

Electronic Supplementary Information (ESI) for

**Visible-light-induced water splitting on hierarchically constructed Z-scheme photocatalyst composed of zinc rhodium oxide and bismuth vanadate**

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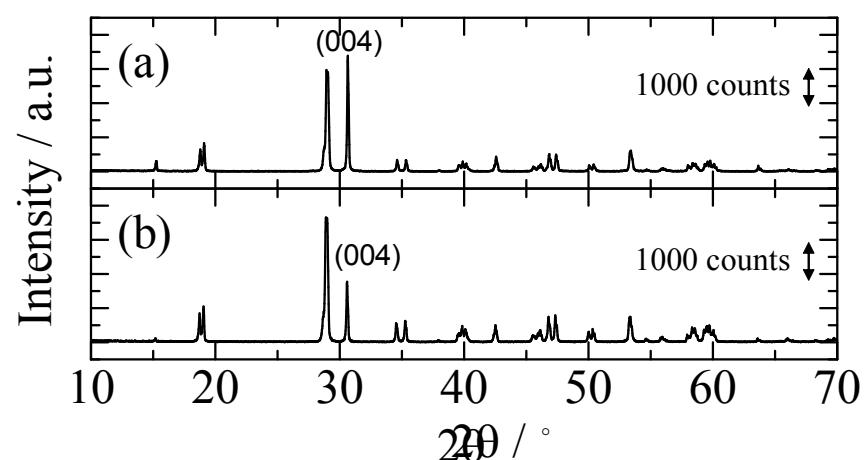
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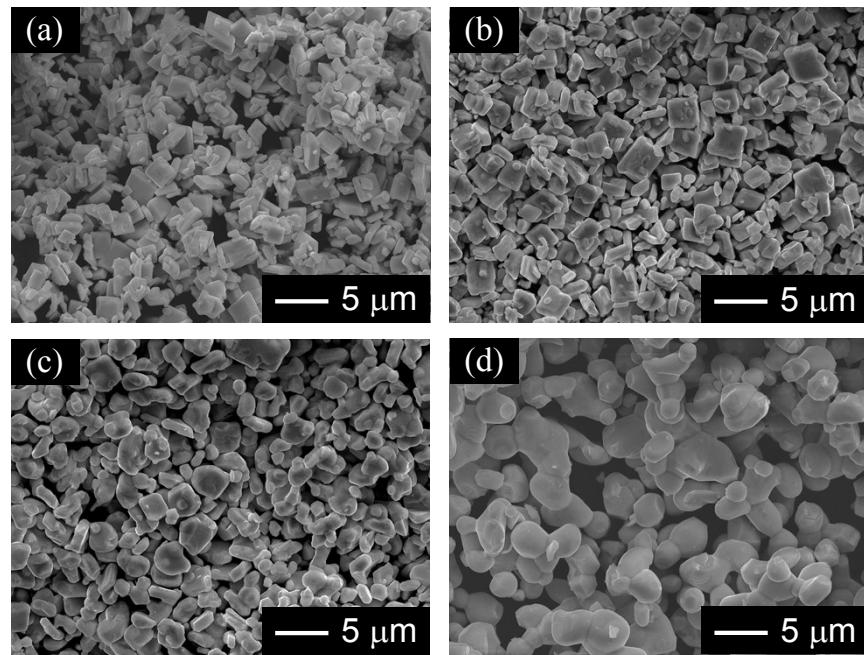
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ESI-1) XRD patterns of  $\text{BiVO}_4$  and  $\text{Au/BiVO}_4$  (Fig. S1).



**Fig. S1** XRD patterns of (a)  $\text{BiVO}_4$  and (b)  $\text{Au/BiVO}_4$ .

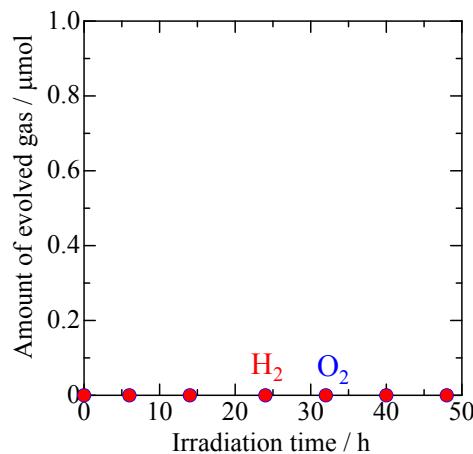
ESI-2) SEM images of  $\text{BiVO}_4$  calcined at various temperatures (Fig. S2).



**Fig. S2** SEM images of  $\text{BiVO}_4$  calcined at (a) 550 °C, (b) 650 °C, (c) 750 °C, and (d) 850 °C,.

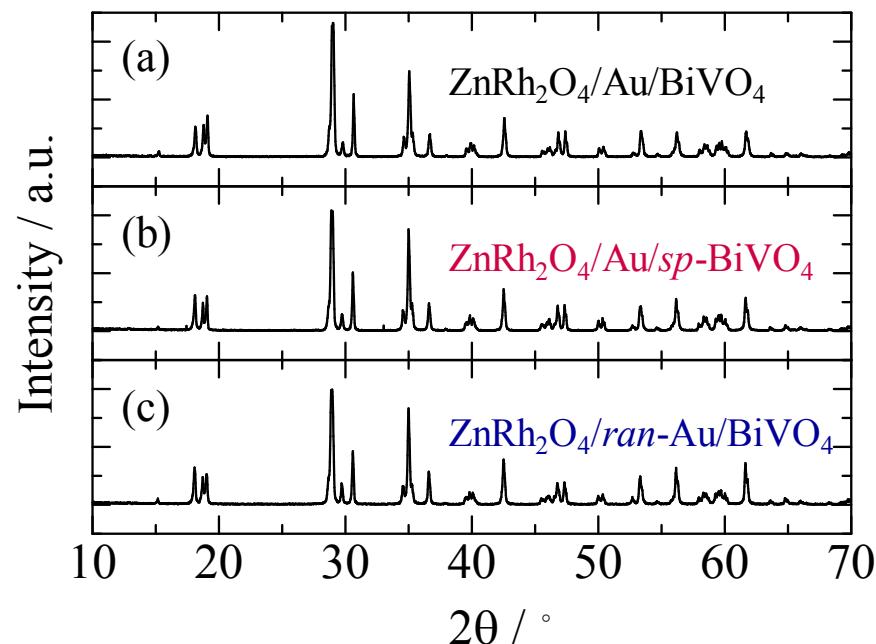
ESI-3) Complementary water-splitting tests (Fig. S3).

Figure S3 shows the time courses of  $H_2$  and  $O_2$  evolution from pure water using directly connected  $ZnRh_2O_4$  and  $BiVO_4$  without Au under irradiation with a xenon (Xe) lamp equipped with a Y-44 optical filter ( $> 420$  nm). Neither  $H_2$  nor  $O_2$  was detected, demonstrating that Au nanoparticles inserted between  $ZnRh_2O_4$  and  $BiVO_4$  are indispensable to split water.



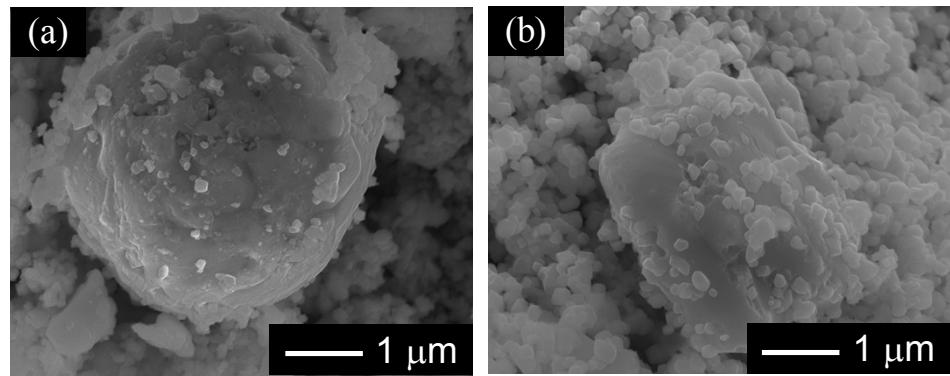
**Fig. S3** Time courses of  $H_2$  (red circles) and  $O_2$  (blue circles) evolution from water in the presence of directly connected  $ZnRh_2O_4$  and  $BiVO_4$  under irradiation with visible light ( $> 420$  nm, Xe lamp + Y-44 filter).

ESI-4) XRD patterns of  $\text{ZnRh}_2\text{O}_4/\text{Au}/\text{BiVO}_4$ ,  $\text{ZnRh}_2\text{O}_4/\text{Au}/sp\text{-}\text{BiVO}_4$ , and  $\text{ZnRh}_2\text{O}_4/ran\text{-}\text{Au}/\text{BiVO}_4$  (Fig. S4).



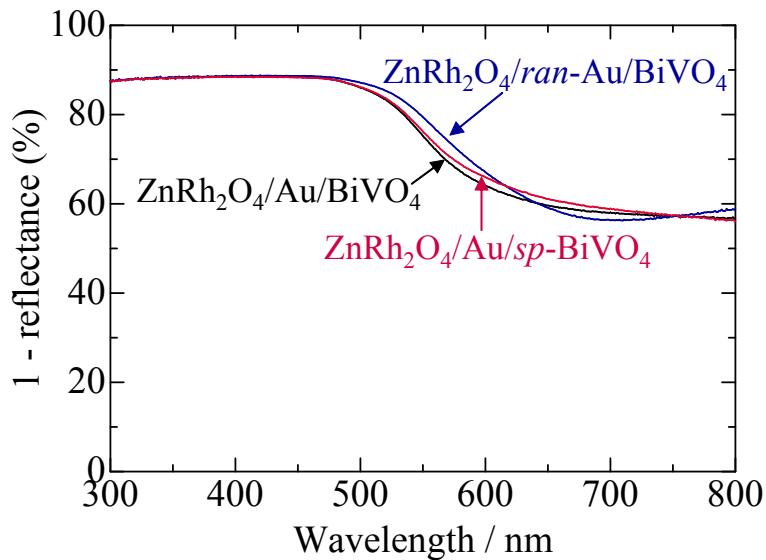
**Fig. S4** XRD patterns of (a)  $\text{ZnRh}_2\text{O}_4/\text{Au}/\text{BiVO}_4$ , (b)  $\text{ZnRh}_2\text{O}_4/\text{Au}/sp\text{-}\text{BiVO}_4$ , and (c)  $\text{ZnRh}_2\text{O}_4/ran\text{-}\text{Au}/\text{BiVO}_4$ .

ESI-5) SEM images of  $\text{ZnRh}_2\text{O}_4/\text{Au}/sp\text{-}\text{BiVO}_4$  and  $\text{ZnRh}_2\text{O}_4/ran\text{-}\text{Au}/\text{BiVO}_4$  (Fig. S5).



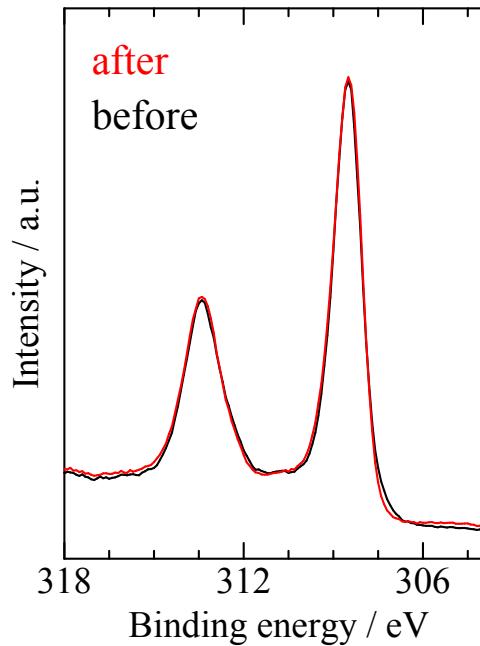
**Fig. S5** SEM images of (a)  $\text{ZnRh}_2\text{O}_4/\text{Au}/sp\text{-}\text{BiVO}_4$  and (b)  $\text{ZnRh}_2\text{O}_4/ran\text{-}\text{Au}/\text{BiVO}_4$ .

ESI-6) UV-vis absorption spectra of of  $\text{ZnRh}_2\text{O}_4/\text{Au}/\text{BiVO}_4$ ,  $\text{ZnRh}_2\text{O}_4/\text{Au}/sp\text{-}\text{BiVO}_4$ , and  $\text{ZnRh}_2\text{O}_4/ran\text{-}\text{Au}/\text{BiVO}_4$  (Fig. S6).



**Fig. S6** UV-vis absorption spectra of of  $\text{ZnRh}_2\text{O}_4/\text{Au}/\text{BiVO}_4$ ,  $\text{ZnRh}_2\text{O}_4/\text{Au}/sp\text{-}\text{BiVO}_4$ , and  $\text{ZnRh}_2\text{O}_4/ran\text{-}\text{Au}/\text{BiVO}_4$ .

ESI-7) XPS spectra of of  $\text{ZnRh}_2\text{O}_4/\text{Au}/\text{BiVO}_4$  before and after the water-splitting experiment (Fig. S7).



**Fig. S7** XPS spectra of Rh 3d region measured for  $\text{ZnRh}_2\text{O}_4/\text{Au}/\text{BiVO}_4$  before (black line) and after (red line) the water-splitting experiment.

ESI-8) Complementary Table for water-splitting tests under monochromic LED lights (Table S1).

**Table S1** Light intensity, O<sub>2</sub> and H<sub>2</sub> generation rates, and AQE values in the presence of ZnRh<sub>2</sub>O<sub>4</sub>/Au/BiVO<sub>4</sub>

Light source	Light intensity / mW cm <sup>-2</sup>	Incident photon rate / h <sup>-1</sup>	O <sub>2</sub> generation rate / μmol h <sup>-1</sup>	H <sub>2</sub> generation rate / μmol h <sup>-1</sup>	AQE(%)
420 nm LED	6.76	$1.04 \times 10^{17}$	$4.34 \times 10^{-2}$	$1.07 \times 10^{-1}$	$5.56 \times 10^{-2}$
470 nm LED	13.7	$2.34 \times 10^{17}$	$8.97 \times 10^{-2}$	$2.01 \times 10^{-1}$	$5.12 \times 10^{-2}$
505 nm LED	12.8	$2.39 \times 10^{17}$	$4.68 \times 10^{-2}$	$1.22 \times 10^{-2}$	$2.62 \times 10^{-2}$
545 nm LED	19.7	$3.98 \times 10^{17}$	$3.52 \times 10^{-3}$	$7.38 \times 10^{-3}$	$1.18 \times 10^{-3}$