

CO₂ Reduction Using Water as an Electron Donor over Heterogeneous Photocatalysts Aiming at Artificial Photosynthesis

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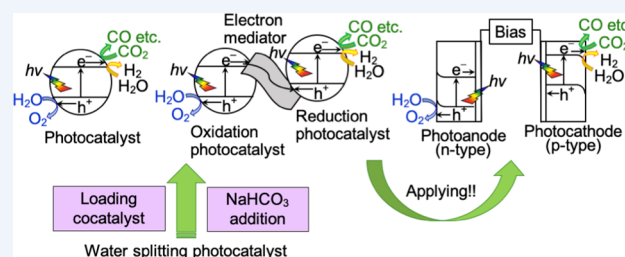
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CONSPECTUS: Photocatalytic and photoelectrochemical CO₂ reduction of artificial photosynthesis is a promising chemical process to solve resource, energy, and environmental problems. An advantage of artificial photosynthesis is that solar energy is converted to chemical products using abundant water as electron and proton sources. It can be operated under ambient temperature and pressure. Especially, photocatalytic CO₂ reduction employing a powdered material would be a low-cost and scalable system for practical use because of simplicity of the total system and simple mass-production of a photocatalyst material.

In this Account, single particulate photocatalysts, Z-scheme photocatalysts, and photoelectrodes are introduced for artificial photosynthetic CO₂ reduction. It is indispensable to use water as an electron donor (i.e., reasonable O₂ evolution) but not to use a sacrificial reagent of a strong electron donor, for achievement of the artificial photosynthetic CO₂ reduction accompanied by ΔG > 0. Confirmations of O₂ evolution, a ratio of reacted e⁻ to h⁺ estimated from obtained products, a turnover number, and a carbon source of a CO₂ reduction product are discussed as the key points for evaluation of photocatalytic and photoelectrochemical CO₂ reduction. Various metal oxide photocatalysts with wide band gaps have been developed for water splitting under UV light irradiation. However, these bare metal oxide photocatalysts without a cocatalyst do not show high photocatalytic CO₂ reduction activity in an aqueous solution. The issue comes from lack of a reaction site for CO₂ reduction and competitive reaction between water and CO₂ reduction. This raises a key issue to find a cocatalyst and optimize reaction conditions defining this research field. Loading a Ag cocatalyst as a CO₂ reduction site and NaHCO₃ addition for a smooth supply of hydrated CO₂ molecules as reactant are beneficial for efficient photocatalytic CO₂ reduction. Ag/BaLa₄Ti₄O₁₅ and Ag/NaTaO₃:Ba reduce CO₂ to CO as a main reduction reaction using water as an electron donor even in just water and an aqueous NaHCO₃ solution. A Rh–Ru cocatalyst on NaTaO₃:Sr gives CH₄ with 10% selectivity (Faradaic efficiency) based on the number of reacted electrons in the photocatalytic CO₂ reduction accompanied by O₂ evolution by water oxidation.

Visible-light-responsive photocatalyst systems are indispensable for efficient sunlight utilization. Z-scheme systems using CuGaS₂, (CuGa)_{1-x}Zn_{2x}S₂, CuGa_{1-x}In_xS₂, and SrTiO₃:Rh as CO₂-reducing photocatalyst, BiVO₄ as O₂-evolving photocatalyst, and reduced graphene oxide (RGO) and Co-complex as electron mediator or without an electron mediator are active for CO₂ reduction using water as an electron donor under visible light irradiation. These metal sulfide photocatalysts have the potential to take part in Z-scheme systems for artificial photosynthetic CO₂ reduction, even though their ability to extract electrons from water is insufficient. A photoelectrochemical system using a photocathode is also attractive for CO₂ reduction under visible light irradiation. For example, p-type CuGaS₂, (CuGa)_{1-x}Zn_{2x}S₂, Cu_{1-x}Ag_xGaS₂, and SrTiO₃:Rh function as photocathodes for CO₂ reduction under visible light irradiation. Moreover, introducing a conducting polymer as a hole transporter and surface modification with Ag and ZnS improve photoelectrochemical performance.



KEY REFERENCES

- Iizuka, K.; Wato, T.; Miseki, Y.; Saito, K.; Kudo, A. Photocatalytic Reduction of Carbon Dioxide over Ag Cocatalyst-Loaded ALa₄Ti₄O₁₅ (A = Ca, Sr, and Ba) Using Water as a Reducing Reagent. *J. Am. Chem. Soc.* 2011, 133, 20863–20868.¹ Ag-cocatalyst for an effective

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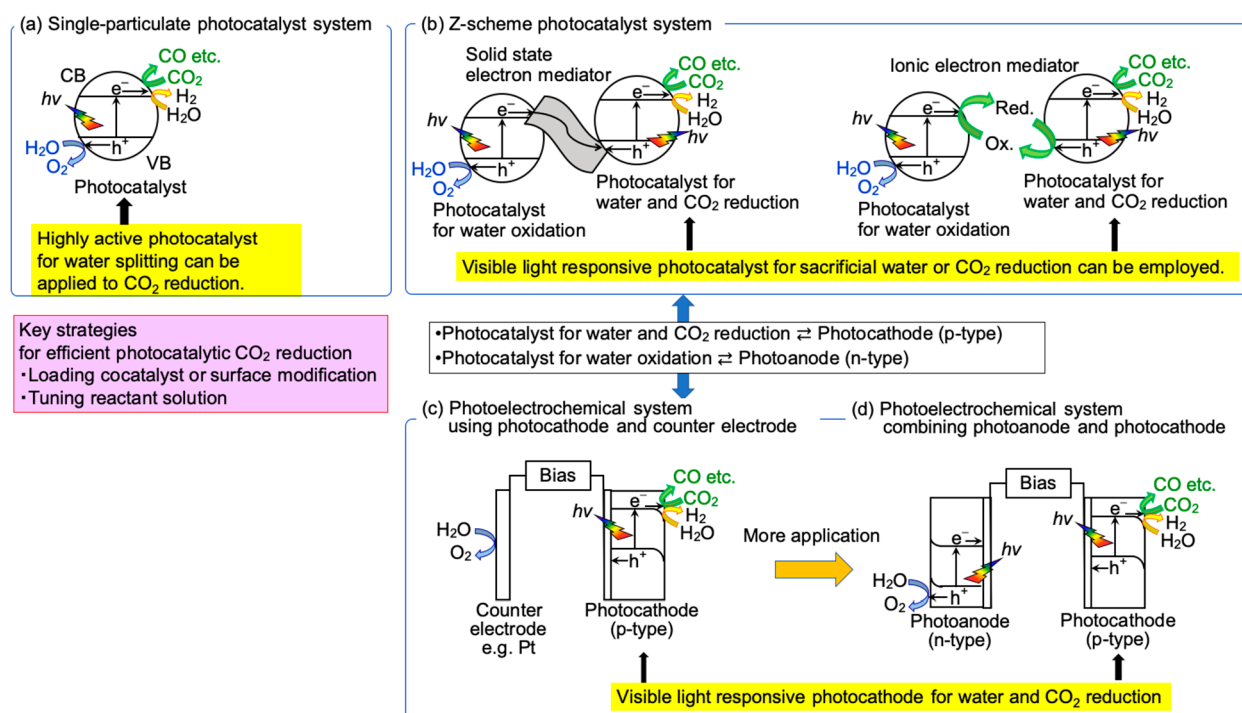


Figure 1. Artificial photosynthetic CO₂ reduction based on a powdered photocatalyst by (a) a single-particulate system, (b) a Z-scheme system, (c) a photoelectrochemical system using a photocathode, and (d) a photoelectrochemical system combining a photocathode and a photoanode.

active site for CO₂ reduction and Ag/BaLa₄Ti₄O₁₅ photocatalyst for CO₂ reduction to form CO as a main reduction product using water as an electron donor even in an aqueous solution.

- Nakanishi, H.; Iizuka, K.; Takayama, T.; Iwase, A.; Kudo, A. Highly Active NaTaO₃-Based Photocatalysts for CO₂ Reduction to Form CO Using Water as the Electron Donor. *ChemSusChem* **2017**, *10*, 112–118.² Ag/NaTaO₃ photocatalyst doped with alkaline earth cations for CO₂ reduction to CO with 90% of selectivity in an aqueous solution with a basic salt for enhancement of hydrated CO₂ molecules supply.
- Iwase, A.; Yoshino, S.; Takayama, T.; Ng, Y. H.; Amal, R.; Kudo, A. Water Splitting and CO₂ Reduction under Visible Light Irradiation Using Z-Scheme Systems Consisting of Metal Sulfides, CoOx-Loaded BiVO₄, and a Reduced Graphene Oxide Electron Mediator. *J. Am. Chem. Soc.* **2016**, *138*, 10260–10264.³ Z-scheme system composed of CuGaS₂ as a reducing photocatalyst and RGO-(CoO_x/BiVO₄) as an O₂-evolving photocatalyst for CO₂ reduction to CO using water as an electron donor under visible light irradiation in an aqueous powder suspension system.
- Yoshino, S.; Iwase, A.; Yamaguchi, Y.; Suzuki, T. M.; Morikawa, T.; Kudo, A. Photocatalytic CO₂ Reduction Using Water as an Electron Donor under Visible Light Irradiation by Z-Scheme and Photoelectrochemical Systems over (CuGa)_{0.5}ZnS₂ in the Presence of Basic Additives. *J. Am. Chem. Soc.* **2022**, *144*, 2323–2332.⁴ Employing (CuGa)_{0.5}ZnS₂ prepared by a flux method in Z-scheme and photoelectrochemical systems with tuning a reactant solution for efficient and stable CO₂ reduction to form CO with 10–20% selectivity using water as an electron donor under visible light.

1. INTRODUCTION

Carbon dioxide capture storage and utilization technology (CCSU) has been encouraged, because CO₂ emission control is a critical issue in the world. Ideally, CO₂ fixation should be realized utilizing renewable energies, such as solar energy, as follows:

- hydrogenation of CO₂ using solar hydrogen
- biological CO₂ fixation
- electrochemical CO₂ reduction utilizing a photovoltaic cell
- photocatalytic and photoelectrochemical CO₂ reduction directly utilizing solar light

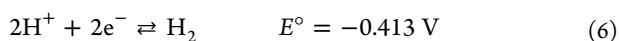
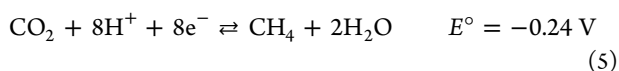
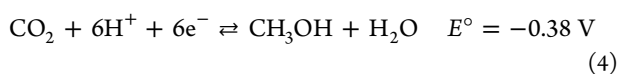
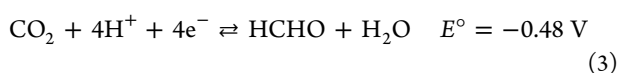
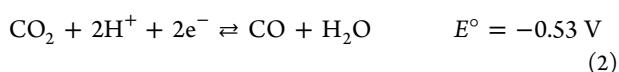
There are advantages and disadvantages to each reaction. Hydrogenation of CO₂ can produce various beneficial chemical compounds with high CO₂ conversion efficiency through a thermal catalytic process on an industrial scale. Much knowledge toward CO₂ hydrogenation has been accumulated in C1 chemistry so far. The hydrogen should be supplied from solar hydrogen production by water splitting with no consumption of fossil resources and no CO₂ emission but not from steam reforming of fossil resources. However, the CO₂ conversion process requires high temperature and pressure to operate the catalytic process. Biological CO₂ fixation is based on natural photosynthesis by plants. Natural photosynthesis involves almost no energy loss for absorbed photon energy conversion. However, the solar energy conversion efficiency is limited because a plant absorbs only a part of the solar spectrum as indicated by its green color. Electrochemical CO₂ reduction is also interesting from the viewpoint of electrocatalysis. The reduction products and the selectivity change with electrode materials even under the same electrolysis conditions. However, electrolyzers and batteries are indispensable for the electrochemical system in addition to a photovoltaic cell. Photocatalytic and photoelectrochemical

CO₂ reduction utilizing solar energy in an aqueous solution is one of the ideal chemical reactions for artificial photosynthesis, because solar energy is directly converted and stored as chemical products. Artificial photosynthesis can be operated under ambient temperature and pressure to produce solar fuels and chemicals and can exceed natural photosynthesis in solar energy conversion efficiency. Especially, a powder-based photocatalyst is attractive because it can be employed for a low-cost and scalable system aimed at artificial photosynthesis.⁵

In this Account, we introduce several types of CO₂ reduction systems, mainly based on particulate photocatalyst materials, using water as an electron donor. Key points for evaluation of photocatalytic and photoelectrochemical CO₂ reduction are also discussed.

2. OVERVIEW OF PHOTOCATALYTIC AND PHOTOELECTROCHEMICAL CO₂ REDUCTION SYSTEMS FOR ARTIFICIAL PHOTOSYNTHESIS

Figure 1 shows various types of photocatalytic and photoelectrochemical systems for artificial photosynthesis.^{6,7} The first is a single-particulate photocatalyst system via one-photon excitation, in which photocatalytic reduction by photo-generated electrons and photocatalytic oxidation by photo-generated holes proceed on one particle (Figure 1a).^{6–9} Photocatalysts of semiconductor materials have a band structure in which a conduction band (CB) is separated from a valence band (VB) with a band gap (BG). The thermodynamic relationship between the band structure of a photocatalyst and the redox potential for the objective reaction is important. The equilibrium potentials relative to the normal hydrogen electrode (NHE) at pH 7 and 298 K for CO₂ reduction and water splitting are as follows:



The conduction band minimum and valence band maximum should locate at more negative and positive levels than redox potentials of objective reactions such as water splitting and CO₂ reduction, respectively. When the energy of the incident photon is larger than that of the band gap, electrons and holes are photogenerated in the conduction band and the valence band, respectively. The photogenerated electrons reduce water and CO₂ to generate H₂ and CO₂ reduction products such as CO, while the photogenerated holes oxidize water to form O₂. The O₂ evolution is a key issue for photocatalytic CO₂ reduction using water as an electron donor. Moreover, since CO₂ reduction competes with water reduction, selective CO₂

reduction is also challenging from the viewpoints of not only thermodynamics but also kinetics. Therefore, the catalytic ability of photocatalyst surface is also a key issue.

The second is a Z-scheme system via a two-photon excitation process consisting of a reducing photocatalyst, an oxidizing photocatalyst, and an electron mediator (Figure 1b).^{10–13} This system mimics natural photosynthesis by a plant. Various photocatalysts that are active for either photocatalytic reduction of water and CO₂ reduction or photocatalytic oxidation of water can be employed to make a Z-scheme system. From this viewpoint, it is meaningful to test photocatalytic CO₂ reduction using sacrificial electron donors such as organic compounds and S²⁻ in order to find potential CO₂-reducing photocatalysts in a part of the Z scheme system, though the sacrificial reaction becomes a downhill reaction ($\Delta G < 0$).

The third is a photoelectrochemical cell.⁷ n-Type and p-type semiconductors may function as O₂-evolving photoanodes and photocathodes to give H₂ and reduction products of CO₂, respectively. The photoelectrochemical cell can be constructed by combining a photoelectrode of a working electrode with a counter electrode (Figure 1c) or combining a photoanode and a photocathode working via two-photon excitation (Figure 1d). External bias can be applied between the photoanode and photocathode to enhance the photoelectrochemical reaction. However, the external bias should be smaller than the theoretical voltage of electrolysis of an objective reaction to achieve artificial photosynthesis from light energy conversion.

In the following sections, several types of the photocatalytic and photoelectrochemical systems shown in Figure 1 are introduced.

3. SINGLE PARTICULATE PHOTOCATALYSTS WITH WIDE BAND GAPS FOR CO₂ REDUCTION USING WATER AS AN ELECTRON DONOR (FIGURE 1a)

3.1. Ag Cocatalyst for CO Formation by Photocatalytic CO₂ Reduction

CO₂ reduction over metal oxide photocatalysts has extensively been investigated. Although TiO₂ has widely been studied for photocatalytic CO₂ reduction, those reports involve critical issues such as lack of quantification of O₂ and small amounts of reduction products such as CH₄ due to low activities. Ishitani et al. reported that CH₄ could come from contaminants adsorbed on TiO₂.¹⁴ In contrast, Sayama and Arakawa have reported that a ZrO₂ photocatalyst (BG = 5.0 eV) produced CO, H₂, and O₂ in stoichiometric amounts in an aqueous medium.¹⁵ Moreover, loading a Cu cocatalyst and adding a bicarbonate ion enhanced the photocatalytic CO₂ reduction. This is the first report to demonstrate photocatalytic CO₂ reduction using water as an electron donor over a particulate photocatalyst. However, the major reduction product was H₂ and the selectivity for CO formation (CO/(H₂ + CO)) was about 12%. In such a background, the author found a highly active Ag cocatalyst for photocatalytic CO₂ reduction to form CO with highly active photocatalysts for water splitting.

BaLa₄Ti₄O₁₅ (BG = 3.9 eV) photocatalyst with a layered perovskite structure was first chosen because NiO_x/BaLa₄Ti₄O₁₅ efficiently split water.¹⁶ The particle is plate shaped in which an edge plane and a basal plane are reduction and oxidation site, respectively, as shown in Figure 2A. The separation of the reduction site from the oxidation site is beneficial for an uphill reaction, because a back reaction of a

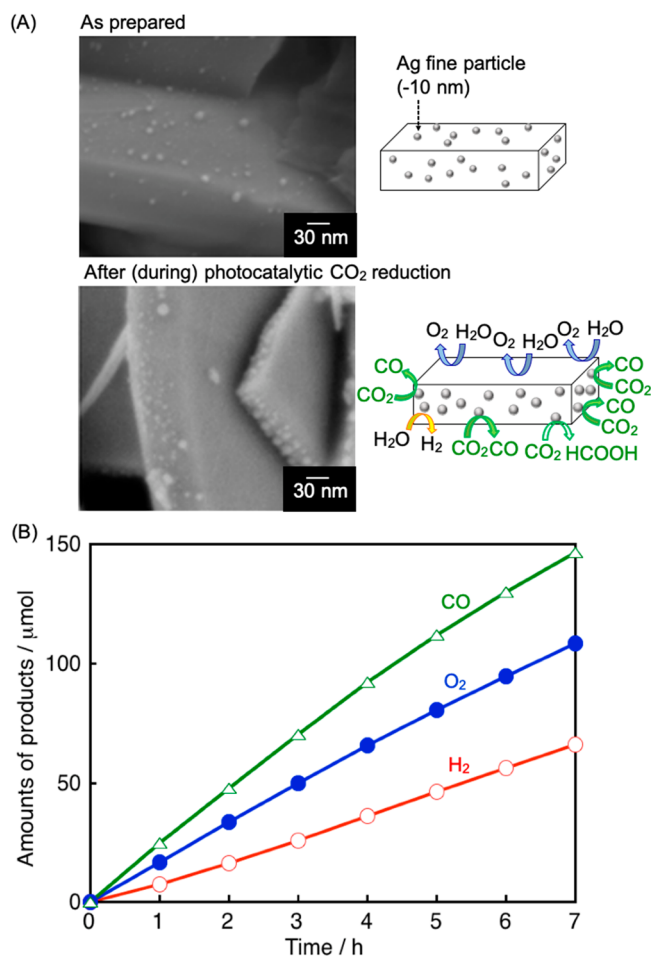


Figure 2. (A) SEM images of Ag/BaLa₄Ti₄O₁₅ before and after photocatalytic CO₂ reduction, and the proposed mechanism. (B) Photocatalytic CO₂ reduction using water as an electron donor under UV light irradiation over Ag(2 wt %)/BaLa₄Ti₄O₁₅.¹ Photocatalyst, 0.3 g; reactant solution, water (360 mL); flow gas, CO₂ (1 atm); light source, 400 W high-pressure mercury lamp; reaction cell, inner irradiation quartz cell. Reproduced with permission from ref 1. Copyright 2011 American Chemical Society.

downhill reaction is suppressed. Ag was found to be a highly active cocatalyst for photocatalytic CO₂ reduction to form CO as shown in Table 1.¹ To compare photocatalytic CO₂ reduction abilities, not only the production rate [mol h⁻¹]

but also the selectivity for CO₂ reduction are essential values. The selectivity is calculated according to eq 8.

$$\text{selectivity [\%]} = 100 \times \left(\frac{\text{number of electrons reacted for objective production}}{\text{sum of all reacted electrons}} \right) \quad (8)$$

The selectivity and the production rate based on the number of reacted electrons are similar to Faradaic efficiency and partial current density, respectively, in an electrochemical reaction. It is noteworthy that CO is the main reduction product with about 70% selectivity, rather than H₂, even in an aqueous medium (Table 1). A small amount of HCOOH was also obtained. It is reasonable that Ag functions as an efficient cocatalyst to form CO judging from its electrocatalysis in aqueous CO₂ solution.^{17,18} The high conduction band level of BaLa₄Ti₄O₁₅ should be important to get an enough driving force for CO₂ reduction and high energy potential of photogenerated electrons applied to the Ag cocatalyst. A liquid-phase reduction method gives higher activity for CO formation than photodeposition and impregnation methods for the Ag cocatalyst loading. There is concern that the Ag cocatalyst may efficiently reduce O₂ produced by water splitting. However, O₂ reduction on the Ag cocatalyst is suppressed more or less, because the reaction is conducted under CO₂ flow conditions smoothly removing the O₂ from the reaction system.

Figure 2A shows SEM images of Ag-cocatalyst before and after photocatalytic CO₂ reduction and a reaction mechanism. BaLa₄Ti₄O₁₅ is a plate-like particle with layered perovskite structure. Ag particles of ~10 nm diameter are loaded on both edge and basal plane by the liquid-phase reduction as prepared. After photocatalytic CO₂ reduction, the number of the Ag cocatalyst particles on the edge increases while Ag particles on the basal plane disappear, because Ag on the basal plane dissolves by photooxidation and is subsequently photo-deposited on the edge by photoreduction during the photocatalytic CO₂ reduction.

Figure 2B shows time courses of CO, H₂, and O₂ evolution by photocatalytic CO₂ reduction over Ag/BaLa₄Ti₄O₁₅. The time courses demonstrate not only activity and durability but also other important points to evaluate photocatalytic CO₂ reduction as discussed below.

It is important to see if O₂ evolves in a stoichiometric amount when the photocatalytic reaction is conducted using

Table 1. Effect of Cocatalyst on CO₂ Reduction Using Water as an Electron Donor under UV Light Irradiation over BaLa₄Ti₄O₁₅ Photocatalyst^{1a}

cocatalyst (wt %)	loading method	activity [μmol h ⁻¹]				CO selectivity (%)	e ⁻ /h ⁺
		H ₂	O ₂	CO	HCOOH		
none		5.3	2.4	0	0	0	1.1
NiO _x (0.5)	impregnation ^b	58	29	0.02	0	0.03	1.0
Ru (0.5)	photodeposition	84	41	0	0	0	1.0
Cu (0.5)	photodeposition	96	45	0.6	0	0.6	1.1
Au (0.5)	photodeposition	110	51	0	0	0	1.1
Ag (1.0)	photodeposition	10	7.0	4.3	0.3	30	1.0
Ag (1.0)	impregnation	8.2	5.7	5.2	0.2	38	1.2
Ag (1.0)	impregnation + H ₂ reduction	5.6	8.7	8.9	0.3	60	0.9
Ag (1.0)	liquid-phase reduction	5.6	12	19	0.4	76	1.0

^aPhotocatalyst, 0.3 g; reactant solution, water (360 mL); flow gas, CO₂ (1 atm); light source, 400 W high-pressure mercury lamp; reaction cell, inner irradiation quartz cell. ^bTreated with H₂ reduction and subsequent oxidation.

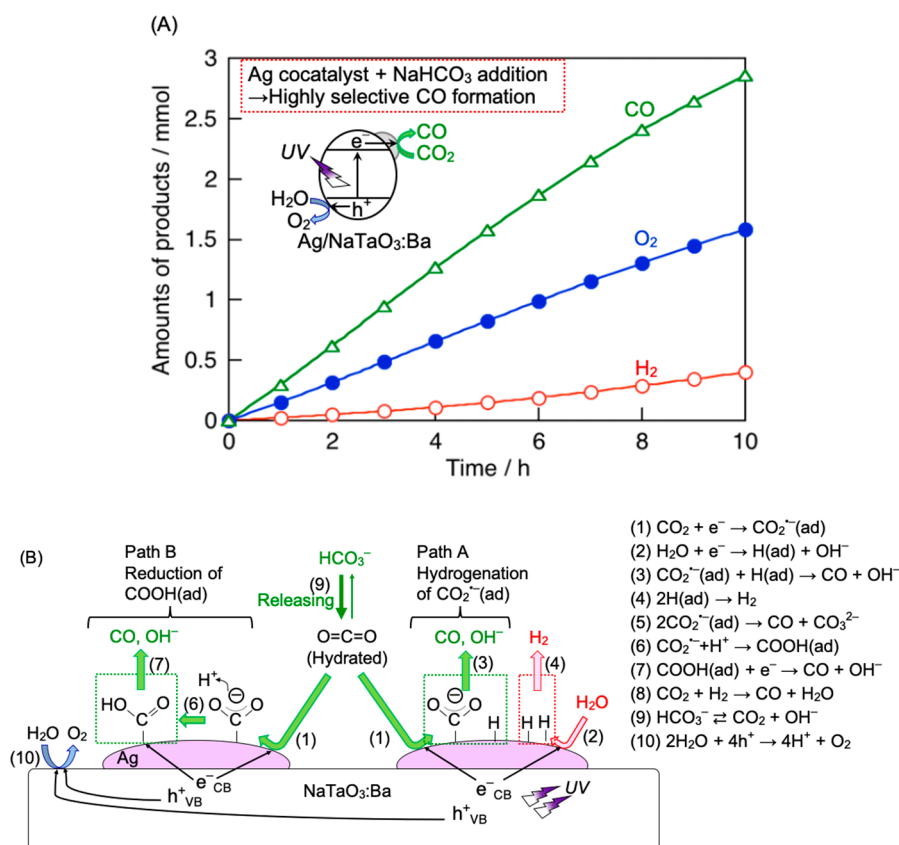


Figure 3. (A) Photocatalytic CO₂ reduction using water as an electron donor under UV light irradiation over Ag/NaTaO₃:Ba. Reactant solution, NaHCO_{3(aq)} (360 mL); flow gas, CO₂ (1 atm); light source, 400 W high-pressure mercury lamp; reaction cell, an inner irradiation quartz cell. (B) Proposed mechanism of photocatalytic CO₂ reduction in the presence of NaHCO₃.² Reproduced with permission from ref 2. Copyright 2017 Wiley.

water as an electron donor for light energy conversion without any strong sacrificial electron donors. CO₂ is reduced by photogenerated electrons on a photocatalyst, while photocatalytic oxidation of water by photogenerated holes simultaneously proceeds as the counterpart as shown in Figures 1a and 2B. It is also important to see if the ratio of reacted electrons to holes estimated from products is unity according to eq 9.

$$\frac{e^-}{h^+} = \frac{\text{(number of reacted electrons calculated from reduction products)}}{\text{(number of reacted holes calculated from oxidation products)}} \quad (9)$$

Unity means that reduction and oxidation products are obtained in a stoichiometric amount. If the e^-/h^+ is not unity, side reactions or noncatalytic but quantitative reactions such as reduction or oxidation of the photocatalyst itself may proceed. In addition, it is necessary to pay attention to whether some products are not detected by the measurement technique employed. The O₂ evolution with at unity e^-/h^+ ratio is satisfied for the present photocatalytic CO₂ reduction over Ag/BaLa₄Ti₄O₁₅ as shown in Table 1 and Figure 2B.

Photocatalytic reaction must proceed by irradiation the energy of which is larger than the band gap energy. The band gap of BaLa₄Ti₄O₁₅ is 3.9 eV, which corresponds to about 320 nm light. This photocatalyst works with use of a quartz reaction cell with a suitable UV lamp, while the activity is negligible using a Pyrex reaction cell. This result indicates that

the photoresponse of the BaLa₄Ti₄O₁₅ photocatalyst is reasonable.

Turnover number defined by eq 10 is also an important indicator to consider if the reaction proceeds photocatalytically.

$$[\text{TON}] = \frac{[\text{molar quantity of products}]}{[\text{molar quantity of active sites}]} \quad (10)$$

Turnover number (TON) indicates how many atoms or molecules react on one active site. TON based on the number of reacted electrons is often used for photocatalysis accompanied by redox reactions according to eq 11.

$$[\text{TON}] = \frac{[\text{number of reacted electrons for objective production}]}{[\text{number of active sites}]} \\ = \frac{[\text{molar quantity of reacted electrons for objective production}]}{[\text{molar quantity of an employed photocatalyst}]} \quad (11)$$

If the TON is too small, we cannot guarantee that it is a photocatalytic reaction because not catalytic but quantitative reactions on the surface of photocatalyst cannot be excluded. In a heterogeneous photocatalyst, the molar quantity of the active site is often replaced with the molar quantity of an employed photocatalyst, because it is difficult to estimate the number of actual active sites on the surface of a photocatalyst.

Table 2. Single Particulate Photocatalysts with Wide Band Gaps for CO₂ Reduction Using Water as an Electron Donor^{1,2,22–24a}

photocatalyst	BG [eV]	crystal structure	Ag cocatalyst (wt %, loading method)	additive	activity [$\mu\text{mol h}^{-1}$]			
					H ₂	O ₂	CO	CO selectivity (%)
CaLa ₄ Ti ₄ O ₁₅	3.9	layered perovskite	Ag (1.0, LPR)	none	3.2	6.6	9.3	72
SrLa ₄ Ti ₄ O ₁₅	3.8	layered perovskite	Ag (1.0, LPR)	none	4.8	5.8	7.1	56
BaLa ₄ Ti ₄ O ₁₅	3.9	layered perovskite	Ag (1.0, LPR)	none	5.6	12	19	76
K ₄ Nb ₆ O ₁₇	3.4	layered	Ag(3.0, LPR)	NaHCO ₃	11	9	8	42
NaTaO ₃	4.0	perovskite	Ag(1.0, PD)	none	32	16	1.4	4.2
NaTaO ₃ :Ba	4.1	perovskite	Ag(3.0, LPR)	NaHCO ₃	24	76	125	84
NaTaO ₃ :Sr	4.1	perovskite	Ag(2.0, LPR)	NaHCO ₃	28	102	176	86
NaTaO ₃ :Ca	4.1	perovskite	Ag(2.0, LPR)	NaHCO ₃	15	84	148	91
AgTaO ₃	3.4	perovskite	none	NaHCO ₃	27	15	4.2	13
KCaSrTa ₅ O ₁₅	4.1	tungsten bronze	Ag(0.5, Imp)	NaHCO ₃	15	46	97	87
K ₃ Ta ₃ B ₂ O ₁₂	4.0	tungsten bronze like	Ag(2.0, PD)	NaHCO ₃	55	32	16.7	23
SrTa ₂ O ₆	4.4	CaTa ₂ O ₆	Ag(3.0, LPR)	NaHCO ₃	95	86	87	48
BaTa ₂ O ₆	4.1	CaTa ₂ O ₆ as main phase	Ag(2.0, LPR)	NaHCO ₃	30	16	7	19
LaTa ₇ O ₁₉	4.1	laminar	Ag(1.0, Imp)	NaHCO ₃	9	17	25	74
CaTa ₄ O ₁₁	4.5	laminar	Ag(1.0, Imp)	NaHCO ₃	31	30	35	53

^aPhotocatalyst, 0.3–1.5 g; reactant solution, water (350–360 mL); flow gas, CO₂ (1 atm); light source, 400 W high-pressure mercury lamp; reaction cell, inner irradiation quartz cell. PD, photodeposition; LPR, liquid-phase reduction; Imp, impregnation.

In some cases, the molar quantities of atoms on the surface, dopant, and cocatalyst are used for the denominator. The TON should be above unity to prove that the reaction proceeds catalytically. Photocatalytic CO₂ reduction over Ag/BaLa₄Ti₄O₁₅ proceeds steadily under UV light irradiation and TON to photocatalyst and cocatalyst reach 1.6 and 7.7, respectively, at 7 h being above unity as shown in Figure 2B.

Products of CO and HCOOH among others must originate from CO₂. However, contaminants on the photocatalyst and some carbon materials constituting the photocatalyst system may become a carbon source.^{14,19} Therefore, confirmation of the carbon source of the obtained products is necessary. One approach is an isotope experiment using ¹³CO₂. Another is a control experiment using an inert gas to confirm that carbon products are not obtained. The reactant solution conditions (i.e., pH) of the control experiment should be similar to those of CO₂ reduction. When ¹³CO₂ is flowed for a photocatalytic reaction over Ag/BaLa₄Ti₄O₁₅, ¹³CO is obtained while ¹²CO is not. In addition, CO is not obtained when Ar instead of CO₂ is supplied. These two results prove CO₂ is the carbon source.

Thus, it is concluded by confirmations of O₂ evolution, the ratio of reacted e⁻ to h⁺ estimated from obtained products, the TON, and the carbon source that the CO₂ reduction photocatalytically proceeds using water as an electron donor over Ag/BaLa₄Ti₄O₁₅.

3.2. Effect of HCO₃⁻ in Water on Photocatalytic CO₂ Reduction

La or alkaline earth metal doped NaTaO₃ (BG = 4.1 eV) with a perovskite structure is also a unique photocatalyst. The doped NaTaO₃ has a surface nanostep structure in which a reduction site is separated from an oxidation site.^{20,21} While NiO/NaTaO₃ with dopant splits water efficiently but does not reduce CO₂, Ag/NaTaO₃:Ba gives CO with about 50% selectivity under UV light upon flowing CO₂ into pure water.² Moreover, with addition of a basic salt into the reactant solution, CO formation rate drastically increases and the selectivity reaches about 90% even in an aqueous solution (Figure 3A). The enhancement of CO₂ reduction with salt

addition is due to efficient supply of hydrated CO₂ molecule reactant and pH control.

A proposed mechanism of photocatalytic CO₂ reduction over Ag/NaTaO₃:Ba in the presence of a basic additive is shown in Figure 3B. It was confirmed that not HCO₃⁻ or CO₃²⁻ but a hydrated CO₂ molecule is a reactant in photocatalytic CO₂ reduction as in electrochemical CO₂ reduction. HCO₃⁻ functions as a buffer for supply of hydrated CO₂ molecules. After the CO₂ adsorbs on the Ag-cocatalyst to make CO₂^{•-}(_{ad}), CO evolves through path A (hydrogenation of CO₂^{•-}(_{ad})) or path B (reduction of COOH(_{ad})). Water is photooxidized to form O₂ on the photocatalyst surface. Thus, adding a basic salt is key for efficient photocatalytic CO₂ reduction with smooth supply of hydrated CO₂ molecules.

3.3. Ag Cocatalyst-Loaded Photocatalysts for Single Particulate Photocatalytic CO₂ Reduction to Form CO

Various metal oxide photocatalysts with different components and crystal structure have been developed for CO₂ reduction based on loading Ag cocatalyst and adding NaHCO₃ strategies from our group as shown in Table 2, for example, CaTa₄O₁₁,²² LaTa₇O₁₉,²² and KCaSrTa₅O₁₅.^{23,24} photocatalysts. In addition, many metal oxide photocatalysts with wide band gaps have been reported for CO₂ reduction such as La₂Ti₂O₇,²⁵ CaTiO₃,²⁶ SrTiO₃:Al,²⁷ Ga₂O₃:Zn,²⁸ and ZnGa₂O₄/Ga₂O₃²⁹ with the Ag cocatalyst from other groups. Substitution of elements is also a beneficial approach to develop new photocatalysts for CO₂ reduction as well as for water splitting. For example, KCaSrTa₅O₁₅ (BG = 4.1 eV) has a tungsten bronze structure, which is similar to a defect type of perovskite structure (A_{1-x}BO₃). K, Ca, and Sr at an A site in KCaSrTa₅O₁₅ can be replaced with various other cations. Sr_xK_yNa_zTa₅O₁₅ and K₂RETa₅O₁₅ (RE = rear earth metal) obtained by the substitution are also active for photocatalytic CO₂ reduction.^{30–32}

3.4. Rh–Ru Cocatalyst for CH₄ Formation by Photocatalytic CO₂ Reduction

Although many photocatalysts have been developed for CO₂ reduction as mentioned above, obtained products are limited to two-electron reduction products such as CO and HCOOH.

Table 3. Sacrificial CO₂ Reduction Using Metal Sulfide Photocatalysts under Visible Light Irradiation^{19a}

metal sulfide	crystal structure	BG, EG [eV]	electron donor	activity [$\mu\text{mol h}^{-1}$]		
				H ₂	CO	HCOOH
CuGaS ₂	chalcopyrite	2.3	K ₂ SO ₃	11	0.25	trace
(AgInS ₂) _{0.22} –(ZnS) _{1.56}	wurtzite	2.3	Na ₂ S + K ₂ SO ₃	16	0.01	0
(AgInS ₂) _{0.1} –(ZnS) _{1.8}	wurtzite	2.6	Na ₂ S	23	0.06	0.10
Ag ₂ ZnGeS ₄	stannite	2.5	Na ₂ S	38	0	0.14
ZnS:Ni(0.1%)	wurtzite + zinc blend	2.3	Na ₂ S	22	trace	4.0
ZnS:Pb(1.0%)	wurtzite + zinc blend	2.4	Na ₂ S	47	0.02	0.96
(ZnS) _{0.9} –(CuCl) _{0.1}	zinc blende	2.9	Na ₂ S	140	0.01	0
ZnGa _{0.5} In _{1.5} S ₄	layered	2.7	Na ₂ S	14	0.01	0

^aPhotocatalyst, 0.2–0.3 g; reactant solution, 0.05–0.1 mol L⁻¹ Na₂S or 0.1 mol L⁻¹ K₂SO_{3(aq)} (120–150 mL) or both; gas, CO₂ (1 atm); light source, 300 W Xe lamp ($\lambda > 420$ nm); irradiation area, 33 cm². BG = band gap, EG = energy gap.

Table 4. Z-Scheme Photocatalyst Systems for CO₂ Reduction Using Water as an Electron Donor under UV or Visible Light Irradiation^{3,4,19,43,46a}

entry	reducing photocatalyst	O ₂ -evolving photocatalyst	mediator	additive (mmol L ⁻¹)	activity [$\mu\text{mol h}^{-1}$]			CO selectivity (%)	e ⁻ /h ⁺
					H ₂	O ₂	CO		
1	CuGaS ₂	RGO–TiO ₂	RGO	none	28.8	11.2	0.15	0.5	1.29
2	CuGaS ₂	RGO–(CoO _x /BiVO ₄)	RGO	none	3.1	1.3	0.04	1.3	1.21
3	Cu _{0.8} Ag _{0.2} GaS ₂	RGO–(CoO _x /BiVO ₄)	RGO	NaHCO ₃ (1)	4.0	1.6	0.03	0.7	1.26
4	CuGa _{0.8} In _{0.2} S ₂	RGO–(CoO _x /BiVO ₄)	RGO	NaHCO ₃ (1)	3.5	1.6	0.04	1.1	1.11
5	(CuGa) _{0.5} ZnS ₂	RGO–(CoO _x /BiVO ₄)	RGO	NaHCO ₃ (1)	3.5	1.9	0.4	11	1.04
6	(CuGa) _{0.5} ZnS ₂	RGO–(CoO _x /BiVO ₄)	RGO	NaHCO ₃ (10)	12.0	6.4	1.8	13	1.08
7	(CuGa) _{0.5} ZnS ₂	RGO–(CoO _x /BiVO ₄)	RGO	KHCO ₃ (10)	8.1	4.6	2.1	20	1.11
8	(CuGa) _{0.5} ZnS ₂	RGO–(CoO _x /BiVO ₄)	RGO	NaHCO ₃ (100)	8.9	3.5	3.2	26	1.73
9	[Ru(dpbbpy)]/ (CuGa) _{0.3} Zn _{1.4} S ₂	BiVO ₄	Co[(tpy) ₂] ^{3+/2+}	NaHCO ₃ (250)	1.7	0.8	2.7	56	3.00
10	SrTiO ₃ :Rh	BiVO ₄	none	none	8.7	4.0	0.018	0.2	1.09
11	Au/SrTiO ₃ :Rh	BiVO ₄	none	none	3.5	1.9	0.031	0.9	0.93

^aPhotocatalyst, 0.1–0.4 g; reactant solution, water (120–150 mL); flow gas, CO₂ (1 atm); light source, 300 W Xe lamp ($\lambda > 300$ nm for TiO₂ and $\lambda > 420$ nm for BiVO₄ systems); irradiation area, 33 cm².

Therefore, it is challenging to demonstrate CO₂ reduction to form CH₄, an eight-electron reduction product, using water as an electron donor. Rh–Ru/NaTaO₃:Sr(1%) continuously produces CH₄, H₂, and O₂ under UV irradiation.³³ The selectivity for CH₄ formation based on the number of reacted electrons is about 10%. The e⁻/h⁺ ratio estimated from obtained products is 1.1, and TON based on CH₄ formation with Rh and Ru cocatalysts is 2.0. No CH₄ is obtained under Ar rather than CO₂ flow. These results prove that CH₄ is obtained by photocatalytic CO₂ reduction using water as an electron donor over the Rh–Ru/NaTaO₃:Sr(1%).

4. Z-SCHEME CO₂ REDUCTION USING WATER AS AN ELECTRON DONOR UNDER VISIBLE LIGHT IRRADIATION (FIGURE 1b)

It is a key issue to construct visible light responsive CO₂ reduction system using water as an electron donor for efficient sunlight utilization beyond the wide band gap photocatalysts. In this section, visible light responsive photocatalysts for CO₂ reduction in the presence of a sacrificial electron donor (Table 3) and application of those photocatalysts to Z-scheme systems for CO₂ reduction using water as an electron donor under visible light (Table 4) are introduced.

4.1. Visible-Light Responsive Metal Sulfide Photocatalysts for CO₂ Reduction Using Sacrificial Electron Donor

Metal sulfide photocatalysts are active for not only water reduction but also CO₂ reduction under visible light using a

sacrificial electron donor. For example, CdS is active for sacrificial CO₂ reduction to form CO in an aqueous solution containing a sacrificial reagent.^{34,35} Metal sulfides with various crystal structures have also been developed for sacrificial CO₂ reduction under visible light irradiation as shown in Table 3.¹⁹ CuGaS₂ and ZnS:Ni photocatalysts are highly active for CO and HCOOH formation, respectively. However, these CO₂ reductions are not artificial photosynthesis because strong sacrificial electron donors are used. Since they cannot oxidize water into O₂ because of self-photooxidation (photocorrosion), single particulate overall water splitting and CO₂ reduction accompanied by O₂ evolution by water oxidation as shown in Figure 1a is difficult. Construction of Z-scheme systems is a beneficial approach to employ metal sulfide photocatalysts showing CO₂ reduction activity combined with an O₂-evolving photocatalyst as shown in Figure 1b.

4.2. Z-Scheme System Employing RGO as a Solid-State Electron Mediator (Figure 4A(a))

A Z-scheme system consisting of CuGaS₂ as a reducing photocatalyst, TiO₂ as an O₂-evolving photocatalyst, and reduced graphene oxide (RGO) as a solid-state electron mediator is active for not only water splitting³⁶ but also CO₂ reduction to form CO (Table 4, entry 1).¹⁹ The carbon source for the CO₂ reduction product should carefully be checked, because RGO is a carbon material. ¹³C formed under ¹³CO₂ flow, indicating that flowed CO₂ was the carbon source. However, ¹²CO was obtained in addition to the ¹³CO.

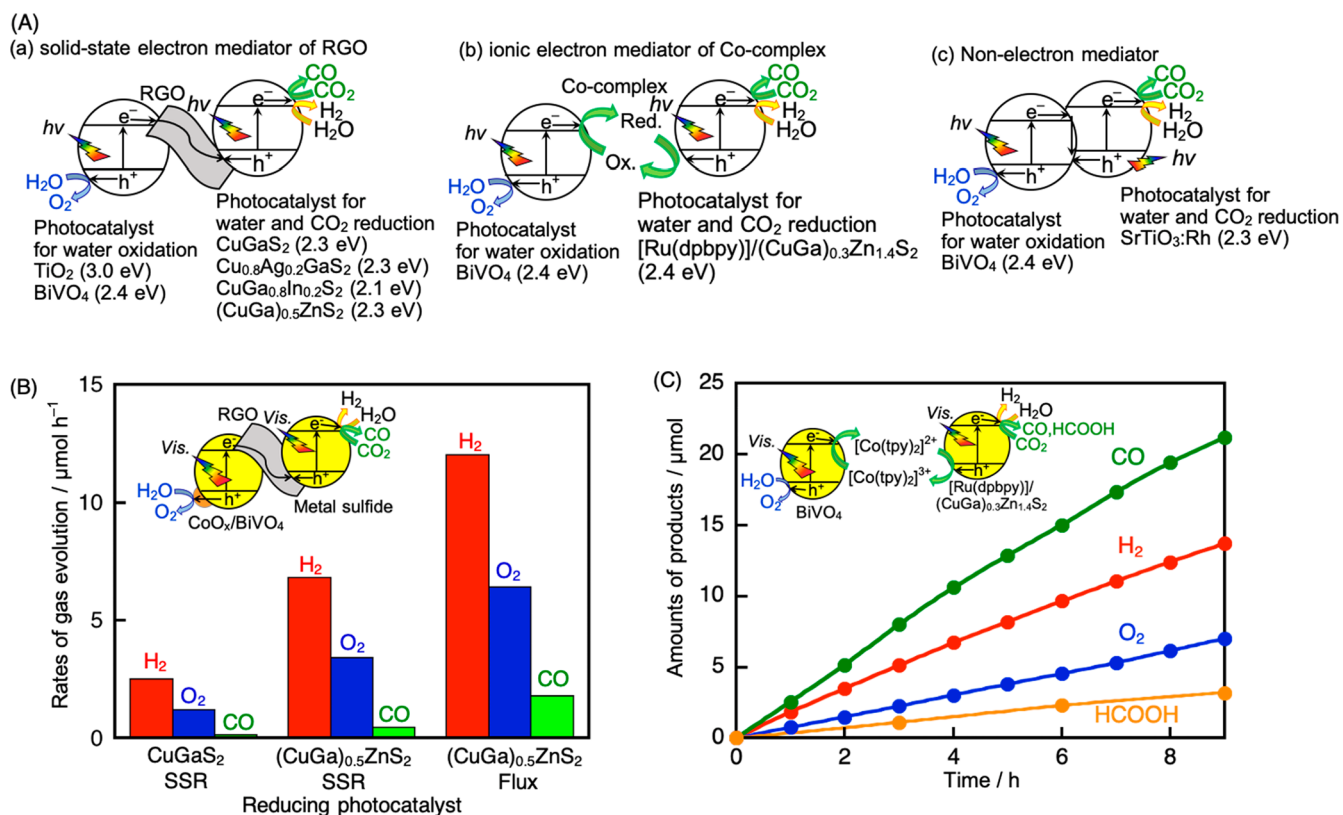


Figure 4. (A) Various types of Z-scheme photocatalysts for CO₂ reduction using water as an electron donor. (B) Z-scheme CO₂ reduction under visible light irradiation using CuGaS₂ or (CuGa)_{0.5}ZnS₂ prepared by a SSR or a flux method combined with RGO-(CoO_x/BiVO₄). Reproduced with permission from ref 4. Copyright 2022 American Chemical Society. (C) Z-scheme CO₂ reduction under visible light irradiation using [Ru(dpbbpy)]/(CuGa)_{0.3}Zn_{1.4}S₂, BiVO₄, and [Co(tpy)₂]^{3+/2+}. Reproduced with permission from ref 43. Copyright 2018 The Royal Society of Chemistry. Photocatalyst, 0.1–0.4 g; reactant solution, NaHCO_{3(aq)} (120–150 mL); flow gas, CO₂ (1 atm); light source, 300 W Xe lamp ($\lambda > 420$ nm); irradiation area, 33 cm².

Moreover, a small amount of CO formed even under Ar gas instead of CO₂. So, a part of CO formed by Z-scheme CO₂ reduction, whereas other CO formed by photooxidation of RGO on TiO₂. The Z-scheme system works only under UV light because of limitations of TiO₂. When visible light responsive RGO-(CoO_x/BiVO₄) is employed instead of RGO-TiO₂, Z-scheme CO₂ reduction to form CO proceeds using water as an electron donor under visible light in an aqueous suspension (Table 4 entry 2).³ CO is not obtained under Ar flow in the Z-scheme system composed of RGO-(CoO_x/BiVO₄) unlike that using RGO-TiO₂. The inhibition of RGO oxidation is due to less oxidation power of holes photogenerated in the valence band of BiVO₄ than that of TiO₂.

Making a solid solution based on CuGaS₂ with p-type character is beneficial to developing a reducing photocatalyst, because the band structure is tunable by a change in the composition of the solid solution.^{6,37} For example, solid solutions of CuGaS₂ with CuInS₂ can absorb longer wavelengths of visible light than CuGaS₂, because In 5s5p orbitals of CuInS₂ lower the conduction band consisting of Ga 4s4p orbitals of CuGaS₂ resulting in band gap narrowing. Red-powdered CuGa_{0.8}In_{0.2}S₂, which absorbs visible light up to 600 nm functions as a CO₂-reducing photocatalyst in the Z-scheme system (Table 4, entry 4). Making a (CuGa)_{1-x}Zn_xS₂ solid solution between CuGaS₂ and ZnS improves CuGaS₂ performance, though the band gap does not become narrower than that of CuGaS₂.³⁸ The Z-scheme system using (CuGa)_{0.5}ZnS₂

prepared by a solid-state reaction (SSR) combined with RGO-(CoO_x/BiVO₄) shows higher water splitting and CO₂ reduction activities than that using CuGaS₂ prepared by SSR (Figure 4B). When the (CuGa)_{0.5}ZnS₂ particle is prepared by a flux method, fine particles of (CuGa)_{0.5}ZnS₂ with a few hundreds of nanometers in size are obtained, while the particle size when prepared by conventional SSR is about 1 μm.³⁹ When the fine particulate (CuGa)_{0.5}ZnS₂ is applied to a Z-scheme system, photocatalytic water splitting and CO₂ reduction are much enhanced (Figure 4B).⁴ The Z-scheme CO₂ reduction activity strongly depends on the reactant solution conditions (Table 4, entries 5–8). Addition of a basic salt not only stabilizes but also enhances Z-scheme CO₂ reduction because of efficient supply of hydrated CO₂ to the photocatalyst surface. We stress that the selectivity for CO formation in the Z-scheme CO₂ reduction reaches 10–20% even using bare metal sulfide without surface modification. Although a Ag cocatalyst is effective for CO₂ reduction to form CO over wide band gap metal oxides as mentioned in section 3, Ag on a metal sulfide does not enhance CO formation in the Z-scheme CO₂ reduction at the present stage, probably due to poisoning of the Ag surface by sulfurization. Therefore, further highly selective CO₂ reduction is expected by introducing a suitable active site and surface modification of the metal sulfide photocatalyst for Z-scheme CO₂ reduction.

4.3. Z-Scheme System Employing a Co-Complex as an Electron Mediator (Figure 4A(b))

Metal complexes have been widely examined as selective CO₂-reducing catalysts in electrochemistry, coordination chemistry, and photochemistry.^{40,41} Recently, hybrid systems combining a metal complex catalyst with semiconductor photocatalyst materials have been studied for highly selective CO₂ reduction in photoelectrochemical and photocatalytic systems.⁴² For example, Z-scheme CO₂ reduction under visible light has been demonstrated using [Ru(dpbpy)]-loaded (CuGa)_{0.3}Zn_{1.4}S₂, BiVO₄, and a Co-complex as an electron mediator (Figure 4C).⁴³ CO evolves as a main reduction product with introduction of the highly active Ru-complex catalyst for CO₂ reduction on (CuGa)_{0.3}Zn_{1.4}S₂. HCOOH is also produced in the reaction. The catalytic activity of a metal complex is usually inhibited in the presence of O₂. Therefore, it is notable that CO₂ reduction and simultaneous O₂ evolution proceed even using a metal complex catalyst with a semiconductor photocatalyst in an aqueous solution, though the amount of O₂ is small compared with a stoichiometric amount.

4.4. Z-Scheme System Driven by Interparticle Electron Transfer without an Electron Mediator (Figure 4A(c))

SrTiO₃:Rh shows high sacrificial H₂ evolution activity, though it does not oxidize water into O₂.⁴⁴ However, SrTiO₃:Rh can be employed to construct a Z-scheme system working via interparticle electron transfer with BiVO₄ without an electron mediator (Figure 4A(c)).^{45,46} The Z-scheme system reduces CO₂ to CO accompanied by H₂ and O₂ under visible light. Loading Ag or Au cocatalyst on SrTiO₃:Rh improves the CO evolution activity (Table 4, entries 10, 11). The suitable pH is around 4, because SrTiO₃:Rh and BiVO₄ particles aggregate well with each other to get good contact between the particles, resulting in smooth electron transfer from BiVO₄ to SrTiO₃:Rh via interparticle electron transfer. It is notable that the Z-scheme CO₂ reduction proceeds using just photocatalyst powders, water, and CO₂ because of self-pH-adjustment by dissolved CO₂.

5. CO₂ REDUCTION ON p-TYPE Cu(I)-CONTAINING METAL SULFIDE PHOTOCATHODES UNDER VISIBLE LIGHT IRRADIATION (FIGURE 1c,d)

A photoelectrochemical CO₂ reduction system is also interesting to construct an artificial photosynthesis system. Photoelectrochemical measurement is generally conducted in a 3-electrode system or a 2-electrode system connected to a potentiostat and a power supply (Figure 5A). Scientifically intrinsic information on the working electrode, for example, an absolute electrode potential, is obtained with the 3-electrode system using a reference electrode. The 2-electrode system is useful for evaluation of cell performance such as open circuit voltage, short circuit current, and energy conversion efficiency. It is meaningless in a photoelectrochemical cell if an externally applied voltage is larger than the theoretical voltage of electrolysis, for example, 1.23 V for water splitting. Applying no external bias is ideal. To compare the performance of a photoelectrode, a current–potential curve is usually measured using the 3-electrode system. In addition, analysis of products by bulk electrolysis is also indispensable, as well as measurement of photocurrent to examine the Faradaic efficiency, that is, electrochemical selectivity. The Faradaic efficiency reveals if the photocurrent is due to desired redox reactions. Moreover,

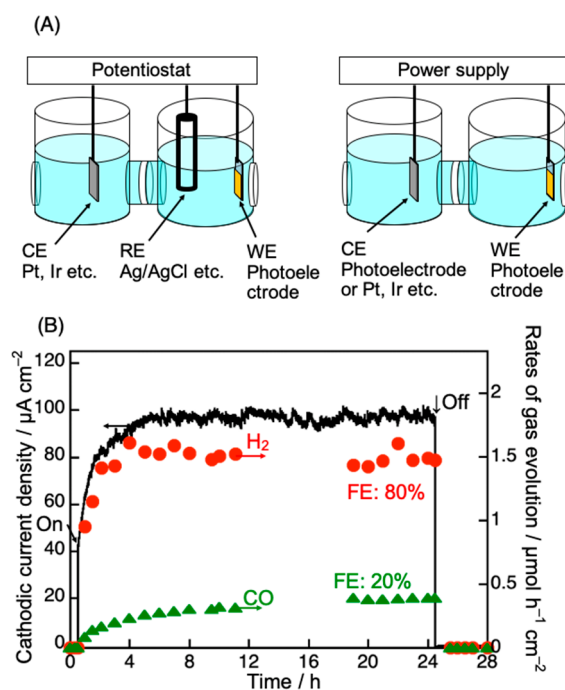


Figure 5. (A) Two-electrode and three-electrode systems for photoelectrochemical CO₂ reduction. (B) Photoelectrochemical CO₂ reduction under visible light irradiation over a (CuGa)_{0.3}Zn_{1.4}S₂ powder-based photocathode. Electrolyte, 0.1 mol L⁻¹ KHCO₃(aq); flow gas, CO₂ (1 atm); light source, 300 W Xe lamp ($\lambda > 420$ nm); applied bias, 0.1 V vs RHE (−0.5 V vs Ag/AgCl (pH 6.9)). Reproduced with permission from ref 4. Copyright 2022 American Chemical Society.

not only the Faradaic efficiency but also a partial photocurrent density (i.e., rate of production) are important to see how fast a certain product is formed. Incident photon to current conversion efficiency (IPCE) and solar energy conversion efficiency are also important.

The photoelectrochemical cell can employ p-type semiconductors as a photocathode even photocorrosive materials. For example, visible light responsive CuGaS₂,⁴⁷ (CuGa)_{0.5}ZnS₂,^{4,38} Cu_{0.8}Ag_{0.2}GaS₂,^{48,49} and Cu₂ZnGeS₄⁵⁰ function as a CO₂-reducing photocathodes. The bare (CuGa)_{0.5}ZnS₂ photocathode reduces CO₂ to CO with high stability under visible light with application of an external bias (Figure 5B).⁴ Faradaic efficiencies for CO and H₂ formation are 20% and 80%, respectively, being almost 100% of total Faradaic efficiency. It is stressed that high CO formation is observed even without cocatalyst and surface modification on the photocathode.

Surface modification with CdS and ZnS of an n-type semiconductor and loading of a cocatalyst improve the performance of p-type Cu_{0.8}Ag_{0.2}GaS₂,⁴⁹ Cu₂ZnGeS₄,⁵¹ and (CuGa_{1-y}In_y)_{1-x}Zn_{2x}S₂ solid solution⁵² photocathodes. Introduction of an electrically conducting polymer such as polypyrrole (PPy) or poly(3,4-ethylenedioxythiophene) (PEDOT) as hole transporter also improves a photocathode composed of a powdered material, because electric contact between the powders and the substrate electrode such as FTO is usually poor.^{53,54} PPy-modified CuGaS₂ gives higher cathodic photocurrent for water and CO₂ reduction than a bare CuGaS₂ photocathode. Moreover, the 2-electrode system combining a PEDOT–CuGaS₂ photocathode and a CoO_x/BiVO₄ photoanode with visible light response also reduces

CO₂ to CO using water as an electron donor under application of a small bias and simulated sunlight irradiation.

6. CONCLUSIONS AND PERSPECTIVES

Artificial photosynthesis is ideal green chemistry and technology to convert and store solar energy to chemical products as an uphill reaction. Solar water splitting to produce H₂ is representative of artificial photosynthesis. Solar water splitting using a powder-based photocatalyst on a large scale (100 m²) has been demonstrated.⁵ It will accelerate the industrial application of solar hydrogen production in the near future. In contrast to solar water splitting, artificial photosynthetic CO₂ utilization using photocatalysts is still at the stage of basic research. However, recent and rapid progress of this research area is hopeful. A variety of photocatalyst and photoelectrode systems for CO₂ utilization has been extensively developed using homogeneous and heterogeneous photocatalyst materials. This Account focused on photocatalytic and photoelectrochemical systems based on particulate photocatalysts for CO₂ reduction as an artificial photosynthesis system working under UV and visible light.

Highly active photocatalysts for water splitting such as BaLa₄Ti₄O₁₅ (BG = 3.9 eV) and doped NaTaO₃ (BG = 4.1 eV) were able to be applied to CO₂ reduction, because they have sufficiently high conduction bands and enough potential for water oxidation to form O₂. The O₂ evolution ability and a suitable cocatalyst working as a reaction center for CO₂ reduction are indispensable for photocatalytic CO₂ reduction using water as an electron donor. Ag and Rh–Ru cocatalysts were developed for CO and CH₄ formation, respectively. Moreover, the photocatalytic activity was increased with optimization of reaction conditions such as tuning of the reactant solution. Metal sulfide photocatalysts with a high conduction band and visible light response are attractive for CO₂ reduction, though they cannot oxidize water. This means that the metal sulfide photocatalyst itself cannot use water as an electron donor to achieve an uphill reaction. However, CuGaS₂, (CuGa)_{1-x}Zn_{2x}S₂, and CuGa_{1-x}In_xS₂ metal sulfide materials were able to be employed as a CO₂-reducing photocatalysts to make a Z-scheme photocatalyst system to achieve photocatalytic CO₂ reduction using water as an electron donor under visible light irradiation. p-Type metal sulfides CuGaS₂, (CuGa)_{1-x}Zn_{2x}S₂, and Cu_{1-x}Ag_xGaS₂ were able to be applied to a photocathode for photoelectrochemical CO₂ reduction, even if their powdered materials were employed.

Strategies to design photocatalytic and photoelectrochemical systems for CO₂ reduction using water as an electron donor under visible light irradiation become clearer as mentioned above. Therefore, it is expected that more efficient photocatalyst and photoelectrode systems can be developed with further extensive study. We believe that photocatalyst and photoelectrode systems for solar CO₂ utilization can be a practical use in the future as well as solar hydrogen production by water splitting.

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REFERENCES

- Iizuka, K.; Wato, T.; Miseki, Y.; Saito, K.; Kudo, A. Photocatalytic Reduction of Carbon Dioxide over Ag Cocatalyst-Loaded ALa₄Ti₄O₁₅ (A = Ca, Sr, and Ba) Using Water as a Reducing Reagent. *J. Am. Chem. Soc.* **2011**, *133*, 20863–20868.
- Nakanishi, H.; Iizuka, K.; Takayama, T.; Iwase, A.; Kudo, A. Highly Active NaTaO₃-Based Photocatalysts for CO₂ Reduction to Form CO Using Water as the Electron Donor. *ChemSusChem* **2017**, *10*, 112–118.
- Iwase, A.; Yoshino, S.; Takayama, T.; Ng, Y. H.; Amal, R.; Kudo, A. Water Splitting and CO₂ Reduction under Visible Light Irradiation Using Z-Scheme Systems Consisting of Metal Sulfides, CoOx-Loaded BiVO₄, and a Reduced Graphene Oxide Electron Mediator. *J. Am. Chem. Soc.* **2016**, *138*, 10260–10264.
- Yoshino, S.; Iwase, A.; Yamaguchi, Y.; Suzuki, T. M.; Morikawa, T.; Kudo, A. Photocatalytic CO₂ Reduction Using Water as an Electron Donor under Visible Light Irradiation by Z-Scheme and Photoelectrochemical Systems over (CuGa)_{0.5}ZnS₂ in the Presence of Basic Additives. *J. Am. Chem. Soc.* **2022**, *144*, 2323–2332.
- Nishiyama, H.; Yamada, T.; Nakabayashi, M.; Maehara, Y.; Yamaguchi, M.; Kuromiya, Y.; Nagatsuma, Y.; Tokudome, H.; Akiyama, S.; Watanabe, T.; Narushima, R.; Okunaka, S.; Shibata, N.; Takata, T.; Hisatomi, T.; Domen, K. Photocatalytic Solar Hydrogen Production from Water on a 100-m² Scale. *Nature* **2021**, *598*, 304–307.
- Kudo, A.; Miseki, Y. Heterogeneous Photocatalyst Materials for Water Splitting. *Chem. Soc. Rev.* **2009**, *38*, 253–278.
- Hisatomi, T.; Kubota, J.; Domen, K. Recent Advances in Semiconductors for Photocatalytic and Photoelectrochemical Water Splitting. *Chem. Soc. Rev.* **2014**, *43*, 7520–7535.
- Chen, S.; Takata, T.; Domen, K. Particulate Photocatalysts for Overall Water Splitting. *Nat. Rev. Mater.* **2017**, *2*, 17050.
- Wang, Q.; Domen, K. Particulate Photocatalysts for Light-Driven Water Splitting: Mechanisms, Challenges, and Design Strategies. *Chem. Rev.* **2020**, *120*, 919–985.
- Bard, A. J. Photoelectrochemistry and Heterogeneous Photocatalysis at Semiconductors. *J. Photochem.* **1979**, *10*, 59–75.
- Kudo, A. Z-Scheme Photocatalyst Systems for Water Splitting under Visible Light Irradiation. *MRS Bull.* **2011**, *36*, 32–38.
- Maeda, K. Z-Scheme Water Splitting Using Two Different Semiconductor Photocatalysts. *ACS Catal.* **2013**, *3*, 1486–1503.
- Wang, Y.; Suzuki, H.; Xie, J.; Tomita, O.; Martin, D. J.; Higashi, M.; Kong, D.; Abe, R.; Tang, J. Mimicking Natural Photosynthesis: Solar to Renewable H₂ Fuel Synthesis by Z-Scheme Water Splitting Systems. *Chem. Rev.* **2018**, *118*, 5201–5241.
- Yui, T.; Kan, A.; Saitoh, C.; Koike, K.; Ibusuki, T.; Ishitani, O. Photochemical Reduction of CO₂ Using TiO₂: Effects of Organic Adsorbates on TiO₂ and Deposition of Pd onto TiO₂. *ACS Appl. Mater. Interfaces* **2011**, *3*, 2594–2600.
- Sayama, K.; Arakawa, H. Photocatalytic Decomposition of Water and Photocatalytic Reduction of Carbon Dioxide over Zirconia Catalyst. *J. Phys. Chem.* **1993**, *97*, 531–533.
- Miseki, Y.; Kato, H.; Kudo, A. Water Splitting into H₂ and O₂ over Niobate and Titanate Photocatalysts with (111) Plane-Type Layered Perovskite Structure. *Energy Environ. Sci.* **2009**, *2*, 306–314.
- Hori, Y.; Wakebe, H.; Tsukamoto, T.; Koga, O. Electrocatalytic Process of CO Selectivity in Electrochemical Reduction of CO₂ at Metal Electrodes in Aqueous Media. *Electrochim. Acta* **1994**, *39*, 1833–1839.
- Hori, Y. Electrochemical CO₂ Reduction on Metal Electrodes. In *Modern Aspects of Electrochemistry*; Vayenas, C. G., White, R. E., Gamboa-Aldeco, M. E., Eds.; Springer: New York, 2008; pp 89–189.
- Takayama, T.; Sato, K.; Fujimura, T.; Kojima, Y.; Iwase, A.; Kudo, A. Photocatalytic CO₂ Reduction Using Water as an Electron Donor by a Powdered Z-Scheme System Consisting of Metal Sulfide and an RGO–TiO₂ Composite. *Faraday Discuss.* **2017**, *198*, 397–407.
- Kato, H.; Asakura, K.; Kudo, A. Highly Efficient Water Splitting into H₂ and O₂ over Lanthanum-Doped NaTaO₃ Photocatalysts with High Crystallinity and Surface Nanostructure. *J. Am. Chem. Soc.* **2003**, *125*, 3082–3089.
- Iwase, A.; Kato, H.; Kudo, A. The Effect of Alkaline Earth Metal Ion Dopants on Photocatalytic Water Splitting by NaTaO₃ Powder. *ChemSusChem* **2009**, *2*, 873–877.
- Takayama, T.; Nakanishi, H.; Matsui, M.; Iwase, A.; Kudo, A. Photocatalytic CO₂ Reduction Using Water as an Electron Donor over Ag-Loaded Metal Oxide Photocatalysts Consisting of Several Polyhedra of Ti⁴⁺, Zr⁴⁺, and Ta⁵⁺. *J. Photochem. Photobiol. A Chem.* **2018**, *358*, 416–421.
- Takayama, T.; Tanabe, K.; Saito, K.; Iwase, A.; Kudo, A. The KCaSrTa₅O₁₅ Photocatalyst with Tungsten Bronze Structure for Water Splitting and CO₂ Reduction. *Phys. Chem. Chem. Phys.* **2014**, *16*, 24417–24422.
- Takayama, T.; Iwase, A.; Kudo, A. Photocatalytic Water Splitting and CO₂ Reduction over KCaSrTa₅O₁₅ Nanorod Prepared by a Polymerized Complex Method. *Bull. Chem. Soc. Jpn.* **2015**, *88*, 538–543.
- Wang, Z.; Teramura, K.; Hosokawa, S.; Tanaka, T. Photocatalytic Conversion of CO₂ in Water over Ag-Modified La₂Ti₂O₇. *Appl. Catal. B Environ.* **2015**, *163*, 241–247.
- Yoshida, H.; Zhang, L.; Sato, M.; Morikawa, T.; Kajino, T.; Sekito, T.; Matsumoto, S.; Hirata, H. Calcium Titanate Photocatalyst Prepared by a Flux Method for Reduction of Carbon Dioxide with Water. *Catal. Today* **2015**, *251*, 132–139.
- Wang, S.; Teramura, K.; Hisatomi, T.; Domen, K.; Asakura, H.; Hosokawa, S.; Tanaka, T. Effective Driving of Ag-Loaded and Al-Doped SrTiO₃ under Irradiation at λ > 300nm for the Photocatalytic Conversion of CO₂ by H₂O. *ACS Appl. Energy Mater.* **2020**, *3*, 1468–1475.
- Teramura, K.; Wang, Z.; Hosokawa, S.; Sakata, Y.; Tanaka, T. A Doping Technique That Suppresses Undesirable H₂ Evolution Derived from Overall Water Splitting in the Highly Selective Photocatalytic Conversion of CO₂ in and by Water. *Chem. - A Eur. J.* **2014**, *20*, 9906–9909.
- Wang, Z.; Teramura, K.; Huang, Z.; Hosokawa, S.; Sakata, Y.; Tanaka, T. Tuning the Selectivity toward CO Evolution in the Photocatalytic Conversion of CO₂ with H₂O through the Modification of Ag-Loaded Ga₂O₃ with a ZnGa₂O₄ Layer. *Catal. Sci. Technol.* **2016**, *6*, 1025–1032.
- Huang, Z.; Teramura, K.; Hosokawa, S.; Tanaka, T. Fabrication of Well-Shaped Sr₂KTa₅O₁₅ Nanorods with a Tetragonal Tungsten Bronze Structure by a Flux Method for Artificial Photosynthesis. *Appl. Catal. B Environ.* **2016**, *199*, 272–281.
- Huang, Z.; Yoshizawa, S.; Teramura, K.; Asakura, H.; Hosokawa, S.; Tanaka, T. Sodium Cation Substitution in Sr₂KTa₅O₁₅

toward Enhancement of Photocatalytic Conversion of CO₂ Using H₂O as an Electron Donor. *ACS Omega* **2017**, *2*, 8187–8197.

(32) Huang, Z.; Teramura, K.; Asakura, H.; Hosokawa, S.; Tanaka, T. Flux Method Fabrication of Potassium Rare-Earth Tantalates for CO₂ Photoreduction Using H₂O as an Electron Donor. *Catal. Today* **2018**, *300*, 173–182.

(33) Soontornchaiyakul, W.; Yoshino, S.; Yamaguchi, Y.; Kudo, A. *Abstracts of Papers, 129th CATSJ Meeting, Kyoto, Japan 2022*, P122.

(34) Fujiwara, H.; Hosokawa, H.; Murakoshi, K.; Wada, Y.; Yanagida, S.; Okada, T.; Kobayashi, H. Effect of Surface Structures on Photocatalytic CO₂ Reduction Using Quantized CdS Nanocrystallites. *J. Phys. Chem. B* **1997**, *101*, 8270–8278.

(35) Kanemoto, M.; Ankyu, H.; Wada, Y.; Yanagida, S. Visible-Light Induced Photofixation of CO₂ into Benzophenone Catalyzed by Colloidal CdS Microcrystallites. *Chem. Lett.* **1992**, *21*, 2113–2114.

(36) Iwashina, K.; Iwase, A.; Ng, Y. H.; Amal, R.; Kudo, A. Z-Schematic Water Splitting into H₂ and O₂ Using Metal Sulfide as a Hydrogen-Evolving Photocatalyst and Reduced Graphene Oxide as a Solid-State Electron Mediator. *J. Am. Chem. Soc.* **2015**, *137*, 604–607.

(37) Kudo, A.; Kato, H.; Tsuji, I. Strategies for the Development of Visible-Light-Driven Photocatalysts for Water Splitting. *Chem. Lett.* **2004**, *33*, 1534–1539.

(38) Kato, T.; Hakari, Y.; Ikeda, S.; Jia, Q.; Iwase, A.; Kudo, A. Utilization of Metal Sulfide Material of (CuGa)_{1-x}Zn_{2x}S₂ Solid Solution with Visible Light Response in Photocatalytic and Photoelectrochemical Solar Water Splitting Systems. *J. Phys. Chem. Lett.* **2015**, *6*, 1042–1047.

(39) Yoshino, S.; Iwase, A.; Ng, Y. H.; Amal, R.; Kudo, A. Z-Schematic Solar Water Splitting Using Fine Particles of H₂-Evolving (CuGa)_{0.5}ZnS₂ Photocatalyst Prepared by a Flux Method with Chloride Salts. *ACS Appl. Energy Mater.* **2020**, *3*, 5684–5692.

(40) Yamazaki, Y.; Takeda, H.; Ishitani, O. Photocatalytic Reduction of CO₂ Using Metal Complexes. *J. Photochem. Photobiol. C Photochem. Rev.* **2015**, *25*, 106–137.

(41) Wang, W.; Himeda, Y.; Muckerman, J. T.; Manbeck, G. F.; Fujita, E. CO₂ Hydrogenation to Formate and Methanol as an Alternative to Photo- and Electrochemical CO₂ Reduction. *Chem. Rev.* **2015**, *115*, 12936–12973.

(42) Maeda, K. Metal-Complex/Semiconductor Hybrid Photocatalysts and Photoelectrodes for CO₂ Reduction Driven by Visible Light. *Adv. Mater.* **2019**, *31*, 1808205.

(43) Suzuki, T. M.; Yoshino, S.; Takayama, T.; Iwase, A.; Kudo, A.; Morikawa, T. 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. *Chem. Commun.* **2018**, *54*, 10199–10202.

(44) Konta, R.; Ishii, T.; Kato, H.; Kudo, A. Photocatalytic Activities of Noble Metal Ion Doped SrTiO₃ under Visible Light Irradiation. *J. Phys. Chem. B* **2004**, *108*, 8992–8995.

(45) Sasaki, Y.; Nemoto, H.; Saito, K.; Kudo, A. Solar Water Splitting Using Powdered Photocatalysts Driven by Z-Schematic Interparticle Electron Transfer without an Electron Mediator. *J. Phys. Chem. C* **2009**, *113*, 17536–17542.

(46) Yoshino, S.; Sato, K.; Yamaguchi, Y.; Iwase, A.; Kudo, A. Z-Schematic CO₂ Reduction to CO through Interparticle Electron Transfer between SrTiO₃:Rh of a Reducing Photocatalyst and BiVO₄ of a Water Oxidation Photocatalyst under Visible Light. *ACS Appl. Energy Mater.* **2020**, *3*, 10001–10007.

(47) Ikeda, S.; Tanaka, Y.; Kawaguchi, T.; Fujikawa, S.; Harada, T.; Takayama, T.; Iwase, A.; Kudo, A. Photoelectrochemical Reduction of CO₂ to CO Using a CuGaS₂ Thin-Film Photocathode Prepared by a Spray Pyrolysis Method. *Chem. Lett.* **2018**, *47*, 1424–1427.

(48) Kaga, H.; Tsutsui, Y.; Nagane, A.; Iwase, A.; Kudo, A. An Effect of Ag(I)-Substitution at Cu Sites in CuGaS₂ on Photocatalytic and Photoelectrochemical Properties for Solar Hydrogen Evolution. *J. Mater. Chem. A* **2015**, *3*, 21815–21823.

(49) Takayama, T.; Iwase, A.; Kudo, A. *Abstracts of Papers, 114th CATSJ Meeting Hiroshima, Japan; 2014*, 1D05.

(50) Ikeda, S.; Fujikawa, S.; Harada, T.; Nguyen, T. H.; Nakanishi, S.; Takayama, T.; Iwase, A.; Kudo, A. Photocathode Characteristics of a Spray-Deposited Cu₂ZnGeS₄ Thin Film for CO₂ Reduction in a CO₂-Saturated Aqueous Solution. *ACS Appl. Energy Mater.* **2019**, *2*, 6911–6918.

(51) Kamimura, S.; Sasaki, Y.; Kanaya, M.; Tsubota, T.; Ohno, T. Improvement of Selectivity for CO₂ Reduction by Using Cu₂ZnSnS₄ Electrodes Modified with Different Buffer Layers (CdS and In₂S₃) under Visible Light Irradiation. *RSC Adv.* **2016**, *6*, 112594–112601.

(52) Hayashi, T.; Niishiro, R.; Ishihara, H.; Yamaguchi, M.; Jia, Q.; Kuang, Y.; Higashi, T.; Iwase, A.; Minegishi, T.; Yamada, T.; Domen, K.; Kudo, A. Powder-Based (CuGa_{1-y}In_y)_{1-x}Zn_{2x}S₂ Solid Solution Photocathodes with a Largely Positive Onset Potential for Solar Water Splitting. *Sustain. Energy Fuels* **2018**, *2*, 2016–2024.

(53) Takayama, T.; Iwase, A.; Kudo, A. *Abstracts of Papers, 96th CSJ Annual Meeting, Kyoto, Japan; 2016*, 1B1-44.

(54) Takayama, T.; Iwase, A.; Kudo, A. *Abstracts of Papers, 118th CATSJ Meeting, Iwate, Japan; 2016*, 3111.

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