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In-situ Pump-Flow-Probe XAFS Study on Single Atom-Pt/CoOOH Photocatalysts under different chemical environment

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1 Introduction

photocatalytic During Heterogeneous hydrogen altering the chemical surroundings of evolution. photocatalysts, for example adding hole scavengers, will have a great impact on their overall efficiency of converting water into hydrogen by solar energy.^[1] In previous work we successfully tracked the excited electron transfer in CoOOH semiconductor to the single-atom (SA) Pt reaction site (SA-Pt/CoOOH) by microsecond (µs) timeresolution pump-flow-probe XAFS (PFP-XAFS) spectroscopy. However, the following questions are left open: 1) how the hole scavengers alter the surface reaction kinetics of photocatalysts; 2) Whether hole scavengers have some impact on the photoexcited carrier transfer from the semiconductor (energy harvester) to Pt (reaction center) in photocatalysts. To find the answers for these two questions, we further study the photogenerated carrier kinetics under different chemical surroundings using PFP-XAFS spectroscopy.

2 Experiment

The SA-Pt/CoOOH photocatalysts were prepared as shown in our previous work.^[2] In-situ PFP-XAFS measurements were carried out at the BL-15A1 beamline station, Photon Factory, where the micro X-ray beam of 20 μ m × 20 μ m X-ray is available. The size is the key factor to realize ~10 µs time resolution in the PFP PFP-XAFS. We used continuous wave (CW) 405 nm laser with total reflection fiber pump and X-ray was used as probe. A 7channel silicon drift detector (SDD) was used for fluorescence signals collection. 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 distance between laser and X-ray spots (*d*) was tuned by the Z stage. To avoid sample damage, SA-Pt/CoOOH suspension was pumped to the laser/X-ray spots in a flow away manner. We prepared different chemical surroundings of pure water (no scavenger) and Na₂SO₃ aqueous solution (with hole scavenger) with N2 bubbling around SA-Pt/CoOOH photocatalysts. For each delay time, Pt L_3 edge XAFS spectrum was first collected at laser off state then under laser on condition.

3 Results and Discussion

The white line of Pt L_3 edge XAFS spectrum corresponds to the transition Pt $2p \rightarrow 5d$. For photocatalysts

under pure water $+ N_2$ bubbling, a maximum reduction of white line intensity was observed under laser on condition at about 10 µs delay time (Fig. 1), indicating the laserexcited electrons localized into Pt 5d orbits after photoexcitation. Notably, with SO32- as excited hole scavengers, the maximum reduction of white line intensity also appeared at 10 µs delay time for Na₂SO₃ solution + N₂ bubbling condition. The difference XAFS spectra, got by subtracting the laser off spectrum from the laser on one, were depicted in Fig. 2. It can been seen that, with hole scavengers, peak intensity of difference XAFS spectra almost decay completely at 25 µs delay time, much faster than that in pure water. These results reveal hole scavengers did not impact the excited electron transfer kinetics from CoOOH to Pt cocatalysts but just accelerated the decay of localized electron in Pt sites, indicating the promotion of surface reaction kinetics by hole scavengers.



Fig. 1 Pt L_3 edge XAFS spectra under (a) pure water + N_2 bubbling and (b) Na_2SO_3 solution + N_2 bubbling.



Fig. 2 Difference XAFS spectra under various delay time for (a) pure water $+ N_2$ bubbling and (b) Na_2SO_3 solution $+ N_2$ bubbling. (c) Time-dependence change of peak intensity at ~11570 eV for difference XAFS spectra.

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<u>References</u>

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