Construction of Z-scheme Type Heterogeneous Photocatalysis Systems for Water Splitting into H_2 and O_2 under Visible Light Irradiation

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The water splitting under visible light irradiation has been achieved by the Z-scheme system constituted of an Fe^{3+}/Fe^{2+} redox couple as an electron relay and two powdered heterogeneous photocatalysts which we have recently developed. The $(Pt/SrTiO_3{:}Rh)$–$(BiVO_4)$ system showed the highest activity with 0.3% of an apparent quantum yield at 440 nm. It can use visible light up to 520 nm.

The water splitting reaction using photoelectrodes[1–5] and photocatalysts[6–8] has been studied as the photon energy conversion. The research has been especially focused on the visible light response from the viewpoint of utilization of the solar energy. It has been reported that some metal oxides function as highly active photocatalysts for water splitting.[6–8] Unfortunately, such photocatalysts cannot use sunlight efficiently because of their large band gaps. On the other hand, there are many reports about H_2 and O_2 production from aqueous solutions containing sacrificial reagents using metal oxide,[6,7,9,10] (oxy)-nitride,[11] and sulfide[7,12] photocatalysts with the visible light response. It can be considered that the overall water splitting reaction is achieved by the combined system. The combined system involving two photoexcitation processes is called 'Z-scheme system' because of the similarity to the photosynthesis scheme in green plants. There are few reports about water splitting using the combined system. Fujihara et al. have reported a two-compartment system.[13] In this system, the H_2 evolution compartment is connected to the O_2 evolution compartment by a Pt wire and an ion-exchange membrane. Sayama et al. have reported the combined system of the photochemical H_2 production and photocatalytic O_2 production,[14a] and the Z-scheme system consisting of $Pt/SrTiO_3{:}Cr/Ta$,[10c] Pt/WO_3, and an IO_3^-/I^- redox couple. The quantum yield is 0.1% at 420.7 nm.[14b] The Z-scheme system can be regarded as one of the candidates for the photocatalysis system aiming at water splitting using the sun light. However, it has significant barriers at this stage. The efficiency of the Z-scheme is quite low. Moreover, the useful light is limited with the wavelength lower than 460 nm corresponding to the band gap of the WO_3 photocatalyst. In the present paper, we report the overall water splitting using the visible-light-driven Z-scheme photocatalysis systems constituted of the Fe^{3+}/Fe^{2+} redox couple and two photocatalysts.

Powders of Pt-loaded $SrTiO_3$ doped with Rh (denoted as $Pt/SrTiO_3{:}Rh$ hereafter) and $BiVO_4$ were prepared according to the previous literatures.[10] A powder of Bi_2MoO_6 was prepared by a reflux method. Other materials were purchased from companies. The photocatalytic reactions were carried out in a gas-closed circulation system as described in previous reports.[10] The sulfuric acid was added into the solution containing iron ions to adjust pH of the solution at 2.4 in order to prevent formation of an iron oxide colloid.

The photocatalytic activities for half reactions are listed in Table 1. Firstly, we investigated the H_2 evolution from an aqueous solution containing Fe^{2+} ions as an electron donor on various photocatalysts. The Pt/TiO_2-anatase did not produce H_2 (Run 1) while $Pt/SrTiO_3$ produced H_2 (Run 2) under UV light irradiation. On the other hand, the H_2 evolution proceeded on Pt-loaded $SrTiO_3{:}Rh$ (Run 3) which is a highly active photocatalyst for the H_2 evolution from an aqueous methanol solution under visible light irradiation.[10d] Thus, it has been revealed that the $Pt/SrTiO_3{:}Rh$ can produce H_2 under visible light irradiation even when Fe^{2+} ions are used as an electron donor.

Secondly, we investigated the O_2 evolution from an aqueous solution containing Fe^{3+} ions as an electron acceptor on various photocatalysts. TiO_2-rutile, $BiVO_4$, Bi_2MoO_6, and WO_3 showed the photocatalytic activities (Runs 4–7). The O_2 evolution has been already reported for TiO_2-rutile[15] and WO_3.[9] We have found that $BiVO_4$ and Bi_2MoO_6 photocatalysts can produce O_2 from an aqueous $FeCl_3$ solution.

Finally, we examined the overall water splitting reaction by 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 (Figure 1). All systems produced H_2 and O_2 in the ratio of 2:1 from an aq $FeCl_3$ solution under visible light irradiation. In the case of the $(Pt/SrTiO_3{:}Rh)$–$(BiVO_4)$ system, an excess amount of O_2 was produced at the initial stage of the reaction as shown in Figure 1a. It was due to the higher efficiency for the O_2 production process on $BiVO_4$ than the H_2 production process on $Pt/SrTiO_3{:}Rh$. After the induction period, evolution of H_2 and O_2 eventually proceeded in the ratio 2:1. It was due to the suppression of O_2 evolution by accumulated Fe^{2+} ions in the solution. On the other hand, H_2 and O_2 evolved in the stoichiometric ratio from the initial stage for the (Pt/

Table 1. Photocatalytic H_2 or O_2 evolution on various photocatalysts from water containing iron ions

Run	Catalyst	Reactant Solution	Incident Light /nm	Activity /µmol h^{-1}	
				H_2	O_2
1	Pt/TiO_2-anatase	$FeCl_2{}^a$	$\lambda > 300$	0	0
2	$Pt/SrTiO_3$	$FeCl_2{}^a$	$\lambda > 300$	2.6	0
3	$Pt/SrTiO_3{:}Rh$	$FeCl_2{}^a$	$\lambda > 420$	16.9	0
4	TiO_2-rutile	$FeCl_3{}^a$	$\lambda > 300$	0	13.4
5	$BiVO_4$	$FeCl_3{}^a$	$\lambda > 420$	0	82.6
6	Bi_2MoO_6	$FeCl_3{}^a$	$\lambda > 420$	0	6.9
7	WO_3	$FeCl_3{}^a$	$\lambda > 420$	0	23.7

Catalyst: 0.1 g, reactant solution: 120 mL, pH 2.4, 300-W Xe-arc lamp, top-irradiation cell with a Pyrex window. [a]2 mmol L^{-1}.

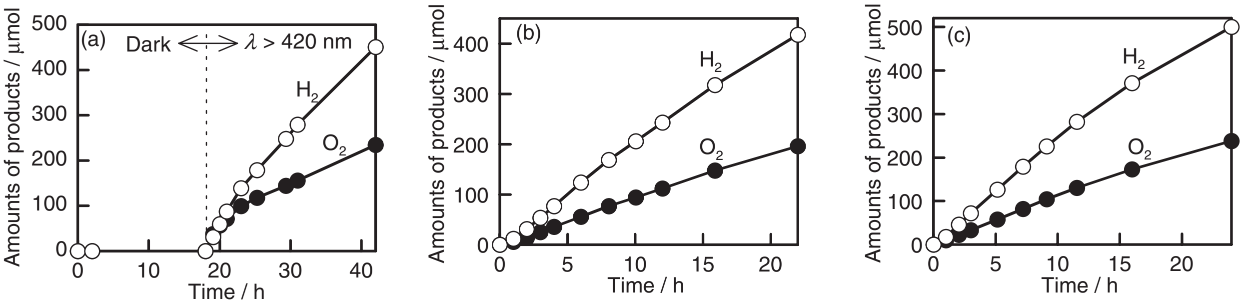

Figure 1. Photocatalytic overall water splitting on (a) (Pt/$SrTiO_3$:Rh)–($BiVO_4$), (b) (Pt/$SrTiO_3$:Rh)–(Bi_2MoO_6), and (c) (Pt/$SrTiO_3$:Rh)–(WO_3) systems. Catalyst: 0.1 g for each component, reactant solution: 2 mmol L^{-1} of an aq $FeCl_3$ solution, 120 mL, pH 2.4, lamp: 300-W Xe-arc lamp ($\lambda > 420$ nm), cell: top-irradiation cell with a Pyrex window.

$SrTiO_3$:Rh)–(Bi_2MoO_6) and –(WO_3) systems. There was no remarkable difference in the activity among the three systems because the reactions on Pt/$SrTiO_3$:Rh limited the overall efficiency of the system. In the present systems, the backward reaction between H_2 and O_2 would be suppressed by separation of evolution sites. The amounts of produced H_2 and O_2 on the (Pt/$SrTiO_3$:Rh)–($BiVO_4$), –(Bi_2MoO_6), and –(WO_3) systems were 1800 and 860 µmol (for 120 h), 418 and 196 µmol (for 22 h), 1240 and 640 µmol (for 158 h), respectively. Thus, the number of reacted electrons/holes became larger than that of Fe^{3+} ions involved in the each case (240 µmol). The overall water splitting had never proceeded in control reactions in which one component of the system, Fe^{3+} ions, photocatalysts, and light, was absent. The reaction also proceeded when an aqueous $FeCl_2$ solution was used. These results conclude the overall water splitting reaction photocatalytically proceeded according to the Z-scheme process. The apparent quantum yields of the present (Pt/$SrTiO_3$:Rh)–($BiVO_4$), –(Bi_2MoO_6), and –(WO_3) systems were 0.3, 0.2, and 0.2% at 440 nm, respectively.[16]

Figure 2 shows the photoresponse of the present systems. In the case of the (Pt/$SrTiO_3$:Rh)–($BiVO_4$) system, the water splitting reaction proceeded under irradiation with the wavelength up to 520 nm, which was consistent with the absorption onsets of $SrTiO_3$:Rh and $BiVO_4$. On the other hand, the (Pt/$SrTiO_3$:Rh)–(WO_3) system was active when it was irradiated with the wavelength shorter than the absorption onset of WO_3. However, the apparent quantum yield of the WO_3 system (0.5%) was higher than that of $BiVO_4$ (0.4%) at 420 nm. It would be due to the fact that WO_3 shielded the light absorbed by Pt/$SrTiO_3$:Rh less effectively than $BiVO_4$.

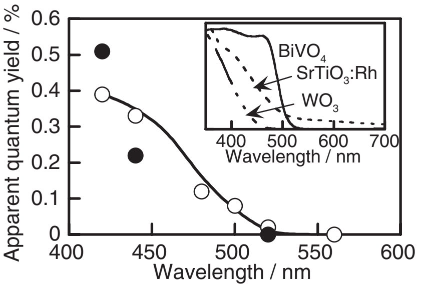

Figure 2. Photoresponse of the Z-scheme photocatalysis systems, (Pt/$SrTiO_3$:Rh)–($BiVO_4$): open marks and (Pt/$SrTiO_3$:Rh)–(WO_3): closed marks. Catalyst: 20 mg for each component, reactant solution: 2 mmol L^{-1} of an aq $FeCl_3$ solution, 120 mL, pH 2.4, lamp: 300-W Xe-arc lamp attached with optical filters in order to extract the monochromatic light from full arc, cell: top-irradiation cell with a Pyrex window. The inset shows diffuse reflection spectra of photocatalysts.

In conclusions, we have found that Pt/$SrTiO_3$:Rh functions as a photocatalyst for the H_2 production using Fe^{2+} ions, and then that $BiVO_4$ and Bi_2MoO_6 are active photocatalysts for the O_2 production using Fe^{3+} ions. We achieved overall water splitting under visible light irradiation by construction of the Z-scheme photocatalysis system using the Fe^{3+}/Fe^{2+} redox couple.

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16 The apparent quantum yield $\Phi_{app}(\%) = \{(R_{H_2} \times 4)/I\} \times 100$ R_{H_2} and I represent the rate of H_2 evolution and the irradiated photon flux, respectively. H_2 is produced by a 4-electron process in the Z-scheme system.

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