Efficient and scalable water splitting on particulate photocatalyst sheets

Qian Wang,[a,b] **Takashi Hisatomi,**[a,b] **Akihiko Kudo,**[c] **Taro Yamada,**[a,b] **Kazunari Domen**[a,b,*]

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

[b]*Japan Technological Research Association of Artificial Photosynthetic Chemical Process (ARPChem), 2-11-9 Iwamotocho, Chiyoda-ku, Tokyo 101-0032, Japan*

[c]*Department of Applied Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan*

**Corresponding author: +81-3-5841-8838, domen@chemsys.t.u-tokyo.ac.jp*

Abstract: Z-scheme water splitting systems, which employ two different semiconductors for H_2 and O_2 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.

Keywords: Water splitting, photocatalysis, hydrogen production

1. Introduction

Development of sunlight-driven water splitting systems with high efficiency, scalability, and cost-competitiveness is a central issue for mass production of solar hydrogen as a renewable and storable energy carrier. Z-scheme photocatalytic systems using two-step photoexcitation of HEP and OEP have been the subject of considerable attention because narrow band gap semiconductors with either a water reduction or oxidation potential can be employed to split water using solar energy. The challenge of developing a redox-mediator-free Z-scheme water splitting system lies in ensuring efficient transfer of electrons between HEP and OEP.[1] 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 continuous conductive layer for efficient electron transfer. Taking the combination of $SrTiO_3$:La,Rh and $BiVO_4$:Mo as a prototype, this work discusses the effectiveness and advantages of the all-solid-state structure design over conventional Z-scheme systems based on interparticle electron transfer in the overall water splitting reaction.

2. Experimental

The photocatalyst sheets were prepared by a particle transfer method.[2] Firstly, a mixture of $SrTiO_3$:La,Rh and $BiVO_4$:Mo powders (10 mg each) were suspended in isopropanol and deposited on a glass substrate (3×3 cm^2). After drying at room temperature, a thin gold[3,4] or carbon layer[5] (300-1000 nm) was deposited by vacuum evaporation or sputtering. The conductive film holding the particulate photocatalysts was bonded to a second glass plate (3×3 cm^2) with an adhesive carbon tape and then lifted off the primary glass plate. The photocatalyst sheet obtained was ultrasonicated in distilled water to remove excess particles piling on the particle layer. Ruthenium as a cocatalyst was loaded on the photocatalyst sheets by photodeposition from $RuCl_3\cdot3H_2O$ dissolved in distilled water (40 mL). The photodeposition reactions were carried out in a Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system under illumination from a Xe lamp with a cutoff filter ($\lambda > 420$ nm). Z-scheme water splitting reactions were carried out in the same closed gas circulation system with top irradiation. The sheet samples (3×3 cm^2) were placed at the bottom of the reaction cell containing the reactant solution (40 mL). The reaction cell was illuminated by a 300 W Xe lamp fitted with a cut-off filter ($\lambda > 420$ nm) or a solar simulator. The amounts of gases produced were measured by gas chromatography.

3. Results and discussion

The SEM-EDX analysis of the photocatalyst sheet prepared by the particle transfer method revealed that both HEP and OEP particles contacted the conductive layer. Thus, electrons could be transferred through the metal between HEP and OEP particles. Simultaneous evolution of H_2 and O_2 occurred at the H_2/O_2 ratio of two under visible light irradiation ($\lambda > 420$ nm). The $SrTiO_3$:La,Rh/Au/$BiVO_4$: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. Furthermore, a high water-splitting activity at ambient pressure was achieved by utilizing carbon as an oxygen-tolerant conductor layer in the photocatalyst sheet systems. The $SrTiO_3$:La,Rh/C/$BiVO_4$:Mo sheets exhibited a STH of 1.0% during unassisted pure-water (pH 6.8) splitting at near-ambient pressure (91 kPa), as shown in Figure 1, because the sputtered carbon conductor was less active with regard to reverse reactions.

This photocatalyst sheet exhibited a water-splitting activity that was twice as high as that of the powder suspension and photoelectrochemical systems in their optimal reaction solutions, because the underlying metal layer efficiently transfers electrons from the OEP to the HEP. The effects of H^+/OH^- concentration overpotentials and of the *IR* drop are reduced in the case of the photocatalyst sheet compared to photoelectrochemical systems, because the HEP and OEP are situated in close proximity to one another. Therefore, the photocatalyst sheet design is well-suited to efficient large-scale applications.

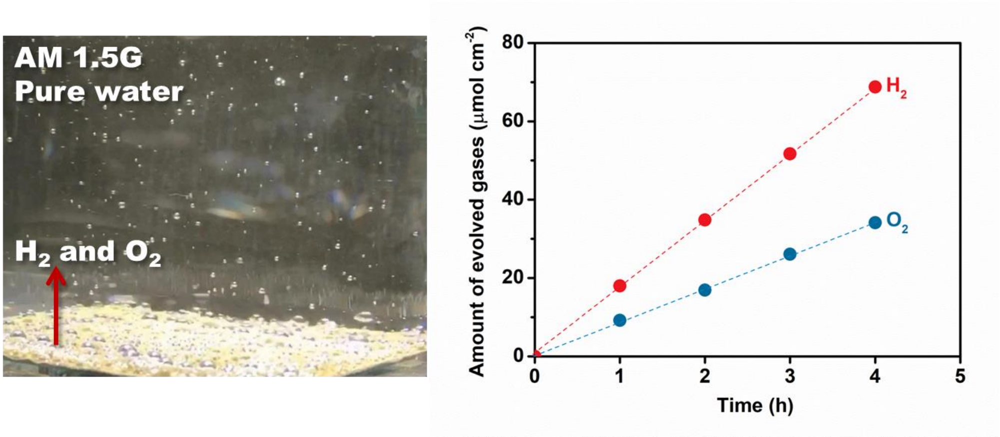

Figure 1. Overall water splitting on $SrTiO_3$:La,Rh/C/$BiVO_4$:Mo sheet under AM 1.5G simulated sunlight irradiation.

4. Conclusions

The photocatalyst sheet recorded by far the highest STH among Z-scheme water splitting systems based on particulate semiconductors. The concept of photocatalyst sheet not only enhances the photocatalytic activity in Z-scheme water splitting but also overcomes the limitations of conventional Z-scheme systems, which necessitate the addition of redox couples, aggregation of photocatalyst particles, or formation of composites for electron relay, thus extending the kinds of photocatalytic materials applicable to the reaction. Our study demonstrates that appropriate device designing extends the potential of particulate photocatalysts in the water splitting reaction and offers a novel and versatile strategy toward sustainable and practical solar fuel production.

References

1. Y. Sasaki, H. Nemoto, K. Saito, A. Kudo, J. Phys. Chem. C 113 (2009) 17536.
2. T. Minegishi, N. Nishimura, J. Kubota, K. Domen, Chem. Sci. 4 (2013) 1120.
3. 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.
4. Q. Wang, T. Hisatomi, M. Katayama, T. Takata, T. Minegishi, A. Kudo, T. Yamada, K. Domen, Faraday Discuss. 197 (2017) 491.
5. 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. 139 (2017) 1675.