

Electronic Supplementary Information (ESI) for

Z-schematic and visible-light-driven CO₂ reduction using H₂O as an electron donor by particulate mixture of Ru-complex/(CuGa)_{1-x}Zn_{2x}S₂ hybrid catalyst, BiVO₄ and electron mediator

Tomiko M. Suzuki,^{*a} Shunya Yoshino,^b Tomoaki Takayama,^b Akihide Iwase,^b Akihiko Kudo,^{* b} and Takeshi Morikawa^a

^a Toyota Central R&D Labs. Inc., 41-1, Yokomichi, Nagakute, Aichi 480-1192, Japan

^b Tokyo University of Science, Department of Applied Chemistry, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

Experimental section

Preparation of metal sulfide semiconductor

(CuGa)_{1-x}Zn_{2x}S₂ solid solutions with various composition ($x=0, 0.2, 0.5, 0.5, 0.7,$ and 0.9) were synthesized by solid-state reaction according to a previously reported method.¹ CuS₂ (Kojundo Chemical Laboratory, 99%), Ga₂S₃ (Kojundo Chemical Laboratory, 99%), and ZnS (Kojundo Chemical Laboratory, 99.999%) were mixed using an agate mortar in the ratio of Cu/Ga/Zn=(1-x): 1.2 (1-x): 1.1 (1-x): 2x. The mixture was sealed in a quartz ampule after evacuation and then calcined at 1073 K for 10 h.

Preparation of BiVO₄ photocatalyst

BiVO₄ was prepared by a liquid-solid state reaction as previously reported.² 20 mmol of

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 10 mmol of V_2O_5 were stirred in 0.5 mol L^{-1} of aqueous nitric acid solution (100 mL) for 72 h. The BiVO_4 powder obtained was collected by filtration and washed with distilled water before drying.

Synthesis of the Ru-complex

$[\text{Ru}(4,4'\text{-diphosphonate-2,2'}\text{-bipyridine})(\text{CO})_2\text{Cl}_2]$ ($[\text{Ru}(\text{dpbpy})]$) was synthesized according to a previously reported method.³

Preparation of $[\text{Ru-dpbpy}]/(\text{CuGa})_{1-x}\text{Zn}_{2x}\text{S}_2$ hybrid photocatalysts

Hybrid photocatalysts consisting of a Ru-complex $[\text{Ru}(\text{dpbpy})]$ and a metal sulfide semiconductor $(\text{CuGa})_{1-x}\text{Zn}_{2x}\text{S}_2$ were prepared by adsorption of the Ru-complex in methanol solution according to a previous report.² UV/vis absorption spectra of the solutions after filtration were acquired using a UV/vis spectrophotometer (Shimadzu UV-3600) and the amount of $[\text{Ru}(\text{dpbpy})]$ adsorbed on $(\text{CuGa})_{1-x}\text{Zn}_{2x}\text{S}_2$ was calculated from each spectrum.

Synthesis of the Co-complex

$[\text{Co}(2,2':6,6'\text{-terpyridine})_2](\text{NO}_3)_2$ ($[\text{Co}(\text{tpy})_2](\text{NO}_3)_2$) was synthesized as follows. 1.5 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Wako Pure Chemical Industry) and 3.0 mmol of 2,2':6,6'-terpyridine (Tokyo Chemical Industry) were dissolved in methanol solution, which was then stirred at room-temperature for 2 h. The solution changed color to dark brown and was then evaporated to dryness. The residue was recrystallized from methanol and diethyl ether.

Characterization

The crystal structures of the photocatalysts were analyzed using X-ray diffraction (XRD; Rigaku, Ultima IV) with Cu K α radiation at 40 kV and 40 mA. Diffuse reflection spectra were obtained using a UV-vis-NIR spectrometer (JASCO, V-780) and were converted from reflectance to absorbance by the Kubelka-Munk method. X-ray photoelectron spectroscopy (XPS; Ulvac-Phi Quantera SXM) measurements were conducted with monochromated Al K α radiation.

Z-schematic photocatalytic CO₂ reduction by the test tube method

Z-schematic photocatalytic CO₂ reduction was conducted according to a previously reported test tube method.⁴⁻⁵ Photocatalytic activity was measured at ambient pressure under CO₂ in 8 mL Pyrex test tubes containing an aqueous solution (4 mL) of 0.02 mmol L⁻¹[Co(tpy)₂]²⁺ and the [Ru(dpby)]/(CuGa)_{1-x}Zn_{2x}S₂ hybrid photocatalyst and BiVO₄ photocatalyst (16 mg in total). After purging with CO₂ for 15 min, the suspensions were irradiated in a rotating apparatus using a 500 W Xe lamp (Ushio UXL-500SX) equipped with filters to produce visible-light in the range of (390 < λ \leq 750 nm at 31 mW/cm²) for a predetermined time at room temperature, in the same manner as reported in a previous study.⁴⁻⁵ The amount of product obtained was determined from gas chromatography (Shimadzu, GC-14A) and ion-exchange chromatography (Dionex, ICS-2000) measurements. More than three runs were performed to obtain average values.

Isotope analysis

Isotope experiments for Z-schematic CO₂ reduction were conducted using ¹³CO₂ (99

at% ^{13}C , ISOTECH) and H_2^{18}O (≥ 98 at% ^{18}O , Taiyo Nippon Sanso). The obtained $\text{H}^{13}\text{COO}^-$ was analyzed using an ion chromatograph interfaced with a time-of-flight mass spectrometer (IC-TOFMS; JEOL JMS-T100LP).⁶ ^{13}CO and $^{18}\text{O}_2$ obtained by catalytic reaction using $^{13}\text{CO}_2$ and H_2^{18}O , respectively, were detected using gas chromatography-mass spectrometry (GC-MS; 6890 and 1973, Agilent Technologies, Inc.).⁶

Z-schematic photocatalytic CO_2 reduction by CO_2 flow system

To confirm O_2 generation, Z-schematic CO_2 reduction was conducted using a batch-type cell under CO_2 gas flow according to a previously reported method.⁷⁻⁸ $[\text{Ru}(\text{dpbpy})]/(\text{CuGa})_{0.3}\text{Zn}_{1.4}\text{S}_2$ (0.4 g) and BiVO_4 (0.2 g) photocatalysts were dispersed in $0.25 \text{ mol L}^{-1} \text{ NaHCO}_3$ and $0.02 \text{ mmol L}^{-1} [\text{Co}(\text{tpy})_2]^{2+}$ aqueous solution (150 mL) in a top irradiation cell with a Pyrex window. 1 atm of CO_2 gas (99.995%) was bubbled into the suspension at a flow rate of ca. 15 mL min^{-1} . The light source was a 300 W Xe-lamp with cut-off filters ($\lambda > 420 \text{ nm}$). The measurement was conducted after pre-irradiation. Products in the gas and liquid phases were analyzed using a gas chromatography (Shimadzu, GC-8A, MS-5A, thermal conductivity detector, Ar carrier for H_2 and O_2 ; GC-8A, MS-13X, flame ionization detector with a methanizer, N_2 carrier for CO) and ion-exchange chromatography (Dionex, ICS-2000), respectively.

Results

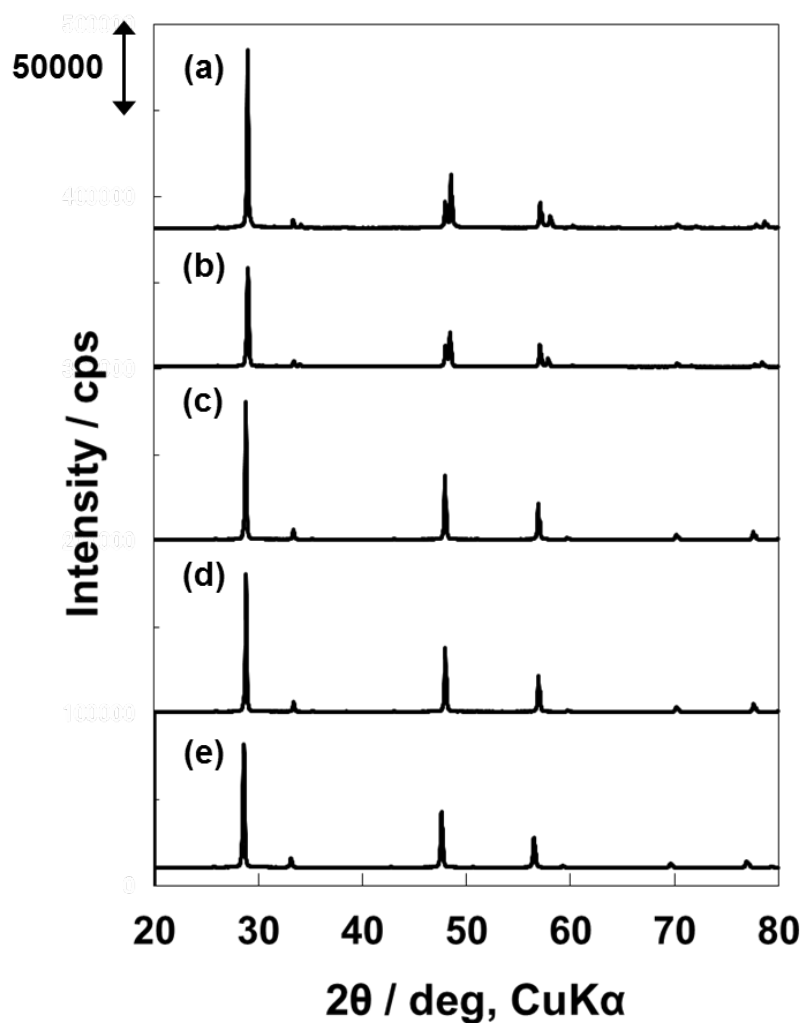


Fig. S1 XRD patterns of $(\text{CuGa})_{1-x}\text{Zn}_{2x}\text{S}_2$ prepared by solid-state reaction at 1073 K; x = (a) 0, (b) 0.2, (c) 0.5, (d) 0.7, and (e) 0.9. 10% excess Ga_2S_3 was added to the starting materials for all samples during synthesis according to the previously reported method.¹

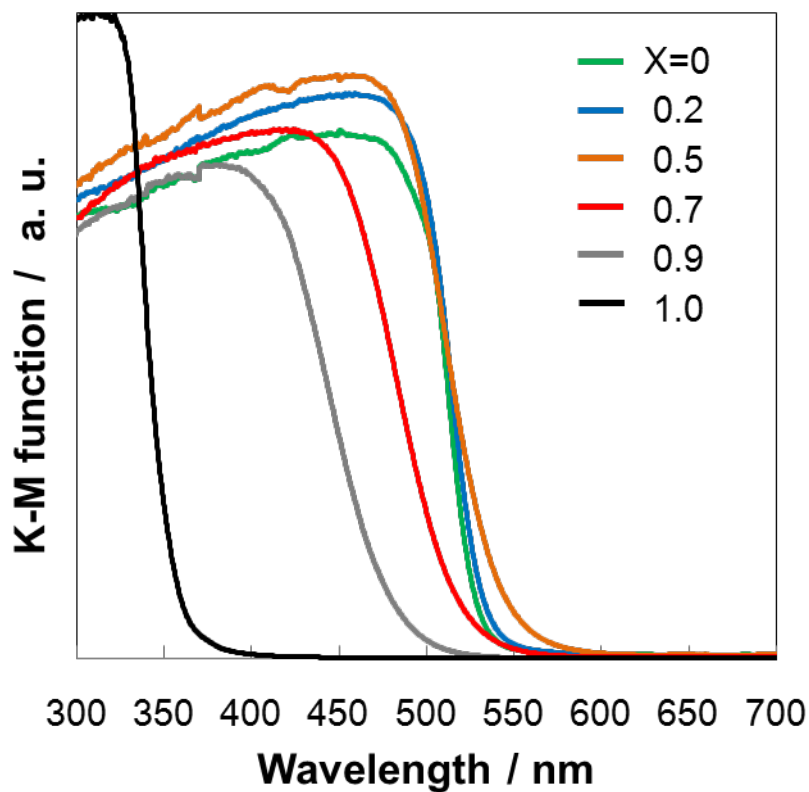


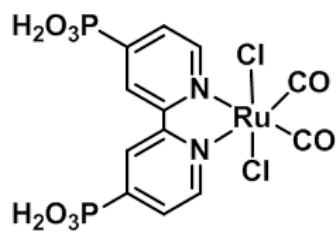
Fig. S2 UV-vis diffuse reflectance spectra of various $(\text{CuGa})_{1-x}\text{Zn}_{2x}\text{S}_2$. Diffuse reflectance spectra were obtained with a UV-vis-NIR spectrometer (JASCO, V-780) equipped with an integrating sphere and were converted from reflection to absorbance by the Kubelka-Munk method.

Table S1 Band gaps (BGs) of various $(\text{CuGa})_{1-x}\text{Zn}_{2x}\text{S}_2$ estimated from UV-vis diffuse reflectance spectra

x	Chemical composition	Crystal phase	BG (eV)
0	CuGaS_2	chalcopyrite	2.33
0.2	$(\text{CuGa})_{0.8}\text{Zn}_{0.4}\text{S}_2$	chalcopyrite	2.30
0.5	$(\text{CuGa})_{0.5}\text{ZnS}_2$	zincblende	2.24
0.7	$(\text{CuGa})_{0.3}\text{Zn}_{1.4}\text{S}_2$	zincblende	2.36
0.9	$(\text{CuGa})_{0.1}\text{Zn}_{1.8}\text{S}_2$	zincblende	2.54
1.0 ^a	ZnS	zincblende	3.50

^a Quoted from previous report⁵

Table S2 Structure of metal-complex [Ru(dpbbpy)] and amount of [Ru(dpbbpy)] adsorbed onto $(\text{CuGa})_{1-x}\text{Zn}_{2x}\text{S}_2$



[Ru(dpbbpy)]

x in $(\text{CuGa})_{1-x}\text{Zn}_{2x}\text{S}_2$	[Ru(dpbbpy)] content (wt%)
0.0	0.08
0.2	0.08
0.5	0.06
0.7	0.03
0.9	0.03

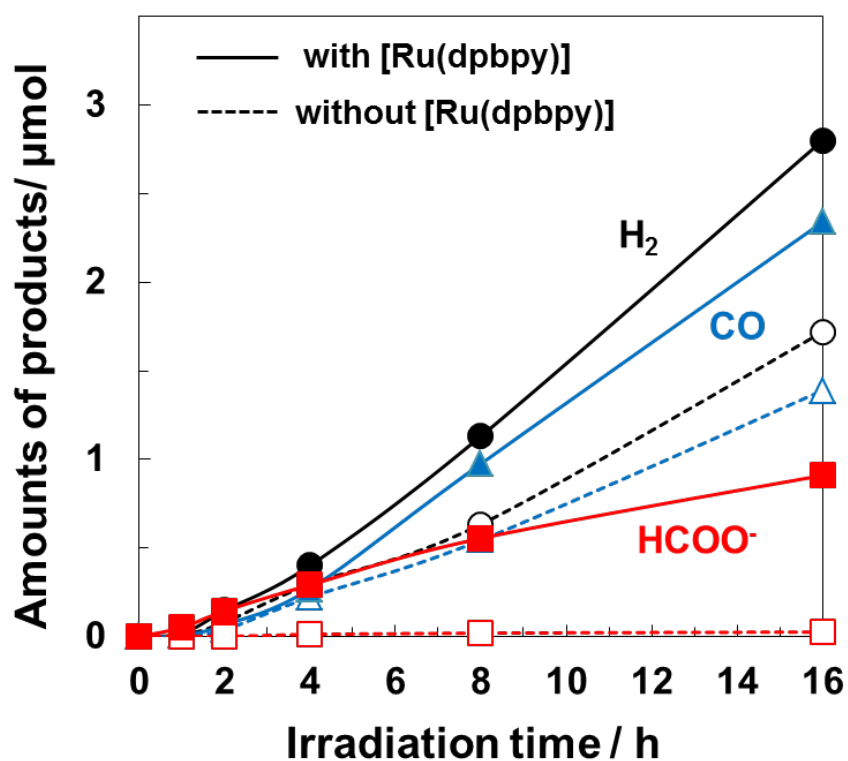


Fig. S3 Effect on Ru-complex catalyst using $(\text{CuGa})_{0.3}\text{Zn}_{1.4}\text{S}_2$ photocatalyst for Z-schematic CO_2 reduction in aqueous solution under visible light irradiation.

Photocatalyst: 10.7 mg $[\text{Ru}(\text{dpbpy})]$ (0.03 wt%)/ $(\text{CuGa})_{0.3}\text{Zn}_{1.4}\text{S}_2$ or $(\text{CuGa})_{0.3}\text{Zn}_{1.4}\text{S}_2$, 5.3 mg BiVO_4 ; reactant solution: 0.02 mmol L^{-1} $[(\text{Co}(\text{tpy})_2)^{2+}]$ containing 0.25 mol L^{-1} NaHCO_3 aqueous solution (4 mL); light source: 500 W Xe lamp with a filter ($390 < \lambda \leq 750 \text{ nm}$); reactor: Pyrex test tube (8 mL).

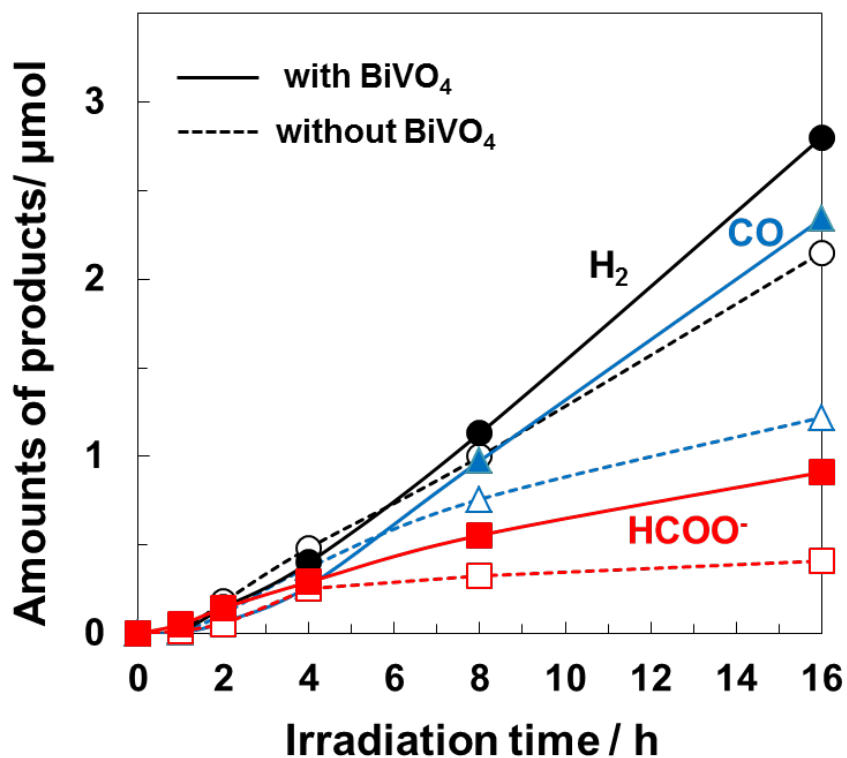


Fig. S4 Effect of BiVO₄ on Z-schematic CO₂ reduction in aqueous solution under visible light irradiation. Photocatalyst: 10.7 mg [Ru(dpby)] (0.03 wt%)/(CuGa)_{0.3}Zn_{1.4}S₂ and/or 5.3 mg BiVO₄; reactant solution: 0.02 mmol L⁻¹ [(Co(tpy)₂)²⁺ containing 0.25 mol L⁻¹ NaHCO₃ aqueous solution (4 mL); light source: 500 W Xe lamp with a filter (390 < λ ≤ 750 nm); reactor: Pyrex test tube (8 mL).

Table S3 Z-schematic CO₂ reduction using Ru-complex ([Ru(dpbpy)]/(CuGa)_{0.5}ZnS₂ hybrid CO₂-reduction photocatalyst and BiVO₄ O₂-evolving photocatalyst containing 0.02 mmol L⁻¹ [Co(tpy)₂]²⁺ in various aqueous solutions under visible light irradiation^a

Entry	[Ru(dpbpy)] content (wt%)	Reactant aqueous solution			Amount of products (μmol)		
		Electrolyte (0.1 mol L ⁻¹)	pH ^b	[Co(tpy) ₂] ²⁺ content (mmol L ⁻¹)	H ₂	CO (TON) ^c	HCOO ⁻ (TON) ^c
S1	0.00	none	4.3	0.02	1.37	0.20	0.03
S2	0.06	none	4.3	0.02	0.71	0.16 (0)	0.03(0)
S3	0.06	none	4.3	0.00	1.45	0.01	0.00
S4	0.00	K ₂ HPO ₄ -KH ₂ PO ₄ ^d	6.3	0.02	0.46	0.23	0.04
S5	0.06	K ₂ HPO ₄ -KH ₂ PO ₄ ^d	6.3	0.02	0.44	0.23 (0)	0.06 (1)
S6	0.00	K ₂ SO ₄	4.8	0.02	0.62	0.16	0.03
S7	0.06	K ₂ SO ₄	4.8	0.02	1.03	0.16 (0)	0.05 (1)
S8	0.00	NaHCO ₃	6.8	0.02	1.51	1.03	0.04
S9	0.06	NaHCO ₃	6.8	0.02	1.14	1.12 (5)	0.20 (19)
S10	0.06	NaHCO ₃	6.8	0.00	1.66	0.15	0.14
S11	0.00	KHCO ₃	6.9	0.02	2.04	1.17	0.04
S12	0.06	KHCO ₃	6.9	0.02	1.31	0.97 (0)	0.20 (19)
S13	0.00	Na ₂ CO ₃	7.1	0.02	2.75	0.98	0.05
S14	0.06	Na ₂ CO ₃	7.1	0.02	1.60	0.74	0.10 (3)

^a Photocatalyst: 8 mg each; reactant solution: 4 mL; light source: 500 W Xe lamp with a filter (390 < λ ≤ 750 nm) for 16 h, reactor: Pyrex test tube (8 mL).

^b After CO₂ bubbling for 10 min.

^c Turnover numbers (TONs) were calculated based on the amount of [Ru(dpbpy)] after detection of the HCOOH or CO amount without [Ru(dpbpy)].

^d Concentration 50 mmol L⁻¹ each.

Table S4 Z-schematic CO₂ reduction using Ru-complex ([Ru(dpbpy)]/(CuGa)_{0.3}Zn_{1.4}S₂ hybrid CO₂-reduction photocatalyst and BiVO₄ O₂-evolving photocatalyst containing 0.02 mmol L⁻¹ mediator in 0.25 mol L⁻¹ NaHCO₃ aqueous solution electron mediator under visible light irradiation ^a

Entry	Electron mediator	[Ru(dpbpy)] content (wt%)	Amount of products (μmol)		
			H ₂	CO (TON) ^b	HCOO ⁻ (TON) ^b
S1	none	0.00	0.19	0.01	0.01
S2	none	0.03	0.66 (80)	0.13(22)	0.27(45)
S3	[Co(bpy) ₃] ²⁺	0.00	0.62	0.29	0.04
S4	[Co(bpy) ₃] ²⁺	0.03	0.80 (30)	0.19 (0)	0.06 (4)
S5	[Co(phen) ₃] ²⁺	0.00	0.02	0.01	0.01
S6	[Co(phen) ₃] ²⁺	0.03	0.07 (9)	0.04 (4)	0.08 (16)
S7	[Co(tpy) ₂] ²⁺	0.00	1.72	1.39	0.04
S8	[Co(tpy) ₂] ²⁺	0.03	2.80 (184)	2.34 (161)	0.91 (147)

^a Photocatalyst: CO₂ reduction photocatalyst 10.7 mg/BiVO₄ 5.3 mg; reactant solution: 4 mL; light source: 500 W Xe lamp with a filter (390 < λ ≤ 750 nm) for 16 h, reactor: Pyrex test tube (8 mL).

^b TON calculated based on the amount of [Ru(dpbpy)] after detection of the HCOOH or CO amount without [Ru(dpbpy)].

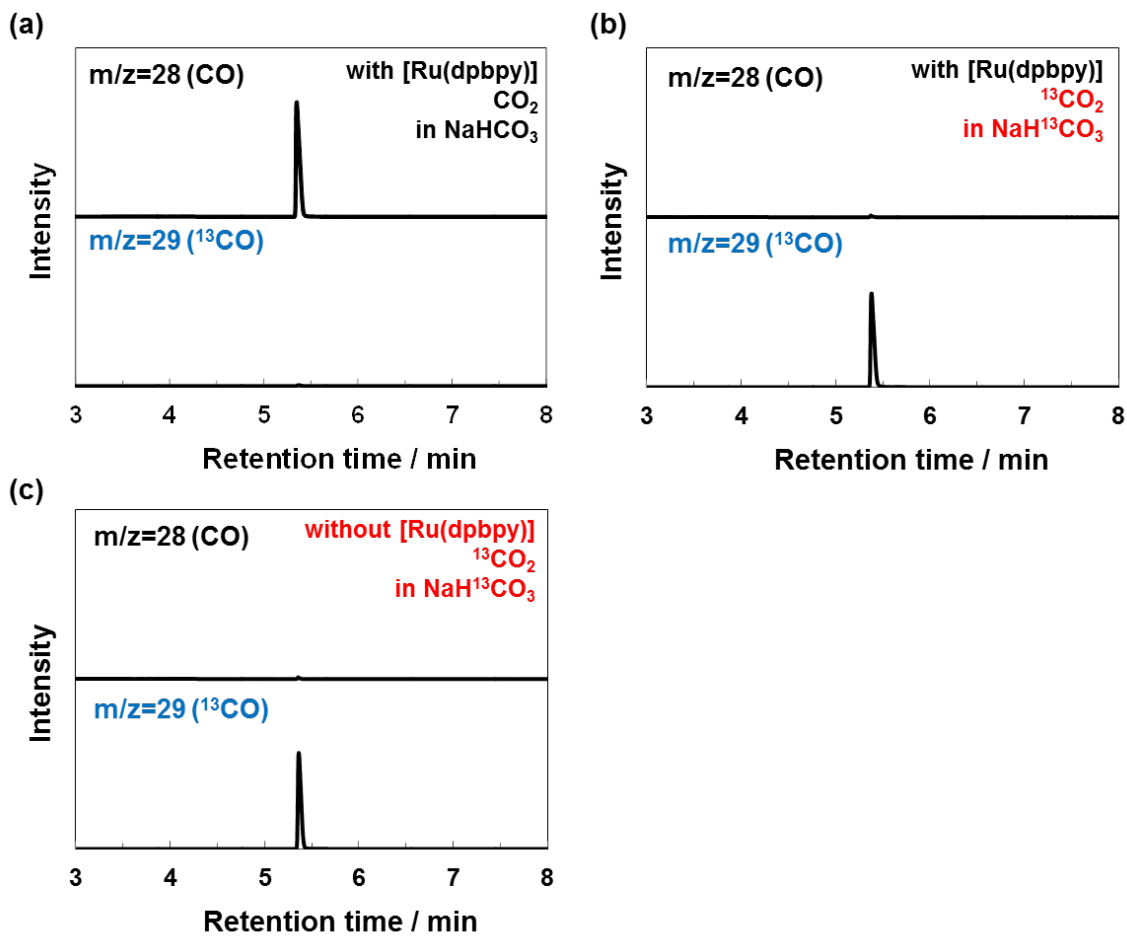


Fig. S5 GC-MS chromatograms of the gas products for (a) CO_2 and (b) $^{13}\text{CO}_2$ photoreduction using the $[\text{Ru}(\text{dpbbpy})]/(\text{CuGa})_{0.3}\text{Zn}_{1.4}\text{S}_2$ - $([\text{Co}(\text{tpy})_2]^{2+})$ - (BiVO_4) system, and (c) $^{13}\text{CO}_2$ reduction using $(\text{CuGa})_{0.3}\text{Zn}_{1.4}\text{S}_2$ - $([\text{Co}(\text{tpy})_2]^{2+})$ - (BiVO_4) system (without $[\text{Ru}(\text{dpbbpy})]$) (detected $m/z=28$ for ^{12}CO and $m/z=29$ for ^{13}CO). Photocatalyst: 10.7 mg of $[\text{Ru}(\text{dpbbpy})]/(\text{CuGa})_{0.3}\text{Zn}_{1.4}\text{S}_2$ and 5.3 mg of BiVO_4 ; solution: 0.02 mmol L^{-1} $([\text{Co}(\text{tpy})_2]^{2+})$ containing 0.25 mmol L^{-1} NaHCO_3 or $\text{NaH}^{13}\text{CO}_3$ aqueous solution (4 mL); reactor: Pyrex glass test tube (8 mL); light source: 500 W Xe lamp ($410 \leq \lambda \leq 750$ nm); irradiation time: 21 h.

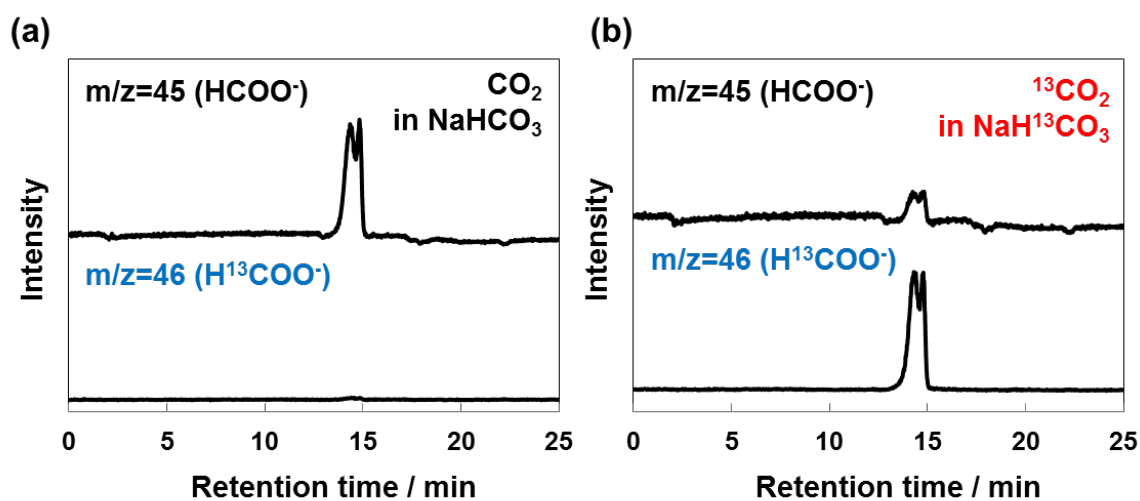


Fig. S6 IC-TOFMS chromatograms of the products for (a) CO_2 and (b) $^{13}\text{CO}_2$ photoreduction using the $[\text{Ru}(\text{dpbpy})]/(\text{CuGa})_{0.3}\text{Zn}_{1.4}\text{S}_2$ - $[\text{Co}(\text{tpy})_2]^{2+}$ - (BiVO_4) system (detected $m/z=45$ for $\text{H}^{12}\text{COO}^-$ and $m/z=46$ for $\text{H}^{13}\text{COO}^-$). Photocatalyst: $[\text{Ru}(\text{dpbpy})]$ (0.03 wt%)/ $(\text{CuGa})_{0.3}\text{Zn}_{1.4}\text{S}_2$ (10.7 mg) and BiVO_4 (5.3 mg); solution: 0.02 mmol L^{-1} $[\text{Co}(\text{tpy})_2]^{2+}$ containing 0.25 mmol L^{-1} NaHCO_3 or $\text{NaH}^{13}\text{CO}_3$ aqueous solution (4 mL); reactor: Pyrex glass test tube (8 mL); light source: 500 W Xe lamp ($410 \leq \lambda \leq 750 \text{ nm}$); irradiation time: 21 h.

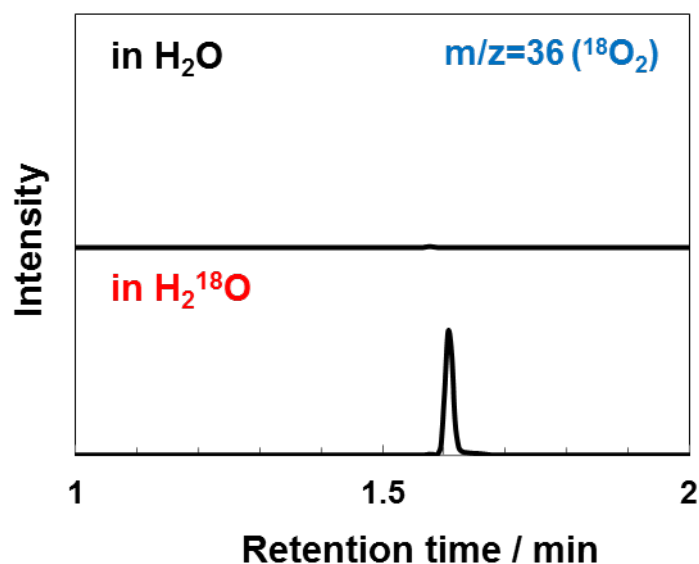


Fig. S7 GC-MS chromatograms of $^{18}\text{O}_2$ products ($m/z=36$) for CO_2 photoreduction over a Z-schematic photocatalyst system consisting of $[\text{Ru}(\text{dpbpy})]/(\text{CuGa})_{0.3}\text{Zn}_{1.4}\text{S}_2$ and BiVO_4 photocatalysts, and $[\text{Co}(\text{tpy})_2]^{3+/2+}$ electron mediator with 0.25 M NaHCO_3 aqueous solution containing (a) H_2O and (b) H_2^{18}O . Photocatalyst: 8 mg of $[\text{Ru}(\text{dpbpy})]/(\text{CuGa})_{0.3}\text{Zn}_{1.4}\text{S}_2$ and 8 mg of BiVO_4 ; solution: 0.02 mmol L^{-1} $[(\text{Co}(\text{tpy})_2)]^{2+}$ containing 0.25 mmol L^{-1} of NaHCO_3 aqueous solution (4 mL); reactor: Pyrex glass test tube (8 mL); light source: 500 W Xe lamp ($410 \leq \lambda \leq 750 \text{ nm}$); irradiation time: 22 h.

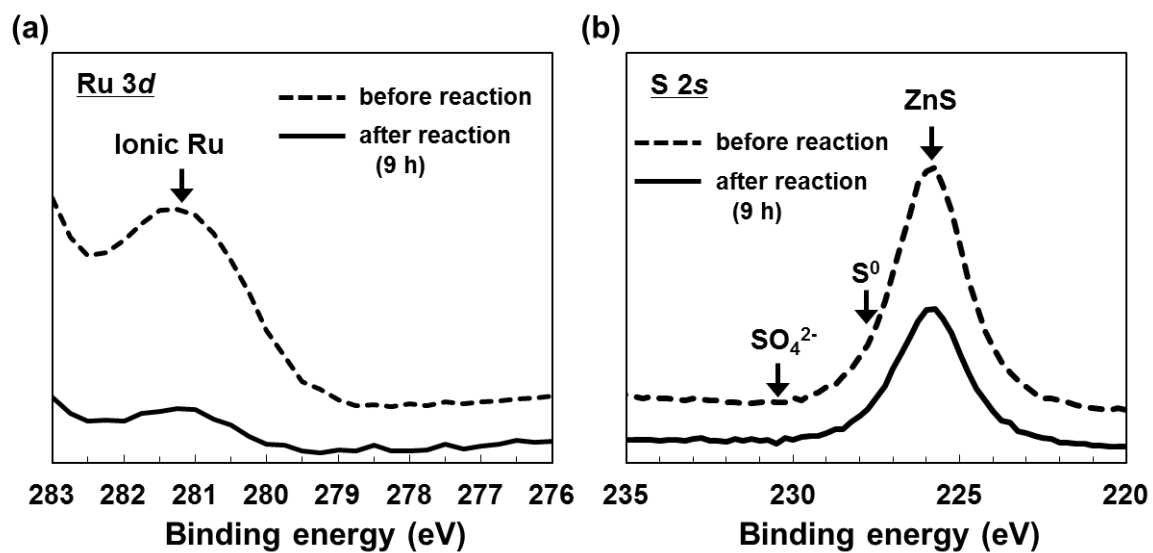


Fig. S8 XPS (a) Ru 3d and (b) S 2s spectra before ([Ru(dpby)]/(CuGa)_{0.3}Zn_{1.4}S₂) and after 9 h Z-schematic ([Ru(dpby)]/(CuGa)_{0.3}Zn_{1.4}S₂ and BiVO₄) photocatalytic reaction (evaluation of Figure 1(b)).

Table S5. Atomic ratio evaluated from XPS data for Z-schematic CO₂ reduction activity of ([Ru(dpbpy)]/(CuGa)_{0.3}Zn_{1.4}S₂)-([Co(tpy)₂]^{3+/2+})-(BiVO₄) system before and after photocatalytic reaction for 9 h (evaluation of Figure 1(b))

Atomic ratio			
Before reaction		After reaction	
Ru/S	Ru/Zn	Ru/S	Ru/Zn
0.0032	0.0044	0.0016	0.0019

References

1. Kato, T.; Hakari, Y.; Ikeda, S.; Jia, Q.; Iwase, A.; Kudo, A. *J. Phys. Chem. Lett.* **2015**, *6*, 1042-1047.
2. Suzuki, T. M.; Iwase, A.; Tanaka, H.; Sato, S.; Kudo, A.; Morikawa, T. *J. Mater. Chem. A* **2015**, *3*, 13283-13290.
3. Anderson, P. A.; Deacon, G. B.; Haarmann, K. H.; Keene, F. R.; Meyer, T. J.; Reitsma, D. A.; Skelton, B. W.; Strouse, G. F.; Thomas, N. C.; Treadway, J. A.; White, A. H. *Inorg. Chem.* **1995**, *34*, 6145-6157.
4. Suzuki, T. M.; Tanaka, H.; Morikawa, T.; Iwaki, M.; Sato, S.; Saeki, S.; Inoue, M.; Kajino, T.; Motohiro, T. *Chem. Commun.* **2011**, *47*, 8673-8675.
5. Suzuki, T. M.; Takayama, T.; Sato, S.; Iwase, A.; Kudo, A.; Morikawa, T. *Appl. Catal., B* **2018**, *224*, 572-578.
6. Sato, S.; Arai, T.; Morikawa, T.; Uemura, K.; Suzuki, T. M.; Tanaka, H.; Kajino, T. *J. Am. Chem. Soc.* **2011**, *133*, 15240-15243.
7. Iwase, A.; Yoshino, S.; Takayama, T.; Ng, Y. H.; Amal, R.; Kudo, A. *J. Am. Chem. Soc.* **2016**, *138*, 10260-10264.
8. Takayama, T.; Sato, K.; Fujimura, T.; Kojima, Y.; Iwase, A.; Kudo, A. *Faraday Discuss.* **2017**, *198*, 397-407.