

Photocatalytic Water Splitting Using Modified GaN:ZnO Solid Solution under Visible Light: Long-Time Operation and Regeneration of Activity

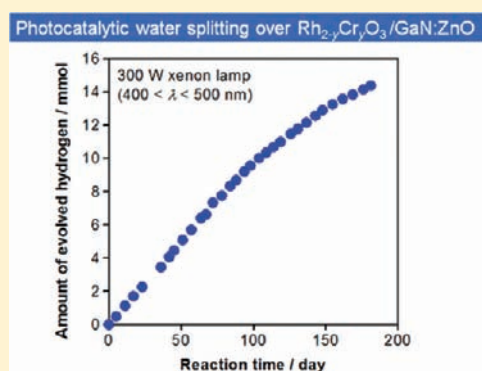
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S Supporting Information

ABSTRACT: Overall water splitting using GaN:ZnO solid solution photocatalyst modified with Rh_{2-y}Cr_yO₃ nanoparticles as H₂ evolution cocatalysts under visible light (400 < λ < 500 nm) was examined with respect to long-term durability and regeneration of photocatalytic activity. The rate of visible light water splitting remained unchanged for 3 months (2160 h), producing H₂ and O₂ continuously at a stoichiometric amount. After 6 months of operation, a 50% loss of the initial activity occurred. Regeneration treatment of deactivated catalysts was attempted by reloading the Rh_{2-y}Cr_yO₃ cocatalyst. The degree of activity regeneration depended on the reloading amount. Up to 80% of the initial activity for H₂ evolution could be recovered under optimal treatment conditions. It was also found that deactivation of GaN:ZnO was suppressed to some extent by prior coloaded of an O₂ evolution cocatalyst, which helped to suppress oxidative decomposition of GaN:ZnO by valence band holes, thereby improving the durability.



1. INTRODUCTION

Photocatalytic water splitting using semiconductor particles has been regarded as one of the most promising means of H₂ production from renewable resources.¹ Many metal oxides have been reported to function as highly active photocatalysts for overall water splitting under UV irradiation ($\lambda < 400$ nm).^{1d} Recent advances in research and development have made visible-light water splitting possible at a measurable reaction rate, which had once been described as a “Holey Grail” in chemistry.^{1b}

These advances have relied exclusively on development of a new photocatalytic material and improvement of performance. Practical applications require not only that the preparation method be refined but that the end product also has long-term durability. Kato et al. demonstrated that overall water splitting using NiO-loaded NaTaO₃ doped with La, which exhibits an apparent quantum yield of 56% at 270 nm, proceeds steadily for longer than 16 days without noticeable degradation.² However, there is no example of photocatalytic overall water splitting in the time scale of months under UV irradiation let alone visible light. Regeneration of the deactivated photocatalyst is also important for photocatalyst stability, but there are only a few studies on this topic.³

Our group has developed solid solutions of GaN and ZnO (denoted as GaN:ZnO) as visible-light-driven photocatalysts for overall water splitting.^{4–9} Upon modification by suitable cocatalysts, GaN:ZnO becomes active for the reaction.^{5–7}

Therefore, research on GaN:ZnO for water splitting has focused on development of an efficient cocatalyst as well as refinement of the preparation conditions for GaN:ZnO to minimize recombination between electrons and holes. Among the cocatalysts examined, Rh_{2-y}Cr_yO₃ exhibits the best performance with stable water splitting behavior for 3 days.^{5c} However, the long-term durability and regeneration of activity for this material have yet to be investigated.

In this study, we conducted visible-light-driven overall water splitting using GaN:ZnO modified with Rh_{2-y}Cr_yO₃ for a time span of 0.5 years. The photocatalytic system was stable for longer than 3 months. Strategies to suppress deactivation and regenerate activity are also discussed.

2. EXPERIMENTAL SECTION

2.1. Preparation of Catalysts. GaN:ZnO solid solution was prepared by a method reported in the literature.⁴ Briefly, a powder mixture of 0.94 g of ZnO (99%, Kanto Chemicals) and 1.08 g of Ga₂O₃ (99.9%, High Purity Chemicals) was heated at 1098 K for 18 h under a NH₃ flow (250 mL·min⁻¹). After nitridation, the sample was cooled to room temperature under NH₃ flow.

The as-prepared GaN:ZnO catalyst was modified with Rh_{2-y}Cr_yO₃ as a cocatalyst for H₂ evolution according to a method described elsewhere.⁵ Briefly, 0.3–0.4 g of GaN-ZnO powder and 3–4 mL of distilled water containing appropriate amounts of Na₃RhCl₆·12H₂O

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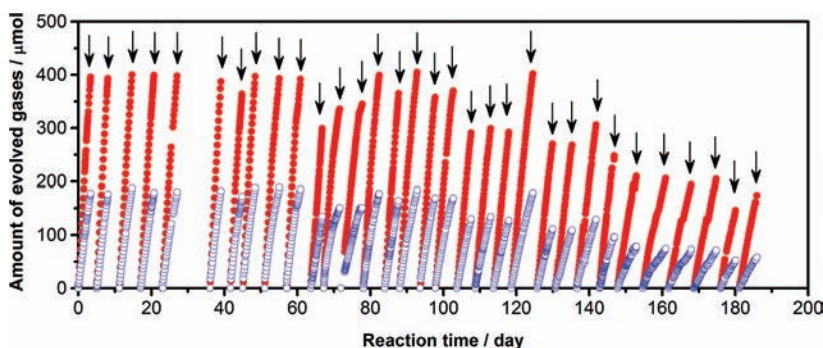


Figure 1. Time course of overall water splitting using $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3/\text{GaN}:\text{ZnO}$ under visible light. Reaction conditions: catalyst, 0.2 g; aqueous H_2SO_4 solution (pH 4.5), 200 mL; light source, xenon lamp (300 W) fitted with a cold mirror (CM-2) and a cutoff filter (L40); reaction vessel, Pyrex top-irradiation type; irradiation wavelength, $400 < \lambda < 500$ nm. Red circles, H_2 ; blue circles, O_2 . Reaction was conducted for a total of 180 days in a closed gas circulation system, which was evacuated several times (as indicated by arrows) to remove the accumulated gases.

(99.9%, Mitsuwa Chemicals) and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.9%, Wako Pure Chemicals) were placed into an evaporating dish over a water bath. The suspension was stirred using a glass rod to complete evaporation, and the resulting powder was collected and heated in air at 623 K for 1 h to convert the rhodium and chromium species to $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$. Rhodium and chromium were loaded at a rate of 2.5 and 2 wt % (metallic content).

Regeneration treatment of deactivated catalysts was attempted by reloading the $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ cocatalyst. The experimental procedure was essentially the same as that described above but with different amounts of $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$.

When a double-cocatalyst system is to be employed for simultaneous water reduction and water oxidation, the typical cocatalysts of choice are, respectively, core/shell-structured $\text{Rh}/\text{Cr}_2\text{O}_3$ and RuO_2 . First, 0.05 wt % RuO_2 was loaded onto $\text{GaN}:\text{ZnO}$ by an impregnation method using RuCl_3 as a precursor, followed by calcination in air at 623 K for 1 h. Then, Rh (2.5 wt %) was photodeposited onto $\text{RuO}_2/\text{GaN}:\text{ZnO}$ using $\text{Na}_3\text{RhCl}_6 \cdot 12\text{H}_2\text{O}$ as the precursor, followed by Cr_2O_3 deposition from a K_2CrO_4 solution (containing 2.0 wt % Cr) according to a method we developed previously.⁶

2.2. Characterization of Catalysts. The prepared samples were studied by powder X-ray diffraction (XRD; RINT-UltimaIII, Rigaku; $\text{Cu K}\alpha$), X-ray photoelectron spectroscopy (XPS; JPS-9000, JEOL), scanning electron microscopy (SEM; S-4700, Hitachi), and transmission electron microscopy with a FEI Tecnai G2 F20 microscope (operating at 200 kV) and a copper grid sample holder. The binding energies determined by XPS were corrected by reference to the $\text{Au}4f_{7/2}$ peak (83.8 eV) for each sample. Elemental analyses (Rh , Cr , Ga , and Zn) were performed by inductively coupled plasma (ICP) mass spectroscopy (HP-4500; Hewlett-Packard).

2.3. Photocatalytic Reactions. Long-time reactions (6 months) were carried out in a Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system at room temperature. Overall water splitting was studied using an aqueous H_2SO_4 solution (pH 4.5, 200 mL) containing 0.2 g of the $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3/\text{GaN}:\text{ZnO}$ powder. The peak catalytic performance of this material for overall water splitting has previously been shown to occur at pH 4.5.^{5c} Reactant solutions were evacuated several times to completely remove any air prior to irradiation under a 300 W xenon lamp fitted with a cutoff filter and a water filter ($400 < \lambda < 500$ nm). The reaction started without mechanical stirring after the catalyst powder formed a sediment on the bottom of the reaction cell. The reactant solution was maintained at room temperature by a water bath during the reaction. The evolved gases were analyzed by gas chromatography. The light intensity of the xenon lamp was measured regularly, and the activity was corrected with respect to the final light intensity.

The apparent quantum yield (AQY) for water splitting was measured using the same experimental setup and estimated as

$$\text{AQY}(\%) = (A \times R/I) \times 100 \quad (1)$$

where A , R , and I represent coefficients based on the reactions (H_2 evolution, 2; O_2 evolution, 4), the H_2 or O_2 evolution rate, and the rate of incident photons, respectively. The total number of incident photons (5×10^{21} photons $\cdot\text{h}^{-1}$, $400 < \lambda < 500$ nm) at the initial stage of the long-term reaction was measured using a calibrated silicon photodiode.

The overall water splitting reaction was also conducted in a Pyrex inner-irradiation reaction vessel under a 450 W high-pressure Hg lamp (USHIO, UM-452) and static air atmosphere. A magnetic stirrer was used to disperse 0.3 g of the cocatalyst-loaded sample in an aqueous H_2SO_4 solution (pH 4.5, 400 mL) or distilled water (pH 6.2, 400 mL). The solution was irradiated using the 450 W high-pressure Hg lamp (USHIO, UM-452) ($\lambda > 300$ nm), which was equipped with a water-cooling jacket (~ 303 K), without initial degassing. For visible light irradiation ($\lambda > 400$ nm), a Pyrex tube filled with aqueous NaNO_2 solution (2 M) was inserted between the lamp and the sample to block UV light. The evolved gases were quantified by volumetric measurement.

3. RESULTS AND DISCUSSION

3.1. Long-Time Reaction Performance. Figure 1 shows the time course of water splitting with $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3/\text{GaN}:\text{ZnO}$ under visible light without stirring the reactant solution. The reaction system was evacuated regularly with adjustment of the pH to 4.5 using H_2SO_4 . Because the incident light intensity gradually decreased with irradiation time in the time scale of months, the amount of gases produced was corrected with respect to the final light intensity (4×10^{21} photons $\cdot\text{h}^{-1}$). The total H_2 evolution in overall water splitting is plotted as a function of time in Figure 2. Both H_2 and O_2 evolved stoichiometrically and steadily for longer than 90 days with an

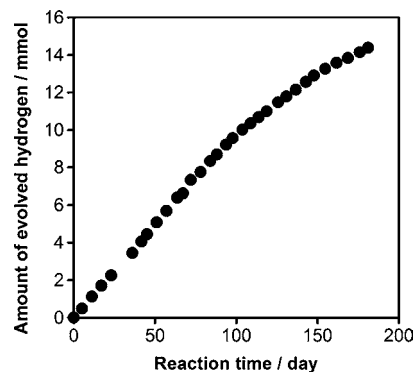


Figure 2. Total H_2 evolution as a function of time. Data corresponds to Figure 1.

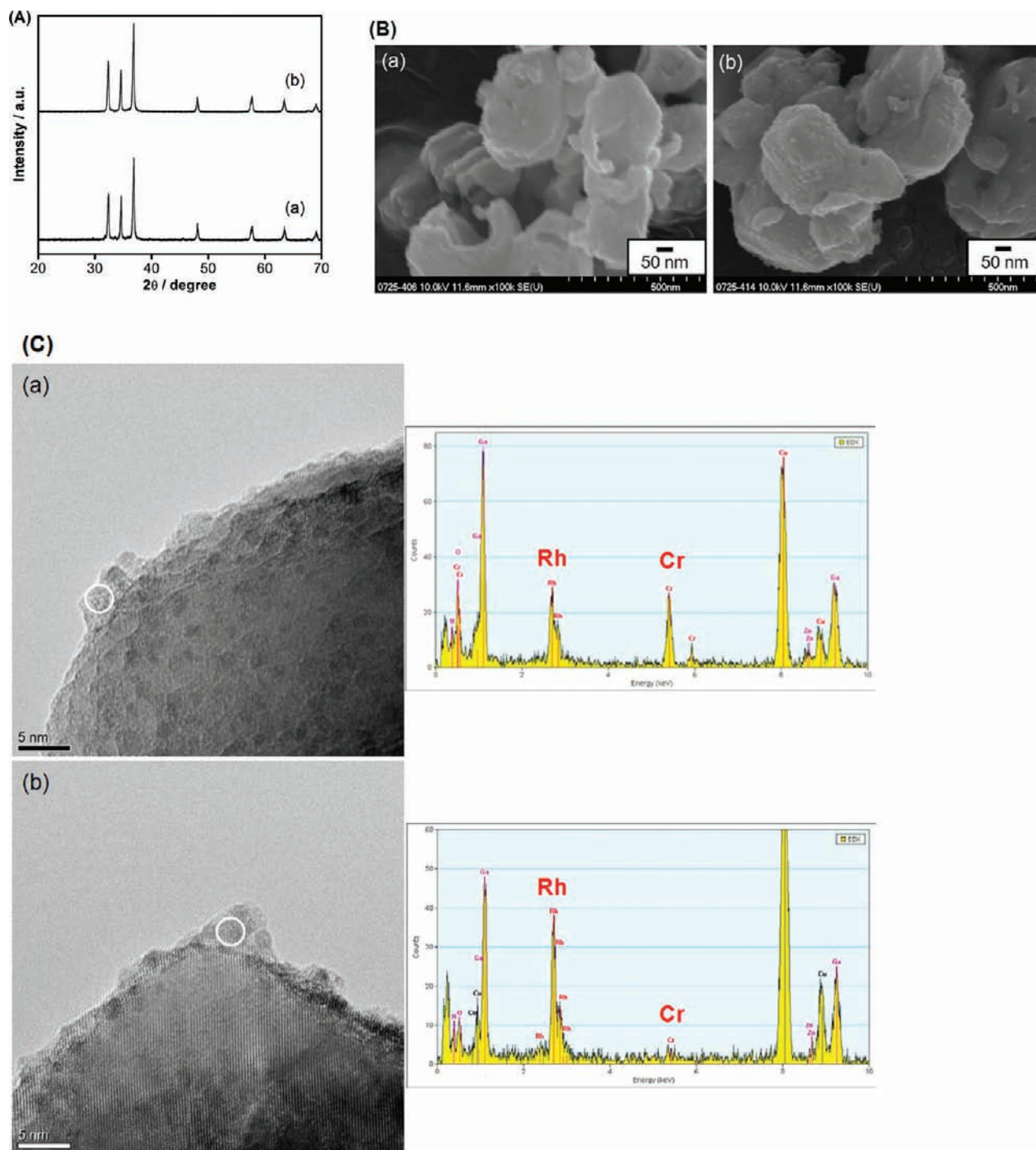


Figure 3. (A) XRD patterns, (B) SEM images, and (C) TEM and combined EDS analyses for catalysts (a) before and (b) after deactivation. White circles in TEM images indicate the spots where EDS analysis was performed. Characterization data shown here was acquired using the sample collected after 60 h of UV irradiation at pH 4.5 (Figure S1, Supporting Information).

apparent quantum yield of ca. 0.16% at 400–500 nm, after which the rates gradually began to drop. After 180 days of operation, 50% of the initial activity was retained. The total production of H₂ and O₂ gases far exceeded the amount of catalyst used (ca. 2.4 mmol), confirming the catalytic cycle with a turnover number, defined as the ratio of the product amount to the total catalyst mass, larger than at least 8. N₂ evolution, which has been sometimes observed in (oxy)nitride-type photocatalysts,^{1b} was negligible in the present case. When the reactant solution was stirred during the reaction, only 20% of

the initial activity was retained after 180 days of reaction. This means that mechanical stirring of the reactant solution contributes to the deactivation of photocatalytic activity, presumably by damaging the photocatalyst surface, although it does not have a significant impact on activity when the reaction time is relatively short (several days).^{5c}

Thus, it was found that Rh_{2-y}Cr_yO₃/GaN:ZnO showed good durability for several months of operation under visible light, as long as mechanical damage due to stirring of the reactant solution was avoided. Matsumura et al. reported that the

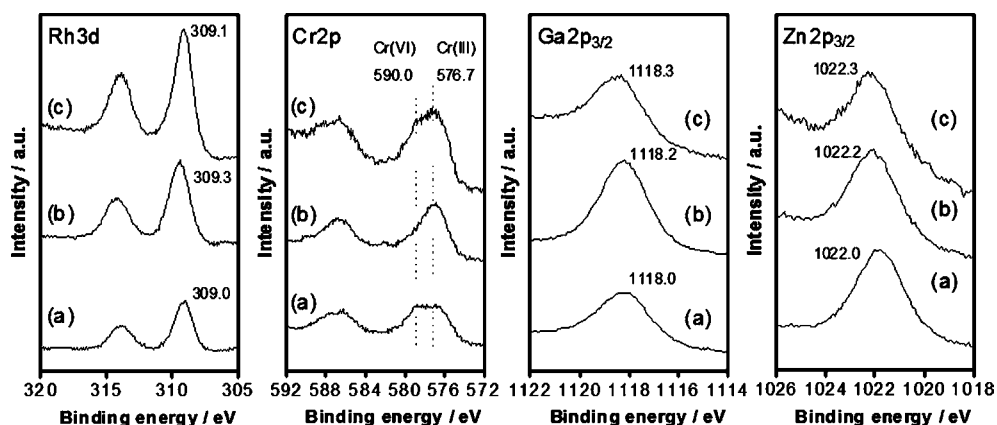


Figure 4. XPS spectra for Rh3d, Cr2p, Ga2p_{3/2}, and Zn2p_{3/2} of Rh_{2-y}Cr_yO₃/GaN:ZnO (a) before and (b) after deactivation (see Figure S1, Supporting Information). Spectrum c is of the deactivated sample after reloading Rh_{2-y}Cr_yO₃ under optimal conditions. Characterization data shown here was acquired using the sample collected after 60 h of UV irradiation at pH 4.5 (Figure S1, Supporting Information).

photocatalytic activity of Pt-loaded CdS was lowered by the damage caused by mechanical grinding, which increased the number of electron–hole recombination centers.¹⁰ The fact that the activity of Rh_{2-y}Cr_yO₃/GaN:ZnO decreased even without stirring indicates that the catalyst structure was damaged to some extent. In order to investigate the cause of the deactivation more effectively and to prepare a sufficient number of samples, we performed “accelerated deactivation”, which employed a high-pressure mercury lamp (450 W) and an inner irradiation-type reaction vessel, giving more intense light than the combination of a 300 W xenon lamp and a top irradiation-type vessel.¹¹ As shown in Figure S1, Supporting Information, 60 h of UV irradiation under continuous stirring in this manner produced ca. 2.5 L of H₂–O₂ mixture with more pronounced deactivation than that observed under xenon lamp irradiation (Figure 2).

3.2. Characterization of Catalysts before and after Deactivation. To determine the factors contributing to deactivation, the reacted catalysts were examined by XRD, SEM, TEM, EDS, and XPS. As shown in Figure 3A, the fresh catalyst and reacted catalyst both exhibited a single-phase diffraction pattern assigned to the hexagonal wurtzite structure, indicating that the original crystal structure was retained even after significant deactivation. However, the intensity of diffraction peaks derived from the *c* axis (i.e., (00*l*) reflections) decreased slightly upon accelerated deactivation, implying that some deactivation (e.g., surface corrosion) occurred on the *c* plane of GaN:ZnO. Although the particle morphology of Rh_{2-y}Cr_yO₃/GaN:ZnO remained largely unchanged (Figure 3B) and no noticeable change was observed in the interface between GaN:ZnO and the loaded Rh_{2-y}Cr_yO₃ (Figure 3C), TEM-EDS analysis indicated that the Cr component in most of the Rh_{2-y}Cr_yO₃ nanoparticles decreased after deactivation (Figure 3C). This is supported by the results of XPS analysis, as will be shown below.

The valence states of the constituent elements of the catalyst were investigated by XPS. We previously studied the change in the valence state of Rh_{2-y}Cr_yO₃/GaN:ZnO reacted for 3 days at various pH conditions, which showed that the Ga and Zn species in the catalyst underwent oxidation to a small extent, judging from the shift in the Ga2p_{3/2} and Zn2p_{3/2} peaks to higher binding energies with decreasing nitrogen concentration in the catalyst surface.^{5c} This strongly suggests that the Ga–N (and/or Zn–N) bond in the catalyst surface partially collapsed

upon reaction with a Ga–O (and/or Zn–O) bond generated as a result of photooxidation by holes and/or hydrolysis. As shown in Figure 4 and Table 1, the deactivated catalyst

Table 1. Surface Atomic Ratios of Rh_{2-y}Cr_yO₃/GaN:ZnO before and after Reaction

entry	catalyst sample	surface atomic ratios ^a			
		Zn/Ga	N/Ga	Rh/Ga	Cr/Ga
1	before reaction	0.29	1.69	0.10	0.17
2	after reaction	0.12	1.18	0.12	0.12
3	after reloading Rh,Cr(50%)	0.11	1.19	0.27	0.26

^aEstimated from XPS measurements. There was an error in estimating the surface atomic ratios from the corresponding XPS peaks, which was typically 0.02–0.03.

prepared in the present study exhibited essentially the same trends as in a previous study.^{5c} Although the Zn/Ga ratio also decreased as a result of the reaction, this decrease is unlikely to contribute significantly to the deactivation. Our previous study revealed that surface Zn species decrease even in a sample exhibiting stable water splitting performance.

These results indicate that Rh_{2-y}Cr_yO₃/GaN:ZnO underwent partial hydrolysis, accompanied by a loss of the Cr component, even at the optimal pH condition if the reaction time was long and the condition was harsh. ICP analysis of the reactant solution after reaction also indicated that the constituent elements of Ga, Zn, Rh, and Cr were eluted from the catalyst during reaction. This would give rise to partial collapse, relaxing the interfacial structure between GaN:ZnO and the loaded Rh_{2-y}Cr_yO₃ nanoparticles. The loosening of the structure hinders prompt electron migration from GaN:ZnO to Rh_{2-y}Cr_yO₃, which has been shown to be one of the slowest steps in overall water splitting using Rh_{2-y}Cr_yO₃/GaN:ZnO.^{8,9} As a result, photocatalytic activity is degraded. It should be also noted that the decrease in the Cr content contributes directly to activity drop, because the water splitting activity of Rh_{2-y}Cr_yO₃/GaN:ZnO is strongly dependent on the amount of Cr.^{5d} When the amount is decreased from the optimal value, the water splitting rate is dropped.

3.3. Regeneration Treatment by Reconstructing Hydrogen Evolution Sites. We examined reloading of the Rh_{2-y}Cr_yO₃ cocatalyst as a regeneration treatment for deactivated Rh_{2-y}Cr_yO₃/GaN:ZnO in an attempt to improve

the water reduction process. Considering the nature of an impregnation method where cocatalyst species are distributed randomly on the surface of a given material it is likely that the reloaded cocatalysts are located both on the "old" cocatalyst and on the surface of GaN:ZnO. Table 2 lists the photocatalytic

Table 2. Effects of Reloading Rh_{2-y}Cr_yO₃ onto Deactivated Rh_{2-y}Cr_yO₃/GaN:ZnO upon Activity for Overall Water Splitting^a

entry	Rh _{2-y} Cr _y O ₃ / GaN:ZnO	reloading amount of Rh and Cr ^b /%	activity ^c / μmol h ⁻¹	
			H ₂	O ₂
1	before reaction		4.6	2.3
2	after reaction		1.4	0.6
3		0 (just calcined)	2.3	1.2
4		10	2.6	1.3
5		50	3.6	1.5
6		80	3.5	1.4
7		100	2.9	0.8
8	before reaction	50	2.2	1.0

^aReaction conditions: catalyst, 0.1 g; aqueous H₂SO₄ solution (pH 4.5), 140 mL; light source, xenon lamp (300 W) fitted with a cold mirror (CM-2) and a cutoff filter (L40); reaction vessel, Pyrex top-irradiation type; irradiation wavelength, 400 < λ < 500 nm. ^bRelative loading amount with respect to the initial loadings (Rh 2.5 wt %, Cr 2.0 wt %). ^cAverage rates of gas evolution in 5 h.

activity of the deactivated sample before and after regeneration treatment. The reloading amount is the ratio of the reloaded metal elements to the initial loadings (Rh 2.5 wt %, Cr 2 wt %). The deactivated sample (entry 2) exhibited water splitting activity but with a 70% loss of the initial activity. It should be noted that the rate of O₂ evolution in water splitting over the deactivated catalyst was smaller than that expected from the stoichiometry. A plausible explanation for such nonstoichiometric production of O₂ observed in the deactivated catalyst is that oxidation reaction sites are in part destroyed as a result of the oxidation of GaN:ZnO by the valence band holes, which are ideally consumed by water oxidation. This idea is supported by the results of XPS analysis (Table 1), which showed that the N/Ga ratio decreased after the water splitting reaction. Just calcination of the deactivated sample recovered the activity to 50% of the initial activity (entry 3), suggesting that the interfacial contact between the cocatalyst and the photocatalyst recovered upon calcination. The water splitting rate was further improved upon reloading Rh_{2-y}Cr_yO₃ cocatalyst. The activity increased with reloading amount, reaching a maximum at 50% of the initial loading amount, beyond which it began to decrease. While up to 80% of the initial activity for H₂ evolution could be recovered at optimal treatment conditions, this treatment was less effective for regenerating O₂ evolution activity. A control experiment showed that reloading treatment of a fresh sample (without deactivation) had a negative impact on activity (entry 8).

As listed in Table 1, the surface atomic ratios of Zn/Ga, N/Ga, and Cr/Ga decreased after the accelerated deactivation procedure while the Rh/Ga ratio remained almost unchanged. On the basis of our previous study on 3 days of operation, which revealed that a decrease in the constituent elements of Cr and N contributes directly to activity drop,^{5c} it is likely that the decrease in N/Ga and Cr/Ga is the main cause of catalyst deactivation in the present case. Reloading of the Rh_{2-y}Cr_yO₃

cocatalyst increased the ratios of Rh/Ga and Cr/Ga, while those of Zn/Ga and N/Ga remained largely unchanged. The recovery of activity by the reloading procedure is thus attributable to reconstruction of H₂ evolution sites as well as improvement in interfacial electron transfer between photocatalyst and cocatalyst induced by heat treatment. XPS results suggested that the activity could not be recovered completely because the damage on the catalyst structure induced by hydrolysis was irreversible. The reloading procedure helped to regenerate the H₂ evolution rate but did not have much influence on O₂ evolution, because it failed to rebuild the damaged surface used for the oxidation reaction.

Further support for the above idea on the cause of deactivation comes from the observation that regeneration treatment of a catalyst deactivated in a similar manner but at pH 6.2 by reloading Rh_{2-y}Cr_yO₃ recovered only 20% of the initial activity. It has been shown that hydrolysis-induced decomposition is more pronounced at pH 6.2 than at pH 4.5, even for shorter reaction times (~3 days),^{5c} which is consistent with the results of the present accelerated deactivation experiment (Figure S1, Supporting Information). The reloading method is clearly less effective if the sample used has already undergone oxidative decomposition.

3.4. Loading an O₂ Evolution Cocatalyst To Suppress Oxidative Decomposition of GaN:ZnO. We reported that the water splitting activity of GaN:ZnO under visible light is improved when an O₂ evolution cocatalyst was loaded in addition to a H₂ evolution cocatalyst.⁷ This is presumably because the O₂ evolution cocatalyst facilitates the water oxidation process on GaN:ZnO. This strategy is expected to be also effective in the present case in suppressing deactivation of GaN:ZnO by improving the selectivity of holes for water oxidation.

To investigate this point, GaN:ZnO photocatalysts loaded with both H₂ and O₂ evolution cocatalysts were deactivated by irradiating with visible light (λ > 400 nm) for about 100 h using a 450 W high-pressure Hg lamp under atmospheric pressure. Table 3 shows the water splitting rates over GaN:ZnO samples

Table 3. Effects of RuO₂ Coloading onto GaN:ZnO Modified with the Core/Shell-Structured Rh/Cr₂O₃ Nanoparticulate Cocatalyst upon Activity for Overall Water Splitting^a

entry	catalyst sample	cocatalyst	activity ^b /μmol h ⁻¹	
			H ₂	O ₂
1	before reaction	Rh/Cr ₂ O ₃	1.8	0.9
2	after reaction		0.9	0.4
3	before reaction	RuO ₂ + Rh/Cr ₂ O ₃	2.9	1.4
4	after reaction		1.9	0.8

^aReaction conditions: catalyst, 0.1 g; aqueous H₂SO₄ solution (pH 4.5), 140 mL; light source, xenon lamp (300 W) fitted with a cold mirror (CM-2) and a cutoff filter (L40); reaction vessel, Pyrex top-irradiation type; irradiation wavelength, 400 < λ < 500 nm. ^bAverage rates of gas evolution in 5 h.

before and after degradation. The activity of GaN:ZnO modified with only the H₂ evolution cocatalyst (Rh/Cr₂O₃ nanoparticles) decreased to ca. 50% after reaction. On the other hand, prior modification with RuO₂ suppressed deactivation, preserving ~70% of the initial activity even after 100 h irradiation. The effectiveness of this strategy was confirmed by

the fact that the amounts of H₂ and O₂ produced by the coloaded samples were larger than those obtained using the sample loaded with only the Rh/Cr₂O₃ core/shell-structured H₂ evolution cocatalyst (see Figure S2, Supporting Information).

Table 4 lists the surface atomic ratios of the samples before and after reaction. N/Ga ratios decreased in both samples after

Table 4. Surface Atomic Ratios of Rh/Cr₂O₃ Core/Shell-Loaded GaN:ZnO with and without Coloaded the RuO₂ Cocatalyst before and after Reaction

entry	catalyst sample	cocatalyst	surface atomic ratios ^a			
			Zn/Ga	N/Ga	Rh/Ga	Cr/Ga
1	before reaction	Rh/Cr ₂ O ₃	0.07	0.87	0.05	0.05
2	after reaction		0.06	0.60	0.04	0.03
3	before reaction	RuO ₂ + Rh/Cr ₂ O ₃	0.08	0.86	0.07	0.08
4	after reaction		0.06	0.67	0.04	0.04

^aEstimated from XPS measurements. There was an error in estimating the surface atomic ratios from the corresponding XPS peaks, which was typically 0.02–0.03.

reaction, regardless of RuO₂ coloaded. However, the degree of the decrease was less pronounced in the coloaded sample than in the sample loaded with only the Rh/Cr₂O₃ cocatalyst. This indicates that the coloaded RuO₂ cocatalyst helped to suppress the oxidative decomposition of GaN:ZnO, thereby improving the durability, although oxidative deactivation could not be completely suppressed at the present stage.

4. CONCLUSION

In this study, a long-time overall water splitting reaction was performed over a period of 0.5 years using Rh_{2-y}Cr_yO₃/GaN:ZnO under visible light (400 < λ < 500 nm). It was found that this material had the ability to photocatalytically split water into H₂ and O₂ without noticeable degradation during the first 3 months of operation with a 50% activity drop after 6 months. The main cause of catalyst deactivation with time was collapse of H₂ evolution sites (i.e., Rh_{2-y}Cr_yO₃ nanoparticles) and hydrolysis of the nitride component by valence band holes as well as mechanical damage caused by stirring the reactant solution. Reloading the Rh_{2-y}Cr_yO₃ cocatalyst with heat treatment onto the deactivated Rh_{2-y}Cr_yO₃/GaN:ZnO regenerated water splitting activity to a certain extent. Coloaded an O₂ evolution cocatalyst onto GaN:ZnO in addition to a H₂ evolution cocatalyst helped to prolong the lifetime of the material.

■ ASSOCIATED CONTENT

Supporting Information

Time courses of water splitting under UV irradiation (λ > 300 nm) using Rh_{2-y}Cr_yO₃/GaN:ZnO; time courses of water splitting under visible light (λ > 400 nm) using Rh/Cr₂O₃-loaded GaN:ZnO with and without RuO₂ coloaded. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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