

Electronic Supplementary Information (ESI)

A zinc-based oxysulfide photocatalyst SrZn₂S₂O capable of reducing and oxidizing water

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Experimental section

Preparation of photocatalysts

SrZn₂S₂O photocatalyst was synthesized using SrO, Zn (Rare Metallic, 99.9%), and S (Rare Metallic, 99.99%) in a stoichiometric ratio.^{S1} SrO was prepared by heating SrCO₃ (Rare Metallic, 99.9%) in an O₂ gas atmosphere at 1573 K overnight. The starting materials were thoroughly mixed in an agate mortar, pressed into a pellet, and heated in an evacuated silica tube at 1273 K for 24 h. A pure sample was obtained by sonicating the product prepared at 1273 K with water in which SrS is readily decomposed and the remaining SrZn₂S₂O was isolated by vacuum filtration. To avoid any additional effect on photocatalytic activity, the collected powders were used without further processing (such as sieving).

ZnS photocatalyst was synthesized by a coprecipitation method according to a previous report.^{S2} Zn(NO₃)₂ (20 mmol Kanto Chemical, >99.0%) and an excess amount of Na₂S·9H₂O (100 mmol, Kanto Chemical, 98–102%) were stirred in water (20 mL) for 17 h at room temperature. Obtained precipitation was heat at 773 K in N₂ gas flow. The Brunauer–Emmett–Teller (BET) specific surface area of the as-synthesized ZnS was determined to be 10 m² g⁻¹.

Cocatalyst-loaded samples were prepared by a previously reported impregnation method.^{S3} The photocatalyst powder was initially dispersed in an aqueous Na₂IrCl₆·6H₂O (Kanto Chemical, >97.0%) solution with stirring. This was followed by evaporation of the solvent and heating at 573 K for 1 h in air.

Characterization

The prepared photocatalysts were studied by powder X-ray diffraction (XRD; Rigaku, MiniFlex 600; Cu K α), UV-visible diffuse reflectance spectroscopy (DRS; JASCO, V-670), scanning electron microscopy (SEM; JSM-IT100LA, JEOL) with an energy dispersive X-ray spectroscopy (EDS) apparatus, transmission electron microscopy (TEM; JEOL, JEM-2010F) and X-ray photoelectron spectroscopy (XPS; Shimadzu, ESCA–3400). The binding energies were corrected with respect to the position of the C 1s peak (285.0 eV) for each sample. The BET surface area was measured using a BELSORP-mini (MicrotracBEL) at liquid nitrogen temperature (77 K).

Photocatalytic reactions

Photocatalytic hydrogen or oxygen evolution reaction was conducted at room temperature using a top-irradiation type cell that was connected to a closed gas circulation system made of glass. 50 mg of sample was dispersed in aqueous Na₂S (10 mM) + Na₂SO₃ (10 mM, FUJIFILM Wako Pure Chemical Co., \geq 95.0%) or AgNO₃ (10 mM, FUJIFILM Wako Pure Chemical, 99.8%) solution (140 mL). After outgassing the reactant solution by a vacuum pump, Ar gas (ca. 5 kPa) was introduced into the reaction system and the solution was irradiated under a 300 W Xe lamp (Cermax, PE300BF) with an output current of 20 A or a solar simulator (ASAHI SPECTRA, HAL–320). The evolved gases during the preparation process were analyzed by a gas chromatography (GL Sciences, GC–3200 with TCD detector; argon carrier gas). A blank test in the aqueous Na₂S–Na₂SO₃ solution without photocatalyst under UV irradiation ($\lambda > 300$ nm) indicated that a very small amount of H₂ (ca. 0.1 μ mol) was produced during 5 h irradiation. This value was negligibly small, as compared to the amount of produced H₂ shown in Fig. 4.

The apparent quantum yield (AQY) was calculated using the following equation:

$$\text{AQY}(\%) = (A \times R/I) \times 100$$

where A , R , and I represent coefficients (2 for H₂ evolution), the H₂ evolution rate, and the rate of incident photons, respectively. The total number of incident photons (6.22 mW) from a 300 W xenon lamp (Asahi Spectra, MAX–303) was measured using a power meter. The irradiation wavelength was controlled by a band-pass filter and water filter ($\lambda = 300$ nm).

Electrochemical impedance measurement

12.5 mg of the as-synthesized SrZn₂S₂O was mixed with 0.1 mL of water, 7.5 μ L of acetylacetone (FUJIFILM Wako Pure Chemicals Co., 99.0+%) and 0.05 mL of octylphenol

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ethoxylate (Aldrich Co., Triton X100) to make a viscous slurry. The mixture was spread onto a conducting glass support (Asahi glass, FTO, fluorine-doped tin oxide) by a squeegee method, and the electrode was heated at 723 K for 1 h in air. Impedance measurements were conducted using an electrochemical analyzer (BAS, ALS604E) in an aqueous phosphate buffered solution. The pH of the solution was adjusted to the desired value with NaOH (Kanto Chemical, $\geq 97.0\%$). The as-prepared SrZn₂S₂O/FTO electrode was employed as a working electrode, in combination with a Ag/AgCl reference electrode and a Pt wire counter electrode. Mott–Schottky plots were prepared at a frequency of 1 kHz.

Isotope tracer experiments

Isotope-labeling experiment for O₂ was performed using 10 mg of IrO₂(1.0 wt%)/SrZn₂S₂O in 1 mL of ¹⁸O-enriched H₂O (Cambridge Isotope Laboratories Inc, ¹⁸O 97%) containing 11 mM AgNO₃. After purging residual air in the test tube with He, irradiation was made using a 500 W Xe lamp for 24 h. Then, the gaseous product was taken using a syringe through a septum, and was analyzed by means of a GC–MS (Shimadzu, QP–2010–Ultra). Unlabeled water oxidation was conducted by the same procedure for comparison but with another GC (Agilent Technologies, 7890B) combined with a MS analyzer (JEOL, JMS700) at the Suzukakedai Materials Analysis Division, Technical Department, Tokyo Institute of Technology.

References

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- S2. S. Kohtani, Y. Ohama, Y. Ohno, I. Tsuji, A. Kudo and R. Nakagaki, *Chem. Lett.*, 2005, **34**, 1056–1057.
- S3. K. Maeda, R. Abe and K. Domen, *J. Phys. Chem. C*, 2011, **115**, 3057–3064.

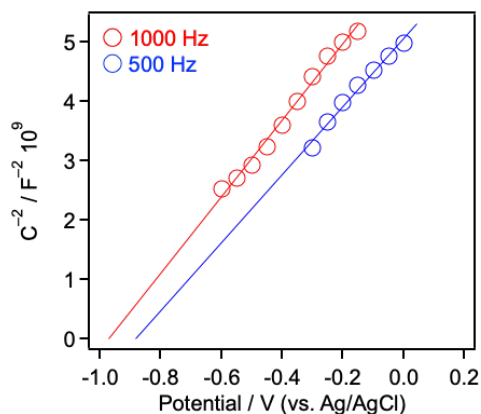


Fig. S1. Mott-Schottky plots of SrZn₂S₂O recorded at different frequencies in aqueous Na₂SO₄ solution (0.1 M, pH 9.0). The flat-band potential values, obtained by extrapolating the linear portion of the Mott-Schottky plots to the x axis intercept, were $-1.0 \sim -0.9$ V vs. Ag/AgCl.

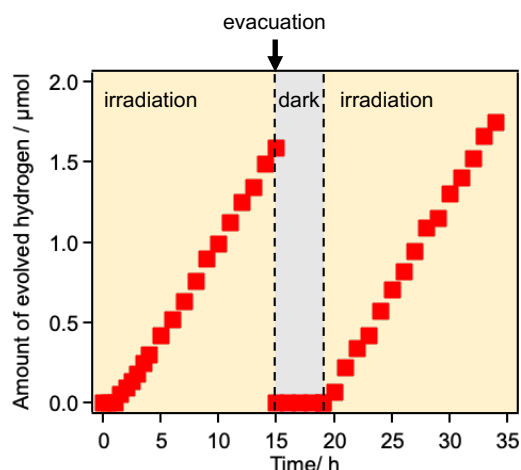


Fig. S2. Time course of H₂ evolution using Pt/SrZn₂S₂O (water-washed) in aqueous Na₂S and Na₂SO₃ mixed solution under simulated sunlight irradiation (AM1.5G, 100 mW cm⁻²). Reaction conditions: catalyst, 20 mg (0.1 wt% Pt photodeposition); reactant solution, aqueous Na₂S (10 mM) and Na₂SO₃ (10 mM), 20 mL. In this experiment, a smaller-capacity top irradiation-type reaction cell was used.

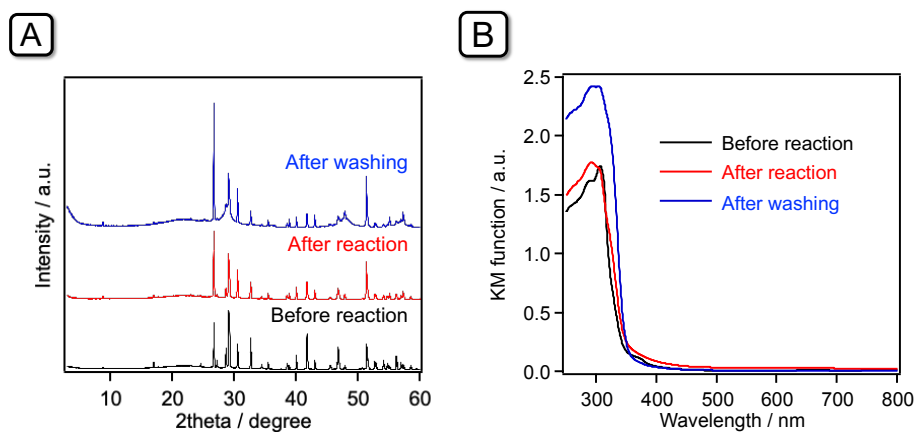


Fig. S3. (A) XRD patterns and (B) UV-visible DR spectra of SrZn₂S₂O before/after reaction and after water washing procedure.

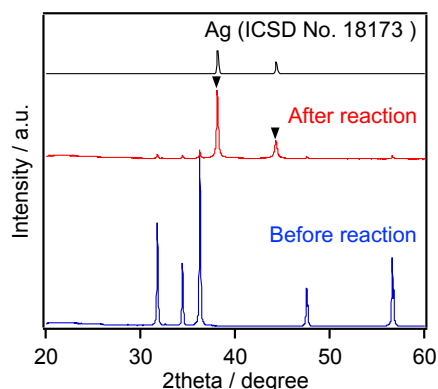


Fig. S4. XRD patterns of IrO₂/ZnO before and after reaction. Inverse triangle indicates peaks due to metallic Ag.

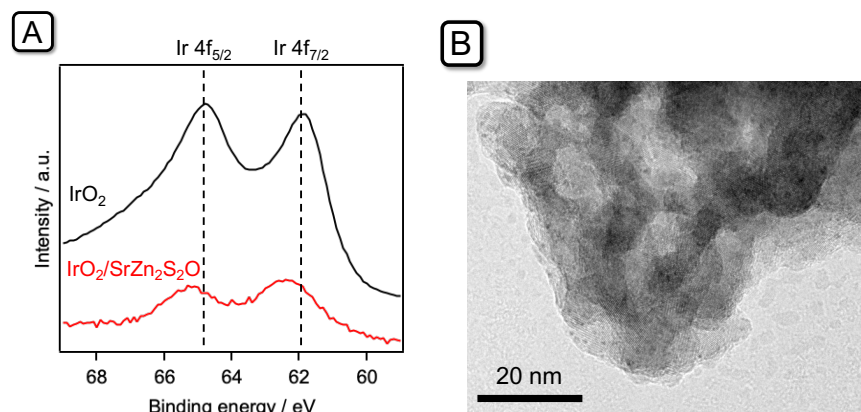


Fig. S5. Characterization of 1.0 wt% IrO₂-loaded SrZn₂S₂O (water-washed). (A) Ir 4f XPS spectrum and (B) TEM image. The Ir 4f XPS spectrum exhibits two major peaks at binding energies of 65.3 and 62.4 eV, which are close to the value of Ir 4f_{5/2} and 4f_{7/2} peaks in the IrO₂ reference spectrum [M. Rubel, R. Haasch, P. Mrozek, A. Wieckowski, C. De Pauli and S. Trasatti, *Vacuum*, 1994, **45**, 423–427]. IrO₂ particles in TEM images were readily distinguishable due to the contrast resulting from the different electron densities for Ir, Sr and Zn.

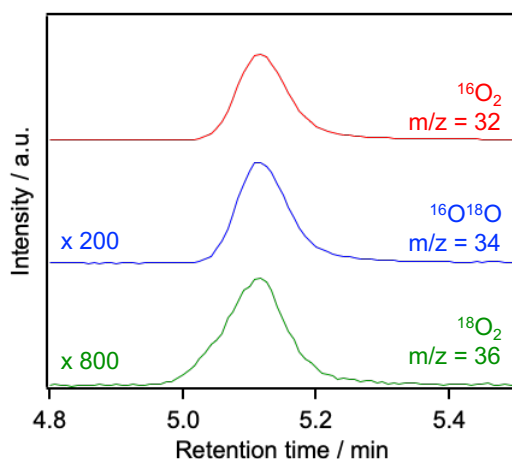


Fig. S6. Typical GC–MS chart of O₂ in gas phase during oxidation of H₂¹⁸O by IrO₂-loaded SrZn₂S₂O (water-washed). Reaction conditions: catalyst, 10 mg (1.0 wt% IrO₂ impregnation); reactant solution, aqueous AgNO₃ (10 mM), 1 mL; light source, high-pressure mercury lamp (400 W).

Table S1. Results of ¹⁸O-enriched water oxidation experiments using IrO₂-loaded SrZn₂S₂O (water-washed)^a

H ₂ O	³⁶ O ₂ / ³² O ₂ ratio in the products (×10 ⁻³)
Unlabeled	0.013 ^b
¹⁸ O-enriched	1.7
-	0.0040 ^c

^a Reaction conditions: the same as that in Fig. S6. ^b This should contain a certain contribution of ³⁶Ar existing in air, suggesting that some contamination of air during the sampling was inevitable. ^c Natural occurrence.