

# Water splitting under visible light irradiation using a GaN:ZnO with Cr<sub>2</sub>O<sub>3</sub> shell/Pb<sub>2</sub>Ru<sub>2</sub>O<sub>7-δ</sub> core as a co-catalyst

Shinya HANYU<sup>\*1 †</sup> Hidenobu SHIROISHI<sup>\*2 ‡</sup>  
 Morihiro SAITO<sup>\*3</sup> Yumi TANAKA<sup>\*4</sup>

## Abstract

Visible-light-driven water photolysis was investigated using a Cr<sub>2</sub>O<sub>3</sub>-shell/Pb<sub>2</sub>Ru<sub>2</sub>O<sub>7-δ</sub>-core co-catalyst supported on GaN:ZnO. Energy-dispersive X-ray spectroscopy mapping analysis suggested that the Pb<sub>2</sub>Ru<sub>2</sub>O<sub>7-δ</sub> and Cr<sub>2</sub>O<sub>3</sub> were uniformly dispersed on the GaN:ZnO. Photocatalytic water splitting with the catalysts was performed under visible-light irradiation. Almost stoichiometric amounts of evolved H<sub>2</sub> and O<sub>2</sub> were confirmed using the Cr<sub>2</sub>O<sub>3</sub>/Pb<sub>2</sub>Ru<sub>2</sub>O<sub>7-δ</sub>/GaN:ZnO catalyst, whereas no gas was evolved when bare GaN:ZnO was used as the catalyst. The amounts of H<sub>2</sub> and O<sub>2</sub> increased with increasing Cr<sub>2</sub>O<sub>3</sub> loadings, which suggests that the recombination between H<sub>2</sub> and O<sub>2</sub> was suppressed by Cr<sub>2</sub>O<sub>3</sub> on Pb<sub>2</sub>Ru<sub>2</sub>O<sub>7-δ</sub>.

**Keywords:** photocatalytic water splitting, GaN:ZnO catalyst, Cr<sub>2</sub>O<sub>3</sub> shell/Pb<sub>2</sub>Ru<sub>2</sub>O<sub>7-δ</sub> core co-catalyst

## 1. Introduction

Sunlight is expected to be used as a future energy source to replace fossil fuels because it irradiates the earth permanently. Water splitting using a visible-light-driven photocatalyst is one way to convert sunlight energy into chemical energy in the form of H<sub>2</sub><sup>(1)</sup>. In 2005, Domen *et al.* reported that a GaN:ZnO semiconductor photocatalyst with RuO<sub>2</sub> as a co-catalyst decomposes water molecules to generate stoichiometric H<sub>2</sub> and O<sub>2</sub><sup>(2)</sup>. To improve the activity of water photolysis, researchers subsequently used Cr<sub>2</sub>O<sub>3</sub>/Rh shell-core or Rh<sub>2-γ</sub>Cr<sub>γ</sub>O<sub>3</sub> as a co-catalyst; these catalysts suppress the H<sub>2</sub>-O<sub>2</sub> recombination reaction<sup>(3)</sup>. However, because precious metals such as Rh are very expensive for practical use, the development of alternative co-catalysts based on inexpensive metals is necessary.

We reported that pyrochlore-type oxides, e.g., A<sub>2</sub>Ru<sub>2</sub>O<sub>7-δ</sub>, (A: Pr, Nd, Sm, Gd, Dy, Yb, Pb) have high catalytic activities both for proton reduction in a Ru(bpy)<sub>3</sub><sup>2+</sup>/methylviologen/catalyst/EDTA system and for water oxidation in a Ru(bpy)<sub>3</sub><sup>2+</sup>/catalyst/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system<sup>(4)</sup>. However, supporting the oxide materials over the semiconductor for overall water splitting is difficult.

In this paper, we report the synthesis of two types of GaN:ZnO photocatalysts loaded with Pb<sub>2</sub>Ru<sub>2</sub>O<sub>7-δ</sub> co-catalyst and Cr<sub>2</sub>O<sub>3</sub>-shell/Pb<sub>2</sub>Ru<sub>2</sub>O<sub>7-δ</sub>-core co-catalyst. The dependence of the amount of H<sub>2</sub> and O<sub>2</sub> evolved on the Cr<sub>2</sub>O<sub>3</sub> loading is investigated by water-splitting experiments using visible-light irradiation.

## 2. Experimental

A GaN:ZnO photocatalyst was prepared according to the method reported in the literature<sup>(2)</sup>. Here 1.08 g of Ga<sub>2</sub>O<sub>3</sub> (Kishida Chemical Co., Ltd) and 0.94 g of ZnO (Wako Chemical Industry Co., Ltd.) were mixed and then heated under flowing NH<sub>3</sub> (200 mL min<sup>-1</sup>) at 1098 K for 14 h. The obtained powder

was then subjected to post-calcination in a static air atmosphere at 873 K for 5 h.

Pb<sub>2</sub>Ru<sub>2</sub>O<sub>7-δ</sub> co-catalyst was loaded onto the surface of the GaN:ZnO photocatalyst using the following procedure: A stoichiometric amount of aqueous solutions of 1.2 × 10<sup>-3</sup> M K<sub>2</sub>RuO<sub>4</sub> and 1.2 × 10<sup>-3</sup> M Pb<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> were mixed with stirring for various times (0, 1, 10, and 60 min) to form the crystal core of Pb<sub>2</sub>Ru<sub>2</sub>O<sub>7-δ</sub>, and the GaN:ZnO photocatalyst was added to the solution. After 24 h of stirring, a precipitate was collected by centrifugation and washed by decantation with Milli-Q® water, followed by drying at 60°C in a vacuum oven for 14 h. The obtained photocatalyst was heat-treated under air at 500°C for 1 h. Assuming that the yield of Pb<sub>2</sub>Ru<sub>2</sub>O<sub>7-δ</sub> on the catalyst was 100%, the loading amount of the co-catalyst was 5 wt%.

The Cr<sub>2</sub>O<sub>3</sub> shell was deposited by a photodeposition method<sup>(3,6)</sup> as follows: Pb<sub>2</sub>Ru<sub>2</sub>O<sub>7-δ</sub>/GaN:ZnO was added to 20% K<sub>2</sub>CrO<sub>4</sub> methanol solution and irradiated under a 100 W mercury lamp (HB100A-1, Sen Light Corp). After the photodeposition, the photocatalyst was collected by centrifugation, washed by decantation with Milli-Q® water, and vacuum-dried at 60°C. The prepared samples were characterized by X-ray diffraction (XRD; D8 ADVANCE, Bruker), field-emission scanning electron microscopy (FE-SEM) with energy-dispersive X-ray spectroscopy (EDX) (FE-SEM: Quanta 250 FEG, FEI; EDX: INCA Energy 250 x-act, Oxford Instruments).

A 12.5 mg of prepared photocatalyst powder was suspended in 30 mL of H<sub>2</sub>SO<sub>4</sub> solution (pH 4.5). After Ar gas was bubbled through the suspension for 30 min, photocatalytic reactions were conducted by visible-light irradiation with four LED lights (Yamazen, MLZ-3; total irradiation area: 10.2 cm<sup>2</sup>; average light intensity: 0.420 kW m<sup>-2</sup>) from four directions with stirring. After 24 h, the amounts of evolved H<sub>2</sub> and O<sub>2</sub> were analyzed by gas chromatography (GC-8A, Shimadzu).

## 3. Results and Discussion

Fig. 1 shows the XRD patterns of the Pb<sub>2</sub>Ru<sub>2</sub>O<sub>7-δ</sub>/GaN:ZnO photocatalyst synthesized at various aging times for the crystal core formation. Focusing on the XRD peaks of the co-catalyst, the Pb<sub>2</sub>Ru<sub>2</sub>O<sub>7-δ</sub> phase was confirmed to be the only phase present in the patterns of the samples aged for 10 and 60 min, whereas both of RuO<sub>2</sub> and Pb<sub>2</sub>Ru<sub>2</sub>O<sub>7-δ</sub> phases and only the RuO<sub>2</sub> phase were observed for the unaged sample and the sample aged for only 1 min, respectively. These results indicate the

<sup>\*1</sup> National Institute of Technology, Tokyo College

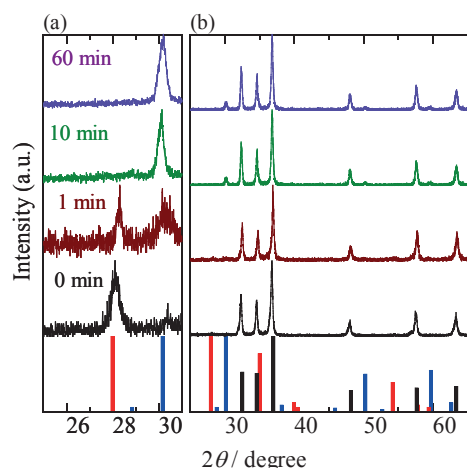
<sup>†</sup> Present Address: Yamanashi University

<sup>\*2</sup> Associate Professor, National Institute of Technology, Tokyo College (1220-2 Kunugida, Hachioji city, Tokyo, JAPAN, 193-0997) <sup>‡</sup>e-mail: h-shiroishi@tokyo-ct.ac.jp

<sup>\*3</sup> Tokyo University of Agriculture and Technology

<sup>\*4</sup> Tokyo University of Science

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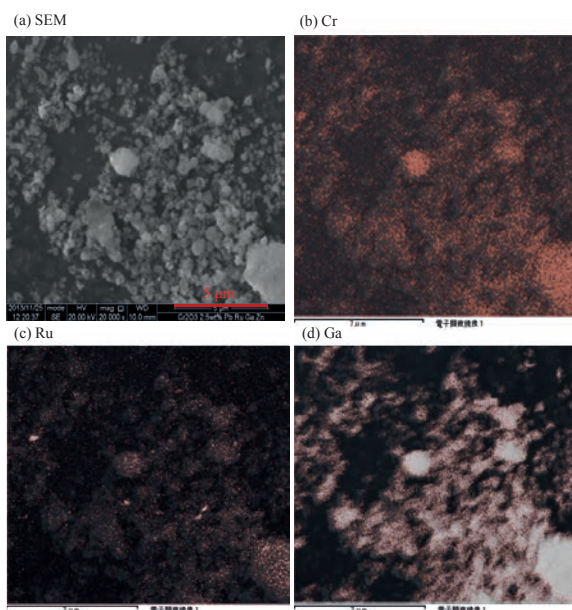


**Fig. 1.** XRD patterns of  $\text{Pb}_2\text{Ru}_2\text{O}_{7-\delta}/\text{GaN:ZnO}$  photocatalysts synthesized at various aging times for the core formation of crystalline  $\text{Pb}_2\text{Ru}_2\text{O}_{7-\delta}$ , together with the reference patterns for —  $\text{RuO}_2$  (#PDS:040-1290), —  $\text{Pb}_2\text{Ru}_2\text{O}_{7-\delta}$  (#PDS:34-0471), and —  $\text{GaN:ZnO}$ : (a) magnified and (b) all patterns.

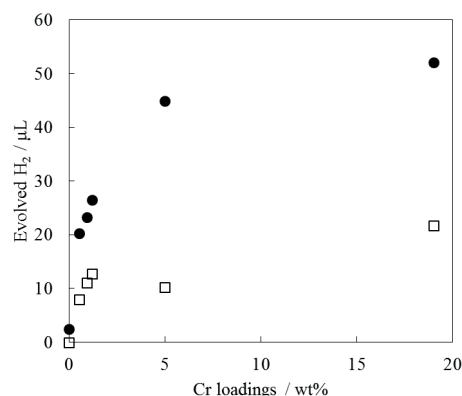
necessity of sufficient aging (longer than 10 min) of the  $\text{K}_2\text{RuO}_4/\text{Pb}_2(\text{NO}_3)_2$  aqueous solution before the addition of  $\text{GaN:ZnO}$  powders for the formation of a single-phased  $\text{Pb}_2\text{Ru}_2\text{O}_{7-\delta}$  core on the  $\text{GaN:ZnO}$  surfaces.

Fig. 2 shows the FE-SEM and EDX elemental mapping images for the catalyst after fabrication of the  $\text{Cr}_2\text{O}_3$  shell. The average particle size of the catalysts was estimated to be  $350 \pm 110$  nm. The distributions of Cr and Ru atoms were approximately consistent with that of Ga atoms, suggesting that  $\text{Pb}_2\text{Ru}_2\text{O}_{7-\delta}$  and  $\text{Cr}_2\text{O}_3$  were supported on  $\text{GaN:ZnO}$ .

Fig. 3 shows the amounts of  $\text{H}_2$  and  $\text{O}_2$  evolved on the series of  $\text{Cr}_2\text{O}_3/\text{Pb}_2\text{Ru}_2\text{O}_{7-\delta}/\text{GaN:ZnO}$  catalysts with various Cr loadings; visible light was irradiated for 24 h. The ratio of evolved  $\text{H}_2$  and  $\text{O}_2$  using  $\text{Cr}_2\text{O}_3/\text{Pb}_2\text{Ru}_2\text{O}_{7-\delta}/\text{GaN:ZnO}$  at Cr loadings greater than 0.36% was close to the stoichiometric value, whereas a small amount of  $\text{H}_2$  and no gas evolution were



**Fig. 2.** (a) FE-SEM image and EDX mapping images of (b) Cr, (c) Ru, and (d) Ga for the  $\text{Cr}_2\text{O}_3/\text{Pb}_2\text{Ru}_2\text{O}_{7-\delta}/\text{GaN:ZnO}$ .



**Fig. 3.** Relationship between Cr loadings and evolved  $\text{H}_2$  (●) and  $\text{O}_2$  (□) after 24 h of light irradiation. Reaction conditions: 12.5 mg photocatalyst, 30 mL pH 4.5  $\text{H}_2\text{SO}_4$  solution.

observed with  $\text{Pb}_2\text{Ru}_2\text{O}_{7-\delta}/\text{GaN:ZnO}$  and  $\text{GaN:ZnO}$ , respectively. The amounts of  $\text{H}_2$  and  $\text{O}_2$  increased with increasing loading amount of  $\text{Cr}_2\text{O}_3$  on the  $\text{GaN:ZnO}$  up to 19 wt% of Cr. This result implies that the  $\text{Cr}_2\text{O}_3$  shell also prevents recombination between evolved  $\text{H}_2$  and  $\text{O}_2$  <sup>(7)</sup>.

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