fixing the X-ray energy and scan the potential as in conventional electrochemical methods (e.g. cyclic voltammetry). It is also possible to preliminary evaluate the effect of light by means of a chronoamperometry while switching on and off the visible light source.

2 – in-situ XAS experiments, in which full XAS spectra are recorded on the same photoelectrode before and after prolongued (at least 1h) photoelectrochemical and photochemical tests

3- differential spectra (in-operando), as described before.

Results are currently under elaboration. However, Figure 2 reports two representative results: Fig. 2A is a FEXRAV of the Cu$_x$O photoelectrode recorded in the dark at the pre-edge peak energy in the XANES for Cu$_2$O. The graph, that also reports the current, clearly shows that below -0.3 V the absorbtion coefficient of the material largely increases, indicating a severe reduction of the material to Cu$_2$O. The second (right side) is a differential XAS spectra recorded on the electrodeposited Cu$_2$O on a Au/FTO support. Figure 2-B shows the response of the Cu$_2$O layer to the illumination by UV-Vis light. The red and the blue line are the XANES spectra acquired in presence and in absence of UV-Vis light respectively. The difference signal ($\Delta\mu$, light-dark) obtained is represented by the green line. Its trend is characterized by a peak-like feature situated at ca. 8980 eV, in correspondence of the allowed $1s \rightarrow 3d_z{}^2$ electronic transition (hybridization between the $2p$ orbitals of oxygen and the$3d_z{}^2$ orbitals of copper occurs). The only reasonable explanation to this feature lies in a larger hole density in the $3d_z{}^2$ states of copper (top of the valence band) in presence of visible light.

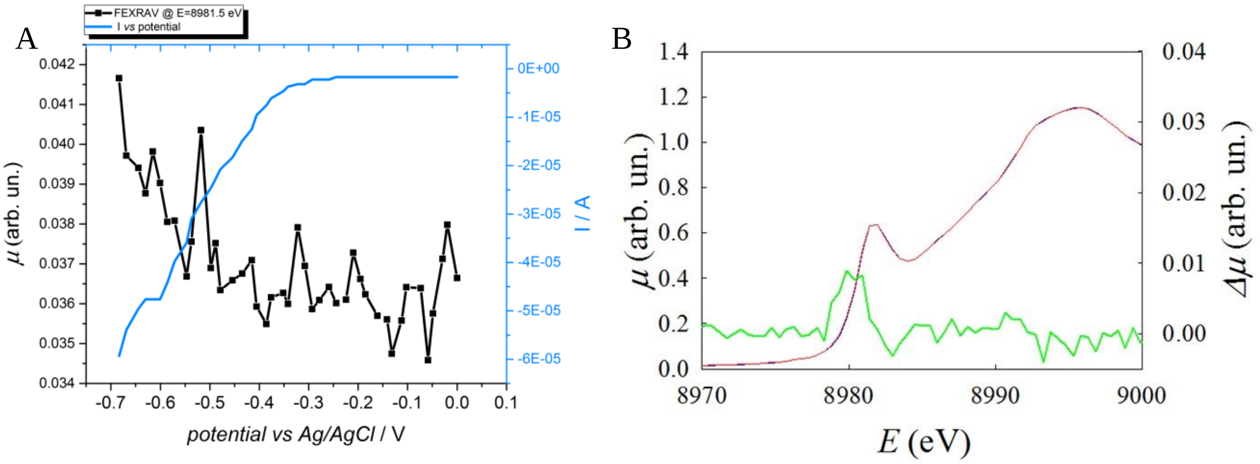

Figure 2. *Left- absorption coefficient and current of a Cu$_x$O photocathode as recorded during a FEXRAV experiment in the dark. Right- Differential spectra (light-dark)of an electrodeposited Cu$_2$O*