

Local Structure of Ruthenium Species as Promoters with TaON-Based Photocatalysts for Oxygen Evolution in Two-Step Water Splitting under Visible Light

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Introduction

Photocatalytic water splitting with visible light has been studied for the past 4 decades as a potential means of converting solar energy into chemical energy in the form of H₂. We reported that RuO₂-loaded TaON is an effective photocatalyst for O₂ evolution to achieve Z-scheme overall water splitting by combining with Pt-loaded TaON as a H₂ evolution photocatalyst using an IO₃⁻/I⁻ shuttle redox mediator.^[1] However, the detailed analysis for RuO₂ loaded on TaON had not been done.

In this study, the structure of Ru species on the TaON surface was investigated by XAFS in an attempt to determine the relationship between the catalyst's structure and its photocatalytic activity for O₂ evolution from a NaIO₃ solution under visible light ($\lambda > 420$ nm).^[2]

Experiments

Ru species as cocatalysts were loaded onto TaON by an impregnation method using (NH₄)₂RuCl₆ as a precursor. The impregnated samples were heat-treated in air for 1 h at 523–723 K. The amount of Ru loading was 0.5 wt%.

XAFS of the Ru-K edge was measured at the NW10A beamline. Appropriate amounts of the samples were packed in polyethylene packs. Using the packs, XAFS was recorded in fluorescent mode at ring energy of 2.5 GeV and stored current 60–40 mA.

Results and Discussion

Figure 1 shows the time courses of O₂ evolution on Ru-impregnated samples calcined at different temperatures. All tested samples produced a measurable amount of O₂ under visible light, regardless of calcination temperature. However, the activity increased with calcination temperature to a maximum at 623 K, beyond which it began to drop significantly.

Figure 2 shows the Fourier transforms (FT) of the *k*³-weighted Ru–K edge EXAFS spectra for the same samples. The samples calcined below 573 K exhibit a peak assigned to the Ru–Cl shell at ca. 2 Å, in addition to a peak appearing at ca. 1.5 Å that is assignable to the first Ru–O shell configuration. This indicates that the structure of (NH₄)₂RuCl₆ is partially preserved upon calcination below 573 K. However, the characteristic peak weakens with increasing calcination temperature, and is almost undetectable at 623 K, in good agreement with the change

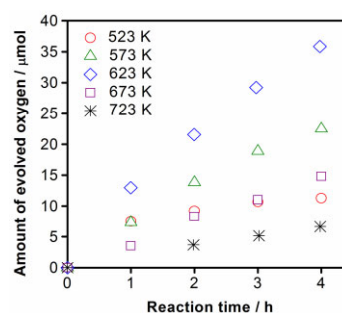


Figure 1. Time courses of O₂ evolution over (NH₄)₂RuCl₆-impregnated TaON calcined at various temperatures. Reaction conditions: catalyst, 50 mg; aqueous NaIO₃ solution, 100 mL (1.0 mM); light source, xenon lamp (300 W) fitted with a cold mirror (CM-1) and a cutoff filter (L42); reaction vessel, Pyrex top-irradiation type; irradiation wavelength, 420 λ <math>< 800</math> nm.

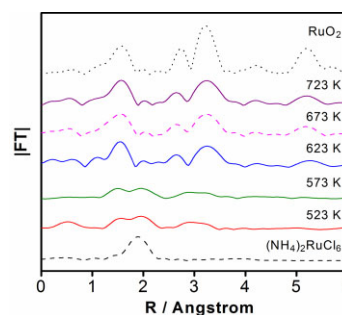


Figure 2. Fourier transforms of *k*³-weighted Ru–K edge EXAFS spectra for (NH₄)₂RuCl₆-impregnated TaON calcined at various temperatures.

in the Ru–K edge XANES spectra (not shown here). In addition, the peaks due to higher shell configuration gradually become stronger with increasing calcination temperature, suggesting that the particle size of RuO₂ increased upon calcination, consistent with the result of SEM observations which were separately done.

It was thus demonstrated that RuO₂ nanoparticles with an optimal distribution, as determined by the preparation conditions, are important for the promotion of O₂ evolution by TaON from an aqueous NaIO₃ solution.

References

- [1] M. Higashi et al., Chem. Lett. 37, 138 (2008).
 - [2] K. Maeda et al., J. Phys. Chem. C 115, 3057 (2011).
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