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Remarkably High Apparent Quantum Yield to Overall Photocatalytic H₂O Splitting Achieved by Utilizing Zn Ion Added Ga₂O₃ Prepared with Dilute CaCl₂ solution

Yoshihisa Sakata,*a Takuya Hayashi, Ryō Yasunaga, Nobuyuki Yanaga, and Hayao Imamura

Remarkably high photocatalytic activity to overall H₂O splitting, where the activity was 32 mmol/h for H₂ production and 16 mmol/h for O₂ 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 Rh₀.₅Cr₁.₅O₃(Rh; 0.₅ wt%)/Zn(3 mol%)-Ga₂O₃ when the Ga₂O₃ was prepared with dilute CaCl₂ 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 H₂O 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 H₂O splitting though photocatalytic activity itself is low. Therefore, various investigations, such as examination of the influence of the preparation conditions of Ga₂O₃ 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 Ga₂O₃ combined with a Rh₅Cr₁₅O₃ co-catalyst has been reported to exhibit extremely high photocatalytic activity to overall H₂O splitting, where the preferable state of the photocatalyst was Rh₀.₅Cr₁.₅O₃(Rh; 0.₅ wt%)/Zn(3 mol%)-Ga₂O₃ and activity was 21 mmol/h and 10.₅ mmol/h for H₂ and O₂, 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-NaTaO₃ photocatalyst reaction carried out under nearly the same conditions, and this has been reported as having the highest efficiency to overall H₂O splitting 10,11. However, the detailed quantum yield and the potential to further improve the photocatalytic activity of overall H₂O splitting have not been investigated so far.

From our previous investigations into improvement of the photocatalytic performance of Ga₂O₃ to H₂O splitting 7, 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 Rh₅Cr₁₅O₃ 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 Ga₂O₃. With respect to the latter, Ga₂O₃ 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 H₂O splitting.

In this study, in order to prepare an effective Ga₂O₃ photocatalyst to overall H₂O 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 H₂ and O₂ in time over (a) Rh₀.₅Cr₁.₅O₃(Rh; 0.₅ wt%)/Ga₂O₃(DI), (b) Rh₀.₅Cr₁.₅O₃(Rh; 0.₅ wt%)/Ga₂O₃(UP-Ca(0.001)), and (c) Rh₀.₅Cr₁.₅O₃(Rh; 0.₅ wt%)/Zn(3 mol%)-Ga₂O₃(UP-Ca(0.001)).]
Ga\(_2\)O\(_3\)\(^2\) in the preparation atmosphere of Ga\(_2\)O\(_3\) photocatalyst on overall photocatalytic \(\text{H}_2\text{O}\) splitting. Here, we report on the influence of Ca ion in the preparation of Ga\(_2\)O\(_3\) and the apparent quantum yields of the photocatalytic reaction over various photocatalysts.

The photocatalyst of Ga\(_2\)O\(_3\) was prepared by an ammonia precipitation method by using distilled and de-ionized water (supplied from EYELA Still Ace SA-2100 E1, resistivity 12 M\(\Omega\) cm at 298 K) and aqueous solutions of CaCl\(_2\) dissolved in ultra-pure water (supplied from Millipore, resistivity 18.2 M\(\Omega\) cm at 298 K). Ga(NO\(_3\))\(_3\) \(\cdot\) \(\text{H}_2\text{O}\) (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\(_2\)O\(_3\). Here, Ga\(_2\)O\(_3\) was prepared by using the de-ionized water is shown as Ga\(_2\)O\(_3\)(UP-Ca(0.001)), and that prepared by using CaCl\(_2\) ultra-pure water solution is shown as Ga\(_2\)O\(_3\)(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\(^6\)\(^7\).

Figure 1 shows the evolution of \(\text{H}_2\) and \(\text{O}_2\) in time by overall photocatalytic \(\text{H}_2\text{O}\) splitting over (a) Rh\(_0.5\)Cr\(_1.5\)O\(_3\)(Rh; 0.5 wt%)/Ga\(_2\)O\(_3\)(UP-Ca(0.001)), and Rh\(_0.5\)Cr\(_1.5\)O\(_3\)(Rh; 0.5 wt%)/Ga\(_2\)O\(_3\)(UP-Ca(0.001)). Photocatalytic \(\text{H}_2\text{O}\) 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 \(\text{H}_2\) and \(\text{O}_2\) were collected in a sampling tube and analyzed by a gas chromatograph.

As shown in Fig. 1, \(\text{H}_2\) and \(\text{O}_2\) are produced constantly with relatively high activity from the beginning of irradiation over all photocatalysts. Particularly, photocatalytic activity improved remarkably high photocatalytic activity can be confirmed if Ga\(_2\)O\(_3\)(UP-Ca(0.001)) with added 3 mol% of Zn ion is applied as the photocatalyst. Then, the photocatalytic property of Zn doped Ga\(_2\)O\(_3\)(UP-Ca(0.001)) to overall \(\text{H}_2\text{O}\) splitting was examined in detail.

![Fig. 2. Photocatalytic evolution of \(\text{H}_2\) and \(\text{O}_2\) in time over Rh\(_0.5\)Cr\(_1.5\)O\(_3\)(Rh; 0.5 wt%)/Zn(3 mol%)-Ga\(_2\)O\(_3\)(UP-Ca(0.001))](image)

Figure 2 shows the evolution of \(\text{H}_2\) and \(\text{O}_2\) in time by overall photocatalytic \(\text{H}_2\text{O}\) splitting over Rh\(_0.5\)Cr\(_1.5\)O\(_3\)(Rh; 0.5 wt%)/Zn(3 mol%)-Ga\(_2\)O\(_3\)(UP-Ca(0.001)). As shown in Fig. 2, \(\text{H}_2\) and \(\text{O}_2\) were produced in the stoichiometric ratio with remarkably high photocatalytic activity and the pressure of the system became 1 atm after 150 min. Moreover, remarkably high photocatalytic activity can be confirmed if the reaction was restarted repeatedly. The values of the activity in a steady state were 32 mmol/h and 16 mmol/h for \(\text{H}_2\) and \(\text{O}_2\), 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\(_2\)O\(_3\)(DI), where the reaction was carried out in the same reaction system in the present study, which has been reported previously\(^5\). Accordingly, the effect of the concentration of CaCl\(_2\) in the preparation solution of Ga\(_2\)O\(_3\) to the photocatalytic activity of Rh\(_0.5\)Cr\(_1.5\)O\(_3\)(Rh; 0.5 wt%)/Zn(3 mol%)-Ga\(_2\)O\(_3\)(UP-Ca) was examined.

![Fig. 3. Photocatalytic activity of overall \(\text{H}_2\text{O}\) splitting on Rh\(_0.5\)Cr\(_1.5\)O\(_3\)(Rh; 0.5 wt%)/Zn(3 mol%)-Ga\(_2\)O\(_3\)(UP-Ca) as a function of the concentration of CaCl\(_2\) in the solution for preparing Ga\(_2\)O\(_3\)](image)
photograph compared with those of Ga2O3(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 Ga2O3(UP-Ca(0.001)) was examined by inductively coupled plasma optical emission spectrometry (ICP-OES; Parkin Elmer Optima 4300DV). From the result of ICP, the amount of Ca ion in Ga2O3(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 Ga2O3(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 Ga2O3(UP-Ca(3.001)) 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 Ga2O3 bulk by the calcination to be a stable state in the Ga2O3(UP-Ca(0.001)) photocatalyst. However, further examinations are necessary to learn the state of the Ca ion in the Ga2O3 bulk and the influences to overall H2O splitting in detail.

Table 1. Photocatalytic performance of Ga2O3 and Zn (3 mol%) doped Ga2O3 prepared with de-ionized water and dilute CaCl2 ultra-pure water solution (0.001 mol/l) to overall H2O splitting

<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>Activity / mmol/h</th>
<th>AQY at 254 nm / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga2O3(DI)7b</td>
<td>7.9</td>
<td>3.9 24</td>
</tr>
<tr>
<td>Ga2O3(UP-Ca0.001)</td>
<td>11 6</td>
<td>--</td>
</tr>
<tr>
<td>Zn(3 mol%)Ga2O3(DI)7b</td>
<td>21 10.5</td>
<td>57</td>
</tr>
<tr>
<td>Zn(3 mol%)Ga2O3(UP- Ca0.001)</td>
<td>32 16</td>
<td>71</td>
</tr>
</tbody>
</table>

(a) Photocatalysts are used in combination with the co-catalyst of Rh0.5Cr1.5O3 (Rh: 0.5 wt%). Ga2O3(DI) is Ga2O3 prepared with de-ionized water and Ga2O3(UP-Ca0.001) is Ga2O3 prepared with CaCl2 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 Ga2O3 and Zn added Ga2O3 combined with Rh0.5Cr1.5O3 (Rh: 0.5 wt%) as the co-catalyst to overall H2O splitting are summarized in Table 1. Table 1 shows the photocatalytic activity as the production rate of H2 and O2 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 H2O 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 H2O splitting to the number of incident photons.

As shown in Table 1, the photocatalytic activity of Ga2O3 noticeably improves if the photocatalyst is prepared with dilute CaCl2 solution. This reflects the influence of Ca ion doping in the bulk of the Ga2O3 photocatalyst if Ga2O3 is prepared with dilute CaCl2 solution as we discussed above. Moreover, remarkably high photocatalytic activity is achieved on the Zn added Ga2O3 if Ga2O3 is prepared by applying a dilute CaCl2 solution. The activity is extremely higher than that of the Zn added Ga2O3 photocatalyst prepared by the method referred to our previous report. These results also suggest that Ca ion in the preparation atmosphere positively influences the prepared Ga2O3 photocatalyst itself to overall H2O splitting. Then, the AQY of overall photocatalytic H2O 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 H2O splitting over the Zn added Ga2O3 photocatalysts exceed 50%. Particularly, the value of the Zn-Ga2O3 (UP-Ca(0.001)) photocatalyst is 71% which is extremely higher than that of NiO/La-NaTaO3, which has been reported as being the photocatalyst showing the highest AQY to overall H2O splitting 8,9.

The results obtained in this study clearly demonstrate that the addition of very small amount of CaCl2 under the preparation atmosphere makes the photocatalytic properties of Ga2O3 itself as well as the overall H2O splitting improve further. Particularly, the photocatalytic activity also improved by the addition of Zn ion and the extremely high activity and AQY can be as observed as shown in Table 1. The control of the addition of CaCl2 in the preparation atmosphere of Ga2O3 is one of the significant factors to improve the photocatalytic activity to the overall H2O splitting.

In conclusion, the photocatalytic property of Rh0.5Cr1.5O3/Ga2O3 to overall H2O splitting was confirmed to improve by applying Ga2O3 prepared by using a dilute CaCl2 solution by the ammonia precipitation method. Moreover, further improvement of photocatalytic performance to H2O splitting was confirmed on Zn added Ga2O3 if Ga2O3 which was prepared with dilute CaCl2 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 H2 and 16 mmol/h for O2 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 Rh0.5Cr1.5O3/Zn-Ga2O3(UP-Ca(0.001)) photocatalyst was 71%, while that over Rh0.5Cr1.5O3/Zn-Ga2O3(DI) was 57%.

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Notes and references

8 X. Wang, Q. Xu, F. Fan, X. Wang, M. Li, Z. Feng, and C. Li, Chem. Asian J. 2013, 8, 2189
Remarkable activity to photocatalytic overall H₂O splitting was achieved by Rh₀.₅Cr₁.₅O₃ (Rh: 0.5 wt%)/Zn(3 mol%)-Ga₂O₅ when Ga₂O₅ was prepared with dilute CaCl₂ solution.