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Scalable water splitting on particulate photocatalyst sheets with a solar-to-hydrogen energy conversion efficiency exceeding 1%

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Photocatalytic water splitting using particulate semiconductors is a potentially scalable and economically feasible technology for converting solar energy into hydrogen. Z-scheme systems based on two-step photoexcitation of a hydrogen evolution photocatalyst (HEP) and an oxygen evolution photocatalyst (OEP) are suited to harvesting of sunlight because semiconductors with either water reduction or oxidation activity can be applied to water splitting reaction. However, it is challenging achieving efficient transfer of electrons between HEP and OEP particles. Here, we present photocatalyst sheets based on La- and Rh-codoped SrTiO$_3$ (SrTiO$_3$:La,Rh$^8$ and Mo-doped BiVO$_4$ (BiVO$_4$:Mo) powders embedded into a gold (Au) layer. Enhancement of the electron relay by annealing and suppression of undesirable reactions through surface modification allow pure water (pH 6.8) splitting with a solar-to-hydrogen energy conversion efficiency of 1.1% and an apparent quantum yield of over 30% at 419 nm. The photocatalyst sheet design enables efficient and scalable water splitting using particulate semiconductors.

The photocatalyst sheet presented in this work, which consists of SrTiO$_3$:La,Rh (La/(La+Sr) = Rh/(Rh+Ti) = 4 mol%) as a HEP and BiVO$_4$:Mo (Mo/V = 0.05 mol%) as an OEP embedded into a Au layer, is hereafter abbreviated as
SrTiO$_3$:La,Rh/Au/BiVO$_4$:Mo. This sheet was fabricated by the particle transfer method (Figure 1a and Methods).$^{9,10}$ In this process, both SrTiO$_3$:La,Rh and BiVO$_4$:Mo particles were embedded into a gold layer, as seen in the top-view scanning electron microscopy and energy dispersive X-ray fluorescence spectroscopy (SEM-EDX) mapping images of the SrTiO$_3$:La,Rh/Au/BiVO$_4$:Mo photocatalyst sheet (Figure 1b-f). Photodeposition was then used to modify the photocatalyst sheet with Ru species as a cocatalyst.$^{11}$ Nanoparticulate Ru species were deposited on the surfaces of SrTiO$_3$:La,Rh and BiVO$_4$:Mo particles, as shown in Supplementary Figure S1, and were likely attributable to Ru and RuO$_x$, respectively, by X-ray photoelectron spectroscopy (XPS) analysis (see Supplementary Figure S2 and the accompanying discussion) and the Pourbaix diagram of Ru in water system.$^{12}$

The mechanism involved in the water splitting reaction on the SrTiO$_3$:La,Rh/Au/BiVO$_4$:Mo sheet is illustrated in Figure 1g.$^9$ When SrTiO$_3$:La,Rh/Au/BiVO$_4$:Mo is irradiated with visible light, photoexcited electrons are generated in the conduction bands of SrTiO$_3$:La,Rh and BiVO$_4$:Mo, whilst positive holes are generated in the donor levels formed by Rh$^{3+}$ ions of SrTiO$_3$:La,Rh and in the valence band of BiVO$_4$:Mo. Electron transfer occurs from the conduction band of BiVO$_4$:Mo to the donor levels of SrTiO$_3$:La,Rh via gold. Meanwhile, the excited
electrons in SrTiO$_3$:La,Rh reduce water to hydrogen on Ru species serving as a hydrogen evolution cocatalyst, and holes in BiVO$_4$ oxidise water to oxygen with the aid of RuO$_x$ species functioning as an oxygen evolution cocatalyst, achieving overall water splitting. Therefore, the ability of the photocatalyst sheet for overall water splitting should be promoted by facilitating the charge transfer through the underlying Au layer. Note that the Au layer is too thick (approximately 350 nm) to induce the surface plasmon resonance below 520 nm, where the SrTiO$_3$:La,Rh/Au/BiVO$_4$:Mo system shows water splitting activity.$^9$

To reduce the contact resistance between the semiconductors and the metal layer, the photocatalyst sheet samples were annealed in air.$^{13,14}$ The activity in Z-scheme water splitting was indeed strongly dependent on the annealing temperature and duration, as shown in Figure 1h and Supplementary Figure S3; it was maximised (almost doubled) upon annealing at 573 K for 20 min. The sample annealed before the deposition of Au (referred to as “pre-annealed”) exhibited similar gas evolution rates to the unannealed sample (Supplementary Figure S4). This rules out the possibility that the heat treatment intensified the junction between the two kinds of semiconductor particles or altered the semiconducting properties of the photocatalysts favourably. The effect of annealing was further investigated through photoelectrochemical (PEC) measurements of
SrTiO$_3$:La,Rh/Au and BiVO$_4$:Mo/Au electrodes. The SrTiO$_3$:La,Rh/Au and BiVO$_4$:Mo electrodes generated cathodic and anodic photocurrents, respectively (see Supplementary Figure S5 and the accompanying discussion). Compared with the pristine electrodes, the electrodes annealed at 573 K for 20 min generated almost twice the photocurrent. These results indicate that the resistance between SrTiO$_3$:La,Rh and BiVO$_4$:Mo particles via the Au layer was reduced by annealing at 573 K for 20 min. However, the water splitting activity decreased sharply when the sample was heated at higher temperatures (673-773 K) and/or for longer durations (30 min), probably because of the volatilization of V$_2$O$_5$. EDX analysis (Supplementary Table S1) revealed that the Bi/V molar ratio of excessively heated samples exceeded that for stoichiometric BiVO$_4$ (Bi/V=1). These samples exhibited a lighter yellow colour than the other samples, as illustrated in Supplementary Figure S6. Notably, the Au layer deposited by electron beam evaporation under heating in vacuo tended to produce approximately 20% higher water splitting activity than that deposited by vacuum evaporation without substrate heating. This is likely due to the in situ desorption of adsorbents on the photocatalyst particles prior to Au deposition.

The overall water splitting rate on the Ru-modified SrTiO$_3$:La,Rh/Au/BiVO$_4$:Mo sheet (7.5 cm$^2$) annealed at 573 K for 20 min was maximised when the amount of RuCl$_3$
added was 0.2 μmol (Supplementary Figure S7), because the Ru species loaded on the photocatalysts not only served as cocatalysts but also blocked incident photons. The solar-to-hydrogen energy conversion efficiency (STH) of the optimally modified sample was 0.29% at 288 K in the initial three hours of the reaction (Supplementary Figure S8). However, it was noted that the water splitting reaction competed with the formation of water from hydrogen and oxygen and the photoreduction of oxygen molecules, typical backward reactions, on the Ru-modified SrTiO$_3$:La,Rh/Au/BiVO$_4$:Mo sheet. The water splitting rate decreased with irradiation time, although it recovered upon degassing the reaction system (Supplementary Figure S8). In addition, the photocatalytic water splitting activity dropped to 23% and 10% when the background reaction pressure was increased from 5 to 10 and 20 kPa, respectively (Supplementary Figure S9), because the hydrogen and oxygen bubbles needed larger numbers of gas molecules to desorb from the photocatalyst sheet at a higher background pressure.

We previously found that Cr$_2$O$_3$ shell capping noble metal nanoparticles suppressed the backward reactions whilst maintaining the function of the noble metal as a hydrogen evolution catalyst. Hence, Cr$_2$O$_3$ was deposited on the Ru-modified SrTiO$_3$:La,Rh/Au/BiVO$_4$:Mo sheet sample by photodeposition. The activity improved with increasing amount of K$_2$CrO$_4$ up to 0.1 μmol for 7.5 cm$^2$-sized samples.
(Supplementary Figure S10). More importantly, after the photodeposition of Cr$_2$O$_3$, the photocatalyst sheet sample maintained a water splitting activity of 78% and 60% at 10 and 20 kPa, respectively (Supplementary Figure S9). No noticeable decrease in photocatalytic activity was observed for at least 10 h (Figure 2a). Moreover, an additional surface modification by recently-developed amorphous titanium oxide (a-TiO$_2$) layers$^{19,20}$ suppressed the background pressure effect further. The photocatalyst sheet samples modified with the Cr$_2$O$_3$ and a-TiO$_2$ layers maintained the water splitting activity of 89% and 86% at 10 and 20 kPa, respectively (Supplementary Figure S9). Suppression of the backward reactions is a critical factor for the activity of photocatalyst sheets because hydrogen and oxygen are generated in close proximity. Hence, the water splitting reaction was carried out at low background pressures at present. However, this problem can be overcome through the development of surface modifications suppressing the backward reactions effectively.

Figure 2b shows the reaction temperature dependence of the photocatalytic water splitting rate on SrTiO$_3$:La,Rh/Au/BiVO$_4$:Mo modified with the cocatalyst Cr$_2$O$_3$/Ru. The water splitting reaction was enhanced monotonically with increasing reaction temperature in the range from 279 to 318 K at a background pressure of 5 kPa. The apparent activation energy of the overall water splitting reaction was 18 kJ mol$^{-1}$, which
was somewhat higher than that observed for Rh$_2$$_{2-x}$Cr$_x$O$_3$-loaded (Ga$_{1-x}$Zn$_x$)(N$_{1-x}$O$_x$) (8 kJ mol$^{-1}$).$^{21,22}$ It is plausible that electron transfer across the Schottky barrier at the BiVO$_4$:Mo/Au interface and hole transfer through the donor levels formed by Rh$^{3+}$ ions in SrTiO$_3$:La,Rh necessitate thermal excitation for effective conduction. Note that the reaction temperature can reach ca. 333 K under solar illumination in practical operating conditions.$^{23-25}$ The STH of the pure water (pH 6.8) splitting reaction using a Cr$_2$O$_3$/Ru-loaded SrTiO$_3$:La,Rh/Au/BiVO$_4$:Mo sheet was 1.0% at 318 K at a background pressure of 5 kPa. Under simulated sunlight (AM 1.5 G) irradiation through Pyrex glass, hydrogen and oxygen bubbles evolved vigorously on the photocatalyst sheet immersed in pure water (pH 6.8) and the gas evolution ceased immediately when the illumination was interrupted, as presented in Supplementary Movie S1 with the original playing speed. The apparent quantum yield (AQY) and STH reached 33% at 419 nm and 1.1%, respectively, at 331 K and 10 kPa (Figure 2a). By comparison, the photocatalyst suspension Z-scheme system consisting of SrTiO$_3$:Rh and BiVO$_4$ powders and Fe$^{3+/2+}$ redox couples exhibited an AQY of 4.2% at 420 nm and an STH of 0.1% under the best reaction conditions.$^{26}$ Clearly, the photocatalyst sheet recorded by far the highest AQY and STH amongst Z-scheme water splitting systems based on particulate semiconductors, in the absence of any external bias. Higher STHs were reported for
photocatalytic water splitting on single materials such as CoO\textsuperscript{27} and CDots/C\textsubscript{3}N\textsubscript{4},\textsuperscript{28} whilst further studies seem to be necessary to confirm the reproducibility.

The present photocatalyst sheet design can be extended to scalable solution processes, for example, screen printing of ink containing an HEP, OEP, and colloidal conductor such as Au and indium tin oxide (Figure 3a and Methods) as long as the HEP and OEP particles are bridged in proximity. This is because, unlike in (photo)electrochemical systems, a continuous conductive layer is not needed, owing to the absence of an external electric circuit. Indeed, a 10×10 cm printed photocatalyst sheet was readily prepared by the screen-printing method, as shown in Figure 3b. In a printed SrTiO\textsubscript{3}:La,Rh/Au colloid (10 wt%)/BiVO\textsubscript{4}:Mo photocatalyst sheet, Au nanoparticles with sizes ranging from several nanometres to 50 nm were dispersed on the surfaces of the SrTiO\textsubscript{3}:La,Rh and BiVO\textsubscript{4}:Mo particles, as shown in Supplementary Figure S11. Au nanoparticles aggregated in significant numbers and bridged the HEP and OEP particles effectively (Supplementary Figure S12). The printed SrTiO\textsubscript{3}:La,Rh/Au colloid/BiVO\textsubscript{4}:Mo sheet produced hydrogen and oxygen from pure water (pH 6.8) in the stoichiometric ratio. The water splitting activity of the printed sheet (Supplementary Figure S13) was enhanced with increasing amount of Au colloid up to 40 wt%, indicating that Au nanoparticle agglomerates effectively served as an
electron conductor between BiVO$_4$:Mo and SrTiO$_3$:La,Rh. The STH of the Ru-loaded printed SrTiO$_3$:La,Rh/Au colloid (40 wt%)/BiVO$_4$:Mo sheet was 0.1% on the basis of the average gas evolution rate during the 13-hour reaction (Figure 3c). This value was rather low because of the difficulty in photodepositing cocatalysts on a thick particle layer (approximately 10 μm) and the presence of a large amount of Au. Nevertheless, the STH obtained here is still very high compared to those of previously reported particulate photocatalytic systems$^{6-8}$ operating in pure water.

It is notable that the photocatalyst sheet exhibited a high water splitting activity in pure water without any supporting electrolytes, buffering reagents, pH adjustment, or applied voltage. On the photocatalyst sheet sample, HEP and OEP particles are physically embedded into a conductor in the immediate vicinity. This configuration is effective in suppressing the generation of concentration overpotentials of H$^+$/OH$^-$ and IR drops between the hydrogen and oxygen evolution sites commonly observed in (photo)electrochemical water splitting. Therefore, the photocatalyst sheet with high activity is scalable as is. Another key advance in photocatalyst sheet systems demonstrated by the present study is the facilitation of electron transfer between HEP and OEP by conductor layers or particles. In the SrTiO$_3$:La,Rh/Au/BiVO$_4$:Mo photocatalyst sheet system, the annealing-induced enhancement in the electric contact
between Au and the semiconductor photocatalysts boosted the gas evolution rates, confirming the importance of electron transfer through the Au layer. In addition, modification of the Ru catalyst with Cr$_2$O$_3$ and a-TiO$_2$ layers effectively suppressed the backward reactions, allowing the photocatalyst sheet systems to maintain a high activity at elevated pressures. The photocatalyst sheet system based on simple and versatile technologies greatly extend the potential of particulate photocatalysts in efficient solar hydrogen production from pure water on a large scale. A gaseous mixture of hydrogen and oxygen is produced on the photocatalyst sheet, but this can be separated safely by introducing the molecular sieving effect of microporous membranes into the system with a minimum energy loss of 1.1\%.\textsuperscript{29,30} Photocatalyst sheet designs with a relatively low cost could thus lead to advances that would enable industrial solar hydrogen production. The STH of the present SrTiO$_3$:La,Rh/Au/BiVO$_4$:Mo system is limited by the short absorption edge wavelengths of SrTiO$_3$:La,Rh and BiVO$_4$:Mo (520 and 540 nm, respectively). Also, the use of Au as a conductor is an economic obstacle to scaling up. The potential of photocatalyst sheet systems can be further extended by employing particulate photocatalysts with narrower bandgap energies and inexpensive conducting materials.
In conclusion, we demonstrated efficient and scalable systems for Z-scheme pure water splitting based on particulate photocatalyst sheets. The SrTiO$_3$:La,Rh/Au/BiVO$_4$:Mo photocatalyst sheet exhibited an AQY of 33% at 419 nm and an STH of 1.1% in overall pure water (pH 6.8) splitting. Moreover, a photocatalyst sheet prepared by screen printing an ink containing SrTiO$_3$:La,Rh, BiVO$_4$:Mo, and a Au colloid exhibited an STH of 0.1%.

References


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Author Contributions


Competing financial interests

The authors declare no competing financial interests.

Figure Legends
Figure 1 | SrTiO₃:La,Rh/Au/BiVO₄:Mo sheet prepared by particle transfer method.

a, Illustration of the preparation of the SrTiO₃:La,Rh/Au/BiVO₄:Mo sheet by the particle transfer method. b-f, top-view SEM-EDX elemental mapping images showing (b) an SEM image, (c) Bi distribution, (d) Sr distribution, (e) Au distribution, and (f) superimposition of (c-e). g, Schematic of overall water splitting on Ru-modified SrTiO₃:La,Rh/Au/BiVO₄:Mo sheet. h, Dependence of overall water splitting activity of Ru-modified SrTiO₃:La,Rh/Au/BiVO₄:Mo photocatalyst sheets on annealing temperature. All samples were annealed for 20 min. “w/o” stands for the pristine sample. The error bars show the standard deviations. Reactions were carried out under Xe lamp (300 W) illumination (λ > 420 nm) at 288 K and 5 kPa.

Figure 2 | Effect of reaction temperature on photocatalytic water splitting rate of the SrTiO₃:La,Rh/Au/BiVO₄:Mo sheet. a, Time courses of the water splitting reaction on a Cr₂O₃/Ru-modified SrTiO₃:La,Rh/Au/BiVO₄:Mo sheet under simulated sunlight (AM 1.5G) at 288 K and 5 kPa (open symbols) and 331 K and 10 kPa (closed symbols).

b, Temperature dependence of the water splitting activity of the Cr₂O₃/Ru-loaded SrTiO₃:La,Rh/Au/BiVO₄:Mo photocatalyst sheet at a background pressure of 5 kPa
under AM 1.5G simulated sunlight. The Au layer was deposited by electron beam evaporation.

**Figure 3 | Printed photocatalyst sheet.** a, A photograph of the ink used for screen printing the photocatalyst sheet. b, The photograph of a 10×10 cm SrTiO₃:La,Rh/Au nanoparticle/BiVO₄:Mo printed sheet. c, Time course of the water splitting reaction using a Ru-modified SrTiO₃:La,Rh/Au colloid (40 wt%)/BiVO₄:Mo printed sheet under simulated sunlight at 288 K and 5 kPa. The sample (6.25 cm²) was photodeposited with RuCl₃·3H₂O (0.17 μmol).

**Methods**

**Synthesis of SrTiO₃:La,Rh and BiVO₄:Mo particles**

SrTiO₃:La,Rh (La/(La+Sr) = Rh/(Rh+Ti) = 4 mol%) was synthesised by a two-step solid state reaction (SSR). In the initial step, SrTiO₃ was prepared by a conventional SSR. SrCO₃ (Kanto Chemicals, 99.9%, heated in air at 573 K for 1 h before use) and rutile-type TiO₂ (Kanto Chemicals, 99.0%) powders were mixed in a mortar at the Sr/Ti ratio of 1.05 and calcined at 1423 K for 10 h. Subsequently, the resulting SrTiO₃ was mixed in ethanol with La₂O₃ (Kanto Chemicals, 99.99%, freshly calcined in air at
BiVO$_4$:Mo (Mo/V = 0.05 mol%) was synthesised via aqueous processes.$^{15}$ Layered Mo-doped K$_3$V$_5$O$_{14}$ was prepared as a precursor by calcining a mixture of K$_2$CO$_3$ (Kanto Chemical, 99.5%), MoO$_3$ (Kanto Chemical, 99.5%), and V$_2$O$_5$ (Wako Pure Chemical, 99.0%) in air at 723 K for 5 h. A suspension of BiONO$_3$ was prepared by adding Bi(NO$_3$)$_3$·5H$_2$O (Kanto Chemical, 99.9%) in distilled water. Mo-doped K$_3$V$_5$O$_{14}$ was added to the suspension of BiONO$_3$, and the suspension was stirred mildly at 343 K for 10 h. The resulting BiVO$_4$:Mo (Mo/V=0.05 mol%) was collected by filtration and washed with distilled water.

The morphologies of the produced samples were characterized by the scanning electron microscope (SEM) images (Supplementary Figure S1). The phases of the samples were confirmed from the X-ray diffraction (XRD) patterns (Supplementary Figure S14). The diffuse reflectance spectra (DRS) of the prepared samples were shown in Supplementary Figure S15.

**Preparation of SrTiO$_3$:La,Rh/Au/BiVO$_4$:Mo photocatalyst sheets**

1273 K for 12 h before use) and Rh$_2$O$_3$ (Kanto Chemicals, 99.9%) and heated at 1373 K for 6 h.
SrTiO$_3$:La,Rh/Au layer/BiVO$_4$:Mo photocatalyst sheets were fabricated by the particle transfer method$^9,10$ by the following procedure: (1) a mixture of SrTiO$_3$:La,Rh and BiVO$_4$:Mo powders (10 mg each) at the optimized mass ratio of 1:1 (Supplementary Figure S16) was suspended in isopropanol (99.9%, 0.5 mL) and drop-cast on a glass substrate (3×3 cm); (2) after drying at room temperature, a thin gold layer (~350 nm) was deposited by thermal vacuum evaporation (VFR-200M/ERH, ULVAC KIKO Inc.) at an evaporation rate of approximately 20 nm s$^{-1}$ under a base pressure of 2.6×10$^{-3}$ Pa or electron beam evaporation (Nexdep, Angstrom Engineering) at an evaporation rate of 2 Å s$^{-1}$ after the chamber was evacuated to a pressure of 2.9×10$^{-4}$ Pa and the substrate was heated to 673 K; (3) the sample was placed on an alumina plate, heated to 473-773 K at 10 K min$^{-1}$ and kept at the target temperature for 10-30 min; (4) the Au film holding the particulate photocatalysts was bonded to a second glass plate (ca. 3×3 cm) with an adhesive carbon tape and then lifted off the primary glass plate; and (5) the photocatalyst sheet obtained was ultrasonicated twice, for 2 min each time, in distilled water to remove excess particles piling up on the particle layer, because outer layer photocatalyst particles which did not contact with the Au layer could have little contribution to the photocatalytic activity.$^9$
SrTiO$_3$:La,Rh/Au colloid/BiVO$_4$:Mo composite prints were fabricated by screen printing. The printing ink was prepared by mixing 60 mg of SrTiO$_3$:La,Rh powder, 60 mg of BiVO$_4$:Mo powder, 133-1200 mg of Au colloid solution (average particle diameter $\approx$ 20 nm, 10 wt% in ethanol, AUSK-2000E, Shinko Kagaku, Japan) and 600 mg of an organic vehicle consisting of $\alpha$-terpineol, 2-(2-butoxyethoxy)ethanol, and acrylic resin (“SPB-TE1”, Soken Chemicals and Engineering Co., Japan) at a weight ratio of 62.5 : 12.5 : 25.0. After evaporation of ethanol, the paste was screen printed on a glass substrate (ca. 3×3 cm). The printed area was controlled to be 2.5×2.5 cm for the measurement of photocatalytic activity. The obtained print was dried at 353 K for 30 min and calcined at 573 K for 30 min.

**Preparation of photoelectrodes**

Photoelectrodes of SrTiO$_3$:La,Rh/Au and BiVO$_4$:Mo/Au were fabricated by a particle transfer method similar to the fabrication of the photocatalyst sheet. SrTiO$_3$:La,Rh or BiVO$_4$:Mo powder (20 mg) was dispersed in isopropanol (0.5 mL) by ultrasonication for 30 min. The suspension was deposited on a glass substrate. Au layers 600-800 nm in thickness were deposited on the semiconductor particles by vacuum evaporation repeatedly to maintain the evaporation rate and operation pressure similar
to the preparation process of the photocatalyst sheet. The deposited Au film was approximately 3 μm in thickness to ensure the continuity and conductivity. The resulting Au film holding the photocatalyst powder was annealed at 573 K for 20 min, peeled off, and processed into electrodes.

**Characterization**

The XRD patterns of the samples were measured with a Rigaku RINT-UltimaIII diffractometer using Cu-Kα source operated at 40 kV and 40 mA. The DRS were obtained using a UV-Vis-NIR spectrometer (V-670, JASCO) and were converted from reflection to absorbance by the Kubelka-Munk method. The SEM images were recorded on the Hitachi SU8020 system at an acceleration voltage of 3 kV. The XPS measurements were carried out using a monochromatic Mg-Kα source (\(hν = 1253.6 \text{ eV}\)) excited at 8 kV and 10 mA. The analysis chamber pressure was \(\sim 10^{-6} \text{ Pa}\). The binding energies were corrected using the C 1s peak (285.0 eV) as a reference. A JEOL JSM-7001FA system was used for the SEM-EDX elemental mapping.

**Photoelectrochemical (PEC) measurements**
Photoelectrochemical water splitting properties of the SrTiO$_3$:La,Rh/Au and BiVO$_4$:Mo/Au photoelectrodes were investigated in the three-electrode configuration using a Ag/AgCl reference electrode (in saturated KCl aqueous solution) and a Pt wire counter electrode. The potential of the working electrode was controlled by a potentiostat (Hokuto Denko, HSV-100). The potential measured to the Ag/AgCl electrode was also expressed in the reversible hydrogen electrode (RHE) scale through calibration. An aqueous solution of 0.1 M Na$_2$SO$_4$ was used as an electrolyte solution under stirring and purging with Ar gas. The pH of the electrolyte solution was adjusted to 6.8 by adding H$_2$SO$_4$ (aq.) or NaOH (aq.) when necessary. The photoelectrodes were irradiated with a 300 W Xe lamp (Lamp house, R300-3J) equipped with a cut-off filter ($\lambda > 420$ nm). Current-potential curves were measured at a scan rate of 10 mV s$^{-1}$ from negative to positive potential for the BiVO$_4$:Mo/Au photoanodes and in the reverse direction for SrTiO$_3$:La/Rh/Au photocathodes.

Photodeposition of cocatalysts and surface modifiers

The photocatalyst sheets were modified with nanoparticulate Ru species by photodeposition because Ru species was known to work more efficiently as a hydrogen evolution cocatalyst than other metal species in Z-scheme water splitting using
SrTiO$_3$:Rh/BiVO$_4$ powder suspension. Subsequently, the photocatalyst sheets were modified with Cr$_2$O$_3$ and a-TiO$_2$ layers successively by photodeposition to suppress the backward reactions. The Cr$_2$O$_3$ and a-TiO$_2$ layers can suppress the backward reactions because oxygen molecules in the reaction solution cannot penetrate the hydrated oxide layers to reach the nanoparticulate noble metal whilst protons and hydrogen molecules can.

In the first step, Ru species were photodeposited on the photocatalyst sheets from RuCl$_3$·3H$_2$O dissolved in distilled water (40 mL). In the second step, the reactant was changed to an aqueous K$_2$CrO$_4$ solution. The amounts of RuCl$_3$·3H$_2$O and K$_2$CrO$_4$ were 0.2 and 0.1 μmol for a photocatalyst sheet sample 7.5 cm$^2$ in size unless otherwise noted. In the third step, an a-TiO$_2$ layer was deposited from a Ti peroxide solution. The Ti peroxide solution was prepared by the following procedures: titanium tetraisopropoxide (10 μL, Kanto Chemical Co., Inc., 97%) and H$_2$O$_2$ (25 μL, Wako Pure Chemical Industries, 30%) were added to distilled water (1 mL). The suspension was subjected to ultrasonication for a few minutes until it turned into a transparent yellow. The photodeposition reactions were conducted in a Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system. Argon gas was introduced into the circulation system as a carrier gas after removing the air. The total background pressure
of argon and water vapour was approximately 5 kPa. The temperature of the reactant solution was maintained at 288 K by cooling water. Photodeposition was performed under a 300 W Xe lamp (Lamp House, R300-3J; irradiation spectra in Supplementary Figure S17) equipped with a cut-off filter ($\lambda > 420$ nm) until steady gas evolution rates were obtained (typically for 5 h). The number of photons ($420 \text{ nm} < \lambda < 540 \text{ nm}$) incident on the photocatalyst sheet ($7.5 \text{ cm}^2$) was measured using a grating spectroradiometer (EKO Instruments Co., Ltd., LS-100) to be $3.9 \times 10^{21}$ photon h$^{-1}$. The amounts of gases produced were measured by gas chromatography (Shimadzu GC-8A with a TCD detector and MS-5A columns and argon carrier gas).

**Overall water splitting reaction**

Z-scheme water splitting reactions were carried out in the same closed gas circulation system with top illumination from a 300 W Xe lamp equipped with a cut-off filter ($\lambda > 420$ nm) or a solar simulator (Asahi Spectra Co., Ltd., HAL-320; irradiation spectra in Supplementary Figure S18). The photocatalyst sheet samples (ca. 7.5 cm$^2$) were placed at the bottom of the reaction cell containing pure water (40 mL). The reaction temperature was kept at 288 K and the background pressure was 5 kPa unless
otherwise noted. The temperature of the reactant solution was raised (lowered) by a water (ice) bath.

Quantum yield measurement

The apparent quantum yield (AQY) of the Z-scheme water splitting based on a two-step photoexcitation process is given by equation (1):

$$\text{AQY} \, (\%) = \frac{4 \times n(\text{H}_2)}{n(\text{photons})} \times 100,$$

(1)

where $n(\text{H}_2)$ and $n(\text{photons})$ denote the number of produced H$_2$ molecules and the number of incident photons, respectively. The water splitting reaction was carried out using the same experimental set-up, except for the use of a band-pass filter with central wavelength of 418.6 nm and full width at half maximum of 9.5 nm. The spatial distribution of the power spectra are presented in Supplementary Figure S17. The number of incident photons illuminated on the photocatalyst sheet was measured using a grating spectroradiometer to be $2.9 \times 10^{20}$ photon h$^{-1}$ (1.7 mA cm$^{-2}$ as the current density if the photon-to-current conversion efficiency was unity).
Solar-to-hydrogen energy conversion efficiency (STH) measurement

The water splitting reaction was carried out under simulated sunlight illumination. The STH is given as

$$STH(\%) = \frac{R(H_2) \times \Delta G_r}{(P \times S) \times 100}, \quad (2)$$

where $R(H_2)$, $\Delta G_r$, $P$, and $S$ denote the rate of hydrogen evolution during the water splitting reaction, the reaction Gibbs energy of the water splitting reaction ($\text{H}_2\text{O (l)} \rightarrow \text{H}_2 (\text{g}) + \frac{1}{2} \text{O}_2 (\text{g})$), the energy intensity of the AM1.5G solar irradiation (100 mW cm$^{-2}$), and the irradiated sample area (7.5 cm$^2$), respectively. Under the pressure of $p$, bubbles generated on a photocatalyst sheet contain hydrogen and oxygen at the pressure of $\frac{2}{3}p$ and $\frac{1}{3}p$, respectively, if the water pressure is ignored. If hydrogen and oxygen behaves as ideal gases, $\Delta G_r$ is calculated to be 226, 220, and 220 kJ mol$^{-1}$ at 288 K and 5 kPa, 318 K and 5 kPa, and 331 K and 10 kPa, respectively. The light source used closely approximates the power spectrum of the standard AM1.5G illumination as shown in Supplementary Figure S18. The energy intensities of the simulated sunlight and the standard AM1.5G were 79.3 and 79.1 mW cm$^{-2}$ over the wavelength range of 350-1100 nm, and 23.2 and 25.5 mW cm$^{-2}$ over 350-540 nm, respectively.