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

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Visible-light-driven Z-schematic CO_2 reduction using H_2O as an electron donor was achieved using a simple mixture of a metalsulfide/molecular hybrid photocatalyst for CO_2 reduction, a water oxidation photocatalyst and a redox-shuttle electron mediator. This is the first demonstration of a highly selective particulate CO_2 reduction system accompanying O_2 generation utilizing a semiconductor/ molecular hybrid photocatalyst.

Photocatalytic CO₂ reduction into useful energy-rich chemicals using water as an electron donor with a particulate system has attracted attention for sustainable and scalable artificial photosynthesis to mitigate global warming and generate useful fuels.¹⁻⁵ Particulate systems are recognized as cost-effective and could be the ultimate tool for CO₂ fixation and solar fuel generation.^{6,7} A photocatalytic Z-scheme (or two-step photoexcitation) system that connects photocatalysts for CO₂ reduction with H₂O oxidation is considered to be a promising approach; however, few particulate Z-scheme systems for CO₂ reduction using water as an electron donor have been reported. Visible-light-driven conversion of CO2 into CO over a combined system of CoO_r-loaded BiVO₄ and metal sulfides with a reduced graphene oxide electron mediator has yet to reach 1% CO selectivity. This is due to competitive H₂ generation and low CO₂ selectivity at metal sulfide surfaces.^{8,9}

A hybrid catalyst of a semiconductor^{10–12} linked with a metal-complex catalyst^{13–15} is promising for visible-light-driven selective CO_2 reduction with regard to high selectivity, depending on the selective coordination of CO_2 molecules to the metal centers of the complexes.^{13,16–22} It is essential that photoexcited electrons in the conduction band (CB) of the semiconductor

transfer to the metal-complex catalyst within the picosecond region, which leads to two-electron reduction of CO₂ at the complex.²³ We previously demonstrated solar formate generation from CO₂ and H₂O using a photocathode of a Ru-complex catalyst linked with Zn-doped InP or N,Zn-codoped Fe2O3 combined with TiO_2 or $SrTiO_{3-x}$ photoanodes, ^{24–26} and confirmed the potential of the system with a solar-to-chemical conversion efficiency of 4.6% over a monolithic Ru-complex-polymer/Si-Ge/ IrO_x electrode.²⁷ Ishitani and colleagues reported photoelectrochemical CO₂ reduction to CO via H₂O oxidation using a photocathode composed of a Ru(II)-Re(I) supramolecular metal complex immobilized on a NiO or CuGaO₂ semiconductor.^{28,29} In contrast, a particulate system for Z-schematic CO_2 reduction using a metal complex combined with a H₂O oxidation reaction has not yet been demonstrated. Efficient electron transfer from the H₂O oxidation site to the CO₂ reduction site without degradation of the catalytic activity for both reactions should be implemented.

To realize Z-schematic CO2 reduction with a particulate system, we focused our attention on metal sulfides as the CO₂ reduction semiconductor because they generally possess long photoexcited carrier lifetimes and narrow band gaps (BGs) originating from the S 3p state, which allows absorption of a substantial amount of visible light. Reisner et al. reported photocatalytic conversion of CO_2 into CO in water with >90% selectivity over a Ni-cyclam catalyst anchored with CdS.¹⁹ We reported CO₂ photoconversion into HCOOH over ZnS:Ni and $(AgIn)_{0.22}Zn_{1.56}S_2$ linked with a Ru-bipyridine catalyst [Ru(4,4'diphosphonate-2,2'-bipyridine)(CO)2Cl2] ([Ru(dpbpy)]).30 These Cd- and Zn-based sulfides are considered to be beneficial when combined with molecular catalysts because of their negative CB minimum (E_{CBM}) positions originating from Cd 5s5p and Zn 4s4p orbitals, respectively, which facilitate fast electron transfer from the CB in a photoexcited state to a metal-complex catalyst due to the greater energy difference (ΔG) between the E_{CBM} and CO2 reduction potential of the metal-complex, which promotes the CO2 reduction reaction. However, these systems conducted half reactions that required triethanolamine as a strong

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[†] Electronic supplementary information (ESI) available: Experimental details, XRD patterns, UV-vis diffuse reflectance spectra, Z-schematic CO₂ reduction using a hybrid photocatalyst, BiVO₄ and a Co-complex, GC-MS chromatograms, IC-TOFMS chromatograms, and XPS spectra. See DOI: 10.1039/c8cc05505j



Fig. 1 (a) Visible-light-driven Z-schematic system for CO₂ reduction consisting of particulate [Ru(dpbpy)] modified (CuGa)_{1-x}Zn_{2x}S₂ hybrid photocatalysts, a BiVO₄ photocatalyst, and a [Co(tpy)₂]^{3+/2+} redox shuttle electron mediator. (b) Z-schematic CO₂ reduction in an aqueous solution with a CO₂ flow system. Conditions: [Ru(dpbpy)]/(CuGa)_{0.3}Zn_{1.4}S₂ (0.4 g) and BiVO₄ (0.2 g); 0.02 mM [Co(tpy)₂]²⁺ containing 0.1 M NaHCO₃ aqueous solution (150 mL) and visible-light ($\lambda > 420$ nm).

sacrificial electron donor. Here, we demonstrate the first particulatebased visible-light-driven Z-scheme system that harmonizes both reactions of CO_2 reduction and H_2O oxidation over a hybrid photocatalyst of a semiconductor/molecular-catalyst.

Fig. 1(a) shows an illustration of the Z-schematic system for photoconversion of CO₂ to CO and HCOO⁻ over [Ru(dpbpy)]modified (CuGa)_{1-x}Zn_{2x}S₂ as a CO₂ reduction hybrid photocatalyst, $[Co(tpy)_2]^{3+/2+}$ (tpy: 2,2':6,2"-terpyridine) as an electron mediator, and BiVO4 as a water oxidation photocatalyst. Fig. 1(b) shows that the simple mixture in an aqueous solution produced CO and HCOO⁻ at almost linear rates together with O₂ generation under visible light irradiation after hours of preirradiation in a CO₂ flow reactor,^{8,9} *i.e.*, the Z-scheme reaction. Although BiVO₄ can photogenerate O_2 , E_{CBM} for BiVO₄ is located at an unfavorably deep position for the reduction reaction of CO_2 and protons.^{8,31} Thus, the CO₂ reduction reaction could occur at the [Ru(dpbpy)]/(CuGa)_{0.3}Zn_{1.4}S₂ photocatalyst, which suggests a Z-scheme mechanism with H₂O as an electron donor, which is discussed later. Although H₂ evolution by proton reduction also proceeded, the CO₂ reduction selectivity to total reductive products (CO, HCOO⁻, H₂) for 9 h reached 64 mol%, significantly higher than the ca. 1% of previous non-molecular particulate Z-scheme systems.^{8,9} The modification of [Ru(dpbpy)] led to the production of HCOO⁻ and the turnover number (TON) of HCOO⁻ evolution was calculated to be 17, assuming that all [Ru(dpbpy)] remained on $(CuGa)_{1-x}Zn_{2x}S_2$ during the photocatalytic reaction.

The key to designing the visible-light-driven Z-schematic system is the hybrid photocatalyst for CO₂ reduction. Thus, a sufficient energy difference ΔG to facilitate fast electron transfer from the semiconductor to the Ru-complex catalyst plays a decisive role.^{16,23} Electron transfer from the water oxidation photocatalyst to the CO₂ reduction photocatalyst is also indispensable. First, the optimal combination of Ru-complex and semiconductor was investigated. A solid solution of CuGaS₂ and ZnS $((CuGa)_{1-x}Zn_{2x}S_2)^{32}$ was selected as the semiconductor for the hybrid photocatalyst because their BG and band position, particularly E_{CBM} , are dominated by Zn 4s4p + Ga 4s4p and are tunable by changing x. This could be beneficial to control the electron transfer rate from the CB to the molecular catalysts. XRD measurements of $(CuGa)_{1-x}Zn_{2x}S_2$ synthesized by a solid-state reaction³² revealed that a single chalcopyrite phase $(x \le 0.2)$ or zincblende structure $(x \ge 0.5)$ was obtained (Fig. S1 and Table S1, ESI⁺). The BG of CuGaS₂ and (CuGa)_{1-x}Zn_{2x}S₂ (x < 1.0) was within the range of 2.24–2.54 eV, which enables absorption of visible light (Fig. S2 and Table S1, ESI[†]). Hybrid catalysts of 0.03–0.08 wt% [Ru(dpbpy)] with the phosphonate ligand (CO₂ reduction potential of *ca.* -1.0 V vs. NHE)³⁰ linked with $(CuGa)_{1-x}Zn_{2x}S_2$ were prepared using an adsorption method³⁰ (Table S2, ESI[†]).

Typical Z-schematic CO₂ reduction was performed by using $[Ru(dpbpy)]/(CuGa)_{1-x}Zn_{2x}S_2$ and BiVO₄ in a test tube filled with [Co(tpy)₂]²⁺ containing aqueous NaHCO₃ solution saturated with CO₂ under visible light irradiation for 16 h. This method is useful to measure the tendency of the sample-dependent product for multiple runs.³³ Fig. 2(a) shows that the CO₂ reduction activity was significantly dependent on the composition of $(CuGa)_{1-x}Zn_{2x}S_2$. For bare $(CuGa)_{1-x}Zn_{2x}S_2$, the amount of CO produced increased with x within the range of $0.0 \le x \le 0.5$, which could be explained by the more negative E_{CBM} and narrower BG (Fig. 2(b) and Fig. S2, ESI⁺), which led to a more efficient electron transfer toward a higher CO₂ reduction rate. Further increase in x ($x \ge 0.7$) decreased CO evolution due to a reduced amount of absorbed photons with a wider BG (\geq 2.36 eV). H₂ evolution induced by the competitive proton reduction increased with *x* within the range of $0.5 \le x \le 0.7$. Replacement of the bare $(CuGa)_{1-x}Zn_{2x}S_2$ with the $[Ru(dpbpy)]/(CuGa)_{1-x}Zn_{2x}S_2$ hybrid photocatalyst not only enhanced the CO formation rate but also induced formate production; [Ru(dpbpy)] is known as a catalyst for the production of formate and CO.^{30,34} [Ru(dpbpy)]/ $(CuGa)_{1-x}Zn_{2x}S_2$ at x = 0.7 showed the highest CO₂ reduction activity for CO and HCOO⁻ production, with TONs (based on product generated by the [Ru(dpbpy)] catalyst) of 214 and 70 after 16 h of reaction, respectively. In the Z-schematic water splitting system composed of metallic Ru-loaded $(CuGa)_{1-x}Zn_{2x}S_2$ for H₂ generation, CoO_x-loaded BiVO₄ for water oxidation and $[Co(tpy)_2]^{2+/3+}$ for electron mediation, the highest water splitting rate was reported at x = 0.2³² In contrast, [Ru(dpbpy)]/ $(CuGa)_{0.8}Zn_{0.4}S_2$ (x = 0.2) showed a negligibly small CO₂ reduction activity. These results suggest that more negative E_{CBM} (with greater x) improves the electron transfer rate for CO₂ reduction at [Ru(dpbpy)].^{16,17,23,30} The CO₂ reduction activity of the hybrid catalyst is in a trade-off relationship between



Fig. 2 (a) Z-Schematic CO₂ reduction using the $(CuGa)_{1-x}Zn_{2x}S_2$ or $([Ru(dpbpy)]/(CuGa)_{1-x}Zn_{2x}S_2)-([Co(tpy)_2]^{3+/2+})-(BiVO_4)$ systems under visible-light irradiation using the test tube method. Conditions: 8 mg of each photocatalyst; 0.02 mM $[Co(tpy)_2]^{2+}$ containing 0.1 M NaHCO₃ aqueous solution (4 mL); visible-light (390 < $\lambda \le$ 750 nm) for 16 h. (b) Estimated band structures of $(CuGa)_{1-x}Zn_{2x}S_2$.

the negative E_{CBM} to facilitate electron transfer to the complex catalyst and the BG to determine the number of photons absorbed; therefore, overall matching in the electron transfer process was successful in the present Z-schematic ([Ru(dpbpy)]/ (CuGa)_{1-x}Zn_{2x}S_2)-([Co(tpy)_2]^{3+/2+})-(BiVO_4) system.

Experimental data used to determine the effective components for the Z-schematic CO_2 reduction are summarized in Table 1. A mixture of BiVO₄ and $[Co(tpy)_2]^{2+}$ produced neither H₂, nor CO, nor $HCOO^-$ due to the unfavorably deep E_{CBM} position (entry 1). The addition of (CuGa)_{0.3}Zn_{1.4}S₂ produced H₂ and CO (entry 2), and [Ru(dpbpy)] modification of (CuGa)_{0.3}Zn_{1.4}S₂ induced HCOO⁻ formation and further improved CO production by the effect of [Ru(dpbpy)] (entry 3, Fig. S3, ESI⁺). The absence of [Co(tpy)₂]²⁺ largely decreased CO and HCOO⁻ generation (entry 4), and removal of BiVO₄ resulted in the termination of both CO and HCOO⁻ formation (entry 5, Fig. S4, ESI[†]). These results indicate that BiVO₄ is necessary for high CO₂ reduction activity, and the presence of $[Co(tpy)_2]^{2+}$ is essential for a high CO and HCOO⁻ formation rate. The absence of NaHCO₃ decreased the formation of both CO and HCOO⁻ (entry 6), and the formation of CO and HCOO⁻ was negligible in the absence of $[Co(tpy)_2]^{2+}$ (entry 7). Among the aqueous electrolyte and Co-complexes, NaHCO₃ and $[Co(tpy)_2]^{2+}$ were evaluated to be the best for the CO₂ reduction selectivity and production rate, respectively (Tables S3 and S4, ESI⁺). It was also confirmed that no reaction occurred without irradiation (entry 8), and that the formation of CO and HCOO⁻ was negligibly small when Ar was bubbled in the solution (entry 9).

 $[Co(tpy)_2]^{2+}$ was reported to act as a $[Co(tpy)_2]^{3+/2+}$ redox shuttle electron mediator connecting two semiconductors for H₂ and O₂ generation in Z-scheme water splitting.³² As inferred from the mechanism of the IO_3^{-}/I^{-} shuttle redox mediator system,^{35,36} it is speculated that $[Co(tpy)_2]^{3+}$ may favorably adsorb onto BiVO₄, while $[Co(tpy)_2]^{2+}$ adsorbs onto $(CuGa)_{0.3}Zn_{1.4}S_2$, mediating electrons between them as a redox shuttle. $[Co(tpy)_2]^{2+}$ was reported to be an electrocatalyst for the reduction of CO₂ to CO in dimethylformamide/H₂O (90/10 v/v) when one terpyridine ligand was eliminated.^{37,38} However, the intrinsic potential for the reaction is too negative (-2.0 V vs. Fc/Fc⁺) compared to the E_{CBM} of $(CuGa)_{0.3}Zn_{1.4}S_2$; therefore, $[Co(tpy)_2]^{2+}$ is not a catalyst in the present case. $[Co(tpy)_2]^{2+}$ did not catalyze CO₂ reduction in an aqueous solution when electrically biased in the E_{CBM} region under visible light irradiation.

Isotope tracer analyses using ${}^{13}\text{CO}_2$ confirmed that the carbon source of evolved CO and HCOO⁻ was dissolved CO₂ (Fig. S5 and S6, ESI†). O₂ was also confirmed to originate from water using H₂¹⁸O (Fig. S7, ESI†), in which the total amount of ${}^{18}\text{O}_2$ and ${}^{16}\text{O}^{18}\text{O}$ was more than 85% of the total dioxygen detected.

Table 1Z-Schematic CO_2 reduction activity of the ([Ru(dpbpy)]/(CuGa)_{0.3}Zn_{1.4}S_2) - ([Co(tpy)_2]^{3+/2+}) - (BiVO_4)system under visible-light irradiation for 16 h^a

Entry	CO ₂ reduction photocatalyst		Mediator	O ₂ evolution photocatalyst	Salt			Amount of products (µmol)		
	$(CuGa)_{0.3}Zn_{1.4}S_2$	[Ru(dpbpy)]	$\overline{[Co(tpy)_2]^{2+}}$	BiVO ₄	NaHCO ₃	Gas	$h\nu$	H_2	СО	$HCOO^{-}$
1				-		CO_2		0.00	0.00	0.00
2				1		CO_2		1.82	0.69	0.02
3				1		CO_2		1.98	1.64	0.37
4				1		CO_2		1.53	0.10	0.10
5						CO_2		1.06	0.79	0.28
6				M		CO_2		3.59	0.56	0.18
7				M		CO_2		2.42	0.01	0.02
8				M		CO_2		0.00	0.00	0.00
9						Ar		0.96	0.01	0.01

^{*a*} Conditions: 8 mg of each photocatalyst; 0.02 mM $[Co(tpy)_2]^{2+}$ containing 0.1 M NaHCO₃ aqueous solution (4 mL); visible-light (390 < $\lambda \le$ 750 nm) for 16 h; Pyrex test tube.

These results explained that CO₂ was reduced to CO and HCOO⁻ using electrons extracted from H₂O molecules. The TON for O₂ evolution with the Co-complex was calculated to be 9 (9 h), which suggests that the Co-complex acted as an electron mediator. A slight deviation from stoichiometric O2 evolution (4-electron reaction) compared with half of the total of $CO + HCOO^{-} + H_2$ (2-electron reactions) in Fig. 1(b) was similarly observed in all-inorganic Z-scheme systems for CO₂ reduction.8,9 Self-photooxidation of (CuGa)1-xZn2xS2 could partially supply electrons for the CO₂ reduction reaction. Further investigations will clarify the overall electron/hole stoichiometry. X-ray photoelectron spectroscopy (XPS) measurements before and after the Z-scheme reaction (in Fig. 1(b)) revealed no change in the chemical state of Ru and sulfur ions (Fig. S8, ESI[†]). Half of the amount of [Ru(dpbpy)] was eliminated from the $(CuGa)_{1-x}Zn_{2x}S_2$ surface according to the change in the Ru/S and Ru/Zn ratios (Table S5, ESI⁺).

In conclusion, a visible-light-driven Z-schematic CO₂ reduction to CO and HCOO⁻ in an aqueous particulate suspension system was achieved using a simple mixture of $[Ru(dpbpy)]/(CuGa)_{1-x}Zn_{2x}S_2$ hybrid, $[Co(tpy)_2]^{2+}$ and BiVO₄. Adjustment of band alignment is essential to the Z-schematic CO₂ reduction reaction accompanying O₂ generation. The very high CO₂ reduction selectivity beyond 60% against competing H₂ generation strongly suggests that the particulate Z-schematic system is feasible to construct selective and efficient photocatalysts for CO₂ fixation and solar fuel generation.

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Conflicts of interest

There are no conflicts to declare.

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