

In-situ Pump-Flow-Probe XAFS Study on Single Atom-Pt/CoOOH Photocatalysts

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1 Introduction

Heterogeneous photocatalytic hydrogen evolution is a promising approach toward a green and sustainable hydrogen economy.^[1] Pt-based cocatalysts play a critical role in the promotion of overall solar-to-hydrogen efficiency during photocatalysis. The electron transfer kinetics between semiconductors and Pt cocatalyst are usually expected to occur in a microsecond time scale,^[2] which is important for understanding the photocatalytic mechanism. But how long it takes for excited electrons transfer between semiconductors and Pt cocatalysts is still an open question since many time-resolved techniques are not locally sensitive nor element-specific. To this goal, we prepared CoOOH semiconductor supported single-atom (SA) Pt sites (SA-Pt/CoOOH) as the semiconductor-cocatalyst photocatalysts and applied microsecond (μs) time-resolution pump-flow-probe XAFS (PFP-XAFS) spectroscopy to SA-Pt/CoOOH for tracking their excited electron transfer kinetics.

2 Experiment

The CoOOH semiconductors were prepared through a hydrothermal method, similar to that reported before.^[3] Single-atom Pt sites are deposited onto CoOOH via a wet chemical approach. *In-situ* PFP-XAFS measurements were carried out at the BL15A1 beamline station, Photon Factory, which has a $20\ \mu\text{m} \times 20\ \mu\text{m}$ X-ray micro-beam^[4] for helpfully achieving $\sim 10\ \mu\text{s}$ time resolution. As shown in Fig. 1, the continuous wave (CW) 405 nm laser was used as pump and X-ray was used as probe during measurements, where fluorescence signals was recorded by a single-channel silicon drift detector (SDD). The delay time after photoexcitation was determined by the equation: $t = d/v$, where the flow speed (v) was measured by the total volume of the effluent sample solution within 30 s and the laser to X-ray spots distance (d) can be tuned by the Z stage. To avoid sample damage, SA-Pt/CoOOH was dispersed into pure water (1 mmol/L) and then was pumped to the laser/X-ray spots in a flow away manner. For each delay time, Pt L_3 edge XAFS spectrum was first collected at laser off state then under laser on condition.

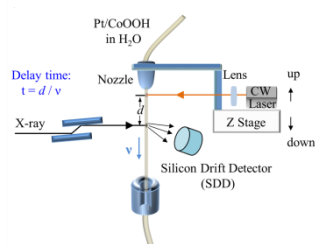


Fig. 1 Schematic of PFP-XAFS measurements.

3 Results and Discussion

The white line of Pt L_3 edge XAFS spectrum corresponds to the transition Pt $2p \rightarrow 5d$. With laser on, a clear reduction of white line intensity was observed under $10\ \mu\text{s}$ delay time for SA-Pt/CoOOH (Fig. 2), which indicates laser-excited electrons localized into Pt $5d$ orbits after photoexcitation. The difference XAFS spectra in Fig. 3a, got by subtracting the laser off spectrum from the laser on one, suggests excited electron transfer between CoOOH and Pt cocatalysts undergoes two processes since different contributions of peak A at 11570 eV and peak B at 11572 eV are obtained. By fitting intensity evolution of peak A and peak B via single- or double- exponential functions (Fig. 3b), the electron transfer from CoOOH to Pt is revealed to occur with a rate constant of $k_1 \approx 0.1\ \mu\text{s}^{-1}$.

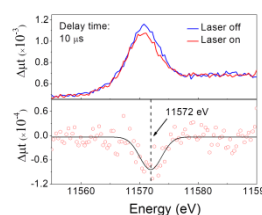
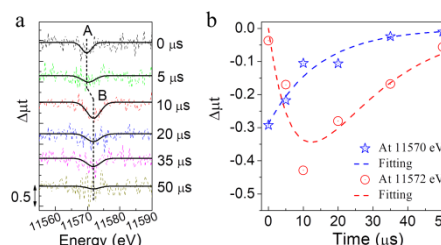
Fig. 2 Upper: Pt L_3 edge XAFS spectra; Lower: difference XAFS spectrum.

Fig. 3 (a) Difference XAFS spectra under various delay time, (b) Evolution of deconvoluted peak intensity.

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