FULL PAPER

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 (ZnRh_2O_4) to serve as a hydrogen (H_2)-evolution photocatalyst in a silver (Ag)-inserted ZnRh_2O_4 and bismuth vanadium oxide ($\text{Bi}_4\text{V}_2\text{O}_{11}$) solid-state photocatalyst ($\text{ZnRh}_2\text{O}_4/\text{Ag}/\text{Bi}_4\text{V}_2\text{O}_{11}$). The amount of deposited Pt was controlled by the photodeposition time to generate Pt-loaded $\text{ZnRh}_2\text{O}_4/\text{Ag}/\text{Bi}_4\text{V}_2\text{O}_{11}$ (Pt/ $\text{ZnRh}_2\text{O}_4/\text{Ag}/\text{Bi}_4\text{V}_2\text{O}_{11}$) containing up to 0.17 wt % of Pt cocatalyst. The prepared Pt/ $\text{ZnRh}_2\text{O}_4/\text{Ag}/\text{Bi}_4\text{V}_2\text{O}_{11}$ 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 H_2 and O_2 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 Pt^0 (metallic Pt) is crucial for enhancing the water-splitting activity of Pt/ $\text{ZnRh}_2\text{O}_4/\text{Ag}/\text{Bi}_4\text{V}_2\text{O}_{11}$.

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1. Introduction

Several photocatalysts and photocatalytic systems aimed at water splitting have been investigated¹⁾ because the generated hydrogen (H_2) 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,²⁾ 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 ($\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$)³⁾ 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 photoexcitation system.

As an alternative to one-step photoexcitation systems, two-step systems, which combine H_2 -evolution photocatalyst (H_2 photocatalyst) and O_2 -evolution photocatalyst (O_2 photocatalyst), are also able to split water under visible-light irradiation.⁴⁾ However, because such two-step systems, which are termed “Z-scheme”, require the presence of a suitable redox mediator, such as iodate ion

(IO_3^-)/iodide ion (I^-) or ferric ion (Fe^{3+})/ferrous ion (Fe^{2+}), 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 (ZnRh_2O_4 , bandgap (E_g) of 1.2 eV) as the H_2 photocatalyst and bismuth vanadate ($\text{Bi}_4\text{V}_2\text{O}_{11}$, E_g of 1.7 eV) as the O_2 photocatalyst.^{5)–8)} In these systems, which were designated $\text{ZnRh}_2\text{O}_4/\text{Ag}/\text{Bi}_4\text{V}_2\text{O}_{11}$ and $\text{ZnRh}_2\text{O}_4/\text{Au}/\text{Bi}_4\text{V}_2\text{O}_{11}$, overall pure-water splitting proceeded via Ag or Au, which mediated the transfer of photoexcited electrons from the conduction band of $\text{Bi}_4\text{V}_2\text{O}_{11}$ to the valence band of ZnRh_2O_4 . 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.^{9)–13)}

In our previous work, the selective photodeposition of Ag or platinum (Pt) as H_2 -favorable cocatalysts onto ZnRh_2O_4 in $\text{ZnRh}_2\text{O}_4/\text{Ag}/\text{Bi}_4\text{V}_2\text{O}_{11}$ resulted in enhanced stoichiometric H_2 and O_2 evolution from pure water.^{14),15)} 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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2. Experimental section

2.1 Sample preparation

ZnRh_2O_4 and $\text{Bi}_4\text{V}_2\text{O}_{11}$ powders were synthesized by a solid-state reaction method. As starting materials, ZnO (Wako, purity 99.0 %) and Rh_2O_3 powders (Kanto Kagaku, purity 99.9 %) were used to synthesize ZnRh_2O_4 , and Bi_2O_3 (Kanto Kagaku, purity 99.9 %) and V_2O_5 powders (Kanto Kagaku, purity 99.0 %) were used to synthesize $\text{Bi}_4\text{V}_2\text{O}_{11}$. 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_2O_4 and $\text{Bi}_4\text{V}_2\text{O}_{11}$ powders, respectively. The $\text{Bi}_4\text{V}_2\text{O}_{11}$ powder was subsequently soaked in distilled water for 20 h with constant stirring, followed by filtration and drying at 65 °C for 12 h.¹⁵⁾

The prepared ZnRh_2O_4 and $\text{Bi}_4\text{V}_2\text{O}_{11}$ powders, and Ag_2O (Kanto Kagaku, purity 99.0 %) powder were thoroughly mixed at a molar ratio of 1.0:1.2:1.0 and were then pressed into pellets of 12 mm in diameter by applying a force of 60 kN. The obtained pellets were heated in air at 750 °C for 2 h and were then ground into a fine powder, which was soaked in a 3 M nitric acid (HNO_3 , Kanto Kagaku) aqueous solution for 5 min. The powder was then filtered, washed thoroughly with distilled water, and dried at 65 °C for 12 h.

Photodeposition of Pt was conducted by dispersing 80 mg $\text{ZnRh}_2\text{O}_4/\text{Ag}/\text{Bi}_4\text{V}_2\text{O}_{11}$ in 40 mL formaldehyde solution (HCHO , 25 vol %) containing 10 mL of 8.65 mM hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, >98.5 %; Kanto Kagaku) as the Pt source. The resulting suspension was deaerated using liquid nitrogen and illuminated by a light-emitting diode (LED) lamp with a wavelength of 850 nm (LEDH60-850; Hamamatsu Photonics) and equipped with an optical filter (IR85N; HOYA) for 4, 20, 35, and 50 h under constant stirring. This light condition was used for the selective photo-excitation of ZnRh_2O_4 , which has an E_g that is 0.5 eV lower than that of $\text{Bi}_4\text{V}_2\text{O}_{11}$ (1.2 vs. 1.7 eV, respectively). The resulting sample was obtained by filtration, washed, and dried at 80 °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 reflection 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 $\text{AQE} (\%) = 100 \times 4 \times \text{H}_2 \text{ generation rate} / \text{incident photon rate}$, because H_2 generation in two-step systems is a four-electron process.¹⁶⁾

3. Results and discussion

3.1 Characterization

The XRD patterns of $\text{Pt}/\text{ZnRh}_2\text{O}_4/\text{Ag}/\text{Bi}_4\text{V}_2\text{O}_{11}$ after 35 h of Pt photodeposition as a representative and bare $\text{ZnRh}_2\text{O}_4/\text{Ag}/\text{Bi}_4\text{V}_2\text{O}_{11}$ were first compared (Fig. 1). The XRD peaks of both samples appeared similar and mainly corresponded to ZnRh_2O_4 and $\text{Bi}_4\text{V}_2\text{O}_{11}$, 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.¹⁴⁾ 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 $\text{ZnRh}_2\text{O}_4/\text{Ag}/\text{Bi}_4\text{V}_2\text{O}_{11}$ and $\text{Pt}/\text{ZnRh}_2\text{O}_4/\text{Ag}/\text{Bi}_4\text{V}_2\text{O}_{11}$ (35-h photodeposition) were next examined (Fig. 2). The $\text{Pt}/\text{ZnRh}_2\text{O}_4/\text{Ag}/\text{Bi}_4\text{V}_2\text{O}_{11}$ spectrum had greater 100-reflectance than that of bare $\text{ZnRh}_2\text{O}_4/\text{Ag}/\text{Bi}_4\text{V}_2\text{O}_{11}$ in the longer wavelength region, a property that is attributable to the photo-deposited Pt.

Elemental analysis by ICP-OES indicated that the Pt amounts were 0.10, 0.12, 0.17, and 0.14 wt % containing

Fig. 1. Powder XRD patterns of $\text{Pt}/\text{ZnRh}_2\text{O}_4/\text{Ag}/\text{Bi}_4\text{V}_2\text{O}_{11}$ after 35 h of Pt photodeposition and bare $\text{ZnRh}_2\text{O}_4/\text{Ag}/\text{Bi}_4\text{V}_2\text{O}_{11}$.

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 ZnRh_2O_4 may have caused a light shading effect, preventing ZnRh_2O_4 from being photoexcited and/or in-

Fig. 2. UV-vis diffuse reflection spectra of Pt/ZnRh₂O₄/Ag/Bi₄V₂O₁₁ after 35 h of Pt photodeposition and bare ZnRh₂O₄/Ag/Bi₄V₂O₁₁.

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 %*1)	Pt ⁰ / %*2)	Pt ²⁺ / %*2)	Pt ³⁺ / %*2)
4	0.10	36 ± 8	57 ± 2	8 ± 6
20	0.12	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: $100 \times \text{Pt}^0 / (\text{Pt}^0 + \text{Pt}^{2+} + \text{Pt}^{3+})$, $100 \times \text{Pt}^{2+} / (\text{Pt}^0 + \text{Pt}^{2+} + \text{Pt}^{3+})$, $100 \times \text{Pt}^{3+} / (\text{Pt}^0 + \text{Pt}^{2+} + \text{Pt}^{3+})$.

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 3d_{5/2} and Ag 3d_{3/2} 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 3d_{5/2} to Ag 3d_{3/2} at 0.667.^{14),17),18)} 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 4f_{7/2}) and 74.6 ± 0.2 eV (Pt 4f_{5/2}) for metallic Pt (Pt⁰), 72.1 ± 0.2 eV (Pt 4f_{7/2}) and 75.6 ± 0.2 eV (Pt 4f_{5/2}) for Pt²⁺, and 73.1 ± 0.2 eV (Pt 4f_{7/2}) and 76.6 ± 0.2 eV (Pt 4f_{5/2}) for Pt³⁺ [Figs. 3(g)–3(j)].^{14),19)} The peak area ratio of Pt 4f_{5/2} to Pt 4f_{7/2} 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 4f_{5/2} and Pt 4f_{7/2}, 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, Pt⁴⁺ 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⁾ Thus, we consider that the Bi₄V₂O₁₁ surface remains unaltered even after the deposition of the cocatalyst. The XPS peaks V 2p_{3/2}, 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 2p_{3/2} spectra were reasonably similar among all of the photocatalysts

Fig. 3. XPS spectra for Ag 3d (Ag 3d_{3/2}, Ag 3d_{5/2}) (a–e) and Pt 4f (Pt 4f_{5/2}, Pt 4f_{7/2}) (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).

Fig. 4. Normalized XPS spectra of bare ZnRh₂O₄/Ag/Bi₄V₂O₁₁ (black lines) and Pt/ZnRh₂O₄/Ag/Bi₄V₂O₁₁ prepared by photodeposition for 4 h (brown lines), 20 h (blue lines), 35 h (red lines), and 50 h (green lines) for Bi 4f (a), V 2p (b), Zn 2p (c), and Rh 3d (d).

[Fig. 4(b)]. In addition, the normalized Zn 2p and Rh 3d peaks of Pt/ZnRh₂O₄/Ag/Bi₄V₂O₁₁ were smaller than those of ZnRh₂O₄/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 monochromatic 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

Fig. 5. Time courses of photocatalytic evolution of H₂ and O₂ from water over 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 ZnRh₂O₄/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	H ₂ generation rate /μmol h ⁻¹	AQE (%)
0 (bare)	3.0	1.7×10^{-2}	1.5×10^{-2}
4	3.2	6.1×10^{-3}	5.2×10^{-3}
20	3.2	2.5×10^{-2}	2.2×10^{-2}
35	3.5	5.0×10^{-2}	4.1×10^{-2}
50	3.0	2.7×10^{-2}	2.5×10^{-2}

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 ZnRh₂O₄/Ag/Bi₄V₂O₁₁ and Pt/ZnRh₂O₄/Ag/Bi₄V₂O₁₁ (50 h photodeposition of Pt) under the same light conditions at a wavelength of 700 nm are included in Fig. 5(d). Both newly prepared photocatalysts evolved H₂ and O₂ from water at a molar ratio of ~2 to 1, indicating that the overall water splitting reaction proceeded. The H₂ and O₂ evolution rates of the newly prepared ZnRh₂O₄/Ag/Bi₄V₂O₁₁ (brown and purple open marks, H₂ generation rate = 1.4×10^{-2} μmol h⁻¹, AQE = 1.2×10^{-2} %) and Pt/ZnRh₂O₄/Ag/Bi₄V₂O₁₁ (brown and purple solid marks, H₂ generation rate = 2.9×10^{-2} μmol h⁻¹, AQE = 2.6×10^{-2} %) in Fig. 5(d) were almost identical within experimental errors to those for the original ZnRh₂O₄/Ag/Bi₄V₂O₁₁ (red and blue open marks) and Pt/ZnRh₂O₄/Ag/Bi₄V₂O₁₁ (red and blue solid marks) in Fig. 5(d). So, we consider that the good reproducibility of the data was confirmed.

The most active photocatalyst for water splitting was prepared by 35 h of Pt photodeposition (Fig. 5, Tables 1

and 2). This finding is plausible because the amount of Pt and proportion of Pt^0 are the largest in $\text{Pt}/\text{ZnRh}_2\text{O}_4/\text{Ag}/\text{Bi}_4\text{V}_2\text{O}_{11}$ (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^{3+} negatively affected the AQE because the photoexcited electrons in ZnRh_2O_4 are consumed by the reduction of Pt^{2+} or Pt^{3+} . Thus, lowering the amount of Pt^{2+} and Pt^{3+} 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 $\text{ZnRh}_2\text{O}_4/\text{Ag}/\text{Bi}_4\text{V}_2\text{O}_{11}$. 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_2O_4 and $\text{Bi}_4\text{V}_2\text{O}_{11}$ are identical, meaning that the numbers of photo-excited electrons in ZnRh_2O_4 and $\text{Bi}_4\text{V}_2\text{O}_{11}$ are identical. Here, we are considering that the cocatalyst Pt is deposited only on the surface of ZnRh_2O_4 , then the shading effect by the deposited Pt should happen only to ZnRh_2O_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_2O_4 in $\text{ZnRh}_2\text{O}_4/\text{Ag}/\text{Bi}_4\text{V}_2\text{O}_{11}$ enhanced the perfor-

mance 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 $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ is expected to promote the formation of Pt^0 . Such investigations are now underway in our laboratory.

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