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Improvement of photocatalytic activity of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ solid solution for overall water splitting by co-loading Cr and another transition metal

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Abstract

Modification with a two-component cocatalyst consisting of Cr and another transition metal was examined in an attempt to improve the photocatalytic activity of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ for overall water splitting. The activity of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ modified with various transition metals is enhanced by co-loading of Cr, although modification with Cr alone is not effective for promoting activity in this reaction. The activity of the co-loaded catalyst is found to be strongly dependent on the amount of loaded Cr, which in turn varies according to the paired transition metal. The improvement in activity is attributed to the formation of suitable reaction sites by intimate interaction between Cr and the paired metal component.
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1. Introduction

Overall water splitting using a heterogeneous photocatalyst is an important reaction that offers an ideal method for supplying hydrogen as a clean and renewable energy carrier. To date, a range of metal oxides and (oxy)nitrides containing either transition metal cations with d^0 electronic configuration (e.g., Ti^{4+}, Nb^{5+}, and Ta^{5+}) or typical metal cations with d^{10} electronic configuration (e.g., Ga^{3+}, Ge^{4+}, and Sn^{4+}) as principal cation components have been reported to be active photocatalysts for overall water splitting [1–25]. This reaction involves three steps: (1) The photocatalyst absorbs photon energy greater than the band gap energy of the material and generates photoexcited electron–hole pairs in the material bulk; (2) the photoexcited charges separate and migrate to the surface without

recombination; and (3) surface-adsorbed species are reduced and oxidized by the photogenerated electrons and holes to produce H_2 and O_2, respectively. The first two steps are strongly dependent on the structural and electronic properties of the photocatalyst, whereas the third step is promoted by the presence of a solid cocatalyst. The cocatalyst is typically a noble metal or metal oxide and is loaded onto the base catalyst as a dispersion of nanoparticles to produce active sites and reduce the activation energy for gas evolution.

To date, various transition metal oxides, including NiO_x [1,3,4,8,9,11,13,14,16], RuO_2 [5,6,12,18–21], IrO_2 [6,15], and RhO_x [2] have been applied as a cocatalyst for photocatalytic overall water splitting. These oxides are inactive for water formation from H_2 and O_2 and thus are well suited for this reaction. Although certain photocatalysts, including $LiTaO_3$ [11] and $K_3Ta_3B_2O_{12}$ [17], have been reported to exhibit high activity without the need for a cocatalyst, in most cases, a cocatalyst is considered indispensable for enhancing the overall efficiency of the reaction. Therefore, the development of a new cocatalyst

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that efficiently promotes photocatalytic overall water splitting remains important.

We have previously reported that the photocatalytic activity of Ni-loaded $K_2La_2Ti_3O_{10}$ for overall water splitting is improved by co-loading Cr [10]. In this case, Cr was the only cocatalyst found to be effective as an additional component for enhancing activity. Recently, the $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ solid solution [19–25] modified with a mixed oxide of Rh and Cr was shown to be an efficient and stable photocatalyst for overall water splitting under visible light irradiation [23–25]. Modification with either Rh or Cr alone did not result in appreciable evolution of H_2 and O_2, suggesting that Cr is an effective component of multielement cocatalysts. This has motivated further investigation of Cr as a cocatalyst in combination with other transition metals.

In the present study, modification of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ by loading with Cr and another transition metal as a cocatalyst was investigated as a means of improving the photocatalytic activity of the system for overall water splitting. The effectiveness of such cocatalysts with other photocatalysts was also examined.

2. Experimental

2.1. Preparation of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ and photocatalytic reactions

The $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ solid solution ($x = 0.12$) was prepared as described previously [19,20]. Production of the solid solution was confirmed by powder X-ray diffraction (XRD; RINT-UltimaIII, Rigaku; Cu$K\alpha$) and energy-dispersive X-ray analysis (EDX; Emax-7000, Horiba).

The cocatalyst, a combination of Cr and one other metal component, was loaded onto the as-prepared $(Ga_{1-x}Zn_x)$ $(N_{1-x}O_x)$ by a co-impregnation method. $Cr(NO_3)_3\cdot9H_2O$ (Wako Pure Chemicals, 99.9%), $Fe(NO_3)_3\cdot9H_2O$ (Kanto Chemicals, 99%), $Co(NO_3)_2\cdot6H_2O$ (Kanto Chemicals, 98%), $Ni(NO_3)_2\cdot6H_2O$ (Kanto Chemicals, 98%), $Cu(NO_3)_2\cdot3H_2O$ (Kanto Chemicals, 99.2%), $(NH_4)_2RuCl_6$ (Aldrich), $Na_3RhCl_6\cdot$ $2H_2O$ (Kanto Chemicals, 97% as Rh), $Rh(NO_3)_3$ (Kanto Chemicals, 99.9%), $(NH_4)_2PdCl_4$ (Kanto Chemicals, 37% as Pd), $Ag(NO_3)_3$ (Kanto Chemicals, 99.8%), $Na_2IrCl_6\cdot6H_2O$ (Kanto Chemicals, 97% as Ir), and $H_2PtCl_6\cdot2H_2O$ (Kanto Chemicals, 97% as Pt) were used as precursors. Impregnation was performed by suspending 0.3–0.4 g of the photocatalyst powder in an aqueous solution containing an appropriate amount of $Cr(NO_3)_3\cdot9H_2O$ and the nitrate or chloride of the paired metal. The solution was then evaporated to dryness over a water bath followed by calcination in air at 623 K for 1 h. Although loading of the cocatalysts by this method is expected to produce the oxide form, the cocatalyst components are simply referred to here by the respective transition metal. In the case of Ni or Ni–Cr cocatalysts, the impregnated catalyst was reduced by exposure to H_2 (20 kPa) at 573 K for 2 h, then oxidized by exposure to O_2 (10 kPa) at 473 K for 1 h in a closed gas circulation system to produce an Ni/NiO (core/shell) double structure [3]. The mor-

phology of the loaded cocatalysts was observed by a scanning electron microscope (Hitachi S-4700).

Water splitting reactions were carried out in a Pyrex inner irradiation-type reaction vessel connected to a glass closed gas circulation and evacuation system. The reaction was performed in distilled water (370–400 mL) containing 0.3 g of the cocatalyst-loaded photocatalyst powder. The reactant solution was first evacuated several times to ensure complete air removal, and then irradiated under a 450 W high-pressure Hg lamp via a Pyrex tube as a light filter ($\lambda > 300$ nm). For visible-light experiments, the Pyrex tube was filled with aqueous 2 M $NaNO_2$ solution to block ultraviolet light ($\lambda > 400$ nm). Before irradiation, it was confirmed that no reaction occurred in the dark. The evolved gases were analyzed by gas chromatography.

The quantum efficiency (Φ) was estimated as described previously [23] and calculated using the following equation: $\Phi(\%) = (2 \times R/I) \times 100$, where R and I represent the number of evolved H_2 molecules and the number of incident photons, respectively. Here Φ is quantum efficiency, where it is assumed that all incident photons are absorbed by the photocatalyst. The number of incident photons was measured using a calibrated Si photodiode.

2.2. Preparation of other photocatalysts and photocatalytic reactions

Preparation of $ZnNb_2O_6$, $NaTaO_3$, and β-Ge_3N_4 photocatalysts and the loading cocatalysts were carried out as described previously [8,9,18]. JRC-TIO-4, supplied by the Catalysis Society of Japan, was used as a TiO_2 catalyst after calcination in air at 673 K for 5 h to remove surface contamination. The TiO_2 catalyst was loaded with Pt (0.5 wt%) by in situ photodeposition using $H_2PtCl_6\cdot2H_2O$ [26]. β-Ga_2O_3 (High Purity Chemicals, 99.9%) was used without further purification, and loading with a NiO cocatalyst was performed as reported in the literature [14]. The crystal structure of these photocatalysts was confirmed by XRD measurements.

Photocatalytic water-splitting reactions over these photocatalysts were carried out in a quartz reaction vessel ($\lambda > 200$ nm) in the same manner as described above. The reactions using TiO_2 were conducted in an aqueous Na_2CO_3 solution (1.9 M, 400 mL) in accordance with the literature [7].

3. Results and discussion

Table 1 gives the photocatalytic activities of the various loaded $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ photocatalysts for overall water splitting under irradiation at ultraviolet (UV) and visible wavelengths ($\lambda > 300$ nm). As reported previously, $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ alone exhibits little photocatalytic activity even under UV irradiation [19,23]. With appropriate modification, however, substantial photocatalytic activity was obtained for simultaneous H_2 and O_2 evolution from pure water. Loading of Ni, Ru, Rh, Ir, or Pt was found to effectively promote overall water splitting, although the rate of O_2 evolution achieved by the Rh- and Ir-modified samples was lower

Table 1
Photocatalytic activity of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ modified with various transition metals for overall water splitting under UV irradiation ($\lambda > 300$ nm)

Cocatalyst		Activity ($\mu mol\, h^{-1}$)	
Element	Loading amount (wt%)	H_2	O_2
Cr	1	0	0
Fe	1	0	0
Co	1	2.0	0
Ni	1.25	126	57
Cu	1	2.0	0
Ru	1	71	27
Rh	1	50	1.6
Pd	1	1.0	0
Ag	1	0	0
Ir	1.5	9.3	3.1
Pt	1	0.9	0.4

Note. Catalyst (0.3 g); distilled water (370–400 mL); light source, high-pressure mercury lamp (450 W); inner irradiation-type reaction vessel made of Pyrex.

Table 2
Photocatalytic activities of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ loaded with Cr and a transition metal for overall water splitting under UV irradiation ($\lambda > 300$ nm)

Cocatalyst		Cr co-loading amount (wt%)	Activity ($\mu mol\, h^{-1}$)	
Element	Loading amount (wt%)		H_2	O_2
Fe	1	1	73	36
Co	1	1	48	24
Ni	1.25	0.125	685	336
Cu	1	1	585	292
Ru	1	0.1	181	84
Rh	1	1.5	3835	1988
Pd	1	0.1	205	96
Ag	1	1	11	2.3
Ir	1.5	0.1	41	17
Pt	1	1	775	357

Note. Catalyst (0.3 g); distilled water (370–400 mL); light source, high-pressure mercury lamp (450 W); inner irradiation-type reaction vessel made of Pyrex.

Fig. 1. Time courses of overall water splitting on $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ loaded with 1 wt% Rh and 1.5 wt% Cr under (A) UV ($\lambda > 300$ nm) and (B) visible light irradiation ($\lambda > 400$ nm). Reactions were performed in pure water (370 mL) with 0.3 g of catalyst powder under illumination from a high-pressure mercury lamp (450 W).

than expected given the stoichiometry. These transition metals have been reported to be active components as cocatalysts for photocatalytic overall water splitting [1–16,18–21]. In contrast, Fe, Co, Cu, Pd, and Ag as cocatalysts did not improve the rate of evolution, suggesting that charge transfer from the $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ bulk to these loaded species does not occur and/or that there are no catalytic sites for gas evolution on the surface of the loaded species.

The photocatalytic activity of the transition metal-loaded catalysts was markedly improved by co-loading Cr. Table 2 lists the photocatalytic activities of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ loaded with both Cr and another transition metal for overall water splitting under UV irradiation ($\lambda > 300$ nm). All of the examples except the Ag–Cr system achieved stoichiometric evolution of H_2 and O_2 from pure water. The largest improvement in activity was obtained by loading the base catalysts with both 1 wt% Rh and 1.5 wt% Cr. The activity of this catalyst system was 2 orders of magnitude higher than the catalysts loaded with 1 wt% Rh under the same reaction conditions. Typical time courses of overall water splitting on the catalyst loaded with 1 wt% Rh and 1.5 wt% Cr are shown in Fig. 1. Under UV irradia-
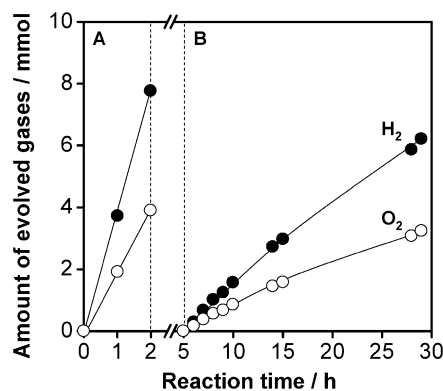
tion ($\lambda > 300$ nm), the catalyst produced H_2 and O_2 linearly and stoichiometrically, and the inner pressure of the reaction system reached approximately atmospheric pressure after 2 h of reaction. After the reaction system was evacuated and the Pyrex-tube light filter filled with aqueous 2 M $NaNO_2$ solution ($\lambda > 400$ nm), stoichiometric H_2 and O_2 evolution was again observed. The total amount of H_2 and O_2 evolved over the entire reaction (21.1 mmol) was substantially greater than the amount of catalyst used in the reaction (3.7 mmol), indicating that the overall water-splitting reaction proceeded catalytically. The maximum quantum efficiency for this reaction was ca. 2.5% at 420–440 nm, as reported previously [23]. The structure of Rh–Cr mixed-cocatalyst and the effects of reaction conditions on photocatalytic behavior have been described elsewhere [24,25]. Note that even though loading with Fe, Co, Cu, Pd, or Ag alone did not make the $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ catalyst active for overall water splitting (see Table 1), co-loading Cr and one of these inactive metal components resulted in measurable photocatalytically activity. Co-loading Cr is considered to facilitate a charge transfer from the $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ bulk to the cocatalyst and/or the creation of catalytic gas evolution sites on the cocatalyst surface. However, the loading amount of Cr in Table 2 may not be optimal except for the Ni–Cr and Rh–Cr system, as discussed later.

The photocatalytic activity of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ loaded with Cr and a transition metal was found to be strongly dependent on the amount of Cr loaded. Fig. 2 shows the dependence of the photocatalytic activity of the catalyst loaded with Ni–Cr and Rh–Cr under UV irradiation ($\lambda > 300$ nm) on the amount of loaded Cr. The activity increased with Cr content to a maximum at a certain loading amount, above which the activity decreased. SEM observation revealed that the particle size of cocatalyst became larger with increasing co-loaded amounts of Cr. The highest activities were obtained at 0.125 wt% Cr with 1.25 wt% Ni and at 1.5 wt% Cr with 1 wt% Rh. These results suggest that the optimal Cr loading differs according to the co-loaded transition metal, and similarly enhanced photocatalytic activity would be expected to result from other transition metal/Cr combinations as cocatalysts with $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$. Inter-

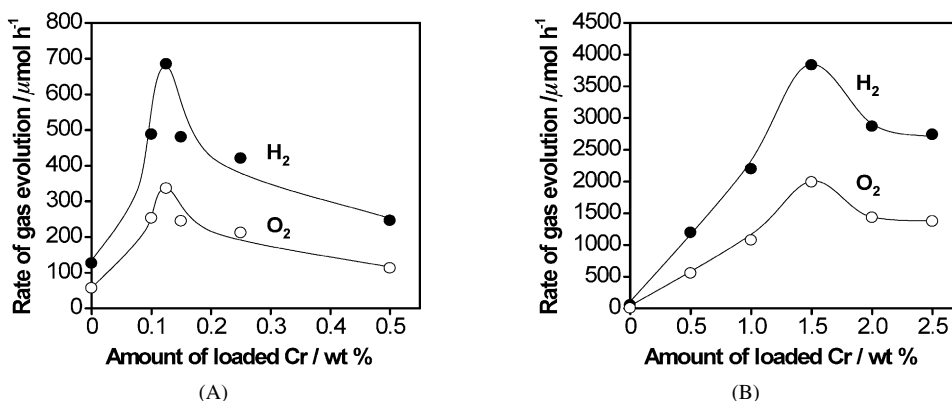Fig. 2. Dependence of photocatalytic activity of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ loaded with (A) Ni–Cr and (B) Rh–Cr for overall water splitting under UV irradiation ($\lambda > 300$ nm) on the amount of loaded Cr. Reactions were performed in pure water (370–400 mL) with 0.3 g of catalyst powder under illumination from a high-pressure mercury lamp (450 W).
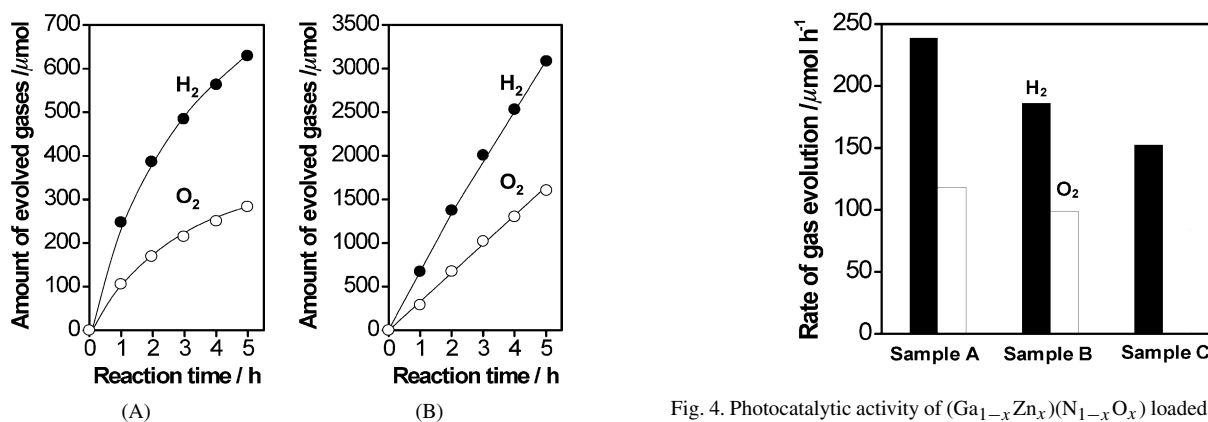

Fig. 3. Time courses of overall water splitting on $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ loaded with (A) Ni and (B) Ni–Cr under UV irradiation ($\lambda > 300$ nm). Reactions were performed in pure water (400 mL) with 0.3 g of catalyst powder under illumination from a high-pressure mercury lamp (450 W).

Fig. 4. Photocatalytic activity of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ loaded with Rh and Cr by various loading methods for overall water splitting under visible light irradiation ($\lambda > 400$ nm). Reactions were performed in pure water (370 mL) with 0.3 g of catalyst powder under illumination from a high-pressure mercury lamp (450 W) via an aqueous 2 M $NaNO_2$ solution filter. Sample A was prepared by simultaneous loading of the two cocatalyst components from one aqueous solution containing both Rh and Cr. Sample B was prepared by suspending the catalyst first in an aqueous solution containing Rh and second in a solution containing Cr. Sample C was prepared in the same manner as Sample B but in the reverse order (Cr then Rh).

estingly, the Cr co-loading is effective not only for enhancing the rates of H_2 and O_2 evolution in overall water splitting, but also for improving the stability of the catalyst. Fig. 3 shows the time courses of water splitting for $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ catalysts loaded with Ni and Ni–Cr. For the Ni-loaded sample, the evolution rates for both H_2 and O_2 were high at the start of the reaction but then decreased as the reaction progressed (Fig. 3A). This degradation of activity is considered due to a change in the state of Ni on the catalyst surface [11]. Kudo et al. reported that immersion of NiO-loaded $NaTaO_3$ in pure water caused NiO nanoparticles to peel off or elute as $Ni(OH)_2$ even without irradiation, resulting in gradual catalyst deactivation [11]. In contrast, $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ loaded with both Ni and Cr produced H_2 and O_2 linearly and stoichiometrically with no noticeable deactivation as the reaction progressed (Fig. 3B). Therefore, co-loading with Cr had the effect of not only enhancing the rates of H_2 and O_2 evolution, but also suppressing deactivation. These results are consistent with those obtained previously for $K_2La_2Ti_3O_{10}$ loaded with both Ni and Cr, which exhibited high durability for overall water splitting over long periods of irradiation [10]. The incorporation of Cr thus appears to modify the intrinsic properties of the paired transition metal component, affording a synergetic improvement in photocatalytic properties. It is of interest that the optimal loading ratio of Ni to Cr for $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ (Ni/Cr = 10) differs from that for $K_2La_2Ti_3O_{10}$ (Ni/Cr = 6) [10], indicating that the optimal Cr load depends on both the transition metal with which it is paired and the base photocatalyst.

If co-loading Cr results in the formation of active species by interaction between the two cocatalyst components, then photocatalytic activity should be affected by the loading method. To examine whether this is the case, $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ catalysts optimally loaded with Rh and Cr were prepared by three different loading methods, and the photocatalytic performance of the three samples compared. Sample A was prepared by simultaneous loading of the two cocatalyst components from one aqueous solution containing both Rh and Cr. Sample B was prepared by suspending the catalyst first in an aqueous solution containing Rh and then in a solution containing Cr. Sample C was prepared in the same way as Sample B but in the reverse order (Cr then Rh). Fig. 4 compares the photocatalytic
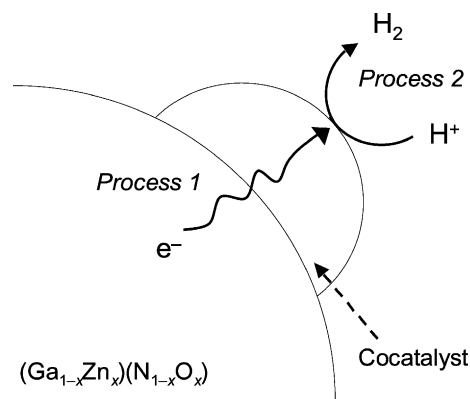
Fig. 5. A schematic illustration of the electron transfer from $(Ga_{1-x}Zn_x)$-$(N_{1-x}O_x)$ to the loaded cocatalyst (Process 1) and the H_2 evolution (Process 2) in the overall water splitting.

activities of the three samples under visible light irradiation ($\lambda > 400$ nm). Although all samples produced H_2 and O_2 stoichiometrically under visible light, Sample A exhibited higher activity than the other samples. Because the two cocatalyst components should be more homogeneously mixed in this sample than in the other samples, this result confirms that close interaction of all components is essential for enhancing the photocatalytic activity by this approach.

On the basis of the above results, we conclude that co-loading of Cr is an effective method for enhancing the photocatalytic activity of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ loaded with various metals/metal oxides for overall water splitting. Taking into account the fact that the Rh and Cr mixed-oxide dispersed on $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ functions as an effective H_2 evolution site [24], other two-component cocatalysts containing Cr also promote H_2 evolution. A schematic illustration of the electron transfer from $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ to the loaded cocatalyst and the H_2 evolution process is depicted in Fig. 5. To achieve efficient H_2 evolution, both photogenerated electron migration to the cocatalyst (process 1) and reduction of surface-adsorbed H^+ followed by H_2 formation (process 2) must proceed smoothly. Accordingly, the addition of Cr should have a positive effect on processes 1 and/or 2 by interacting with the co-loaded metal component (although at present, which process is enhanced is not clear). Presumably, the addition of Cr would change the electronic state and chemical properties of the paired metal. In addition, various factors (e.g., band edge potential [13] and work function [27] of the photocatalyst and the loaded species) have been reported to affect the efficiency of electron transfer. Therefore, the difference in the band edge potential and the work function between $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ and the loaded cocatalyst containing Cr may affect the activity. Therefore, the mechanism of enhanced activity from the addition of Cr seems complicated. Further investigation, including theoretical calculations, is currently underway.

Overall water-splitting reactions using other photocatalysts modified with the Rh–Cr cocatalyst were also carried out. It has been confirmed that the water formation from H_2 and O_2 does not occur on Rh and Cr co-loaded photocatalysts [24]. Table 3 gives the photocatalytic activities of various photocat-

Table 3
Photocatalytic activities of photocatalysts with and without cocatalysts for overall water splitting under UV irradiation ($\lambda > 200$ nm)

Photocatalyst	Cocatalyst (loading amount, wt%)	Activity ($\mu mol\,h^{-1}$)	
		H_2	O_2
TiO_2[a]	None	3.4	0
	Pt (0.5 wt%)	221	109
	Rh (1 wt%)–Cr (1.5 wt%)	39	17
$ZnNb_2O_6$	None	8.9	0
	NiO (0.5 wt%)	75	14
	Rh (1 wt%)–Cr (1.5 wt%)	213	104
$NaTaO_3$	None	120	52
	NiO (0.05 wt%)	1508	736
	Rh (1 wt%)–Cr (1.5 wt%)	568	227
β-Ga_2O_3	None	131	62
	NiO (2 wt%)	248	112
	Rh (1 wt%)–Cr (1.5 wt%)	612	307
β-Ge_3N_4	None	2.0	0
	RuO_2 (1 wt%)[b]	1356	681
	Rh (1 wt%)–Cr (1.5 wt%)[c]	4510	2176

Note. Catalyst (0.3 g); distilled water (370–400 mL); light source, high-pressure mercury lamp (450 W); inner irradiation-type reaction vessel made of quartz.
[a] In an aqueous Na_2CO_3 solution (1.9 M).
[b] In an aqueous H_2SO_4 solution of pH 0, and 0.5 g of photocatalyst powder was used.
[c] In an aqueous H_2SO_4 solution of pH 4.5.

alysts for overall water splitting with and without a cocatalyst using a quartz irradiation vessel. In all cases, the activities of the photocatalysts loaded with a conventional cocatalyst (e.g., Pt, NiO_x, or RuO_2) were much greater than those of the unloaded catalysts, as reported previously [7–9,14,18]. Loadings with Rh–Cr also resulted in enhanced H_2 and O_2 evolution in overall water splitting, indicating that the Rh–Cr cocatalyst functions as an effective cocatalyst for promoting overall water splitting not only on $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ but also on other photocatalysts, regardless of electronic configuration or type of photocatalyst. Note that the results reported in Table 3 were obtained without optimizing the catalyst system or reaction conditions, and that each loading and reaction condition might not be optimal because (1) the surface areas of these photocatalysts differ; (2) the optimal loading of Rh and Cr varies in each photocatalyst, as suggested by the results of Ni–Cr co-loaded $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ and $K_2La_2Ti_3O_{10}$ mentioned above; and (3) in general, the optimal reaction condition for a certain photocatalyst depends on the type of loaded cocatalyst [19,23]. Therefore, the activities of these photocatalysts would be expected to be further improved by refining the loading methods and reaction conditions.

4. Conclusion

Modification of the $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ photocatalyst with both Cr and another transition metal was shown to be effective in improving the photocatalytic activity of the catalytic system for overall water splitting. This increased activity, attributed to the interaction between Cr and the other transition metal component in the cocatalyst, was also demonstrated to

be applicable to other photocatalysts, regardless of electronic configuration or type of photocatalyst.

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