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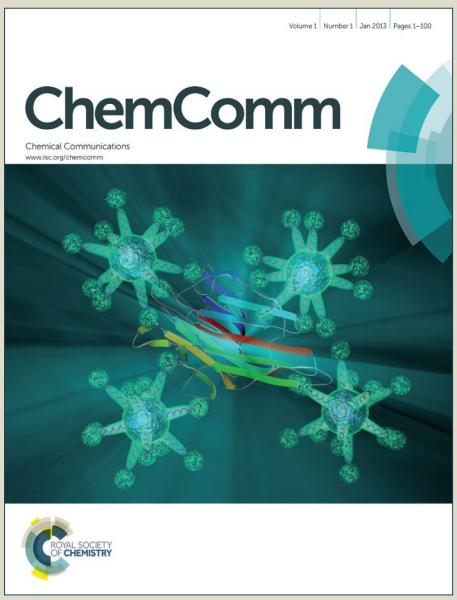

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Remarkably High Apparent Quantum Yield to Overall Photocatalytic H_2O Splitting Achieved by Utilizing Zn Ion Added Ga_2O_3 Prepared with Dilute $CaCl_2$ solution

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Remarkably high photocatalytic activity to overall H_2O splitting, where the activity was 32 mmol/h for H_2 production and 16 mmol/h for O_2 production under irradiation from a 450 W high-pressure Hg lamp and apparent quantum yield (AQY) was 71% under irradiation at 254 nm, was achieved by utilizing a photocatalyst of $Rh_{0.5}Cr_{1.5}O_3$(Rh; 0.5 wt%)/Zn(3 mol%)-Ga_2O_3 when the Ga_2O_3 was prepared with dilute $CaCl_2$ aqueous solution having a concentration of 0.001 mol/l.

Gallium oxide is reported to be one of the simple oxide photocatalysts that exhibit photocatalytic activity to overall H_2O splitting and has been extensively studied [1-9]. Although the band gap of this photocatalyst is too wide (4.4 eV evaluated from UV spectrum) to carry out a photocatalytic reaction under visible light irradiation, the photocatalyst has sufficiently high potential for photocatalytic overall H_2O splitting though photocatalytic activity itself is low. Therefore, various investigations, such as examination of the influence of the preparation conditions of Ga_2O_3 and modification of the surface and the bulk have been examined in order to improve photocatalytic performances [2,4,6]. As a result, Zn ion added Ga_2O_3 combined with a $Rh_yCr_{2-y}O_3$ co-catalyst has been reported to exhibit extremely high photocatalytic activity to overall H_2O splitting, where the preferable state of the photocatalyst was $Rh_{0.5}Cr_{1.5}O_3$(Rh; 0.5 wt%)/Zn(3 mol%)-Ga_2O_3 and activity was 21 mmol/h and 10.5 mmol/h for H_2 and O_2, respectively, under irradiation from a 450 W high-pressure Hg lamp in an inner-irradiation type photoreaction cell[4]. Activity has been confirmed to be at the same level as that of a NiO/La-$NaTaO_3$ photocatalyst reaction carried out under nearly the same conditions, and this has been reported as having the highest efficiency to overall H_2O splitting[10,11] . However, the detailed quantum yield and the potential to further improve the photocatalytic activity of overall H_2O splitting have not been investigated so far.

From our previous investigations into improvement of the photocatalytic performance of Ga_2O_3 to H_2O splitting[4], the following two particular points are important; one is the control of the surface states by combining an effective co-catalyst for suppressing the reverse chemical process that occurs over the surface and the other is the modification of the bulk state to prevent the recombination and the mobility of electrons and holes that are produced by irradiation of the bulk of the photocatalyst. The former was achieved by the combination of a $Rh_yCr_{2-y}O_3$ co-catalyst, and the latter was achieved by the addition of a small amount of metal ions such as Ca, Zn, Cr, Sr, and Ba ions, in particular, Zn ion to Ga_2O_3. With respect to the latter, Ga_2O_3 containing a small amount of metal ions that have a positive influence on the improvement of the photocatalytic activity has the potential to further improve the activity to H_2O splitting.

In this study, in order to prepare an effective Ga_2O_3 photocatalyst to overall H_2O splitting, we investigated the influence of the preparation conditions on the photocatalytic performance. In particular, we studied the influence of small amounts of metal ions in the preparation atmosphere by the ammonia precipitation method on photocatalytic performance based on the latter point described above. In this respect, we investigated the influence of the co-existence of small amounts of Ca ion, which are also reported to be the secondly effective additive for improving the photocatalytic activity of

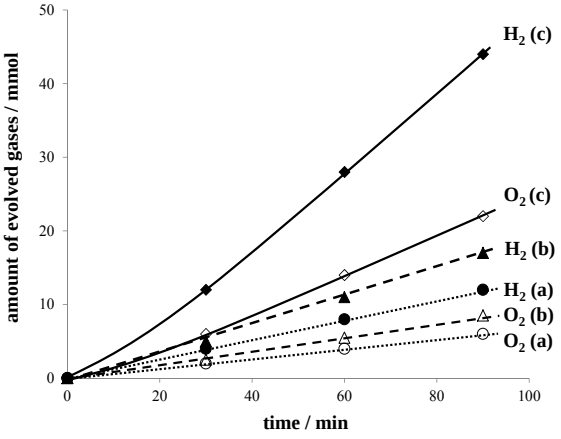

Fig. 1, Photocatalytic evolution of H_2 and O_2 in time over (a) $Rh_{0.5}Cr_{1.5}O_3$(Rh; 0.5 wt%)/Ga_2O_3(DI), (b) $Rh_{0.5}Cr_{1.5}O_3$(Rh; 0.5 wt%)/Ga_2O_3(UP-Ca(0.001)), and (c) $Rh_{0.5}Cr_{1.5}O_3$(Rh; 0.5 wt%)/Zn(3 mol%)-Ga_2O_3(UP-Ca(0.001))

Ga_2O_3,[2] in the preparation atmosphere of Ga_2O_3 photocatalyst on overall photocatalytic H_2O splitting. Here, we report on the influence of Ca ion in the preparation of Ga_2O_3 and the apparent quantum yields of the photocatalytic reaction over various photocatalysts.

The photocatalyst of Ga_2O_3 was prepared by an ammonia precipitation method by using distilled and de-ionized water (supplied from EYELA Still Ace SA-2100 E1, resistivity 12 MΩ cm at 298 K) and aqueous solutions of $CaCl_2$ dissolved in ultra-pure water (supplied from Millipore, resistivity 18.2 MΩ cm at 298 K). $Ga(NO_3)_3$ nH_2O (99.9%, obtained from High Purity Chemicals) (12.6 g) was dissolved in the de-ionized water or various concentrations of $CaCl_2$ ultra-pure water solution (200 ml). Hydroxylation was carried out by dripping ammonium hydroxide solution to have a final pH value of 9. The produced hydroxide was filtered and calcinated at 1273 K for ten hours to obtain Ga_2O_3. Here, Ga_2O_3 prepared by using the de-ionized water is shown as Ga_2O_3(DI) and that prepared by using $CaCl_2$ ultra-pure water solution is shown as Ga_2O_3(UP-Ca(concentration/mol/l)). The details of the addition of Zn ion and the combination of a $Rh_{0.5}Cr_{1.5}O_3$ co-catalyst are shown in the previous reports[4,6].

Figure 1 shows the evolution of H_2 and O_2 in time by overall photocatalytic H_2O splitting over (a) $Rh_{0.5}Cr_{1.5}O_3$(Rh; 0.5 wt%)/Ga_2O_3(DI), (b) $Rh_{0.5}Cr_{1.5}O_3$ (Rh; 0.5 wt%)/Ga_2O_3(UP-Ca(0.001)), and $Rh_{0.5}Cr_{1.5}O_3$ (Rh; 0.5 wt%)/ Zn(3 mol%)-Ga_2O_3(UP-Ca(0.001)). Photocatalytic H_2O splitting was performed in an inner-irradiation type photoreaction cell connected to an isovolumetric closed gas circulation system (dead volume 1.7 l) equipped with a vacuum line and a gas chromatograph sample inlet. The prepared photocatalyst (1 g) was suspended in thoroughly outgassed ultra-pure water (0.65 l) by magnetic stirring in the cell and the suspension was irradiated by a high-pressure Hg lamp (USHIO UM-452, 450 W). The evolved H_2 and O_2 were collected in a sampling tube and analyzed by a gas chromatograph.

As shown in Fig. 1, H_2 and O_2 are produced constantly with relatively high activity from the beginning of irradiation over all photocatalysts. Particularly, photocatalytic activity improved significantly by applying Ga_2O_3 (UP-Ca(0.001)) as the photocatalyst. Moreover, remarkably high photocatalytic activity can be confirmed if Ga_2O_3 (UP-Ca(0.001)) with added 3 mol% of Zn ion is applied as the photocatalyst. Then, the photocatalytic property of Zn doped Ga_2O_3 (UP-Ca(0.001)) to overall H_2O splitting was examined in detail.

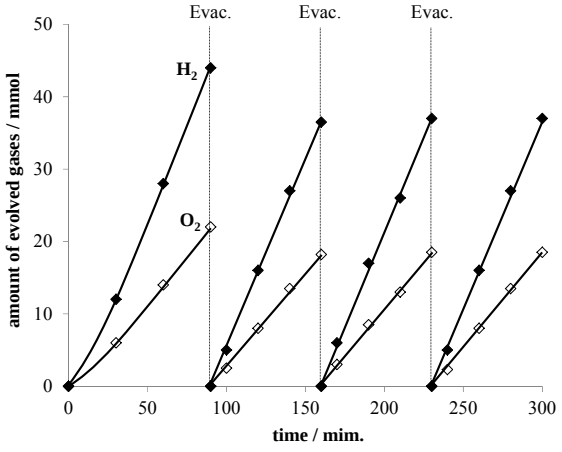

Fig. 2, Photocatalytic evolution of H_2 and O_2 in time over $Rh_{0.5}Cr_{1.5}O_3$(Rh; 0.5 wt%)/Zn(3 mol%)-Ga_2O_3(UP-Ca(0.001))

Figure 2 shows the evolution of H_2 and O_2 in time by overall photocatalytic H_2O splitting over $Rh_{0.5}Cr_{1.5}O_3$ (Rh; 0.5 wt%)/ Zn(3 mol%)-Ga_2O_3(UP-Ca(0.001)). As shown in Fig. 2, H_2 and O_2 were produced in the stoichiometric ratio with remarkably high photocatalytic activity and the pressure of the system became 1 atmosphere within 1.5 hours at the first run. Thereafter, the photocatalytic reaction was carried out for 80 minutes followed by the evacuation of the system and the reaction was restarted. From the result in Fig. 2, it is also confirmed that H_2 and O_2 were produced with remarkable high activity if the reaction was restarted repeatedly. The values of the activity in a steady state were 32 mmol/h and 16 mmol/h for H_2 and O_2, respectively. These values are extremely high compared with the activity of $Rh_{0.5}Cr_{1.5}O_3$ (Rh; 0.5 wt%)/Zn(3 mol%)-Ga_2O_3(DI), where the reaction was carried out in the same reaction system in the present study, which has been reported previously[4]. Accordingly, the effect of the concentration of $CaCl_2$ in the preparation solution of Ga_2O_3 to the photocatalytic activity of $Rh_{0.5}Cr_{1.5}O_3$ (Rh; 0.5 wt%)/ Zn(3 mol%)-Ga_2O_3(UP-Ca) was examined.

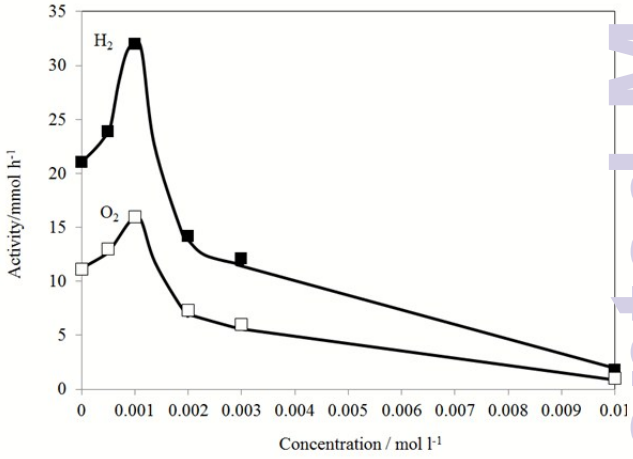

Fig. 3, Photocatalytic activity of overall H_2O splitting on $Rh_{0.5}Cr_{1.5}O_3$(Rh; 0.5 wt%)/Zn(3 mol%)-Ga_2O_3(UP-Ca) as a function of the concentration of $CaCl_2$ in the solution for preparing Ga_2O_3

Figure 3 shows the photocatalytic activity of $Rh_{0.5}Cr_{1.5}O_3$ (Rh; 0.5 wt%)/ Zn(3 mol%)-Ga_2O_3(UP-Ca) to overall photocatalytic H_2O splitting as a function of the concentration of $CaCl_2$ in the preparation solution. As shown in Fig. 3, the photocatalytic activity depends on the concentration of $CaCl_2$ in the preparation solution. In particular, the activity improves with the increase of the concentration of $CaCl_2$ and becomes the maximum value at 0.001 mol/l, while the activity decreases as the concentration is increased above 0.001 mol/l. From the result in Fig. 3, it is noticed that application of Ga_2O_3 prepared with the dilute $CaCl_2$ solution by the ammonia precipitation method is effective for the photocatalytic activity of Zn added Ga_2O_3 to overall H_2O splitting. In this case, the Ca ion in the preparation atmosphere probably positively influences the photocatalytic performance of Zn added Ga_2O_3.

Accordingly, the state of Ga_2O_3(UP-Ca(0.001)), which was the preferable Ga_2O_3 of the Zn added Ga_2O_3 photocatalyst for overall H_2O splitting as shown in Fig. 3, was investigated. The crystallography and the morphology of Ga_2O_3 were examined by XRD (Rigaku RINT-2200) and SEM (JEOL JSM-7600F). Any significant change could not be observed in the XRD pattern and the morphology of the Ga_2O_3 particles of Ga_2O_3 (UP-Ca(0.001)) in SEM

photograph compared with those of Ga_2O_3(UP-Ca(0)) (See Fig. S1 and Fig. S2 in supporting information). Energy dispersed X-ray emission spectrum (EDS) was also measured. From the result of EDS, the spectrum attributed to Ca can be observed as very small peak (See Fig. S3 in supporting information). Then, the content of Ca ion in the prepared Ga_2O_3(UP-Ca(0.001)) was examined by inductively coupled plasma optical emission spectroscopy (ICP-OES; Parkin Elmer Optima 4300DV). From the result of ICP, the amount of Ca ion in Ga_2O_3 (UP-Ca(0.001)) was 0.89 mol% to Ga ion. From these results, it is notice that small amount of Ca ion may disperse homogeneously in the bulk of Ga_2O_3(UP-Ca(0.001)). Therefore, the influences of the added Ca ion in the bulk were difficult to observe clearly in the XRD pattern and the SEM photograph. On the other hand, the photocatalyst of Ga_2O_3 (UP-Ca(0.001)) was prepared by the calcination of hydroxide precursor, where the small amount of Ca ion dispersed homogeneously in gallium hydroxide, at 1273 K. This means that the added Ca ion strongly interacted with Ga_2O_3 bulk by the calcination to be a stable state in the Ga_2O_3(UP-Ca(0.001)) photocatalyst. However, further examinations are necessary to learn the state of the Ca ion in the Ga_2O_3 bulk and the influences to overall H_2O splitting in detail.

Table 1. Photocatalytic performance of Ga_2O_3 and Zn (3 mol%) doped Ga_2O_3 prepared with de-ionized water and dilute $CaCl_2$ ultra-pure water solution (0.001 mol/l) to overall H_2O splitting

Photocatalysts[(a)]	Activity / mmol/h[(b)]		AQY at 254 nm / %
	H_2	O_2	
Ga_2O_3(DI)[6]	7.9	3.9	24
Ga_2O_3(UP-Ca0.001)	11	6	--
Zn(3 mol%)-Ga_2O_3(DI)[4]	21	10.5	57
Zn(3 mol%)-Ga_2O_3(UP-Ca0.001)	32	16	71

(a) Photocatalysts are used in combination with the co-catalyst of $Rh_{0.5}Cr_{1.5}O_3$(Rh; 0.5 wt%). Ga_2O_3(DI) is Ga_2O_3 prepared with de-ionized water and Ga_2O_3(UP-Ca0.001) is Ga_2O_3 prepared with $CaCl_2$ ultra-pure water solution having a concentration of 0.001 mol/l.
(b) Photocatalytic activity is evaluated in an inner-irradiation type photoreaction cell under irradiation from a 450 W high-pressure Hg lamp.

The photocatalytic activities of various Ga_2O_3 and Zn added Ga_2O_3 combined with $Rh_{0.5}Cr_{1.5}O_3$ (Rh; 0.5 wt%) as the co-catalyst to overall H_2O splitting are summarized in Table 1. Table 1 shows the photocatalytic activity as the production rate of H_2 and O_2 under irradiation by a 450 W high-pressure Hg lamp in an inner-irradiation type photoreaction cell and the apparent quantum yield (AQY). The apparent quantum yield (AQY) for photocatalytic H_2O splitting was measured by using a top-irradiation type photoreaction cell connected to a closed gas circulation system (dead volume 0.4 l). Irradiation was carried out by a 450 W high-pressure Hg lamp through a water-cooling jacket made of quartz, a 20 mm diameter slit and a bandpass filter (λ=254 nm, obtained from Edmund Optics). The incident photocurrent was measured by using a calibrated silicon photodiode (made by Hamamatsu Photonics) at the level of the water-gas interface, and photon flow was calculated by the photocurrent. The AQY was expressed as a percentage of the number of photons used for H_2O splitting to the number of incident photons.

As shown in Table 1, the photocatalytic activity of Ga_2O_3 noticeably improves if the photocatalyst is prepared with dilute $CaCl_2$ solution. This reflects the influence of Ca ion doping in the bulk of the Ga_2O_3 photocatalyst if Ga_2O_3 is prepared with dilute $CaCl_2$ solution as we discussed above. Moreover, remarkably high photocatalytic activity is achieved on the Zn added Ga_2O_3 if Ga_2O_3 is prepared by applying a dilute $CaCl_2$ solution. The activity is extremely higher than that of the Zn added Ga_2O_3 photocatalyst prepared by the method referred to our previous report. These result also suggest that Ca ion in the preparation atmosphere positively influences the prepared Ga_2O_3 photocatalyst itself to overall H_2O splitting. Then, the AQY of overall photocatalytic H_2O splitting under irradiation at 254 nm was evaluated. The results are also listed in Table 1. As shown in Table 1, the values of the AQY are correlated with the corresponding photocatalytic activities. From the results, it is noticed that the values of AQY of overall H_2O splitting over the Zn added Ga_2O_3 photocatalysts exceed 50%. Particularly, the value of the Zn-Ga_2O_3 (UP-Ca(0.001)) photocatalyst is 71% which is extremely higher than that of NiO/La-$NaTaO_3$, which has been reported as being the photocatalyst showing the highest AQY to overall H_2O splitting[8,9].

The results obtained in this study clearly demonstrate that the addition of very small amount of $CaCl_2$ under the preparation atmosphere makes the photocatalytic performances of Ga_2O_3 itself to the overall H_2O splitting improve further. Particularly, the photocatalytic activity also improved by the addition of Zn ion and the extremely high activity and AQY can be observed as shown in Table 1. The control of the addition of $CaCl_2$ in the preparation atmosphere of Ga_2O_3 is one of the significant factors to improve the photocatalytic activity to the overall H_2O splitting.

In conclusion, the photocatalytic property of $Rh_{0.5}Cr_{1.5}O_3/Ga_2O_3$ to overall H_2O splitting was confirmed to improve by applying Ga_2O_3 prepared by using a dilute $CaCl_2$ solution by the ammonia precipitation method. Moreover, further improvement of photocatalytic performance to H_2O splitting was confirmed on Zn added Ga_2O_3 if Ga_2O_3 which was prepared with dilute $CaCl_2$ solution was used. The photocatalytic activity in an inner-irradiation type photoreaction cell under irradiation of a high-pressure Hg lamp reached over 32 mmol/h for H_2 and 16 mmol/h for O_2 production, respectively, which was extremely higher than the photocatalytic activity we have reported previously. Then, the apparent quantum yield was evaluated under irradiation of monochromatic light at 254 nm using a top irradiation type cell. The value over the $Rh_{0.5}Cr_{1.5}O_3$/Zn-Ga_2O_3(UP-Ca(0.001)) photocatalyst was 71%, while that over $Rh_{0.5}Cr_{1.5}O_3$/Zn-Ga_2O_3(DI) was 57%.

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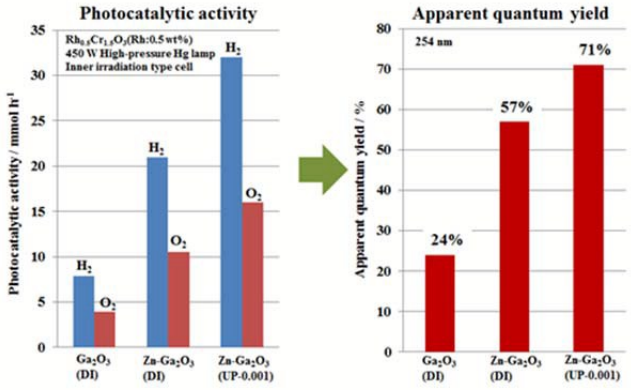

Remarkable activity to photocatalytic overall H_2O splitting was achieved by $Rh_{0.5}Cr_{1.5}O_3$(Rh; 0.5 wt%)/Zn(3 mol%)-Ga_2O_3 when Ga_2O_3 was prepared with dilute $CaCl_2$ solution.