

Charge transfer in the cocatalyst-loaded SrTiO₃:Al photocatalyst under UV irradiation studied by *in situ* conversion-electron-yield soft-X-ray absorption spectroscopy

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1 Introduction

In situ observation of catalytic processes provides critical insights into catalytic mechanisms. Various spectroscopies, including X-ray absorption spectroscopy (XAS), have been applied to study catalysts due to their ability to provide detailed information on the geometric and electronic structures of active sites with high element selectivity. Soft X-ray absorption spectroscopy (SXAS) using the electron-yield method offers surface-sensitive information on chemical states of catalysts and reactants. However, the electron-yield SXAS is typically conducted under vacuum due to limited electron penetration in gases. To address this, the conversion-electron-yield (CEY) method allows SXAS measurements under ambient conditions. We developed a compact CEY-SXAS cell for *in situ* observation of photocatalysts under UV-Vis irradiation. Using this cell, we studied Rh/Cr₂O₃-CoOOH/STO samples [1], revealing photoinduced hole transfer to CoOOH, essential for promoting charge separation and hole transfer to the OER site.

2 Experiment

In situ SXAS measurements were performed at BL-13A in the Photon Factory (KEK-PF) using a modified CEY mode cell, enabling UV-Vis irradiation of sample surfaces (Fig. 1).

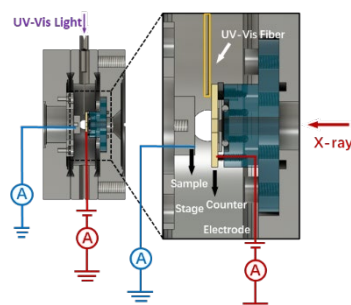


Fig. 1: A CEY-SXAS cell modified for introduction of UV-Vis lights. The UV-Vis lights are introduced via a fiber of which exit is opened to the sample stage. Reproduced with permission from Ref. 2). Copyright 2024 American Chemical Society.

The cell includes a fiber port for UV-Vis light, an ultrathin Si₃N₄ membrane window for soft X-rays introduction, which separates ambient-pressure He inside

from UHV condition of the beamline. UV-Vis lights from a Hg-Xe source were delivered through a fiber. The cell's sample stage and Au-coated counter electrode, separated by 1 mm, were connected to picoammeters to measure surface-sensitive XAS signals. Incident X-ray intensity was monitored with an Au mirror or mesh. Two types of SXAS measurements, TEY mode under vacuum and CEY mode with He gas or He/water vapor mixture, were conducted. In TEY mode, spectra were obtained by measuring sample drain current under vacuum. In CEY mode, secondary electrons and He cations were generated, and CEY-SXAS spectra were obtained by measuring drain currents with applied bias voltages.

3 Results and Discussion

A fresh sample of the photocatalyst was mounted in the CEY cell, and measurements were conducted in dark conditions and under UV irradiation for 15 minutes, followed by the introduction of saturated water vapor. The Co-L SXA spectra results are shown in Fig. 2A, with magnified Co L₃-edge peak changes in Fig. 2B.

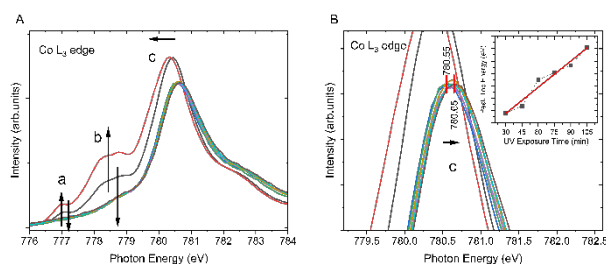


Figure 2: Co L-edge CEY-SXA spectra taken for the Rh/Cr₂O₃-CoOOH/STO:Al photocatalyst under a dark condition and UV-Vis irradiation with and without saturated water vapor. (A): The dark condition (dark) and under UV-Vis irradiation without the water vapor (red) and time evolution under UV-Vis irradiation with the water vapor (from 30 min to 105 min). (b): Magnified spectra for the main peak c. Inset: peak position shift of the main peak c as a function of the UV-Vis exposure time. Reproduced with permission from Ref. 2). Copyright 2024 American Chemical Society.

Under UV-Vis light without water vapor, Co reduction is evident, with increased pre-edge peaks a and b and a slight shift to lower energy side of the main peak c.

Introducing water vapor under UV-Vis irradiation oxidizes Co from Co^{2+} to Co^{3+} , indicated by the disappearance of pre-edge peaks and a shift of the main peak to higher energy side. DFT calculations confirm that water adsorption at OH-vacant Co sites stabilizes photoinduced holes, facilitating the oxidation of Co^{2+} to Co^{3+} . Prolonged UV-Vis irradiation further shifts the Co^{3+} peak, suggesting continuous hole transfer and slight Co oxidation without forming Co^{4+} .

We also found that Rh/ Cr_2O_3 , is crucial to act as an electron sink to trap photoinduced electrons and promote efficient hole transfer to the surface of the CoOOH site to further oxidize Co. Without the presence of HER site to trap the photoinduced electrons, it is assumed that a major part of photoinduced charge carriers undergoes charge recombination at the photocatalyst surface and the remaining electrons are accumulated on the CoOOH surface to reduce Co.

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References

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Research Achievements

1. JVSS 2023 Student Award based on this study.

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