

A new photocatalytic water splitting system under visible light irradiation mimicking a Z-scheme mechanism in photosynthesis

Kazuhiro Sayama^a, Kazuaki Mukasa^b, Ryu Abe^a, Yoshimoto Abe^b, Hironori Arakawa^{a,*}

^a Photoreaction Control Research Center (PCRC), National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

^b Faculty of Science and Technology, Science University of Tokyo, Yamazaki 2641, Noda, Chiba 278-8514, Japan

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Abstract

We studied the water splitting into H₂ and O₂ using two different semiconductor photocatalysts and a redox mediator, mimicking the Z-scheme mechanism of the photosynthesis. It was found that the H₂ evolution took place on a Pt–SrTiO₃ (Cr–Ta-doped) photocatalyst using an I[−] electron donor under the visible light irradiation. The Pt–WO₃ photocatalyst showed an excellent activity of the O₂ evolution using an IO₃[−] electron acceptor under visible light. Both H₂ and O₂ gases evolved in the stoichiometric ratio (H₂/O₂ = 2) for more than 250 h under visible light using a mixture of the Pt–WO₃ and the Pt–SrTiO₃ (Cr–Ta-doped) powders suspended in NaI aqueous solution. It is for the first time that the stoichiometric water splitting occurred over oxide semiconductor photocatalysts under the visible light irradiation. We proposed a two-step photo-excitation mechanism using a pair of I[−]/IO₃[−] redox mediators. The quantum efficiency of the stoichiometric water splitting was ca. 0.1% at 420.7 nm. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Semiconductor photocatalyst; Water splitting; Visible light; Redox mediator; Z-Scheme reaction; Artificial photosynthesis

1. Introduction

Artificial photosynthesis systems have been intensively investigated because the construction of an efficient system for the solar energy conversion and storage is one of the challenging subjects to solve the global energy problem. The water splitting into H₂ and O₂ stoichiometrically (H₂/O₂ = 2) is the most fundamental and important reaction in the artificial photosynthesis. Many semiconductor photocatalysts such as M–TiO₂ (M: Pt, Rh, NiO_x) [1–3], M-titanate (M: RhO_x, NiO_x) [4,5], ZrO₂ [6], Ni-niobate [7], Ni-tantalate [8] have been reported for water splitting under the UV light irradiation. The reaction mechanism in the conventional system is shown in Fig. 1(a). The energy of the UV light occupies only 4% of the total solar energy and that of the visible light (>400 nm) occupies about half. Therefore, the development of the photocatalyst system working under the visible light irradiation is indispensable from the view point of efficient solar energy utilization, but such a reliable and reproducible photocatalyst system has not been established yet. The observation of the stoichiometric O₂ evolution is very important for the

real catalytic reaction; however, the descriptions on the O₂ evolution in some early works were obscure while the H₂ formation was observed under visible light. Most of oxide semiconductors are stable and have an ability for O₂ evolution, but most semiconductors which could absorb visible light such as WO₃ could not show the activity of H₂ evolution because the conduction band potentials were more positive than the water reduction potential to H₂ [9]. Exceptionally, a few mixed or doped oxide semiconductors for H₂ evolution have been reported using sacrificial reagents such as methanol under visible light [12–14]. However, the overall water decomposition into H₂ and O₂ under visible light has not yet been realized in the conventional mechanism. Most of semiconductors such as sulfides and carbides except oxides are not stable enough to be used for this purpose.

On the other hand, in natural photosynthesis of green plants, carbohydrate and O₂ are formed from CO₂ and water using the so-called Z-scheme reaction composed of two photo-excitation centers and many redox mediators under the visible light. In order to realize the photocatalytic water splitting into H₂ and O₂ stoichiometrically under the visible light irradiation, we have been investigating the mimicking system of the Z-scheme mechanism using reversible redox mediators (Ox/Red), not using some irreversible sacrificial

* Corresponding author. Tel.: +81-298-61-4410; fax: +81-298-61-6771.
E-mail address: h.arakawa@aist.go.jp (H. Arakawa).

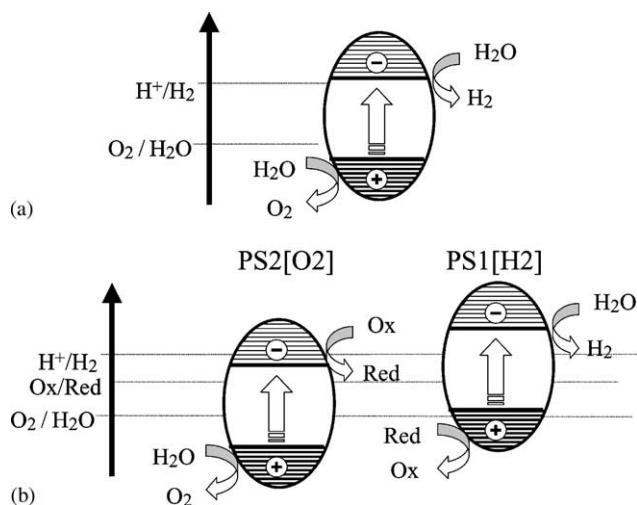
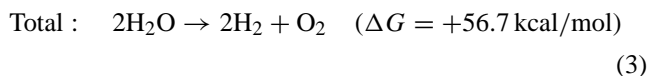
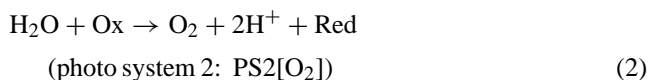
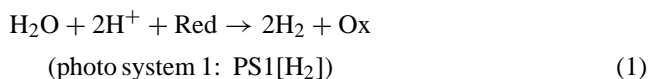


Fig. 1. Reaction mechanism of the photocatalytic water splitting into H_2 and O_2 : (a) the conventional photocatalytic reaction mechanism (one-step photo-excitation system) and (b) the reaction mechanism mimicking the Z-scheme system (the two-step photo-excitation system).

reagents:



In order to realize the Z-scheme reaction, developments of redox mediators and its appropriate reaction conditions are very important. So far, in the study of artificial photosynthesis, irreversible sacrificial reagents such as methanol, triethanolamine for H_2 evolution or peroxides for O_2 evolution have been usually used, but a few studies using reversible redox mediators are reported [15–17]. Matsumura and coworkers [15] reported the photocatalytic water decomposition using platinum electrodes and a cation-exchange membrane in a two-compartment reactor, where H_2 was evolved on Pt– TiO_2 (anatase) photocatalyst suspended in a Br_2/Br^- redox mediator solution and O_2 was evolved on TiO_2 (rutile) in a Fe^{3+}/Fe^{2+} redox mediator solution. We realized the water decomposition using a RuO_2 – WO_3 photocatalyst and Fe^{3+}/Fe^{2+} redox in a one-pot reactor, however, UV light less than 280 nm was essential because H_2 was evolved by direct photo-excitation of Fe^{2+} ion as PS1[H_2] [16] Next, we developed an IO_3^-/I^- redox system with a mixture of Pt– TiO_2 (anatase) and TiO_2 (rutile) photocatalysts as PS1[H_2] and PS2[O_2], respectively [17]. The H_2 evolution occurred on Pt– TiO_2 (anatase) photocatalyst with the oxidation of I^- to IO_3^- , and the O_2 evolution occurred on TiO_2 (rutile) with the reduction of IO_3^- to I^- in a one-pot cell under UV light. Here, we would like to report the photocatalytic

properties of various semiconductors which utilize the visible light using IO_3^-/I^- redox mediator in detail.

2. Experimental

2.1. Materials

Commercial WO_3 powder supplied from Koujundo Chemical was used as one of semiconductors for O_2 evolution. Various mixed-oxide semiconductors such as $BiWO_6$, $In_2O_3(ZnO)_9$, $InNbO_4$ and so on were prepared using the published procedure [12,13]. The powder of $SrTiO_3$ doped with Cr and Ta ions was prepared by the following solid state calcination method [14]. Powders of Cr_2O_3 (Cr: 1 mol% of Ti), Ta_2O_5 (Ta: 1 mol% of Ti), $SrCO_3$ and TiO_2 were mixed well in a mortar with distilled water (20 ml/10 g powder), and dried and fired at $1100^\circ C$ in air for 1 h. Then, the powder was mixed in a mortar again and fired at $1100^\circ C$ in air for 19 h. Pt-loaded catalyst was prepared by the photo-deposition method from a H_2PtCl_6 aqueous solution.

2.2. Photocatalytic reaction and characterization

The photocatalytic reaction was performed in a one-pot glass cell connected to a closed gas-circulating system. The visible light was irradiated using a Xe lamp (300 W, CERMAX-LX-300) through various cutoff filters (HOYA Glass). The total light power was 3.1 W (with 420 nm cutoff filter, window area: 16 cm^2), and it was measured by a thermopile power meter (Scientech, 38-2uv5). A mixture of catalyst powder (0.2 g), distilled water (250 ml) and NaI (100 mmol/l) or $NaIO_3$ (4 mmol/l) in the cell was degassed completely, and then argon gas (100 Torr) was introduced into the system. The evolution of H_2 and O_2 was detected by on-line gas chromatography (TCD, molecular sieve 5A, argon carrier). The I^- , IO_3^- and I_3^- ions were analyzed by ion-chromatography (Shimadzu, HIC-6A) and UV–Vis spectroscopy (Shimadzu, 3101PC). Absorption spectra of semiconductors were obtained using the UV–Vis spectrometer equipped with an integration sphere, and were converted from reflection to absorbance by the Kubelka–Munk method. The quantum efficiency (QE) was measured using a band-pass filter (λ_{max} : 420.7 nm, $\lambda_{\text{half-width}}$: 15.7 nm, Nihon Shinku Kougaku) and a light power meter (Advantest, Si diode, TQ8210).

3. Results and discussion

3.1. Hydrogen evolution from NaI aqueous solution (PS1[H_2])

First, the H_2 evolution on various photocatalysts using I^- ion as a reversible electron donor under visible light was

investigated. The Pt–TiO₂ (anatase) photocatalyst showed a good activity under the UV light [17] but it could not work under the visible light through 420 nm cutoff filter due to the large bandgap energy (ca. 3.0 eV). There is no simple oxide semiconductor that can utilize the visible light and that has a negative conduction band potential to produce H₂ at the same time. Generally, the conduction band originates from d- or s-orbital of metal atom, and the valence band of metal oxide semiconductor originates from 2p orbital of oxygen and is located at a highly positive potential. There are some reports on the relationship between the flat-band potential (E_{fb}) of oxide semiconductors and the bandgap energy (E_g) [9–11]. Scaife [9] indicated the following relationship experimentally:

$$E_{fb} \text{ (vs. NHE)} = 2.94 - E_g \text{ (eV)} \quad (4)$$

The conduction band potential of n-type semiconductors is almost the same as the flat-band potential, and the bandgap energy of semiconductor that can utilize the visible light is less than 3 eV. Therefore, the conduction band potentials of most of oxide semiconductors that can utilize the visible light are positive, i.e., the electron on the conduction band cannot reduce water to H₂. These discussions describe the difficulty of the water splitting reaction under visible light using oxide semiconductor photocatalysts. However, Scaife [9] also reported that a few oxide semiconductors containing transition metal ions such as Cr³⁺, Ni²⁺ and Fe³⁺ did not obey Eq. (4) exceptionally. Moreover, recently, there are some reports on unique mixed-oxide semiconductor photocatalysts that could produce H₂ under the visible light using sacrificial reagents such as methanol [12–14]. The methanol played as an irreversible and effective hole scavenger. On the other hand, I[−] ion is a reversible and mild electron donor; therefore, there was no evidence that these mixed-oxide semiconductor photocatalyst can evolve H₂ using I[−] ion under visible light. Then, we tested many semiconductor photocatalysts including these mixed-oxide semiconductors such as In₂O₃(ZnO)₉ [12], InNbO₄ [13], InTaO₄ [13], SrTiO₃ (Cr–Ta-doped) [14] and so on for the H₂ formation from NaI aqueous solution under visible light, as shown in Table 1. It was found that most photocatalysts could not evolve H₂ at all, but that only Pt-loaded oxide semiconductors containing Cr³⁺ such as SrTiO₃ (Cr–Ta-doped), CaTiO₃ (Cr–Ta-doped) and CrTaO₄ showed activities for H₂ evolution. Among them, the Pt-loaded SrTiO₃ (Cr–Ta-doped) showed the highest activity. This catalyst was reported by Kudo and coworkers [14] as an effective photocatalyst for H₂ evolution using methanol sacrificial reagent; however, the activities of this catalyst using redox mediators such as I[−] ion have not been investigated. The time course of the H₂ evolution is shown in Fig. 2. The initial rate of H₂ evolution was 0.8 μmol/h, but the rate decreased gradually and the reaction appeared to stop after 30 h from the start of irradiation. The H₂ formation was completely suppressed when a small amount of NaIO₃ (1 mmol/l) was added to the NaI reaction solution (100 mmol/l). Since the IO₃[−] ion is

Table 1
The H₂ evolution from NaI aqueous solution over various photocatalysts under visible light (>420 nm)^a

Semiconductor	Dopant (1 mol%)	Amount of the evolved H ₂ ^b (μmol/22 h)
Bi ₂ WO ₆	–	0
In ₂ O ₃ (ZnO) ₉	–	0
α-Fe ₂ O ₃	–	0
CrTaO ₄	–	tr
InTaO ₄	–	0
InNbO ₄	–	0
SrTiO ₃	Cr, Ta	8.0
SrTiO ₃	Cr	2.3
SrTiO ₃	Ta	0
SrTiO ₃	Cr, Bi	2.8
CaTiO ₃	Cr, Ta	0.8
BaTiO ₃	Cr, Ta	0
NaTaO ₃	Cr, Ti	0

^a Pt loading: 0.3 wt.%, NaI solution: 0.1 mol/l.

^b The total amount of the evolved H₂ gas for 22 h.

electron acceptor, the reduction of IO₃[−] formed by the oxidation of I[−] during the H₂ evolution reaction may compete with the reduction of H⁺ to H₂, resulting in the decreased of the H₂ evolution rate in Fig. 2. Moreover, the Pt loading was essential for the H₂ evolution. It is speculated that the loaded Pt acted as a H₂ evolution site because Pt has the lowest over-voltage for H₂ production in the water electrolysis. On the other hand, in the case of the oxidative reaction, the hole in the valence band had a potential for both the reactions; the I[−] oxidation and the water oxidation to O₂. However, the O₂ evolution was not detected in any cases. The non-doped Pt–SrTiO₃ had an excellent activity for O₂ evolution using NaIO₃ electron acceptor, but the Pt–SrTiO₃ (Cr–Ta-doped) photocatalyst hardly produced O₂ gas from the NaIO₃ aqueous solution, suggesting that the Cr and Ta doping prevent the O₂ formation. This characteristic is favorable for the Z-scheme reaction mentioned in Section 3.3.

Fig. 3 shows the absorption spectra of (a) SrTiO₃ and (b) SrTiO₃ (Cr–Ta-doped). The non-doped SrTiO₃ absorbed UV light up to 395 nm, and the bandgap was estimated to be 3.1 eV. The absorption band of the doped semiconductor was very broad and extended to more than 700 nm. The H₂

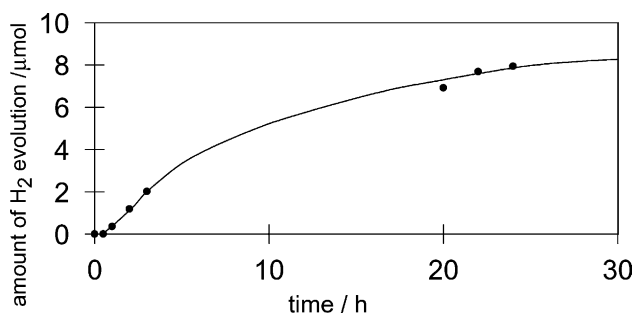


Fig. 2. Time course of the H₂ evolution on Pt (0.3 wt.%)–SrTiO₃ (Cr–Ta doped, 1 mol%) from NaI aqueous solution (100 mmol/l) under visible light (>420 nm).

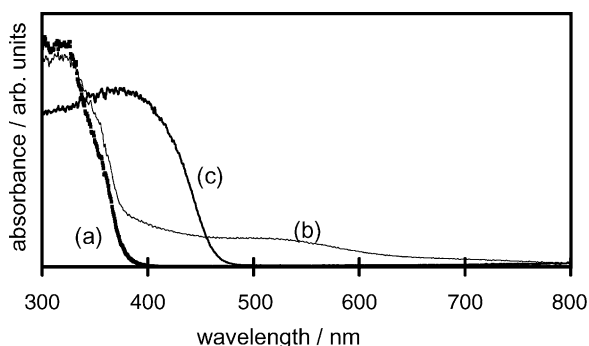


Fig. 3. The absorption spectra of (a) SrTiO₃, (b) SrTiO₃ (Cr–Ta-doped) and (c) WO₃.

evolution was observed on the Pt-loaded SrTiO₃ (Cr–Ta-doped) under visible light even through 460 nm cutoff filter. The SrTiO₃ doped with Ta alone did not absorb visible light; therefore, the Cr doping caused the visible light response. By considering the stable valence under the condition of the semiconductor preparation and the ion radii of Ti⁴⁺ (0.75 Å), Sr²⁺ (1.32 Å), Cr³⁺ (0.76 Å) and Ta⁵⁺ (0.78 Å), it is considered that the doped Cr³⁺ and Ta⁵⁺ ions were substituted for Ti⁴⁺ atom, rather than Sr²⁺ atom. The activity of the SrTiO₃ catalyst doped with Cr and Ta was much higher than that doped with Cr only, as shown in Table 1. Similar behavior was observed in the case of the H₂ evolution using methanol sacrificial reagent [14]. It is speculated that the substitution of Cr³⁺ for Ti⁴⁺ may cause some defects of the lattice in the SrTiO₃ crystal structure due to the lack of the positive charge, and that the co-doping of Ta⁵⁺ may neutralize the total charge.

Scaife [9] found irregular behaviors of some mixed-oxide semiconductors containing Cr³⁺ or Ni²⁺ ion against Eq. (4). These semiconductors had a small bandgap to utilize the visible light and had a negative conduction band potential. He considered that a partially occupied d-orbital of these transition metals modulated the valence band potential. We also speculated the Cr doping modulated the valence band potential negatively; however, a further discussion must be awaiting the information about the real band structure of SrTiO₃ (Cr–Ta-doped), which is now under investigation.

3.2. Oxygen evolution from NaIO₃ aqueous solution (PS2[O₂])

We studied next the O₂ evolution on various photocatalysts using IO₃[−] ion as a reversible electron acceptor. The TiO₂ (rutile) photocatalyst showed an excellent activity under UV light [17] but it could not work under visible light. We tested many semiconductor photocatalysts, e.g., simple oxide semiconductors (WO₃, In₂O₃, Bi₂O₃, Fe₂O₃, etc.) and mixed-oxide semiconductors (BiVO₄, CuWO₄, NiWO₄, SrWO₄, etc.). It was found that the Pt-loaded WO₃ catalyst showed the best activity under the visible light irradiation among them. The H₂ gas was not formed at all. The conduc-

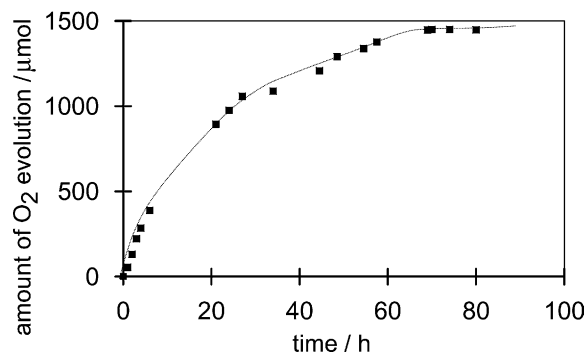


Fig. 4. Time course of the O₂ evolution on Pt (0.5 wt.%)–WO₃ from NaIO₃ aqueous solution (250 ml, 4 mmol/l).

tion band potential of WO₃ is +0.09 V (vs. NHE, pH = 7) [11] and the redox potential of H⁺/H₂ and IO₃[−]/I[−] pairs are −0.41 and 0.67 V (vs. NHE, pH = 7), respectively. Therefore, the electron in the conduction band of WO₃ has an ability to reduce IO₃[−] to I[−], but it cannot reduce H⁺ to H₂. The valence band potential of WO₃ is very positive (ca. 2.79 V vs. NHE, pH = 7) compared to the O₂/H₂O potential (0.82 V vs. NHE, pH = 7), therefore the hole of the valence band of WO₃ has an ability of not only the O₂ formation from water but also the I[−] oxidation to IO₃[−]. Fig. 4 shows the time course of the O₂ evolution on Pt (0.5 wt.%)–WO₃. The total amount of evolved O₂ was ca. 1.5 mmol. The amount of IO₃[−] was 1 mmol in the initial solution; therefore, the maximum O₂ evolution was 1.5 mmol when all IO₃[−] was converted to I[−]. The O₂ evolution took place until all IO₃[−] ions were mostly consumed even if much amount of I[−] was accumulated in the solution during the reaction. It is considered that the backward reaction, re-oxidation of the produced I[−] to IO₃[−] by hole in the valence band, was very slow on Pt–WO₃ in this reaction condition compared to the water oxidation to O₂. The absorption spectrum of the WO₃ semiconductor is shown in Fig. 3(c). Though there was a small absorption skirt up to 480 nm, the main absorption was located at less than 460 nm, suggesting the bandgap of the WO₃ was estimated to be ca. 2.7 eV. The O₂ gas was evolved under the visible light even through 440 nm cutoff filter, but it was negligible through 460 nm cutoff filter, suggesting that the dependence of the activity on the wavelength of the incident light was almost in accord with the absorption spectrum.

The loading of co-catalysts such as Pt and RuO₂ on WO₃ was essential for the photocatalytic O₂ evolution using IO₃[−] electron acceptor. The WO₃ photocatalyst without any co-catalysts had the ability of O₂ evolution when other electron acceptors such as Fe³⁺, NO₃[−] and Ag⁺ ions [16,18] were used instead of IO₃[−] ion, suggesting that the O₂ evolution site was present on the WO₃ surface. The selectivities of the reduced products were much dependent on each co-catalyst. The formation of I[−] took place mainly on Pt–WO₃, while the formation of I₃[−] was negligible on Pt–WO₃, while large amount of I₃[−] was formed on RuO₂–WO₃ and IrO₂–WO₃. There is a report that not only Pt but also RuO₂ played

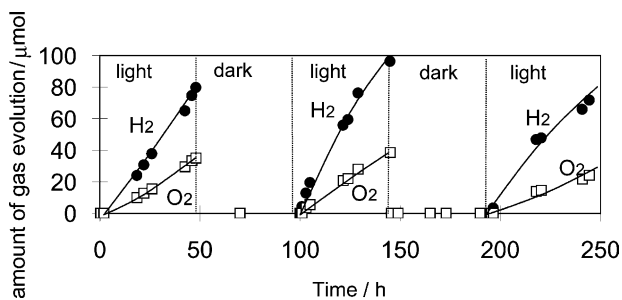


Fig. 5. Photocatalytic decomposition of water into H_2 and O_2 under the visible light (>420 nm). Pt (0.3 wt.%)– $SrTiO_3$ doped with Cr and Ta (1 mol% of Ti, respectively): 0.2 g, Pt (1 wt.%)– WO_3 : 0.2 g, initial reaction solution: NaI aqueous solution (100 mmol/l, pH = 7.0). The magnetic stirring was continued during the light irradiation and in dark.

as reduction site on n-type semiconductors [19]. From all results, it is speculated that the co-catalyst promoted the reduction of IO_3^- ion to I^- .

3.3. The water splitting reaction into H_2 and O_2 using IO_3^-/I^- redox mediator ($PS1[H_2] + PS2[O_2]$)

Finally, we studied the combination of the $PS1[H_2]$ and the $PS2[O_2]$ for the stoichiometric water splitting into H_2 and O_2 . It was found that both H_2 and O_2 gases evolved under visible light using a mixture of the Pt– WO_3 and Pt– $SrTiO_3$ (Cr–Ta-doped) powders in NaI aqueous solution, as shown in Fig. 5. The stoichiometric ratio of H_2 and O_2 ($H_2/O_2 = 2$) was constant from the start of irradiation to more than 250 h, and no change in the catalysts was observed. It is for the first time that the stoichiometric water splitting took place over oxide semiconductor photocatalysts under the visible light irradiation. The presence of the three components, the photocatalyst for H_2 evolution, the photocatalyst for O_2 evolution and NaI, was essential for the stoichiometric water splitting into H_2 and O_2 , suggesting a synergistic effect of two different photocatalysts in NaI aqueous solution. In the case of the Pt– TiO_2 (anatase) and TiO_2 (rutile) system [17] the IO_3^-/I^- redox pair was mainly contributed to the water splitting reaction. Therefore, we speculated the reaction mechanism as shown in Fig. 6. The reaction mechanism was similar to the Z-scheme reaction in the natural photosynthesis, in other words, we could

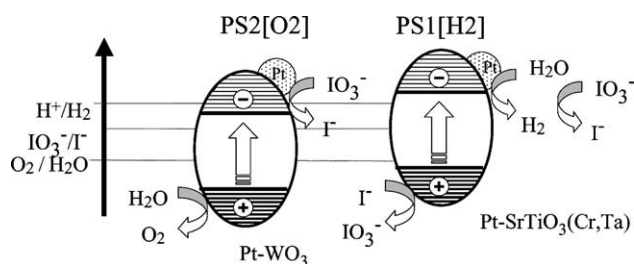


Fig. 6. Speculated reaction mechanism using IO_3^-/I^- redox mediator.

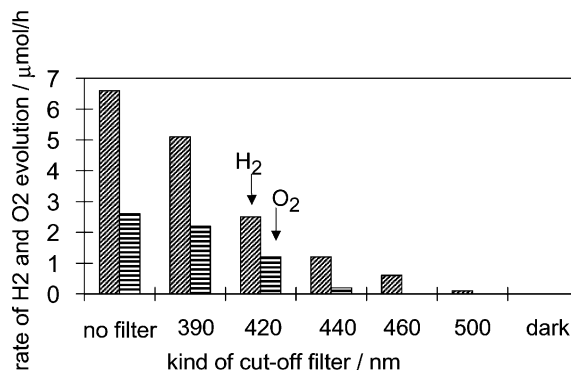


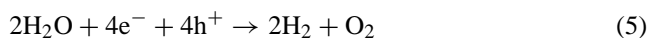
Fig. 7. Dependence of gas evolution rate on the wavelength of the irradiated light.

succeed in the construction of the artificial photosynthesis system. After the reaction, the concentration of I^- ion (100 mmol/l) was not changed, and the formation IO_3^- ion was negligible. It is suggested that the equilibrium ratio of IO_3^-/I^- was almost zero during the water splitting reaction. It should be noted that the H_2 evolution rate over the mixture of Pt– $SrTiO_3$ (Cr–Ta-doped) and Pt– WO_3 ($2.5 \mu\text{mol/h}$) was higher than that over Pt– $SrTiO_3$ (Cr–Ta-doped) alone ($0.8 \mu\text{mol/h}$ at initial activity in Fig. 2). It is considered that the concentration of the IO_3^- ion formed on Pt– $SrTiO_3$ (Cr–Ta-doped) was kept very low because Pt– WO_3 reduced IO_3^- to I^- promptly. As for the other redox species except I^- and IO_3^- , it was found that I_2 (or I_3^-) did not contribute to the water splitting reaction. Because the activity of H_2 formation using I_2 as electron donor and that of O_2 formation using I_2 as electron acceptor were negligible. The formation of IO^- was not observed in the solution after the reaction, however, it is a very unstable species and the redox potential of $E(IO^-/I^-)$ is 0.74 V (vs. NHE, pH = 7). Therefore the possibility of the contribution of IO^- redox could not be completely excluded now.

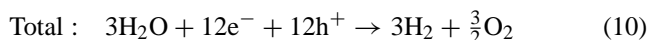
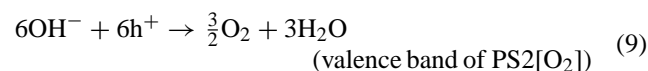
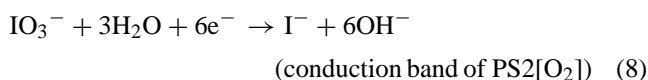
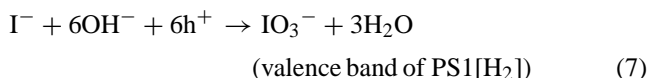
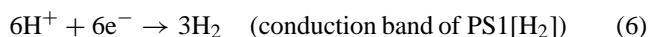
Fig. 7 shows the dependence of the rate of gas evolution on the wavelength of the light irradiation. The activity decreased as the wavelength of the cutoff filter increased. When a 460 nm cutoff filter was used, the O_2 evolution could not be observed because the Pt– WO_3 catalyst could not work at >460 nm. Domen and coworkers [20] reported that the H_2 and O_2 gases were formed by a mechanical energy of the stirring. No mechano-catalytic reaction occurred in our system however because any gas evolution was not observed by the rotating of the magnetic stirring rod without irradiation.

In order to determine the QE, the rate of gas evolution under the monochromatic light (0.057 W) through a 420.7 nm band-pass filter was measured. The photon flux was calculated to be $721.5 \mu\text{mol/h}$. A Pyrex glass plate was put just before the power meter to correct the reflection at the window of the Pyrex reactor; however, the losses by the transmission and scattering by the catalyst powder were not corrected. Therefore, the actual value of the photon flux adsorbed by the catalyst itself was smaller than this value. The rates of

H₂ and O₂ evolution were 0.21 and 0.11 μmol/h, respectively. In the case of the overall water splitting reaction in the conventional mechanism (Fig. 1(a)), four electron–hole pairs are needed to produce two H₂ molecules (Eq. (5)), suggesting that two photons are needed for one H₂:



On the other hand, in the case of the overall water splitting reaction in the Z-scheme system, eight electron–hole pairs are needed to produce two H₂ molecules (Eq. (11)), suggesting that four photons are needed for one H₂:



Therefore, the QE of the overall water splitting reaction in the Z-scheme system was calculated to be ca. 0.1% at 420.7 nm by the following equation:

$$\text{QE of the overall water splitting reaction in the Z-scheme system (\%)} = \frac{(\text{H}_2 [\text{mmol/h}] \times 4 \times 100)}{\text{photon flux } [\mu\text{mol/h}]} \quad (12)$$

3.4. Comparison between the Z-scheme reaction (two-step) system and the conventional (one-step) system

The two-step photo-excitation reaction system mimicking the Z-scheme reaction of the photosynthesis has some advantages over the conventional one-step system as follows: (1) the combinations of redox mediators and semiconductors are abundant. We can investigate some efficient reactions in each of PS1[H₂] and PS2[O₂] separately and then can link PS1[H₂] and PS2[O₂] together. (2) When the redox potential of Ox/Red couple is located between the potentials of H⁺/H₂ and O₂/H₂O, the change of chemical potential (ΔG) in each PS reaction is smaller than that in the total reaction (+56.7 kcal/mol). Therefore, PS1[H₂] and PS2[O₂] may take place more easily compared to the direct water decomposition. (3) The separate evolution of H₂ and O₂ gas is possible in the Z-scheme mechanism using a simple membrane filter to avoid the mixing of two catalysts, while both gases evolve on one photocatalyst particle simultaneously as a detonating gas in the conventional mechanism. (4) A dye photocatalyst or a dye-sensitized semiconductor photocatalyst can be applied as PS1[H₂] [21]. In the case of the

dye-sensitized solar cell, the dye injected into the conduction band of TiO₂ semiconductor effectively using I[−] electron donor [22]. On the other hand, it is difficult for a simple dye photocatalysts to produce O₂ gas in the conventional one-step system because the O₂ evolution is four-electron process. (5) We proposed an economical H₂ production system using the photocatalysis–electrolysis hybrid system [23]. The O₂ evolution took place on semiconductor photocatalyst with the reduction of redox mediators such as Fe³⁺ ion under the solar light, as the same as PS2[O₂], and the H₂ evolution took place by electrolysis with the reductive mediator such as Fe²⁺ under a very small voltage compared to the conventional electrolysis. Therefore the study on the PS2[O₂] is very meaningful economically.

The disadvantages of the two-step system are: first that twice the number of photons must be used to evolve the same amount of H₂ compared to the one-step system. However, if the absorption wavelength regions of PS1[H₂] and PS2[O₂] are different significantly, this disadvantage is not serious. Secondly, the two-step system is more complicated than the one-step one. Therefore, some processes such as the recovery of deactivated catalysts from the solution may be difficult, and the possibility of an undesirable side-reaction such as the I₂ formation may be increased.

Now, the QE was still low, however, a further development will be anticipated because the study of the Z-scheme reaction using two photocatalysts has just started. For example, the efficiency will increase if the side-reaction on Pt–SrTiO₃ (Cr–Ta doped), IO₃[−] reduction by electron, is suppressed by means of the modification of the reduction site.

4. Conclusion

The stoichiometric water splitting into H₂ and O₂ (H₂/O₂ = 2) over oxide semiconductor photocatalysts under the visible light irradiation could be demonstrated for the first time. Both H₂ and O₂ gases evolved under visible light using a mixture of Pt–WO₃ and Pt–SrTiO₃ (Cr–Ta-doped) powders in NaI aqueous solution for more than 250 h. We proposed the two-step photo-excitation mechanism using I[−]/IO₃[−] redox mediator, which was similar to the Z-scheme reaction in the natural photosynthesis. The QE of the stoichiometric water splitting was ca. 0.1% at 420.7 nm.

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