Water splitting and CO₂ 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 CO₂ 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 H₂-evolving photocatalyst in Z-scheme systems for water splitting by combining them with a suitable electron mediator and an O₂-evolving photocatalyst. The Z-scheme systems also showed the activity for CO₂ reduction accompanied by reasonable O₂ evolution under visible light irradiation.

Keywords: artificial photosynthesis, visible light, photocatalyst.

1. Introduction

Artificial photosynthetic water splitting and CO₂ reduction are a promising chemical reaction to address energy and environmental issues. 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. A photocatalyst which is active for either H₂ or O₂ 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 CO₂ reduction accompanied by O₂ 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 H₂ and O₂ 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 H₂ and O₂. 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 SrTiO₃ and BiVO₄ are active photocatalysts for sacrificial H₂ and O₂ evolution under visible light irradiation, respectively. Therefore, the SrTiO₃:Rh as an H₂-evolving photocatalyst and BiVO₄ as an O₂-evolving photocatalyst were combined with suitable electron mediators to construct Z-scheme system. When Fe³⁺/²⁺ and Co³⁺/²⁺ complex redox couples were employed as an ionic electron mediator, steady H₂ and O₂ evolution with a stoichiometric amount were observed under visible light and sunlight irradiation. Interestingly, the ionic redox mediator was not necessary to achieve Z-schematic water splitting, when the
solution was controlled to acidic condition. 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.

Photocorrosive metal sulfides were successfully used as an H₂-evolving photocatalyst in Z-scheme systems for water splitting. In more detail, the combination of (CuGa)₂₅ ZnS₂ as an H₂-evolving photocatalyst, BiVO₄ as an O₂-evolving photocatalyst, and Co³⁺/²⁺ complex as an electron mediator functioned as a Z-scheme system for water splitting under visible light irradiation. The combination of CuGaS₂ as an H₂-evolving photocatalyst, RGO as a solid-state electron mediator, and either TiO₂ or BiVO₄ as an O₂-evolving photocatalyst also worked as a Z-scheme system for water splitting. The Z-scheme systems with RGO also showed the activity for CO₂ reduction to produce CO with H₂ and O₂ evolution due to water splitting. Developed Z-scheme systems were summarized in Figure 1.

![Diagram of Z-scheme systems for water splitting and CO₂ reduction accompanied by O₂ evolution.](image)

**Figure 1** Various Z-scheme systems for water splitting and CO₂ reduction accompanied by O₂ evolution.

4. Conclusions

Upon using the Rh-doped SrTiO₃ and BiVO₄ photocatalysts, various kinds of Z-scheme systems for water splitting were successfully constructed. Photocorrosive metal sulfides were successfully used as an H₂-evolving photocatalyst in Z-scheme systems with suitable electron mediators. The Z-scheme system with RGO also showed the activity for CO₂ reduction to produce CO. Thus, we have developed various Z-scheme systems for artificial photosynthetic water splitting and CO₂ reduction.

References