

Experiment Report Form



	Experiment title: In-operando EXAFS, XANES and FEXRAV of photoelectrochemical water splitting architectures	Experiment number: CH-4209
Beamline:	Date of experiment: from: 17/11/2015 to: 25/12/2015	Date of report:
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Report:

In a previous experiment ad BM08 (CH-3511), we collected significant experimental evidences for the oxidation states assumed by Ir in hydrous iridium oxide electrodes (EIROF) when used as catalysts for water oxidation to oxygen, a reaction of paramount importance in electrochemistry and in particular for the production of hydrogen by water electrolyses or photoelectrochemical water splitting. In CH-3511 we focused our attention on EIROF as anode in an electrochemical cell. In the present experiment we studied EIROF as overlayer in photoanodes (n-type semiconductor) for photoelectrochemical water splitting, a device capable of producing high purity hydrogen converting sunlight into chemical energy.

We consider the last system since the role of photoelectrodes overlayers is controversial: it can in principle act as both a catalyst (thus promoting the redox reaction occurring at the photoelectrode) or as defect quencher and modifier of the semiconductor electron density (thus favoring the charge separation and transfer towards the solution).

In order to better understand the role of overlayer, and in particular of IrO_x, one of the most studied in the literature, in-operando XAS is an optimal technique.

To this aim, we deposited EIROF onto α-Fe₂O₃ (hematite), a low-cost n-type semiconductor and one of the most promising photoanodes for water splitting. The hematite band energies needs for the application of an "extra" potential (bias) in order to observe a photocurrent related to water splitting.

During the experiment, XAS spectra at the Ir L_{III} edge have been collected while the photoelectrode was kept under working conditions (quasi-in-operando), i.e. immersed in solution, connected to a potentiostat together with a counter electrode (where water is reduced to hydrogen) and illuminated with a 400 nm LED.

In order to evidence the change in the chemical surrounding and oxidation state of Ir caused by the illuminated semiconductor, a software built on the beamline allowed to collect spectra in dark and light conditions simultaneously: for each point (for each X-Ray energy value), acquisition was performed both in presence and in absence of UV-Vis light. The great advantage of this system is that errors associated to possible different instrumental conditions can be avoided.

In addition, a new cell was developed and its picture is reported in Fig. 1. The cell, prepared by means of a 3D printer, allowed the effective illumination of the photoelectrode by both visible and X-ray photons.

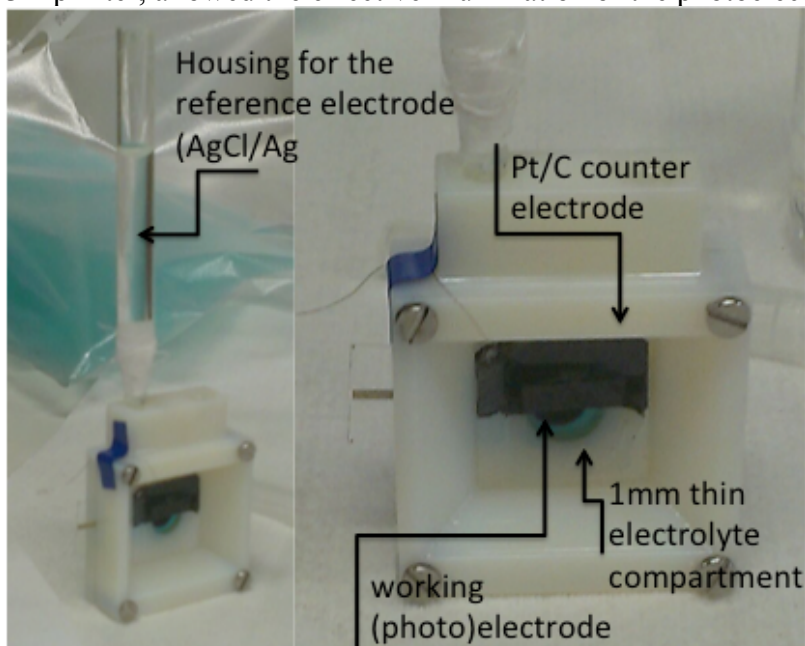


Figure 1 Picture and description of the spectro/photoelectrochemical cell

The spectro-electrochemical cell shown in Fig.1 allows to use a three-electrodes configuration and contains the electrolyte solution. A mylar window serves as support for Pt/C (used as counter electrode) and as window for X-rays / visible light. The experiments were conducted controlling the electrochemical instrumentation (CH Instrument 633D potentiostat/galvanostat) from the control room.

The data are still under elaboration but both XANES/EXAFS analysis and FEXRAV clearly shows the change of Ir charge state during due to photogeneration of charge carriers at the semiconductor: the XANES peaks area is higher under illumination, indicating a partial depletion of 5d electrons in the IrO_x overlayer (Fig. 2a). This occurs particularly when the external bias favours water splitting, i.e. at 1.4 V (vs. the reversible hydrogen electrode, RHE), as shown in Fig. 2b.

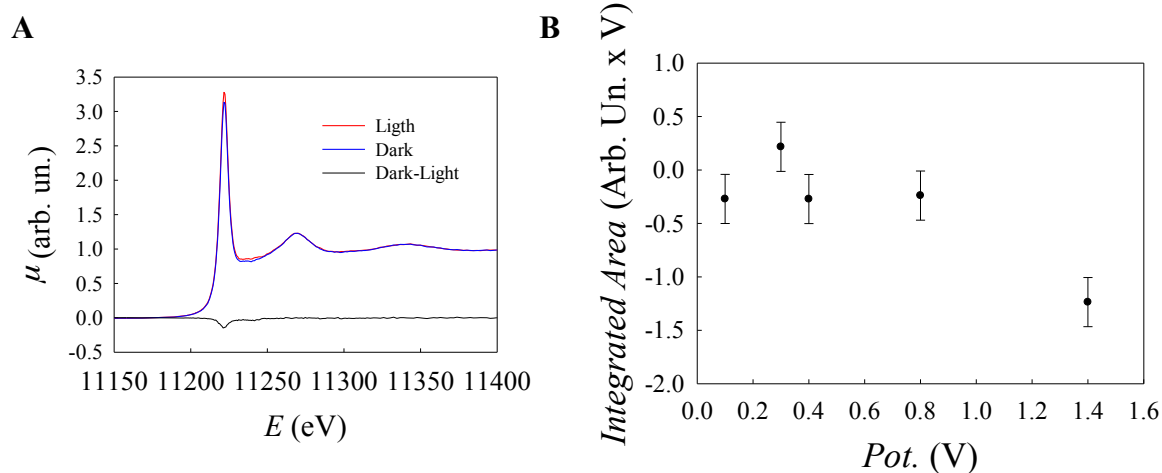


Figure 2: (A) XAS spectra of IrO_x (deposited on hematite) at 1.4 V (RHE) in light and dark. (B) Area of the differential XANES peak as a function of the applied potential.