

# Scalable and Efficient Pure-Water Splitting on Particulate Photocatalyst Sheets

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Solar-driven water splitting is a promising approach for producing hydrogen as a clean and sustainable energy carrier. Z-scheme water splitting systems, which employ two different semiconductors for H<sub>2</sub> and O<sub>2</sub> evolution, are capable of utilizing visible light more efficiently than a single-component photocatalyst because the energy required for driving each photocatalyst can be reduced. A major challenge in developing high-performing Z-scheme water splitting systems lies in achieving efficient transfer of electrons between the hydrogen evolution photocatalyst (HEP) and oxygen evolution photocatalyst (OEP). Herein, we report an all-solid-state device for redox-mediator-free Z-scheme water splitting, that is, a photocatalyst sheet consisting of HEP and OEP particles and a conductive layer for efficient electron relay.<sup>[1,2]</sup>

The SrTiO<sub>3</sub>:La,Rh/Au/BiVO<sub>4</sub>:Mo sheets were prepared by a particle transfer method. The SEM-EDX analysis of the photocatalyst sheet prepared revealed that both HEP and OEP particles contacted the gold layer. Thus, electrons could be transferred through the Au between HEP and OEP particles. Simultaneous evolution of H<sub>2</sub> and O<sub>2</sub> occurred at the H<sub>2</sub>/O<sub>2</sub> ratio of two under visible light irradiation ( $\lambda > 420$  nm). The enhancement in the electric contact between Au and the semiconductor photocatalysts by annealing boosted the gas evolution rates, confirming the importance of the electron transfer through the Au layer. The SrTiO<sub>3</sub>:La,Rh/Au/BiVO<sub>4</sub>:Mo photocatalyst sheet exhibited an AQY of 33% at 419 nm in overall pure water (pH 6.8) splitting at 331 K and 10 kPa. The STH was calculated to be

1.1% on the basis of the average rate of gas evolution over the ten-hour reaction. Nevertheless, the photocatalytic water-splitting activity of the SrTiO<sub>3</sub>:La,Rh/Au/BiVO<sub>4</sub>:Mo sheets dramatically decreased with increasing background pressure because of reverse reactions involving molecular oxygen. Hence, surface modification using Cr<sub>2</sub>O<sub>3</sub> and amorphous titanium oxide (a-TiO<sub>2</sub>) layers are necessary in order to suppress the reverse reactions. Furthermore, a high water-splitting activity at ambient pressure were achieved by utilizing carbon as an oxygen-tolerant conductor layer in the photocatalyst sheet systems.<sup>[3]</sup> The SrTiO<sub>3</sub>:La,Rh/C/BiVO<sub>4</sub>:Mo sheets exhibited a STH of 1.0% during unassisted pure-water (pH 6.8) splitting at 331 K and 91 kPa, as shown in Figure 1, because the sputtered carbon conductor was less active with regard to reverse reactions.

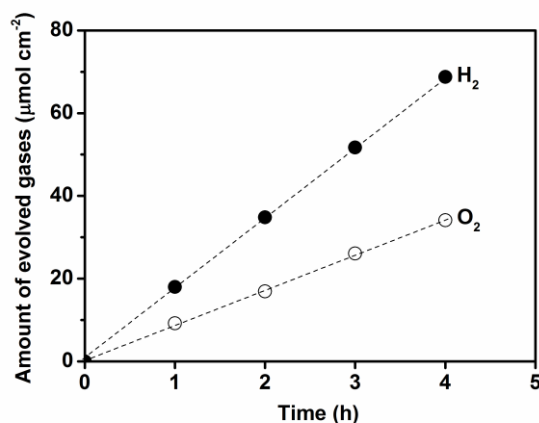


Fig. 1. A time course of water splitting on a SrTiO<sub>3</sub>:La,Rh/C/BiVO<sub>4</sub>:Mo photocatalyst sheet modified with Cr<sub>2</sub>O<sub>3</sub>/Ru under simulated sunlight (AM 1.5G) at 331 K and 91 kPa.

## REFERENCES

- [1] Q. Wang, T. Hisatomi, Q. Jia, H. Tokudome, M. Zhong, C. Wang, Z. Pan, T. Takata, M. Nakabayashi, N. Shibata, Y. Li, I. D. Sharp, A. Kudo, T. Yamada, K. Domen, *Nature Mater.* 15 (2016) 611.
- [2] Q. Wang, Y. Li, T. Hisatomi, M. Nakabayashi, N. Shibata, J. Kubota, K. Domen, *J. Catal.* 328 (2015) 308.
- [3] Q. Wang, T. Hisatomi, Y. Suzuki, Z. Pan, J. Seo, M. Katayama, T. Minegishi, H. Nishiyama, T. Takata, K. Seki, A. Kudo, T. Yamada, K. Domen, *J. Am. Chem. Soc.*, DOI 10.1021/jacs.6b12164.