

Photocatalyst materials for water splitting

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Abstract

photocatalytic

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Introduction

The importance of hydrogen energy has recently been recognized again, especially by the spread of a fuel cell from the viewpoint of an environmental issue. However, hydrogen is industrially produced by steam reforming of hydrocarbons such as methane. Dihydrogen has to be produced from water using a natural energy if one thinks of the environmental issue. Therefore, water splitting using a photocatalyst is a challenging reaction because it is one of the ultimate reactions to solve energy and environmental issues. Water splitting using photocatalysts is not a new theme. Water splitting has been studied in the research fields of catalysis, electrochemistry, photochemistry, organic and inorganic chemistry, etc. for about 30 years since the Honda–Fujishima effect was reported using a TiO₂ semiconductor electrode [1].

1- Basis of photocatalytic reactions

Many heterogeneous Photocatalyst have semiconducting properties because photocatalytic reactions proceed. Semiconductors have the band structure in which the conduction band is separated from the valence band by a band gap with a suitable width. When light of which the energy is larger than the band gap is irradiated, electrons and holes are generated in the conduction and valence bands, 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 a width of the band gap and potentials of the conduction and valence bands. The bottom level of the conduction band has to be more negative than the redox potential of H⁺/H₂ (0V vs. NHE), while the top level of the valence band be more positive than the redox potential of O₂/H₂O (1.23V). Therefore, the band gap should be larger than 1.23eV.

2- General view of photocatalyst materials for water splitting

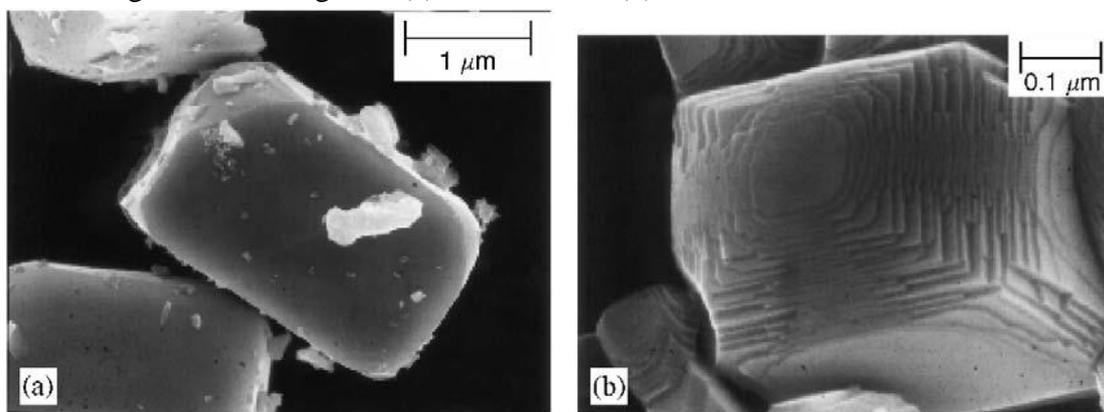
SrTiO₃ with the perovskite structure has also been used as a photocatalyst. Domen and co-workers have reported that NiO-loaded SrTiO₃ powder can decompose pure water into H₂ and O₂.10) The treatment by H₂ reduction and subsequent O₂

oxidation is indispensable for activation of the NiO/SrTiO₃ photocatalyst. The NiO co-catalyst for H₂ evolution is particularly characteristic because it does not cause the back reaction between H₂ and O₂, being different from Pt. The excellent NiO co-catalyst has often been employed also for other photocatalysts for water splitting. Besides the titanate photocatalysts, ZrO₂(12) and NiO/Ta₂O₅(13) have been reported to show high activities.

3- Tantalate photocatalysts for water splitting [8–11]

Most of reported photocatalysts for water splitting had been titanates [12]. So, it is important to develop new types of photocatalyst materials. On the other hand, it has been reported that some oxides with structural regularities such as layered and tunneling structures are active [3,4]. Then, new photocatalyst materials, except for titanates, These materials were synthesized by solid-state reactions or a flux method. These tantalate photocatalysts are active even without co-catalysts. Moreover, loading a NiO co-catalyst which works as a H₂ evolution site drastically improves the photocatalytic activity. LiTaO₃ was most active among the naked alkali and alkaline earth tantalates. Among tantalates loaded with a NiO co-catalyst, NiO/NaTaO₃ was most active. Therefore, the authors tried to improve the activity by some modifications.

- Fig. 1. SEM images of (a) NaTaO₃ and (b) NaTaO₃: La.

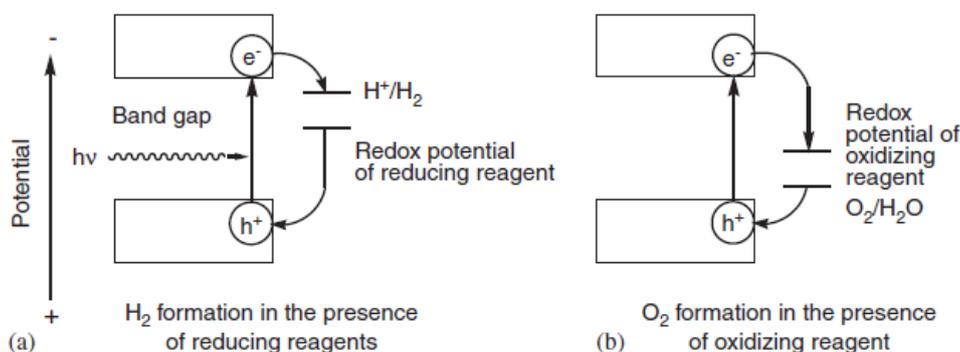


4- Visible light driven photocatalysts working under visible light irradiation for H₂ or O₂ evolution

Water splitting into H₂ and O₂ in stoichiometric amounts is a tough reaction because of an uphill reaction. Sacrificial reagents are often used as half reactions of the water splitting in order to evaluate photocatalytic abilities. The role of sacrificial reagents in photocatalytic reactions is shown in Fig. 2. When the photocatalytic reaction is carried out in aqueous solutions including easily oxidizable reducing reagents such as alcohol, S²⁻, and SO₃²⁻, photogenerated holes irreversibly oxidize the reducing reagents instead of water. It makes the electrons in the photocatalyst rich and a H₂ evolution reaction is enhanced. On the other hand, in the presence of electron acceptors such as Ag⁺ and Fe³⁺, the photogenerated electrons in the conduction band are consumed by them and an O₂ evolution reaction is enhanced. These reactions using sacrificial reagents are regarded as half reactions and often employed for test

reactions of photocatalytic H₂ or O₂ evolution. However, one should know that the results do not guarantee a photocatalyst to be active for overall water splitting into H₂ and O₂ in the absence of sacrificial reagents. Photocatalytic reactions mentioned below were carried out in the presence of sacrificial reagents.

- Fig. 2. Scheme of photocatalytic H₂ or O₂ evolution in the presence of sacrificial reagents.



4.1. Metal sulfide photocatalysts working under visible light irradiation for H₂ evolution from aqueous solutions containing sacrificial reagents [17]

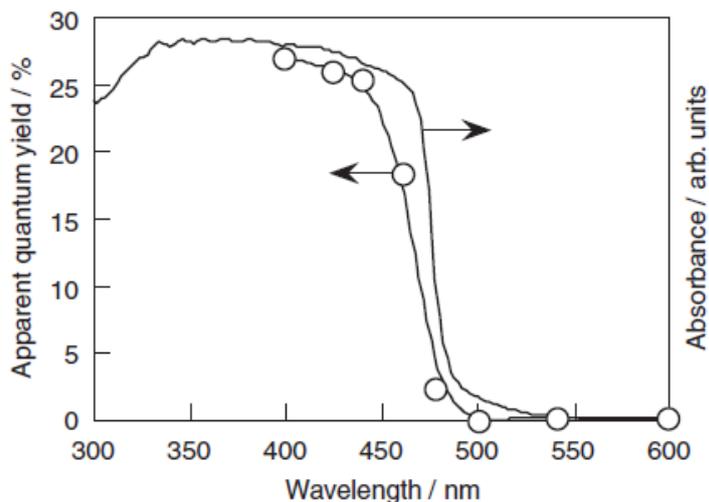
Although metal sulfides usually have a problem of photocorrosion, they are attractive as photocatalysts with visible light response. The representative photocatalyst is CdS which is active for H₂ evolution under visible light irradiation. The photocorrosion is considerably suppressed in the presence of sacrificial reagents.

On our surveying metal sulfides, AgGaS₂ and AgInZnXSX₂ showed activities for photocatalytic H₂ evolution from aqueous solution containing sacrificial reagents of Na₂S and K₂SO₃ under visible light irradiation without Pt co-catalysts.

Calcoplylite-type material AgGaS₂ with a 2.6 eV band gaps showed the photocatalytic activity for H₂ evolution from an aqueous Na₂S and K₂SO₃ solution under visible light irradiation. Loading noble metal co-catalysts to the AgGaS₂ dramatically improved the photocatalytic activity. The onset of the action spectrum agreed with that of the diffuse reflection spectrum indicating that the H₂ evolution proceeded with the band gap excitation as shown in Fig. 3. The Rh (1 wt%)-loaded AgGaS₂ photocatalyst gave ca. 25% of the quantum yield at 440 nm. The electronic band structure study using a plane-wave-based density functional method revealed that the valence band consisted of a hybrid orbital of S 3p and Ag 4d, and the conduction band is composed of a hybrid orbital of S 3p + Ga 4s4p.

AgInZnXSX₂ of Wurtzite-type solid solutions between ZnS and AgInS₂ showed activities for photocatalytic H₂ evolution from aqueous solutions containing sacrificial reagents of K₂SO₃ under visible light irradiation without Pt co-catalysts [17].

Fig. 3. Diffuse reflection and action spectra of Rh/AgGaS₂ photocatalyst. Catalyst: 0.3 g, an aqueous sulfite and sulfide solution: Na₂S (0.1 mol dm⁻³) and K₂SO₃ (0.5 mol dm⁻³), 150 ml, light source: 300W Xe lamp with band-pass filter and cut-off filter.



The diffuse reflectance spectra of the $\text{AgInZnXSX}+2$ solid solution photocatalysts successively shifted with the change in the composition X ($X = 2.10$) as shown in Fig. 4. The band gaps of the catalysts estimated from the onsets of the visible light absorption bands were 2–2.4 eV ($X = 2.10$). The photocatalytic H_2 evolution depended on the composition as shown in Fig. 5.

Pt-loaded AgInZn7S9 (2.3 eV) showed the highest activity for the H_2 evolution. The rate of H_2 evolution was 944 mol/h and the quantum yield at 420 nm was 20%. Scanning electron microscope observation revealed that the $\text{AgInZnXSX}+2$ solid solution photocatalyst possessed the surface nano-step structure and a Pt co-catalyst was selectively photodeposited on the edge of the step structure. This unique surface nano-structure seems to contribute to the high photocatalytic ability.

Fig. 4. Diffuse reflectance spectra of $(\text{AgIn})\text{XZn}_2(1-X)\text{S}_2$ photocatalysts.

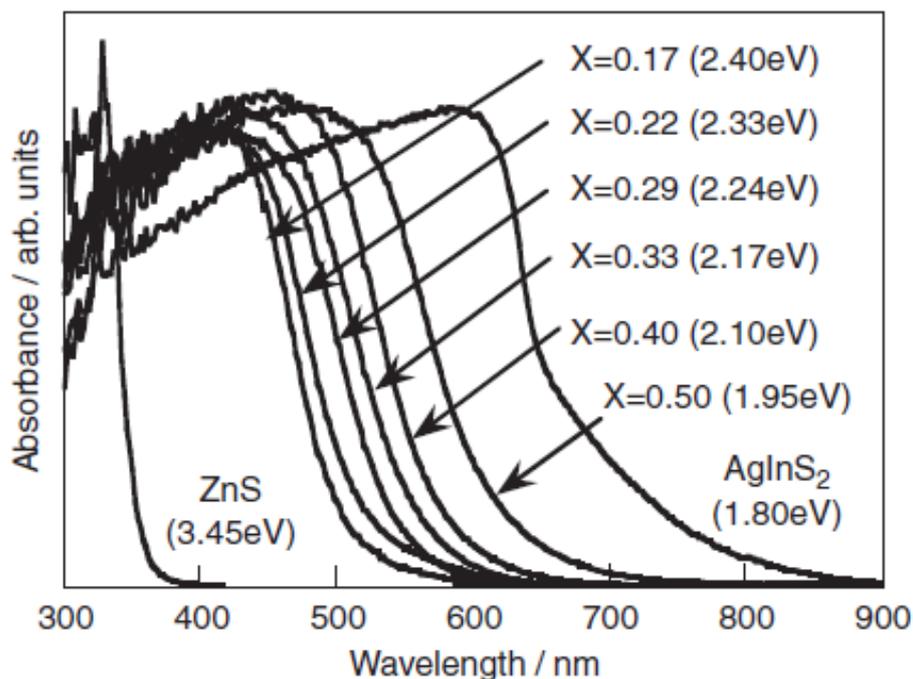
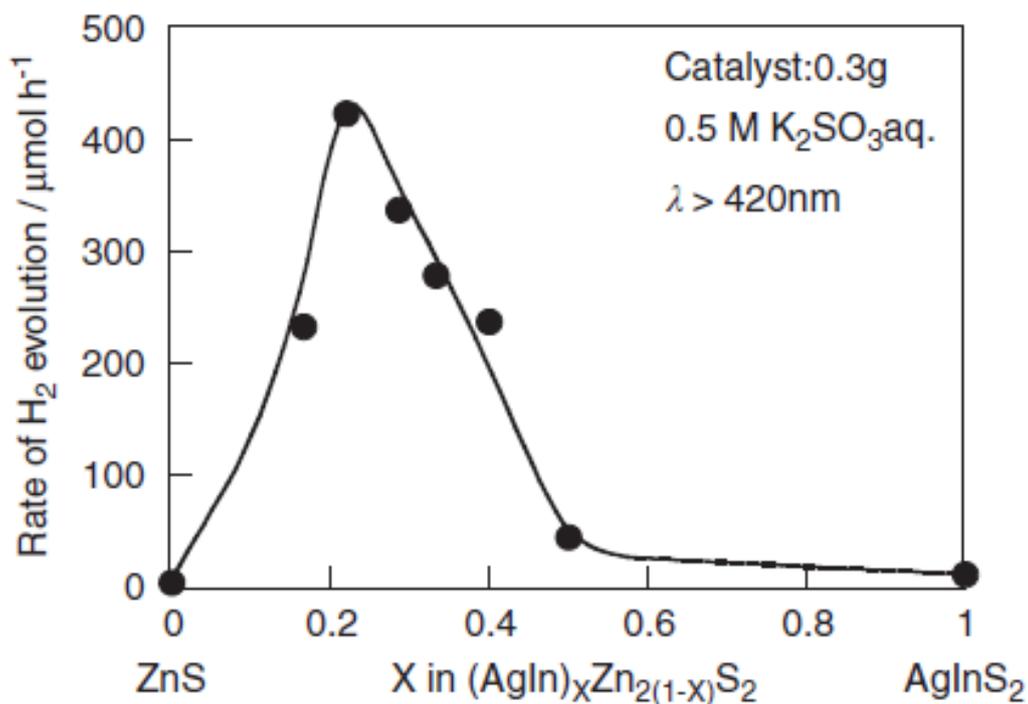


Fig. 5. Dependence of photocatalytic activities for H₂ evolution from an aqueous K₂SO₃ solution over Pt(3wt%)/(AgIn)_XZn_{2(1-X)}S₂ solid solutions upon the value of X.



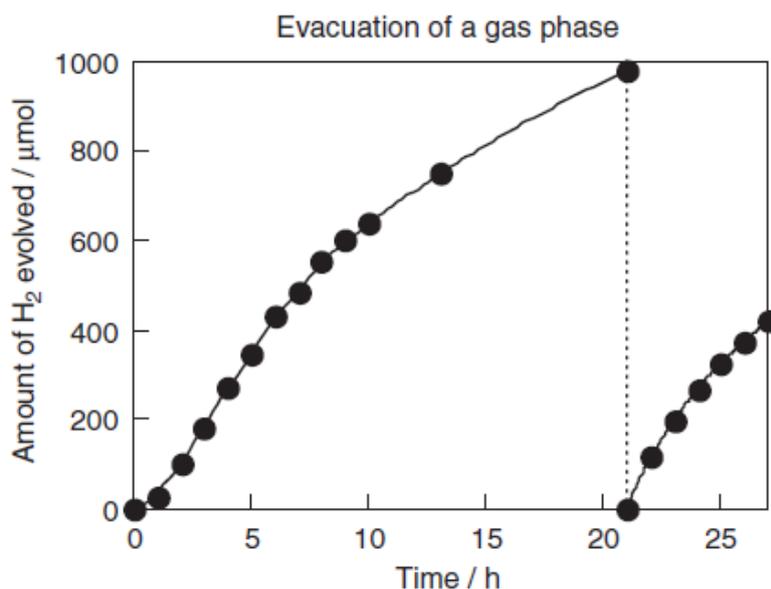
4.2. Metal oxide photocatalysts working under visible light irradiation for H₂ evolution from aqueous solutions containing sacrificial reagents [18]

The creation of visible light response by doping some transition metal ions into photocatalysts working under ultraviolet irradiation has been studied for a long time.

The base photocatalyst was mainly TiO₂ [19]. The doping of transition metal ions with partially filled d-orbitals colors TiO₂ photocatalysts. However, in most of the cases, the dopant worked as a recombination center between photogenerated electrons and holes resulting in the drastic decrease in the photocatalytic activity even under the ultraviolet irradiation.

The author's group has paid attention to SrTiO₃ as a host photocatalyst besides TiO₂. Rh-doped SrTiO₃ possessed an intense absorption band in the visible light. The Rh-doped SrTiO₃ loaded with Pt co-catalysts produced H₂ from an aqueous methanol solution under visible light irradiation as shown in Fig. 6 [18]. The Rh (1%)-doped SrTiO₃ photocatalyst loaded with a Pt co-catalyst (0.1 wt%) gave 5.2% of the quantum yield at 420 nm for the H₂ evolution reaction. The visible light response was due to the transition from the electron donor level formed by the Rh ions to the conduction band composed of Ti3d orbitals of SrTiO₃.

Fig. 6. H₂ evolution from an aqueous methanol (10 vol%) solution under visible light irradiation (wavelength > 440 nm) over a Pt(0.1wt%)/SrTiO₃: Rh(1%) photocatalyst. Catalyst: 0.3 g, reactant solution: 150 ml, light source: 300W Xe lamp with cut-off filters (L42 + Y44).

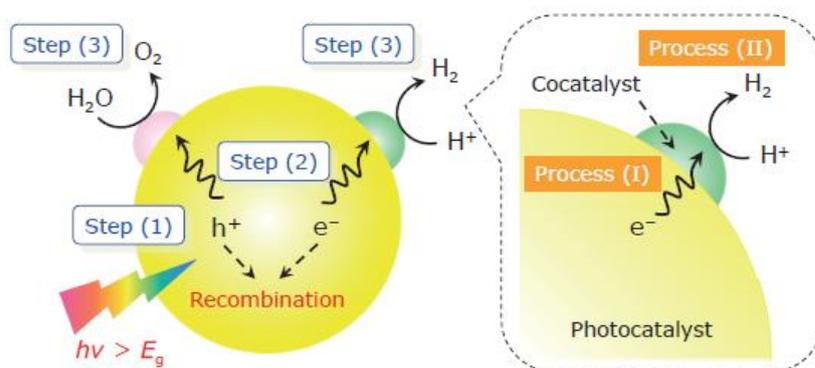


5- Factors Affecting Photocatalytic Activity.

As shown in Figure 2, overall water splitting on a semiconductor photocatalyst, typically with the size of several hundreds of nanometers to several micrometers, occurs in three steps: (1) the photocatalyst absorbs light energy greater than the band-gap energy of the material, generating photoexcited electron-hole pairs in the bulk material, (2) the photogenerated carriers separate and move to the surface without recombination, and (3) adsorbed species undergo reduction and oxidation by reaction with the photogenerated electrons and holes to produce H₂ and O₂, respectively. The first two steps depend strongly on the structural and electronic properties of the semiconductor photocatalyst. High crystallinity in general has a positive impact on activity, because the density of defects, which serve as recombination centers between

photogenerated electrons and holes, decreases with increasing crystallinity. One can also enhance photocatalytic activity by reducing the particle size of a photocatalyst, because the diffusion length for photogenerated electron-hole pairs can be shortened. On the other hand, the third step is promoted by a cocatalyst loaded on the photocatalyst surface. The cocatalyst is typically a noble metal (e.g., Pt, Rh) or transition metal oxide (e.g., NiOx, RuO₂) and is loaded onto the photocatalyst surface as a dispersion of nanoparticles (typically <50 nm in size) to produce active sites and reduce the activation energy for gas evolution.[14,15] In most cases, cocatalysts are loaded for the promotion of H₂ evolution, presumably because most photocatalysts are unable to activate hydrogen on the surface. As illustrated in Figure 2, the loaded cocatalysts extract photogenerated electrons from the photocatalyst (process I) and host active sites for gas evolution (process II). Therefore, the overall efficiency of a given photocatalytic system is dependent on the loaded cocatalyst. In particular, the structural characteristics and intrinsic catalytic properties of a cocatalyst for H₂ (or O₂) evolution are important. For example, Pt is well known as an excellent reduction catalyst of protons to form H₂ molecules. However, a photocatalyst modified with a Pt cocatalyst does not always show the highest activity among analogues loaded with other metals (e.g., Ru and Rh). This suggests that the contribution of process (I) to the overall efficiency can be more important than that of process (II). For example, Ru-loaded TaON was reported to give a much higher activity for H₂ evolution from aqueous methanol solution than a Pt-loaded one.[16] Because no report has yielded a systematic understanding of which process, I or II, is more important in a specific case, one must consider both processes when designing an efficient photocatalytic system. It is thus important to design both the bulk and surface properties of the material carefully so as to obtain a high activity for photocatalytic overall water splitting.

Figure 2. Processes involved in photocatalytic overall water splitting on a semiconductor particle. A schematic illustration of electron transfer from a photocatalyst to the loaded cocatalyst (Process I) and H₂ evolution (Process II) in the reaction is also shown.



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