

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

Akihiko Kudo

Water splitting to produce H_2 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 $SrTiO_3$:Rh of a H_2-evolving photocatalyst, and O_2-evolving photocatalysts with and without electron mediators. These photocatalyst systems showed activities for water splitting into H_2 and O_2 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 H_2O from evolved H_2 and O_2.

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 H_2 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 H_2 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 H_2 and O_2 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^+/H_2 (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 O_2/H_2O (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 $ZnGeN_2$-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 H_2-evolving photocatalyst, an O_2-evolving photocatalyst, and an electron mediator, as shown in Figure 1. Photocatalysts that are active only for half reactions of water splitting (sacrificial H_2 and O_2 evolution reactions) can be employed for the construction of the z-scheme: that is the merit of the z-scheme. There

Akihiko Kudo, Tokyo University of Science, Japan; a-kudo@rs.kagu.tus.ac.jp
DOI: 10.1557/mrs.2010.3

© 2011 Materials Research Society
https://doi.org/10.1557/mrs.2010.3 Published online by Cambridge University Press

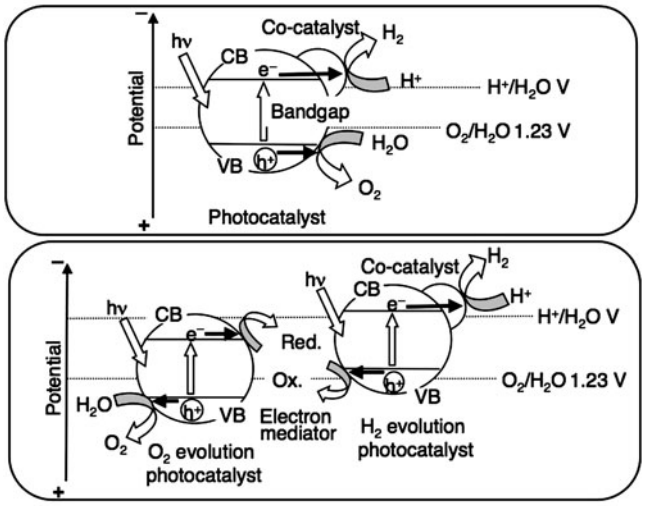


Figure 1. Single- and two-particulate photocatalyst systems for water splitting into H_2 and O_2. CB, conduction band; VB, valence band; *h*, Planck's constant; ν, frequency.

are many reports about visible-light-driven photocatalysts that show the activities for H_2 and O_2 evolution from water containing sacrificial reagents (electron donor and acceptor reagents), for example, WO_3,[14] $BiVO_4$,[15] Cr and Sb co-doped TiO_2 (TiO_2:Cr,Sb),[16] $AgNbO_3$,[17] Cr and Ta co-doped $SrTiO_3$ ($SrTiO_3$:Cr,Ta),[18] Rh-doped $SrTiO_3$ ($SrTiO_3$:Rh),[19] $SnNb_2O_6$,[20] Cr-doped $PbMoO_4$ ($PbMoO_4$:Cr),[21] Rh and Sb co-doped TiO_2 (TiO_2:Rh,Sb),[22] $Sm_2Ti_2S_2O_5$,[23] Ta_3N_5,[8] and TaON.[24] These photocatalysts are inactive for overall water splitting into H_2 and O_2 in the absence of sacrificial reagents. However, overall water splitting has been attained by constructing a z-scheme photocatalysis system composed of H_2- and O_2-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 $SrTiO_3$ co-doped with Cr and Ta (Pt/$SrTiO_3$:Cr,Ta) for the H_2-evolving photocatalyst with Pt/WO_3 for the O_2-evolving photocatalyst can split water into H_2 and O_2 in stoichiometric amounts under visible light irradiation in the presence of an IO_3^-/I^- redox couple. Oxynitride photocatalysts TaON, $CaTa_2O_2N$, and $BaTa_2O_2N$ can be used as H_2-evolving photocatalysts with a Pt/WO_3 of an O_2-evolving photocatalyst. These photocatalyst systems respond to about 450 nm of light, which is limited by the bandgap of WO_3. The system of Pt/TaON with RuO_2/TaON is a unique combination and is active up to 500 nm. Coumarin dye adsorbed on a $K_4Nb_6O_{17}$ photocatalyst with a wide bandgap works as an H_2-evolving photocatalyst through a dye sensitization process. ZrO_2 modification of TaON on an H_2-evolving photocatalyst improves the activity. The z-scheme system consisting of Pt/$SrTiO_3$:Rh and $BiVO_4$ or Bi_2MoO_6 or WO_3 is also active in the presence of a Fe^{3+}/Fe^{2+} redox couple. The system of Pt/$SrTiO_3$:Rh and $BiVO_4$ responds to 520-nm light, which corresponds to the bandgaps of $SrTiO_3$:Rh and $BiVO_4$. The system of $SrTiO_3$:Rh and $BiVO_4$ 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 $SrTiO_3$:Rh is employed as a H_2-evolving photocatalyst.

In this article, the z-scheme systems consisting of $SrTiO_3$:Rh of an H_2-evolving photocatalyst and O_2-evolving photocatalysts with and without electron mediators are reviewed and discussed in detail.

Construction of a z-scheme system composed $SrTiO_3$:Rh and O_2-evolving photocatalysts

The photocatalytic activities for half reactions of water splitting are listed in **Tables II** and **III**. Table II shows the H_2 evolution from an aqueous solution containing Fe^{2+} ions as an electron donor on various photocatalysts. This reaction is based on sacrificial H_2 evolution. The Pt/TiO_2-anatase did not produce H_2, while $Pt/SrTiO_3$ produced H_2 under UV light irradiation. On the other hand, the H_2 evolution proceeded on Pt-loaded $SrTiO_3$:Rh, which was a highly active photocatalyst for the H_2 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^-
$Pt/CaTaO_2N$	Pt/WO_3	IO_3^-/I^-
$Pt/BaTaO_2N$	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_2MoO_6	$Fe^{3+/2+}$
Pt/$SrTiO_3$:Rh	WO_3	$Fe^{3+/2+}$
Coumarin/$K_4Nb_6O_{17}$	Pt/WO_3	IO_3^-/I^-
Pt/ZrO_2/TaON	Pt/WO_3	IO_3^-/I^-

Table II. H_2 evolution over visible-light-driven photocatalysts using Fe^{2+} 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%)/$SnNb_2O_6$	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.

https://doi.org/10.1557/mrs.2010.3 Published online by Cambridge University Press

O_2 evolution from an aqueous solution containing Fe^{3+} ions as an electron acceptor on various photocatalysts. This reaction is based on sacrificial O_2 evolution. TiO_2-rutile, $BiVO_4$, Bi_2MoO_6, and WO_3 showed reasonable photocatalytic activities. These results of sacrificial H_2 and O_2 evolution reactions led to the construction of the z-scheme photocatalysis systems consisting of the Pt/$SrTiO_3$:Rh photocatalyst, the O_2-photocatalyst ($BiVO_4$, Bi_2MoO_6, and WO_3), and the Fe^{3+}/Fe^{2+} redox couple as an electron relay, as shown in Figure 1.[26] In this scheme, Fe^{3+} is reduced by electrons photogenerated in the conduction band of $BiVO_4$, while Fe^{2+} is oxidized by holes photogenerated in the electron donor levels formed by doped Rh in $SrTiO_3$:Rh. The result is that iron ions are not consumed, but instead are cycled during the photocatalytic water splitting. All systems produced H_2 and O_2 in the ratio of 2:1 from an aqueous $FeCl_3$ solution under visible light irradiation, as shown in **Figure 2**. The solution contained Fe^{3+} and Fe^{2+} 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.

Table III. O_2 evolution over visible-light-driven photocatalysts using Fe^{3+} as an electron acceptor.

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_2MoO_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/$SrTiO_3$:Rh)-(WO_3)-($FeCl_3$) 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 $1.3 \leq pH \leq 2.5$, 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-$FeCl_3$-$HClO_4$ was obtained when the pH was adjusted with hydrochloric acid. The highest activity was obtained in the aqueous $FeCl_3$-H_2SO_4 solution with pH 2.4. The low pH is indispensable for suppression of hydrolysis of Fe^{3+} to form hydroxide precipitation. The sulfate ions create $[Fe(H_2O)_5(SO_4)]^+$ species around pH 2.4. This iron complex or cluster covers the surface of a Pt co-catalyst to suppress back-reactions to form H_2O from evolved H_2 and O_2 because the back-reactions easily proceed to form water from evolved H_2 and O_2 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 H_2 formation on the surface of a photocatalyst (Figure 1). Oxide photocatalysts that show reasonable activities for H_2 evolution under visible light irradiation are only $SrTiO_3$:Cr,Ta[18] and $SrTiO_3$:Rh.[19] These materials are indispensable for construction of z-scheme systems using only oxide materials. So, $SrTiO_3$:Rh is implied as a H_2-evolving photocatalyst. The activities of z-scheme photocatalysis systems consisting of

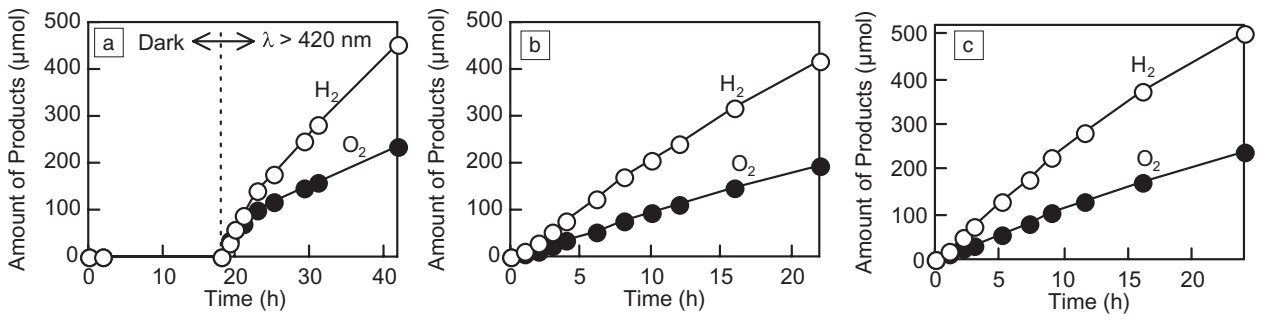


Figure 2. Photocatalytic overall water splitting on (a) (Pt/$SrTiO_3$:Rh)-($BiVO_4$), (b) (Pt/$SrTiO_3$:Rh)-(Bi_2MoO_6), and (c) (Pt/$SrTiO_3$:Rh)-(WO_3) systems.[26] Photocatalytic water splitting into H_2 and O_2 in stoichiometric amounts under visible light irradiation was accomplished by constructing z-schemes. Catalyst: 0.1 g for each component, reactant solution: 2 mmol L^{-1} of an aqueous $FeCl_3$ solution, 120 mL, pH 2.4, lamp: 300 W Xe-arc lamp (wavelength, λ > 420 nm) cell: top-irradiation cell with a Pyrex window. The notation of (Pt/$SrTiO_3$:Rh)-($BiVO_4$) indicates the mixture of Pt/$SrTiO_3$:Rh and $BiVO_4$ powders.

https://doi.org/10.1557/mrs.2010.3 Published online by Cambridge University Press

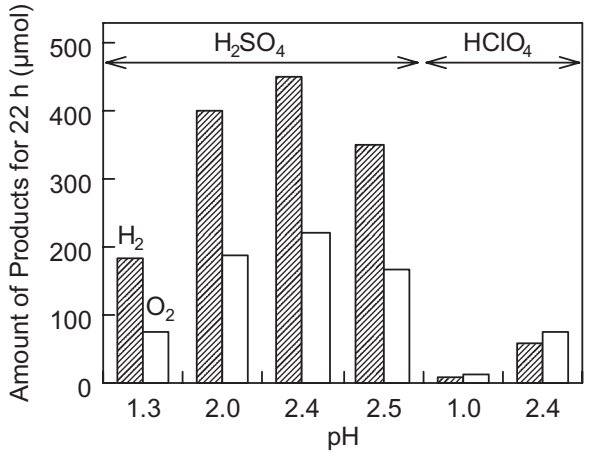


Figure 3. Dependence of photocatalytic activity of the (0.5 wt%Pt/$SrTiO_3$:1 at%Rh)-(WO_3) system on pH under visible light irradiation.[28] Photocatalytic activity for water splitting using a z-scheme system employing iron ions as an electron mediator strongly depends on pH and acids, suggesting that the $[Fe(H_2O)_5(SO_4)]^+$ species suppress a back-reaction to form H_2O from evolved H_2 and O_2 on a Pt co-catalyst. Catalyst: 0.1 g for each component, reactant solution: 2 mmol L^{-1} of $FeCl_3$, 120 mL, light source: 300 W Xe-arc lamp with a cutoff filter (wavelength, $\lambda > 420$ nm) cell: top-irradiation cell with a Pyrex window.

$SrTiO_3$:Rh loaded with various co-catalysts and WO_3 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 $SrTiO_3$: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 $SrTiO_3$:Rh powder. The metal salts decompose with calcination in air at suitable temperatures to produce a co-catalyst-loaded $SrTiO_3$:Rh photocatalyst. When Ni, Ru, Rh, and Pt co-catalysts were loaded on $SrTiO_3$:Rh, water splitting was enhanced in comparison with a non-loaded system, which was due to the enhancement of H_2 production. Au co-catalysts are also effectve.[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 H_2 to O_2 deviated from stoichiometry when H_2 production was poor. It was due to the dominance of O_2 production on the WO_3 photocatalyst at the initial stage of the reaction using an aqueous $FeCl_3$ solution.[28]

The RuO_2 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 RuO_2 co-catalyst strongly depended on the condition of RuO_2. 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 H_2-evolution site

Figure 5 shows time courses of photocatalytic overall water splitting on the (Pt/$SrTiO_3$:Rh)-($BiVO_4$) and (Ru/$SrTiO_3$:Rh)-($BiVO_4$) systems using an Fe^{3+}/Fe^{2+} electron mediator.[28,31] Because this reaction was carried out in a gas-closed circulation system, the evolved H_2 and O_2 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

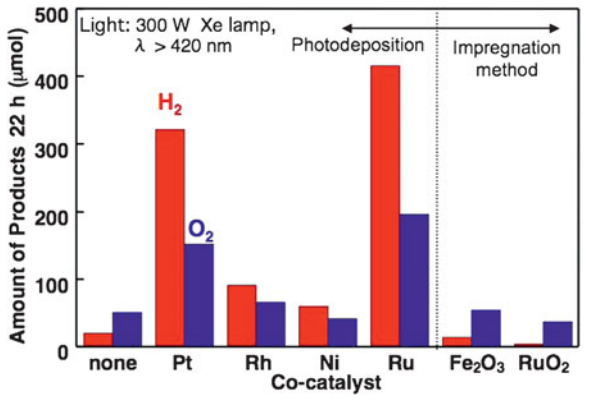


Figure 4. Effect of co-catalysts loaded on $SrTiO_3$:Rh of a H_2-evolving photocatalyst on water splitting by using a z-scheme combined with WO_3 of an O_2-evolving photocatalyst.[31] A photodeposited Ru co-catalyst is effective for $SrTiO_3$:Rh of a H_2-evolving photocatalyst z-scheme system. Catalyst: 0.05 g for each component, reactant solution: 2 mmol L^{-1} of $FeCl_3$, 120 mL, light source: 300 W Xe-arc lamp with a cutoff filter (wavelength, $\lambda > 420$ nm) cell: top-irradiation cell with a Pyrex window.

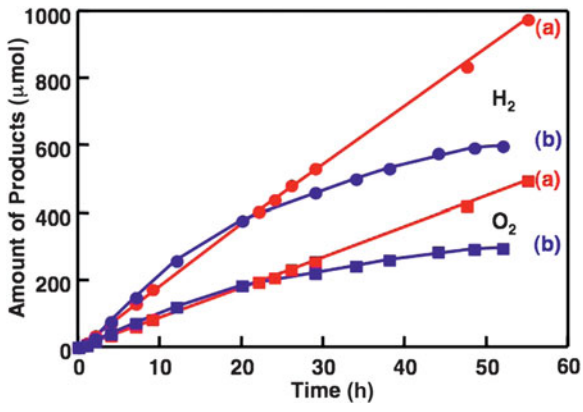
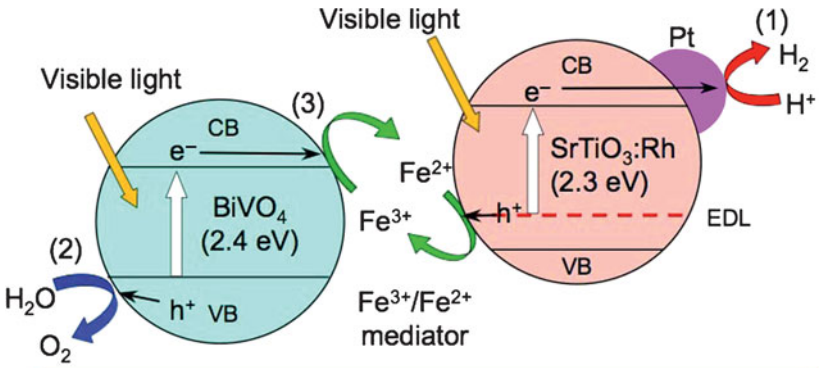


Figure 5. Photocatalytic overall water splitting on (a) the (0.7 wt%Ru/$SrTiO_3$:Rh)-($BiVO_4$) system and (b) the (0.1 wt%Pt/$SrTiO_3$:Rh)-($BiVO_4$) system.[31] A Ru co-catalyst for a $SrTiO_3$:Rh H_2-evolving photocatalyst has stable activity for water splitting compared to a Pt co-catalyst. Catalyst: 50 mg each, reactant solution: 2 mmol L^{-1} of aqueous $FeCl_3$ solution, 120 mL, pH 2.4, light source: 300 W Xe-arc lamp (wavelength, $\lambda > 420$ nm), cell: top-irradiation cell with a Pyrex glass window.

https://doi.org/10.1557/mrs.2010.3 Published online by Cambridge University Press

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 H_2 and O_2, 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 H_2 and O_2. 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 ($Pt/SrTiO_3$:Rh)-($BiVO_4$) and ($Ru/SrTiO_3$:Rh)-($BiVO_4$) systems in the dark, as shown in **Figure 7**. Twenty torrs of H_2 and 10 torrs of O_2 were introduced into the system with the catalyst suspension. The decreases in pressures of the gases were monitored. Remarkable decreases in pressure of H_2 and O_2 due to water formation were observed in the Pt co-catalyst system when Fe^{3+} ions were absent (triangles in Figure 7a). In the presence of Fe^{3+} ions, the decreases in pressure of the gases in the system employing the Pt co-catalyst were remarkably suppressed at pH 2.4, because $[Fe(H_2O)_5(SO_4)]^+$ and $[Fe(H_2O)_5(OH)]^{2+}$ ions cover the Pt surface, although the gas consumption was still observed slightly (triangles in Figure 7b).[16] The ratio of H_2 consumption to O_2 was more than two, indicating that a reduction of Fe^{3+} ions by H_2 proceeds. In contrast, H_2 and O_2 were not consumed in the system employing the Ru co-catalyst in the absence and presence of Fe^{3+} ions (circles in Figure 7a and 7b).



$2H_2 + O_2 \rightarrow 2H_2O$	on Pt co-catalyst (dark)	(1)
$H_2 + 2Fe^{3+} \rightarrow 2H^+ + 2Fe^{2+}$	on Pt co-catalyst (dark)	(1)
$O_2 + e^- \rightarrow O_2^-$	on Pt co-catalyst and $BiVO_4$ (irradiation)	(1,3)
$Fe^{2+} + h^+ \rightarrow Fe^{3+}$	on $BiVO_4$ (irradiation)	(2)
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	on Pt co-catalyst (irradiation)	(1)

Figure 6. Undesirable back-reactions for water splitting using a z-scheme photocatalyst system. "Dark" and "irradiation" in the figure indicate that the reactions proceed under dark and irradiation conditions, respectively. CB, conduction band; VB, valence band; EDL, electron donor level formed by Rh^{3+}.

Z-scheme systems without electron mediators for solar water splitting

An electron mediator plays an important role in electron transfer from an O_2-evolving photocatalysts to a H_2-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 $SrTiO_3$ loaded with Ru co-catalyst and O_2-evolving photocatalysts work for overall water splitting into H_2 and O_2 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 H_2-photocatalyst of $Ru/SrTiO_3$:Rh and various O_2-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 $SrTiO_3$:Rh powder is

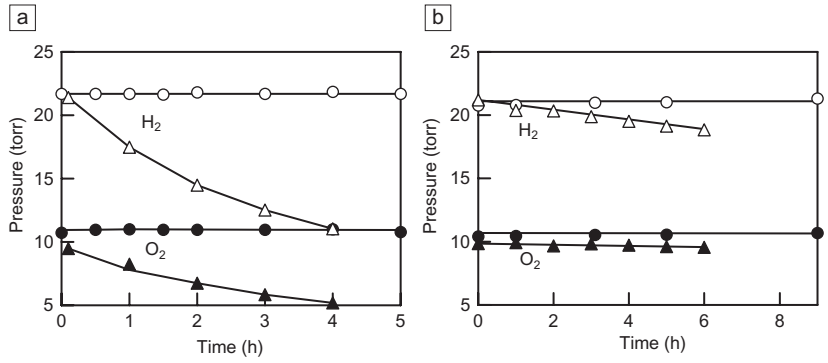


Figure 7. Consumption of H_2 and O_2 due to back-reactions (a) without Fe^{3+} ions and (b) with 2 mmol L^{-1} aqueous $FeCl_3$ solution on the (0.3 wt% $Pt/SrTiO_3$:Rh)-($BiVO_4$) (triangles) and (0.7 wt% $Ru/SrTiO_3$:Rh)-($BiVO_4$) (circles) systems in the dark.[31] A back-reaction to form H_2O from H_2 and O_2 barely proceeds on a Ru co-catalyst, showing that the Ru co-catalyst is effective for photocatalytic water splitting under the specified experimental conditions. Open symbols: H_2, closed symbols: O_2. Catalyst: 50 mg each, reactant solution: 120 mL, pH = 2.4 adjusted by H_2SO_4.

https://doi.org/10.1557/mrs.2010.3 Published online by Cambridge University Press

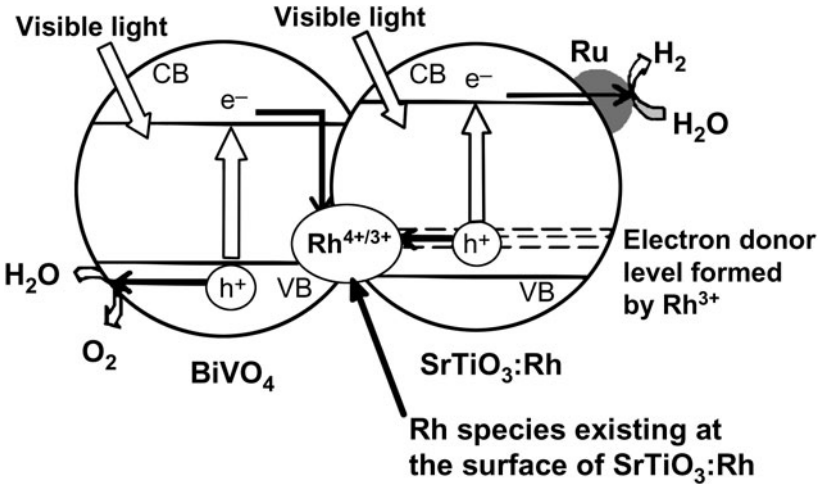


Figure 8. Mechanism of water splitting using the z-scheme photocatalysis system driven by electron transfer between Ru/$SrTiO_3$:Rh and $BiVO_4$ photocatalysts.[37] Z-scheme-type water splitting proceeds with interparticle electron transfer from $BiVO_4$ to $SrTiO_3$:Rh through the Rh species on the surface. CB, conduction band; VB, valence band.

positive at pH 3.5, while that of $BiVO_4$ 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/$SrTiO_3$:Rh and $BiVO_4$ gave the highest activity under visible light irradiation. The overall water splitting preceded 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 $SrTiO_3$:Rh photocatalyst, overall water splitting did not proceed because of the enhanced backward reaction of water formation from evolved H_2 and O_2 or their intermediates. An electron mediator of Fe^{3+}/Fe^{2+} was indispensable for the z-scheme photocatalysis system employing the Pt-loaded $SrTiO_3$:Rh photocatalyst, as mentioned previously.[26,28] Moreover, other H_2-photocatalysts, except Ru/$SrTiO_3$: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.

Table IV. Overall water splitting using z-scheme photocatalysis systems composed of various powdered H_2- and O_2-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_2MoO_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 H_2SO_4 solution, pH 3.5, 120 mL, light source; 300-W Xe-arc lamp, cell; top-irradiation cell with a Pyrex glass window.

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 H_2 or O_2 evolution. The efficiency can be improved by finding stable oxide photocatalysts with narrow bandgaps, especially for H_2 evolution. Moreover, H_2 can be obtained separately from O_2

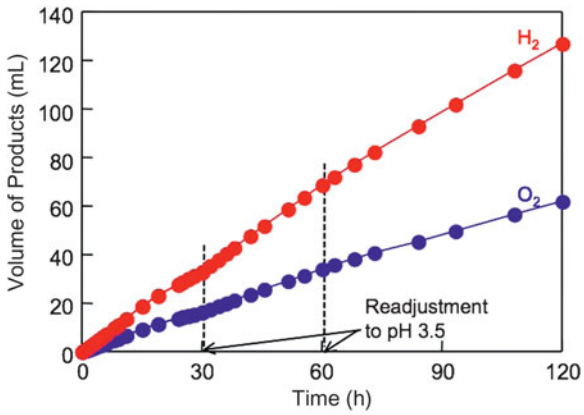


Figure 9. Solar water splitting into H_2 and O_2 using the z-scheme (Ru/$SrTiO_3$:Rh)-($BiVO_4$) system.[37] Solar water splitting for over 120 h was achieved with the z-scheme system without an electron mediator. Catalyst: 0.1 g each. Reactant solution: aqueous H_2SO_4 solution, pH 3.5, 180 mL. Light source: a solar simulator with an AM-1.5 filter (100 mW cm^{-1}). Irradiated area: 33 cm^2

https://doi.org/10.1557/mrs.2010.3 Published online by Cambridge University Press

using a z-scheme system consisting of a powder-suspension system because a H_2-evolving photocatalyst is different from an O_2-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.

References

1. A. Fujishima, K. Honda, *Nature* **238**, 37 (1972).
2. O. Khaselev, J.A. Turner, *Science* **280**, 425 (1998).
3. M. Grätzel, *Nature* **414**, 338 (2001).
4. S. Licht, *J. Phys. Chem. B* **105**, 6281 (2001).
5. A. Kudo, *Int. J. Hydrogen Energy* **32**, 2673 (2007).
6. K. Domen, M. Hara, J.N. Kondo, T. Takata, *Bull. Chem. Soc. Jpn.* **73**, 1307 (2000).
7. H. Arakawa, K. Sayama, *Catal. Surveys Jpn.* **4**, 75 (2000).
8. K. Maeda, K. Domen, *J. Phys. Chem. C* **111**, 7851 (2007).
9. F.E. Osterloh, *Chem. Mater.* **20**, 35 (2008).
10. A. Kudo, Y. Miseki, *Chem. Soc. Rev.* **38**, 253 (2009).
11. Y. Inoue, *Energy Environ. Sci.* **2**, 364 (2009).
12. K. Maeda, K. Teramura, D. Lu, T. Takata, N. Saito, Y. Inoue, K. Domen, *Nature* **440**, 295 (2006).
13. Y. Lee, H. Terashita, Y. Shimodaira, K. Teramura, M. Hara, H. Kobayashi, K. Domen, M. Yashima, *J. Phys. Chem. C* **111**, 1042 (2007).
14. J.R. Darwent, A. Mills, *J. Chem. Soc., Faraday Trans. 2* **78**, 359 (1982).
15. A. Kudo, K. Omori, H. Kato, *J. Am. Chem. Soc.* **121**, 11459 (1999).
16. H. Kato, A. Kudo, *J. Phys. Chem. B* **106**, 5029 (2002).
17. H. Kato, H. Kobayashi, A. Kudo, *J. Phys. Chem. B* **106**, 12441 (2002).
18. T. Ishii, H. Kato, A. Kudo, *J. Photochem. Photobiol. A* **163**, 181 (2004).
19. R. Konta, T. Ishii, H. Kato, A. Kudo, *J. Phys. Chem. B* **108**, 8992 (2004).
20. Y. Hosogi, K. Tanabe, H. Kato, H. Kobayashi, A. Kudo, *Chem. Lett.* **33**, 28 (2004).
21. Y. Shimodaira, H. Kato, H. Kobayashi, A. Kudo, *Bull. Chem. Soc. Jpn.* **80**, 885 (2007).
22. R. Niishiro, R. Konta, H. Kato, W.J. Chun, K. Asakura, A. Kudo, *J. Phys. Chem. C* **111**, 17420 (2007).
23. A. Ishikawa, T. Takata, J.N. Kondo, M. Hara, H. Kobayashi, K. Domen, *J. Am. Chem. Soc.* **124**, 13547 (2002).
24. D. Yamashita, T. Takata, M. Hara, J.N. Kondo, K. Domen, *Solid State Ionics.* **172**, 591 (2004).
25. K. Sayama, K. Mukasa, R. Abe, Y. Abe, H. Arakawa, *Chem. Commun.* 2416 (2001).
26. H. Kato, M. Hori, R. Konta, Y. Shimodaira, A. Kudo, *Chem. Lett.* **33**, 1348 (2004).
27. R. Abe, T. Takata, H. Sugihara, K. Domen, *Chem. Commun.* 3829 (2005).
28. H. Kato, Y. Sasaki, A. Iwase, A. Kudo, *Bull. Chem. Soc. Jpn.* **12**, 2457 (2007).
29. M. Higashi, R. Abe, A. Ishikawa, T. Takata, B. Ohtani, K. Domen, *Chem. Lett.* **37**, 138 (2008).
30. M. Higashi, R. Abe, K. Teramura, T. Takata, B. Ohtani, K. Domen, *Chem. Phys. Lett.* **452**, 120 (2008).
31. Y. Sasaki, A. Iwase, H. Kato, A. Kudo, *J. Catal.* **259**, 133 (2008).
32. R. Abe, K. Shinmei, K. Hara, B. Ohtani, *Chem. Commun.* **3577** (2009).
33. K. Maeda, M. Higashi, D. Lu, R. Abe, K. Domen, *J. Am. Chem. Soc.* **132**, 5858 (2010).
34. S. Ogura, M. Kohno, K. Saito, Y. Inoue, *Phys. Chem. Chem. Phys.* **1**, 179 (1999).
35. Y. Lee, H. Terashima, Y. Shimodaira, K. Teramura, M. Hara, H. Kobayashi, K. Domen, M. Yashima, *J. Phys. Chem. C* **111**, 1042 (2007).
36. T. Sakata, K. Hashimoto, T. Kawai, *J. Phys. Chem.* **88**, 5214 (1984).
37. Y. Sasaki, H. Nemoto, K. Saito, A. Kudo, *J. Phys. Chem. C* **113**, 17536 (2009). □

JANIS

Cryogenic Systems



Does your research require low temperatures? Contact Janis today. Our engineers will assist you in choosing the best system for your application.

- 10 mK to 800 K
- Cryocoolers
- LHe/LN_2 Cryostats
- Magnet Systems
- Dilution Refrigerator Systems
- Micro-manipulated Probe Stations

Janis Research Company
2 Jewel Drive Wilmington, MA 01887 USA
TEL +1 978 657-8750 FAX +1 978 658-0349 sales@janis.com
Visit our website at www.janis.com



Transparent conductive oxide film deposition on semiconductor wafers, solar wafers, and glass panels up to 300mm x 300mm.

Accelerate your research and development with fully characterized ITO, AZO, ZnO, and ultrathin Ag.

ADVANCED FILM SERVICES

828 Charcot Avenue • San Jose • CA • 95131 • USA
www.advancedfilmservices.com

https://doi.org/10.1557/mrs.2010.3 Published online by Cambridge University Press