



	Experiment title: In-operando XAS study of photocatalytic water splitting: state of catalytic sites as a function of irradiation and applied potential.	Experiment number: 30-02-1045
Beamline: BM30	Date of experiment: from: 05/06/2013 to: 11/06/2013	Date of report: 25/08/2013
Shifts: 21	Local contact(s): Olivier Proux	<i>Received at ESRF:</i>
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Report:

Developing efficient methods of photocatalytic water splitting under sunlight is a great scientific challenge. Recently developed promising systems for this purpose, responding to visible light, are based on modified titania, nitrides and oxynitrides semiconductors such as carbon nitride C_3N_4 . While these materials provide photo generation of electron-hole pairs, production of H_2 at their surface requires the presence of catalytic sites of bi-functional character. One type of sites (Pt) is necessary to recombine hydrogen atoms, whereas another (co-catalyst) is to oxidize water and to produce oxygen (Co or Ru oxides and complexes). Applying external bias to a photo catalyst drastically changes its performance due to changes of relative positions of electronic bands. The key to understand the relationship between properties of materials and photo catalytic properties is closely related to the determination of the valence, and coordination of active species under real conditions, with a maximum of control over the state of the system. In the present run, we studied in operando the evolution of supported platinum and cobalt species on TiO_2 and C_3N_4 during photo catalytic reaction of hydrogen production from methanol. Variation of Pt and Co state upon exposure to methanol, UV illumination and external potential were observed.

In order to measure the XANES/EXAFS spectra on a working photo catalyst with simultaneous application of controlled potential, we developed a dedicated in situ photoelectrochemical cell (Fig. 1, 2). Measurements were carried out on semiconductor catalysts which were supported on a FTO-covered glass electrode, applied as a working electrode of a three electrode potentiostat (Fig. 2). An electrolyte was put at the cell bottom in a specially designed Teflon reservoir, in order to have the border of the liquid at the level of cell window. X-ray beam penetrated through a kapton window to hit the menisci zone where FTO –supported semiconductor (SC) was well wetted by an electrolyte, but narrow enough to provide good signal from the SC sample (i.e. to avoid total absorption of the beam by an electrolyte). Counter electrode and reference electrode were immersed in the electrolyte in a close proximity to the working electrode. To activate the photocatalysts, UV or visible light from a Xenon lamp was directed on the sample by means of an optic fiber. The cell was flushed by helium and eventually vapors of an organic reagent (methanol). The products were analysed by mass spectrometer (Fig. 3).

In the present run we succeeded for the first time to observe simultaneously the effects of light and applied potential on the state of Pt and Co species on the surface of TiO_2 and C_3N_4 working catalysts. With this respect the results of the run represent a step forward in the methodology of in operando studying of water splitting catalysts. Thus, kinetics of photodeposition CoPi phase and of Pt on titania was followed at controlled light intensity and potential bias (Fig. 4, 5). The relationship between the influence of both

parameters was evidenced. Photocurrents and hydrogen production were measured as a function of light intensity/wavelength and potential. Otherwise, open circuit potential was followed at the same time with illumination and photoactivity. At the same time tangible changes in the XAS spectra of the co-catalysts were observed. For instance, oxidation of platinum under the reaction conditions and applied anodic potential was demonstrated by XANES.

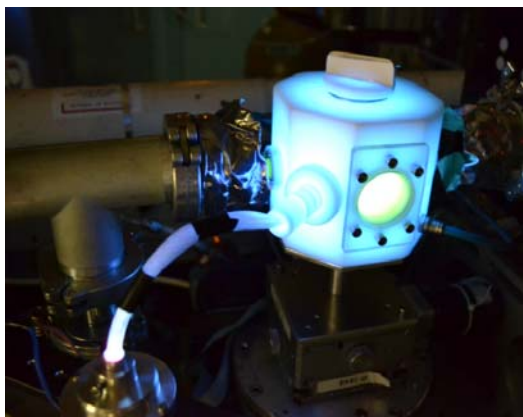


Fig. 1 In situ cell on the BM30 line

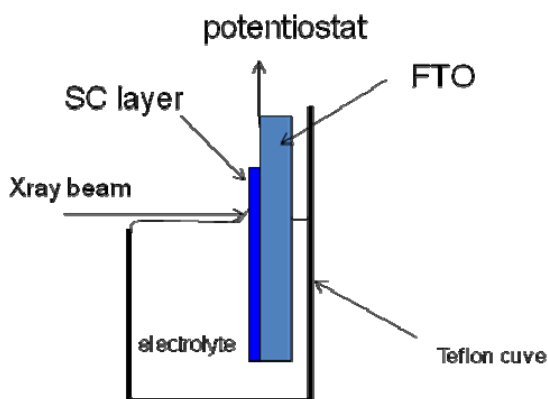


Fig. 2 General principle of XAS measurements

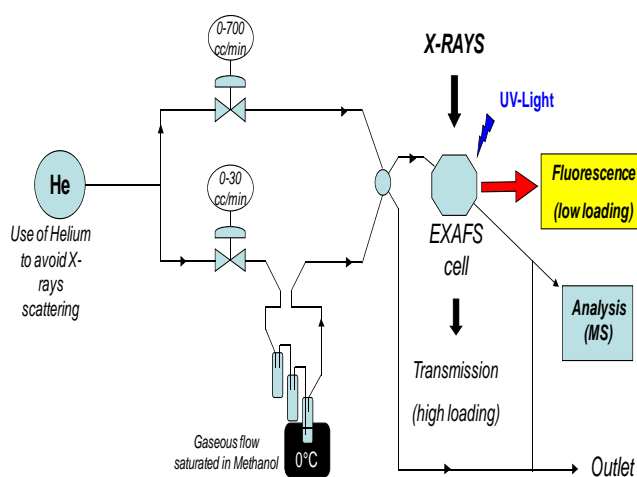


Fig. 3. In situ XAS coupled with photocatalytic test (potentiostat not shown here).

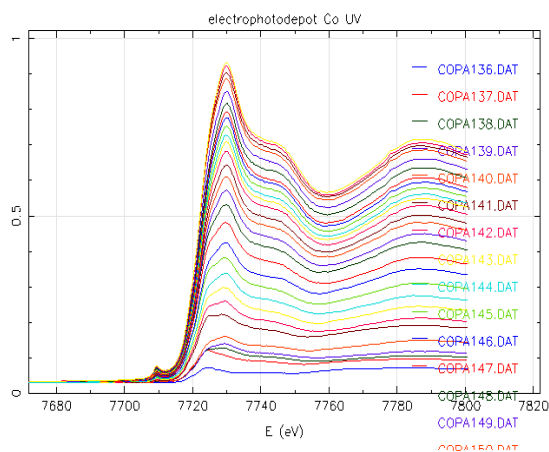


Fig. 4 Photoelectrodeposition of CoPi on TiO₂ vs time.

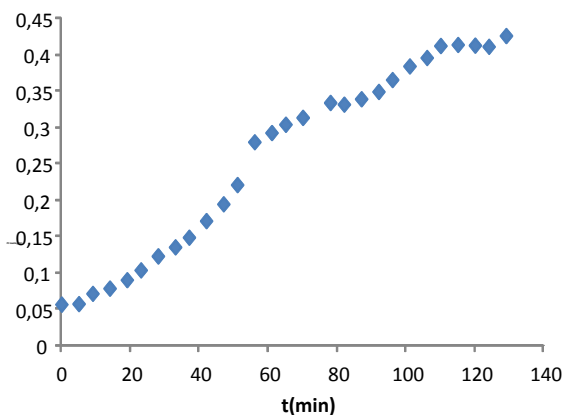
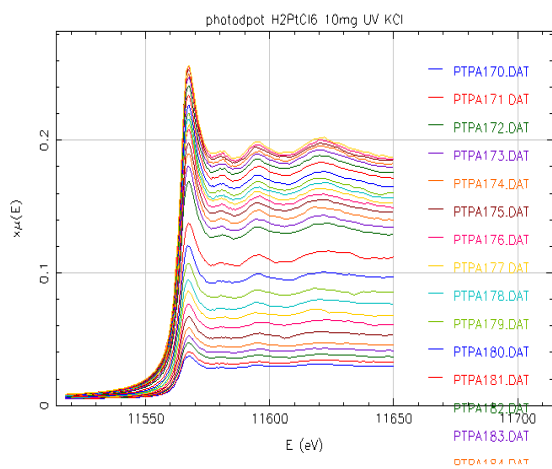


Fig. 5 Kinetics of photodeposition of Pt on titania from hexachloroplatonate solution. XAS spectra (left) and the amount of deposited Pt (right) derived from the time dependence of edge jump.