

Water splitting under visible light irradiation using a GaN:ZnO with Cr_2O_3 shell/Pb₂Ru₂O_{7- δ} core as a co-catalyst

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Abstract

Visible-light-driven water photolysis was investigated using a Cr_2O_3 -shell/Pb₂Ru₂O_{7- δ}-core co-catalyst supported on GaN:ZnO. Energy-dispersive X-ray spectroscopy mapping analysis suggested that the Pb₂Ru₂O_{7- δ} and Cr₂O₃ were uniformly dispersed on the GaN:ZnO. Photocatalytic water splitting with the catalysts was performed under visible-light irradiation. Almost stoichiometric amounts of evolved H₂ and O₂ were confirmed using the Cr₂O₃/Pb₂Ru₂O_{7- δ}/GaN:ZnO catalyst, whereas no gas was evolved when bare GaN:ZnO was used as the catalyst. The amounts of H₂ and O₂ increased with increasing Cr₂O₃ loadings, which suggests that the recombination between H₂ and O₂ was suppressed by Cr₂O₃ on Pb₂Ru₂O_{7- δ}.

Keywords: photocatalytic water splitting, GaN:ZnO catalyst, Cr2O3 shell/Pb2Ru2O7-6 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 $H_2^{(1)}$. In 2005, Domen *et al.* reported that a GaN:ZnO semiconductor photocatalyst with RuO₂ as a co-catalyst decomposes water molecules to generate stoichiometric H₂ and $O_2^{(2)}$. To improve the activity of water photolysis, researchers subsequently used Cr₂O₃/Rh shell–core or Rh_{2–y}Cr_yO₃ as a co-catalyst; these catalysts suppress the H₂–O₂ recombination reaction⁽³⁾. 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., $A_2Ru_2O_{7-\delta}$, (A: Pr, Nd, Sm, Gd, Dy, Yb, Pb) have high catalytic activities both for proton reduction in a Ru(bpy)₃²⁺/methylviologen/ catalyst/EDTA system and for water oxidation in a Ru(bpy)₃²⁺/ catalyst/K₂S₂O₈ system⁽⁴⁾. 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 Pb₂Ru₂O_{7- δ} co-catalyst and Cr₂O₃-shell/Pb₂Ru₂O_{7- δ}-core co-catalyst. The dependence of the amount of H₂ and O₂ evolved on the Cr₂O₃ 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⁽²⁾. Here 1.08 g of Ga₂O₃ (Kishida Chemical Co., Ltd) and 0.94 g of ZnO (Wako Chemical Industry Co., Ltd.) were mixed and then heated under flowing NH₃ (200 mL min⁻¹) at 1098 K for 14 h. The obtained powder

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

Pb₂Ru₂O_{7- δ} 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^{-3} M K₂RuO₄ and 1.2×10^{-3} M Pb₂(NO₃)₂ were mixed with stirring for various times (0, 1, 10, and 60 min) to form the crystal core of Pb₂Ru₂O_{7- δ}, 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 Pb₂Ru₂O_{7- δ} on the catalyst was 100%, the loading amount of the co-catalyst was 5 wt%.

The Cr₂O₃ shell was deposited by a photodeposition method^(3,6) as follows: Pb₂Ru₂O_{7- δ}/GaN:ZnO was added to 20% K₂CrO₄ 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 H₂SO₄ 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 cm²; average light intensity: 0.420 kW m⁻²) from four directions with stirring. After 24 h, the amounts of evolved H₂ and O₂ were analyzed by gas chromatography (GC-8A, Shimadzu).

3. Results and Discussion

Fig. 1 shows the XRD patterns of the $Pb_2Ru_2O_{7-\delta}/GaN:ZnO$ photocatalyst synthesized at various aging times for the crystal core formation. Focusing on the XRD peaks of the co-catalyst, the $Pb_2Ru_2O_{7-\delta}$ phase was confirmed to be the only phase present in the patterns of the samples aged for 10 and 60 min, whereas both of RuO₂ and $Pb_2Ru_2O_{7-\delta}$ phases and only the RuO₂ phase were observed for the unaged sample and the sample aged for only 1 min, respectively. These results indicate the

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Fig. 1. XRD patterns of Pb₂Ru₂O_{7- δ}/GaN:ZnO photocatalysts synthesized at various aging times for the core formation of crystalline Pb₂Ru₂O_{7- δ}, together with the reference patterns for —RuO₂ (#PDS:040-1290), —Pb₂Ru₂O_{7- δ} (#PDS:34-0471), and —GaN:ZnO: (a) magnified and (b) all patterns.

necessity of sufficient aging (longer than 10 min) of the $K_2RuO_4/Pb_2(NO_3)_2$ aqueous solution before the addition of GaN:ZnO powders for the formation of a single-phased Pb₂Ru₂O_{7- δ} core on the GaN:ZnO surfaces.

Fig. 2 shows the FE-SEM and EDX elemental mapping images for the catalyst after fabrication of the Cr₂O₃ shell. The average particle size of the catalysts was estimated to be 350 ± 110 nm. The distributions of Cr and Ru atoms were approximately consistent with that of Ga atoms, suggesting that Pb₂Ru₂O_{7- δ} and Cr₂O₃ were supported on GaN:ZnO.

Fig. 3 shows the amounts of H₂ and O₂ evolved on the series of $Cr_2O_3/Pb_2Ru_2O_{7-\delta}/GaN:ZnO$ catalysts with various Cr loadings; visible light was irradiated for 24 h. The ratio of evolved H₂ and O₂ using $Cr_2O_3/Pb_2Ru_2O_{7-\delta}/GaN:ZnO$ at Cr loadings greater than 0.36% was close to the stoichiometric value, whereas a small amount of H₂ 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 Cr₂O₃/Pb₂Ru₂O_{7-δ}/GaN:ZnO.



Fig. 3. Relationship between Cr loadings and evolved $H_2(\bullet)$ and $O_2(\Box)$ after 24 h of light irradiation. Reaction conditions: 12.5 mg photocatalyst, 30 mL pH 4.5 H₂SO₄ solution.

observed with $Pb_2Ru_2O_{7-\delta}/GaN:ZnO$ and GaN:ZnO, respectively. The amounts of H_2 and O_2 increased with increasing loading amount of Cr_2O_3 on the GaN:ZnO up to 19 wt% of Cr. This result implies that the Cr_2O_3 shell also prevents recombination between evolved H_2 and O_2 ⁽⁷⁾.

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