

Z-scheme photocatalyst systems for water splitting under visible light irradiation

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Water splitting to produce H₂ using sunlight is a form of artificial photosynthesis in that light energy is converted to chemical energy. As such, water splitting using powdered photocatalysts has attracted attention in the framework of energy and environmental issues. This article reviews z-scheme photocatalyst systems for water splitting under visible light irradiation, especially focused on the systems consisting of SrTiO₃:Rh of a H₂-evolving photocatalyst, and O₂-evolving photocatalysts with and without electron mediators. These photocatalyst systems showed activities for water splitting into H₂ and O₂ in a stoichiometric amount under visible light irradiation and even under sunlight irradiation. The photocatalytic activity was sensitive to pH. The optimum pH was 2.4 when iron ions were used as electron mediators. Co-catalysts also affected the activity. The photodeposited Ru co-catalyst gave an excellent performance. The best performance achieved by the pH adjustment and the selection of a co-catalyst was obtained mainly by suppression of back reactions to form H₂O from evolved H₂ and O₂.

Introduction

Energy and environmental issues on a global level are important topics. It is indispensable to construct clean energy systems in order to solve these issues. Solar H₂ production from water is one of the most promising processes. Semiconductor electrodes^{1–5} and photocatalysts^{4–11} will be useful for solar water splitting. Solar water splitting using a powdered photocatalyst is a strong candidate for practical large-scale use for a H₂ production system because of its simplicity of fabrication.

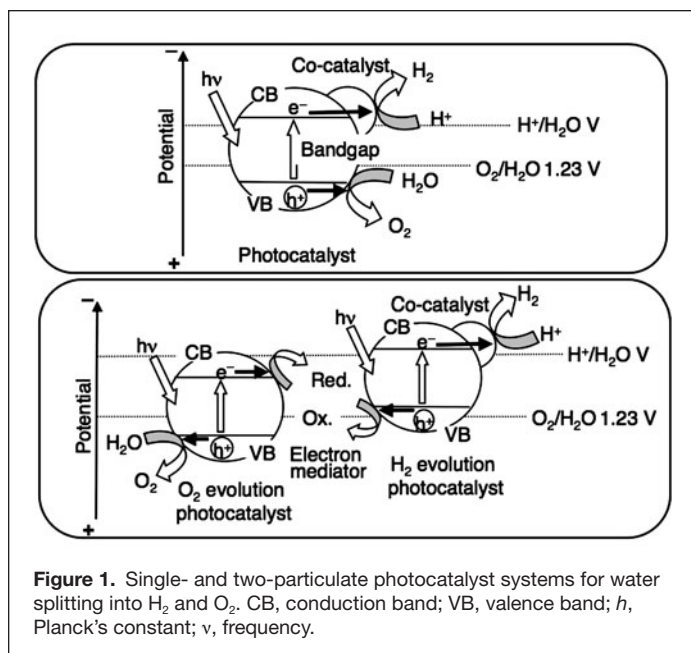
Photon energy is converted to chemical energy accompanied by a largely positive change in the Gibbs free energy through water splitting. This reaction is similar to photosynthesis by green plants from the viewpoint of an uphill reaction with a positive change in the Gibbs free energy. Therefore, photocatalytic water splitting into H₂ and O₂ in a stoichiometric ratio is regarded as artificial photosynthesis. Artificial photosynthesis is an attractive and challenging theme in chemistry. Although many oxide photocatalysts have been reported for water splitting, they only respond to UV irradiation.^{4–11} The number of photocatalysts that are active for water splitting under visible light irradiation is very limited. Therefore, it is important to develop improved visible-light-driven photocatalyst materials for solar water splitting.

There are two types of photocatalyst systems for water splitting under visible light irradiation, as shown in **Figure 1**.

A single-particulate photocatalyst system is one example. Important points in the single-particulate semiconductor photocatalyst system are the width of the bandgap and levels of the conduction and valence bands. The bottom level of the conduction band has to be more negative than the redox potential of H⁺/H₂ (0 V versus NHE [normal hydrogen electrode]), while the top level of the valence band needs to be more positive than the redox potential of O₂/H₂O (1.23 V). The bandgap of a visible-light-driven photocatalyst should be narrower than 3.0 eV ($\lambda > 415$ nm). Therefore, suitable band engineering is necessary for tuning the band positions of photocatalyst materials for water splitting under visible light irradiation. Some oxynitride photocatalysts such as GaN-ZnO and ZnGeN₂-ZnO solid solutions are active for water splitting as a single-particulate photocatalyst.^{12,13} See the Maeda and Domen article in this issue.

Two-photon systems, as seen in photosynthesis by green plants (z-scheme), are another way to achieve overall water splitting. The z-scheme is composed of a H₂-evolving photocatalyst, an O₂-evolving photocatalyst, and an electron mediator, as shown in Figure 1. Photocatalysts that are active only for half reactions of water splitting (sacrificial H₂ and O₂ evolution reactions) can be employed for the construction of the z-scheme: that is the merit of the z-scheme. There

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are many reports about visible-light-driven photocatalysts that show the activities for H₂ and O₂ evolution from water containing sacrificial reagents (electron donor and acceptor reagents), for example, WO₃,¹⁴ BiVO₄,¹⁵ Cr and Sb co-doped TiO₂ (TiO₂:Cr,Sb),¹⁶ AgNbO₃,¹⁷ Cr and Ta co-doped SrTiO₃ (SrTiO₃:Cr,Ta),¹⁸ Rh-doped SrTiO₃ (SrTiO₃:Rh),¹⁹ SnNb₂O₆,²⁰ Cr-doped PbMoO₄ (PbMoO₄:Cr),²¹ Rh and Sb co-doped TiO₂ (TiO₂:Rh,Sb),²² Sm₂Ti₂S₂O₅,²³ Ta₃N₅,⁸ and TaON.²⁴ These photocatalysts are inactive for overall water splitting into H₂ and O₂ in the absence of sacrificial reagents. However, overall water splitting has been attained by constructing a z-scheme photocatalysis system composed of H₂- and O₂-photocatalysts and a suitable electron mediator.^{25–33} **Table I** summarizes reported z-scheme photocatalyst systems that work for water splitting under visible light irradiation. Combined systems of Pt co-catalyst loaded SrTiO₃ co-doped with Cr and Ta (Pt/SrTiO₃:Cr,Ta) for the H₂-evolving photocatalyst with Pt/WO₃ for the O₂-evolving photocatalyst can split water into H₂ and O₂ in stoichiometric amounts under visible light irradiation in the presence of an IO₃⁻/I⁻ redox couple. Oxynitride photocatalysts TaON, CaTa₂O₂N, and BaTa₂O₂N can be used as H₂-evolving photocatalysts with a Pt/WO₃ of an O₂-evolving photocatalyst. These photocatalyst systems respond to about 450 nm of light, which is limited by the bandgap of WO₃. The system of Pt/TaON with RuO₂/TaON is a unique combination and is active up to 500 nm. Coumarin dye adsorbed on a K₄Nb₆O₁₇ photocatalyst with a wide bandgap works as an H₂-evolving photocatalyst through a dye sensitization process. ZrO₂ modification of TaON on an H₂-evolving photocatalyst improves the activity. The z-scheme system consisting of Pt/SrTiO₃:Rh and BiVO₄ or Bi₂MoO₆ or WO₃ is also active in the presence of a Fe³⁺/Fe²⁺ redox couple. The system of Pt/SrTiO₃:Rh and BiVO₄ responds to 520-nm light, which corresponds to the bandgaps of SrTiO₃:Rh and BiVO₄. The

system of SrTiO₃:Rh and BiVO₄ corresponds to the longest light wavelength with relatively high activity among z-scheme systems, shown in Table I. It also shows activity for solar water splitting. Moreover, this z-scheme system works without an electron mediator only when SrTiO₃:Rh is employed as a H₂-evolving photocatalyst.

In this article, the z-scheme systems consisting of SrTiO₃:Rh of an H₂-evolving photocatalyst and O₂-evolving photocatalysts with and without electron mediators are reviewed and discussed in detail.

Construction of a z-scheme system composed SrTiO₃:Rh and O₂-evolving photocatalysts

The photocatalytic activities for half reactions of water splitting are listed in **Tables II** and **III**. Table II shows the H₂ evolution from an aqueous solution containing Fe²⁺ ions as an electron donor on various photocatalysts. This reaction is based on sacrificial H₂ evolution. The Pt/TiO₂-anatase did not produce H₂, while Pt/SrTiO₃ produced H₂ under UV light irradiation. On the other hand, the H₂ evolution proceeded on Pt-loaded SrTiO₃:Rh, which was a highly active photocatalyst for the H₂ evolution from an aqueous methanol solution under visible light irradiation.¹⁹ Table III shows the

Table I. Z-scheme-type photocatalysts for water splitting under visible light irradiation.

H ₂ -Evolving Photocatalyst	O ₂ -Evolving Photocatalyst	Electron Mediator
Pt/SrTiO ₃ :Cr, Ta	Pt/WO ₃	IO ₃ ⁻ /I ⁻
Pt/TaON	RuO ₂ /TaON	IO ₃ ⁻ /I ⁻
Pt/CaTaO ₂ N	Pt/WO ₃	IO ₃ ⁻ /I ⁻
Pt/BaTaO ₂ N	Pt/WO ₃	IO ₃ ⁻ /I ⁻
Pt/TaON	Pt/WO ₃	IO ₃ ⁻ /I ⁻
Pt/SrTiO ₃ :Rh	BiVO ₄	Fe ^{3+/2+}
Pt/SrTiO ₃ :Rh	Bi ₂ MoO ₆	Fe ^{3+/2+}
Pt/SrTiO ₃ :Rh	WO ₃	Fe ^{3+/2+}
Coumarin/K ₄ Nb ₆ O ₁₇	Pt/WO ₃	IO ₃ ⁻ /I ⁻
Pt/ZrO ₂ /TaON	Pt/WO ₃	IO ₃ ⁻ /I ⁻

Table II. H₂ evolution over visible-light-driven photocatalysts using Fe²⁺ as an electron donor.

Photocatalyst	Light (nm)	H ₂ (μmol h ⁻¹)
Pt(0.3 wt%)/TiO ₂ (anatase)	λ > 300	0
Pt(0.3 wt%)/SrTiO ₃	λ > 300	2.6
Pt(0.5 wt%)/SrTiO ₃ :Rh(1 at.%)	λ > 420	13.7
Pt(0.3 wt%)/SnNb ₂ O ₆	λ > 420	0.1
Pt(0.5 wt%)/(CuIn) _{0.05} Zn _{0.9} S	λ > 420	3.2

Catalyst: 0.1 g, reactant solution: 120 mL, pH: 2.4, top-window reaction cell, 300-W Xe-arc lamp.

O₂ evolution from an aqueous solution containing Fe³⁺ ions as an electron acceptor on various photocatalysts. This reaction is based on sacrificial O₂ evolution. TiO₂-rutile, BiVO₄, Bi₂MoO₆, and WO₃ showed reasonable photocatalytic activities. These results of sacrificial H₂ and O₂ evolution reactions led to the construction of the z-scheme photocatalysis systems consisting of the Pt/SrTiO₃:Rh photocatalyst, the O₂-photocatalyst (BiVO₄, Bi₂MoO₆, and WO₃), and the Fe³⁺/Fe²⁺ redox couple as an electron relay, as shown in Figure 1.²⁶ In this scheme, Fe³⁺ is reduced by electrons photogenerated in the conduction band of BiVO₄, while Fe²⁺ is oxidized by holes photogenerated in the electron donor levels formed by doped Rh in SrTiO₃:Rh. The result is that iron ions are not consumed, but instead are cycled during the photocatalytic water splitting. All systems produced H₂ and O₂ in the ratio of 2:1 from an aqueous FeCl₃ solution under visible light irradiation, as shown in Figure 2. The solution contained Fe³⁺ and Fe²⁺ in a suitable ratio under steady state.

Factors affecting activity of z-scheme photocatalyst systems

Photocatalytic activities of water splitting using z-scheme systems are affected by pH, co-catalysts, and electron mediators.¹⁰ These factors are discussed in the following sections.

Photocatalyst	BG (eV)	Light (nm)	O ₂ (μmol h ⁻¹)
TiO ₂ (rutile)	3.0	λ > 300	13.4
TiO ₂ :Cr/Sb	2.3	λ > 420	0
BiVO ₄	2.4	λ > 420	82.6
AgNbO ₃	2.8	λ > 420	2.3
Bi ₂ MoO ₆	2.7	λ > 420	6.9
WO ₃	2.8	λ > 420	23.7

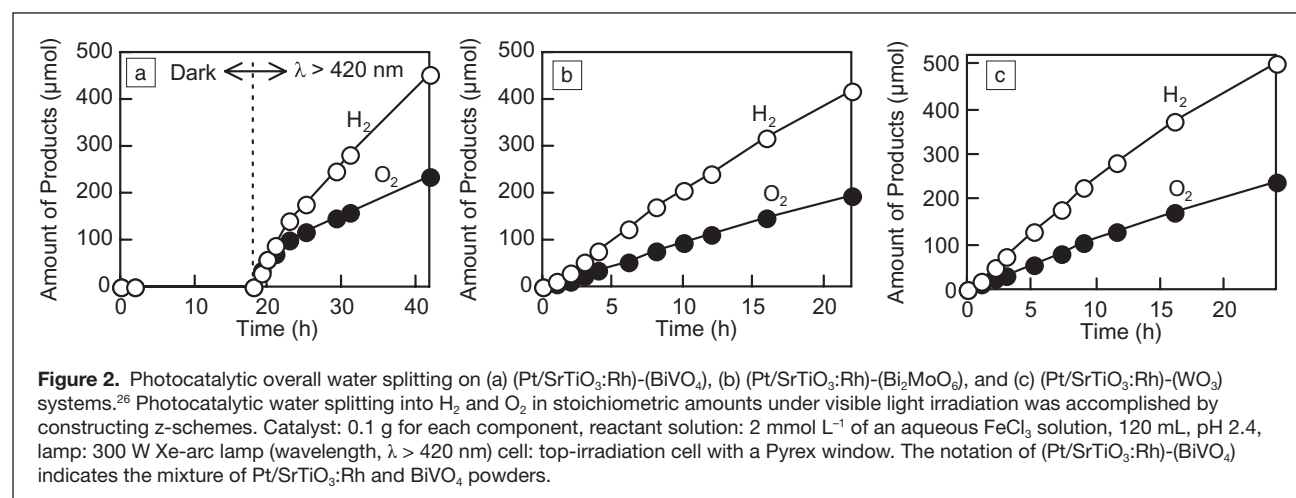
Catalyst: 0.1 g, reactant solution: 120 mL, pH: 2.4, top-window reaction cell, 300-W Xe-arc lamp.

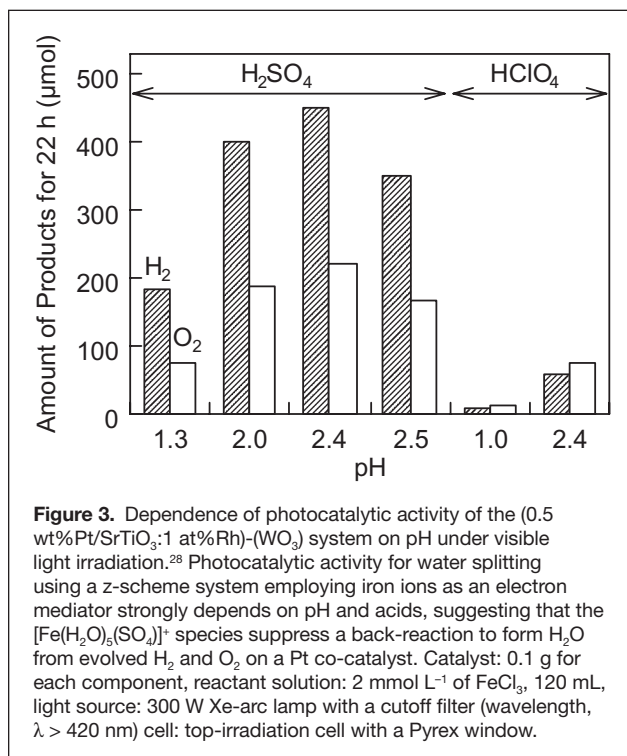
Effect of pH on the photocatalytic activity for water splitting

Each reaction step in a z-scheme, shown in Figure 1, is affected by pH. For example, reactivity and the nature of an electron mediator strongly depend on the pH.^{25,28} Figure 3 shows the effect of pH on photocatalytic water splitting using the (Pt/SrTiO₃:Rh)-(WO₃)-(FeCl₃) system.²⁸ Here, the pH was adjusted using sulfuric acid, perchloric acid, or hydrochloric acid. The photocatalytic activity of the present z-scheme system was sensitive to pH and the kind of an acid used for pH control. When sulfuric acid was used for the pH adjustment, the z-scheme system showed activity in the pH range 1.3 ≤ pH ≤ 2.5, although the activity depended on the pH. The optimum pH was 2.4. On the other hand, when the pH was adjusted with perchloric acid, the z-scheme system showed activity at pH 2.4, although the activity was only one sixth of that when sulfuric acid was used. A similar activity to pH-2.4-FeCl₃-HClO₄ was obtained when the pH was adjusted with hydrochloric acid. The highest activity was obtained in the aqueous FeCl₃-H₂SO₄ solution with pH 2.4. The low pH is indispensable for suppression of hydrolysis of Fe³⁺ to form hydroxide precipitation. The sulfate ions create [Fe(H₂O)₅(SO₄)]⁺ species around pH 2.4. This iron complex or cluster covers the surface of a Pt co-catalyst to suppress back-reactions to form H₂O from evolved H₂ and O₂ because the back-reactions easily proceed to form water from evolved H₂ and O₂ for water splitting of the uphill reaction, as mentioned in the next section.

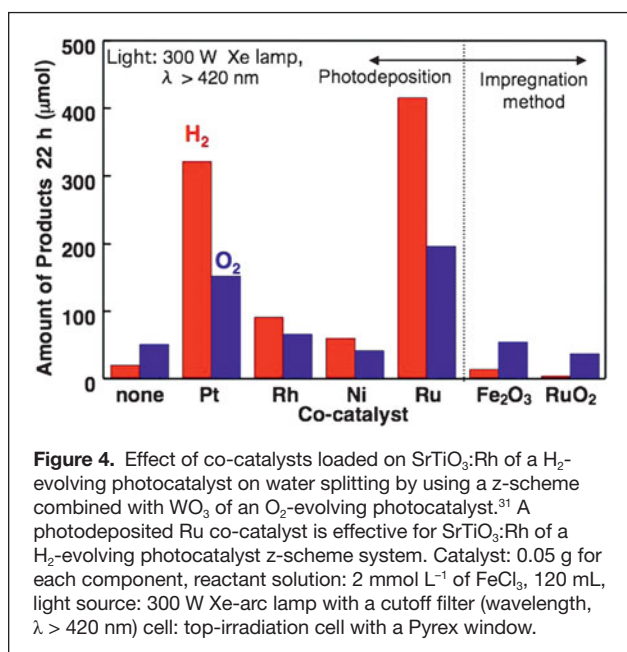
Effect of co-catalysts on the photocatalytic activity for water splitting

A co-catalyst plays an important role in providing reaction sites for H₂ formation on the surface of a photocatalyst (Figure 1). Oxide photocatalysts that show reasonable activities for H₂ evolution under visible light irradiation are only SrTiO₃:Cr,Ta¹⁸ and SrTiO₃:Rh.¹⁹ These materials are indispensable for construction of z-scheme systems using only oxide materials. So, SrTiO₃:Rh is implied as a H₂-evolving photocatalyst. The activities of z-scheme photocatalysis systems consisting of





SrTiO₃:Rh loaded with various co-catalysts and WO₃ for overall water splitting are shown in **Figure 4**.³¹ These co-catalysts were loaded by photodeposition and impregnation methods. In the photodeposition method, metal ions are reduced by electrons photogenerated in a photocatalyst to form metallic particles on the surface. In the impregnation method, after the SrTiO₃:Rh powder is added to an aqueous solution containing metal species, the water is evaporated, resulting in metal salts loading onto the surface of the SrTiO₃:Rh powder. The metal salts

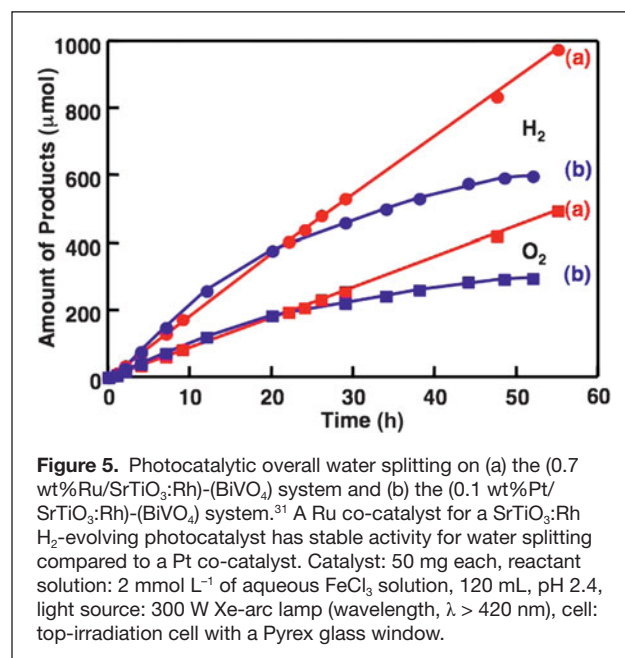


decompose with calcination in air at suitable temperatures to produce a co-catalyst-loaded SrTiO₃:Rh photocatalyst. When Ni, Ru, Rh, and Pt co-catalysts were loaded on SrTiO₃:Rh, water splitting was enhanced in comparison with a non-loaded system, which was due to the enhancement of H₂ production. Au co-catalysts are also effective.³¹ The system employing a photodeposited Ru co-catalyst showed high photocatalytic performance as well as the system employing a Pt co-catalyst. The ratios of evolved H₂ to O₂ deviated from stoichiometry when H₂ production was poor. It was due to the dominance of O₂ production on the WO₃ photocatalyst at the initial stage of the reaction using an aqueous FeCl₃ solution.²⁸

The RuO₂ co-catalyst has often been used for overall water splitting.^{11,34–36} The Ru co-catalyst formed after photodeposition was effective, whereas that loaded by an impregnation method was not effective in the present z-scheme system. The effect of the RuO₂ co-catalyst strongly depended on the condition of RuO₂. X-ray photoelectron spectroscopy and scanning electron microscopy analyses indicated that the surface of the photodeposited Ru co-catalyst was oxidized by air or water. This is the reason why the Ru co-catalyst is superior to Pt, as mentioned in the next section.

Comparison of a Ru co-catalyst with a Pt co-catalyst as a H₂-evolution site

Figure 5 shows time courses of photocatalytic overall water splitting on the (Pt/SrTiO₃:Rh)-(BiVO₄) and (Ru/SrTiO₃:Rh)-(BiVO₄) systems using an Fe³⁺/Fe²⁺ electron mediator.^{28,31} Because this reaction was carried out in a gas-closed circulation system, the evolved H₂ and O₂ accumulated in the system. In the early stage, the activity of the system employing the Pt co-catalyst was slightly higher than that employing the Ru co-catalyst. However, the activity of the system employing the

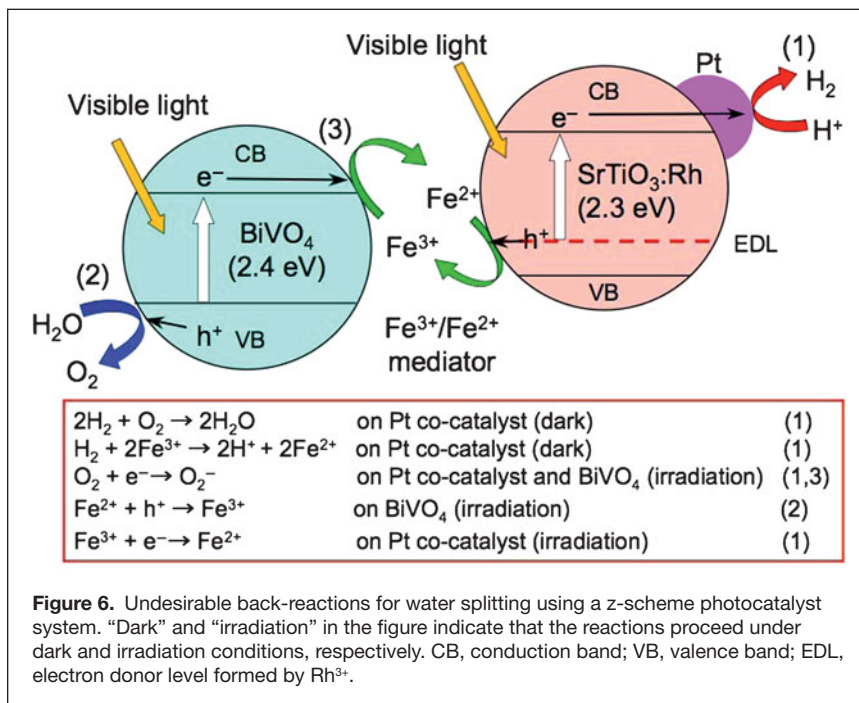


Pt co-catalyst gradually decreased after 10 hours, and eventually the reaction almost stopped after 50 hours. In contrast, the reaction steadily proceeded for a long time in the system employing the Ru co-catalyst even under relatively high pressures of evolved H₂ and O₂, indicating that back-reactions barely proceeded on the Ru co-catalyst during the photocatalytic water-splitting process. There was a significant advantage for the system employing the Ru co-catalyst.

The difference in deactivation between Ru and Pt co-catalysts is due to back-reactions that were caused by the increase in the pressures of evolved H₂ and O₂. The back-reactions are suppressed in the system employing the Ru co-catalyst in comparison with the system employing the Pt co-catalyst. Possible back-reactions are illustrated in **Figure 6**. Back-reactions (1) in Figure 6 were examined with the suspension of the (Pt/SrTiO₃:Rh)-(BiVO₄) and (Ru/SrTiO₃:Rh)-(BiVO₄) systems in the dark, as shown in **Figure 7**. Twenty torrs of H₂ and 10 torrs of O₂ were introduced into the system with the catalyst suspension. The decreases in pressures of the gases were monitored. Remarkable decreases in pressure of H₂ and O₂ due to water formation were observed in the Pt co-catalyst system when Fe³⁺ ions were absent (triangles in Figure 7a). In the presence of Fe³⁺ ions, the decreases in pressure of the gases in the system employing the Pt co-catalyst were remarkably suppressed at pH 2.4, because [Fe(H₂O)₅(SO₄)]⁺ and [Fe(H₂O)₅(OH)]²⁺ ions cover the Pt surface, although the gas consumption was still observed slightly (triangles in Figure 7b).¹⁶ The ratio of H₂ consumption to O₂ was more than two, indicating that a reduction of Fe³⁺ ions by H₂ proceeds. In contrast, H₂ and O₂ were not consumed in the system employing the Ru co-catalyst in the absence and presence of Fe³⁺ ions (circles in Figure 7a and 7b).

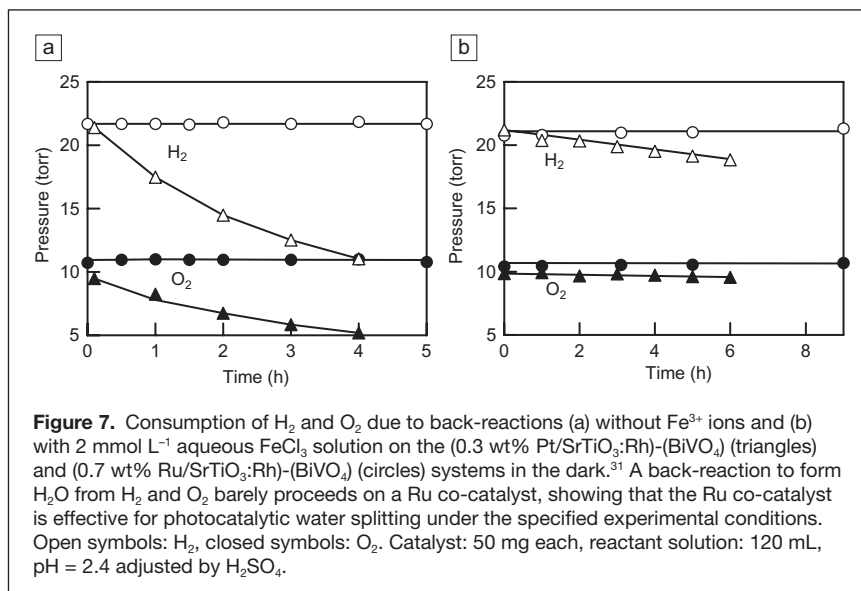
Z-scheme systems without electron mediators for solar water splitting

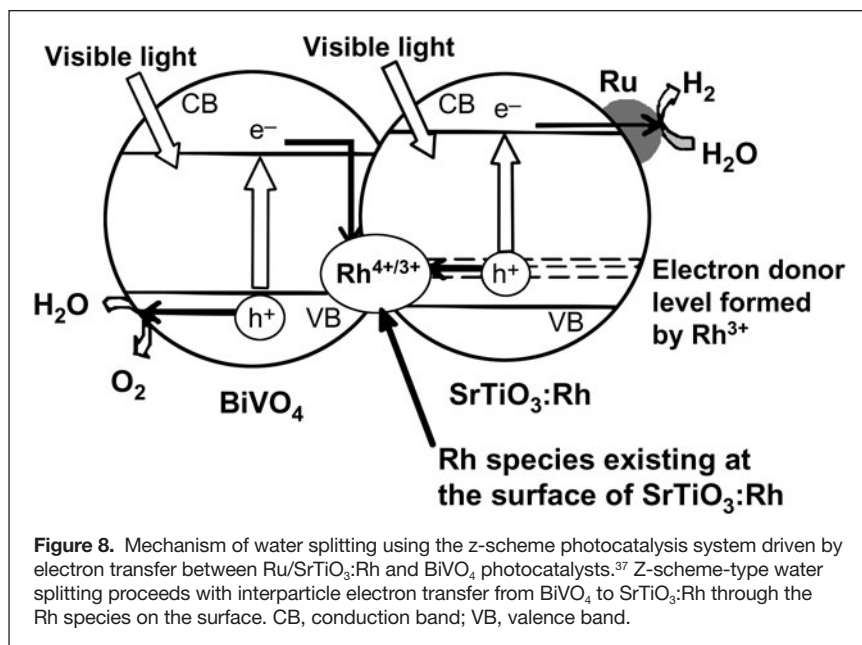
An electron mediator plays an important role in electron transfer from an O₂-evolving photocatalysts to a H₂-evolving photocatalyst, as shown in Figure 1. However, the electron mediator also produces negative effects, as shown in Figure 6. Moreover, if an electron mediator has color, part of the visible light is absorbed by the electron mediator. A suitable combination between photocatalysts and the electron mediator is required, as shown in Table I. So, a z-scheme system without an



electron mediator has attracted our attention in eliminating this limitation.

The present z-schemes consisting of Rh-doped SrTiO₃ loaded with Ru co-catalyst and O₂-evolving photocatalysts work for overall water splitting into H₂ and O₂ in a stoichiometric ratio under visible light irradiation without any electron mediators, according to the scheme as shown in **Figure 8** and in **Table IV**.³⁷ In this process, the contact between the H₂-photocatalyst of Ru/SrTiO₃:Rh and various O₂-photocatalysts is indispensable. The best contact was achieved at pH 3.5 with aggregation of these particles. It was reasonable judging from the zeta potentials of those particles at which the surface charges were neutral. The surface charge of the SrTiO₃:Rh powder is





positive at pH 3.5, while that of BiVO₄ is negative, resulting in the aggregation of these powders by an electrostatic force. Thus, various combinations of z-scheme systems have been developed for water splitting, as shown in Table IV. Among them, the combination of Ru/SrTiO₃:Rh and BiVO₄ gave the highest activity under visible light irradiation. The overall water splitting proceeded steadily over 120 h even using a solar simulator AM-1.5 as a light source, as shown in Figure 9. When the Pt co-catalyst was loaded on the SrTiO₃:Rh photocatalyst, overall water splitting did not proceed because of the enhanced

Table IV. Overall water splitting using z-scheme photocatalysis systems composed of various powdered H₂- and O₂-photocatalysts without electron mediators.

H ₂ -photocatalyst	O ₂ -photocatalyst	Incident light (nm)	Activity (μmol h ⁻¹)	
			H ₂	O ₂
Ru/SrTiO ₃ :Rh	BiVO ₄	>420	40	19
Pt/SrTiO ₃ :Rh	BiVO ₄	>420	1.3	0
Ru/SrTiO ₃ :Cr,Ta	BiVO ₄	>420	0.3	0.1
Ru/SrTiO ₃	BiVO ₄	>300	0.05	0
Ru/TiO ₂ (anatase)	BiVO ₄	>300	Trace	0
Ru/SrTiO ₃ :Rh	AgNbO ₃	>420	1.9	0.7
Ru/SrTiO ₃ :Rh	Bi ₂ MoO ₆	>420	12	5.2
Ru/SrTiO ₃ :Rh	TiO ₂ :Cr,Sb	>420	6.7	3.3
Ru/SrTiO ₃ :Rh	TiO ₂ :Rh,Sb	>420	5.1	2.2
Ru/SrTiO ₃ :Rh	WO ₃	>420	5.7	2.4
Ru/SrTiO ₃ :Rh	SrTiO ₃	>300	19	8.2
Ru/SrTiO ₃ :Rh	TiO ₂ (rutile)	>300	67	31

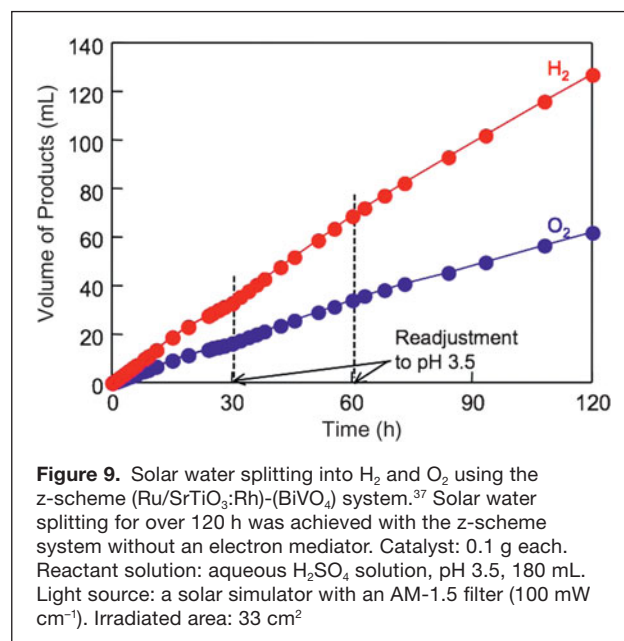
Reaction conditions: reactant solution; aqueous H₂SO₄ solution, pH 3.5, 120 mL, light source; 300-W Xe-arc lamp, cell; top-irradiation cell with a Pyrex glass window.

backward reaction of water formation from evolved H₂ and O₂ or their intermediates. An electron mediator of Fe³⁺/Fe²⁺ was indispensable for the z-scheme photocatalysis system employing the Pt-loaded SrTiO₃:Rh photocatalyst, as mentioned previously.^{26,28} Moreover, other H₂-photocatalysts, except Ru/SrTiO₃:Rh, could not function for overall water splitting, indicating that doped Rh significantly participated in not only the formation of the impurity level in the forbidden band for visible light response but also the electron transfer between photocatalyst particles.

Summary

Research of photocatalytic water splitting has progressed, with an increased understanding of materials phenomena. Highly efficient photocatalyst materials for water

splitting under UV irradiation have been developed. Moreover, water splitting under visible light irradiation has been achieved with several photocatalyst materials. Water splitting using powdered photocatalysts is the simplest way for sunlight energy conversion to chemical energy, which requires water, sunlight, and powder. Z-scheme photocatalysts are promising systems for solar water splitting. Although the efficiency is low at the present stage, z-scheme photocatalyst systems can work using sun light. The z-scheme system can employ a variety of photocatalysts that are active for either H₂ or O₂ evolution. The efficiency can be improved by finding stable oxide photocatalysts with narrow bandgaps, especially for H₂ evolution. Moreover, H₂ can be obtained separately from O₂



using a z-scheme system consisting of a powder-suspension system because a H₂-evolving photocatalyst is different from an O₂-evolving photocatalyst. Thus, the z-scheme system is different from a one-particle system, as shown in Figure 1, and its capability is a significant property of the z-scheme photocatalyst system. Alternatively, photoelectrochemical cells for solar water splitting can be constructed using the materials employed for the z-scheme photocatalyst systems. The achievement of photocatalytic water splitting for practical use will contribute to an ultimate solution for energy and environmental issues.

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