

Real-time probing of charge-transfer induced interfacial fields in a dye-semiconductor system using time-resolved XPS

Johannes Mahl^{1,2}, Stefan Nepp^{1,3}, Friedrich Roth^{4,5}, Andrey Shavorskiy^{6,7}, Nils Huse^{2,5}, Hendrik Bluhm^{1,7}, Wolfgang Eberhardt^{5,7}, and Oliver Gessner¹

¹Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720 USA

²Physics Department Universität Hamburg, 22607 Hamburg, Germany

³Helmholtz-Zentrum Berlin für Materialien und Energie, 14109 Berlin, Germany

⁴Institute for Experimental Physics, TU Bergakademie Freiberg, 09599 Germany

⁵Center for Free-Electron Laser Science DESY, 22607 Hamburg, Germany

⁶MAX IV Laboratory, 225 94 Lund, Sweden

⁷Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720 USA

Abstract. Photo-induced charge carrier dynamics and transient interfacial fields at the interface between N3 polypyridine complexes and films of nanocrystalline ZnO are probed by picosecond time-resolved X-ray photoelectron spectroscopy.

1 Introduction

Interfacial charge transfer is a fundamental component of natural and engineered processes ranging from biological function to catalytic applications. In particular, heterogeneous systems involving molecular and crystalline phase components attract significant attention due to the possibility to assemble “chemical machineries” from a wide variety of tailored, molecular-scale building blocks. Here, we probe photoinduced charge-transfer dynamics in films of N3-sensitized ZnO using picosecond time-resolved X-ray photoelectron spectroscopy (tr-XPS). Exploiting the elemental site specificity and chemical sensitivity of XPS, we track the evolution of interfacial electronic configurations from both sides of the N3-ZnO interface by monitoring the C1s photoline associated with the dye molecule and the Zn3d line associated with the semiconductor substrate. The measurements give access to injection and recombination timescales as well as transient potential energy differences across the interface with atomic-scale site-sensitivity, providing a comprehensive picture of the fundamental dynamics that ultimately define the efficiency of the photoinduced processes.

2 Experimental Setup

A 10 ps laser “pump” pulse with 532 nm wavelength induces HOMO–LUMO excitations in the N3 dye molecules attached to films of nanocrystalline ZnO. The temporal evolution of

the interfacial potentials is probed by monitoring time-dependent changes in the C1s and Zn3d XPS spectra recorded with 70 ps X-ray “probe” pulses from the Advanced Light Source (ALS). The setup implemented at beamline 11.0.2 of the ALS uses a time-stamping technique to simultaneously record XPS signals from an extended X-ray pulse train [1]. Typical excitation laser fluences are on the order of ~ 1 mJ/cm².

3 Results and Discussion

Both, the C1s and Zn3d lines exhibit rigid shifts to higher binding energies following laser excitation. Figure 1a shows the amplitudes of these shifts for both lines as a function of pump-probe delay. The solid lines are fits to the data using a bi-exponential decay model

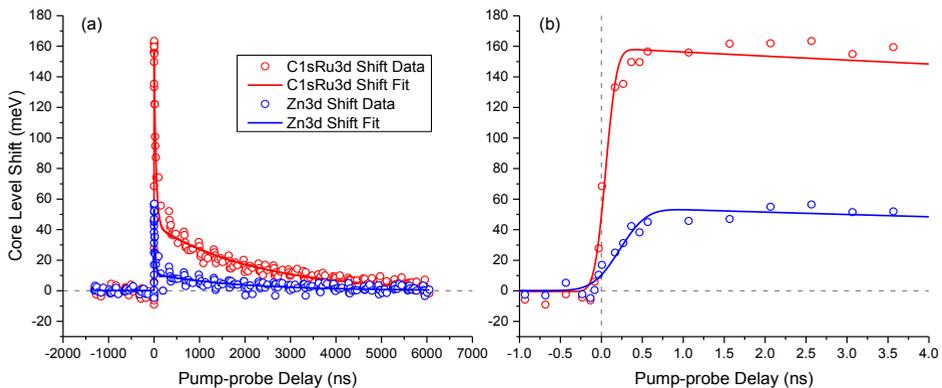


Fig. 1. a) Photoinduced binding energy shifts for dye-associated C1s photoelectrons (red) and substrate-associated Zn3d photoelectrons (blue) due to charge-transfer and recombination dynamics at an N3-ZnO interface. b) Magnified view of dynamics during the first few nanoseconds.

for the falling edges and broadened step functions for the rising edges, convoluted with a Gaussian instrument response function. The resulting decay constants are 42 ns and 2.2 μ s for the C1s line (red) and 26 ns and 1.9 μ s for the Zn3d line (blue). Interestingly, the initial Zn3d response is ~ 200 ps slower than the C1s response as can be seen in Fig. 1b, which shows a magnified view of the trends across the first few nanoseconds. This time lag is comparable to the characteristic timescale for free charge carrier generation in photoexcited N3-ZnO heterostructures as determined by transient infrared absorption [2] and transient THz photoconductivity [3, 4] measurements.

The observed tr-XPS signals may be interpreted in terms of contributions from interfacial and intraband dynamics (Fig. 2). Separation of electrons and holes during charge transfer from the dye molecules to the semiconductor substrate is expected to create interfacial dipole moments on sub-ps timescales.[5] The subsequent release of electrons from the interfacial region into the substrate conduction band, however, may proceed on significantly longer timescales [2-4]. Eventually, injection of electrons into the ZnO conduction band affects the screening of surface charges and, therefore, the band bending towards the interface. This effect modifies the effective binding energies of photoelectrons emitted from all electronic levels of all atoms on both sides of the interface.

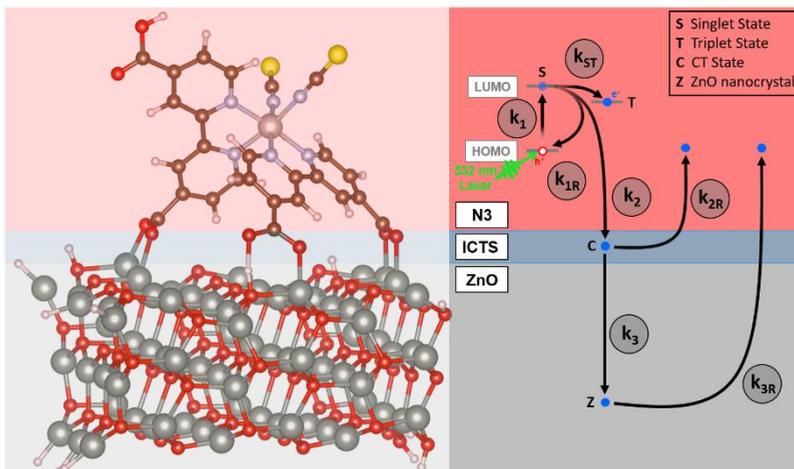


Fig. 2. Left: Predicted dominant binding motif of N3 dye molecules on wurtzite ZnO substrate. Right: Relevant rates contributing to interfacial charge-transfer and relaxation dynamics following photoinduced HOMO-LUMO excitation of the N3 dye. Labels mark molecular singlet [S] and triplet [T] states, interfacial charge-transfer states [C], and delocalized conduction band states [Z]. Electron-hole recombination rates involving different states are indicated by an index R.

Transient interfacial dipoles, however, may affect photolines emerging from different interfacial sites by different amounts. The tr-XPS measurements are, therefore, sensitive to both interfacial and intraband dynamics with the former mostly reflected in the difference between the C1s and Zn3d responses and the latter in the overall shape of the signal transients. In particular, the bi-exponential decay reflects the electron-hole recombination dynamics across the interfacial space charge layer [1]. A coupled rate equation model will be used to connect electronic processes proceeding on a variety of length- and timescales to produce a comprehensive picture of all stages of photoinduced interfacial charge-transfer and relaxation dynamics.

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