Supporting Information

Metal sulfide photocatalyst composed of ubiquitous elements for solar hydrogen production

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Experimental detail

First principle calculation

Our electronic structure calculations were based on the density-functional theory (DFT). The exchangecorrelation energy functional was represented by a hybrid functional suggested by Heyd, Scuseria, and Ernzerhof (HSE).¹ The mixing parameter for Hartree-Fock exchange was set to 25 % as suggested in the original paper. Projector-augmented wave pseudopotentials were employed as implemented in the VASP code.^{2,3} The van der Waals interactions are taken into account using the scheme suggested by Tkatchenko and Scheffler.⁴ The valence configurations of the pseudo-potentials were $5s^25p^2$ for tin and $3s^23p^4$ for sulfur. The energy cutoff for the plane-wave basis set expansion was set at 500 eV. A Monkhorst-Pack k-point set of $2\times6\times6$ was used for the relaxation of 8-atom unit cell of SnS (space group *Pnma*) where x axis is vertical to layers, while $6\times6\times4$ was used for 3-atom unit cell of SnS₂ (space group *P-3m1*).

For calculations of SnS (010) surface, we created a slab model with 9 layers including 72 atoms. We also constructed a SnS₂ (001) surface with 7 layers including 42 atoms. The vacuum thickness was set at 20 Å. The mid layer of each slab was fixed to represent bulk region and both sides of the slab were relaxed for atomic positions until residual forces were below 0.02 eV/Å. The k-points were sampled at $4 \times 2 \times 1$ for SnS (010) and $4 \times 6 \times 1$ for SnS₂ (001).

The relative position of the averaged electrostatic potential V_{ae} in the mid layer of SnS (010) and SnS₂ (001) were estimated with respect to the vacuum level.

Vacuum(SnS) - Vae(SnS slab) = 71.21 eV

 $Vacuum(SnS_2) - Vae(SnS_2 slab) = 79.43 eV$

 $\Delta Vae = Vacuum(SnS) - Vae(SnS slab) - [Vacuum(SnS_2) - Vae(SnS_2 slab)] = 8.22 \text{ eV}.$

We also estimated the valence band maximum (VBM) of SnS and SnS₂ with respect to V_{ae} from the bulk

calculations,

VBM - Vae(SnS bulk) = 66.18 eV

 $VBM - Vae(SnS_2 bulk) = 72.23 eV$

The valence band and conduction band offsets were given by

VBM offset = 66.18 + 8.22 - 72.23 = 2.17 eV

CBM offset = VBM offset + $Eg(SnS) - Eg(SnS_2) = 1.15 \text{ eV}$

where band gap (Eg) of SnS and SnS₂ are 1.25 eV and 2.27 eV, respectively.

The ionization potential is also given by the following formula,

IP(SnS) = VBM - Vae(SnS bulk) - [Vacuum(SnS) - Vae(SnS slab)] = -5.02 eV

 $IP(SnS_2) = VBM - Vae(SnS_2 bulk) - [Vacuum(SnS_2) - Vae(SnS_2 slab)] = -7.20 eV$

References:

1. J. Heyd, G. Scuseria and M. Ernzerhof, J. Chem. Phys., 118, 8207-8215 (2003).

2. G. Kresse and J. Hafner, Phys. Rev. B 47, 558-561 (1993).

3. G. Kresse, and J. Furthmüller, Phys. Rev. B 54, 11169-11186 (1996).

4. A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. 102, 073005 (2009).

Fabrication of SnS and SnS₂ electrodes

Mesoporous TiO₂ film of 7 µm thickness was prepared onto a fluorine doped tin oxide (FTO glass) substrates by screen-printing using commercial (P25, Degussa) TiO₂ powder for paste, followed by annealing at 450 °C for 1 h. Prior to TiO₂ mesoporous film coating, a dense TiO₂ passivation layer was coated over FTO substrates by spin coating with a metal alkoxide solution, which was composed of 1.5 mL titanium tetraisopropoxide, 30 mL ethanol, 0.3 mL polyethylene glycol dimethylether, and 0.1 mL of a 1 M HNO₃ aqueous solution. After the spin coating of the alkoxide solution, the substrates were dried at 80 °C for 20 min. The thickness of the TiO₂ passivation layer was determined to be 50 nm. The SnS quantum dots were deposited on mesoporous TiO₂ electrodes by successive ionic layer adsorption and reaction (SILAR) method. Solutions containing Sn²⁺ (solution A) or S²⁻ (solution B) were prepared for SILAR deposition. In solution A, 1.2 mmol Sn²⁺ ions were dissolved in a mixture of ethylene glycol (10 mL) and 2, 2', 2"-nitrilotriethanol (2 mL). In solution B, 1 mmol Na₂S was dissolved in 10 mL water. A TiO₂ electrode was immersed into solution, and then immersed for 30s into solution B, washed with water. This two-step immersion procedure is termed as one SILAR cycle. The crystallite growth of SnS was controlled by repeating the SILAR cycles. After several SILAR cycles, the electrodes were finally washed with ethanol and dried at 80 °C in air for 10 min.

The SnS_2 nanoparticles were deposited on a mesoporous TiO_2 electrode by a hydrothermal method. A mesoporous TiO_2 electrode was placed in 20 mL of aqueous solution containing 2.5 mmol of $SnCl_4 \cdot 5H_2O$, 2.5 mmol of citric acid, and 5 mmol of thioacetamide, and heated at 130-170°C for 12h in an autoclave. After the hydrothermal reaction, the container was cooled to room temperature naturally and the electrode was washed with water for several times and dried in the air at 80 °C for 1h. We have optimized the hydrothermal

temperature by photocurrent performance, and optimum temperature was 150 °C in the present study.

For the XRD analysis, powder forms of SnS and SnS_2 were used because the amount and crystallite size of grafted SnS and SnS₂ on mesoporous TiO₂ were too small to determine the crystal phase. SnS and SnS₂ powder sample were prepared by mixing the same solutions as SILAR method and gathering precipitates from hydrothermal reaction, respectively.

Experimental procedure for SiO₂ coating

Thin SiO₂ layer was coated over SnS QDs/TiO₂ electrode by a sol-gel method using the tetraethylolthosilicate (TEOS) dissolved in ethanol solution as a precursor material. The SnS grafted TiO₂ electrode was dipped into the solution for 1min and kept in the air for 30 min leading to hydrolysis. The dipping and hydrolysis procedures were conducted twice, and the samples were dried under 80 °C for 2h in air. After the drying procedure, the samples were annealed in nitrogen gas atmosphere for 10 min at 300 °C. Coating and annealing conditions were optimized by the results of photo-stability. The concentration of TEOS was also optimized through the evaluation of photo-stability, and its optimum concentration was 0.1 M.

Characterization

The crystal phase was determined using an X-ray diffraction meter (XRD; Rigaku SmartLab). The morphology of the materials was examined using a field emission electron scanning microscope (FE-SEM; S-4700, Hitachi Co.) and a transmission electron microscope (TEM; JEM-2010F, JEOL) equipped with an energy dispersive X-Ray spectroscope (EDX). The absorption spectra of the electrodes were measured using a spectrophotometer (V-660, Jasco Ltd.) in diffuse reflectance mode. X-ray photoelectron spectroscopy analysis was conducted to determine the chemical states of tin sulfides and the existence of thin SiO₂ layer onto SnS QDs by using Mg K α X-rays (XPS; model ESCA-5500MT, Perkin Elmer Instruments). Ionization potential (valence band potential of semiconductor) was determined by using ultraviolet photoelectron spectroscopy (UPS, model AC-5 photoemission yield spectroscopy in air, RIKEN KEIKI Co. Ltd.).

Photo-electrochemical measurement

SnS and SnS₂ electrodes were sealed in a sandwich cell with 30 µm spacer and equipped with a Pt counter electrode. The electrode area was 0.25 cm². An aqueous solution containing 0.24 M Na₂S and 0.34 M Na₂SO₃ was used as an electrolyte for photochemical measurement. The photocurrent response under rest potential was measured by a potentiostat (HSV-110; Hokuto Denko Co.). AM 1.5 solar simulator (PEC-L11; Peccell Co.) equipped with a 300 W Xe lamp and AM 1.5 filter was used as a light source. And the range of the light wavelength was above 420 nm using UV-cut off filter (Y-43; Asahi Techno Glass). Photo current densities were recorded under the chopped light irradiation.

Photocatalytic hydrogen evolution measurement

Measurement of photocatalytic hydrogen evolution was examined in a closed gas-circulating system connected to an on-line gas chromatogram system with a thermal conductivity detector (TCD). For the

wireless photocatalytic reaction, Pt layer was inserted at the interface between FTO layer and mesoporous TiO₂ layer as a catalytic site for hydrogen production. Hydrogen production properties of SnS and SnS₂ films were evaluated under wireless condition without any bias application. The catalytic Pt layer was deposited on a FTO glass by DC magnetron sputtering (MSP-30T; Shinku Device Ltd.), and the thickness of Pt layer was estimated to be 25 nm by considering the deposition rate and deposition time. Hydrogen production properties were performed in an electrolyte solution containing 0.24 M Na₂S and 0.34 M Na₂SO₃, used as an oxidation sacrificial agent. Visible light was irradiated by using 150 W Xe lamp passed through a UV-cut off filter (Y-43; Asahi Techno Glass).

Quantum efficiency was determined according to the following equation (1):

Quantum efficiency =
$$\frac{(\text{number of reacted electrons})}{\int (\text{photon flux}) \times (\text{absorption coefficient}) \cdot d\lambda}$$
(1)

The photon flux and absorption coefficient of the electrode films were measured using a spectro-radiometer (USR-40D, Ushio Co.) and spectrophotometer (V-660, Jasco, Ltd.), respectively. The number of reacted electrons was determined based on the assumption that for water splitting, hydrogen evolution involves the two-electron reduction of protons.

Turnover number was estimated by the reacted electrons for hydrogen production versus SnS QDs amount. The loaded SnS QDs amount was calculated by the weight change after SILAR cycles.



Fig. S1 Calculated band dispersion and density of states (DOS) for SnS (a) and SnS_2 (b).



Fig. S2 Cross sectional SEM images for mesoporous TiO_2 electrode (a) and (b).TEM image of SnS loaded TiO_2 (c) and SnS_2 loaded TiO_2 (d), respectively. The panel (e) shows point EDX spectra of the SnS loaded TiO_2 on point (i) and point (ii), which are indicated in panel (c). Pt thin layer was inserted between FTO and TiO_2 interface as a cocatalytic layer for hydrogen production.



Fig. S3 XPS survey spectra for SnS and SnS_2 electrodes, which were fabricated under optimum conditions for photo-electrochemical performance.



Fig. S4 Photos of tin sulfides loaded electrode. (a) SnS with different SILAR cycles, and (b) SnS_2 with different hydrothermal temperature.



Fig. S5 Current densities under chopped light irradiation. (a) SnS, SnS_2 , and bare TiO_2 electrodes, and (b) SnS electrodes with different SILAR cycles. Photocurrent was decreased by photo-corrosion of SnS QDs, thus the photocurrent data at the second chopped light condition were plotted in Figure 4 (a).



Fig. S6 Photocatalytic hydrogen evolution results including control experiments. Visible light was irradiated through a UV cut-off filter, and a bias potential was not applied on the electrode. The electrolyte solution contained Na₂S and Na₂SO₃ as sacrificial agents for the oxidation reaction. Pt layer insertion was required to evolve hydrogen as a cocatalyst layer.



Fig. S7 TEM image of SiO_2 coated electrode (a), and XPS spectra for Si-2p orbital for SiO_2 coated SnS and SnS without SiO_2 coating.



Fig. S8 Photocurrent density versus irradiation time. (a): effect of TEOS concentration for SiO_2 coating, (b): effect of annealing temperature for hydrolysis of TEOS in argon atomosphere.