in situ XAFS analysis of Ru cocatalyst deposited on SrTiO$_3$:Rh photocatalyst

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Introduction

Overall water splitting under visible light irradiation has been achieved by Z-scheme type photocatalysis systems composed of two kinds of photocatalysts, Pt/SrTiO$_3$:Rh and BiVO$_4$, and an Fe$^{3+}$/Fe$^{2+}$ electron mediator[1,2]. The authors have recently found that Ru is a better cocatalyst than Pt for use in the Z-scheme systems because Ru is inactive for reverse reactions between H$_2$ and O$_2$ or Fe$^{3+}$[3]. Characterization of the Ru cocatalyst is important to clear the mechanism.

In the present research, the authors carried out in situ XAFS analysis for Ru cocatalysts deposited on the SrTiO$_3$:Rh photocatalyst using suspension system with visible light irradiation.

Experiments

XAFS measurement at Ru K-edge was carried out for Ru/SrTiO$_3$:Rh and RuCl$_3$-SrTiO$_3$:Rh suspension systems containing methanol using a glass cell with and without visible light irradiation. Concentration of Ru in the suspension was 100 ppm. The suspended solution was continuously stirred by a magnetic stirrer during XAFS measurements. XAFS spectra were mainly collected in a fluorescence mode using a multi-channel solid state detector. The incident beam was monitored by an ionization chamber filled with N$_2$(50%)/Ar(50%).

Results

EXAFS measurements using dried disk samples have revealed that Ru cocatalysts were deposited as oxide clusters on SrTiO$_3$:Rh photocatalysts in the samples prepared by a photodeposition method. However, this result does not guarantee that the Ru oxide cluster is the active cocatalyst in photocatalytic reactions. There is a possibility that Ru oxide clusters can be reduced by photogenerated electrons under working condition because the Ru cocatalyst functions as reduction sites to produce hydrogen molecules. Thus, it has been revealed from in situ EXAFS that the Ru oxide cluster is an active cocatalyst for SrTiO$_3$:Rh.

Next, in situ EXAFS of irradiated RuCl$_3$-SrTiO$_3$:Rh suspension containing methanol was measured to clarify the change in the Ru state in the photodeposition process (Fig. 1). Contribution of Ru-Cl bonds was dominantly observed in an aqueous RuCl$_3$ solution. Ru-O bonds appeared when SrTiO$_3$:Rh powder was dispersed in the solution. But, the contribution of Ru-Cl bonds still remained. It indicates that hydrolysis takes place partly due to rising pH with elution of Sr ions. In the irradiated suspension, the contribution of Ru-Cl bonds disappeared and the EXAFS of the suspension became similar to that of Ru oxide cluster in the dried Ru/SrTiO$_3$:Rh sample. Thus, it has been found that Ru oxide cluster formed in the photodeposition process even in the presence of methanol.

![Fig. 1 EXAFS of (a) an aqueous RuCl$_3$ solution (100 ppm) containing 10 vol% of methanol, RuCl$_3$-SrTiO$_3$:Rh suspension; (b) in the dark, (c) under irradiation, and (d) a dried Ru/SrTiO$_3$:Rh disk.](image)

References


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