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Solar water splitting over Rh₄₋₅Cr₁₋₅O₃-loaded AgTaO₃ of a valence-band-controlled metal oxide photocatalyst
Solar water splitting over Rh\textsubscript{0.5}Cr\textsubscript{1.5}O\textsubscript{3}-loaded AgTaO\textsubscript{3} of a valence-band-controlled metal oxide photocatalyst†

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Improvement of water splitting performance of AgTaO\textsubscript{3} (BG 3.4 eV) of a valence-band-controlled photocatalyst was examined. Survey of cocatalysts revealed that a Rh\textsubscript{0.5}Cr\textsubscript{1.5}O\textsubscript{3} cocatalyst was much more effective than Cr\textsubscript{2}O\textsubscript{3}, RuO\textsubscript{2}, NiO and Pt for water splitting into H\textsubscript{2} and O\textsubscript{2} in a stoichiometric amount. The optimum loading amount of the Rh\textsubscript{0.5}Cr\textsubscript{1.5}O\textsubscript{3} cocatalyst was 0.2 wt%. The apparent quantum yield (AQY) at 340 nm of the optimized Rh\textsubscript{0.5}Cr\textsubscript{1.5}O\textsubscript{3}(0.2 wt%)/AgTaO\textsubscript{3} photocatalyst reached to about 40%. Rh\textsubscript{0.5}Cr\textsubscript{1.5}O\textsubscript{3}(0.2 wt%)/AgTaO\textsubscript{3} gave a solar to hydrogen conversion efficiency (STH) of 0.13% for photocatalytic water splitting under simulated sunlight irradiation. Bubbles of gases evolved by the solar water splitting were visually observed under atmospheric pressure at room temperature.

Introduction

Photocatalytic solar water splitting is an important reaction because it has the potential for solving resources, energy and environmental issues. Hence, many researchers have aimed to develop water splitting systems of a one-step photoexcitation type and a two-step photoexcitation type (Z-scheme) with visible-light-driven powdered photocatalysts.1–4 The simplicity of the one-step photoexcitation type will be an advantage in practical use. Domen and co-workers have reported that (oxy)nitride and oxysulfide photocatalysts such as GaN–ZnO,7–8 ZnGeN\textsubscript{2}–ZnO,9 LaMg\textsubscript{11}Ta\textsubscript{12}O\textsubscript{33}N\textsubscript{11}–13 TaON,14 CaTaO\textsubscript{3}N\textsubscript{15} TaN\textsubscript{2} (ref. 16) and Y\textsubscript{2}Ti\textsubscript{2}O\textsubscript{5}S\textsubscript{2} (ref. 17) show activities for one-step photoexcitation type water splitting under visible light irradiation. We have also reported that Rh,Sb-codoped SrTiO\textsubscript{3} of a metal oxide photocatalyst shows the water splitting activity under visible light irradiation by loading of an IrO\textsubscript{2} cocatalyst.18 Although above visible-light-responsive photocatalysts split water under sunlight irradiation, their solar energy conversion efficiencies (solar to hydrogen conversion efficiency, STH) do not reach the level for practical use due to low apparent quantum yields (AQY). In terms of the high AQY, NiO-loaded La-doped NaTaO\textsubscript{3} (ref. 19) (BG 4.1 eV), Rh\textsubscript{0.5}Cr\textsubscript{1.5}O\textsubscript{3}-loaded Zn,Ca-codoped Ga\textsubscript{2}O\textsubscript{3} (ref. 20) (BG 4.6 eV) and MoO\textsubscript{3},RhCrO\textsubscript{2}-coloaded Al-doped SrTiO\textsubscript{3} (ref. 21) (BG 3.2 eV) show the AQYS of 56% at 270 nm, 71% at 254 nm and 69% at 365 nm, for photocatalytic water splitting under UV irradiation, respectively. However, only Al-doped SrTiO\textsubscript{3} can respond to sunlight (λ > 300 nm) with STH of 0.4%.22 Thus, the development of sunlight-driven photocatalysts with one-step photoexcitation for water splitting is an important research topic.

We have reported that a AgTaO\textsubscript{3} photocatalyst (BG 3.4 eV) shows water splitting activity under UV irradiation by loading of a NiO cocatalyst.23 The characteristics of AgTaO\textsubscript{3} is the valence band maximums formed by Ag 4d orbitals which are located above the bands formed by O 2p orbitals, and hence the band gap of AgTaO\textsubscript{3} is relatively narrow among the metal oxides containing Ta. AgTaO\textsubscript{3} is expected to respond to sunlight judging from the band gap of 3.4 eV, while the water splitting under sunlight irradiation has not been achieved yet. Moreover, the crystal structure of perovskite for AgTaO\textsubscript{3} is the same as that for SrTiO\textsubscript{3} and NaTaO\textsubscript{3} photocatalysts with high activities for water splitting. These backgrounds motivate us to investigate solar water splitting using the AgTaO\textsubscript{3} photocatalyst.

A cocatalyst is one of the most effective factors for improvement of the photocatalytic activity. Actually, the water splitting activity of AgTaO\textsubscript{3} is drastically improved by loading of a NiO cocatalyst which is widely used in water splitting over metal oxides.24 Recently, Rh\textsubscript{0.5}Cr\textsubscript{1.5}O\textsubscript{3} has also arisen as a potential candidate cocatalyst for water splitting over metal oxides.25,26 In the present study, we investigated the loading effect of various cocatalysts on water splitting over AgTaO\textsubscript{3}. Solar water splitting was also demonstrated using the AgTaO\textsubscript{3} with the optimized cocatalyst.

Experimental

Preparation of photocatalysts

AgTaO\textsubscript{3} was synthesized by a solid-state reaction using Ag\textsubscript{2}O (Kanto Chemical; 99.0%) and Ta\textsubscript{2}O\textsubscript{5} (Rare Metallic; 99.99%) as
starting materials. The starting materials were mixed in an alumina mortar in a ratio of Ag : Ta = 1 + x : 1 (x = 0, 0.03, 0.05, 0.07). The mixture was calcined in air at 1173–1373 K for 5–20 h in an alumina crucible. The calcined materials were washed with 1 mol L⁻¹ of an aqueous HNO₃ solution in ultrasonication for 1 h in order to remove Ag metals deposited on the surface of AgTaO₃.

A Pt cocatalyst was loaded in situ by a photoelectrodeposition method using an aqueous H₂PtCl₆ (Tanaka Kikinzoku; 37.7 wt% as Pt) solution. NiO,²¹ RuO₂ (ref. 24) and Cr₂O₃ (ref. 25) of cocatalysts were loaded on AgTaO₃ photocatalysts by an impregnation method using Ni(NO₃)₂·6H₂O (Wako Pure Chemical; 98.0%), RuCl₃·3H₂O (Aldrich; 99%), Cr(NO₃)₃·9H₂O (Kanto Chemical; 98.0–103.0%). AgTaO₃ powder was suspended in aqueous solutions dissolving Ni(NO₃)₂ or Cr(NO₃)₃, and an acetone solution dissolving RuCl₃·3H₂O in porcelain crucibles. The AgTaO₃-suspended solutions were dried up on a water bath and subsequently calcined in an electric furnace with conditions of 543 K–1 h for NiO, 673 K–2 h for RuO₂ and 623 K–1 h for Cr₂O₃. Rh₀.₅Cr₁.₅O₃ (ref. 25) cocatalyst was loaded by a simple impregnation method using Cr(NO₃)₃·9H₂O and Rh(NO₃)₃ (Kanto Chemical; >80.0% as anhydrous). AgTaO₃-suspended aqueous solution containing both Rh(NO₃)₃ and Cr(NO₃)₃ was dried up and subsequently calcined at 623 K for 1 h. It is reported that Rh₀.₅Cr₁.₅O₃ of a mixed oxide is naturally formed on a photocatalyst by this process.²⁶ The loading amount of Rh₀.₅Cr₁.₅O₃ was controlled by adjusting the amount of starting materials.

Characterization

The crystal structure of the synthesized AgTaO₃ was identified by powder X-ray diffraction (Rigaku; MiniFlex6000). The elemental composition of the synthesized AgTaO₃ was measured by an X-ray fluorescence spectrometer (Rigaku; NEX DE). A Diffuse reflection spectrum was measured using a UV-vis-NIR spectrometer with an integrating sphere (Jasco; UbestV-570) and was converted from refection to absorbance spectrum (Fig. S3†). The peaks due to the surface plasmonic resonance a little bit smaller than that before the washing (Fig. S2†). The absorption due to the surface plasmonic resonance was measured using a silicon detector (Asahi Spectra). The photon flux of the monochromatic light through the long-pass filters was measured using a silicon diode head (OPHIR; PD300-UV head and NOVA display). An AQY and a solar to hydrogen conversion efficiency (STH) were estimated using the following eqn (2) and (3).

\[
\text{AQY} = 100 \times \frac{[\text{the number of reacted electrons or holes}]}{[\text{the number of incident photons}]} = 100 \times \frac{[\text{the number of evolved H₂ molecules}]}{[\text{the molar quantity of AgTaO₃}]} \times \frac{2}{[\text{the number of incident photons}]} \quad (2)
\]

\[
\text{STH} = 100 \times \frac{[\Delta G'(\text{H₂O})/\text{kJ mol}^{-1}]}{[\text{rate of H₂ evolution/\text{mol h}^{-1}]} \times \text{[irradiation time/s]} \times [\text{solvent energy (AM1.5G)/mW cm}^{-2}]} \times \frac{[\text{irradiation area/cm}^{2}]}{237} \times \frac{[\text{rate of H₂ evolution/\text{mol h}^{-1}]} \times (3600 \times 100 \times 25) \times 100} \quad (3)
\]

Results and discussion

XRD measurement confirmed that trigonal AgTaO₃ with a perovskite structure was successfully synthesized in a single phase as previously reported (Fig. S1†). The peaks due to metallic Ag were not observed in XRD patterns of AgTaO₃ both before and after washing with an aqueous HNO₃ solution. However, the absorption due to the surface plasmonic resonance of Ag was observed in diffuse reflectance spectra of the AgTaO₃ before and after the washing (Fig. S2†). The absorption due to the surface plasmonic resonance after the washing was a little bit smaller than that before the washing. Therefore, metallic Ag on the surface would be removed by the washing but the amount of removed Ag was quite small. Actually, atomic ratios of Ag to Ta in the AgTaO₃ after the washing were calculated to be 1.00 and 0.99 from XPS and XRF measurements, respectively. These results indicate that the ratios of Ag to Ta on the surface and in the bulk were almost stoichiometric even if after the washing. The absorption edge of AgTaO₃ was around 380 nm in a diffuse reflectance spectrum (Fig. S3†), indicating 3.4 eV of the band gap. Scanning electron microscope observation revealed that the size of AgTaO₃ particles was from several hundreds nm to several μm (Fig. S4†).

Table 1 shows the activities for photocatalytic water splitting over AgTaO₃, loaded with various cocatalysts under UV irradiation. Non-loaded AgTaO₃ produced only a small amount of H₂.
Without O2 evolution. In other words, water splitting did not proceed. In contrast, all AgTaO3 loaded with various cocatalysts produced both H2 and O2. However, the amount of evolved H2 was more than a stoichiometric amount when NiO, RuO2 and Pt were loaded. When Cr2O3 and Rh0.5Cr1.5O3 were loaded, the stoichiometric amounts of H2 and O2 evolved, indicating that ideal water splitting proceeded. In particular, the activity of AgTaO3 was greatly improved by loading of the Rh0.5Cr1.5O3 cocatalyst. This result is appropriate because Rh0.5Cr1.5O3 is known as an effective cocatalyst for photocatalytic water splitting. It is reported that Cr2O3 does not work as a cocatalyst for photocatalytic water splitting but Ag coloaded with Cr works as a cocatalyst.25 In the present case, only Cr2O3-loaded AgTaO3 showed the water splitting activity. This is probably because a small amount of metallic Ag still remained on the surface of AgTaO3 even after washing with an aqueous HNO3 solution and a Ag–Cr cocatalyst was formed by loading of Cr2O3 as an effective cocatalyst. We optimized the loading amount of the Rh0.5Cr1.5O3 cocatalyst and synthesis conditions of AgTaO3. The water splitting activity of AgTaO3 slightly depended on synthesis conditions and 1273 K – 15 h was the best condition for the activity (Table S1†). In addition, the activity was insensitive for an excess amount of Ag. On the other hand, the activity much depended on the loading amount of Rh0.5Cr1.5O3 cocatalyst and 0.2 wt% was optimum (Table 1). The optimized Rh0.5Cr1.5O3(0.2 wt%)/AgTaO3 stably and continuously produced H2 and O2 using a Xe lamp (Fig. 1).

Table 1 Photocatalytic water splitting over AgTaO3 loaded with various cocatalysts under UV irradiation

<table>
<thead>
<tr>
<th>Cocatalyst (wt%)</th>
<th>Loading method</th>
<th>H2 (µmol h⁻¹)</th>
<th>O2 (µmol h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>—</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>Rh0.5Cr1.5O3(0.05)</td>
<td>Impregnation (623 K – 1 h)</td>
<td>56</td>
<td>28</td>
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<tr>
<td>Rh0.5Cr1.5O3(0.1)</td>
<td>Impregnation (623 K – 1 h)</td>
<td>38</td>
<td>162</td>
</tr>
<tr>
<td>Rh0.5Cr1.5O3(0.2)</td>
<td>Impregnation (623 K – 1 h)</td>
<td>400</td>
<td>192</td>
</tr>
<tr>
<td>Rh0.5Cr1.5O3(0.3)</td>
<td>Impregnation (623 K – 1 h)</td>
<td>217</td>
<td>111</td>
</tr>
<tr>
<td>Cr2O3(0.13)</td>
<td>Impregnation (623 K – 1 h)</td>
<td>1.8</td>
<td>0.9</td>
</tr>
<tr>
<td>RuO2(0.2)</td>
<td>Impregnation (673 K – 2 h)</td>
<td>1.6</td>
<td>0.5</td>
</tr>
<tr>
<td>NiO(0.2)</td>
<td>Impregnation (543 K – 1 h)</td>
<td>18</td>
<td>4</td>
</tr>
<tr>
<td>Pt(0.2)</td>
<td>Photodeposition (in situ)</td>
<td>45</td>
<td>4</td>
</tr>
</tbody>
</table>

*Photocatalyst: 0.3 g, reactant solution: distilled water (120 mL), cell: top-irradiation cell with a Pyrex window, light source: 300 W Xe-arc lamp (λ > 300 nm).

That for Rh2O3 (308.3 eV) but that for Rh0.5Cr1.5O3 (308.9 eV).26 The slightly positive shift in the binding energy was also observed for the Rh0.5Cr1.5O3 loaded on GaN-ZnO (309.1 eV).26 These results indicate that the loaded Rh0.5Cr1.5O3 on AgTaO3 in the present study was similar to that on GaN–ZnO. Additionally, the TEM image of Rh0.5Cr1.5O3 cocatalysts did not change so much after photocatalytic water splitting. On the other hand, in the XPS spectra, the Rh 3d5/2 peak for Rh0.5Cr1.5O3 loaded on GaN–ZnO was more than a stoichiometric amount when NiO, RuO2 and Pt were loaded. When Cr2O3 and Rh0.5Cr1.5O3 were loaded, the stochiometric amounts of H2 and O2 evolved, indicating that ideal water splitting proceeded. This observation indicated that the photocatalyst was activated by partial reduction of Rh in loaded Rh0.5Cr1.5O3 cocatalyst to the metallic form during the induction period in Fig. 1.

An action spectrum of water splitting on the optimized Rh0.5Cr1.5O3(0.2 wt%)/AgTaO3 was measured, as shown in Fig. 3. The maximum AQY was 38% at 340 nm. As far as we know, the AQY is the highest among one-step photoexcitation type water splitting using metal oxide photocatalysts with valence bands consisting of metal cation orbitals. In order to compare the activity of Rh0.5Cr1.5O3(0.2 wt%)/AgTaO3 with that

Fig. 1 Photocatalytic water splitting over Rh0.5Cr1.5O3(0.2 wt%)/AgTaO3. AgTaO3 was synthesized by a solid state reaction at 1273 K for 15 h without excess Ag. Rh0.5Cr1.5O3 was loaded by an impregnation method at 623 K for 1 h. Photocatalyst: 0.3 g, reactant solution: distilled water (120 mL), cell: top-irradiation cell with a Pyrex window, light source: 300 W Xe-arc lamp (λ > 300 nm).

Fig. 2 TEM images of Rh0.5Cr1.5O3(0.2 wt%)/AgTaO3 (a) before and (b) after photocatalytic water splitting under UV irradiation using a 300 W Xe-arc lamp. AgTaO3 was synthesized by a solid state reaction at 1273 K for 15 h without excess Ag. Rh0.5Cr1.5O3 was loaded by an impregnation method at 623 K for 1 h.
of highly active NiO/NaTaO₃:La₄ photocatalytic water splitting over Rh₀.₅Cr₁.₅O₃(0.₂ wt%)/AgTaO₃ was carried out in an inner-irradiation reaction cell made of quartz equipped with a 400 W high pressure Hg-lamp using 1 g of photocatalyst powder suspended in 340 mL of distilled water, as shown in Fig. 4. Evolution rates of H₂ and O₂ were 20 mmol h⁻¹ and 10 mmol h⁻¹, respectively. The activity of Rh₀.₅Cr₁.₅O₃(0.₂ wt%)/AgTaO₃ was similar to that of NiO/NaTaO₃:La₄ This reaction catalytically proceeded because TON was 47. Thus, Rh₀.₅Cr₁.₅O₃(0.₂ wt%)/AgTaO₃ interestingly showed the high activity for water splitting even without doping unlike La-doped NaTaO₃, Zn,Ca-codoped Ga₂O₃, and Al-doped SrTiO₃, suggesting that AgTaO₃ itself has good potential for water splitting. One possible explanation about the potential of AgTaO₃ will be the distortion of its crystal structure. The Ta–O–Ta bond angle of AgTaO₃ (164 degree) is very similar to that of NaTaO₃ (163 degree). The similarity in the lattice distortion between AgTaO₃ and NaTaO₃ causes a similar property of a conduction band of AgTaO₃ to a highly active NaTaO₃. Therefore, mobility of photogenerated charges and a reduction potential of water reduction of AgTaO₃ should be similar to those of NaTaO₃. Additionally, the valence band of NaTaO₃ is formed by only O 2p orbitals, whereas that of AgTaO₃ is formed by hybridized orbitals between Ag 4d and O 2p. Therefore, photogenerated holes in AgTaO₃ could migrate more easily than those in NaTaO₃. These positive factors in AgTaO₃ gave high photocatalytic activity.

Water splitting proceeded over the Rh₀.₅Cr₁.₅O₃(0.₂ wt%)/AgTaO₃ photocatalyst even under simulated sunlight irradiation, as shown in Fig. 5. H₂ and O₂ were steadily evolved with the rates of 486 mL m⁻² h⁻¹ and 247 mL m⁻² h⁻¹, respectively. The STH was estimated to be 0.13%. Additionally, we were able to watch evolved bubbles when Rh₀.₅Cr₁.₅O₃(0.₂ wt%)/AgTaO₃ on the bottom of the reaction cell was irradiated with simulated sunlight under 1 atm at room temperature. The STH of Rh₀.₅Cr₁.₅O₃(0.₂ wt%)/AgTaO₃ is lower than those of TiO₂/CoOOH/RhCrO₃/ SrTiO₃:Al (STH = 0.4%) and SrTiO₃:RhₙLaₙAu-BiVO₄:Mo photocatalyst sheet (STH = 1.1%), whereas it is higher than those of Z-schematic water splitting using SrTiO₃:Rh of a H₂-evolving photocatalyst, BiVO₄ of an O₂-evolving photocatalyst, and ionic electron mediators such as Fe⁴⁺/²⁺ and [Co(bpy)]³⁺/²⁺. Thus, we successfully achieved highly efficient one-step photoexcitation type solar water splitting using Rh₀.₅Cr₁.₅O₃(0.₂ wt%)/AgTaO₃ of a valence-band-controlled metal oxide photocatalyst.

**Conclusions**

Rh₀.₅Cr₁.₅O₃(0.₂ wt%)-loaded AgTaO₃ has arisen as a photocatalyst for solar water splitting in a suspension system. The
AQY of Rh$_{0.5}$Cr$_{1.5}$O$_3$(0.2 wt%)/AgTaO$_3$ was about 40% at 340 nm. The activity of Rh$_{0.5}$Cr$_{1.5}$O$_3$(0.2 wt%)/AgTaO$_3$ was similar to that of NiO/NaTaO$_2$:La under the same experimental condition, using 1 g of photocatalyst powder suspended in 340 mL of distilled water, in an inner-irradiation cell made of quartz equipped with a 400 W high pressure Hg-lamp. AgTaO$_3$ seems to have good potential for water splitting because Rh$_{0.5}$Cr$_{1.5}$-O$_3$(0.2 wt%)/AgTaO$_3$ showed the high AQY even without doping of elements. Rh$_{0.5}$Cr$_{1.5}$O$_3$(0.2 wt%)/AgTaO$_3$ also showed the photocatalytic activity for water splitting under simulated sunlight irradiation with the STH of 0.13%. The AQY and STH of Rh$_{0.5}$Cr$_{1.5}$O$_3$(0.2 wt%)/AgTaO$_3$ were the highest for one-step photoexcitation type water splitting using a valence-band-controlled metal oxide photocatalyst. Thus, it was clarified that a metal oxide photocatalyst with a valence band consisting of metal cation orbitals rather than O 2p could be utilized as a photocatalyst for highly efficient water splitting. The knowledge is expected to be applied to visible-light-driven photocatalysts.

Conflicts of interest
There are no conflicts to declare.

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Notes and references