

Time-Domain *In Situ* X-ray Studies of Interfacial Charge Transfer

Proposal for an ALS Approved Program (AP) to use Beamlines 11.0.2 and 8.0.1 for 3 Years

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Abstract

This AP will establish picosecond time-resolved *in situ* X-ray photoelectron spectroscopy (XPS) and picosecond time-resolved *in operando* X-ray absorption spectroscopy (XAS) techniques at the Advanced Light Source (ALS) and employ them in a diverse research program on charge transfer and fundamental chemistry in energy-challenge relevant interfacial systems. The program is aimed at providing new insight into the chemical and electronic dynamics that are associated with photocatalytic and photovoltaic activity in thin films of transition metal complexes, semiconductor nanocrystals and nanorods, molecular heterojunctions, molecule/semiconductor interfaces, as well as buried molecule/semiconductor and semiconductor/semiconductor interfaces. In particular, the correlated dynamics that connect interfacial charge transfer, molecular oxidation state changes, transient interfacial dipole layers, and dynamic band structure alignments will be investigated with the unique site-specificity of inner-shell transitions and under environmental conditions that approach real-world applications.

Request: 50% (≈fifteen 8-hour shifts/cycle) of two-bunch beam time at BL 11.0.2, 5% (≈fifteen 8-hour shifts/cycle) of multi-bunch beam time at BL 11.0.2, and 5% (≈fifteen 8-hour shifts/cycle) of multi-bunch beam time at BL 8.0.1

Justification for an AP request

- The AP will establish new capabilities for time-resolved *in situ* and *in operando* X-ray spectroscopy studies at the ALS that will be made available to other users.
- The AP will amplify the payoff to ALS from recent investments into both a picosecond laser system (DUETTO) and a suite of *in situ* X-ray photoelectron spectroscopy (XPS) and *in operando* X-ray absorption spectroscopy (XAS) techniques.
- The AP will lay the groundwork for future spectroscopy techniques that will exploit the unique capabilities of an upgraded, diffraction limited ALS (ALS-U).
- The AP will significantly enhance the capability of the two groups to conduct joint beam times on complementary topics that rely on the same experimental resources, enabling the most efficient use of ALS beam time and resources.
- Both PIs are leaders in their fields and have already demonstrated the synergistic effects that are enabled by collaborative beam times.
- An LBNL project scientist (Stefan Neppel) is associated with the AP, ensuring on-the-floor expert support to external users of the new resources for the duration of the AP.

Background and Motivation

At the heart of many emerging sunlight-to-fuel and sunlight-to-electricity concepts are interfacial processes that require an optimized, concerted flow of charge and energy on the molecular level. Processes evolving on spatial and temporal scales spanning orders of magnitudes have to be connected in order to gain a comprehensive understanding of the fundamental dynamics and scaling laws that enable molecular, interfacial, and macroscopic charge and energy transport. Soft X-ray spectroscopy techniques are particularly well suited to monitor electronic and chemical states of matter with the elemental site-specificity and chemical sensitivity that is required to test and improve our fundamental understanding of interfacial chemistry and photophysics in complex systems. Over the past ~10 years the ALS has invested substantially into the development of (semi-)static *in situ* and *in operando* XPS and XAS techniques that are currently deployed at many other synchrotron radiation facilities. More recently, ALS joined a multi-divisional initiative at Lawrence Berkeley National Laboratory (LBNL) to implement a mobile picosecond laser system (DUETTO) at the ALS for multi-color experiments. Gessner coordinated the selection and implementation of the laser system. His group has been the driving force of the first series of experiments,¹⁻⁶ it made the system available to other user groups,² and it led the first steps toward time-domain *in operando* X-ray studies of interfacial photoelectrochemistry.⁶ A particularly successful proof-of-principle study emerged from a collaborative effort between the Gessner and Eberhardt groups, whose complementary capabilities and scientific interests align very productively such that only three Director's Discretionary shifts were required to implement a new type of time-resolved X-ray studies on charge-transfer in model systems for organic photovoltaic materials.² This is an opportune moment to join the scientific and technical expertise of the Gessner and Eberhardt groups and to provide them with the organizational backbone for a research program that will significantly contribute to the continued leadership of ALS in the field of soft X-ray enabled interfacial chemical dynamics studies. The proposed technological and scientific developments are well aligned with the vision for an upgraded, diffraction-limited ALS-U, which builds on extensive advances in *in situ/operando* techniques applied in both the time- and energy-domains.⁷

The AP is envisioned to create new capabilities and user resources at the ALS by leveraging equipment, know-how, and personnel of the Gessner and Eberhardt groups well beyond the capacity of the synchrotron radiation facility alone. In particular, interfacing the DUETTO laser system with existing *in situ/operando* X-ray spectroscopy techniques will create a unique infrastructure for X-ray studies of transient electronic and chemical configurations in complex systems with short (<100 ps) to intermediate (~ms) life times. Additionally, the Gessner group will make a recently constructed and commissioned transient X-ray absorption endstation available to users that has been specifically designed for synchrotron-based *in situ/operando* optical-pump/X-ray-probe studies. Over the course of the past two years, the mobile DUETTO system has been successfully operated at several ALS beamlines including, in particular, BL 11.0.2 and BL 8.0.1. A series of feasibility studies has demonstrated that the system can be installed and operated on-demand at various beamlines within the tight schedule of a multi-user facility.^{1,3,4,6} Concurrent with the implementation of the laser system, Gessner and collaborators have developed novel time-stamping data acquisition techniques that enable picosecond time-resolved XPS and XAS experiments in both two-bunch and multi-bunch operating modes of the ALS with a temporal resolution only limited by the ALS bunch length (~70 ps FWHM).^{1,3} Most recently, the group has commissioned a transient X-ray absorption setup that is specifically

designed for time-resolved studies of radiation-sensitive materials and to accommodate existing *in situ/operando* techniques. All these efforts were entirely supported by General User Proposals (GUPs) and three Director's Discretionary shifts. They have created the necessary technical and intellectual infrastructure for an AP proposal. As a result of this AP, the demonstrated capabilities of the DUETTO laser system and the accompanying time-resolved spectroscopy techniques and endstations will be developed into a diverse set of experiments and create new user resources.

Beyond merely providing equipment, the two groups are sufficiently well established to provide personnel support to incoming users. In particular, former postdoc and Humboldt Fellow Stefan Neppel from the Gessner group, who has been instrumental in the implementation of the laser system, has recently been promoted to a Project Scientist position. This will ensure continued on-the-floor expert support for the project over the entire duration of the AP and a strong LBNL-based resource for future application developments. Significant know-how has also been acquired by the Eberhardt group, which is currently engaged with three postdoctoral research assistants (Tiberiu Arion, Friedrich Roth, Hyun Ook Seo) in the project. Through an AP program, these personnel resources would become available to support future user programs through collaborative beam times.

The novel technical capabilities described above have been developed in close collaboration with the responsible instrument scientists Hendrik Bluhm (BL 11.0.2), Jinghua Guo, and Wanli Yang (BL 8.0.1), with whom the technical feasibility of the studies proposed herein has been coordinated. Francesca Toma and Ian Sharp from the Joint Center for Artificial Photosynthesis (JCAP) will provide well-characterized, high-quality thin film and plasmonic nanostructure samples. An ongoing collaboration with David Prendergast and Chaitanya Das Pemmaraju (Molecular Foundry and Chemical Sciences Division, LBNL) will ensure cutting-edge theory support for the interpretation of the acquired X-ray spectra.⁸ The request for 50% of two-bunch time at BL 11.0.2 is based on the consideration that, traditionally, this low average flux mode is rather unpopular with other XPS users while it is beneficial for some of the time-resolved studies proposed herein.

Science Case

I. Novel photovoltaic materials and architectures

Photo-induced generation, migration, exchange, and trapping of charge carriers at interfaces between solids, molecules, and liquids, and in nanoscale heterojunction structures are of central importance for the vast majority of emerging solar energy-conversion technologies. Monitoring the evolution of the interfacial electronic structure as it proceeds in *real time*, under *realistic conditions*, and *with the atomic-site specificity and chemical sensitivity of X-ray spectroscopy* holds great promise for improving our fundamental understanding of the reaction mechanisms that underlie the function of such devices. Hybrid systems based on dye-sensitized semiconductor nanostructures, organic/inorganic halide perovskite material combinations, and molecular donor-acceptor blends are attracting particular attention and are the focus of the first part of this AP.

I. A. Electron dynamics in solvated dye-sensitized semiconductor nanostructures

Previous time-resolved XPS experiments by the Gessner group at the ALS^{1,3} and the LCLS⁸

have provided deeper insight into the coupled electronic dynamics proceeding at interfaces consisting of dye molecules attached to nanostructured semiconductor (SC) electrodes (Fig. 1). The scientific driver of these studies is the quest for a deeper understanding of the enabling and limiting factors for efficient photo-induced charge injection from the dye chromophore into the SC substrate, suppressed recombination across the dye-SC interface, and efficient reduction of the dye by a surrounding electrolyte bath, all of which are critical enabling factors for dye-sensitized solar cells (DSSCs) and envisioned photocatalytic applications. A key advance enabled by this AP will be to extend the previous ultrahigh vacuum (UHV)-based studies toward

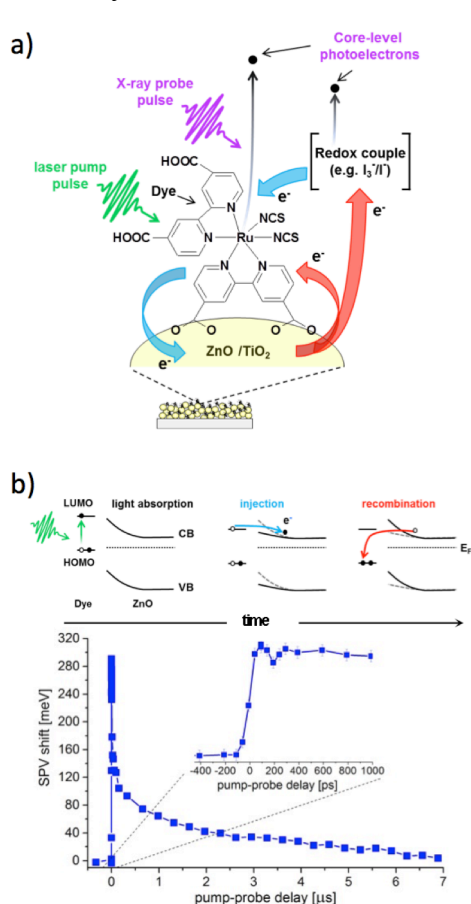


Figure 1. (a) Intended (blue) and parasitic (red) charge transfer and relaxation processes in DSSCs. The green and purple pulses indicate the optical pump and X-ray probe steps, respectively, of the planned experiments. (b) Picosecond time-resolved transient SPV response of an N3 sensitized ZnO electrode and its relation to the interfacial charge transfer dynamics.

the formation of a Helmholtz double layer at the SC-liquid junction and the electrolyte-mediated dye regeneration reaction, which are not accessible in UHV measurements. In particular, the sensitivity of tr-XPS to transient oxidation states will shed new light on the complex, presumably stepwise redox chemistry¹² that is currently poorly understood. The tr-APXPS experiments will be performed at BL 11.0.2, which has already been used for the UHV based tr-XPS studies. The

solvated systems that probe the electrolyte-mediated redox chemistry in addition to the dye-SC charge dynamics under conditions approaching real-world applications. The studies will employ the high-pressure capabilities of the XPS analyzers at BL 11.0.2 to perform time-resolved ambient-pressure X-ray photoemission (tr-APXPS) experiments on solvated dye-SC interfaces. Studies will be performed as a function of electrode composition (TiO_2 vs. ZnO), dye architecture (conventional vs. donor-pi-acceptor designs⁹), wetting conditions (background-gas adsorption¹⁰ vs. meniscus¹¹ techniques) and different redox species (I_2 vs. LiI). The element specificity of tr-APXPS will provide a real-time perspective of the interfacial dynamics from well-localized atomic-sites within the chromophore, the semiconductor substrate, and the electrolyte.

A visible picosecond “pump” pulse will initiate the interfacial charge transfer process (Fig. 1a). The temporal evolution of the photo-excited charges and molecular oxidation states will be reflected in the transient core-level shifts of tr-XPS spectra recorded at various delays relative to the pump pulse.^{1,8} Additionally, the intrinsic sensitivity of XPS to changes in the interfacial band bending will be exploited to probe the time-dependent charge carrier concentrations at the SC-molecule and SC-electrolyte interfaces through transient surface photo-voltage (SPV) measurements^{1,3} (Fig. 1b). The temporal evolution of SPV responses and chemical shifts will monitor parasitic recombination channels (electron – electrolyte), population dynamics of interfacial trap states, dielectric screening mediated by the electrolyte,

tr-APXPS experiments will be complemented by tr-APXAS measurements that provide additional site-specific information on the temporal evolution of the unoccupied and occupied states of the chromophore and the redox couple in the course of the photochemical reaction. The tr-APXAS signal will be acquired in Auger electron yield mode, which does not require any reconfiguration of the existing setup available at the beamline.¹³

I. B. Charge separation and recombination in organometal halide perovskites

Organometal halide perovskite semiconductors currently attract enormous attention as photoactive materials for solar photovoltaic and photocatalytic applications due to both high photon-to-current conversion efficiency and a rapid, ongoing increase in performance. In particular, devices based on organolead triiodide perovskites ($\text{CH}_3\text{NH}_3\text{PbI}_3$, Fig. 2) have been reported to reach conversion efficiencies exceeding 20%. A key difference between perovskite based cells

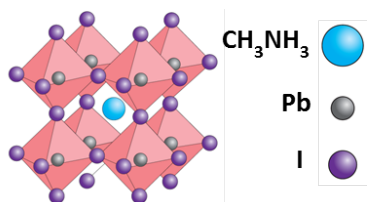


Figure 2. Crystal structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films.

and the DSSCs discussed in the previous section is that the perovskite film can simultaneously act as the light absorber and the charge transport layer, thereby eliminating the need for regenerating electrolytes in the cell design. These properties facilitate simple planar device architectures (Fig. 3) in which the perovskite film is sandwiched between a hole-transporting medium (HTM) and an electron-transporting medium (ETM) for efficient separation of photo-generated electron-hole pairs inside the perovskite layer. Despite first successes, very little is known about the underlying photophysics and charge carrier dynamics of perovskite based devices.¹⁴ Empirically, it has been found that both the film morphology and the substitution of small fractions of the iodine atoms with different halogen ions such as chlorine can substantially influence the carrier lifetimes and light-absorption of perovskite films.¹⁵ However, fundamental questions remain regarding the nature and location of the charge recombination centers within the perovskite lattice, as well as the relative importance of the interfacial electron/hole transfer and trapping processes at the perovskite-HTM and perovskite-ETM interfaces.¹⁶

Experiments employing tr-XPS and tr-XAS can significantly improve our understanding of this new class of photovoltaic systems by providing element-specific insight into the transient charge distributions within the perovskite structure. Initial experiments will focus on the I3p/I3d/Cl2p and Pb4p/Pb4d/Pb4f inner-shell transitions of bare $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films to characterize the intrinsic charge carrier dynamics of perovskites. The photo-excited state in these materials is known to exhibit significant ligand-to-metal charge transfer character, which implies dynamic charge rearrangement within the perovskite unit cell associated with a transient depletion of electrons at the halide ions and a corresponding accumulation of electronic charge near the Pb sites.¹⁶ The capability of tr-XAS to track such a spatial and temporal evolution of charges in the condensed phase has recently been demonstrated by Chergui and co-workers for TiO_2 nanoparticles.¹⁷ The carrier dynamics will be studied as a function of chlorine admixture, humidity and exposure to UV light. In particular, moisture and UV exposure have been identified as the main degradation

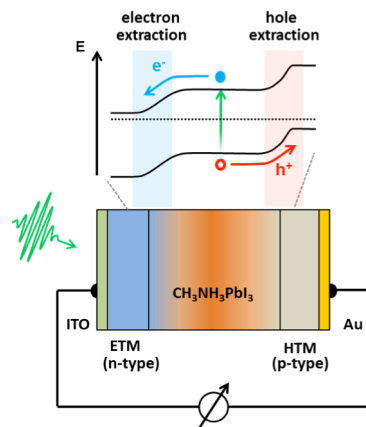


Figure 3. Structure and charge separation mechanism of perovskite solar cells.

mechanisms for perovskite-based solar cells, which currently pose the greatest hurdle toward their commercialization and warrant the application of *in situ/operando* techniques to investigate the underlying chemistry. Comparison of tr-XPS and tr-XAS results will be used to clarify the impact of surface defects on the overall charge recombination dynamics. Bulk and interfacial charge transfer processes will be disentangled by depositing perovskite films on prototypical HTM and ETM substrates, such as Spiro-OMeTAD and TiO₂, respectively. The light-induced evolution of the band bending within the buried charge extraction regions (Fig. 3) is expected to give rise to a characteristic p-type (hole extraction) and n-type (electron extraction) SPV response that will be mapped onto the tr-XPS signals from the perovskite capping layer (see section I-A).

There is growing evidence that the charge transport and recombination characteristics of perovskites are strongly affected by the presence of an external electric field, giving rise to a hysteresis in the current-voltage behavior of the cells. A variety of explanations have been proposed such as photo-induced formation of trap states, migration of halide ions in the lattice and the formation of ferroelectric domains inside the perovskite.^{18,19} All models indicate that the electronic response is coupled to dynamical structural rearrangements in the perovskite. To elucidate the origin of this phenomenon, *in operando* tr-XAS experiments will be developed that probe the electronic and structural dynamics of perovskite films in response to an external bias. This effort will build on a recent demonstration of *in operando* tr-XAS in a photo-electrochemical cell as described in section II.

I. C. Organic photoreceptors and photovoltaics

Self-assembled donor-acceptor nanostructures based on organic molecules are another type of photoactive materials that continue to inspire high hopes for cheap, sustainable energy solutions, yet, have so far fallen short of their (theoretical) full potential. Preferential conductivity for electrons or holes in organic electronics is usually achieved by mixing molecular compounds with different electronic functionalities. Some typical donor and acceptor materials are shown in Fig. 4. Conceptually, three steps determine the function of an organic photocatalytic (OPC) or organic photovoltaic (OPV) system: 1) The absorption of a photon in the chromophore resulting in the creation of an excitonic (polaronic) state in the electron donor, 2) the separation of charges at the interface between the electron donor and acceptor phases, and 3) the motion of charge carriers to electrodes (in OPV) or the transfer to adsorbed H₂O in photosynthetic hydrolysis.

Evidently, the charge transfer process between the (typically organic) chromophore and the electron acceptor is central to understand and control the functionality of organic photoreceptor systems. This applies to organic photovoltaics, organic photoconductors and even photosynthesis in biological systems. While it has been demonstrated for a large variety of OPVs that charge

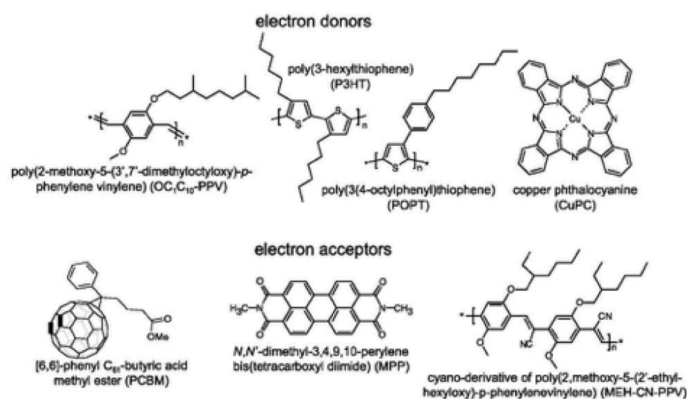


Figure 4. Selection of organic electron donor and acceptor materials.

transfer is energetically enabled,²⁰⁻²⁴ very little, if any information is available about the time dependence of the crucial charge transfer process^{25,26} and how this time scale is influenced by design criteria such as the chemical composition and the morphology of the system.²⁴

The Eberhardt and Gessner groups have recently demonstrated that tr-XPS offers the unique opportunity to investigate the photo-induced interfacial charge transfer in bi-layer donor-acceptor systems with exquisite site-specificity and a temporal resolution limited only by the light source.² Valence band PES, in contrast, is not necessarily specific to the spatial location of the excited electronic state. Fig. 5 illustrates a central result of the tr-XPS study performed at BL 11.0.2 of the ALS. The system consisted of a thin (~ 2 monolayers) layer of electron accepting C_{60} atop a

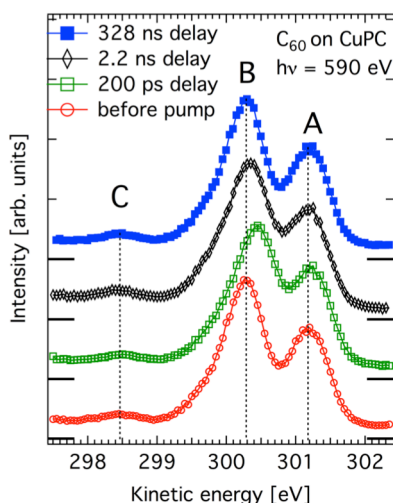


Figure 5. Picosecond time-resolved XPS spectra ($h\nu = 590$ eV) of the bi-layer system of C_{60} on CuPC recorded at ALS BL 11.0.2. The colors indicate spectra before the optical pump pulse arrival (red) and at pump-probe delays of 200 ps (green), 2.2 ns (black), and 328 ns (blue). The C1s line associated with the C_{60} phase (feature B) exhibits a transient shift toward higher kinetic energies, while the CuPC-associated C1s lines (features A, C) remain unaffected by the optical excitation.

multi-layer of copper-phthalocyanine (CuPC) chromophores. Peak B in these spectra is largely due to C1s emission from C_{60} whereas peaks A and C emerge from CuPC. Peak B shifts by about 200 meV to higher kinetic energies (lower binding energies) when the XPS spectrum is recorded 200 ps after the film has been excited by an optical (532 nm) laser pulse. The transient shift

diminishes with increasing pump-probe delay. Evidently, electron arrival in the C_{60} domain leads to a characteristic energy shift of the C1s line from the electron acceptor. This feature can be exploited as a site-specific marker to directly monitor the interfacial charge transfer by recording intensity variations of the peak shift as a function of the time delay between the optical laser excitation of the CuPC chromophore and the core electron emission from the electron acceptor.

Within the framework of this AP we will investigate the charge transfer dynamics as a function of the morphology of the system. In particular, more application relevant systems will be studied by extending the experiments to bulk heterostructures, which are required for efficient light absorption. The morphology of bulk mixtures depends crucially on the mixing ratio while, interestingly, the static electronic properties of the heterojunctions do not.²⁴ Nevertheless, we expect different charge transfer times in intermixed bulk phases in comparison with thin-layered systems due to the exciton diffusion, which has to occur over larger distances in the bulk phases.

Material dependent trends will be investigated by substituting PCBM for C_{60} and using other chromophores such as MnPC, which has a different electronic structure compared to most other PC's. The studies will be extended to other optically active organic systems such as TTF-TCNQ, a polymer based model organic conductor system. The C1s XPS structure of this system is quite complex, but other atomic constituents, such as sulfur and nitrogen, exhibit sharp core levels and are specific to only one of the molecular constituents. Using tr-XAS on BL 8.0.1 will provide important complementary information on the dynamical processes, in particular, for the initial photoexcited states prior to the charge transfer process. Chemical states may also be more readily resolved in the NEXAFS spectra than in XPS, since the assignment of specific core hole excited

states has been established rather well for NEXAFS.

II. Photocatalytic systems – *in operando* studies of photocatalytic water splitting

Among renewable energy technologies, photocatalysis has the particularly appealing potential to directly convert solar energy into storable fuels. One of the most intensely studied photoanode materials for water-splitting applications in photoelectrochemical cells (PECs) is hematite ($\alpha\text{-Fe}_2\text{O}_3$) due to its natural abundance, chemical stability, and relatively narrow band gap of ~ 2.1 eV, which facilitates photon absorption across a large portion of the solar spectrum. In a PEC, photo-generated holes have to diffuse toward the anode-electrolyte interface where they ultimately drive the water oxidation reaction. Despite a large body of electrochemical and optical spectroscopy studies, a comprehensive atomic orbital scale picture of the electronic processes that enable and limit the water-splitting reaction in PECs has not yet emerged. While many studies indicate that surface states have a significant impact on the water oxidation efficiency, a controversy exists regarding the chemical character of the interfacial hole-states and the role they play in the electrochemical reaction.²⁷ Time-resolved X-ray spectroscopy can provide entirely new insight into the concerted electronic and nuclear dynamics in PECs.

Gessner and collaborators have recently demonstrated the feasibility of picosecond time-resolved *in operando* XAS at the ALS (Fig. 6).⁶ These proof-of-principle experiments with a working hematite photoanode show that (i) the water-oxidation reaction can be efficiently driven with 10 ps/355 nm laser pulses (Fig. 6c), (ii) the PEC cells maintain their functionality even after prolonged laser exposure, and (iii) picosecond tr-XAS spectra can be efficiently collected from the semiconductor-liquid interface by simultaneously recording data across a several nanosecond wide time window using the newly developed time-tagging approach (Fig. 6d). Within this AP

we will further develop and employ this novel technique to not only identify the chemical character of the holes that accumulate at the solid-liquid interface,²⁸ but also to monitor the evolution of their concentration over time and as a function of bias potential.

The dynamic response of prototypical electrode materials such as hematite, TiO_2 , WO_3 and BiVO_4 will be investigated by probing the O1s levels and the metal absorption edges (Fe2p, Ti2p, W4p V2p, Bi4d). The studies will be extended to probe novel material design strategies

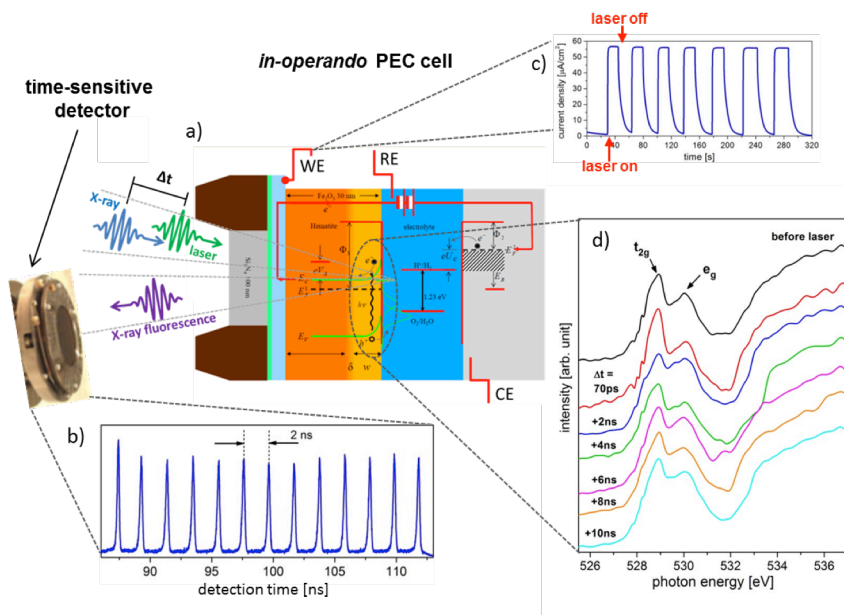


Figure 6. Demonstration of *in operando* tr-XAS of interfacial photo-electrochemistry. (a) Combination of an *in situ* photoelectrochemical (PEC) cell, time-resolved X-ray fluorescence detector and the synchronized DUETTO laser system. (b) Time-resolved bunch structure of the ALS. (c) Laser-induced photocurrent of the PEC cell. (d) Preliminary tr-XAS results at the O K-edge of a working hematite photoanode (WE).

for PECs such as: (i) nano-structuring of the photoanode to minimize recombination losses during charge carrier diffusion and (ii) coating of the photoanode with catalysts that enhance charge separation and increase the lifetime of photo-generated holes at the electrode-liquid interface. Particularly promising results have been obtained with hematite electrodes decorated with cobalt adatoms and IrO_2 nanoparticles.²⁹ The element-specific perspective provided by tr-XAS is uniquely suited to decipher the microscopic mechanisms underlying the chemical function(s) of such overlays.

Most recently, plasmonic-based devices based on combinations of metal nanoparticles (NP) and SC nanocrystals are attracting significant attention. The key idea is to couple the tunable wideband absorption characteristics of metal NPs with efficient charge carrier separation at a metal-SC interface to produce the free charge carriers required for catalytic activity (Fig. 7a).

Moskovits and co-workers recently demonstrated an autonomous solar water-splitting device based on an array of gold nanorods that are lined with a cobalt-based oxygen evolution catalyst (Co-OEC) along their sidewalls and capped with a layer of TiO_2 and Pt nanoparticles (Fig. 7b).³⁰ While providing a beautiful demonstration of the key concepts of plasmonic photocatalysis, the overall yield of the system's photosynthetic activity is rather low (~0.1 - 0.25 % photon-to-hydrogen yield). Within this AP we will develop the capability to test some of the fundamental hypotheses on charge carrier creation, transport, localization, and catalytic activity in plasmonic photocatalytic systems with time-domain X-ray spectroscopy techniques.

The efficient separation and transport of catalytically active charge carriers and their sufficiently long retention/life times at redox-active sites are closely related to the (transient) interfacial band structure (Fig. 8). At the metal-SC interface, band-bending is expected to lead to

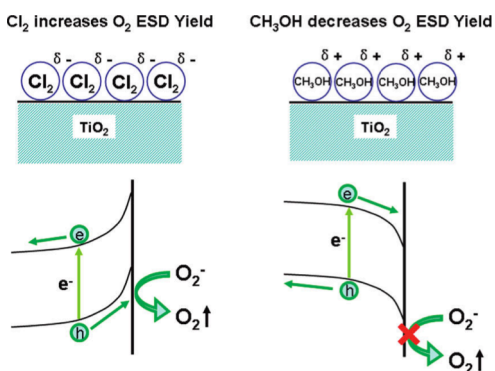


Figure 8. Band bending at semiconductor surfaces strongly impacts interfacial charge-transfer probabilities and carrier lifetimes.

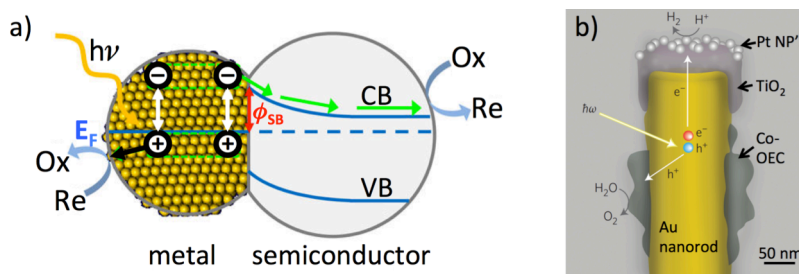


Figure 7. (a) Concept and (b) implementation of nanoscale plasmonic photocatalytic heterostructures. Metal nanoparticles serve as plasmonic light absorbers, creating hot charge carriers, which are separated at interfaces between metal and semiconductor nanostructures.

a Schottky barrier that facilitates efficient charge separation. At both SC-liquid or SC-molecule interfaces, band bending can strongly affect the carrier lifetimes.³¹ The very concept of nanoscale Schottky barriers and electronic interfaces, however, is a matter of intense research and no universal, quantitatively accurate model exists.³²⁻³⁴ Moreover, the ultrafast dynamic variations of nanoscale interfacial electronic structures are virtually unexplored. Optical pump / X-ray probe tr-XPS and tr-XAS experiments will be employed to monitor transient surface photovoltages (SPV) and interfacial charge carrier concentrations of SC components at

vacuum and buried interfaces. First experiments will be performed on TiO₂ films sensitized with Au nanoparticles. For this system, reversible spectral changes have been recently been observed in the pre-edge region of the Ti-related XAS signals under continuous laser excitation resonant with the localized surface plasmon resonance (LSPR) of the Au nanoparticles.³⁵ The results point toward a significant modification of the TiO₂ electronic structure in response to the hot electron injection from the Au. Tr-XAS at the Ti-L and O-K edges will be used to clarify the population dynamics and atomistic origin of the trapping sites at the SC surface, while the temporal evolution of the band-alignment at the metal-SC interfaces will be monitored with tr-XPS via the transient SPV effect.

Building on these proof-of-concept experiments, we will extend our studies to arrays of gold nanorods capped with layers of either TiO₂ or a Co-OEC (Fig. 7b). Based on the concepts described above, oxidizing and reducing interfaces are expected to exhibit opposite SPV effects upon free-charge carrier induced band flattening (Fig. 8).^{33,36} Note that the dynamics of buried metal-SC interfaces may be observed by tr-XPS even if the layers of SC materials are thicker than the photoelectron escape depth since the electronic bands are pinned to the buried interface.^{1,37} In the next stage, caps and sidewall coatings will be applied using different materials. Picosecond to microsecond tr-XPS and tr-XAS studies will monitor the appearance, trapping and relaxation dynamics of electrons and holes at the critical interfaces with site specificity. Co2p and Ti2p lines will be used to study the transient charge carrier concentrations at both metal-SC interfaces *independently*. Comparison of experiments using two and three materials will provide insight as to which degree multiple interfacial dynamics in nanoscale systems can be treated independently by focusing only on dynamics in an idealized half system (oxidizing vs. reducing). In the next stage, critical links and differences between electronic dynamics in isolated and solvated nanorod assemblies will be investigated, which are particularly important with respect to their catalytic activity.

Previous Scientific Accomplishments / Track Record

Both PIs have an extensive track record in synchrotron-, ultrafast laser-, and X-ray free-electron laser based science. The bestowal of a DOE Early Career Award in 2012 has enabled Gessner to implement several novel time-domain X-ray spectroscopy techniques at the ALS¹⁻⁶ and LCLS^{5,8} to study interfacial charge dynamics in condensed phase systems. The work has recently been recognized by the 2014 LBNL Director's Award for Exceptional Scientific Achievement. Eberhardt has been an internationally recognized leader in the field of synchrotron and laser based materials science for ~30 years. In particular, he has studied the electronic and magnetic properties of molecules, clusters, and solids by photoemission and (fs-laser) time resolved photoemission spectroscopy and other synchrotron radiation related techniques.³⁸⁻⁴²

Justification for particular beamlines

Beamlines 8.0.1 and 11.0.2 are uniquely suited for the proposed tr-XAS and tr-XPS studies, respectively, due to both their photon characteristics and available/compatible experimental endstations. The time-tagging approach relies on time-resolved detectors that are available at these beamlines as part of the ambient pressure XPS at BL 11.0.2 and the newly developed TXA setup, which is compatible with BL 8.0.1. The photon energy ranges of the beamlines give access to the most important core-levels of materials used in electrodes (e.g. Zn2p, Ti2p), electrolytes (e.g. I3d) and molecular components (e.g. C1s, S2p, N1s, Ru3d).

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