Supplementary Information

Ultrafine $Zn_{1-x}Cu_xS$ ($0 \leq x \leq 0.066$) nanocrystallites for photocatalytic H_2 evolution under visible light irradiation

Zongwei Mei,[*a, b] **Shuxin Ouyang,**[b] **Yuanjian Zhang,**[c] **Tetsuya Kako.** [a, b]

a Department of Chemistry, Graduate School of Science, Hokkaido University, Sapporo, Japan. Fax: (+81)-29-860-4958; E-mail: MEI.Zongwei@nims.go.jp

b Catalytic Materials Group, Research Unit for Environmental Remediation Materials, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.

c School of Chemistry and Chemical Engineering, Southeast University 211189, Nanjing, P. R. China.

Experimental Section

All the reagents consist of sodium sulfide nonahydrate ($Na_2S·9H_2O$), zinc acetate dihydrate ($(CH_3OO)_2Zn·2H_2O$), thiourea (H_2NCSNH_2), copper (II) acetate monohydrate ($(CH_3COO)_2Cu·H_2O$), and cadmium chloride 2.5-hydrate ($CdCl_2·2.5H_2O$). They were analytical grade and used without further treatment.

Synthesis of $Zn_{1-x}Cu_xS$ by complexing-wet-chemical method

In a typical procedure, white ZnS deposition was firstly fabricated by adding 100 ml of $Na_2S·9H_2O$ (0.06 mol/L) into 200 ml of $(CH_3OO)_2Zn·2H_2O$ (0.02 mol/L) drop by drop and then the solution was magnetically stirred for 30 min. After that, the white products were washed with distilled water for 5 times and separated by centrifuge, respectively. Secondly, the white ZnS was dispersed into 100 ml of distilled water for 10 min by a ultrasonic method before adding 50 ml of H_2NCSNH_2 (0.4 mol/L) and $(CH_3COO)_2Cu·H_2O$ (0.0032 mol/L) into it. Thirdly, the whole solution was added into a three-neck flask (500 ml) and vigorously stirred by a mechanical stirrer at 300 r/min for 72 h at 85 °C. Finally, the yellow products were cleaned by distilled water and ethanol for several times, respectively. Then the products were dried in air. The other $Zn_{1-x}Cu_xS$ were prepared by the same way just changing the starting molar ratio of Cu^{2+}/Zn^{2+} (6%, 5%，3%, and 2%). As reference, $Zn_{1-x}Cu_xS$-I was synthesized by the same way but there was not H_2NCSNH_2 added in the second step, the molar ratio of Cu^{2+}/Zn^{2+} was 4%.

Synthesis of CdS and ZnS

As comparison, CdS was synthesized by the same way mentioned above. At first, 4 mmol of $CdCl_2 \cdot 2.5H_2O$ was dissolved into 200 ml of distilled water, then 100 ml of $Na_2S \cdot 9H_2O$ (0.06 mol/L) was added into the solution drop by drop. The final solution was magnetically stirred for 30 min. The synthesized orange CdS were separated and cleaned with distilled water for 5 times by centrifuge. After that, the cleaned CdS was dispersed into 100 ml of distilled water for 10 min by ultrasonic method, then 50 ml of H_2NCSNH_2 (0.4 mol/L) was quickly added into the dispersed CdS solution. Finally, the mixture was transferred into 500 ml of three-neck flask and constantly heated at 85°C for 72 h. The final orange CdS was cleaned by distilled water and ethanol for several times, respectively. Then the products were dried in air for further characterization. ZnS was synthesized by the same way using $Na_2S \cdot 9H_2O$ and $(CH_3OO)_2Zn \cdot 2H_2O$ as the starting materials.

Synthesis of $Zn_{1-x}Cu_xS$-II by coprecipitation method

4 mmol $(CH_3OO)_2Zn \cdot 2H_2O$ and 0.16 mmol $(CH_3COO)_2Cu \cdot H_2O$ was dissolved into 100 ml distilled water, then 50 ml of $Na_2S \cdot 9H_2O$ (0.12 mol/L) was added into that solution drop by drop. After that, the whole solution was vigorously stirred in a three-neck flask at room temperature for 72 h. The products were cleaned by distilled water and ethanol for several times and dried in air for further characterization.

Characterization

Powder X-ray diffraction (XRD) characterization was performed by using Rint-2000 diffractometer (Rigaku Co., Japan) operating at 40 kV and 30 mA for Cu Kα radiation (λ = 1.5406 Å). Inductively coupled plasma optical emission spectrometer (ICP-OES) characterization for Zn and Cu elements was operated on IRIS Advantage (Nippon

Jarrell-Ash Co., Japan), while the characterization of S element was carried out on Carbon/Sulfur determinator CS-444LS (LECO Co. USA). The BET surface area was measured by nitrogen adsorption at 77 K with a BELSORP II Surface Area Analyzer (Bel Japan Co., Japan). X-ray Photoelectron Spectroscopy (XPS) experiments were performed in type Theta probe using monochromatized Al Kα at hν = 1486.6 eV. The UV-visible diffuse reflection spectra were recorded on a UV-2500PC recording spectrophotometer (Shimadzu Co., Japan). The reflectance spectra were converted into absorption spectra using Kubelka-Munk equation. Transmission electron microscope (TEM) and high-resolution TEM (HRTEM) were operated on JEM-2100F (JEOL).

Apparent quantum efficiency (AQE) was calculated by the following equation:

$$\begin{aligned} AQE(\%) &= \frac{\text{The number of reacted electrons}}{\text{The number of incident photons}} \times 100\% \\ &= \frac{\text{The number of evolved H}_2\text{ molecules } \times 2}{\text{The number of incident photons}} \times 100\% \end{aligned}$$

Tab. S1

Starting molar ratio of Cu^{2+}/Zn^{2+}	**Element (mass %)**			**Molar ratio of**	**Molar ratio of Cu/Zn**
	Zn	**Cu**	**S**	**Zn:Cu:S**	**(*x* value of $Zn_{1-x}Cu_xS$)**
6%	53.3±0.3	3.4±0.1	28.2±0.2	0.927:0.061:1	0.066
5%	55.2±0.1	2.6±0.3	28.9±0.2	0.937:0.051:1	0.054
4%	55.7±0.1	2.8±0.1	28.8±0.2	0.950:0.047:1	0.049
3%	57.1±0.1	1.9±0.1	28.9±0.2	0.969:0.033:1	0.034
2%	57.9±0.1	1.0±0.2	28.8±0.1	0.986:0.018:1	0.018

Tab. S1 ICP-OES and Carbon/Sulfur Determinator characterization for Zn, Cu, and S elements.

Tab. S2

Sample	S_{BET} (m^2/g)
$Zn_{0.982}Cu_{0.018}S$	212.4
$Zn_{0.966}Cu_{0.034}S$	223.0
$Zn_{0.951}Cu_{0.049}S$	201.1
$Zn_{0.946}Cu_{0.054}S$	192.9
$Zn_{0.934}Cu_{0.066}S$	183.2

Tab. S2 Surface areas of samples characterized by Brunauer-Emmett-Teller (BET) gas sorptometry.

Fig. S1

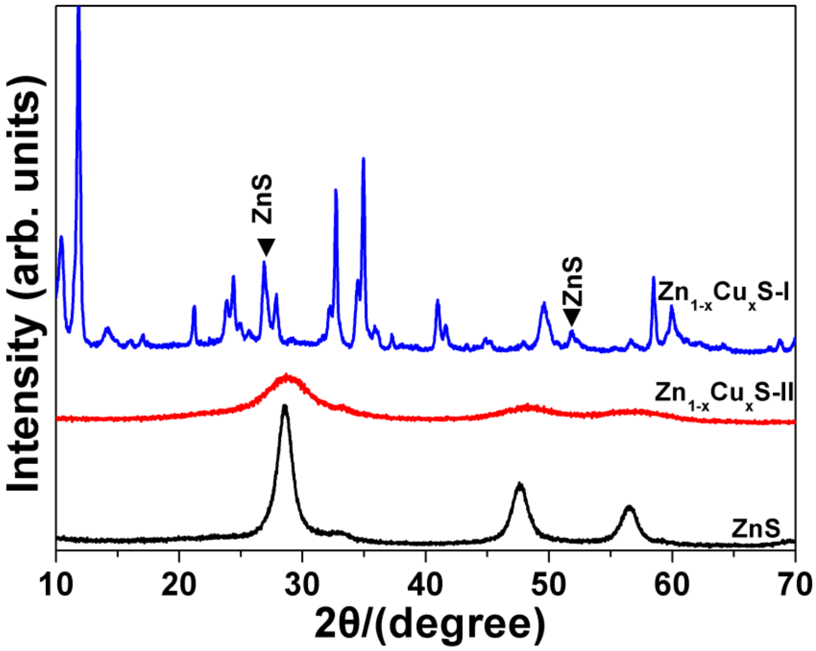

Fig. S1 XRD patterns of (a) $Zn_{1-x}Cu_xS$-I synthesized without thiourea from ZnS precursor at 85 °C for 72 h, (b) $Zn_{1-x}Cu_xS$-II synthesized by coprecipitation method, and (c) cubic ZnS synthesized in this study.

Fig. S2

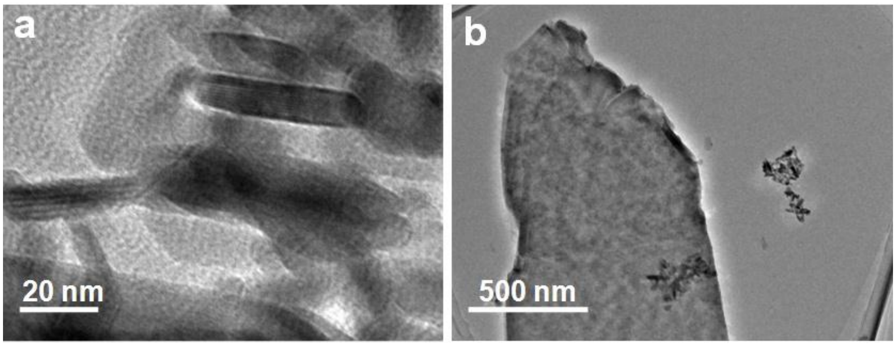

Fig. S2 TEM images of $Zn_{1-x}Cu_xS$-I synthesized without thiourea from ZnS precursor at 85 °C for 72 h.

Fig. S3

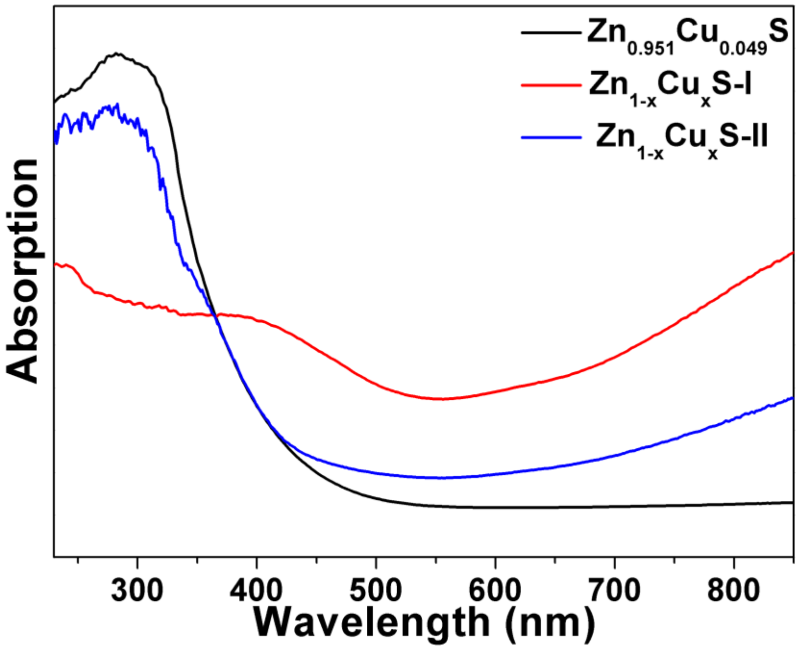

Fig. S3 UV-vis absorption spectra of (a) $Zn_{0.951}Cu_{0.049}S$ synthesized by complexing-wet-chemical method at 85 °C for 72 h, (b) $Zn_{1-x}Cu_xS$-I synthesized without thiourea from ZnS precursor at 85 °C for 72 h, and (c) $Zn_{1-x}Cu_xS$-II synthesized by coprecipitation method at room temperature for 72 h.

Fig. S4

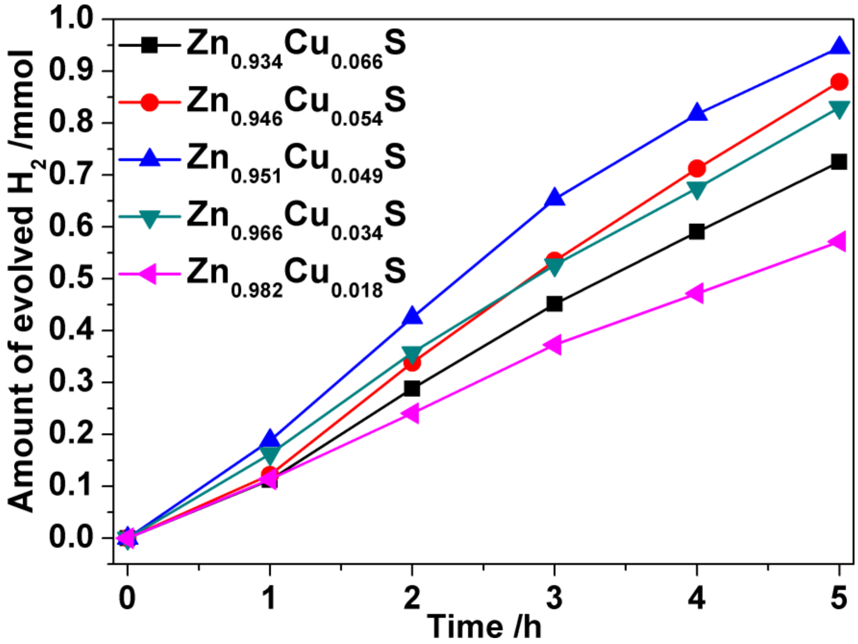

Fig. S4 Time course of photocatalytic H_2 evolution of $Zn_{1-x}Cu_xS$ ($0.018 \leq x \leq 0.066$) without cocatalyst from Na_2S (0.35 M)/K_2SO_3 (0.25 M) aqueous solution under visible-light irradiation (λ > 400 nm). Light source: 300 W of Xe lamp; Light filter: L42.

Fig. S5

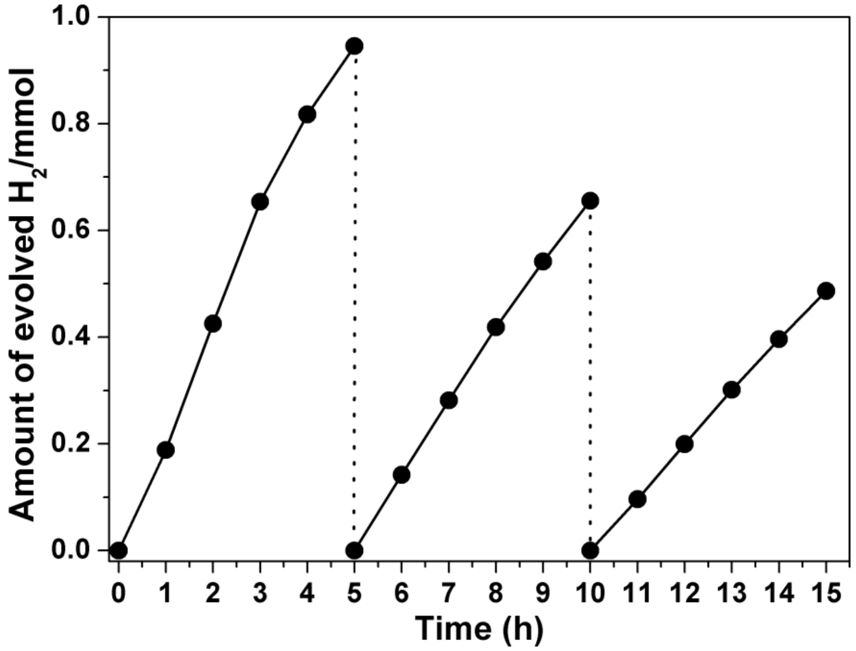

Fig. S5. Amount of H_2 evolved at each run for $Zn_{0.951}Cu_{0.049}S$.