

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

Author: Qian Wang, Takashi Hisatomi, Qingxin Jia, Hiromasa Tokudome, Miao Zhong, Chizhong Wang, Zhenhua Pan, Tsuyoshi Takata, Mamiko Nakabayashi, Naoya Shibata, Yanbo Li, Ian D. Sharp, Akihiko Kudo, Taro Yamada & Kazunari Domen

Additional information(追加情報) :

This is the author's accepted version of the manuscript.

The definitive version is published in Nature Materials doi:10.1038/nmat4589 (2016).

The final version published is available online at

<http://www.nature.com/nmat/journal/vaop/ncurrent/abs/nmat4589.html>

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

List of authors

Qian WANG,^{1,2} Takashi HISATOMI,^{1,2} Qingxin JIA,^{1,2} Hiromasa TOKUDOME,^{2,3}
Miao ZHONG,^{1,2} Chizhong WANG,¹ Zhenhua PAN,¹ Tsuyoshi TAKATA,⁴ Mamiko
NAKABAYASHI,⁵ Naoya SHIBATA,⁵ Yanbo LI,⁶ Ian D. SHARP,⁶ Akihiko KUDO,⁷
Taro YAMADA,^{1,2} Kazunari DOMEN^{1,2,*}

Affiliation and full postal address

1 Department of Chemical System Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

2 Japan Technological Research Association of Artificial Photosynthetic Chemical Process (ARPCHEM), 5-1-5 Kashiwanoha, Kashiwa-shi, Chiba 277-8589, Japan

3 Research Institute, TOTO Ltd., 2-8-1 Honson, Chigasaki, Kanagawa 253-8577, Japan

4 Global Research Center for Environment and Energy Based on Nanomaterials Science (GREEN), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba-shi, Ibaraki 305-0044, Japan

5 Institute of Engineering Innovation, The University of Tokyo, 2-11-16 Yayoi,

Bunkyo-ku, Tokyo 113-8656, Japan

6 Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, 1

Cyclotron Road, Berkeley, CA 94720, United States

7 Department of Applied Chemistry, Tokyo University of Science, 1-3 Kagurazaka,

Shinjuku-ku, Tokyo 162-8601, Japan

***Corresponding author**

Professor Kazunari DOMEN

Department of Chemical System Engineering, School of Engineering, The University of

Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Tel: +81-3-5841-1148

Fax: +81-3-5841-8838

E-mail: domen@chemsys.t.u-tokyo.ac.jp

Photocatalytic water splitting using particulate semiconductors is a potentially scalable and economically feasible technology for converting solar energy into hydrogen.¹⁻³ 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.^{4,5} However, it is challenging achieving efficient transfer of electrons between HEP and OEP particles.^{6,7} Here, we present photocatalyst sheets based on La- and Rh-codoped SrTiO₃ (SrTiO₃:La,Rh)⁸ and Mo-doped BiVO₄ (BiVO₄: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 SrTiO₃:La,Rh (La/(La+Sr) = Rh/(Rh+Ti) = 4 mol%) as a HEP and BiVO₄:Mo (Mo/V = 0.05 mol%) as an OEP embedded into a Au layer, is hereafter abbreviated as

SrTiO₃:La,Rh/Au/BiVO₄:Mo. This sheet was fabricated by the particle transfer method (Figure 1a and Methods).^{9,10} In this process, both SrTiO₃:La,Rh and BiVO₄: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 SrTiO₃:La,Rh/Au/BiVO₄: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 SrTiO₃:La,Rh and BiVO₄: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 SrTiO₃:La,Rh/Au/BiVO₄:Mo sheet is illustrated in Figure 1g.⁹ When SrTiO₃:La,Rh/Au/BiVO₄:Mo is irradiated with visible light, photoexcited electrons are generated in the conduction bands of SrTiO₃:La,Rh and BiVO₄:Mo, whilst positive holes are generated in the donor levels formed by Rh³⁺ ions of SrTiO₃:La,Rh and in the valence band of BiVO₄:Mo. Electron transfer occurs from the conduction band of BiVO₄:Mo to the donor levels of SrTiO₃:La,Rh via gold. Meanwhile, the excited

electrons in SrTiO₃:La,Rh reduce water to hydrogen on Ru species serving as a hydrogen evolution cocatalyst, and holes in BiVO₄ 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 SrTiO₃:La,Rh/Au/BiVO₄: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

SrTiO₃:La,Rh/Au and BiVO₄:Mo/Au electrodes. The SrTiO₃:La,Rh/Au and BiVO₄: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 SrTiO₃:La,Rh and BiVO₄: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 V₂O₅.^{15,16} EDX analysis (Supplementary Table S1) revealed that the Bi/V molar ratio of excessively heated samples exceeded that for stoichiometric BiVO₄ (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 SrTiO₃:La,Rh/Au/BiVO₄:Mo sheet (7.5 cm²) annealed at 573 K for 20 min was maximised when the amount of RuCl₃

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.¹¹ 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 $\text{SrTiO}_3\text{:La,Rh/Au/BiVO}_4\text{:Mo}$ 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_2O_3 shell capping noble metal nanoparticles suppressed the backward reactions whilst maintaining the function of the noble metal as a hydrogen evolution catalyst.^{17,18} Hence, Cr_2O_3 was deposited on the Ru-modified $\text{SrTiO}_3\text{:La,Rh/Au/BiVO}_4\text{:Mo}$ sheet sample by photodeposition. The activity improved with increasing amount of K_2CrO_4 up to 0.1 μmol for 7.5 cm^2 -sized samples

(Supplementary Figure S10). More importantly, after the photodeposition of Cr_2O_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_2O_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 $\text{SrTiO}_3\text{:La,Rh/Au/BiVO}_4\text{:Mo}$ modified with the cocatalyst $\text{Cr}_2\text{O}_3\text{/Ru}$. 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-y}Cr_yO₃-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 BiVO₄:Mo/Au interface and hole transfer through the donor levels formed by Rh³⁺ ions in SrTiO₃: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 Cr₂O₃/Ru-loaded SrTiO₃:La,Rh/Au/BiVO₄: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 SrTiO₃:Rh and BiVO₄ 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^{27} and $\text{CDots/C}_3\text{N}_4$,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 $\text{SrTiO}_3\text{:La,Rh/Au}$ colloid (10 wt%)/ $\text{BiVO}_4\text{:Mo}$ photocatalyst sheet, Au nanoparticles with sizes ranging from several nanometres to 50 nm were dispersed on the surfaces of the $\text{SrTiO}_3\text{:La,Rh}$ and $\text{BiVO}_4\text{:Mo}$ 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 $\text{SrTiO}_3\text{:La,Rh/Au}$ colloid/ $\text{BiVO}_4\text{:Mo}$ 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 BiVO₄:Mo and SrTiO₃:La,Rh. The STH of the Ru-loaded printed SrTiO₃:La,Rh/Au colloid (40 wt%)/BiVO₄: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 systems⁶⁻⁸ 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 SrTiO₃:La,Rh/Au/BiVO₄: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_2O_3 and $\alpha\text{-TiO}_2$ 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%.^{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 $\text{SrTiO}_3\text{:La,Rh/Au/BiVO}_4\text{:Mo}$ system is limited by the short absorption edge wavelengths of $\text{SrTiO}_3\text{:La,Rh}$ and $\text{BiVO}_4\text{:Mo}$ (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 SrTiO₃:La,Rh/Au/BiVO₄: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 SrTiO₃:La,Rh, BiVO₄:Mo, and a Au colloid exhibited an STH of 0.1%.

References

1. Chen, X., Shen, S., Guo, L. & Mao, S. Semiconductor-based photocatalytic hydrogen generation. *Chem. Rev.* **110**, 6503–6570 (2010).
2. Walter, M. G. *et al.* Solar water splitting cells. *Chem. Rev.* **110**, 6446–6473 (2010).
3. Pinaud, B. A. *et al.* Technical and economic feasibility of centralized facilities for solar hydrogen production via photocatalysis and photoelectrochemistry. *Energy Environ. Sci.* **6**, 1983–2002 (2013).
4. Hisatomi, T., Kubota, J. & Domen, K. Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting. *Chem. Soc. Rev.* **43**, 7520–7535 (2014).

5. Yuan, Y.-P., Ruan, L.-W., Barber, J., Joachim, Loo S. C. & Xue, C. Hetero-nanostructured suspended photocatalysts for solar-to-fuel conversion. *Energy Environ. Sci.* **7**, 3934–3951 (2014).
6. Maeda, K. Z-scheme water splitting using two different semiconductor photocatalysts. *ACS Catalysis* **3**, 1486–1503 (2013).
7. Sasaki, Y., Nemoto, H., Saito, K. & Kudo, A. Solar water splitting using powdered photocatalysts driven by Z-schematic interparticle electron transfer without an electron mediator. *J. Phys. Chem. C* **113**, 17536–17542 (2009).
8. Wang, Q., Hisatomi, T., Ma, S. S. K., Li, Y. & Domen, K. Core/shell structured La- and Rh-codoped SrTiO₃ as a hydrogen evolution photocatalyst in Z-scheme overall water splitting under visible light irradiation. *Chem. Mater.* **26**, 4144–4150 (2014).
9. Wang, Q. *et al.* Z-scheme water splitting using particulate semiconductors immobilized onto metal layers for efficient electron relay. *J. Catal.* **328**, 308–315 (2015).
10. Minegishi, T., Nishimura, N., Kubota, J. & Domen, K. Photoelectrochemical properties of LaTiO₂N electrodes prepared by particle transfer for sunlight-driven water splitting. *Chem. Sci.* **4**, 1120–1124 (2013).

11. Sasaki, Y., Iwase, A., Kato, H. & Kudo, A. The effect of co-catalyst for Z-scheme photocatalysis systems with an $\text{Fe}^{3+}/\text{Fe}^{2+}$ electron mediator on overall water splitting under visible light irradiation. *J. Catal.* **259**, 133–137 (2008).
12. Piela, P., Eickes, C., Brosha, E., Garzon, F. & Zelenay, P. Ruthenium crossover in direct methanol fuel cell with Pt-Ru black anode. *J. Electrochem. Soc.* **151**, A2053-A2059 (2004).
13. Luther, B. *et al.* Investigation of the mechanism for ohmic contact formation in Al and Ti/Al contacts to n-type GaN. *Appl. Phys. Lett.* **70**, 57–59 (1997).
14. Hsu, C.-Y., Lan, W.-H. & Wu, Y. S. Effect of thermal annealing of Ni/Au ohmic contact on the leakage current of GaN based light emitting diodes. *Appl. Phys. Lett.* **83**, 2447–2449 (2003).
15. Kudo, A., Omori, K. & Kato, H. A novel aqueous process for preparation of crystal form-controlled and highly crystalline BiVO_4 powder from layered vanadates at room temperature and its photocatalytic and photophysical properties. *J. Am. Chem. Soc.* **121**, 11459–11467 (1999).
16. Berglund, S. P., Flaherty, D. W., Hahn, N. T., Bard, A. J. & Mullins, C. B. Photoelectrochemical oxidation of water using nanostructured BiVO_4 films. *J. Phys. Chem. C* **115**, 3794–3802 (2011).

17. Maeda, K. *et al.* Noble-metal/Cr₂O₃ core/shell nanoparticles as a cocatalyst for photocatalytic overall water splitting. *Angew. Chem. Int. Ed.* **45**, 7806–7809 (2006).
18. Yoshida, M. *et al.* Role and function of noble-metal/Cr-layer core/shell structure cocatalysts for photocatalytic overall water splitting studied by model electrodes. *J. Phys. Chem. C* **113**, 10151–10157 (2009).
19. Takata, T., Pan, C., Nakabayashi, M., Shibata, N. & Domen, K. Fabrication of a core–shell-type photocatalyst via photodeposition of group IV and V transition metal oxyhydroxides: An effective surface modification method for overall water splitting. *J. Am. Chem. Soc.* **137**, 9627–9634 (2015).
20. Xu, J., Pan, C., Takata, T. & Domen, K. Photocatalytic overall water splitting on the perovskite-type transition metal oxynitride CaTaO₂N under visible light irradiation. *Chem. Commun.* **51**, 7191–7194 (2015).
21. Dionigi, F. *et al.* Gas phase photocatalytic water splitting with Rh_{2–y}Cr_yO₃/GaN:ZnO in μ-reactors. *Energy Environ. Sci.* **4**, 2937–2942 (2011).
22. Hisatomi, T., Minegishi, T. & Domen, K. Kinetic assessment and numerical modeling of photocatalytic water splitting toward efficient solar hydrogen production. *Bull. Chem. Soc. Jpn.* **85**, 647–655 (2012).

23. Wohlgemuth, J. H., Cunningham, D. W., Monus, P., Miller, J. & Nguyen, A. Long term reliability of photovoltaic modules. Photovoltaic energy conversion, Conference record of the 2006 IEEE 4th world conference on. *IEEE*. **2**, 2050–2053 (2006).
24. Kurtz, S. *et al.* Evaluation of high-temperature exposure of photovoltaic modules. *Prog. Photovoltaics Res. Appl.* **19**, 954–965 (2011).
25. Pihosh, Y. *et al.* Photocatalytic generation of hydrogen by core-shell $\text{WO}_3/\text{BiVO}_4$ nanorods with ultimate water splitting efficiency. *Sci. Rep.* **5**, 11141–11150 (2015).
26. Kato, H., Sasaki, Y., Shirakura, N. & Kudo, A. Synthesis of highly active rhodium-doped SrTiO_3 powders in Z-scheme systems for visible-light-driven photocatalytic overall water splitting. *J. Mater. Chem. A* **1**, 12327–12333 (2013).
27. Liao, L. *et al.* Efficient solar water-splitting using a nanocrystalline CoO photocatalyst. *Nat. Nanotechnol.* **9**, 69–73 (2014).
28. Liu, J. *et al.* Metal-free efficient photocatalyst for stable visible water splitting via a two-electron pathway. *Science* **347**, 970–974 (2015).
29. Caro, J. & Noack, M. Zeolite membranes—Recent developments and progress. *Microporous Mesoporous Mater.* **115**, 215–233 (2008).

30. Li, H., Haas-Santo, K., Schygulla, U. & Dittmeyer, R. Inorganic microporous membranes for H₂ and CO₂ separation—Review of experimental and modeling progress. *Chem. Eng. Sci.* **127**, 401–417 (2015).

Acknowledgements

This work was financially supported by the Artificial Photosynthesis Project of the New Energy and Industrial Technology Development Organization (NEDO) and Grants-in-Aids for Specially Promoted Research (No. 23000009) and for Young Scientists (A) (No. 15H05494) and the A3 Foresight Program of Japan Society for the Promotion of Science (JSPS). A part of this work was conducted at Research Hub for Advanced Nano Characterization, The University of Tokyo, with the support of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. T.T. performed work at GREEN, NIMS supported through the Development of Environmental Technology using Nanotechnology from the Ministry of Education, Culture, Sports, Science and Technology (MEXT). I. D. Sharp and Y. Li performed work at the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0004993.

Author Contributions

Q. W., T. H., Y. L. and K. D. conceived the photocatalyst sheet design. Q. W. prepared SrTiO₃:La,Rh and the photocatalyst sheet, conducted XRD, DRS, XPS, and SEM characterizations and the water splitting reactions. T. H. and K. D. supervised the experimental work. Q. J. prepared the BiVO₄:Mo particles. H. T. prepared the printed photocatalyst sheets. M. Z. and C. W. performed the PEC measurements. Q.W., Z. P., and T. T. conducted the surface modification with a-TiO₂. M. N. and N. S. conducted the SEM-EDX elemental mapping measurements. Q. W., Y. L., and I. D. S. carried out the electron beam evaporation. Q. W., T. H., Q. J., H. T., Y. L., A. K., T. Y., and K. D. discussed the results. Q. W. and T. H. wrote the manuscript with contributions from the other coauthors.

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 ($\lambda > 420$ 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).⁸ 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

1273 K for 12 h before use) and Rh_2O_3 (Kanto Chemicals, 99.9%) and heated at 1373 K for 6 h.

$\text{BiVO}_4\text{:Mo}$ (Mo/V = 0.05 mol%) was synthesised via aqueous processes.¹⁵ Layered Mo-doped $\text{K}_3\text{V}_5\text{O}_{14}$ was prepared as a precursor by calcining a mixture of K_2CO_3 (Kanto Chemical, 99.5%), MoO_3 (Kanto Chemical, 99.5%), and V_2O_5 (Wako Pure Chemical, 99.0%) in air at 723 K for 5 h. A suspension of BiONO_3 was prepared by adding $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Kanto Chemical, 99.9%) in distilled water. Mo-doped $\text{K}_3\text{V}_5\text{O}_{14}$ was added to the suspension of BiONO_3 , and the suspension was stirred mildly at 343 K for 10 h. The resulting $\text{BiVO}_4\text{:Mo}$ (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 $\text{SrTiO}_3\text{:La,Rh/Au/BiVO}_4\text{:Mo}$ photocatalyst sheets

SrTiO₃:La,Rh/Au layer/BiVO₄:Mo photocatalyst sheets were fabricated by the particle transfer method^{9,10} by the following procedure: (1) a mixture of SrTiO₃:La,Rh and BiVO₄: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

SrTiO₃:La,Rh/Au colloid/BiVO₄:Mo composite prints were fabricated by screen printing. The printing ink was prepared by mixing 60 mg of SrTiO₃:La,Rh powder, 60 mg of BiVO₄: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 α -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 \times 3 cm). The printed area was controlled to be 2.5 \times 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 SrTiO₃:La,Rh/Au and BiVO₄:Mo/Au were fabricated by a particle transfer method similar to the fabrication of the photocatalyst sheet. SrTiO₃:La,Rh or BiVO₄: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-K α 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-K α source ($h\nu = 1253.6$ eV) excited at 8 kV and 10 mA. The analysis chamber pressure was $\sim 10^{-6}$ 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 SrTiO₃:La,Rh/Au and BiVO₄: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 Na₂SO₄ 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 H₂SO₄ (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 BiVO₄:Mo/Au photoanodes and in the reverse direction for SrTiO₃: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

SrTiO₃:Rh/BiVO₄ powder suspension.¹¹ Subsequently, the photocatalyst sheets were modified with Cr₂O₃ and a-TiO₂ layers successively by photodeposition to suppress the backward reactions. The Cr₂O₃ and a-TiO₂ 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.¹⁷⁻²⁰

In the first step, Ru species were photodeposited on the photocatalyst sheets from RuCl₃·3H₂O dissolved in distilled water (40 mL). In the second step, the reactant was changed to an aqueous K₂CrO₄ solution. The amounts of RuCl₃·3H₂O and K₂CrO₄ were 0.2 and 0.1 μmol for a photocatalyst sheet sample 7.5 cm² in size unless otherwise noted. In the third step, an a-TiO₂ layer was deposited from a Ti peroxide solution.²⁰ The Ti peroxide solution was prepared by the following procedures: titanium tetraisopropoxide (10 μL, Kanto Chemical Co., Inc., 97%) and H₂O₂ (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 cm^2) was measured using a grating spectroradiometer (EKO Instruments Co., Ltd., LS-100) to be 3.9×10^{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):

$$\text{AQY (\%)} = [4 \times n(\text{H}_2)] / n(\text{photons}) \times 100, \quad (1)$$

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 2.9×10^{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

$$STH(\%) = (R(\text{H}_2) \times \Delta G_r) / (P \times S) \times 100, \quad (2)$$

where $R(\text{H}_2)$, ΔG_r , P , and S denote the rate of hydrogen evolution during the water splitting reaction, the reaction Gibbs energy of the water splitting reaction ($\text{H}_2\text{O} (\text{l}) \rightarrow \text{H}_2 (\text{g}) + 1/2 \text{O}_2 (\text{g})$), 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, ΔG_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.