A Thesis for the Degree of Ph.D. in Science

Development of Surface/Interface Sensitive *in situ* Soft X-ray Absorption Spectroscopy Techniques and Their Application to Studies on Photocatalytic System

February 2025

Graduate School of Science and Technology

Keio University

Wang Zi 王梓

別表６
（３）

Keio University

Thesis Abstract

No.

Registration Number	☑ "KOU" □ "OTSU" No. *Office use only	Name	WANG, Zi

Thesis Title

Development of Surface/Interface Sensitive *in situ* Soft X-ray Absorption Spectroscopy Techniques and Their Application to Studies on Photocatalytic System

Thesis Summary

This thesis investigates the surface reactions and the interfacial properties on photocatalyst surfaces under gas and liquid environments using in situ soft X-ray absorption spectroscopy (sXAS). By integrating advanced synchrotron-based techniques with new experimental setups, this work explores photoinduced charge transfer during photocatalytic water splitting under realistic working conditions and interactions at photocatalyst-water interfaces. This thesis consists of the following 6 chapters.

Chapter 1: General introductions

This chapter provides an overview of the scientific background relevant to this study, including heterogeneous catalysis, *in situ* X-ray absorption spectroscopy, and photocatalytic water splitting. It outlines the fundamental principles and the current challenges in the field, highlighting the importance of studying interfacial properties under operando conditions.

Chapter 2: Research Methodology

This chapter details the experimental and theoretical techniques employed in this study. It covers soft X-ray absorption spectroscopy (sXAS) with different measurement modes, X-ray photoelectron spectroscopy (XPS), and the specific synchrotron beamlines utilized for the experiments. Additionally, the chapter introduces the computational simulations performed using density functional theory (DFT) to complement the experimental observations.

Chapter 3: Charge Transfer in the Co-catalyst loaded Al-doped $SrTiO_3$ Photocatalyst under Ambient Pressure Conditions

This chapter focuses on the development of *in situ* sXAS methodologies. The newly developed conversion electron yield (CEY) cell enables direct probing of photoinduced charge transfer from the photocatalyst, Al-doped $SrTiO_3$, to the co-catalyst cobalt oxyhydroxide (CoOOH) at oxygen evolution reaction (OER) sites. Spectral changes observed at the Co L-edge under varying conditions reveal the critical role of water molecules and hydrogen evolution reaction (HER) sites in facilitating photoexcited hole transfer to CoOOH surfaces, thereby enhancing photocatalytic efficiency through effective charge separation.

Thesis Abstract

No.

Chapter 4: XAS Measurement Under Liquid Condition and Water/Toluene Structure Near Au Surface

This chapter extends the surface-sensitive insights to liquid environments by introducing a solid-liquid interface-sensitive sXAS cell designed for total electron yield (TEY) and total ion yield (TIY) measurements. Systematic studies on the Au-H_2O interface demonstrate the sensitivity of sXAS spectra to both interfacial and bulk water regions across multiple detection modes, including TEY-sample side, TEY-counter electrode side, TEY-dual electrode, and TIY. The results highlight the capability of electron and ion yield modes to selectively probe interfacial and bulk regions in solid-liquid systems, providing valuable insights into surface chemistry.

Chapter 5: Solid-Liquid Interface Structure of STO and CoOOH in Liquid Water

This chapter presents further advancements in the solid-liquid interface-sensitive sXAS analysis of $SrTiO_3$ (STO) and CoOOH surfaces in contact with water. The findings reveal significant differences in the electronic structure of these materials under liquid conditions compared to vacuum. Specifically, CoOOH surfaces exhibit a high-spin state in liquid water, while STO surfaces show partial electron filling of t_{2g} orbitals due to interactions with water lone pairs. Additionally, the interfacial water structure was found to differ significantly from bulk water, displaying an ice-like structure on STO and a water structure with reduced isolated OH groups on CoOOH.

Chapter 6: Concluding Remarks

The final chapter summarizes the key findings of this thesis and highlights the contributions made to the field of photocatalysis and surface chemistry. The chapter also outlines potential future research directions aimed at further advancing synchrotron-based studies of surface reactions and interfacial properties.