Electronic Supplementary Information (ESI) for

Facile synthesis of a red light-inducible overall water-splitting photocatalyst using gold as a solid-state electron mediator

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ESI-1) Detailed preparation and characterization procedures.

A powdered photocatalyst composed of ZnRh₂O₄, Bi₄V₂O₁₁, and Au (ZnRh₂O₄/Au/Bi₄V₂O₁₁) was prepared using the following method. First, ZnRh₂O₄ and Bi₄V₂O₁₁ powders were synthesized using a solid-state reaction method. As starting materials, commercial ZnO (Wako, purity 99.0%) and Rh₂O₃ (Kanto Kagaku, purity 99.9%) powders were used for ZnRh₂O₄, and Bi₂O₃ (Kanto Kagaku, purity 99.9%) and V₂O₅ (Kanto Kagaku, purity 99.0%) powders were used for Bi₄V₂O₁₁. Stoichiometric amounts of the starting materials for both materials were wet-ball-milled for 20 h in polyethylene bottles using zirconium dioxide (ZrO₂) balls as the milling medium. The resulting mixtures were calcined at 1150 °C for 24 h and 850 °C for 8 h to obtain ZnRh₂O₄ and Bi₄V₂O₁₁ powders, respectively, which were then thoroughly ground.

The prepared ZnRh₂O₄ and commercial Au (nanopowder (<100-nm particle size), Aldrich, purity 99.9%) were wet-ball-milled at a molar ratio of 1 : 0.15 in an identical manner as described above, and then calcined at 850 °C for 2 h to form ZnRh₂O₄/Au. The prepared ZnRh₂O₄/Au and Bi₄V₂O₁₁ were again mixed (molar ratio of ZnRh₂O₄ : Au : Bi₄V₂O₁₁ = 1 : 0.15 : 0.20) in an identical manner as described above, except that the milling medium was not used and the ball-milling time was reduced to 4 h from 20 h, to generate ZnRh₂O₄/Au, which was then calcined at 850 °C for 2 h to form ZnRh₂O₄/Au/Bi₄V₂O₁₁.

As only repeated ball-milling and calcination steps were used to form $ZnRh_2O_4/Au/Bi_4V_2O_{11}$, this represents a facile synthesis procedure.

The crystal structures of the prepared powders were determined by X-ray diffraction (XRD) using a PW-1700 instrument (PANalytical). UV-visible absorption (UV-vis) spectra were obtained by the diffuse reflection method using a spectrometer (V-650, Jasco) with barium sulfate (BaSO₄) as the reflectance standard. A scanning electron microscope (SEM, JSM-6500F, JEOL Ltd.) was used to observe the morphology of the prepared photocatalysts. A scanning transmission electron microscope (STEM, Tecnai Osiris, FEI) and an energy-dispersive X-ray spectrometry (EDS) were also utilized for elemental mapping.

Photocatalytic overall water-splitting tests were conducted in a gas-closed circulation system. ZnRh₂O₄/Au/Bi₄V₂O₁₁ composite powder (60 mg) was suspended in 12 mL pure water (pH unadjusted) under an argon atmosphere (50 kPa) and constant stirring using a magnetic stirrer. Light-emitting diode (LED) lamps with wavelengths of 610 (LEDH60-610, Hamamatsu Photonics), 700 (LEDH60-700, Hamamatsu Photonics), and 740 nm (LEDH60-740, Hamamatsu Photonics) were used for light irradiation. The amounts of evolved H₂ and O₂ were monitored using an online gas chromatograph (GC-8A, Shimadzu). The apparent quantum efficiency (AQE) values were calculated using the amount of evolved O₂ and the equation: AQE (%) = $100 \times 8 \times O_2$ generation rate/incident photon rate, because O₂ generation in the two-step system is a eighthole process. The AQE values were also calculated using the amount of evolved H₂ and of evolved H₂ and the equation: AQE (%) = $100 \times 4 \times H_2$ generation rate/incident photon rate, because H₂ generation in this system is a four-electron process (after reference, Y. Sasaki, H. Nemoto, K. Saito and A. Kudo, *J. Phys. Chem. C*, 2009, **113**, 17536–17542.). Then the average AQE values for overall pure-water splitting over ZnRh₂O₄/Au/Bi₄V₂O₁₁ were obtained. ESI-2) XRD and SEM characterization (Fig. S1, Fig. S2).



Fig. S1 XRD pattern of $ZnRh_2O_4/Au/Bi_4V_2O_{11}$.



Fig. S2 SEM images of (a) $ZnRh_2O_4/Au/Bi_4V_2O_{11}$, (b) Au, (c) $ZnRh_2O_4$, (d) $ZnRh_2O_4/Au$ (Au particles are indicated by white arrows), and (e) $Bi_4V_2O_{11}$.

ESI-3) STEM observation of as-prepared $ZnRh_2O_4/Au/Bi_4V_2O_{11}$ (before the overall pure-water splitting test, images of the newly-prepared $ZnRh_2O_4/Au/Bi_4V_2O_{11}$) and that of $ZnRh_2O_4/Au/Bi_4V_2O_{11}$ after the overall pure-water splitting test (Fig. S3, Fig. S4).

We performed the STEM observation again for the newly-prepared $ZnRh_2O_4/Au/Bi_4V_2O_{11}$ photocatalyst, and the STEM image (Figs. S3a) and EDS element maps (Figs. S3b–S3d) of Bi, Zn, and Au, respectively, are shown for the as-prepared photocatalyst. Fig. S3e is the overlapped color image of Figs. S3b-S3d. Figure S3f shows the atomic percentages of Zn, Rh, Bi, V, and Au measured along the line from the area of $ZnRh_2O_4$ (A) to that of $Bi_4V_2O_{11}$ (B). The atomic percentages of Zn and Rh decreased at the boundary of $ZnRh_2O_4$ and Au, and those of Bi and V increased at the boundary of Au and $Bi_4V_2O_{11}$. Accordingly, the percentage of Au increased and decreased at the boundaries of $ZnRh_2O_4$ and Au, and $Bi_4V_2O_{11}$, respectively. This result indicates that Au existed at the interface between $ZnRh_2O_4$ and $Bi_4V_2O_{11}$. Note that the Au particle size in Figs. S3 was ~80 nm and that in Figs. 2 was ~300 nm, indicating that the Au particle size ranged from nearly one hundred nanometer to several hundreds of nanometers.

We also performed the STEM observation for the $ZnRh_2O_4/Au/Bi_4V_2O_{11}$ photocatalyst after the water-splitting reaction for ~311 h under exactly the same light condition as in Fig. 3b. Although the H₂ and O₂ generation behaviors are not shown here, we confirmed that the evolved H₂ and O₂ molar ratio from water was 2 to 1. The STEM image (Figs. S4a) and EDS element maps (Figs. S4b–S4d) of Bi, Zn, and Au, respectively, are shown. Fig. S4e is the overlapped color image of Figs. S4b-S4d. Figure S4f shows the atomic percentages of Zn, Rh, Bi, V, and Au along the line from the ZnRh₂O₄ (A) to Bi₄V₂O₁₁ area (B). Similar to Fig. 2g and Fig. S3f, the atomic percentages of Zn and Rh decreased at the ZnRh₂O₄-Au boundary, and those of Bi and V increased at the Au-Bi₄V₂O₁₁ boundary. Accordingly, the percentage of Au increased and decreased at the ZnRh₂O₄-Au and Au-Bi₄V₂O₁₁ boundaries, respectively. The Au particle size was ~200 nm in the image, which is within the range of Au particle sizes as mentioned above.

 $ZnRh_2O_4/Au/Bi_4V_2O_{11}$ does not appear to have changed even after the water-splitting reaction for ~311 h, and Au was detected between the $ZnRh_2O_4$ and $Bi_4V_2O_{11}$ particles. Thus, we concluded that $ZnRh_2O_4/Au/Bi_4V_2O_{11}$ was stable up to at least ~311 h.



Fig. S3 STEM images of newly- and as-prepared $ZnRh_2O_4/Au/Bi_4V_2O_{11}$. STEM image (a), and EDS element maps (b–e), in which blue (b), red (c), and yellow (d) colors correspond to Bi, Zn, and Au, respectively. (e) is the overlapped image of (b), (c), and (d). In (a), the line along which elemental analysis was performed is shown (A to B). Atomic percentages of Bi, V, Zn, Rh, and Au measured from the area of $Bi_4V_2O_{11}$ (A) to that of $ZnRh_2O_4$ (B) (f).



400 nm



Fig. S4 STEM images of $ZnRh_2O_4/Au/Bi_4V_2O_{11}$ after the water-splitting reaction for ~311 h with the same light condition in Fig. 3b. STEM image (a), and EDS element maps (b–e), in which blue (b), red (c), and yellow (d) colors correspond to Bi, Zn, and Au, respectively. (e) is the overlapped image of (b), (c), and (d). In (a), the line along which elemental analysis was performed is shown (A to B). Atomic percentages of Bi, V, Zn, Rh, and Au measured from the area of $Bi_4V_2O_{11}$ (A) to that of $ZnRh_2O_4$ (B) (f).

ESI-4) Complementary water-splitting tests (Fig. S5, Fig. S6).

Figure S5 shows the time courses of H₂ and O₂ evolution from pure water using only $ZnRh_2O_4/Au$ under irradiation with a xenon (Xe) lamp equipped with a Y-44 optical filter (> 420 nm). Neither H₂ nor O₂ were detected, demonstrating that $ZnRh_2O_4/Au$ cannot split pure water by itself. Figure S6 shows the time courses of H₂ and O₂ evolution from pure water using only $Au/Bi_4V_2O_{11}$ under irradiation with identical visible light to that used in Fig. S5. Neither H₂ nor O₂ were detected, demonstrating that $Au/Bi_4V_2O_{11}$ also cannot split pure water by itself.

Notably, we have reported that neither $ZnRh_2O_4$ nor $Bi_4V_2O_{11}$ can split pure water to produce H_2 and O_2 under visible light (> 420 nm, Xe lamp + Y-44 filter). In addition, we examined purewater splitting over the $ZnRh_2O_4$ - $Bi_4V_2O_{11}$ direct hetero-junction ($ZnRh_2O_4/Bi_4V_2O_{11}$) photocatalyst (without Au) irradiated with visible light (> 420 nm, Xe lamp + Y-44 filter). O_2 was not detected and only a negligible amount of H_2 was observed (R. Kobayashi, K. Kurihara, T. Takashima, B. Ohtani and H. Irie, J. Mater. Chem. A, 2016, 4, 3061–3067).



Fig. S5 Time courses of H_2 (red circles) and O_2 (blue circles) evolution from pure water in the presence of $ZnRh_2O_4/Au$ under irradiation with visible light (> 420 nm, Xe lamp + Y-44 filter).



Fig. S6 Time courses of H_2 (red circles) and O_2 (blue circles) evolution from pure water in the presence of Au/Bi₄V₂O₁₁ under irradiation with visible light (> 420 nm, Xe lamp + Y-44 filter).

ESI-5) Comparisons of water-splitting activity of $ZnRh_2O_4/Au/Bi_4V_2O_{11}$ prepared by three different procedures (Fig. S7).

Three types of powdered photocatalysts composed of $ZnRh_2O_4$, $Bi_4V_2O_{11}$, and Au $(ZnRh_2O_4/Au/Bi_4V_2O_{11})$ were prepared and compared. For the comparison, we utilized $ZnRh_2O_4$ calcined at 1000 °C for 24 h in place of the sample calcined at 1150 °C for 24 h, and the same $Bi_4V_2O_{11}$ and Au as described in the main text.

[ZnRh₂O₄/Au]/Bi₄V₂O₁₁: ZnRh₂O₄/Au/Bi₄V₂O₁₁ was prepared as described in the main text, except that ZnRh₂O₄ was calcined at 1000 °C for 24 h. In this method, the connection between ZnRh₂O₄ and Au was firstly formed, followed by the preparation of ZnRh₂O₄/Au/Bi₄V₂O₁₁. The photocatalyst prepared in this manner is described as [ZnRh₂O₄/Au]/Bi₄V₂O₁₁.

ZnRh₂O₄/[Au/Bi₄V₂O₁₁]: ZnRh₂O₄/Au/Bi₄V₂O₁₁ was prepared by forming the connection between Au and Bi₄V₂O₁₁ first and then forming ZnRh₂O₄/Au/Bi₄V₂O₁₁. Specifically, the prepared Bi₄V₂O₁₁ and Au were wet-ball-milled at a molar ratio of 1 : 0.20 for 20 h in polyethylene bottles using ZrO₂ balls as the milling medium and were then calcined at 850 °C for 2 h to form Au/Bi₄V₂O₁₁. The prepared ZnRh₂O₄ and Au/Bi₄V₂O₁₁ were again mixed (a molar ratio of ZnRh₂O₄ : Au : Bi₄V₂O₁₁ = 1 : 0.15 : 0.20) in an identical manner as described above to form Au/Bi₄V₂O₁₁, except that the milling medium was not used and a ball-milling time of 4 h was used instead of 20 h. The obtained sample was then calcined at 850°C for 2 h to form ZnRh₂O₄/Au/Bi₄V₂O₁₁. The photocatalyst prepared in this manner is described as ZnRh₂O₄/[Au/Bi₄V₂O₁₁].

[ZnRh₂O₄/Au/Bi₄V₂O₁₁]: ZnRh₂O₄/Au/Bi₄V₂O₁₁ was prepared in one step. The prepared ZnRh₂O₄ (calcined at 1000 °C for 24 h), Bi₄V₂O₁₁ and Au were wet-ball-milled at a molar ratio of 1 : 0.15 : 0.20 for 20 h in polyethylene bottles using the milling medium, and were then calcined at 850 °C for 2 h to form ZnRh₂O₄/Au/Bi₄V₂O₁₁. The photocatalyst prepared in this manner is described as [ZnRh₂O₄/Au/Bi₄V₂O₁₁].

The time courses of H₂ and O₂ evolution from pure water by the three types of powdered photocatalysts under visible-light irradiation (> 420 nm, Xe lamp + Y-44 filter) are shown in Fig. S7. Under these conditions, H₂ was not detected and only a negligible amount of O₂ was observed in the presence of $[ZnRh_2O_4/Au/Bi_4V_2O_{11}]$, demonstrating that the water-splitting reaction did not occur. However, the linear generation of H₂ and O₂ at a molar ratio of 2 to 1 was observed in the presence of $[ZnRh_2O_4/Au]/Bi_4V_2O_{11}$ and $ZnRh_2O_4/[Au/Bi_4V_2O_{11}]$, indicating that the overall water-splitting proceeded in these systems. The H₂ and O₂ evolution rates of $[ZnRh_2O_4/Au]/Bi_4V_2O_{11}$ were slightly larger than those of $ZnRh_2O_4/[Au/Bi_4V_2O_{11}]$. This result is plausible when we consider that Au on $Bi_4V_2O_{11}$ without connection to $ZnRh_2O_4$ would not function as an electron acceptor, but could serve this role on $ZnRh_2O_4$ without connection $Bi_4V_2O_{11}$. However, more detailed studies are needed to determine which photocatalyst (ZnRh₂O₄ or $Bi_4V_2O_{11}$) holds a greater amount of Au between these two photocatalysts.



Fig. S7 Time courses of H_2 and O_2 evolution from pure water by the three types of powdered photocatalysts under visible-light irradiation (> 420 nm, Xe lamp + Y-44 filter).

ESI-6) H_2 and O_2 generation rates under different LED light sources, incident photon rates, and AQE values for overall pure-water splitting (Table S1).

Table S1 Incident photon rates, H_2 and O_2 generation rates, AQE values obtained from H_2 and O_2 generation rates, average AQE values for overall pure-water splitting over $ZnRh_2O_4/Au/Bi_4V_2O_{11}$.

LED Light	Light intensity / mW	Incident photon rate / μmol h ⁻¹	$H_2~$ generation rate / $\mu mol~h^{\text{-1}}$	AQE from H ₂ (%)	O_2 generation rate / μ mol h ⁻¹	AQE from O ₂ (%)	Average AQE (%)
610 nm ^{a)}	9.8	1.8×10 ²	1.9×10 ⁻²	4.2×10 ⁻²	7.8×10 ⁻³	3.5×10 ⁻²	(3.8±0.4)×10 ⁻²
700 nm ^{a)}	2.4×10 ¹	5.0×10 ²	7.5×10 ⁻³	6.0×10 ⁻³	3.8×10 ⁻³	6.2×10 ⁻³	(6.1±0.1)×10 ⁻³
740 nm ^{a)}	5.1×10 ¹	1.1×10 ³	3.4×10 ⁻³	1.2×10 ⁻³	1.6×10 ⁻³	1.1×10 ⁻³	(1.2±0.0)×10 ⁻³
700 nm ^{b1)}	6.6×10 ¹	1.1×10 ³	1.6×10 ⁻²	4.5×10 ⁻³	6.7×10 ⁻³	3.8×10 ⁻³	(4.2±0.4)×10 ⁻³
700 nm ^{b2)}			1.6×10 ⁻²	4.5×10 ⁻³	8.8×10 ⁻³	5.0×10 ⁻³	(4.8±0.3)×10 ⁻³

^{a)} data from Fig. 3a

^{b)} data from Fig. 3b, ^{b1)} 1st cycle, ^{b2)} 2nd cycle

ESI-7) Turnover numbers for H_2 - and O_2 -evolution over $ZnRh_2O_4/Au/Bi_4V_2O_{11}$.

We prepared ZnRh₂O₄/Au/Bi₄V₂O₁₁ with a molar ratio of 1:0:15:0.20 (the composition ratio for preparation). In the present study, 60 mg of ZnRh₂O₄/Au/Bi₄V₂O₁₁ composite contains 1.0×10^2 , 1.5×10^1 , and 2.0×10^1 µmol of ZnRh₂O₄, Au, and Bi₄V₂O₁₁, respectively. Not shown here, but we confirmed ~1.0×10¹ and ~5.0 µmol of the evolved H₂ and O₂ so far under the same reaction conditions in Fig. 3b. We calculated the TON values of H₂ generation with respect to Au and ZnRh₂O₄, and that of O₂ generation with respect to Au and Bi₄V₂O₁₁ because we are presumably considering that H₂ is evolved over either Au or ZnRh₂O₄ and that O₂ is over Bi₄V₂O₁₁. The turnover number (TON) values of H₂ generation with respect to ZnRh₂O₄ and Au were 1.0×10^{-1} and 6.7×10^{-1} , respectively, and the TON value of O₂ generation with respect to Bi₄V₂O₁₁ was 2.5×10^{-1} . Those TON values did not exceed 1. However, they are just the apparent TON values, not the actual TON values, due to following reasons.

We can presumably consider from the SEM image in Fig. S2a that a lot of isolated $ZnRh_2O_4$ or $ZnRh_2O_4/Au$ powders, not connecting to $Bi_4V_2O_{11}$, existed in 60 mg of the $ZnRh_2O_4/Au/Bi_4V_2O_{11}$ composite. Such the isolated $ZnRh_2O_4$ and $ZnRh_2O_4/Au$ do not contribute to the water-splitting reaction as demonstrated in Fig. S5. Even though $ZnRh_2O_4/Au$ is connected to $Bi_4V_2O_{11}$, unless Au is inserted between $ZnRh_2O_4$ and $Bi_4V_2O_{11}$, that is, if $ZnRh_2O_4$ is directly connected to $Bi_4V_2O_{11}$ – $ZnRh_2O_4/Au$), it is probable that such the composite also do not contribute to the water-splitting reaction (ESI-4⁺). We do not know how to estimate the actual amount of $ZnRh_2O_4/Au/Bi_4V_2O_{11}$ composite participating in the water-splitting reaction out of 60 mg of the composite served for the water-splitting test. So we are currently unable to calculate the actual TON.