A heterojunction photocatalyst composed of zinc rhodium oxide, single crystal-derived bismuth vanadium oxide, and silver for overall pure-water splitting under visible light up to 740 nm.

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Electronic Supporting Information (ESI) for

**Heterojunction Photocatalyst Composed of Zinc Rhodium Oxide, Single Crystal-Derived Bismuth Vanadium Oxide, and Silver for Overall Pure-Water Splitting under Visible Light up to 740 nm**

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ESI. 1  Description of previously developed overall water-splitting photocatalysts.

Numerous groups have attempted to identify powdered photocatalysts that are able to split water into $\text{H}_2$ and $\text{O}_2$ at a molar ratio of $\sim 2 : 1$ (overall water splitting) under visible-light irradiation for the efficient utilization of sunlight energy. One major approach for visible-light sensitization is to construct a system composed of a single photocatalyst with a controlled electric band structure and a suitable cocatalyst.8-16 The most well-known example of such a system is gallium nitride (GaN)–zinc oxide (ZnO) solid solution reported by Domen et al.8-11 More recently, several novel photocatalysts have been developed,12-19 including nanocrystalline CoO, which exhibits visible-light sensitivity even in the absence of a cocatalyst.17 Pan et al.18 also developed a complex photocatalyst, titanium-and-silicon amorphous oxyhydroxide $(\text{MO}_{2-m}\text{(OH)}_{2m}\text{xH}_2\text{O})$-coated Rh–Cr oxide $(\text{RhCrO}_y)$-loaded lanthanum–magnesium–tantalum oxynitride $(\text{LaMg}_x\text{Ta}_{1-x}\text{O}_{1+3x}\text{N}_{2-3x})$ solid solution, which has an $E_g$ of 2.03 eV and is reported to function at wavelengths up to 600 nm. Liu et al.19 synthesized a carbon nanodot (CDot)–carbon nitride (C$_3$N$_4$) nanocomposite as a metal-free photocatalyst and demonstrated that this material is capable of overall water splitting when irradiated with visible light with a wavelength of 630±20 nm, which is the longest reported wavelength for overall water splitting using this approach.

Another approach for visible-light sensitization is the construction of systems composed of two photocatalysts that are both sensitive to visible light, called “Z-scheme” systems. Previous studies on Z-scheme photocatalysts are described in the main text.

ESI. 2  Back-reflection Laue pattern of s-$\text{Bi}_4\text{V}_2\text{O}_{11}$ (Fig. S1).

![Back-reflection Laue pattern of s-$\text{Bi}_4\text{V}_2\text{O}_{11}$](image)

**Fig. S1** Back-reflection Laue pattern taken from the normal to plate surface of a single $\text{Bi}_4\text{V}_2\text{O}_{11}$ crystal. Black spots correspond to the Laue pattern. The visible white markings were due to flaws in the film.
ESI. 3 Photos of pulverized s-Bi$_4$V$_2$O$_{11}$, as-prepared ZnRh$_2$O$_4$, and ZnRh$_2$O$_4$/Ag/p-Bi$_4$V$_2$O$_{11}$ after HNO$_3$ treatment (Fig. S2).

Fig. S2 Photos showing pulverized s-Bi$_4$V$_2$O$_{11}$ (a), as-prepared ZnRh$_2$O$_4$ (b), and ZnRh$_2$O$_4$/Ag/p-Bi$_4$V$_2$O$_{11}$ after HNO$_3$ treatment (c).
ESI. 4 Comparison of s-Bi$_4$V$_2$O$_{11}$ and p-Bi$_4$V$_2$O$_{11}$ regarding UV-vis and PA spectra, and AQE (Fig. S3).

The PA spectrum intensity of s-Bi$_4$V$_2$O$_{11}$ was larger than that of p-Bi$_4$V$_2$O$_{11}$, corresponding to their UV-visible absorption capability. The reasons for the observation are still unknown; however, the higher true absorption capability of s-Bi$_4$V$_2$O$_{11}$ would be one reason for the enhanced AQE, as well as the higher crystallinity and anisotropy. Similar to the case of s-Bi$_4$V$_2$O$_{11}$, the AQE values for O$_2$ evolution of p-Bi$_4$V$_2$O$_{11}$ coincided with the PA absorption spectrum, but not with the UV-vis absorption spectrum.

![Graph showing comparison of AQE and PA intensity spectra for s-Bi$_4$V$_2$O$_{11}$ and p-Bi$_4$V$_2$O$_{11}$](image)

**Fig. S3** Action spectra for O$_2$ evolution by the half reaction of water over s-Bi$_4$V$_2$O$_{11}$ (solid circles) and p-Bi$_4$V$_2$O$_{11}$ (open circles) in the presence of Ce$^{4+}$. The data are the same as those in Fig. 7. The normalized UV-visible absorption spectra of s-Bi$_4$V$_2$O$_{11}$ (red solid line) and p-Bi$_4$V$_2$O$_{11}$ (red broken line), and the normalized PA spectra of p-Bi$_4$V$_2$O$_{11}$ (blue solid line) and p-Bi$_4$V$_2$O$_{11}$ (blue broken line) are also shown.
Overall pure-water splitting over ZnRh$_2$O$_4$/Ag/s-Bi$_4$V$_2$O$_{11}$ irradiated with visible light (>420 nm) (Fig. S4). Comparison of ZnRh$_2$O$_4$/Ag/s-Bi$_4$V$_2$O$_{11}$ before and after performing the water-splitting reaction (Figs. S5 and S6).

**Fig. S4** Time courses of photocatalytic evolution of H$_2$ and O$_2$ from pure water over ZnRh$_2$O$_4$/Ag/s-Bi$_4$V$_2$O$_{11}$ irradiated with visible light (>420 nm).

We measured the XRD pattern of ZnRh$_2$O$_4$/Ag/s-Bi$_4$V$_2$O$_{11}$ powder after performing the water-splitting reaction under the conditions used in Fig. S4. Notably, however, the XRD pattern did not change after the reaction, as shown in Fig. S5. Also note that the XRD pattern in Fig. S5 denoted as “Before water splitting” is the same as that presented in Fig. 3.

**Fig. S5** XRD patterns of HNO$_3$-treated ZnRh$_2$O$_4$/Ag/s-Bi$_4$V$_2$O$_{11}$ before and after performing the water-splitting reaction.
STEM imaging and EDS-based elemental mapping of ZnRh$_2$O$_4$/Ag/Bi$_4$V$_2$O$_{11}$ after the water-splitting reaction (Fig. S4) were also performed (Figs. S6a–S6e). In the STEM image of ZnRh$_2$O$_4$/Ag/Bi$_4$V$_2$O$_{11}$ before the water-splitting reaction (Figs. 6a and 6b), s-Bi$_4$V$_2$O$_{11}$ and ZnRh$_2$O$_4$ particles were clearly distinguishable (Figs. S6a and S6b) based on size. Although the number of ZnRh$_2$O$_4$ particles that were not attached to the Bi$_4$V$_2$O$_{11}$ surface before the water-splitting reaction appeared to have decreased after the reaction, Ag was distributed (Fig. S6e) between the Bi (Fig. S6c) and Rh sites (Fig. S6d), as was observed in Figs. 6c-6e. ZnRh$_2$O$_4$/Ag/Bi$_4$V$_2$O$_{11}$ did not appear to have changed even after performing the water-splitting reaction, and Ag was detected between the ZnRh$_2$O$_4$ and Bi$_4$V$_2$O$_{11}$ particles.

**Fig. S6** STEM images of ZnRh$_2$O$_4$/Ag/s-Bi$_4$V$_2$O$_{11}$ after performing the water-splitting reaction under the conditions in Fig. S4. STEM image (a), its enlargement (b), and EDS element maps (c-e), in which the blue (c), red (d), and yellow (e) colors correspond to Bi, Rh, and Ag, respectively.
ESI. 6  O₂ generation rates under different LED light sources, normalized photon numbers, and QE values for overall pure-water splitting (Table S1).

**Table S1** O₂ generation rates, normalized photon numbers, and QE values for overall pure-water splitting over ZnRh₂O₄/Ag/s-Bi₄V₂O₁₁.

<table>
<thead>
<tr>
<th>Light source</th>
<th>Light intensity / mW cm⁻²</th>
<th>O₂ generation rate / μmol h⁻¹</th>
<th>AQE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>545 nm LED</td>
<td>1.54</td>
<td>1.31×10⁻²</td>
<td>3.45×10⁻²</td>
</tr>
<tr>
<td>610 nm LED</td>
<td>1.40</td>
<td>8.97×10⁻³</td>
<td>2.33×10⁻²</td>
</tr>
<tr>
<td>700 nm LED</td>
<td>4.00</td>
<td>1.36×10⁻²</td>
<td>1.07×10⁻²</td>
</tr>
<tr>
<td>740 nm LED</td>
<td>3.06</td>
<td>3.32×10⁻³</td>
<td>3.25×10⁻³</td>
</tr>
</tbody>
</table>
ESI. 7  Energy band diagram and charge transfer process for ZnRh$_2$O$_4$/Ag/Bi$_4$V$_2$O$_{11}$ (Scheme S1).

The band edge positions of ZnRh$_2$O$_4$, Ag, and Bi$_4$V$_2$O$_{11}$ are described in Scheme S1a and were determined as described in our previous paper.$^{27}$ The band alignments of ZnRh$_2$O$_4$, Ag, and Bi$_4$V$_2$O$_{11}$ before and after the mixing and calcination of Ag and ZnRh$_2$O$_4$, and Ag and Bi$_4$V$_2$O$_{11}$ are shown in Scheme S1b. It should be noted that the uncertainty in the band edge positions for ZnRh$_2$O$_4$, Ag, and Bi$_4$V$_2$O$_{11}$ would correspond to a few tenths of an eV. In addition, various values for the work function of Ag have been reported depending on the surface states and measuring technique used. Further, although we could not determine the Fermi potentials of ZnRh$_2$O$_4$ and Bi$_4$V$_2$O$_{11}$, photogenerated holes in the VB of Bi$_4$V$_2$O$_{11}$ and photoexcited electrons in the CB of ZnRh$_2$O$_4$ evolved O$_2$ and H$_2$, respectively, from water. Scheme S1b was revised to show that holes in the VB of Bi$_4$V$_2$O$_{11}$ and electrons in the CB of ZnRh$_2$O$_4$ have thermodynamic potentials that allow for O$_2$ and H$_2$ evolution, respectively. Thus, the illustration in Scheme 1 was revised from our previous paper.$^{27}$

Scheme S1  Band edge positions of ZnRh$_2$O$_4$, Ag and Bi$_4$V$_2$O$_{11}$ (a) and their band alignments before and after the mixing and calcination of Ag and ZnRh$_2$O$_4$, and Ag and Bi$_4$V$_2$O$_{11}$ (b). The charge transfer processes are also shown.