NW10A/2006G326

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+}. 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 was carried out for $SrTiO_3$:Rh suspension containing $RuCl_3$ and methanol in a glass cell with and without visible light irradiation. Concentration of Ru in the suspension was 30-100 ppm. The suspended solution was continuously stirred by a magnetic stirrer during XAFS measurements. The incident and transmitted X-ray beams were monitored by ionization chambers filled with N_2(50%)/Ar(50%) and Kr, respectively. The fluorescent X-ray was monitored by a Lytle detector or a solid state detector.

Results

EXAFS measurement in Ru(5wt%)/Al_2O_3-water suspension systems was conducted to confirm reliability of XAFS measurement in the suspension systems. Figure 1 shows EXAFS oscillations at Ru K-edge of Ru(5wt%)/Al_2O_3 disk and suspended solutions with 6000 and 300 ppm of the Ru concentration. The 6000 ppm suspension solution was measured in a conventional transmission mode, while another suspended solution was measured in a fluorescence mode using the Lytle detector. Both of the EXAFS oscillations of suspension solutions were similar to that of the disk sample. Thus, it has demonstrated that EXAFS measurement can be applied to the suspension systems even under the stirring condition.

The obvious change was observed in XANES when a $RuCl_3$-$SrTiO_3$:Rh suspended solution was irradiated with visible light (Fig. 2). It is due to the photodeposition of a Ru cocatalyst from $RuCl_3$ on $SrTiO_3$:Rh with visible light excitation. XANES of photodeposited Ru/$SrTiO_3$:Rh was similar to that of RuO_2, indicating that the Ru cocatalyst was deposited not as metallic Ru but as RuO_x. Thus, in situ XAFS analysis revealed the chemical species of the photodeposited Ru cocatalyst although the mechanism of the oxidative photodeposition of RuO_x from Ru^{3+} in the presence of methanol, which works as a scavenger of photogenerated holes in $SrTiO_3$:Rh, is not clear at this stage.

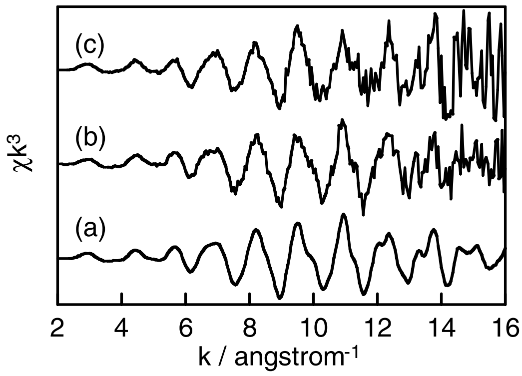

Fig. 1 EXAFS oscillations of Ru(5wt%)/Al_2O_3; (a) disk sample, (b) 6000 ppm suspension in the transmission mode, and (c) 300 ppm suspension in the fluorescence mode with the Lytle detector.

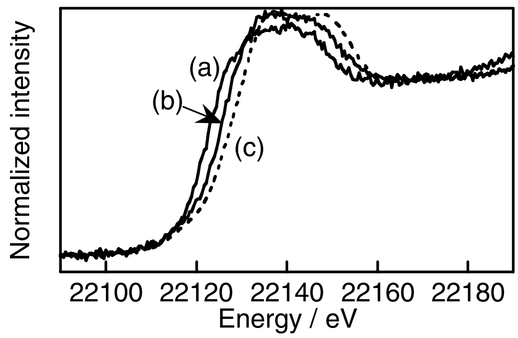

Fig. 2 XANES of 30 ppm $RuCl_3$-$SrTiO_3$:Rh suspension solutions (a) before and (b) after visible light irradiation, and (c) RuO_2 disk.

References

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