Modification of Oxysulfides with Two Nanoparticulate Cocatalysts to Achieve Enhanced Hydrogen Production from Water with Visible Light

Fuxiang Zhang, Kazuhiko Maeda, Tsuyoshi Takata, Kazunari Domen*
Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-Ku, Tokyo 113-8656, Japan; Tel.: +81-3-5481-1148; Fax: +81-3-5481-8838
E-mail: domen@chemsys.t.u-tokyo.ac.jp

1. Experimental Details

1.1. Preparation of photocatalysts

The synthesis of Ag_2S-modified $Sm_2Ti_2S_2O_5$ (denoted as "Ag-$Sm_2Ti_2S_2O_5$") was similar to our previously reported synthesis of the parent $Sm_2Ti_2S_2O_5$.[1] The synthesis involved calcination of an amorphous oxide precursor (denoted as "Ag@$Sm_2Ti_2O_7$") prepared by the polymerized complex (PC) method under H_2S flow.

The typical synthesis of an oxide precursor was as follows: 0.02 mol titanium tetrasiopropoxide was dissolved in 0.2 mol ethylene glycol at room temperatures, and 0.3 mol anhydrous citric acid was then added and heated at 333 K until it was completely dissolved. Subsequently, 0.02 mol $Sm(NO_3)_3.6H_2O$, 20 mL methanol, and a calculated amount of $AgNO_3$ (Ag content was calculated according to the molar ratio of Ag/Ti atoms) were then added to the solution in order. The mixture was stirred at 403 K until a transparent gel was formed. The polymer was carbonized at elevated temperatures, stopping at 523 K, 573 K, and 623 K for 1 h each, and finally calcined at 773 K for 12 h to completely remove carbon.

The as-obtained amorphous oxide precursor was subject to sulfurization at different temperatures for 1 h under a flow of H_2S (10 mL/min). Post-calcination in air at 573 K for 2 h was adopted before using the catalyst, in order to remove any sulfur species that may have adsorbed on the surface of the photocatalyst. A similar procedure was used to prepare $Gd_2Ti_2S_2O_5$ and Ag_2S-modified $Gd_2Ti_2S_2O_5$ (Ag-$Gd_2Ti_2S_2O_5$) photocatalysts.

1.2. Deposition of cocatalysts

In this work, rhodium was mainly used as a cocatalyst for H_2 evolution, and was deposited by *in-situ* photodeposition or impregnation. The *in situ* photodeposition method was mainly employed to optimize the Ag content and sulfurization temperature. The corresponding optimal values were found at 1 mol% ($Ag_2S/Sm_2Ti_2S_2O_5$) and 1223 K, respectively. Thus, unless otherwise stated, the Ag-$Sm_2Ti_2S_2O_5$ photocatalyst discussed here refers to sample containing 1 mol% Ag_2S with sulfurization at 1223 K for 1 h.

In the impregnation process, the experimental procedure was as follows. 0.3 g of catalyst powder was immersed in an aqueous solution of $RhCl_3{\cdot}xH_2O$ (Aldrich, 38-40%) (1 wt% Rh), and sonicated for ca. 10 min. After the solution was completely evaporated in a water bath, the resulting powder was collected and heated with H_2 gas (ca. 20 kPa) at 623 K for 1 h in a gas circulation system similar to that used for the photocatalysis tests. A similar procedure was adopted to impregnate platinum.

1.3. Catalyst Characterization

The as-prepared samples were characterized by X-ray powder diffraction (XRD, Geiger-flex

RAD-B, Rigaku; Cu kα), field-emission scanning electron microscopy (FE-SEM; S-4700, Hitachi), ultraviolet-visible diffuse spectroscopy (JASCO, V-670 spectrophotometer), high-resolution transmission electron microscopy (HRTEM; JEM-2010F, JEOL), X-ray photoelectron spectroscopy (XPS; JPS-9000, JEOL), and X-ray absorption near-edge spectroscopy (XANES). XANES measurements were carried out in the NW10A beamline of the Photon Factory (High Energy Accelerator Research Organization, Tsukuba, Japan) using a ring energy of 2.5 GeV and a stored current of 60–40 mA (Proposal No. 2008G150) for measurement of the Ag–K edge spectra. The X-ray absorption spectra were measured in transmission or fluorescence mode at room temperature with a Si(111) two-crystal monochromator. Data reduction was performed using the REX2000 program (Rigaku Corporation). The binding energies determined by XPS were corrected by reference to the C 1s peak (285 eV) for each sample. The Brunauer-Emmett-Teller (BET) surface area was measured using a BELSORP-mini instrument (BEL Japan) at 77 K.

1.4. Photocatalytic Reactions

Reactions were carried out in a Pyrex inner-irradiation-type reaction vessel connected to a glass closed gas circulation system. 400 mL of 0.05 M Na_2S-Na_2SO_3 containing 0.20 g of the cocatalyst-loaded sample was used for the H_2 evolution. Prior to the reactions, the reactant solution was evacuated several times to remove air completely, and then irradiated under a 450 W high-pressure Hg lamp ($\lambda > 400$ nm using 2 M $NaNO_2$). A flow of cooling water was used to maintain the reactant solution at room temperatures. The evolved gases were analyzed by gas chromatography.

1.5. Quantum efficiency measurement

The apparent quantum efficiency (AQE) was measured with the use of a Pyrex top-irradiation-type reaction vessel and a 300 W xenon lamp fitted with a 440 nm band-pass filter. Photoreduction of H^+ to H_2 was examined using an aqueous solution (200 mL) containing 0.20 g 1 wt% Rh/Ag-$Sm_2Ti_2S_2O_5$ and 0.05 M Na_2S-Na_2SO_3 reagents. The number of photos reaching the solution was measured using an Si photodiode: the rate of total incident photos at 440 nm was typically 1.71×10^{20} photos·h^{-1}. The quantum efficiency (Φ) was calculated using the following equation:

$$\Phi\ (\%) = (AR/I) \times 100$$

where A, R, and I are coefficients (here H_2 evolution, 2), the H_2 evolution rate, and the rate of absorption of incident photos, respectively. Here Φ is the apparent quantum efficiency. It was assumed that all incident photos were adsorbed by the suspension.

1.6. Photoelectrochemical measurements

$Sm_2Ti_2S_2O_5$ and Ag-$Sm_2Ti_2S_2O_5$ electrodes were prepared by pasting a viscous slurry onto a piece of conducting glass, following our previously reported procedure.[2] Typically, a mixture of 0.1 g of as-prepared powder, 10 μL of acetylacetone (Kanto Chemicals), 10 μL of Triton-X (Aldrich, USA), and 100 μL of distilled water was ground in an agate mortar to prepare a viscous slurry. This slurry was then pasted onto fluorine-doped tin-oxide (FTO) glass slides to prepare a 1×3 cm^2 electrode, which was calcined in air at 573 K for 1 h before measurement.

Measurements were performed using a conventional Pyrex electrochemical cell, with a platinum wire as a counter electrode and an Ag/AgCl reference electrode under potentiostat control (HSV-100, Hokuto Denko, Japan). Current-voltage curves were measured in an aqueous solution containing 0.01 M Na_2S-Na_2SO_3. The electrolyte solution was purged with nitrogen prior to the measurements, and

was maintained at room temperature by a flow of cooling water during the measurements. A 300 W xenon lamp with a wavelength of 420-800 nm was used as the light source.

References

1. A. Ishikawa, Y. Yamada, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, and K. Domen, *Chem. Mater.,* 2003, **15**, 4442-4446.
2. K. Maeda, N. Nishimura, and K. Domen, *Appl. Catal. A:Gen,* 2009, **370**, 88-92.

2. Results of characterizations

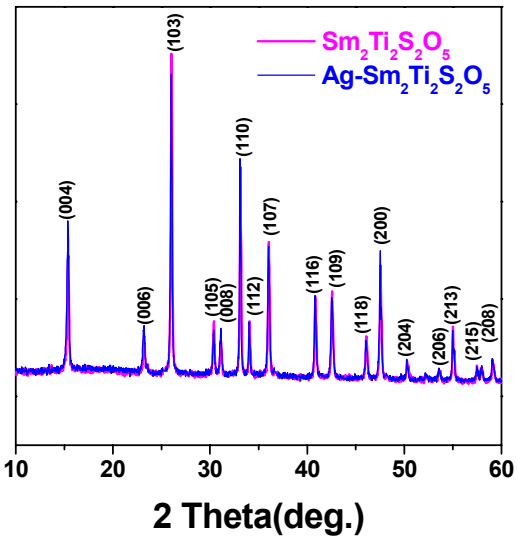

Fig. S1. XRD patterns of $Sm_2Ti_2S_2O_5$ and Ag-$Sm_2Ti_2S_2O_5$ photocatalysts.

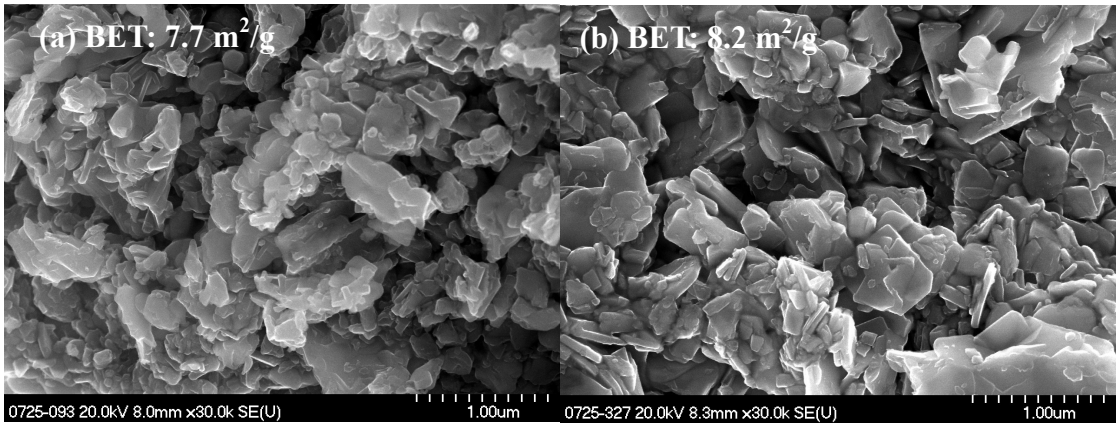

Fig. S2. Typical SEM images of (a) $Sm_2Ti_2S_2O_5$ and (b) Ag- $Sm_2Ti_2S_2O_5$.

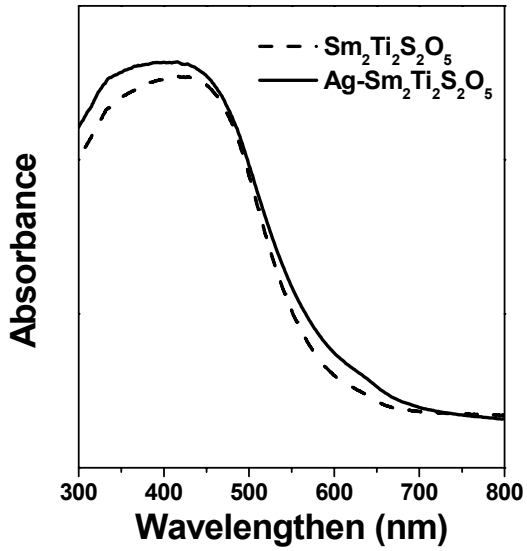

Fig. S3. UV-Vis spectra of $Sm_2Ti_2S_2O_5$ and Ag-$Sm_2Ti_2S_2O_5$ photocatalysts.

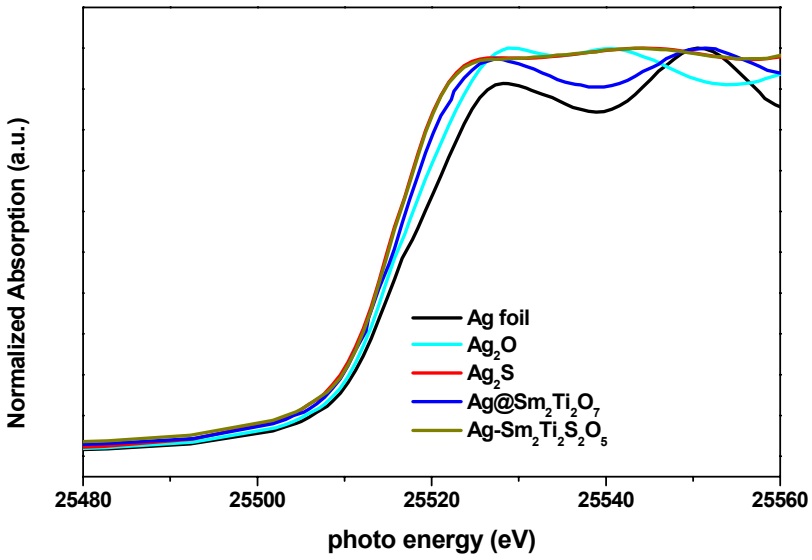

Fig. S4. Ag–K edge XANES spectra for Ag-$Sm_2Ti_2S_2O_5$, its oxide precursor Ag@$Sm_2Ti_2O_7$, and several reference spectra.

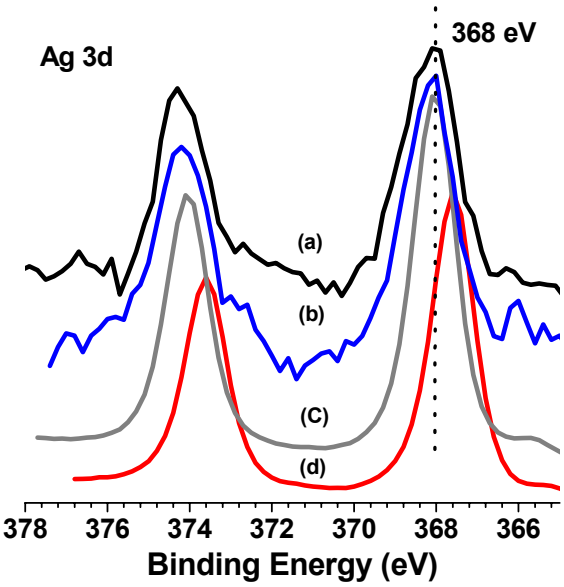

Fig. S5. XPS spectra for Ag-$Sm_2Ti_2S_2O_5$: (a) before H_2 evolution, (b) after H_2 evolution and references of (c) Ag_2S and (d) Ag powder.

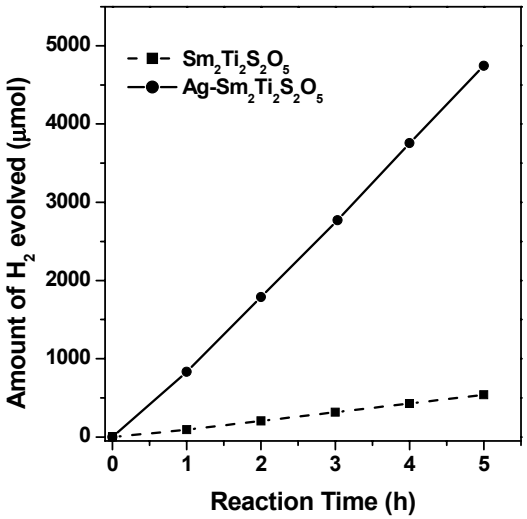

Fig. S6. Time courses of H_2 evolution on $Sm_2Ti_2S_2O_5$ and Ag-$Sm_2Ti_2S_2O_5$ photocatalysts under visible light. Reaction conditions: catalyst, 0.2 g (1 wt% Rh cocatalyst); aqueous Na_2S-Na_2SO_3 solution (400 mL, 0.05 M); light source, 450 W Hg lamp with an $NaNO_2$ (2 M) solution filter ($\lambda > 400$ nm).