

Toward Ultrafast *In Situ* X-Ray Studies of Interfacial Photoelectrochemistry

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Abstract: Picosecond time-resolved *in situ* X-ray absorption and X-ray photoelectron spectroscopy techniques for atomic site-specific real-time studies of interfacial photoelectrochemistry are developed. First experiments monitor electronic dynamics of dye-sensitized nanocrystals and at hematite-electrolyte interfaces.

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1. Introduction

Interfacial photoelectrochemistry is governed by the flow of charge, mass, and energy among molecules and between molecules and condensed phase substrates. By definition, the quest for a deeper understanding of interfacial photochemical processes is directly related to the capability to monitor non-equilibrium dynamics of complex systems in electronically and/or vibrationally excited states. Time-domain X-ray spectroscopy techniques offer new opportunities to unravel the fundamental electronic dynamics that underlie the chemical and electronic interactions in processes such as photoelectrochemical water splitting or photovoltaic power generation. The simultaneous element specificity and chemical sensitivity of X-ray transitions in combination with the time-structure of accelerator-based X-ray light sources provides real-time access to transient oxidation states and local bonding motives with atomic pinpoint accuracy.

Time-resolved X-ray photoelectron spectroscopy (TRXPS) and time-resolved X-ray absorption spectroscopy (TRXAS) provide complementary information on interfacial dynamics. TRXPS is particularly surface sensitive and, in combination with ambient pressure photoelectron spectroscopy (APPES) techniques, provides a detailed picture of the interaction of the first few molecular monolayers with a condensed phase substrate. Time-resolved X-ray absorption spectroscopy (TRXAS) is sensitive to both surface and bulk dynamics and, in particular, lends itself to *in situ/operando* applications in which the X-ray spectroscopic signatures of the sample are recorded under device-like operating conditions. The implementation of both TRXPS and TRXAS at the Advanced Light Source (ALS) is presented. Showcase applications include photoinduced electronic dynamics in films of N3 dye-sensitized ZnO nanocrystals and at hematite/electrolyte interfaces in working photoelectrochemical (PEC) cells.

2. Experiments and results

The ALS based experiments are enabled by a combination of three fundamental components: i) APPES and *in situ* XAS techniques, ii) a mobile high-repetition rate, high-power picosecond laser system, iii) time-stamping data acquisition techniques enabled by time-sensitive detectors. The laser system provides 10 ps long “pump” pulses that initiate interfacial processes, which are monitored by ~70 ps “probe” pulses from the ALS. The laser system is synchronized to the ALS bunch structure and is used at a variety of beamlines (BL). At BL 11.0.2, an APPES enabled electron analyzer is interfaced with a time- and position-sensitive detector that marks every registered electron with a unique time stamp. Post-processing of the data provides picosecond TRXPS spectra extending over microsecond time ranges, all recorded simultaneously and making use of the entire X-ray fluence of the ALS in either multi-bunch or two-bunch operating mode [1,2]. A recent proof-of-principle study at the Linac Coherent Light Source (LCLS) demonstrated the potential of femtosecond TRXPS to monitor interfacial electron dynamics at N3-sensitized films of ZnO nanocrystals during photoinduced charge injection [1,3]. The ALS based experiments extend these studies to the picosecond to microsecond domain, giving access to the recombination dynamics during the last phase of the working cycle of dye-sensitized solar cells. TRXPS fingerprints of both injection and recombination dynamics will be discussed as well as the potential of *ab initio* constrained density functional theory (DFT) calculations to interpret the experimental results on a molecular level.

A schematic of the TRXAS experiment (BL 8.0.1 and BL 6.3.1) is shown in Fig. 1a. The laser system is operated at either 532 nm or 355 nm output wavelength, producing pump pulses with up to 8 MHz repetition rate and up to 75 μJ pulse energy at 100 kHz repetition rate. The repetition rate and pulse energy of the laser system can be set during operation, providing the crucial capability to efficiently tune the delicate balance of all operating parameters of photoactive interfaces. Both the laser and the ALS X-ray beams are focused into a PEC cell, designed for *in operando* X-ray absorption studies of photoelectrochemical processes [4]. The cell contains a semi-transparent

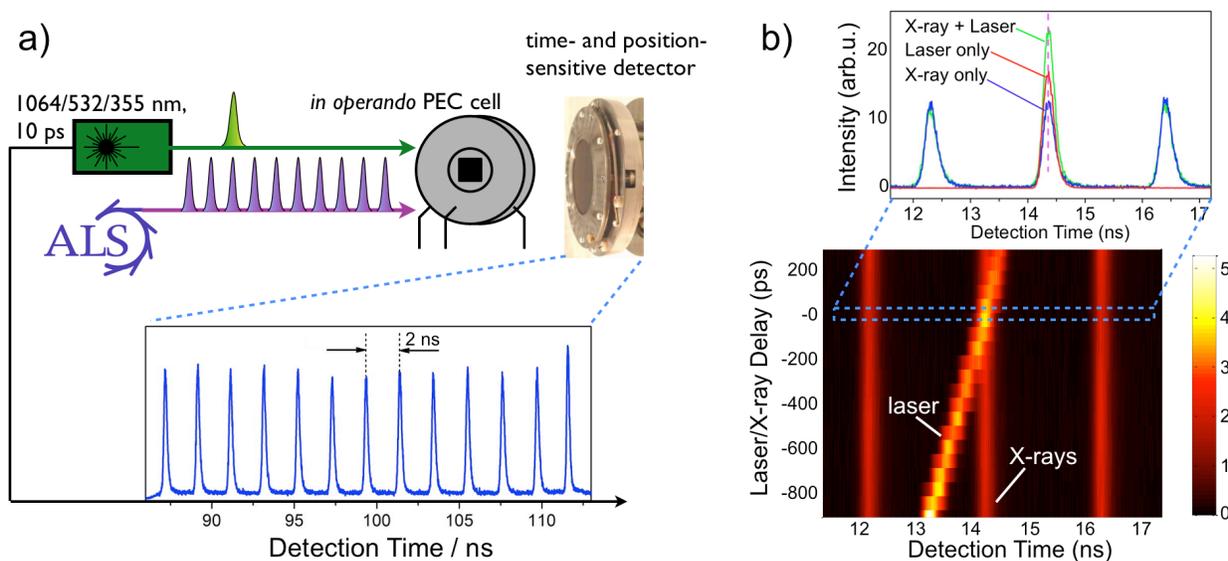


Fig. 1. (a) Setup for picosecond time-resolved *in situ* X-ray absorption spectroscopy of interfacial photoelectrochemistry. A high-repetition rate picosecond laser system is synchronized to the ALS bunch train. Laser and X-ray pulses are incident on an *in situ* photoelectrochemical (PEC) cell. The total X-ray fluorescence yield is recorded by a time- (and position-) sensitive detector, enabling the acquisition of picosecond time-resolved X-ray absorption spectra over microsecond time ranges and taking advantage of the full multi-bunch X-ray flux of the ALS. (b) Demonstration of picosecond time-resolution by scanning the laser pump / X-ray probe delay.

~ 30 nm thick hematite ($\alpha\text{-Fe}_2\text{O}_3$) working electrode attached to a ~ 100 nm thick silicon nitride (Si_3N_4) window with a 10 nm thick Au film and a 2 nm Cr layer. The other side of the hematite film is exposed to a reservoir filled with an aqueous NaOH electrolyte. The electrical circuit of the PEC cell is completed by a Pt counter electrode and an Ag/AgCl reference electrode in the reservoir. Near-edge X-ray absorption fine structure (NEXAFS) spectra of the assembly are recorded by monitoring the total X-ray fluorescence yield emerging through the Si_3N_4 window as a function of the incident X-ray photon energy. A time- (and position-) sensitive fluorescence detector provides a unique time stamp for every detected fluorescence photon, enabling a clear distinction of fluorescence signals from all ALS bunches in either multi-bunch (Fig. 1a, bottom) or two-bunch operating mode. The picosecond time resolution of the setup is demonstrated in Fig. 1b. To record the false color map, the PEC was oriented at an angle at which the laser back reflection from the cell was incident on the fluorescence detector. The map shows the detected total light intensity as a function of time (horizontal axis) and the delay between the optical pump pulse and one of the X-ray probe pulses (vertical axis). The upper part of Fig. 1b illustrates the time-dependent signals at zero pump-probe delay when either only X-rays, or only the pump laser, or both X-ray and laser pulses are incident on the cell. After the timing calibration, the PEC cell is rotated such that the laser back reflection does not overlap with the TRXAS signal. NEXAFS and TRXAS spectra of working PEC cells will be discussed in the context of the interfacial hole dynamics that are critical for the efficiency of photoelectrochemical water splitting.

3. References

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