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Time-Resolved X-Ray Photoelectron Spectroscopy Techniques For Real-Time Studies Of Interfacial Charge Transfer Dynamics

Andrey Shavorskiy^a, Amy Cordones^b, Josh Vura-Weis^b, Katrin Siefertmann^c, Daniel Slaughter^c, Felix Sturm^c, Fabian Weise^c, Hendrik Bluhm^d, Matthew Strader^e, Hana Cho^e, Ming-Fu Lin^{b,c}, Camila Bacellar^{b,c}, Champak Khurmi^c, Marcus Hertlein^a, Jinghua Guo^a, Tolek Tyliczszak^a, David Prendergast^f, Giacomo Coslovich^e, Joseph Robinson^{e,g}, Robert A. Kaindl^e, Robert W. Schoenlein^{c,e}, Ali Belkacem^c, Thorsten Weber^c, Daniel M. Neumark^{b,c}, Stephen R. Leone^{b,c,h}, Dennis Nordlundⁱ, Hirohito Ogasawaraⁱ, Anders R. Nilssonⁱ, Oleg Krupin^{g,j}, Joshua J. Turner^g, William F. Schlotter^g, Michael R. Holmes^g, Philip A. Heimann^g, Marc Messerschmidt^g, Michael P. Minitti^g, Martin Beye^k, Sheraz Gul^l, Jin Z. Zhang^l, Nils Huse^m, and Oliver Gessner^c

^aAdvanced Light Source, Lawrence Berkeley National Laboratory; ^bDepartment of Chemistry, University of California Berkeley; ^cUltrafast X-ray Science Laboratory, Chemical Sciences Division, Lawrence Berkeley National Laboratory; ^dChemical Sciences Division, Lawrence Berkeley National Laboratory; ^eMaterials Sciences Division, Lawrence Berkeley National Laboratory; ^fMolecular Foundry, Lawrence Berkeley National Laboratory; ^gLinac Coherent Light Source, SLAC National Accelerator Laboratory; ^hDepartment of Physics, University of California Berkeley; ⁱSLAC National Accelerator Laboratory; ^jEuropean XFEL GmbH; ^kHelmholtz-Zentrum Berlin fuer Materialien und Energie GmbH; ^lDepartment of Chemistry and Biochemistry, University of California Santa Cruz; ^mMax-Planck Research Department for Structural Dynamics at the University of Hamburg, CFEL

Abstract. X-ray based spectroscopy techniques are particularly well suited to gain access to local oxidation states and electronic dynamics in complex systems with atomic pinpoint accuracy. Traditionally, these techniques are applied in a quasi-static fashion that usually highlights the steady-state properties of a system rather than the fast dynamics that often define the system function on a molecular level. Novel x-ray spectroscopy techniques enabled by free electron lasers (FELs) and synchrotron based pump-probe schemes provide the opportunity to monitor intramolecular and interfacial charge transfer processes in real-time and with element and chemical specificity. Two complementary time-domain x-ray photoelectron spectroscopy techniques are presented that are applied at the Linac Coherent Light Source (LCLS) and the Advanced Light Source (ALS) to study charge transfer processes in N3 dye-sensitized ZnO semiconductor nanocrystals, which are at the heart of emerging light-harvesting technologies.

Keywords: Ultrafast Spectroscopy, X-ray Photoelectron Spectroscopy, Dye-Sensitized Nanostructures, Free Electron Lasers.

PACS: 82.80.Pv, 82.53.Mj, 88.40.hj, 78.47.J

INTRODUCTION

Intramolecular and interfacial charge transfer is a fundamental component of the working cycle of naturally occurring and engineered energy conversion and storage solutions. The goal to improve efficiencies

of photovoltaic devices, photocatalytic processes, and battery technologies, for example, is intimately linked with the capability to characterize and ultimately control charge transfer processes on a molecular level. Dye-sensitized solar cells are a particularly prominent example for the emerging technologies of so-called molecular photovoltaics. Some of the most successful

dye sensitized solar cell designs are based on the attachment of Ruthenium complexes such as Ruthenium 535 (cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II), also called N3) to zinc oxide or titanium dioxide nanostructures (Fig. 1a). Critical for the functionality of the cell is the fast electron transfer from the dye to the substrate, which has to be orders of magnitude more efficient than exciton recombination in the dye and electron back-transfer from the substrate to the dye. Despite two decades of significant research efforts, a unified picture of the time scales that govern the fundamental electronic dynamics in these cells is still lacking. Such a picture would include time scales for metal-to-ligand charge transfer (MLCT) within the dye, electron injection into the nanostructured substrate, subsequent electronic relaxation dynamics within the substrate, and electron-hole recombination by Coulomb interaction between the oxidized dye and the semiconductor substrate. Time-domain and energy-domain studies indicate the involvement of multiple time scales ranging from less than a few femtoseconds [1] to many picoseconds [2] and even microseconds [3] but it is not clear in all cases which

physical processes are associated with the observed time scales.

The combination of visible lasers and accelerator-based x-ray light sources such as free electron lasers (FELs) and synchrotron radiation light sources provide the opportunity to gain a deeper understanding of the electronic dynamics in complex interfacial systems by applying core-level spectroscopy techniques in time-resolved experiments [4]. The element specificity of core-level transitions combined with the femtosecond to picosecond time duration of the x-ray pulses provide a unique perspective on electronic dynamics in photovoltaic systems with an unprecedented combination of temporal and spatial resolution. Here, we describe two time-resolved x-ray photoelectron spectroscopy (TRXPS) experiments performed at the Linac Coherent Light Source (LCLS) at SLAC National Accelerator Laboratory and the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. The goal of the experiments is to explore the potential of TRXPS for time-domain studies of interfacial electronic dynamics in dye-sensitized semiconductor nanostructures.

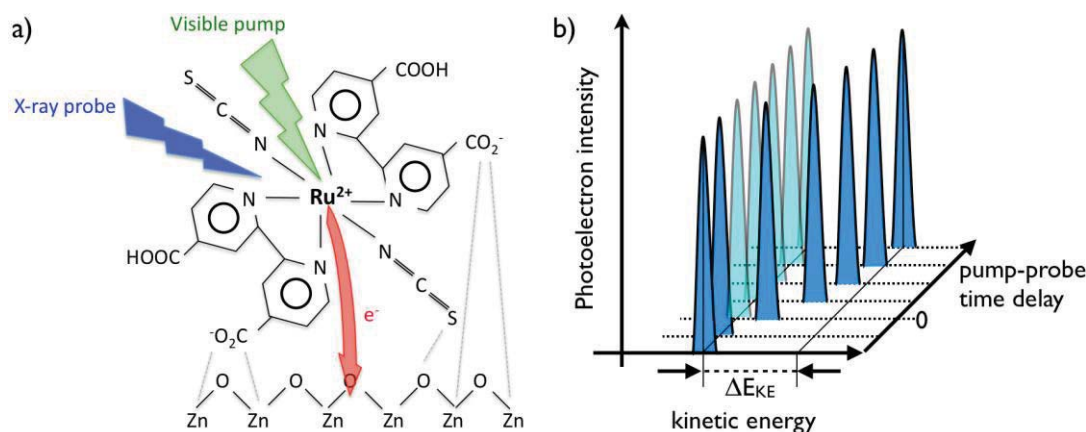


FIGURE 1. Fundamental concept of TRXPS to monitor (a) electronic dynamics in dye-sensitized nanocrystals by (b) a transient chemical shift in the inner-shell photoelectron spectrum.

Fig. 1 illustrates the fundamental concept of the experiments. Visible (~530 nm) laser pulses are employed to stimulate electronic dynamics in N3 dye-sensitized films of semiconductor nanoparticles (ZnO or TiO₂, Fig. 1a). The induced electronic dynamics are probed by recording inner-shell photoelectron spectra for different time delays between the exciting laser pulse and the probing x-ray pulse provided by the FEL or synchrotron light source (Fig. 1b). The key idea of TRXPS is that the valence electron dynamics in the vicinity of a specific atom induce a time-dependent chemical shift [5] in the kinetic energies of photoelectrons emitted from the tightly bound inner

shells of this atom. The kinetic energies of inner-shell photoelectrons are directly related to the binding energies of the core levels and are therefore element-specific. Therefore, TRXPS provides a unique element-specific view of the interfacial valence electron dynamics in complex systems.

TRXPS EXPERIMENT AT THE LINAC COHERENT LIGHT SOURCE (LCLS)

LCLS is the first free electron laser that produces femtosecond duration x-ray pulses with photon energies in the keV range [6]. The Soft X-ray

Materials Science (SXR) instrument of the LCLS provides x-ray pulses with photon energies between 480 eV and 2000 eV [7]. It is equipped with a monochromator with a resolving power $E/\Delta E=3300 - 5000$. The monochromator is a critical component for TRXPS experiments since it provides the sub-eV photon energy bandwidth that is required to resolve small chemical shifts in photoelectron spectra. Fig. 2 illustrates the TRXPS experiment at the LCLS SXR instrument. A visible pump-pulse with a wavelength of

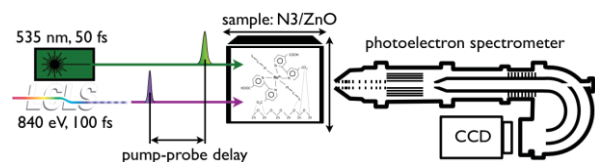


FIGURE 2. TRXPS setup at the LCLS SXR instrument.

535 nm and a pulse duration of 50 fs (FWHM) is used to induce electronic dynamics in the sample that consists of a film of N3 dye-sensitized ZnO nanocrystals supported by a 0.5 mm thick Si(100) wafer. The sample is mounted in shallow incidence geometry inside the Surface Chemistry Endstation of the SXR instrument, which is equipped with a hemispherical electron energy analyzer (R3000, VG-Scienta). The LCLS is tuned to provide x-ray probe-

pulses at a nominal photon energy of 850 eV and sub-100 fs pulse duration (FWHM). Space charge effects in the photoelectron spectra are minimized by attenuating the x-ray beam by $\sim 6-8$ orders of magnitude using Mg foils. Sample damage effects are reduced by moving the sample between consecutive measurements.

Fig. 3a shows two photoelectron spectra in the vicinity of ~ 290 eV binding energy. The red spectrum is observed when a visible pump pulse with a fluence of ~ 0.8 mJ/cm² is incident on the sample 1 ps before the x-ray probe pulse. The black spectrum is recorded without a pump pulse. The pump-on and pump-off spectra are recorded simultaneously by operating the visible laser at half the repetition rate of the LCLS (60 Hz and 120 Hz, respectively) and separating the data sets after the measurement. The data acquisition time for the spectra shown in Fig. 3 was 16 minutes. Three main features can be readily distinguished in the photoelectron spectra: two C1s⁻¹ photolines, one from the carboxyl groups, the other from the pyridine rings, and the Ru3d_{5/2}⁻¹ photoline from the transition metal center of the dye [8]. The separation of the two C1s⁻¹ photolines demonstrates the time-independent sensitivity of XPS to the local valence electron environment of specific atomic sites.

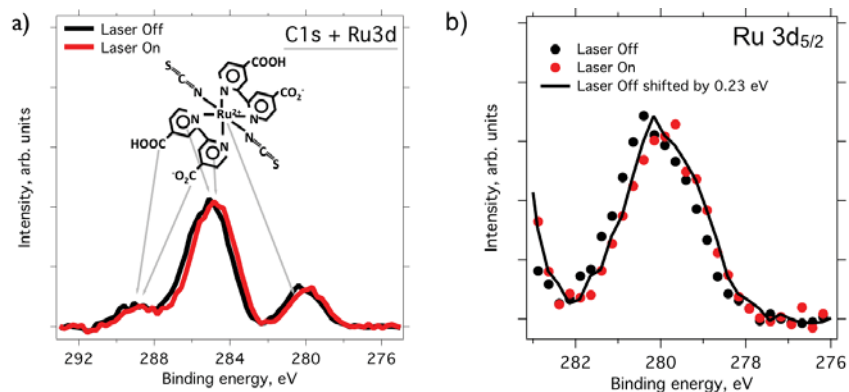


FIGURE 3. Transient shift of the inner-shell photoelectron spectrum of N3-sensitized ZnO nanocrystals observed at the LCLS. Red and black traces are measured with and without the pump laser incident on the sample, respectively. A magnified view of the Ru 3d_{5/2}⁻¹ peak region in (a) is shown in (b) together with a copy of the black trace shifted by 0.23 eV to lower binding energies (black line).

The red trace can be approximated by shifting the black trace by 0.23 eV toward lower binding energies (black line in Fig. 3b). We associate this shift of the entire spectrum with a transient change of the electric potential of the sample on a macroscopic scale rather than with local electronic dynamics in the dye molecules. This interpretation is supported by a test experiment in which the exciting laser beam and the probing x-ray beam are incident on spatially separated

regions of the sample, leading to the same transient energy shift in the XPS spectrum (not shown). A similar spectral shift has previously been observed for the Si 2p⁻¹ photoline in TRXPS experiments on pure silicon where the shift has been interpreted as the result of a transient surface photovoltage (SPV) effect [9,10]. Note that the 2.3 eV photon energy of the pump laser in the LCLS experiment is sufficient to bridge the 1.1 eV band gap in silicon but not the 3.3 eV band gap

in the ZnO nanocrystals. The micron-thick nanocrystal film is largely transparent to visible light, enabling efficient free charge carrier generation in the silicon support by the pump pulse. We therefore interpret the transient shift in the XPS spectrum in Fig. 3 as the result of a transient SPV at the interface between the Si wafer and the dye-sensitized nanocrystal film.

TRXPS EXPERIMENT AT THE ADVANCED LIGHT SOURCE (ALS)

A synchrotron based TRXPS experiment that is complementary to the LCLS experiment is shown in Fig. 4. The XPS setup consists of a hemispherical electron energy analyzer (PHOIBOS 150 NAP, SPECS), and a computer-controlled sample positioning system mounted in a high vacuum chamber. The setup is located at the Molecular Environmental Science beamline 11.0.2 of the ALS, which provides x-rays with photon energies between 100 eV and 2000 eV [11]. For the TRXPS experiments

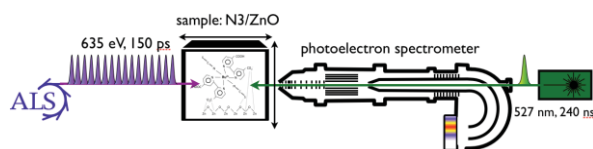


FIGURE 4. TRXPS setup at the ALS Molecular Environmental Science beamline 11.0.2.

described here, visible (527 nm) light pulses from a diode-pumped, Q-switched ND:YLF laser are routed into the vacuum chamber through a vacuum viewport at the back of the hemispherical analyzer and along the central axis of the electrostatic lens system. The pulse duration is 240 ns (FWHM). The last aperture along the laser beam path is the 0.3-1.0 mm diameter entrance aperture of the photoelectron spectrometer. The coaxial arrangement of the laser beam and the lens system of the electron analyzer significantly simplifies the alignment procedure of the pump-probe experiment. In order to achieve spatial overlap between the visible pump-pulse and the x-ray probe-pulse it is sufficient to maximize the XPS signal by optimizing the sample position and x-ray beam pointing.

In order to perform TRXPS experiments during the multi-bunch operating mode of the ALS, electrons emerging from the exit of the hemispherical analyzer are imaged by means of a fast time- and position-sensitive detector instead of the conventional combination of a phosphor screen and a CCD camera. The details of this novel detection scheme are discussed in a different publication [12]. Fig. 5 shows two XPS spectra of an N3-sensitized ZnO nanocrystal

film supported by a 0.5 mm thick Si(100) wafer. The black trace (round markers) is recorded before the pump pulse is incident on the sample, the red trace 2-3 μ s after the pump pulse arrival. The pump pulse fluence on the sample is ~ 7 mJ/cm². Similar to the

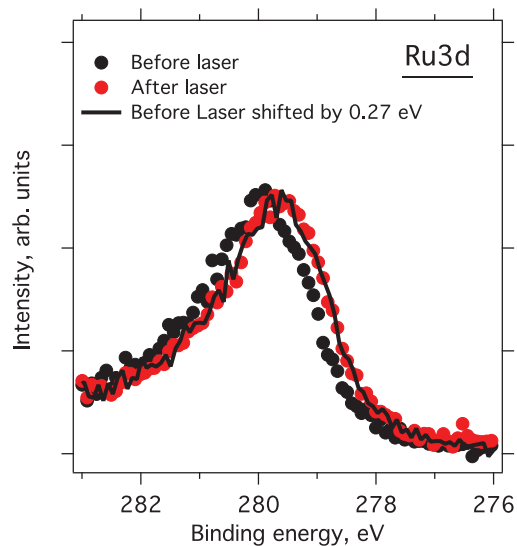


FIGURE 5. Transient shift of the inner-shell photoelectron spectrum of N3-sensitized ZnO nanocrystals observed at the ALS. Red and black symbols are measured with and without the pump laser incident on the sample, respectively. The black line is a copy of the black trace shifted by 0.27 eV to lower binding energies.

LCLS measurements, the pump laser induces a shift of ~ 0.27 eV of the entire spectrum toward lower binding energies (black line). Note that Long and co-workers reported transient SPV relaxation time scales on the order of microseconds, which explains the similarities between the results of the femtosecond time-resolved measurements at the LCLS and the nanosecond time-resolved experiments at the ALS. Future refinements in the experiments and analysis techniques will grant access to the more subtle electronic dynamics that take place at the interface between the molecular dyes and the semiconductor nanocrystal substrates.

SUMMARY

Time resolved x-ray photoelectron spectroscopy (TRXPS) experiments are operational at the Advanced Light Source, Lawrence Berkeley National Laboratory and the Linac Coherent Light Source at SLAC National Accelerator Laboratory. Test experiments with films of dye-sensitized semiconductor nanocrystals supported by silicon wafers reveal a transient shift of the XPS spectrum that is ascribed to a previously observed transient surface photovoltage

effect in the Si support. In particular the results of the LCLS experiments demonstrate that space charge effects in FEL-based measurements can be sufficiently minimized to enable femtosecond time-resolved XPS measurements that are sensitive to spectral shifts in the sub-eV range. Future refinements in the experiments and analysis techniques will exploit the full potential of TRXPS to monitor interfacial electronic dynamics in dye-sensitized semiconductor nanocrystals with element specificity and femtosecond time resolution.

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