Photocatalytic Activity of RuS_2/SiO_2 for Water Decomposition

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Hydrogen and oxygen were produced, respectively, from water in the presence of sacrificial reagents by photocatalytic reaction using RuS_2 powder catalyst under UV light irradiation for the first time. Photocatalytic activity of RuS_2 significantly improved by support on SiO_2.

Sulfide semiconductors able to absorb visible light (e.g. CdS) are attractive in photoelectrochemically converting light energy into electrical or chemical energy. These compounds are generally unstable in an aqueous solution under light irradiation due to self-oxidation by photogenerated holes (photocorrosion). Ruthenium disulfide (RuS_2) is highly stable against photocorrosion and absorbs visible light well, suggesting potentially good efficiency in photoelectrochemical energy conversion.

Ezzaouia et al. reported that single-crystal RuS_2 electrodes with a band gap (Eg) of 1.85 eV and a flat band potential (E_{fb}) of –0.48 V vs. SHE were stable photoanodes in water oxidation in an aqueous electrolyte.[1] Ashokkumar et al. studied the photoelectrochemical behavior of TiO_2 electrodes coated with RuS_2 particles, concluding that the Eg of RuS_2 particles was 2.8 eV and the E_{fb} was –0.6 V vs. NHE.[2] On the other hand, photocatalytic reactions using powder RuS_2 catalyst have not been investigated so far. The Eg and the E_{fb} of RuS_2 and its high stability suggest the possibility of producing hydrogen and oxygen through the photocatalytic decomposition of water over a RuS_2 powder catalyst. This letter reports, for the first time, the photocatalytic activity of RuS_2 for water decomposition.

RuS_2 was prepared by mixing a 0.15 mM (1 M = mol dm^{-3}) acetonitrile solution of $RuCl_3$ and a 1.3 M Na_2S aqueous solution. The mixture was stirred continuously for 15 h at room temperature to form a RuS_2 black precipitate. Supported RuS_2 was prepared as follows: $RuCl_3$ was supported on SiO_2 (Davison #57) by the incipient wetness of the aqueous solution. $RuCl_3$ supported on SiO_2 was treated in a H_2S stream at 400°C for 4 h. The prepared RuS_2 and supported RuS_2 were analyzed using X-ray diffraction (XRD) and X-ray fluorescence (XRF). 0.2 wt% of Pt-promoted RuS_2 and RuS_2/SiO_2 were also prepared by in situ photoreductive decomposition of H_2PtCl_6 onto the RuS_2 catalyst in an aqueous suspension. With 0.4 g of the photocatalyst used for the reactions. Photocatalytic reactions were conducted in a closed gas circulation system connected to an inner-irradiation reactor (solution: 400 mL). A high-pressure Hg lamp (400 W) was used as the light source (pyrex glass filter: >300 nm irradiation). A $NaNO_2$ aq filter was used for reactions under visible light irradiation. Both 2.7 mmol of Na_2S and 5.5 mmol of Na_2SO_3 were added to the solution as sacrificial reagents to form hydrogen. To form oxygen, 3.8 mmol $AgNO_3$ was used as the electron acceptor. The resulting hydrogen and oxygen were quantitatively analyzed using a gas chromatograph.

XRD and XRF results for prepared catalysts suggested that RuS_2 was formed by the reaction of $RuCl_3$ with Na_2S or H_2S. Hydrogen was formed over RuS_2 catalysts under UV light irradiation (>300 nm) in the Na_2S/Na_2SO_3 aqueous solution, with photocatalytic activity depending markedly on the catalyst (Figure 1). In the 1 wt% RuS_2/SiO_2 catalyst (non-Pt loading catalyst), 213 μmol of hydrogen was produced in 46 h of light irradiation. Only 0.7 μmol of hydrogen was produced on a nonsupported RuS_2 catalyst in 23 h, however. These results suggest that small RuS_2 particles highly dispersed on a SiO_2 support show high photocatalytic activity for hydrogen formation. The hydrogen yield over a 1 wt% RuS_2/SiO_2 catalyst in 46 h, 213 μmol, reached approximately 9 times amount of RuS_2, 24 μmol, supported on SiO_2, suggesting that real catalytic hydrogen formation proceeded over a RuS_2 catalyst.

Metals and oxides loaded over semiconductor photocatalysts are known to markedly enhance hydrogen and oxygen formation.[3–7] Hydrogen formation was not enhanced with Pt loading in the RuS_2/SiO_2 photocatalyst system, however, which yielded 188 μmol of hydrogen in 46 h (Figure 1). It is found that the photocatalytic hydrogen formation can proceed over a RuS_2 catalyst without loaded Pt, suggesting the remarkable effect of RuS_2 as a hydrogen evolution catalyst having a low overpotential for hydrogen formation.

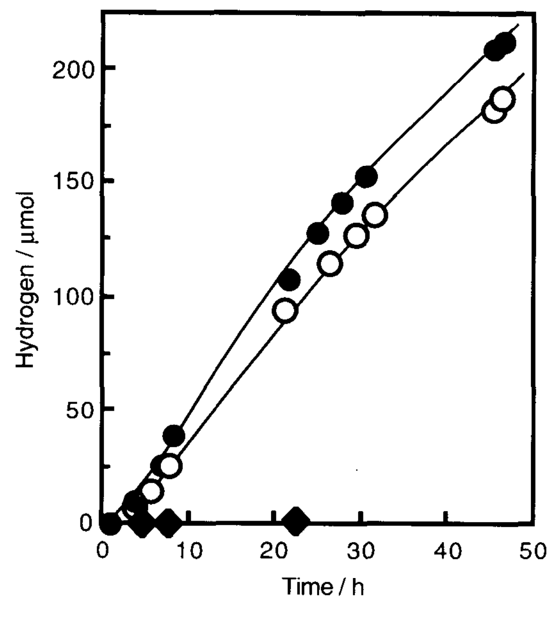

Figure 1. Hydrogen formation over RuS_2 catalysts under UV irradiation (>300 nm) in a Na_2S/Na_2SO_3 aqueous solution: (◆) RuS_2; (●) 1 wt% RuS_2/SiO_2; (○) 0.2 wt% Pt/1wt% RuS_2/SiO_2, photocatalyst 0.4 g.

Figure 2 shows oxygen evolution over RuS_2 photocatalysts under UV irradiation (>300 nm) in a $AgNO_3$ aqueous solution. No oxygen was formed over a nonsupported RuS_2 catalyst. Oxygen was, however, formed over 1 wt% RuS_2/SiO_2 and 0.2 wt% Pt/1 wt% RuS_2/SiO_2 catalysts, with the yields increasing with increasing irradiation time. Oxygen was not produced under irradiation in a SiO_2 suspension of a $AgNO_3$ solution. These results suggest that oxygen was produced over small RuS_2 particles supported on a SiO_2. Oxygen evolved, 121 μmol, in 25 h over a 1 wt% RuS_2/SiO_2 catalyst greatly exceeded the stoichiometric amount of supported RuS_2, 24 μmol. This suggests that oxygen is formed photocatalytically over a RuS_2/SiO_2 catalyst similarly to hydrogen. Dimitrijevic et al. reported that oxygen formed over Rh_2O_3/CdS photocatalysts under visible light irradiation.[8] CdS is unstable, however, in an aqueous solution under irradiation due to photocorrosion.

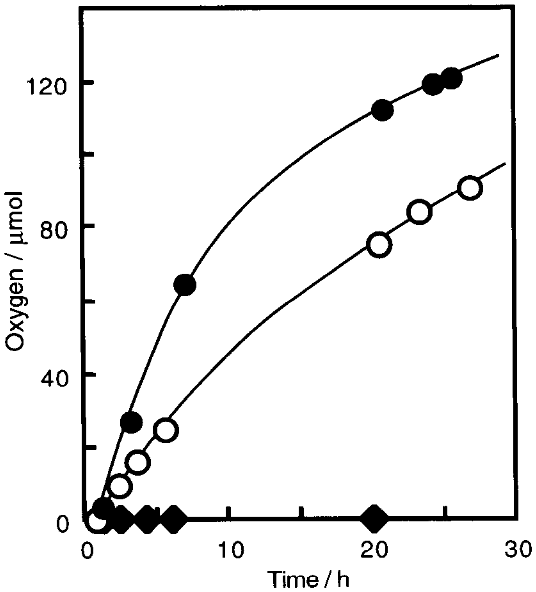

Figure 2. Oxygen formation over RuS_2 catalysts under UV light irradiation (>300 nm) in a $AgNO_3$ aqueous solution: (◆) RuS_2; (●) 1 wt% RuS_2/SiO_2; (○) 0.2 wt% Pt/1 wt% RuS_2/SiO_2, photocatalyst 0.4 g.

It is concluded that SiO_2-supported RuS_2 can potentially decompose water to hydrogen and oxygen, respectively. It was reported that the Eg of RuS_2 particles increased due to the size effect compared to that of single-crystal RuS_2.[2] The Eg of SiO_2-supported RuS_2 would be larger than that of nonsupported RuS_2 by the size effect, resulting in an increase of photocatalytic activity. The photocatalytic activity of a 1 wt% RuS_2/SiO_2 catalyst for hydrogen and oxygen formation under visible light irradiation (>400 nm) were quite low though it has an enough potential to decompose water theoretically. For example, the hydrogen yield was 1.3 μmol in 20 h. Low activity under visible light irradiation may be due to an increased Eg due to the size effect. At present, hydrogen and oxygen were not produced simultaneously in the absence of sacrificial reagents. Detailed studies of RuS_2 photocatalytic systems are now being studied.

References and Notes

1 H. Ezzaouia, R. Heindl, R. Parsons, and H. Tributsch, *J. Electroanal. Chem.*, **145**, 279 (1983).
2 M. Ashokkumar, A. Kudo, and T. Sakata, *Bull. Chem. Soc. Jpn.*, **68**, 2491 (1995).
3 J. M. Lehn, J. P. Sauvage, and R. Ziessle, *Nouv. J. Chim.*, **4**, 623 (1980).
4 K. Domen, S. Naito, T. Ohnishi, K. Tamaru, and M. Soma, *J. Phys. Chem.*, **86**, 3657 (1982).
5 A. Kudo, A. Tanaka, K. Domen, K. Maruya, K. Aika, and T. Ohnishi, *J. Catal.*, **111**, 67 (1988).
6 K. Sayama and H. Arakawa, *J. Photochem. Photobiol. A: Chem.*, **77**, 243 (1994).
7 T. Sakata, K. Hashimoto, and T. Kawai, *J. Phys. Chem.*, **88**, 5214 (1984).
8 N. M. Dimitrijevic, S. Li, and M. Grätzel, *J. Am. Chem. Soc.*, **106**, 6565 (1984).