

## Effect of the valence state of Rh in Rh/Cr<sub>2</sub>O<sub>3</sub> (core/shell) cocatalyst with GaN:ZnO solid solution on activity for visible-light water splitting

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### Introduction

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 H<sub>2</sub>. It is necessary to modify a photocatalyst with a H<sub>2</sub> evolution cocatalyst such as Rh/Cr<sub>2</sub>O<sub>3</sub> (core/shell) nanoparticles (NPs) to achieve water splitting with reasonable rates.<sup>[1]</sup>

In these core/shell cocatalysts, the physicochemical state of the core seems to be important, because the core loaded directly on a photocatalyst induces photogenerated electrons from the conduction band of the photocatalyst and hosts active sites for H<sub>2</sub> evolution. XAFS is a suitable method to study relationship between structure and activity of nanoparticulate cocatalysts.<sup>[1b]</sup> The purpose of this study is to clarify the effect of the valence state of Rh in Rh/Cr<sub>2</sub>O<sub>3</sub> (core/shell) NPs with GaN:ZnO on activity for water splitting using XAFS.

### Experiments

Modification of GaN:ZnO with Rh NPs to form the core was carried out by an impregnation method using Rh(NO<sub>3</sub>)<sub>3</sub> as the precursor.<sup>[2]</sup> The Rh-species impregnated sample was then subject to heating either in H<sub>2</sub> at 523 K for 2 h or in air at 623 K for 1 h. Cr<sub>2</sub>O<sub>3</sub> shell was formed over the Rh NPs by a photodeposition method, yielding Rh/Cr<sub>2</sub>O<sub>3</sub> core/shell-structured NPs.<sup>[1]</sup>

XAFS of the Rh-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

Table 1 lists photocatalytic water splitting activity of Cr<sub>2</sub>O<sub>3</sub>/Rh/GaN:ZnO under visible light ( $\lambda > 400$  nm). The activity increased with increasing Rh loading to 0.25 wt%, beyond which it began to decline by further loading. Scanning electron microscopy observation revealed that the density of the introduced Rh NPs on the GaN:ZnO surface increased with increasing Rh loading. The abrupt increase in activity with Rh loading from 0 to 0.25 wt% was therefore attributed to an increase in the density of active sites for H<sub>2</sub> evolution. On the other hand, the decrease in activity at higher Rh loadings is probably related to excess coverage of the Rh NPs deposited on GaN:ZnO. Such excess loading can cause an inner-filter effect, contributing to a decrease in activity.

It is noted that the sample prepared by air-calcination shows lower activity (entry 6) than the H<sub>2</sub>-reduced sample (entry 5). As shown in Figure 1, XANES analysis

indicated that the H<sub>2</sub>-reduced sample was less oxidized than the air-calcined sample that was similar to the Rh<sub>2</sub>O<sub>3</sub> reference. Although the valence state of Rh in the H<sub>2</sub>-reduced sample is dissimilar to that in Rh foil reference, these results indicate that metallic Rh is a better cocatalyst (core) for H<sub>2</sub> evolution than the oxidized state.

Table 1. Photocatalytic activity of Cr<sub>2</sub>O<sub>3</sub>/Rh/GaN:ZnO for overall water splitting under visible irradiation ( $\lambda > 400$  nm)<sup>[a]</sup>

Entry	Loading method	Loaded Rh / wt%	Activity / $\mu\text{mol h}^{-1}$	
			H <sub>2</sub>	O <sub>2</sub>
1	Imp. → H <sub>2</sub> -reduction	0	0	0
2	Imp. → H <sub>2</sub> -reduction	0.1	17	7.9
3	Imp. → H <sub>2</sub> -reduction	0.25	149	72
4	Imp. → H <sub>2</sub> -reduction	0.5	115	56
5	Imp. → H <sub>2</sub> -reduction	1.0	91	45
6	Imp. → Air-calcination	1.0	70	36

[a] Reaction conditions: catalyst, 0.15 g; distilled water, 370–400 mL; light source, high-pressure mercury lamp (450 W) via aqueous NaNO<sub>2</sub> solution filter to cut ultraviolet light; reaction vessel, Pyrex inner-irradiation type.

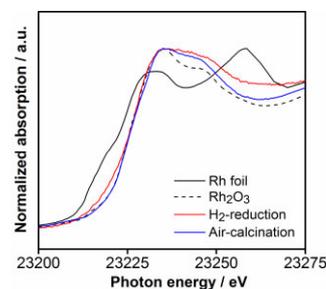


Figure 1. Rh-K edge XANES spectra for Cr<sub>2</sub>O<sub>3</sub>/Rh/GaN:ZnO. Rh was loaded by impregnation, followed by heating either in H<sub>2</sub> (20 kPa) at 523 K for 2 h or in air at 623 K for 1 h.

Our recent study also showed that highly dispersed Rh core NPs give higher water splitting activity.<sup>[3]</sup> Based on these findings, we are now developing a method to prepare metallic Rh NPs on GaN:ZnO with high dispersion.

### References

- [1] (a) K. Maeda et al., *Angew. Chem., Int. Ed.* 45, 7806 (2006). (b) K. Maeda et al., *J. Phys. Chem. C* 111, 7554 (2007).
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