Selective loading of platinum cocatalyst onto zinc rhodium oxide in a silver-inserted heterojunction overall water-splitting photocatalyst consisting of zinc rhodium oxide and bismuth vanadium oxide

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Platinum (Pt) was selectively photodeposited onto zinc rhodium oxide (ZnRh2O4) to serve as a hydrogen (H2)-evolution photocatalyst in a silver (Ag)-inserted ZnRh2O4 and bismuth vanadium oxide (Bi4V2O11) solid-state photocatalyst (ZnRh2O4/Ag/Bi4V2O11). The amount of deposited Pt was controlled by the photodeposition time to generate Pt-loaded ZnRh2O4/Ag/Bi4V2O11 (Pt/ZnRh2O4/Ag/Bi4V2O11) containing up to 0.17 wt% of Pt cocatalyst. The prepared Pt/ZnRh2O4/Ag/Bi4V2O11 photocatalysts were able to catalyze the overall pure-water splitting reaction under irradiation with red light at a wavelength of 700 nm and enhanced the stoichiometric evolution of H2 and O2 from water at Pt amounts exceeding 0.12 wt% of Pt. The apparent quantum efficiency of the water-splitting reaction was highest at 0.17 wt% of Pt. In addition to the loading amount of Pt, the loading of Pt as Pt⁰ (metallic Pt) is crucial for enhancing the water-splitting activity of Pt/ZnRh2O4/Ag/Bi4V2O11.

Key-words : Overall pure water-splitting, Platinum, Cocatalyst, Two-step photoexcitation

1. Introduction

Several photocatalysts and photocatalytic systems aimed at water splitting have been investigated because the generated hydrogen (H2) gas is a versatile and clean energy carrier. Since the first report of overall water splitting at wavelengths up to ~480 nm over a solid solution of gallium nitride-zinc oxide and a mixed oxide of rhodium and chromium as a cocatalyst, most research on powdered photocatalysts has focused on increasing the sensitivity of these one-step systems to longer wavelengths of visible light to allow the more efficient utilization of solar energy. Recently, a yttrium titanium oxysulfide (Y2Ti2O5S2) was demonstrated to be capable of overall water splitting under irradiation at ~630 nm, which is the longest wavelength reported to date for a one-step photocatalytic system.

As an alternative to one-step photocatalytic systems, two-step systems, which combine H2-evolution photocatalyst (H2 photocatalyst) and O2-evolution photocatalyst (O2 photocatalyst), are also able to split water under visible-light irradiation. However, because such two-step systems, which are termed “Z-scheme”, require the presence of a suitable redox mediator, such as iodate ion (IO3⁻)/iodide ion (I⁻) or ferric ion (Fe³⁺)/ferrous ion (Fe²⁺), these systems are not able to split pure water.

To achieve overall pure-water splitting under irradiation with visible light, we developed two-step solid-state Z-scheme photocatalysts by inserting either silver (Ag) or gold (Au) as an electron mediator between zinc rhodium oxide (ZnRh2O4, bandgap (Eg) of 1.2 eV) as the H2 photocatalyst and bismuth vanadate (Bi4V2O11, Eg of 1.7 eV) as the O2 photocatalyst. In these systems, which were designated ZnRh2O4/Ag/Bi4V2O11 and ZnRh2O4/Au/Bi4V2O11, overall pure-water splitting proceeded via Ag or Au, which mediated the transfer of photoexcited electrons from the conduction band of Bi4V2O11 to the valence band of ZnRh2O4. These photocatalysts were capable of utilizing visible light at wavelengths up to 740 nm, which represents nearly the entire visible light spectrum and to our knowledge, is the longest wavelength reported to date. Several recent studies have described similar heterojunction photocatalysts, demonstrating the potential of these systems for overall water splitting.

In our previous work, the selective photodeposition of Ag or platinum (Pt) as H2-favorable cocatalysts onto ZnRh2O4 in ZnRh2O4/Ag/Bi4V2O11 resulted in enhanced stoichiometric H2 and O2 evolution from pure water. Here, we evaluated the dependence of the apparent quantum efficiency (AQE) of the overall water splitting activity on the amount and valency of Pt.

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FULL PAPER

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2. Experimental section

2.1 Sample preparation

ZnRh$_2$O$_4$ and Bi$_4$V$_2$O$_{11}$ powders were synthesized by a solid-state reaction method. As starting materials, ZnO (Wako, purity 99.0%) and Rh$_2$O$_3$ powders (Kanto Kagaku, purity 99.9%) were used to synthesize ZnRh$_2$O$_4$, and Bi$_2$O$_3$ (Kanto Kagaku, purity 99.9%) and V$_2$O$_5$ powders (Kanto Kagaku, purity 99.0%) were used to synthesize Bi$_4$V$_2$O$_{11}$. Stoichiometric amounts of both pairs of starting materials were thoroughly mixed, and the resulting mixtures were calcined in air at 1150 °C for 24 h and 850 °C for 8 h to obtain ZnRh$_2$O$_4$ and Bi$_4$V$_2$O$_{11}$ powders, respectively. The Bi$_4$V$_2$O$_{11}$ powder was subsequently soaked in distilled water for 20 h with constant stirring, followed by filtration and drying at 65 °C for 12 h.

Photodeposition of Pt was conducted by dispersing 80 mg ZnRh$_2$O$_4$/Ag/Bi$_4$V$_2$O$_{11}$ in 40 mL formaldehyde solution (HCHO, 25 vol%) containing 10 mL of 8.65 mM hexachloroferroic acid (H$_2$PtCl$_6$.6H$_2$O, >98.5%; Kanto Kagaku) aqueous solution for 5 min. The powder was then filtered, washed thoroughly with distilled water, and dried at 65 °C overnight.

2.2 Characterizations

The crystal structures of the prepared powders were determined by X-ray diffraction (XRD) using a PW-1700 instrument (Panalytical). Ultraviolet–visible absorption (UV–vis) spectra were obtained by the diffuse reflectance method using a spectrometer (V-650, Jasco) with barium sulfate (BaSO$_4$) as the reflectance standard. The amounts of photodeposited Pt were evaluated by inductively coupled plasma optical emission spectrometry (ICP-OES, SPS3500 DD, Hitachi). The Bi 4f, V 2p, Zn 2p, Rh 3d, Ag 3d, and Pt 4f core levels were measured by X-ray photoelectron spectroscopy (XPS; Axis-Ultra, Shimadzu). The XPS peaks were calibrated using the C 1s peak derived from a hydrocarbon surface contaminant with a binding energy of 284.5 eV. To quantitatively evaluate the valencies of Ag and Pt contained in the photocatalyst, peak deconvolution was performed using a Gaussian lineshape.

2.3 Photocatalytic water splitting tests

Photocatalytic overall water splitting tests were performed in a gas-closed circulation system. The composite photocatalysts (60 mg) were suspended in 12 mL pure water (distilled water, pH unadjusted) under constant magnetic stirring in an argon atmosphere (50 kPa) after repeated evacuation until reaching 2.5 Pa. An LED lamp with a wavelength of 700 nm (LEDH60-700, Hamamatsu Photonics) was used for light irradiation. The amounts of evolved H$_2$ and O$_2$ were monitored using an online gas chromatograph (GC-8A, Shimadzu).

AQE was calculated using the amount of evolved H$_2$ and the equation AQE (%) = 100 × $\frac{4}{2}$ $\times$ H$_2$ generation rate/incident photon rate, because H$_2$ generation in two-step systems is a four-electron process.

3. Results and discussion

3.1 Characterization

The XRD patterns of Pt/ZnRh$_2$O$_4$/Ag/Bi$_4$V$_2$O$_{11}$ after 35 h of Pt photodeposition as a representative and bare ZnRh$_2$O$_4$/Ag/Bi$_4$V$_2$O$_{11}$ were first compared (Fig. 1). The XRD peaks of both samples appeared similar and mainly corresponded to ZnRh$_2$O$_4$ and Bi$_4$V$_2$O$_{11}$, with the trace peaks being ascribed to an unknown Ag oxide (likely AgVO$_3$). Other photodeposited photocatalysts indicated the similar XRD patterns. Notably, peaks corresponding to Ag and Pt peaks were not observed, indicating that the amounts of residual Ag and photodeposited Pt were too low for detection. These observations are consistent with those reported previously. The XPS results demonstrated that Ag existed as Ag$^0$ (metallic Ag) and Pt as Pt$^0$, Pt$^{2+}$, and Pt$^{3+}$. The implications of these findings are discussed below.

The UV–vis diffuse reflection spectra of bare ZnRh$_2$O$_4$/Ag/Bi$_4$V$_2$O$_{11}$ and Pt/ZnRh$_2$O$_4$/Ag/Bi$_4$V$_2$O$_{11}$ (35-h photo-deposition) were next examined (Fig. 2). The Pt/ZnRh$_2$O$_4$/Ag/Bi$_4$V$_2$O$_{11}$ spectrum had greater 100-reflectance than that of bare ZnRh$_2$O$_4$/Ag/Bi$_4$V$_2$O$_{11}$ in the longer wavelength region, a property that is attributable to the photodeposited Pt.

Elemental analysis by ICP-OES indicated that the Pt amounts were 0.10, 0.12, 0.17, and 0.14 wt% containing...
in the photocatalysts with Pt photodeposition times of 4, 20, 35, and 50 h, respectively (Table 1). The amount of deposited Pt increased to 0.17 wt% with increasing photodeposition time up to 35 h, but then decreased. As a possible reason for this result, increasing the amount of Pt on ZnRh2O4 may have caused a light shading effect, preventing ZnRh2O4 from being photoexcited and/or in-
creasing Pt detachment at a rate that exceeded Pt deposition. To determine the valency of Ag and Pt in the prepared photocatalysts, a peak deconvolution method was applied to the Ag 3d and Pt 4f peaks (Fig. 3). In Figs. 3(a)–3(e), all of the photocatalysts were deconvoluted by one pair of Ag 3d peaks by fixing the Ag 3d5/2 and Ag 3d3/2 peaks, which are attributable to metallic Ag (Ag0) and had binding energies of 368.6 ± 0.1 and 374.6 ± 0.1 eV, respectively, and by fixing the peak area ratio of Ag 3d5/2 to Ag 3d3/2 at 0.667.14) These results indicate that Ag exists as metallic particles when inserted between ZnRh2O4 and Bi4V2O11 in ZnRh2O4/Ag/Bi4V2O11 and Pt/ZnRh2O4/Ag/Bi4V2O11. In contrast, the Pt 4f peaks were deconvoluted by three pairs of Pt 4f peaks with binding energies of 71.1 ± 0.2 eV (Pt 4f5/2) and 74.6 ± 0.2 eV (Pt 4f7/2) for metallic Pt (Pt0), 72.1 ± 0.2 eV (Pt 4f5/2) and 75.6 ± 0.2 eV (Pt 4f7/2) for Pt2+, and 73.1 ± 0.2 eV (Pt 4f5/2) and 76.6 ± 0.2 eV (Pt 4f7/2) for Pt3+. Figs. 3(g)–3(j)14) The peak area ratio of Pt 4f5/2 to Pt 4f7/2 for Pt0, Pt2+, and Pt3+ was fixed at 0.75. The total Pt0, Pt2+, and Pt3+ areas were determined by summing the corresponding deconvolution areas of Pt 4f5/2 and Pt 4f7/2, and the atomic ratios of Pt0, Pt2+, and Pt3+ vs. total Pt were then calculated (Table 1). Thus, although the major Pt species that functioned as the cocatalyst was Pt0, Pt2+ was not fully reduced to Pt0.

We previously demonstrated by elemental mapping using scanning transmission electron microscopy and energy-dispersive X-ray spectrometry that Pt is specifically photodeposited onto ZnRh2O4.14) We consider that the Bi4V2O11 surface remains unaltered even after the deposition of the cocatalyst. The XPS peaks V 2p3/2, Zn 2p, and Rh 3d were normalized for all of the photocatalysts using the peak areas of Bi 4f [Figs. 4(a)–4(d)]. The peak areas in the normalized V 2p3/2 spectra were reasonably similar among all of the photocatalysts.

### Table 1. Pt weight percentage in Pt/ZnRh2O4/Ag/Bi4V2O11, and percentages of Pt0, Pt2+, and Pt3+ including in the photodeposited Pt

| Photodeposition time/h | Pt (wt.%) | Pt0 (wt.%) | Pt2+ (wt.%) | Pt3+ (wt.%) |
|------------------------|----------|------------|-------------|-------------|
| 4                      | 0.10     | 36 ± 8     | 57 ± 2      | 8 ± 6       |
| 20                     | 0.16     | 43 ± 2     | 42 ± 3      | 16 ± 5      |
| 35                     | 0.17     | 62 ± 2     | 27 ± 2      | 12 ± 1      |
| 50                     | 0.14     | 61 ± 1     | 32 ± 0      | 7 ± 1       |

*1 Obtained by ICP-OES.
*2 Average values of the two times Pt 4f measurements for each Pt/ZnRh2O4/Ag/Bi4V2O11, and their peak deconvolution. Figures 3(g)–3(j) are one of the series of Pt 4f data and their deconvolution results out of two measurements. Value obtained using: 100 × Pt0/(Pt0 + Pt2+ + Pt3+), 100 × Pt2+/(Pt0 + Pt2+ + Pt3+), 100 × Pt3+/(Pt0 + Pt2+ + Pt3+).

![Fig. 2. UV-vis diffuse reflection spectra of Pt/ZnRh2O4/Ag/Bi4V2O11 after 35 h of Pt photodeposition and bare ZnRh2O4](image2.png)

![Fig. 3. XPS spectra for Ag 3d (Ag 3d5/2, Ag 3d3/2) (a–c) and Pt 4f (Pt 4f5/2, Pt 4f7/2) (f–j) of ZnRh2O4/Ag/Bi4V2O11 (a, f), and Pt/ZnRh2O4/Ag/Bi4V2O11 prepared with Pt photodeposition times of 4 h (b, g), 20 h (c, h), 35 h (d, i), and 50 h (e, j). The blue open circles in the lower part of each plot were generated by subtracting the background (gray line, upper) from the experimental XPS data (black open plots, upper). The blue open plots closely coincided with the fitted curves (light blue lines, which represent the sum of the contributions obtained by deconvolution (red, green, and brown lines)).](image3.png)
[Fig. 4(b)]. In addition, the normalized Zn 2p and Rh 3d peaks of Pt/ZnRh2O4/Ag/Bi4V2O11 were smaller than those of ZnRhO2/Ag/Bi4V2O11 [Figs. 4(c) and 4(d)]. These surface-sensitive XPS results are consistent with the speculation that Pt was selectively deposited onto ZnRh2O4.

3.2 Photocatalytic water splitting tests

The time courses of H2 and O2 evolution from Pt/ZnRh2O4/Ag/Bi4V2O11 after Pt photodeposition for 4, 20, 35, and 50 h were compared with bare ZnRh2O4/Ag/Bi4V2O11 under monochromic light irradiation at 700 nm (Fig. 5). All of the photocatalysts evolved H2 and O2 from water at a molar ratio of ~2 to 1, indicating that the overall water-splitting reaction proceeded. Notably, the H2 and O2 evolution rates initially decreased (4 h photodeposition), then increased (20 and 35 h photodeposition), and then decreased again (50 h photodeposition). The factors influencing these phenomena are discussed below.

To estimate the AQE values (Table 2), the total number of incident photons from the 700 nm LED light source was calculated from light intensities and the H2 evolution rates were calculated by a least squares method from the slopes of the plots in Figs. 5(a)–5(d). The obtained AQE values for H2 and O2 evolution were almost identical because the H2 and O2 evolution ratio was ~2 to 1.

It should be noted that we can strictly compare the dependence of the water splitting efficiency on the amount of Pt cocatalyst because all the data shown by solid red and blue marks (i.e., evolved H2 and O2) in Figs. 5(a)–5(d) were obtained over Pt/ZnRh2O4/Ag/Bi4V2O11 photocatalysts prepared from the same batch of ZnRh2O4/Ag/Bi4V2O11. To confirm the reproducibility of the data, ZnRh2O4/Ag/Bi4V2O11 was prepared from the very beginning following the same procedure, and then Pt was photodeposited for 50 h under the same conditions. The H2 and O2 evolution vs. irradiation time from Pt/ZnRh2O4/Ag/Bi4V2O11 prepared by Pt photodeposition of 4 h (a), 20 h (b), 35 h (c), and 50 h (d) under irradiation with 700 nm LED light (solid marks with solid lines). The evolution of H2 and O2 over bare ZnRhO2/Ag/Bi4V2O11 is also shown for comparison (open marks with broken lines). In (d), confirmation of the data reproducibility shown by brown and purple marks.

Table 2. Light intensities, H2 generation rates, and AQE values for overall pure-water splitting over ZnRh2O4/Ag/Bi4V2O11 and Pt/ZnRh2O4/Ag/Bi4V2O11

| Photo-deposition time/h | Light intensity/mW cm^-2 | H2 generation rate/µmol h^-1 | AQE/% |
|-------------------------|--------------------------|------------------------------|-------|
| 0 (bare)                | 3.0                      | 1.7 x 10^-2                  | 1.5 x 10^-2 |
| 4                       | 3.2                      | 6.1 x 10^-3                  | 5.2 x 10^-3 |
| 20                      | 3.2                      | 2.5 x 10^-2                  | 2.2 x 10^-2 |
| 35                      | 3.5                      | 5.0 x 10^-2                  | 4.1 x 10^-2 |
| 50                      | 3.0                      | 2.7 x 10^-2                  | 2.5 x 10^-2 |
and 2). This finding is plausible because the amount of Pt and proportion of Pt\(^0\) are the largest in Pt/ZnRh\(_2\)O\(_4\)/Ag/Bi\(_4\)V\(_2\)O\(_{11}\) (35 h photodeposition). It is reasonable to consider that the AQE tended to increase in the measurement range up to 0.17 wt% Pt and that presence of Pt\(^2+\) or Pt\(^4+\) negatively affected the AQE because the photoexcited electrons in ZnRh\(_2\)O\(_4\) are consumed by the reduction of Pt\(^2+\) or Pt\(^4+\). Thus, lowering the amount of Pt\(^2+\) and Pt\(^4+\) is expected to increase the AQE. Compared to the AQE of the photocatalyst prepared by the 35-h photodeposition of Pt, that of the 50-h photodeposited photocatalyst decreased due to the lower amount of Pt despite the similar portion of Pt\(^0\). In contrast, the AQE of 20-h photodeposited photocatalyst decreased due to the lower portion of Pt\(^0\) and lower amount of Pt. However, in both cases, the AQE values remained higher than that of bare ZnRh\(_2\)O\(_4\)/Ag/Bi\(_4\)V\(_2\)O\(_{11}\). The AQE values of 20-h and 50-h photodeposited photocatalysts became similar although the Pt amount and Pt\(^0\) portion of the 50-h photodeposited photocatalyst were larger than those of the 20-h photocatalyst. This would be attributable to coarsening of Pt particles loaded at 50 h. The photocatalyst prepared using 4-h photodeposition, which had the lowest AQE value, because of the lower amount of Pt and the lower proportion of Pt\(^0\).

These findings demonstrate the importance of having the fine Pt cocatalyst loaded with Pt\(^0\). We cannot give a clear explanation why the AQE of 4-h photodeposited photocatalyst was lower than that of bare photocatalyst. In the two-photon excitation system like the present study, the activity should be the best, when the absorbed photon numbers by ZnRh\(_2\)O\(_4\) and Bi\(_4\)V\(_2\)O\(_{11}\) are identical, meaning that the numbers of photo-excited electrons in ZnRh\(_2\)O\(_4\) and Bi\(_4\)V\(_2\)O\(_{11}\) are identical. Here, we are considering that the cocatalyst Pt is deposited only on the surface of ZnRh\(_2\)O\(_4\), then the shading effect by the deposited Pt should happen only to ZnRh\(_2\)O\(_4\). So, the negative effect of the Pt loading in the two-photon excitation system is the deviation from the balance of the photon number contributing to the intended reactions by the two constituent photocatalysts, causing the decrease in the activity. It is well-known that the positive effect of Pt loading is the electron accumulation in Pt, causing the effective electrons-and-holes separation, followed by the effective utilization of photo-excited electrons for reducing protons to produce H\(_2\). So, we are just speculating that the negative effect overwhelmed the positive effect in the 4-h photodeposited photocatalyst. Then, in the 20-h photodeposited photocatalyst, the positive effect overwhelmed the negative effect with increasing the activity accompanied by increasing the amount of loaded Pt. Under these conditions, although the deposition of Pt did not always increase the AQE, we can conclude that Pt functions as the cocatalyst for the overall water-splitting reaction.

4. Conclusions

The selective photodeposition of Pt as a cocatalyst onto ZnRh\(_2\)O\(_4\) in ZnRh\(_2\)O\(_4\)/Ag/Bi\(_4\)V\(_2\)O\(_{11}\) enhanced the performance of water splitting when the amount of Pt exceeded 0.12 wt%. The photodeposition of Pt in the form of Pt\(^0\) was essential to enhance the water-splitting activity. Following the Pt photodeposition procedure, photoirradiation at wavelengths up to 850 nm in the presence of HCHO and absence of H\(_2\)PtCl\(_6\)/H\(_2\)O is expected to promote the formation of Pt\(^0\). Such investigations are now underway in our laboratory.

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