Z-Schematic Water Splitting into H 2 and O 2 Using Metal Sulfide as a Hydrogen-Evolving Photocatalyst and Reduced Graphene Oxide as a Solid-State Electron Mediator

5 AUTHORS, INCLUDING:

Yun Hau Ng
University of New South Wales
75 PUBLICATIONS 2,093 CITATIONS

Rose Amal
University of New South Wales
333 PUBLICATIONS 9,687 CITATIONS

Z-Schematic Water Splitting into H₂ and O₂ Using Metal Sulfide as a Hydrogen-Evolving Photocatalyst and Reduced Graphene Oxide as a Solid-State Electron Mediator

Katsuya Iwashina,[†] Akihide Iwase,[†,‡] Yun Hau Ng,[§] Rose Amal,[§] and Akihiko Kudo*[†,‡]

[†]Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

[‡]Photocatalysis International Research Center, Research Institute for Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda-shi, Chiba-ken 278-8510, Japan

[§]ARC Centre of Excellence for Functional Nanomaterials, School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

S *Supporting Information*

ABSTRACT: Z-schematic water splitting was successfully demonstrated using metal sulfide photocatalysts that were usually unsuitable for water splitting as single particulate photocatalysts due to photocorrosion. When metal sulfide photocatalysts with a p-type semiconductor character as a H₂-evolving photocatalyst were combined with reduced graphene oxide-TiO₂ composite as an O₂-evolving photocatalyst, water splitting into H₂ and O₂ in a stoichiometric amount proceeded. In this system, photogenerated electrons in the TiO₂ with an n-type semiconductor character transferred to the metal sulfide through a reduced graphene oxide to achieve water splitting. Moreover, this system was active for solar water splitting.

Solar water splitting using photocatalysts has been paid attention as a potential system for clean hydrogen production.[1] To utilize sunlight efficiently, development of visible-light-responsive photocatalysts is indispensable. Many metal sulfides respond to visible light because the band gaps of metal sulfides are generally narrower than those of corresponding metal oxides due to shallower valence bands formed by S 3p orbitals than those formed by O 2p orbitals. Metal sulfide photocatalysts show high activity for H₂ evolution from an aqueous solution containing sulfur compounds of sacrificial reagents under visible light irradiation.[2] In the absence of the sacrificial reagents, however, photogenerated holes oxidize the metal sulfide itself rather than water resulting in no O₂ evolution and photocorrosion. Thus, the metal sulfide photocatalysts cannot split water into H₂ and O₂ as a single particulate photocatalyst. Therefore, we are interested in construction of a photocatalyst system using the metal sulfides for water splitting.

Z-scheme photocatalyst is one of the systems for water splitting under visible light irradiation. Photocatalysts that are active for sacrificial H₂ and O₂ evolution can be used to construct the Z-scheme system. Z-schematic water splitting proceeds accompanied by an electron transfer from an O₂-evolving photocatalyst to a H₂-evolving photocatalyst. Ionic electron mediators such as IO_3^-/I^-, $Fe^{3+/2+}$, and $Co(bpy)_3^{3+/2+}$

are generally used for Z-scheme systems.[3] These ionic electron mediators efficiently transfer electrons by adsorption onto the surfaces of photocatalysts. However, usable photocatalysts are limited because suitable adsorbing and desorbing properties of ionic electron mediators on photocatalysts are required and backward reactions by ionic electron mediators may proceed. For example, when a metal sulfide photocatalyst is combined with an iron ion electron mediator, the iron ions are deposited on the surface of the metal sulfide as iron sulfides. Our group reported that reduced graphene oxide (RGO) of a conductive solid-state material promotes electron transfer between photocatalyst particles in a Z-scheme system for water splitting.[4] In the system with RGO, adsorbing and desorbing properties required for the systems employing ionic electron mediators can be neglected because electrons migrate by interparticle electron transfer. Therefore, it is expected that RGO can be used to construct Z-scheme systems consisting of various photocatalysts including metal sulfides. This potential property of RGO motivates us to utilize metal sulfide photocatalysts with highly efficient H₂ evolution ability as a H₂-evolving photocatalyst in a Z-scheme system for water splitting.

In the present study, Z-scheme systems consisting of various metal sulfides as a H₂-evolving photocatalyst and RGO-TiO₂ (rutile) composite as an O₂-evolving photocatalyst were constructed. Factors dominating the activity for photocatalytic water splitting were investigated. The effects of cocatalysts and the loading method on the Z-schematic water splitting were also studied.

Table 1 shows photocatalytic activities for Z-schematic water splitting using various metal sulfides as a H₂-evolving photocatalyst and RGO-TiO₂ composite as an O₂-evolving photocatalyst. Only H₂ evolved due to photocorrosion, when ZnS, AgGaS₂, AgInS₂, Ag₂ZnGeS₂, and Ag₂ZnSnS₂ were employed as a H₂-evolving photocatalyst (entries 1−5 in Table 1). In contrast, H₂ and O₂ evolved in a stoichiometric amount, when CuGaS₂, CuInS₂, Cu₂ZnGeS₂, and Cu₂ZnSnS₂ were employed as a H₂-evolving photocatalyst (entries 6−11 in Table 1). All of the metal sulfides working as a H₂-evolving

Table 1. Overall Water Splitting Using Z-Scheme Photocatalyst Systems Consisting of Various Metal Sulfide Photocatalysts of a H_2-Evolving Photocatalyst and RGO-TiO_2 (Rutile) Composite of an O_2-Evolving Photocatalyst[a]

entry	H_2-photocatalyst (metal sulfide photocatalyst)	amount of Pt loaded (wt %)	loading method	initial activity (μmol h^{-1}) H_2	O_2
1	ZnS	0.3	photodeposition	0.8	0
2	AgGaS$_2$	0.3	photodeposition	12.5	0
3	AgInS$_2$	0.3	photodeposition	0.3	0
4	Ag$_2$ZnGeS$_4$	0.3	photodeposition	6.1	0
5	Ag$_2$ZnSnS$_4$	0.3	photodeposition	0.4	0
6	CuGaS$_2$	0.3[b]	photodeposition	19.8	10.3
7	CuGaS$_2$	0.3[b]	impregnation + H_2 red[c]	7.7	3.3
8	CuGaS$_2$	0.1[b]	adsorption	56.2	25.0
9	CuInS$_2$	0.3	photodeposition	9.9	4.5
10	Cu$_2$ZnGeS$_4$	0.3	photodeposition	17.4	7.8
11	Cu$_2$ZnSnS$_4$	0.3	photodeposition	6.3	2.9

[a]Conditions: 0.05 g each; water without pH adjustment (120 mL); 300 W Xe lamp full-arc; top-irradiation cell with a Pyrex window. [b]Determined by ICP. [c]Heat-treated at 473 K for 1 h in H_2.

photocatalyst in the Z-scheme system in Table 1 are known as a p-type semiconductor.[5] Photoelectrochemical properties of the metal sulfide photocatalyst materials used in Table 1 were measured to investigate the relationship between the semiconductor character and Z-schematic water splitting activity as shown in Figure 1A. The metal sulfides working as a H_2-evolving photocatalyst in the Z-scheme system gave cathodic photocurrents. TiO_2 of a well-known n-type semiconductor gave an anodic photocurrent. Photoelectrochemical cells for water splitting can be constructed by a combination of a p-type photocathode with an n-type photoanode as shown in Figure 1B. It is indispensable for water splitting without an external bias that the potential at which the cathodic photocurrent overlaps with the anodic photocurrent exists. Onset potentials of cathodic photocurrent over the metal sulfides working as a H_2-evolving photocatalyst in the Z-scheme system possessed more positive than that of anodic photocurrent over TiO_2. This indicates that photogenerated electrons in TiO_2 with n-type semiconductor character transferred to metal sulfides with p-type semiconductor character through RGO as shown in Figure 1C being similar to Figure 1B. Electron transfers between semiconductors and RGO have previously been observed.[4,6] When the metal sulfides with n- or i-type semiconductor properties were used in the system of entries 1−5 in Table 1, water splitting did not proceed.

In order to clarify that the water splitting proceeds by Z-schematic electron transfer, the control experiments were carried out using the Pt-loaded CuGaS$_2$ and RGO-TiO$_2$ composite system showing the highest activity for water splitting as shown in Table 2. Without RGO, the photocatalytic activity was low, and H_2 and O_2 did not evolve in a stoichiometric amount (entry 2 in Table 2), indicating that RGO was necessary for smooth electron transfer from O_2- to H_2-evolving photocatalysts. Water splitting did not proceed using either Pt-loaded CuGaS$_2$ or RGO-TiO$_2$ composite (entries 4 and 5 in Table 2). These results indicate that a combination of Pt-loaded CuGaS$_2$ with RGO-TiO$_2$ composite was indispensable for the Z-schematic water splitting.
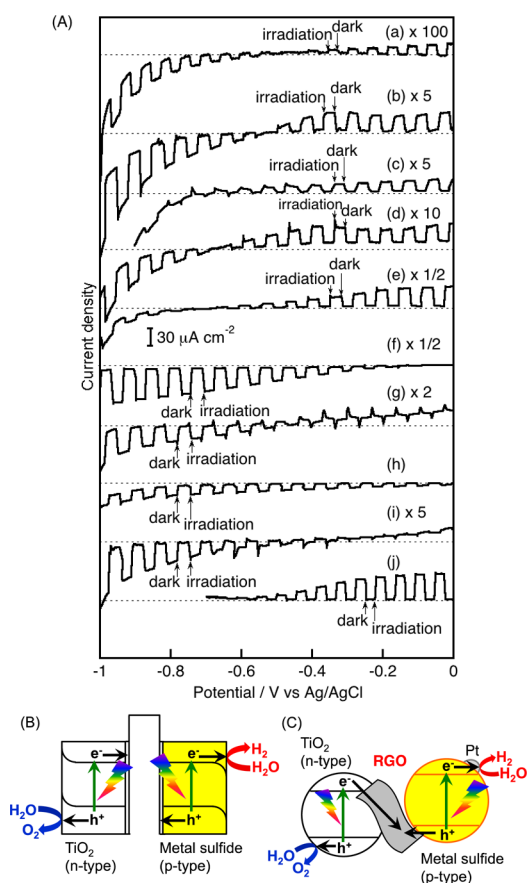

Figure 1. (A) Current vs potential curves of (a) ZnS, (b) AgGaS$_2$, (c) AgInS$_2$, (d) Ag$_2$ZnGeS$_4$, (e) Ag$_2$ZnSnS$_4$, (f) CuGaS$_2$, (g) CuInS$_2$, (h) Cu$_2$ZnGeS$_4$, (i) Cu$_2$ZnSnS$_4$, and (j) TiO$_2$ photoelectrodes: (a,j) λ > 300 nm and (b−i) λ > 420 nm. Electrolyte, (0.1 mol L^{-1} K$_2$SO$_4$ aq.) + (0.05 mol L^{-1} KH$_2$PO$_4$ aq.) + (0.05 mol L^{-1} NaH$_2$PO$_4$ aq.); sweep rate, 20 mV s^{-1}; sweep direction, −1 → 0 V vs Ag/AgCl; light source, 300 W Xe lamp. Dashed line represents 0 A for each electrode. (B) Photoelectrochemical system consisting of a metal sulfide photocatalyst electrode with a p-type semiconductor character and TiO$_2$ photoelectrode for water splitting with applying no bias. (C) Z-scheme system consisting of a Pt-loaded metal sulfide photocatalyst with a p-type semiconductor character and RGO-TiO$_2$ composite photocatalyst for water splitting.

Table 2. Z-Schematic Water Splitting Using Pt-Loaded CuGaS$_2$ and RGO-TiO$_2$ Composite Photocatalysts[a]

entry	H_2-photocatalyst	O_2-photocatalyst	initial activity (μmol h^{-1}) H_2	O_2
1	Pt/CuGaS$_2$	RGO-TiO$_2$	19.8	10.3
2	Pt/CuGaS$_2$	TiO$_2$	1.4	0.3
3	CuGaS$_2$	RGO-TiO$_2$	6.9	0.8
4	Pt/CuGaS$_2$	none	0.2	0
5	none	RGO-TiO$_2$	trace	0

[a]Conditions: 0.05 g each; water without pH adjustment (120 mL); 300 W Xe lamp full-arc; top-irradiation cell with a Pyrex window.

A cocatalyst plays an important role in enhancement of a photocatalytic reaction.[7] When nonloaded CuGaS$_2$ was combined with RGO-TiO$_2$ composite, H_2 and O_2 did not evolve in stoichiometric amounts (entry 3 in Table 2) suggesting that the H_2 evolution was mainly due to photocorrosion. Therefore, various metal cocatalysts were loaded on
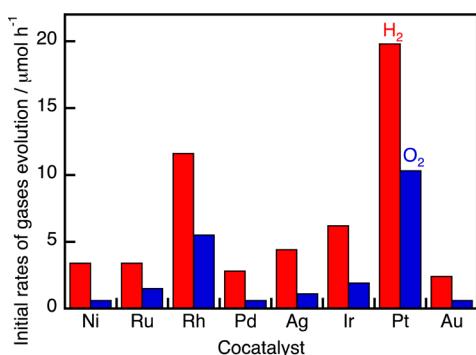
Figure 2. Z-schematic water splitting using $CuGaS_2$ with various metal cocatalysts (0.3 wt %) and RGO-TiO_2 composite. Conditions: 0.05 g each; water without pH adjustment (120 mL); 300 W Xe lamp full-arc; top-irradiation cell with a Pyrex window.

Figure 3. Z-schematic water splitting using $CuGaS_2$ with adsorbed Pt and RGO-TiO_2 composite under (A) 300 W Xe lamp full-arc and (B) simulated sunlight (100 mW cm^{-2} adjusted with an AM-1.5 filter) irradiation. Conditions: 0.05 g of Pt(0.1 wt %)-loaded $CuGaS_2$ and (A) 0.05 g and (B) 0.1 g of RGO-TiO_2 composite; water without pH adjustment (120 mL); top-irradiation cell with a Pyrex window; irradiated area, 33 cm^2.

the $CuGaS_2$ powder as shown in Figure 2. Water splitting proceeded in a stoichiometric amount, when Pt, Ru, and Rh were employed as a cocatalyst. Pt was the most effective cocatalyst. In contrast, Ni, Pd, Ag, Ir, and Au did not function as a cocatalyst.

Loading effects of the cocatalyst affect its size, degree of dispersion, and chemical states.[8] Therefore, the effects of the loading method for a Pt cocatalyst on the photocatalytic activity were examined as shown in Table 1. The order of photocatalytic activity was adsorption > photodeposition > impregnation + H_2 red method. XPS revealed that Pt cocatalysts were loaded as PtS_x by photodeposition and adsorption methods, and as metallic Pt by an impregnation + H_2 red method (Figure S1). The PtS_x worked more effectively than the metallic Pt in the present Z-scheme employing metal sulfide photocatalysts. The Pt particles loaded on $CuGaS_2$ were observed by SEM. Pt particles with 20−50 nm of the size were observed for the photodeposition and impregnation + H_2 red methods, while no Pt particles were observed for the adsorption method (Figure S2). However, ICP-AES measurement revealed that 0.1 wt % of Pt was loaded on $CuGaS_2$ by the adsorption method, while 0.3 wt % of Pt was loaded by the photodeposition and impregnation + H_2 red methods. Moreover, XPS also indicated the presence of Pt particles loaded by adsorption (Figure S1). These results indicate that the adsorbed Pt should be fine particles. The fine Pt particles on $CuGaS_2$ photocatalyst would function as an efficient reduction site to produce H_2.

The Z-scheme photocatalyst system consisting of $CuGaS_2$ with adsorbed Pt and RGO-TiO_2 composite continuously split water into H_2 and O_2 for 12 h as shown in Figure 3A, giving 1.3% of the apparent quantum yield under 380 nm of a monochromatic light irradiation. The rates of gases evolution became slower with the irradiation time probably due to the hydrolysis of $CuGaS_2$, exfoliation of RGO, and a certain degree of photocorrosion. The hydrolysis and photocorrosion of $CuGaS_2$ were confirmed by XPS (Figure S3). After water splitting, the Ga 3d peak at 19.3 eV corresponding to the Ga in Ga_2S_3 drastically decreased accompanied by the increase in the peak at 20.8 eV corresponding to the Ga in Ga_2O_3 (Figure S3A). The S 2p peaks at 164.2 and 165.6 eV corresponding to the elemental S formed by photocorrosion also increased after water splitting (Figure S3B). Moreover, the hydrolysis and photocorrosion of $CuGaS_2$ happened at only the surface judging from no significant difference in XRD pattern between before and after water splitting. The exfoliation of RGO has
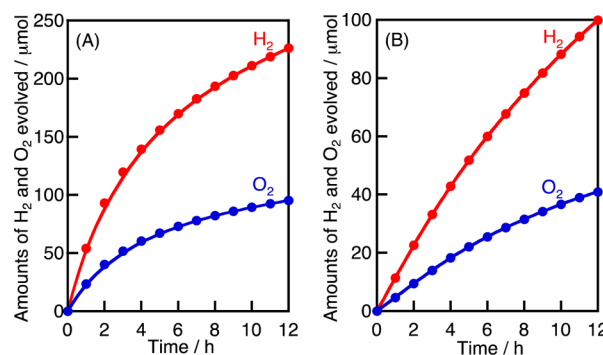
been reported by the careful observation of the reactant solution after water splitting.[4] Black-colored stuff was actually floated on the reactant solution only after water splitting in the present system. However, the turnover numbers of reacted electrons to carbon atoms in RGO (assumed to contain pristine graphitic carbon), to S atoms on the surface of $CuGaS_2$, and to the molar amount of $CuGaS_2$ were 2.2, 477, and 1.8 at 12 h, respectively. These turnover numbers larger than the unity indicate that this Z-schematic water splitting photocatalytically proceeded. The present Z-scheme system consisting of $CuGaS_2$ with adsorbed Pt and RGO-TiO_2 composite split water even under simulated sunlight irradiation as shown in Figure 3B. Solar energy conversion efficiency of this Z-scheme system at the initial stage was determined to be 0.023%. Thus, Z-schematic water splitting employing metal sulfides as a H_2-evolving photocatalyst was successfully achieved under simulated sunlight.

We have successfully demonstrated Z-schematic water splitting using various metal sulfides as a H_2-evolving photocatalyst and RGO-TiO_2 composite as an O_2-evolving photocatalyst. The key factor lies in the combination of p-type and n-type semiconductor photocatalysts. In the present Z-scheme, fine Pt particles loaded by an adsorption method was effective as the H_2 evolution site. The present results provide new and significant knowledge to construct efficient solar water splitting systems employing various metal sulfides with high activities for H_2 evolution.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, XPS spectra, SEM images, and XRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*a-kudo@rs.kagu.tus.ac.jp

Notes

The authors declare no competing financial interest.

■ **ACKNOWLEDGMENTS**

■ **REFERENCES**

(1) (a) Kudo, A.; Kato, H.; Tsuji, I. *Chem. Lett.* **2004**, *33*, 1534. (b) Osterloh, E. F. *Chem. Mater.* **2008**, *20*, 35−54. (c) Kudo, A.; Miseki, Y. *Chem. Soc. Rev.* **2009**, *38*, 253−278. (d) Chen, X.; Shen, S.; Guo, L.; Mao, S. S. *Chem. Rev.* **2010**, *110*, 6503.

(2) (a) Mau, A. W.-H.; Huang, C.-B.; Kakuta, N.; Bard, A. J.; Campion, A.; Fox, M. A.; White, J. M.; Webber, S. E. *J. Am. Chem. Soc.* **1984**, *106*, 6537. (b) Kudo, A.; Sekizawa, M. *Catal. Lett.* **1999**, *58*, 241. (c) Lei, Z.; You, W.; Liu, M.; Zhou, G.; Takata, T.; Hara, M.; Domen, K.; Li, C. *Chem. Commun.* **2003**, *17*, 2142. (d) Tsuji, I.; Kato, H.; Kobayashi, H.; Kudo, A. *J. Am. Chem. Soc.* **2004**, *126*, 13406. (e) Tsuji, I.; Kato, H.; Kobayashi, H.; Kudo, A. *J. Phys. Chem. B* **2005**, *109*, 7323. (f) Tsuji, I.; Kato, H.; Kudo, A. *Chem. Mater.* **2006**, *18*, 1969. (g) Kudo, A. *Int. J. Hydrogen Energy* **2006**, *31*, 197. (h) Yan, H.; Yang, J.; Ma, G.; Wu, G.; Zong, X.; Lei, Z.; Shi, J.; Li, C. *J. Catal.* **2009**, *266*, 165. (i) Tsuji, I.; Shimodaira, Y.; Kato, H.; Kobayashi, H.; Kudo, A. *Chem. Mater.* **2010**, *22*, 1402. (j) Kaga, H.; Saito, K.; Kudo, A. *Chem. Commun.* **2010**, *46*, 3779. (k) Zhang, K.; Guo, L. *Catal. Sci. Technol.* **2013**, *3*, 1672. (l) Kaga, H.; Kudo, A. *J. Catal.* **2014**, *310*, 31.

(3) (a) Abe, R.; Sayama, K.; Domen, K.; Arakawa, H. *Chem. Phys. Lett.* **2001**, *344*, 339. (b) Maeda, K.; Higashi, M.; Lu, D.; Abe, R.; Domen, K. *J. Am. Chem. Soc.* **2010**, *132*, 5858. (c) Kato, H.; Sasaki, Y.; Iwase, A.; Kudo, A. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 2457. (d) Sasaki, Y.; Kato, H.; Kudo, A. *J. Am. Chem. Soc.* **2013**, *135*, 5441.

(4) Iwase, A.; Ng, Y. H.; Ishiguro, Y.; Kudo, A.; Amal, R. *J. Am. Chem. Soc.* **2011**, *133*, 11054.

(5) (a) Tell, B.; Shay, J. J. *J. Appl. Phys.* **1972**, *43*, 2469. (b) Levcenco, S.; Dumcenco, D.; Huang, Y. S.; Tiong, K. K.; Du, C. H. *Opt. Mater.* **2011**, *34*, 183. (c) Ito, K.; Nakazawa, T. *Jpn. J. Appl. Phys.* **1988**, *27*, 2094.

(6) (a) Ng, Y. H.; Lightcap, I.; Goodwin, K.; Matsumura, M.; Kamat, P. V. *J. Phys. Chem. Lett.* **2010**, *1*, 2222. (b) Ng, Y. H.; Iwase, A.; Kudo, A.; Amal, R. *J. Phys. Chem. Lett.* **2010**, *1*, 2607.

(7) Maeda, K. *J. Photochem. Photobiol. C: Photochem. Rev.* **2011**, *12*, 237.

(8) Maeda, K.; Sakamoto, N.; Ikeda, Y.; Ohtsuka, H.; Xiong, A.; Ku, D.; Kanehara, M.; Teranishi, T.; Domen, K. *Chem.—Eur. J.* **2010**, *16*, 7750.