

Operando and Time-Resolved X-Ray Absorption Spectroscopy for the Study of Photoelectrode Architectures



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ABSTRACT

Photoelectrocatalytic processes (e.g. water splitting) are particularly interesting as a method of solar to chemical energy conversion. The catalytic process is driven by transient changes in the semiconductor material's properties, such as the metal oxidation state, the local reconstruction of catalytic sites or charge recombination processes. Here, we report a novel experimental technique for performing pump and probe time-resolved hard X-ray absorption spectroscopy in electrochemical conditions under UV–vis irradiation: pump and probe XAS enables the study of processes occurring in pico- to microseconds time scale by probing the local electronic properties of a selected atom. The described technique was developed using α -Fe₂O₃/IrO_x as a model photoelectrode.

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1. Introduction

Solar energy conversion is based on the efficient separation of photogenerated charge carriers and their consequent utilization. Whether the collected charges are used for electricity generation (i.e., solar cells) or for driving chemical reactions (i.e. photocatalytic water splitting), the study of the multiple processes involving generation and recombination of charges is fundamental to increase the yield of solar light conversion.

Interaction of light with semiconductors may yield in electron and hole separation: electrons are promoted from the valence band into the conduction band leaving holes behind. This process is a first and fundamental step in all semiconductor-based photoelectrochemical and photocatalytic reactions like water splitting. Photogenerated electrons and holes can recombine (in non-radiative or radiative way) and dissipate energy as heat, may be trapped at nonreactive (e^-_{tr} , h^+_{tr}) or reactive (e^-_r , h^+_r) surface sites

and eventually react with substrates adsorbed at the material surface (electron donors D or electron acceptors A), as presented in Fig. 1 [1]. The efficiency of interfacial charge transfer (photoelectrochemical reactions or photosensitization processes [2]) is determined by a competition between charge separation, recombination and trapping. Such processes occur on the femto-, pico- and nanosecond time scales (see Fig. 1). Their investigation with the correct time resolution is therefore crucial for the correct understanding of the photoelectrochemical as well as the photocatalytic reactions.

In turn, this information can be used for the design of more efficient photoelectrodes. *In situ* or *operando* (in an electrochemical cell and under irradiation) studies are particularly useful because many features of photoelectrodes are intimately coupled to the properties of the liquid-phase electrolyte. On the other hand, *ex situ* studies provide complementary characterizations of the materials used for photoelectrodes. Several tools, based on electrochemical or spectroscopic techniques, are available for studying ultrafast processes occurring during photoelectrochemical reactions. Transient absorption spectroscopy, laser flash photolysis and time-resolved diffuse reflectance spectroscopy are commonly used. Flash photolysis is a pump-probe method, in

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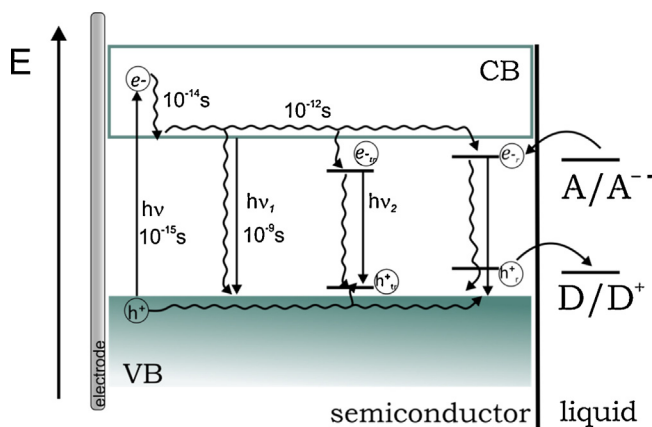


Fig. 1. Primary processes occurring at a photoelectrode immersed in an electrolyte solution upon irradiation. Based on [1,3].

which a sample is firstly excited by a strong pump pulse of light from a laser with nano- to femtosecond width: the fate of the electron-hole couple can then be investigated by several methods. Such technique can be used for investigating the carrier dynamics (e.g. dynamics of charge injection [3,4]). Ultrafast spectroscopic techniques, such as Transient Absorption Spectroscopy (TAS), can probe optical, electronic, or vibrational characteristic on the subnanosecond time scale. Measurement of transient absorption spectra requires a pulsed laser light source for exciting the material and a probe beam (UV, Vis, IR, X-ray) [5]. Time resolution in pump-probe TAS is limited by the duration of the laser pulse ($\approx 30\text{--}50$ fs, or even few fs pulses [6]) and the time delay between pump and probe can be of the order of ns. Anyhow, an alternative technique with pulsed pump and continuous probe allows measurements above the nanosecond time scale. Transient spectroscopy has been widely employed for the investigation of various photoelectrode materials such as γ - and α - Fe_2O_3 [7], CdS nanocluster multilayer assembly [8] or photosensitized TiO_2 [9]. Such experiments allow to directly observe many interesting phenomena such as dynamics of photogenerated charges under electrochemical condition [7,8], plasmon induced electron transfer [10], electron scattering during the interparticle electron transition or relaxation dynamics and recombination processes [7,8]. Moreover, trapped electrons and holes, reactive species and quasi-free electrons can be identified using such techniques.

Time-resolved TAS under photoelectrochemical conditions allowed to shine light over several fundamental issues related to the water splitting reaction. By tuning the timescale of the probe it has been possible to investigate charge recombination or transfer processes from the picoseconds to the milliseconds-seconds regimes. While in the first case, ultrafast charge recombination phenomena were investigated [11], the longer timescale has been used to determine the kinetics of the water splitting reaction and to provide some suggestions on how this is influenced by the presence of an overlayer atop the semiconductor [12,13].

Through these investigations, Tang et al. [13] have discussed the role of overlayers on hematite photoanodes, ultrafast charge carrier recombination and trapping [11], the role of back electron-hole recombination at the FTO/semiconductor interface on water oxidation [14], the four-hole chemistry associated to water oxidation at TiO_2 and hematite surfaces [13], and the rate law analysis of water oxidation on the hematite surface [15].

Time-resolved terahertz spectroscopy and time-resolved microwave conductivity are other useful methods for the characterization of photoelectrodes with enhanced temporal resolution [16,17]. The first one allows studying the charge carrier dynamics in semiconductors with sub-picosecond resolution. Due to the use of energy

in the range of a few to 100 meV, this method is sensitive to the response of free carriers, excitons or polarons and it allows studying processes as phonon resonances and intraband transitions as well as monitoring the non-equilibrium time evolution of carriers with picosecond temporal resolution. Similarly, time resolved microwave conductivity is an outstanding tool for investigating the dynamics of charge carrier in polymers or semiconductors [18]. Other ultrafast techniques include time-resolved X-ray Photoelectron Spectroscopy (XPS) and time-resolved X-Ray Diffraction (XRD) to study the surface and bulk composition and structure of photoelectrodes.

X-ray Absorption Spectroscopy (XAS) includes a number of highly selective, well-established techniques for studying the electronic and atomic structure of matter. In contrast to all the above described methods, XAS is element selective, probing a target atom and its surroundings. XAS can be particularly useful for the investigation of the charge transfer processes occurring in materials for solar-energy conversion, when used as a probe for the electronic species excited by a pump beam [10,19].

The scheme for time-resolved pump (optical) – probe (X-ray) technique is shown in Fig. 2. The pump pulse delivers UV–vis light to a semiconductor, while the probe X-ray pulse from a synchrotron source follows the pump with a controlled delay and interrogates the excited system. Examples of time-resolved XAS experiments combining laser and synchrotron radiation for the analysis of the dynamics of photoexcited states with subnanosecond temporal resolution can be found in studies from the micro-XAS beamline at SLS [20] or at the BACH beamline at Elettra [21–23]. The width of the X-ray pulse is typically short enough to investigate dynamic processes occurring in the time scale from 60 ps up to 0.5 μs . Time resolved XAS experiments require single-bunch, few-bunches (or hybrid modes) operation modes of the storage ring. However, operating at variable repetition rate, the use of multi-bunch filling pattern of the storage rings has been also developed [21]. This technique enabled the study of transient changes of the structurally relevant 2p–4s (L_{III}) XAS spectra during the phase transition of crystalline germanium within a time scale of picoseconds [21].

Time-resolved pump and probe XAS enables understanding different phenomena than in the case of TAS. Pump and probe TAS technique allows to follow the transient signal relative to electron or holes, while time-resolved XAS allows to probe the oxidation states of the absorber (in the X-Ray Absorption Near Edge Structure – XANES- region) and its local structure, including the number and nature of surrounding atoms and the relevant bond length (Extended X-Ray Absorption Fine Structure EXAFS).

Here we report a time-resolved photo-spectro-electrochemical experiment conducted on an α - Fe_2O_3 (hematite)/ IrO_x , that is used in the Oxygen Evolution Reaction (OER) in alkaline media:



Even though our final goal is the understanding of the role of the overlayer in the charge transfer from hematite to water during

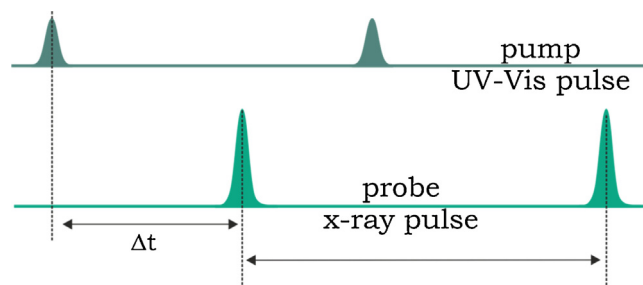


Fig. 2. Pictorial scheme (not in scale) of time-resolved pump and probe XAS. The pump duration was set to 60 ns, while the probe one is of 100 ps (see the Section 2). The distance between the X-ray bunches in the 4 bunches mode is of 700 ns.

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