Water splitting and CO_2 reduction using newly developed Z-scheme photocatalyst systems

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Abstract: Construction of Z-scheme systems is a promising way to achieve artificial photosynthetic water splitting and CO_2 reduction. Various Z-scheme systems for water splitting under visible light irradiation were constructed by development of novel electron mediators and photocatalysts. Note that photocorrosive metal sulfides were successfully used as an H_2-evolving photocatalyst in Z-scheme systems for water splitting by combining them with a suitable electron mediator and an O_2-evolving photocatalyst. The Z-scheme systems also showed the activity for CO_2 reduction accompanied by reasonable O_2 evolution under visible light irradiation.
Keywords: artificial photosynthesis, visible light, photocatalyst.

1. Introduction

Artificial photosynthetic water splitting and CO_2 reduction are a promising chemical reaction to address energy and environmental issues.[1] Z-scheme systems have been extensively studied to achieve such reactions. The Z-scheme system is composed of two different photocatalysts and a suitable electron mediator.[1-3] A photocatalyst which is active for either H_2 or O_2 evolution can be used in the system, and hence various kinds of photocatalyst will be a candidate. Combination of photocatalysts and an electron mediator is also an important factor to construct the Z-scheme system.

In the present study, various Z-scheme systems for water splitting were developed by combining various photocatalysts and electron mediators with each other. The Z-scheme system was also applied to CO_2 reduction accompanied by O_2 evolution using water as an electron source.

2. Experimental

Metal oxides and metal sulfides were prepared by a solid-state reaction and a liquid-solid-state reaction. Physicochemical properties of the synthesized powder were analyzed using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV-vis-NIR spectroscopy, and scanning electron microscope (SEM).

Photocatalytic activities for water splitting and sacrificial H_2 and O_2 evolution were evaluated using a gas-closed-circulation system. In this system, the gas sampling port from the reactor is directly connected to an online gas chromatograph (TCD, MS-5A, Ar carrier gas) for measuring the evolved H_2 and O_2. The photocatalyst was irradiated using a 300-W Xe lamp (Perkin Elmer, CERMAX PE-300BBF) with a long-pass filter and a solar simulator (Asahi spectra, HAL-320).

3. Results and discussion

Rh-doped $SrTiO_3$ and $BiVO_4$ are active photocatalysts for sacrificial H_2 and O_2 evolution under visible light irradiation, respectively.[4,5] Therefore, the $SrTiO_3$:Rh as an H_2-evolving photocatalyst and $BiVO_4$ as an O_2-evolving photocatalyst were combined with suitable electron mediators to construct Z-scheme system. When $Fe^{3+/2+}$ and $Co^{3+/2+}$ complex redox couples were employed as an ionic electron mediator, steady H_2 and O_2 evolution with a stoichiometric amount were observed under visible light and sunlight irradiation.[6,7] Interestingly, the ionic redox mediator was not necessary to achieve Z-schematic water splitting, when the solution was controlled to acidic condition.[8] The activity was improved by formation of a composite of photocatalysts and incorporation of a reduced graphene oxide (RGO) as a solid-state electron mediator.[9,10]

Photocorrosive metal sulfides were successfully used as an H_2-evolving photocatalyst in Z-scheme systems for water splitting. In more detail, the combination of $(CuGa)_{0.5}ZnS_2$ as an H_2-evolving photocatalyst, $BiVO_4$ as an O_2-evolving photocatalyst, and $Co^{3+/2+}$ complex as an electron mediator functioned as a Z-scheme system for water splitting under visible light irradiation.[11] The combination of $CuGaS_2$ as an H_2-evolving photocatalyst, RGO as a solid-state electron mediator, and either TiO_2 or $BiVO_4$ as an O_2-evolving photocatalyst also worked as a Z-scheme system for water splitting.[12,13] The Z-scheme systems with RGO also showed the activity for CO_2 reduction to produce CO with H_2 and O_2 evolution due to water splitting.[13,14] Developed Z-scheme systems were summarized in Figure 1.

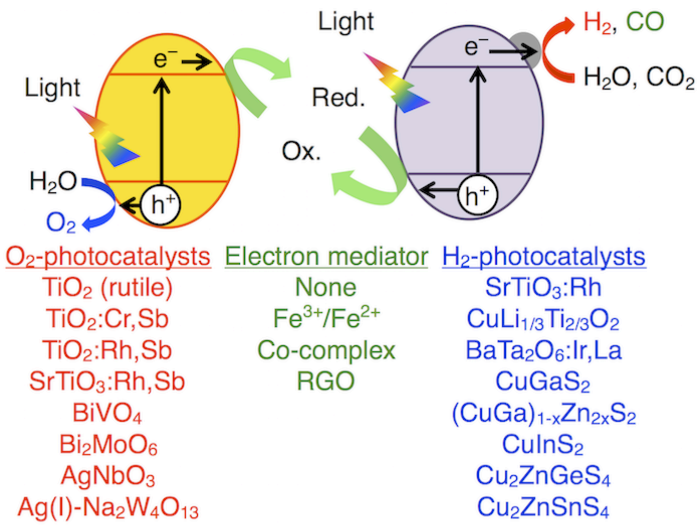

Figure 1 Various Z-scheme systems for water splitting and CO_2 reduction accompanied by O_2 evolution.

4. Conclusions

Upon using the Rh-doped $SrTiO_3$ and $BiVO_4$ photocatalysts, various kinds of Z-scheme systems for water splitting were successfully constructed. Photocorrosive metal sulfides were successfully used as an H_2-evolving photocatalyst in Z-scheme systems with suitable electron mediators. The Z-scheme system with RGO also showed the activity for CO_2 reduction to produce CO. Thus, we have developed various Z-scheme systems for artificial photosynthetic water splitting and CO_2 reduction.

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