Photocatalysis

# Visible-Light-Induced $H_2$ Evolution from an Aqueous Solution Containing Sulfide and Sulfite over a ZnS–$CuInS_2$–$AgInS_2$ Solid-Solution Photocatalyst**

*Issei Tsuji, Hideki Kato, and Akihiko Kudo**

The photocatalytic splitting of water to generate $H_2$ and $O_2$ has attracted attention as a clean energy system. An important feature of this system is that it does not require complicated devices: the photocatalysts are simply placed in water, irradiated with sunlight, and then hydrogen is produced by a photocatalytic reaction. This water-splitting reaction does not depend on fossil fuels, and is therefore an ideal method to produce clean hydrogen fuel. The reaction is also attractive from the viewpoint of achieving an artificial

---

[*] I. Tsuji, H. Kato, Prof. A. Kudo
Department of Applied Chemistry
Faculty of Science
Tokyo University of Science
1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601 (Japan)
Fax: (+81) 33235-2214
E-mail: a-kudo@rs.kagu.tus.ac.jp
Prof. A. Kudo
Core Research for Evolutional Science and Technology
Japan Science and Technology Agency (CREST, JST)
4-1-8 Honcho, Kawaguchi-shi, Saitama 332-001 (Japan)

[**] This work was supported by Core Research for Evolutional Science and Technology (CREST), a Grant-in-Aid for the Priority Area Research (No. 417) from the Ministry of Education, Culture, Science, and Technology, and the Tokyo Ohka Foundation for the Promotion of Science and Technology.

DOI: 10.1002/ange.200500314

photosynthesis, which converts light into chemical energy. Many active photocatalysts for splitting water under UV irradiation have been reported. In particular, the NiO-loaded $NaTaO_3$:La photocatalyst showed extremely high activity, and the quantum yield amounted to 56% at 270 nm.[1] However, photocatalysts with wide band gaps (3 eV or above) do not absorb visible light, which is a large part of the solar spectrum. It is indispensable to develop highly active photocatalysts with a visible-light response.

A Pt-loaded CdS photocatalyst showed high activity for the evolution of hydrogen from aqueous solutions containing $S^{2-}$ and $SO_3^{2-}$ ions as sacrificial electron donors, under visible-light irradiation, even though most sulfide photocatalysts are unstable during the water-splitting reaction.[2–4] The sacrificial reagents make up half of the water-splitting reaction and they are routinely used as a test to make sure that the photocatalytic materials can reduce $H_2O$ to $H_2$. Sacrificial electron donors that irreversibly consume photogenerated holes may promote hydrogen evolution. If the reaction could be turned into a practical application for the production of hydrogen gas from by-products such as hydrogen sulfide and sulfur dioxide, which are emitted in hydrogenation and flue-gas desulfurization processes at chemical plants, it would be especially interesting in light of current energy and environmental concerns.[5,6]

Photocatalysts driven by visible light that show high activity for hydrogen evolution, with the exception of the Pt-loaded CdS photocatalyst, have not been investigated until recently. We have succeeded in developing several photocatalysts that are driven by visible light by doping transition-metal ions such as $Ni^{2+}$ and $Cu^{2+}$, as well as $Pb^{2+}$ into ZnS, which is a highly active photocatalyst for hydrogen evolution under UV/Vis irradiation, even without the presence of a Pt co-catalyst.[7–11] Specifically, Ni- and Cu-doped ZnS photocatalysts showed a high activity for hydrogen evolution without the presence of any co-catalysts, and their apparent quantum yields were 1.3 and 3.7%, respectively, at 420 nm. We also developed solid-solution photocatalysts between ZnS (wide band gap) and $MInS_2$ (M = Cu, Ag; narrow band gap). The energy structures of the solid solutions were controllable by the change in their compositions. At 420 nm, the apparent quantum yields of Pt-loaded $(AgIn)_{0.22}Zn_{1.56}S_2$ (band gap 2.3 eV) and Pt-loaded $(CuIn)_{0.09}Zn_{1.82}S_2$ (band gap 2.3 eV) amounted to 20% and 13%, respectively.[12,13]

We have recently found that the $ZnS–CuInS_2–AgInS_2$ solid solution was a highly active photocatalyst that exhibited an absorption band over a wider wavelength range than $ZnS–AgInS_2$ and $ZnS–CuInS_2$ solid solutions. Herein, we report the evolution of hydrogen over a Ru-loaded $ZnS–CuInS_2–AgInS_2$ solid solution photocatalyst under visible-light irradiation. We also demonstrate hydrogen production under solar-light irradiation (air mass (AM) = 1.5).

Figure 1 shows X-ray diffraction patterns of the previously reported solid solution photocatalysts $(CuIn)_{0.09}Zn_{1.82}S_2$ (**1**) and $(AgIn)_{0.22}Zn_{1.56}S_2$ (**2**) and the solid solution $(CuAg)_{0.15}In_{0.3}Zn_{1.4}S_2$ (**3**). The crystal structure of the solid solution **1** between ZnS and $CuInS_2$ was a zinc-blende, low-temperature phase of ZnS (Figure 1 a). The solid solution **2** between ZnS and $AgInS_2$ exhibited the wurtzite structure of a high-temperature phase of ZnS (Figure 1 b). For **3**, which can be regarded as a solid solution of three sulfides ($ZnS–AgInS_2–CuInS_2$), diffraction patterns similar to those of both zinc-blende and wurtzite were obtained. The main peaks indicated the presence of zinc blende along with a negligible amount of unidentified impurities. The diffraction peaks of (111) and (222) planes were relatively intensive, thus indicating an anisotropic shape of the powder.

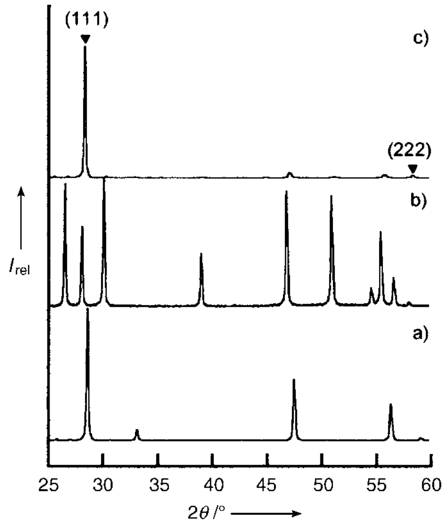

***Figure 1.*** X-ray diffraction patterns (XRD) of the solid solution **1** (a), **2** (b), and **3** (c).

Figure 2 shows SEM images of the solid solution **3**. The small particles were about 200 nm in size (Figure 2 a), and the average particle size of the solid solution was relatively small compared with those of the solid-solution photocatalysts **1** and **2** (several micrometers). Some of these small particles were platelike. Extremely large Plate-shaped particles, such as that shown in Figure 2 b, were also observed in relatively large numbers. Therefore, we suggest that the anisotropy in

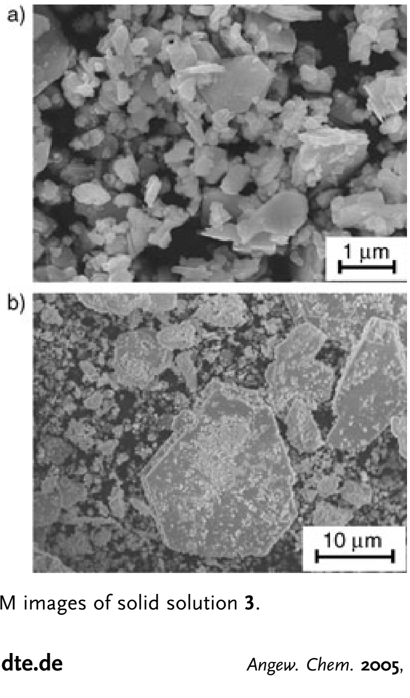

***Figure 2.*** SEM images of solid solution **3**.

the XRD pattern is due to the presence of such particles. The surface area of the solid solution was 3.3 $m^2 g^{-1}$.

Figure 3 shows diffuse reflection spectra of the solid solutions and ZnS. The ZnS photocatalyst with a wide band gap (3.5 eV) had an UV absorption band. Unlike ZnS, the solid solutions of ZnS and $MInS_2$ (M = Cu, Ag) had visible-light absorption bands; those bands with steep edges were due to band-gap transitions. The solid solutions **1** and **2** were able to use visible light up to 500 nm and thus the estimated band-gap energies are 2.4 eV. The absorption edge of the solid solution **3** was at a longer wavelength than those of other solid solutions. The color of the powder of **3** was dark orange. Taking into account the efficient use of visible light in a large part of the solar spectrum, we believe that this solid solution, with its long wavelength absorption band, is an attractive photocatalyst for hydrogen evolution.

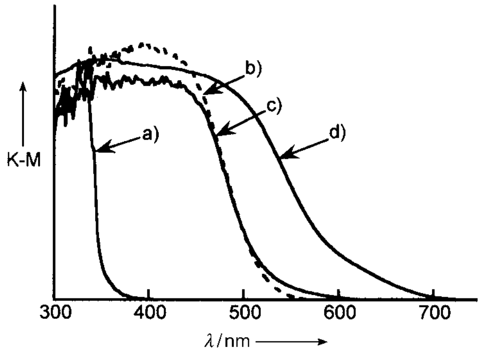

***Figure 3.*** Diffuse reflection spectra of ZnS (a) and the solid solutions **1** (b), **2** (c), and **3** (d). K–M = diffuse reflection spectra converted into absorbance by the Kubelka–Munk method (arbitrary units).

When a Ru co-catalyst was loaded, the solid solution **3** effected hydrogen evolution under visible-light irradiation. The rate of hydrogen evolution was extremely high (2.3 $mmol\,h^{-1}$) under irradiation from a 300-W Xe lamp with a 420 nm cut-off filter. The optimized photocatalytic activities of the solid solutions **1** and **2** were 0.94 $mmol\,h^{-1}$ and 1.16 $mmol\,h^{-1}$, respectively. The solid solution **3** produced hydrogen more efficiently than the solid solutions **1** and **2**. Vigorous evolution of hydrogen bubbles was observed over the photocatalyst particles irradiated with visible light.

Figure 4 shows $H_2$ evolution under simulated sunlight irradiation (AM 1.5) from an aqueous solution containing the sacrificial reagents $SO_3^{2-}$ and $S^{2-}$ over a Ru-loaded $(CuAg)_{0.15}In_{0.3}Zn_{1.4}S_2$ (**3**) solid-solution photocatalyst. Even under these conditions, the photocatalyst produced hydrogen gas efficiently. The initial rate of hydrogen evolution was 8.2 $L\,m^{-2}h^{-1}$, which was estimated from the irradiated area (33 $cm^2$). Although a slight deactivation was observed during the photocatalytic reaction, the activity remained comparatively stable over 20 h when the reaction solution was replaced periodically with fresh solution. As there were no significant changes in the XRD patterns of the catalyst before and after the reaction, we conclude that the slight deactivation was due to a change in the surface state and/or poisoning by products. The solid solution showed higher activity than the well-known Pt-loaded CdS photocatalyst with wurtzite structure under the same reaction conditions (Figure 4). Its activity was also higher than that of the previously reported Pt-loaded $(AgIn)_{0.22}Zn_{1.56}S_2$ (**2**) solid solution photocatalyst (3.3 $L\,m^{-2}h^{-1}$).[12]

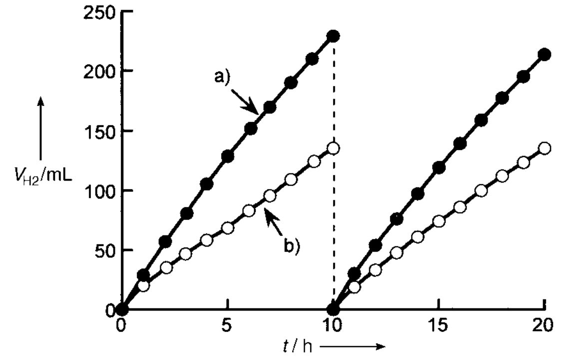

***Figure 4.*** Photocatalytic $H_2$ evolution from an aqueous $K_2SO_3$ (0.25 $mol\,L^{-1}$) $Na_2S$ (0.35 $mol\,L^{-1}$) solution (150 mL) under simulated sunlight irradiation over solid solution photocatalyst **3** loaded with 0.75 wt% Ru (a) and the Pt-black-loaded (2 wt%) CdS photocatalyst (b). Catalyst: 0.3 g; solar simulator: 300-W Xe short arc lamp with an AM-1.5 filter; reaction cell: top-window pyrex cell; irradiated area: 33 $cm^2$.

Figure 5 shows an action spectrum for hydrogen evolution from an aqueous solution containing $K_2SO_3$ and $Na_2S$ over a Ru-loaded $(CuAg)_{0.15}In_{0.3}Zn_{1.4}S_2$ (**3**) photocatalyst. The onset of the action spectrum "hydrogen evolution" agreed approximately with onset of the diffuse reflection spectrum. It was revealed that the visible-light response for hydrogen evolution was due to a band-gap transition between the valence and conduction bands; this band gap and thus the transition could be altered by making a solid solution. The visible-light response might be derived from the contribution of Cu 3d, Ag 4d, and S 3p orbitals to the valence band and that of In 5s5p and Zn 4s4p orbitals to the conduction band, respectively, as

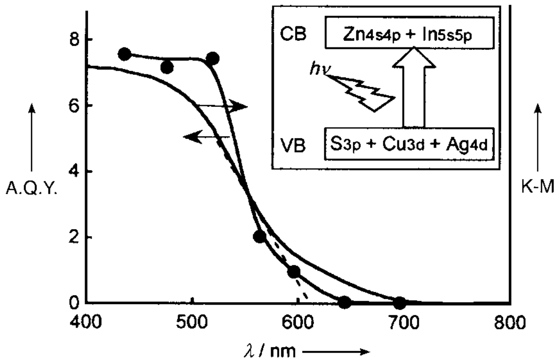

***Figure 5.*** Action spectrum of $H_2$ evolution from an aqueous $K_2SO_3$ (0.25 $mol\,L^{-1}$) $Na_2S$ (0.35 $mol\,L^{-1}$) solution (150 mL) over the solid solution **3** loaded with 0.75 wt% Ru. Catalyst: 0.3 g; light source: 300-W Xe lamp with cut-off and band-pass filters; reaction cell: top-window Pyrex cell. A.Q.Y. = apparent quantum yield. K–M = diffuse reflection spectra converted into absorbance by the Kubelka–Munk method (arbitrary units).

in the cases of the ZnS–$AgInS_2$ and ZnS–$CuInS_2$ solid solutions. Hydrogen did not evolve through absorption of light in the region around 650–700 nm. This result indicates that a visible-light absorption band, which might be due to impurities and defects, was not responsible for the photocatalytic reaction. The comparatively high average quantum yield of 7.4 % was obtained under monochromatic irradiation at 440, 480, and 520 nm.

In summary, we report that a ZnS–$CuInS_2$–$AgInS_2$ solid solution **3** is a highly active photocatalyst for the evolution of hydrogen under visible-light irradiation from an aqueous solution containing sulfide and sulfite. The activity of the solid solution that contained Cu and Ag atoms was higher than that of the previously reported ZnS–$MInS_2$ (M = Cu or Ag) solid solutions **1** and **2**. Although the quantum yield of the ZnS–$CuInS_2$–$AgInS_2$ solid solution was lower than that of the ZnS–$MInS_2$ (M = Cu or Ag) solid-solution photocatalysts, the former had higher activity when irradiated from a solar simulator. A sulfide photocatalyst that is able to produce hydrogen efficiently, even under solar-light irradiation would be an attractive functional material. Although it has not yet reached the level that it has a practical use, if quantum yields and activities can be further improved, this series of solid solutions could be used in photocatalytic hydrogen production.

## Experimental Section

**3**: An aqueous solution of $Zn(NO_3)_2 \cdot 6H_2O$ (Wako Pure Chemicals; 99.0 %), $AgNO_3$ (Tanaka Kikinzoku; 99.8 %), and $In(NO_3)_3 \cdot 3.6H_2O$ (Kojundo Chemical; 99.9 %) was purged with $N_2$ gas. An excess ($\approx$10 %) of $In(NO_3)_3$, was added to the solution, followed by CuCl, freshly prepared by reduction of $CuCl_2 \cdot 2H_2O$ (Wako Pure Chemicals; 99.0 %) with metallic Cu. Purging the reaction mixture with $H_2S$ gas resulted in a grayish brown precipitate. The mixture was stirred for 15 h, washed with deionized water, and dried in air. The obtained powder was sealed in a quartz ampoule together with a small quantity of sulfur (about 1 wt %). The sealed ampoule was evacuated and heated over the course of 20 h to 600 °C and held at this temperature for 2 h. The phase of the product was confirmed by X-ray diffraction (Rigaku; MiniFlex). Surface areas were determined by BET (Brunauer–Emmett–Teller) measurement (Coulter; SA3100). Diffuse reflection spectra were obtained with a UV/Vis/NIR spectrometer (Jasco; Ubest U-570) and were converted from reflection to absorbance by the Kubelka–Munk method. Photocatalyst powders were observed by scanning electron microscopy (JEOL: JSM-6700F).

Photocatalytic reactions were conducted in a gas-closed circulation system. The photocatalyst powder (0.3 g) was dispersed by a magnetic stirrer in an aqueous solution (150 mL) containing $K_2SO_3$ and $Na_2S$ as electron donors in a pyrex cell with a window on the top. The mixture was irradiated with visible light ($\lambda \geq 420$ nm) through a cut-off filter (HOYA; L42) from a 300-W Xe lamp (ILC technology; CERMAX LX-300). Ru co-catalyst was loaded by a photodeposition method in situ. An appropriate amount of $(NH_4)_2RuCl_6$ (Wako Pure Chemicals) was dissolved in an aqueous $K_2SO_3$ solution, the photocatalyst powder was added and the aqueous solution was irradiated under visible light for 20–30 min; subsequently, $Na_2S$ was added into the solution. The optimum amount of the co-catalyst was about 0.7 wt %. Hydrogen production was measured by using on-line gas chromatography (Shimadzu; GC-8A, MS-5 A column, TCD, Ar carrier). The apparent quantum yields defined by Equation (1) were measured by using combined band-pass (Kenko) and cut-off (HOYA) filters, and a photodiode (OPHIRA: PD300-UV head and NOVA power monitor).

$$\begin{aligned}\text{A.Q.Y. [\%]} &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \\ &= \frac{\text{number of evolved } H_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100\end{aligned} \quad (1)$$

A solar simulator (YAMASHITA DENSO; YSS-80QA) was also used to test the photocatalytic reaction (AM 1.5). In this case, the amount of hydrogen gas evolved was determined by a volumetric measurement.

Received: January 27, 2005

**Keywords:** green chemistry · heterogeneous catalysis · hydrogen · photocatalysis

[1] H. Kato, K. Asakura, A. Kudo, *J. Am. Chem. Soc.* **2003**, *125*, 3082–3089.
[2] A. W.-H. Mau, C. B. Huang, N. Kakuta, A. J. Bard, *J. Am. Chem. Soc.* **1984**, *106*, 6537.
[3] M. Matsumura, S. Furukawa, Y. Saho, H. Tsubomura, *Phys. Chem.* **1985**, *89*, 1327.
[4] J. F. Reber, M. Rusek, *Phys. Chem.* **1986**, *90*, 824.
[5] S. C. March, L. Borrell, J. Gimenez, R. Simarro, J. M. Andujar, *Int. J. Hydrogen Energy* **1992**, *17*, 683.
[6] C. A. Linkous, T. E. Mingo, N. Z. Muradov, *Int. J. Hydrogen Energy* **1993**, *18*, 203.
[7] J. F. Reber, K. Meier, *J. Phys. Chem.* **1984**, *88*, 5903.
[8] H. Kisch, J. Bucheler, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2378.
[9] A. Kudo, M. Sekizawa, *Catal. Lett.* **1999**, *58*, 241.
[10] A. Kudo, M. Sekizawa, *Chem. Commun.* **2000**, 1371.
[11] I. Tsuji, A. Kudo, *J. Photochem. Photobiol. A* **2003**, *156*, 249.
[12] I. Tsuji, H. Kato, H. Kobayashi, A. Kudo, *J. Am. Chem. Soc.* **2004**, *126*, 13406.
[13] I. Tsuji, H. Kato, H. Kobayashi, A. Kudo, *J. Phys. Chem. B*, **2005**, *109*, 7323.