Supporting information

Enhanced Z-schematic water splitting using $(CuGa)_{0.5}ZnS_2$ H_2-evolving photocatalyst with a post-treatment in aqueous solutions

Akihide Iwase, Koki Yagishita

Experimental

Synthesis of photocatalysts

$(CuGa)_{0.5}ZnS_2$ was synthesized by a solid-state reaction, as previously reported.[1] Starting materials of Cu_2S (Kojundo Chemical, 99%), Ga_2S_3 (Kojundo Chemical, 99.99%), and ZnS (Rare Metal Chemical, 99.99%) in an atomic ratio of Cu/Ga/Zn=1:1.2:2.4 were mixed in an agate mortar. The mixed starting materials were encapsulated in a quartz tube after evacuation and was subsequently calcined at 1073 K for 10h. The obtained $(CuGa)_{0.5}ZnS_2$ powder (0.11 g) was stirred at room temperature for 10 minutes in 20 mL of water, an aqueous NaOH solution (1.0 mol L^{-1}), and aqueous Na_2S solutions (1.0, 2.0 mol L^{-1}) for surface treatments.

$BiVO_4$ was synthesized from Bi_2O_3 (Kanto Chemical, 99.9%) and V_2O_5 (Kanto Chemical, 99.0%) by a liquid-solid-state reaction, as previously reported.[2] Bi_2O_3 (5 mmol) and V_2O_5 (5 mmol) were vigorously stirred in a 1.0 mol L^{-1} aqueous HNO_3 solution (50 mL) at room temperature for 48 hours. A CoO_x cocatalyst was loaded on the obtained $BiVO_4$ by an impregnation method.[3] The $BiVO_4$ powder (0.5 g) and 80 mmol L^{-1} aqueous $Co(NO_3)_2$ solution (0.53 mL) were placed in a porcelain crucible and dried. The impregnated powder was calcined at 673 K for 2 h in the air to obtain CoO_x(0.5 wt%)-loaded $BiVO_4$ ($CoO_x/BiVO_4$). An RGO-incorporated $CoO_x/BiVO_4$ (RGO-$CoO_x/BiVO_4$) was prepared by photocatalytic reduction of a graphene oxide (NiSiNa materials, Rap eGO) over $CoO_x/BiVO_4$ under visible light irradiation.[3] A graphene oxide (GO)-dispersed solution (10 mg mL^{-1}, 1.5 mL), $CoO_x/BiVO_4$ (0.3 g), and methanol (20 mL) were added into water (20 mL). The suspension was irradiated with visible light using a 300 W Xe lamp (LuxteL, CeraLux CL-300BF) with a long-pass filter (HOYA, L42) for 3 hours in an atmosphere of N_2.

Characterization

The crystal phases of the synthesized $(CuGa)_{0.5}ZnS_2$ and $BiVO_4$ were analyzed on an X-ray diffractometer (Rigaku, MiniFlex). Diffuse reflectance spectra were obtained

using a UV-vis-NIR spectrometer (JASCO, V-650) equipped with an integrating sphere and were converted from reflection to K-M function by the Kubelka-Munk method. Morphology and particle size of the photocatalyst powder were observed using a scanning electron microscope (Hitachi, S-5200).

Photocatalytic reactions

Z-schematic water splitting was carried out under 1 atm of Ar gas flow. $(CuGa)_{0.5}ZnS_2$ (0.05 g) and RGO-CoO_x/$BiVO_4$ (0.05 g) were dispersed in water (120 mL) in a top-irradiation cell with a Pyrex window. Sacrificial H_2 evolution was carried out using a gas-tight circulation system. $(CuGa)_{0.5}ZnS_2$ (0.2 g) was dispersed in an aqueous solution (120 mL) containing Na_2S (0.1 mol L^{-1}) and K_2SO_3 (0.5 mol L^{-1}). A 300 W Xe arc lamp with a long-pass filter (HOYA, L42) was used as a light source for visible light irradiation. The amounts of evolved gases were determined using an online gas chromatograph (Shimadzu, GC-8A, TCD detector, MS-5A column, Ar carrier).

References

1. T. Kato, Y. Hakari, S. Ikeda, Q. Jia, A. Iwase and A. Kudo, *J. Phys. Chem. Lett.*, 2015, **6**, 1042-1047.

2. A. Iwase, H. Kato, A. Kudo, *J. Sol. Energy Eng.*, 2010, **132**, 21106.

3. A. Iwase, S. Yoshino, T. Takayama, Y. H. Ng, R. Amal and A. Kudo, *J. Am. Chem. Soc.*, 2016, **138**, 10260-10264.

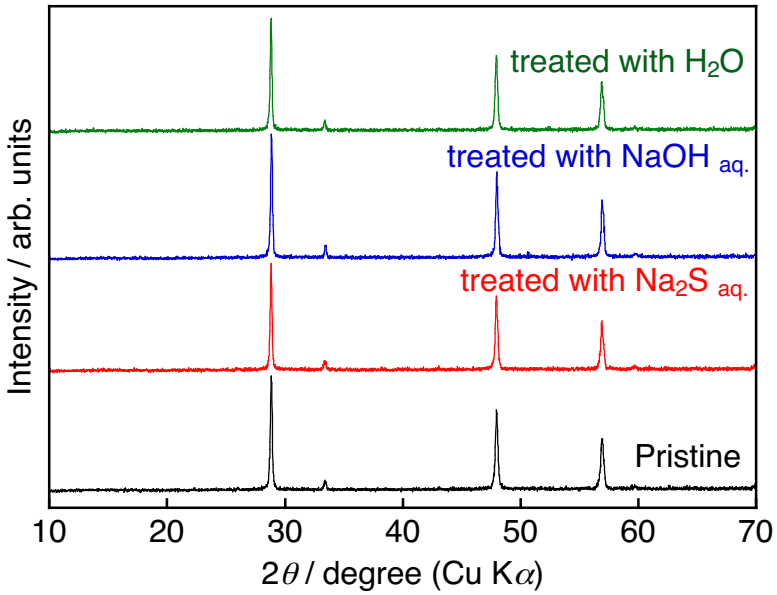

Figure S1 XRD patterns of pristine $(CuGa)_{0.5}ZnS_2$ (black) and $(CuGa)_{0.5}ZnS_2$ treated in a 2.0 mol L^{-1} aqueous Na_2S solution (red), a 1.0 mol L^{-1} aqueous NaOH solution (blue), and water (green).

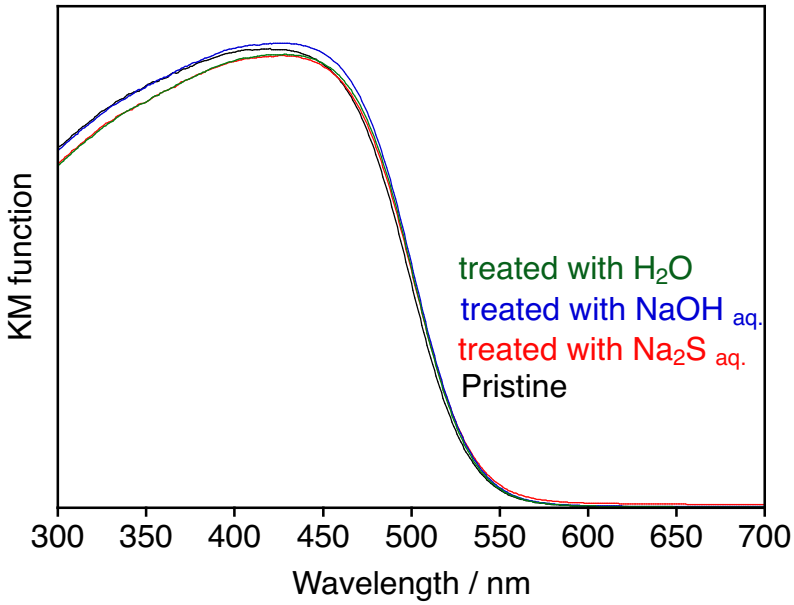

Figure S2 Diffuse reflectance spectra of pristine $(CuGa)_{0.5}ZnS_2$ (black) and $(CuGa)_{0.5}ZnS_2$ treated in a 2.0 mol L^{-1} aqueous Na_2S solution (red), a 1.0 mol L^{-1} aqueous NaOH solution (blue), and water (green).

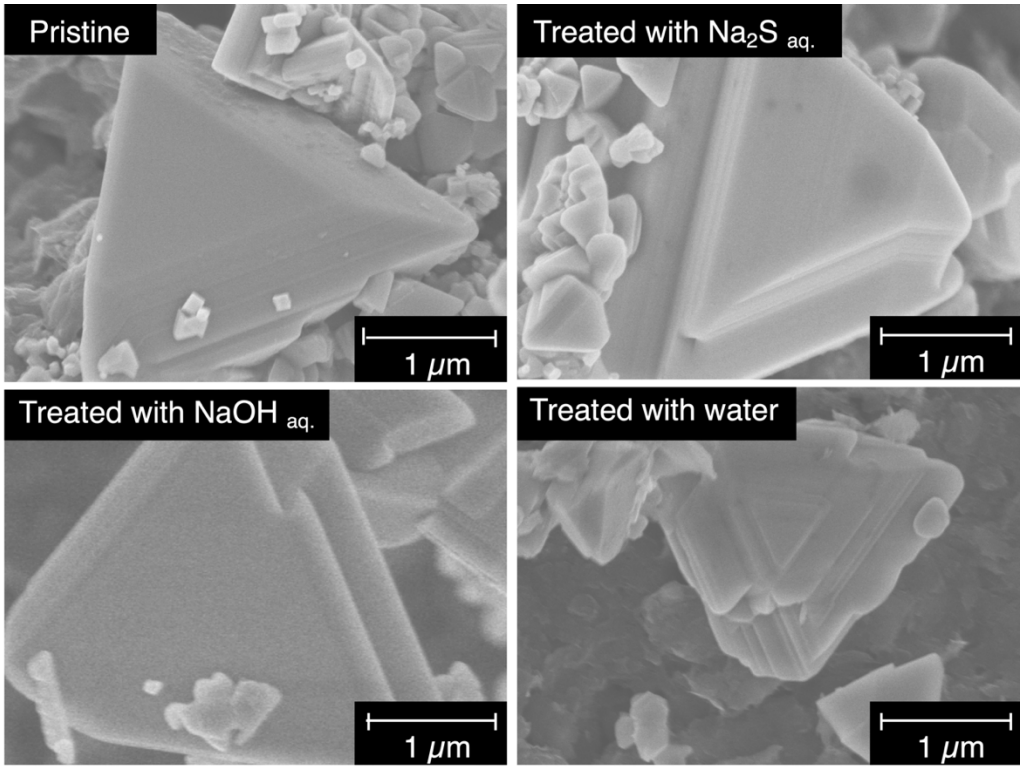

Figure S3 SEM images of pristine $(CuGa)_{0.5}ZnS_2$ and $(CuGa)_{0.5}ZnS_2$ treated in a 2.0 mol L^{-1} aqueous Na_2S solution, a 1.0 mol L^{-1} aqueous NaOH solution, and water.

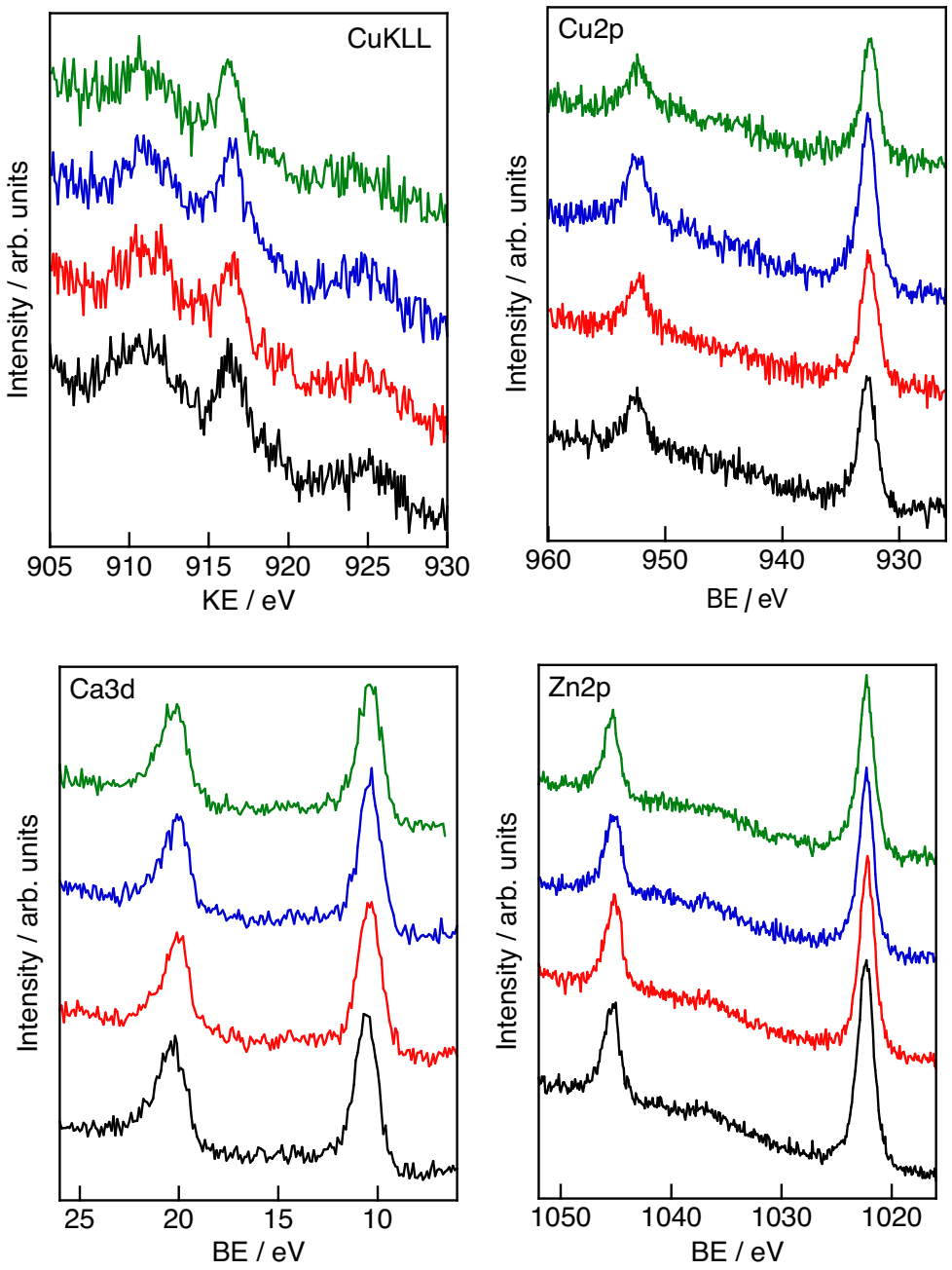

Figure S4 Auger spectra for Cu $L_3M_{4,5}M_{4,5}$ and X-ray photoelectron spectra for Cu2p, Ga3d, and Zn2p in pristine $(CuGa)_{0.5}ZnS_2$ (black) and $(CuGa)_{0.5}ZnS_2$ treated in a 2.0 mol L^{-1} aqueous Na_2S solution (red), a 1.0 mol L^{-1} aqueous NaOH solution (blue), and water (green).

Table S1 Atomic ratio at the surface estimated by XPS of $(CuGa)_{0.5}ZnS_2$ with and without a treatment in aqueous solutions

Treatment	Atomic ratio		
	Ga/Cu	Zn/Cu	S/Cu
–	0.24	3.47	0.51
2.0 mol L^{-1} $Na_2S_{aq.}$	0.23	2.87	0.42
1.0 mol L^{-1} $NaOH_{aq.}$	0.17	2.05	0.33