

## Photocatalysis and solar hydrogen production\*

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*Abstract:* Photocatalytic water splitting is a challenging reaction because it is an ultimate solution to energy and environmental issues. Recently, many new powdered photocatalysts for water splitting have been developed. For example, a NiO (0.2 wt %)/NaTaO<sub>3</sub>:La (2 %) photocatalyst with a 4.1-eV band gap showed high activity for water splitting into H<sub>2</sub> and O<sub>2</sub> with an apparent quantum yield of 56 % at 270 nm. Overall water splitting under visible light irradiation has been achieved by construction of a Z-scheme photocatalysis system employing visible-light-driven photocatalysts, Ru/SrTiO<sub>3</sub>:Rh and BiVO<sub>4</sub> for H<sub>2</sub> and O<sub>2</sub> evolution, and an Fe<sup>3+</sup>/Fe<sup>2+</sup> redox couple as an electron relay. Moreover, highly efficient sulfide photocatalysts for solar hydrogen production in the presence of electron donors were developed by making solid solutions of ZnS with AgInS<sub>2</sub> and CuInS<sub>2</sub> of narrow band gap semiconductors. Thus, the database of powdered photocatalysts for water splitting has become plentiful.

*Keywords:* Photocatalysts; water splitting; solar light; hydrogen; metal oxides; metal sulfides.

### INTRODUCTION

Hydrogen is an ideal clean energy as well as a raw material in many chemical industries. Hydrogen is mainly produced by steam reforming of hydrocarbons such as methane in industry. Hydrogen must be produced from water using renewable energy sources such as solar light, if one considers the energy and environmental issues. Photocatalytic water splitting is one of the candidates for solar hydrogen production. When one considers the usage of solar energy, one encounters difficulty due to the low density of the energy. A large area should be used in order to harvest a reasonable amount of solar energy. The photocatalytic water splitting will be advantageous for the large-scale application of solar hydrogen production because of its simplicity.

Photocatalysis is classified into two categories. One is the application to the improvement of the living environment such as anti-stain, self-cleaning, and superhydrophilicity properties [1]. TiO<sub>2</sub> photocatalysts are widely used for these applications, and many industrial products have been made. Another direction of photocatalysis is light energy conversion as represented by water splitting. Water splitting using light energy has been studied for a long time using powder and electrode systems since the Honda–Fujishima effect was reported [2,3]. Although it is under basic research, it is still a challenging topic. This research field has made remarkable progress recently. It is no doubt that photocatalytic water splitting will contribute to green–sustainable chemistry. The final target of this research field is to achieve an artificial photosynthesis and solar hydrogen production from water.

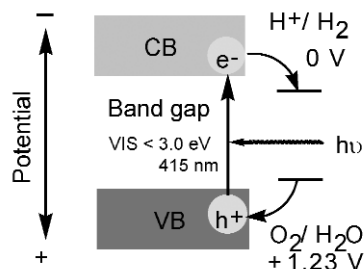
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\*Pure Appl. Chem. 79, 1831–2100. An issue of reviews and research papers based on lectures presented at the 1<sup>st</sup> International IUPAC Conference on Green–Sustainable Chemistry, held in Dresden, Germany, 10–15 September 2006.

The present paper focuses on the development of new photocatalyst materials in order to make a photocatalyst library. New materials of photocatalysts that the author and coworkers have found are reviewed.

## BASIS OF PHOTOCATALYTIC REACTION

Water splitting proceeds on heterogeneous photocatalysts with semiconductor properties as schematically shown in Fig. 1. Semiconductors have the band structure in which the conduction band (CB) is separated from the valence band (VB) by a suitable band gap. When light (of which the energy is larger than the band gap) is irradiated, electrons and holes are generated in the CBs and VBs, respectively. The photogenerated electrons and holes cause redox reactions similarly to electrolysis. Water molecules are reduced by the electrons to form hydrogen and are oxidized by the holes to form oxygen for overall water splitting. Important points in the semiconductor photocatalyst materials are the width of the band gap and energy levels of the CBs and VBs. The bottom level of the CB has to be more negative than the redox potential of  $\text{H}^+/\text{H}_2$  (0 V vs. NHE), while the top level of the VB has to be more positive than the redox potential of  $\text{O}_2/\text{H}_2\text{O}$  (1.23 V). Therefore, the band gap should be wider than 1.23 eV.



**Fig. 1** Principle of water splitting on semiconductor photocatalysts.

In general, the VBs of stable oxide semiconductor photocatalysts based on metal cations with  $d^0$  and  $d^{10}$  configurations are composed of O 2p orbitals. The energy levels are considerably more positive (ca. +3eV) than the oxidation potential of  $\text{H}_2\text{O}$ . Therefore, the band gaps of oxide semiconductor photocatalysts for water splitting inevitably become wider than 3 eV. Thus, these oxide photocatalysts respond to only UV light.

Water splitting using photocatalysts would seem to be simple and easy as shown in Fig. 1. However, it is a very tough reaction because of an up-hill reaction in which back reactions easily proceed. The band structure is merely a thermodynamic requirement, but not a sufficient condition. Some important factors are actually concerned with the photocatalytic properties as shown in Fig. 2. Photogenerated electrons and holes have to be separated and migrate to the surface. This process is strongly affected by bulk properties such as crystallinity. The better the crystallinity is, the less the number of defects which often work as recombination sites between photogenerated electrons and holes, resulting in increases in the life time and mobility. On the other hand, the number and quality of the active sites for redox reactions by photogenerated electron and hole pairs are kinetically affected by surface properties. For example, the number of the active site usually depends on the surface area. Even if the photogenerated electrons and holes possess thermodynamically sufficient potentials for water splitting, they will have to recombine with each other if the active sites for the redox reactions do not exist on the surface. Therefore, a cocatalyst such as Pt, NiO, and  $\text{RuO}_2$  is often loaded on the surface in order to introduce the active site. Thus, suitable bulk and surface properties, and energy structure are required for photocatalysts. So, it is understandable that photocatalysts should be highly functional materials.

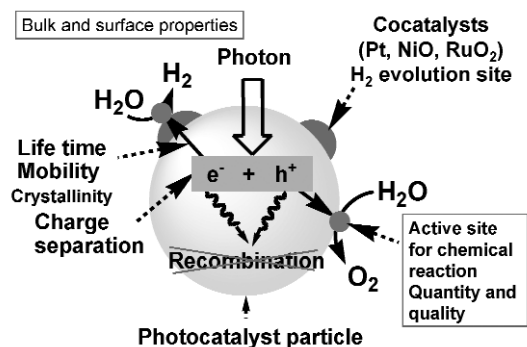


Fig. 2 Processes for photocatalytic reaction in powdered system.

## HISTORY OF THE DISCOVERY OF PHOTOCATALYST MATERIALS

During the 1970s and the first half of the 1980s, the photocatalysts used for the research of water splitting were mainly  $\text{TiO}_2$  and  $\text{SrTiO}_3$ . The  $\text{TiO}_2$  photocatalyst is active when it is modified with a cocatalyst and the reaction is carried out in a suitable aqueous solution or a gas phase. No activity is obtained if native  $\text{TiO}_2$  powder is dispersed in water. Beginning in the second half of the 1980s, new photocatalyst materials, such as  $\text{K}_4\text{Nb}_6\text{O}_{17}$  [4–6],  $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$  [7],  $\text{BaTi}_4\text{O}_9$  [8],  $\text{ZrO}_2$  [9], and  $\text{Ta}_2\text{O}_5$  [10], other than  $\text{TiO}_2$  and  $\text{SrTiO}_3$ , were found for water splitting. Many tantalate photocatalysts have been found since the second half of the 1990s [11]. Moreover, many oxide photocatalysts consisting of the metal cations  $\text{Ga}^{3+}$ ,  $\text{In}^{3+}$ ,  $\text{Ge}^{4+}$ ,  $\text{Sn}^{4+}$ , and  $\text{Sb}^{5+}$ , with  $d^{10}$  configuration, and assisted with  $\text{RuO}_2$  as a cocatalyst have recently been reported [12–16]. Non-oxide  $\text{Ge}_3\text{N}_4$  with a  $\text{RuO}_2$  cocatalyst was also found to be a photocatalyst [17].

Thus, the database of photocatalysts for water splitting has become plentiful. Highly efficient photocatalytic water splitting has been achieved. However, these photocatalysts consisting of  $d^0$  and  $d^{10}$  metal cations respond to only UV light because of their wide band gaps ( $\text{BG} > 3.0 \text{ eV}$ ).

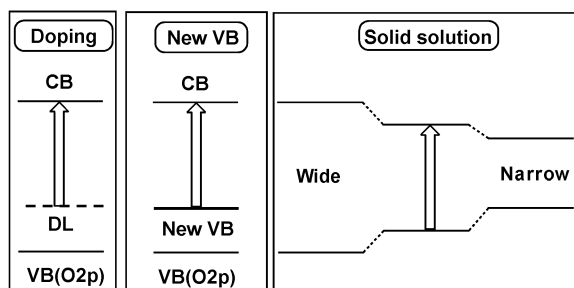
Highly active photocatalysts for  $\text{H}_2$  or  $\text{O}_2$  evolution under visible light irradiation, even in the presence of sacrificial reagents, were only  $\text{Pt/CdS}$  [18–20] and  $\text{WO}_3$  [21] during the first half of the 1990s. The materials for visible-light-driven photocatalysts had been quite limited. However, many oxides [22,23], oxynitrides [24–31], and oxysulfides [32–34] have recently been found to be active for  $\text{H}_2$  and  $\text{O}_2$  evolution under visible light irradiation in the presence of sacrificial reagents.

Recently, water splitting has been achieved by several photocatalyst systems. Two-photon systems, as seen in photosynthesis by green plants (Z-scheme), have been reported. Combined systems, with  $\text{Pt/SrTiO}_3\text{:Cr,Ta}$  or  $\text{Pt/TaON}$  for the  $\text{H}_2$  evolution photocatalyst, and  $\text{WO}_3$  for the  $\text{O}_2$  evolution photocatalyst, can split water into  $\text{H}_2$  and  $\text{O}_2$  in stoichiometric amounts in the presence of an  $\text{IO}_3^-/\text{I}^-$  redox couple [35–37].  $\text{Cr-Rh}$  oxide/ $\text{GaN}:\text{ZnO}$ , which is a solid solution of  $\text{GaN}$  and  $\text{ZnO}$ , is also an active photocatalyst for overall water splitting [38].

## STRATEGY FOR DESIGN OF VISIBLE-LIGHT-DRIVEN PHOTOCATALYSTS

Stable oxide semiconductor photocatalysts based on the metal cations with  $d^0$  and  $d^{10}$  configurations usually respond to only UV light as mentioned above. Suitable band engineering is needed in order to develop photocatalysts for water splitting under visible light irradiation. The strategies are shown in Fig. 3.

Doping of transition-metal cations has often been attempted to prepare visible-light-driven photocatalysts. Here, doping often means replacement with a foreign element at a crystal lattice point of the host material. The host material for the doping is usually a  $\text{TiO}_2$  photocatalyst. However, although the



**Fig. 3** Band engineering for design of visible-light-driven photocatalysts.

white powder becomes colored with doping of transition-metal cations, in general, the photocatalytic activity drastically decreases because of formation of recombination centers between photogenerated electrons and holes, even under band gap excitation. Therefore, doping is regarded as an unsuitable method. However, if metal cations are properly doped, visible light response is actually obtained as mentioned below.

In the doped photocatalysts, the formation of recombination sites by the dopant is more or less inevitable. Moreover, the level formed by the dopant is usually discrete and thus inconvenient for the migration of holes formed there. Therefore, the formation of a VB by orbitals not associated with O 2p but with other elements is indispensable for oxide photocatalysts in order to design visible-light-driven photocatalysts.

Making a solid solution is also one of the strategies. Band gaps and the energy levels can be controlled by changing the ratio of wide and narrow band gap semiconductors.

## NEW PHOTOCATALYST MATERIALS FOR WATER SPLITTING

### Photocatalyst library

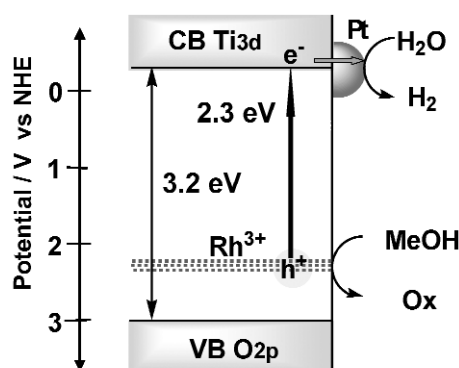
Table 1 shows photocatalyst materials that the present author and coworkers have found. The photocatalytic reactions are classified into overall water splitting into H<sub>2</sub> and O<sub>2</sub> without any sacrificial reagents, and H<sub>2</sub> or O<sub>2</sub> evolution in the presence of sacrificial reagents. Many tantalates and niobates with wide band gaps show the activities for overall water splitting under UV irradiation [39–51]. In the presence of sacrificial reagents, many metal cation-doped oxides [52–56], VB-controlled oxides [57–64], and metal sulfides [65–74] show activities for H<sub>2</sub> or O<sub>2</sub> evolution under visible light irradiation. It is important to make such a photocatalyst library in order to look at the overview of materials and get information for design of new materials.

**Table 1** Photocatalyst library.

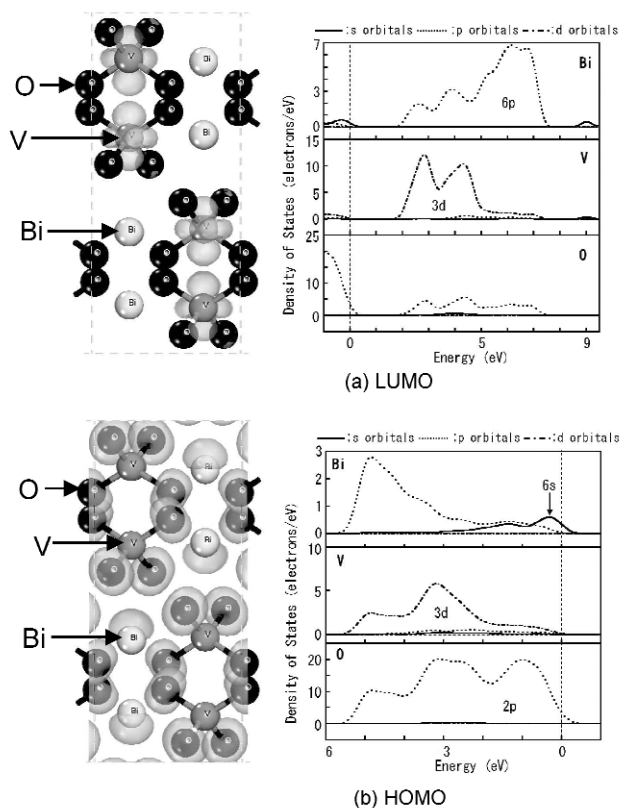
UV-responsive photocatalysts	Visible-light-responsive photocatalysts		
	H <sub>2</sub> evolution (sacrificial)	O <sub>2</sub> evolution (sacrificial)	Overall water splitting
ZnNb <sub>2</sub> O <sub>6</sub> [39]	SrTiO <sub>3</sub> :Cr,Sb [52]	TiO <sub>2</sub> :Cr,Sb [52]	SrTiO <sub>3</sub> :Rh–BiVO <sub>4</sub> [76]
Sr <sub>2</sub> Nb <sub>2</sub> O <sub>7</sub> [40]	SrTiO <sub>3</sub> :Cr,Ta [53]	TiO <sub>2</sub> :Ni,Nb [55]	SrTiO <sub>3</sub> :Rh–Bi <sub>2</sub> MoO <sub>6</sub> [76]
Cs <sub>2</sub> Nb <sub>4</sub> O <sub>11</sub> [41]	SrTiO <sub>3</sub> :Rh [54]	PbMoO <sub>4</sub> :Cr [56]	SrTiO <sub>3</sub> :Rh–WO <sub>3</sub> [76]
Ba <sub>5</sub> Nb <sub>4</sub> O <sub>15</sub> [42]	SnNb <sub>2</sub> O <sub>6</sub> [57]	BiVO <sub>4</sub> [58–61]	
ATaO <sub>3</sub> (A = Li, Na, K) [43,44]	ZnS:Cu [65]	Bi <sub>2</sub> MoO <sub>6</sub> [62]	
NaTaO <sub>3</sub> :A (A = Ln, Ca, Sr, Ba) [45,46]	ZnS:Ni [66]	Bi <sub>2</sub> WO <sub>6</sub> [63]	
ATA <sub>2</sub> O <sub>6</sub> (A = Mg, Ca, Sr, Ba) [43]	ZnS:Pb,Cl [67]	AgNbO <sub>3</sub> [51]	
Sr <sub>2</sub> Ta <sub>2</sub> O <sub>7</sub> [40,47]	NaInS <sub>2</sub> [68]	Ag <sub>3</sub> VO <sub>4</sub> [64]	
K <sub>3</sub> Ta <sub>3</sub> Si <sub>2</sub> O <sub>13</sub> [48]	AgGaS <sub>2</sub> [69]	In <sub>2</sub> O <sub>3</sub> (ZnO) <sub>3</sub> [75]	
K <sub>3</sub> Ta <sub>3</sub> B <sub>2</sub> O <sub>12</sub> [49]	CuInS <sub>2</sub> –AgInS <sub>2</sub> –ZnS [70–74]		
K <sub>2</sub> LnTa <sub>5</sub> O <sub>15</sub> [50]	In <sub>2</sub> O <sub>3</sub> (ZnO) <sub>3</sub> [75]		
AgTaO <sub>3</sub> [51]			

Codoping is sometimes a suitable method to get visible light response. For example, TiO<sub>2</sub> codoped Sb with Cr is active for O<sub>2</sub> evolution, whereas only Cr-doped TiO<sub>2</sub> is inactive as usual [52]. The codoping contributes to the compensation of the charge and distortion resulting in the suppression of recombination centers.

A remarkable photocatalyst in Table 1 is Rh-doped SrTiO<sub>3</sub> [54]. It is one of the rare oxide photocatalysts that can produce H<sub>2</sub> under visible light irradiation. The visible light response is due to the transition from an electron donor level consisting of Rh 4d orbitals to the conduction band of STiO<sub>3</sub> as shown in Fig. 4. This photocatalyst shows the highest activity when the doping amount is ca. 1 %. The amount of 1 % is not small as a doping level. The Rh dopant forms a discrete level or a subband.

**Fig. 4** Mechanism of H<sub>2</sub> evolution over Pt/SrTiO<sub>3</sub>:Rh under visible light irradiation.

Another unique photocatalyst is VB-controlled  $\text{BiVO}_4$  [58–61]. It can be prepared under ambient condition in aqueous media. It is an environmental-friendly process. It can produce  $\text{O}_2$  under visible light irradiation. The Bi 6s orbitals in  $\text{BiVO}_4$  contribute to the formation of the top of the VB (near the highest occupied molecular orbital, HOMO) as shown in Fig. 5. The CB is composed of V3d orbitals as usual.



**Fig. 5** Contour maps and densities of states of  $\text{BiVO}_4$  photocatalyst. (a) lowest unoccupied molecular orbital (LUMO) and (b) HOMO.

### Highly efficient water splitting into $\text{H}_2$ and $\text{O}_2$ on tantalate photocatalyst

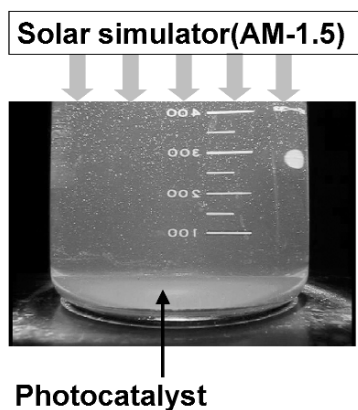
$\text{NiO}/\text{NaTaO}_3$  is the most active for water splitting among tantalate photocatalysts [11]. The photocatalytic activity of  $\text{NiO}/\text{NaTaO}_3$  increases remarkably with doping of lanthanoid and alkaline earth metal cations [45,46]. The doping of La makes the life time of photogenerated electrons long; that was confirmed by time-resolved infrared absorption spectroscopy [77]. An optimized  $\text{NiO}$  (0.2 wt %)/ $\text{NaTaO}_3$ :La (2 %) photocatalyst shows high activity, with an apparent quantum yield of 56 % for water splitting [45]. Under irradiation of the light from a 200-W Xe–Hg lamp,  $\text{H}_2$  and  $\text{O}_2$  evolve in the form of bubbles, without any sacrificial reagents, as shown in Fig. 6. This photocatalyst responds to only UV light. It should be stressed that this photocatalyst has demonstrated the highly efficient water splitting even using a powdered system.



**Fig. 6** Water splitting over NiO/NaTaO<sub>3</sub>:La photocatalyst under UV irradiation. Light source: 200-W Xe–Hg Lamp.

### Solar hydrogen production using water and abundant sulfur compounds on metal sulfide photocatalysts

We have examined the photophysical and photocatalytic properties of solid solutions of sulfides based on ZnS according to the band engineering as shown in Fig. 3 [70–74]. Solid solutions consisting of combinations of CuInS<sub>2</sub>, AgInS<sub>2</sub>, and ZnS show the high photocatalytic activities for H<sub>2</sub> evolution from aqueous sulfide and sulfite solutions under visible light irradiation. The diffuse reflectance spectra for AgInS<sub>2</sub>–CuInS<sub>2</sub>–ZnS shift monotonically with the composition of the solid solution. This indicates that the levels of the CB consisting of Zn 4s–4p and In 5s–5p, and of the VB consisting of Cu 3d, Ag 4d, and S 3p, shift with the varying composition. Ru/Cu<sub>0.25</sub>Ag<sub>0.25</sub>In<sub>0.5</sub>ZnS<sub>2</sub> especially shows excellent activity for the H<sub>2</sub> evolution solution (8 L/m<sup>2</sup>·h) with a solar simulator (AM-1.5). Hydrogen is observed in the form of bubbles as shown in Fig. 7. These sulfide solid solution photocatalysts can utilize visible light of wavelengths up to about 700 nm. The activity is higher than that of the well-known Pt/CdS photocatalyst, which can utilize visible light up to 520 nm. Moreover, toxic elements such as cadmium are not included in the photocatalysts. These photocatalysts will be able to be used for the recovery of hydrogen from water and abundant sulfur compounds in nature, and petroleum and mining industries as shown in Fig. 8.



**Fig. 7** Solar H<sub>2</sub> production on Ru/Cu<sub>0.25</sub>Ag<sub>0.25</sub>In<sub>0.5</sub>ZnS<sub>2</sub> photocatalyst from an aqueous K<sub>2</sub>SO<sub>3</sub>+Na<sub>2</sub>S solution using a solar simulator (AM-1.5).

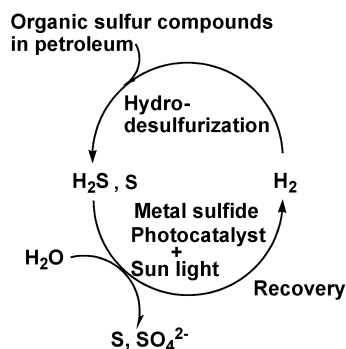


Fig. 8  $H_2$  recovering system using metal sulfide photocatalysts.

### Solar hydrogen production from water using visible-light-driven photocatalysts

It is mentioned that  $SrTiO_3:Rh$  and  $BiVO_4$  are remarkable photocatalysts working under visible light irradiation. The system in which  $SrTiO_3:Rh$  is combined with  $BiVO_4$  in the presence of an  $Fe^{3+}/Fe^{2+}$  redox couple shows activity for overall water splitting under visible light irradiation according to the scheme as shown in Fig. 9 [76]. This Z-scheme system responds to 520-nm light, corresponding with the absorption edges of  $SrTiO_3:Rh$  and  $BiVO_4$ , and is active even with a solar simulator as shown in Fig. 10. In other words, although the efficiency is low, solar hydrogen production from water has been accomplished using a powdered photocatalyst system with visible light response.

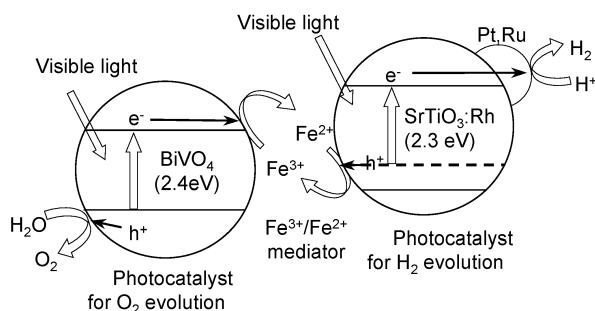


Fig. 9 Z-scheme photocatalyst system for solar hydrogen production.

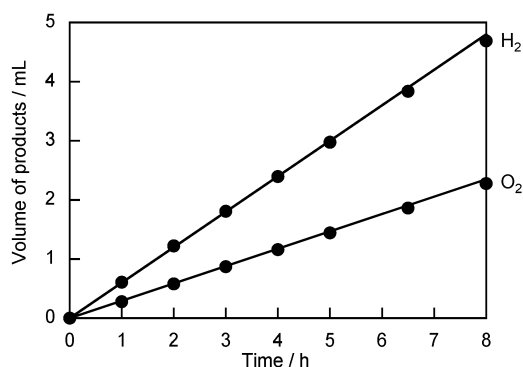


Fig. 10 Solar hydrogen production from water using a  $(Ru/SrTiO_3:Rh)-(BiVO_4)-FeCl_3$  photocatalyst system. Catalyst: 50 mg each solution: 120 mL; light source: AM-1.5 ( $100 \text{ mW cm}^{-2}$ ); irradiated area:  $33 \text{ cm}^2$ .



## CONCLUDING REMARKS

The target for efficiency of water splitting into H<sub>2</sub> and O<sub>2</sub> can be said to be 30 % in terms of quantum yield at 600 nm in this research field. This means that we have to develop highly active photocatalysts with a 2-eV band gap. At the present stage, although the NiO/NaTaO<sub>3</sub>:La photocatalyst shows a high quantum yield, it responds to only UV light. The wavelength is far from the target. The sulfide solid solution photocatalysts AgInS<sub>2</sub>-CuInS<sub>2</sub>-ZnS show relatively high active for solar hydrogen production in the presence of electron donors, but not for overall water splitting. The new powdered photocatalyst systems, Ru/SrTiO<sub>3</sub>:Rh-BiVO<sub>4</sub>, respond to 520 nm for overall water splitting and solar hydrogen production from water. The respondent wavelength is somewhat close to the target. However, the quantum yield is still low compared with the target. We still have to continue the research and make further breakthroughs for solar hydrogen production from water. It will be also important to construct the operating system for photocatalytic hydrogen production, as well as the development of photocatalyst materials. The achievement will lead to an ultimate green-sustainable chemistry.

## ACKNOWLEDGMENTS

This work was supported by the Core Research for Evolutional Science and Technology (CREST) program of the Japan Science and Technology (JST) Agency, and a Grant-in-Aid (no. 14050090) for Priority Area Research (no. 417) from the Ministry of Education, Culture, Science, and Technology. The author thanks Dr. Kato, Dr. Tsuji, Ms. Omori, and Ms. Konta for their experiments, and Prof. Kobayashi (Kyoto Institute of Technology) and Dr. Shimodaira for DFT calculations.

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