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## Z-Schematic and visible-light-driven CO<sub>2</sub> reduction using H<sub>2</sub>O as an electron donor by a particulate mixture of a Ru-complex/(CuGa)<sub>1-x</sub>Zn<sub>2x</sub>S<sub>2</sub> hybrid catalyst, BiVO<sub>4</sub> and an electron mediator†

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**Visible-light-driven Z-schematic CO<sub>2</sub> reduction using H<sub>2</sub>O as an electron donor was achieved using a simple mixture of a metal-sulfide/molecular hybrid photocatalyst for CO<sub>2</sub> reduction, a water oxidation photocatalyst and a redox-shuttle electron mediator. This is the first demonstration of a highly selective particulate CO<sub>2</sub> reduction system accompanying O<sub>2</sub> generation utilizing a semiconductor/molecular hybrid photocatalyst.**

Photocatalytic CO<sub>2</sub> 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.<sup>1–5</sup> Particulate systems are recognized as cost-effective and could be the ultimate tool for CO<sub>2</sub> fixation and solar fuel generation.<sup>6,7</sup> A photocatalytic Z-scheme (or two-step photoexcitation) system that connects photocatalysts for CO<sub>2</sub> reduction with H<sub>2</sub>O oxidation is considered to be a promising approach; however, few particulate Z-scheme systems for CO<sub>2</sub> reduction using water as an electron donor have been reported. Visible-light-driven conversion of CO<sub>2</sub> into CO over a combined system of CoO<sub>x</sub>-loaded BiVO<sub>4</sub> and metal sulfides with a reduced graphene oxide electron mediator has yet to reach 1% CO selectivity. This is due to competitive H<sub>2</sub> generation and low CO<sub>2</sub> selectivity at metal sulfide surfaces.<sup>8,9</sup>

A hybrid catalyst of a semiconductor<sup>10–12</sup> linked with a metal-complex catalyst<sup>13–15</sup> is promising for visible-light-driven selective CO<sub>2</sub> reduction with regard to high selectivity, depending on the selective coordination of CO<sub>2</sub> molecules to the metal centers of the complexes.<sup>13,16–22</sup> It is essential that photoexcited electrons in the conduction band (CB) of the semiconductor

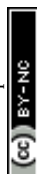
transfer to the metal-complex catalyst within the picosecond region, which leads to two-electron reduction of CO<sub>2</sub> at the complex.<sup>23</sup> We previously demonstrated solar formate generation from CO<sub>2</sub> and H<sub>2</sub>O using a photocathode of a Ru-complex catalyst linked with Zn-doped InP or N,Zn-codoped Fe<sub>2</sub>O<sub>3</sub> combined with TiO<sub>2</sub> or SrTiO<sub>3-x</sub> photoanodes,<sup>24–26</sup> 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<sub>x</sub> electrode.<sup>27</sup> Ishitani and colleagues reported photoelectrochemical CO<sub>2</sub> reduction to CO *via* H<sub>2</sub>O oxidation using a photocathode composed of a Ru(II)-Re(I) supramolecular metal complex immobilized on a NiO or CuGaO<sub>2</sub> semiconductor.<sup>28,29</sup> In contrast, a particulate system for Z-schematic CO<sub>2</sub> reduction using a metal complex combined with a H<sub>2</sub>O oxidation reaction has not yet been demonstrated. Efficient electron transfer from the H<sub>2</sub>O oxidation site to the CO<sub>2</sub> reduction site without degradation of the catalytic activity for both reactions should be implemented.

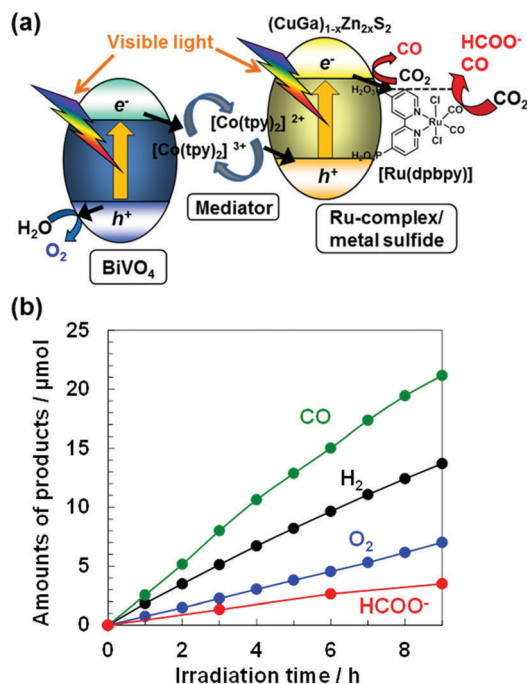
To realize Z-schematic CO<sub>2</sub> reduction with a particulate system, we focused our attention on metal sulfides as the CO<sub>2</sub> reduction semiconductor because they generally possess long photoexcited carrier lifetimes and narrow band gaps (BGs) originating from the S 3p state, which allows absorption of a substantial amount of visible light. Reisner *et al.* reported photocatalytic conversion of CO<sub>2</sub> into CO in water with >90% selectivity over a Ni-cyclam catalyst anchored with CdS.<sup>19</sup> We reported CO<sub>2</sub> photoconversion into HCOOH over ZnS:Ni and (AgIn)<sub>0.22</sub>Zn<sub>1.56</sub>S<sub>2</sub> linked with a Ru-bipyridine catalyst [Ru(4,4'-diphosphonate-2,2'-bipyridine)(CO)<sub>2</sub>Cl<sub>2</sub>] ([Ru(dppbpy)]).<sup>30</sup> These Cd- and Zn-based sulfides are considered to be beneficial when combined with molecular catalysts because of their negative CB minimum (*E*<sub>CBM</sub>) 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 ( $\Delta G$ ) between the *E*<sub>CBM</sub> and CO<sub>2</sub> reduction potential of the metal-complex, which promotes the CO<sub>2</sub> 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 CO<sub>2</sub> reduction using a hybrid photocatalyst, BiVO<sub>4</sub> and a Co-complex, GC-MS chromatograms, IC-TOFMS chromatograms, and XPS spectra. See DOI: 10.1039/c8cc05505j





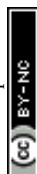
**Fig. 1** (a) Visible-light-driven Z-schematic system for CO<sub>2</sub> reduction consisting of particulate [Ru(dpbpy)] modified (CuGa)<sub>1-x</sub>Zn<sub>2x</sub>S<sub>2</sub> hybrid photocatalysts, a BiVO<sub>4</sub> photocatalyst, and a [Co(tpy)]<sub>2</sub><sup>3+/2+</sup> redox shuttle electron mediator. (b) Z-schematic CO<sub>2</sub> reduction in an aqueous solution with a CO<sub>2</sub> flow system. Conditions: [Ru(dpbpy)]/(CuGa)<sub>0.3</sub>Zn<sub>1.4</sub>S<sub>2</sub> (0.4 g) and BiVO<sub>4</sub> (0.2 g); 0.02 mM [Co(tpy)]<sub>2</sub><sup>2+</sup> containing 0.1 M NaHCO<sub>3</sub> aqueous solution (150 mL) and visible-light ( $\lambda > 420$  nm).

sacrificial electron donor. Here, we demonstrate the first particulate-based visible-light-driven Z-scheme system that harmonizes both reactions of CO<sub>2</sub> reduction and H<sub>2</sub>O oxidation over a hybrid photocatalyst of a semiconductor/molecular-catalyst.

Fig. 1(a) shows an illustration of the Z-schematic system for photoconversion of CO<sub>2</sub> to CO and HCOO<sup>-</sup> over [Ru(dpbpy)]-modified (CuGa)<sub>1-x</sub>Zn<sub>2x</sub>S<sub>2</sub> as a CO<sub>2</sub> reduction hybrid photocatalyst, [Co(tpy)]<sub>2</sub><sup>3+/2+</sup> (tpy: 2,2':6,2''-terpyridine) as an electron mediator, and BiVO<sub>4</sub> as a water oxidation photocatalyst. Fig. 1(b) shows that the simple mixture in an aqueous solution produced CO and HCOO<sup>-</sup> at almost linear rates together with O<sub>2</sub> generation under visible light irradiation after hours of pre-irradiation in a CO<sub>2</sub> flow reactor,<sup>8,9</sup> *i.e.*, the Z-scheme reaction. Although BiVO<sub>4</sub> can photogenerate O<sub>2</sub>,  $E_{\text{CBM}}$  for BiVO<sub>4</sub> is located at an unfavorably deep position for the reduction reaction of CO<sub>2</sub> and protons.<sup>8,31</sup> Thus, the CO<sub>2</sub> reduction reaction could occur at the [Ru(dpbpy)]/(CuGa)<sub>0.3</sub>Zn<sub>1.4</sub>S<sub>2</sub> photocatalyst, which suggests a Z-scheme mechanism with H<sub>2</sub>O as an electron donor, which is discussed later. Although H<sub>2</sub> evolution by proton reduction also proceeded, the CO<sub>2</sub> reduction selectivity to total reductive products (CO, HCOO<sup>-</sup>, H<sub>2</sub>) for 9 h reached 64 mol%, significantly higher than the *ca.* 1% of previous non-molecular particulate Z-scheme systems.<sup>8,9</sup> The modification of [Ru(dpbpy)] led to the production of HCOO<sup>-</sup> and the turnover number (TON) of HCOO<sup>-</sup> evolution was calculated to be 17, assuming that all [Ru(dpbpy)] remained on (CuGa)<sub>1-x</sub>Zn<sub>2x</sub>S<sub>2</sub> during the photocatalytic reaction.

The key to designing the visible-light-driven Z-schematic system is the hybrid photocatalyst for CO<sub>2</sub> reduction. Thus, a sufficient energy difference  $\Delta G$  to facilitate fast electron transfer from the semiconductor to the Ru-complex catalyst plays a decisive role.<sup>16,23</sup> Electron transfer from the water oxidation photocatalyst to the CO<sub>2</sub> reduction photocatalyst is also indispensable. First, the optimal combination of Ru-complex and semiconductor was investigated. A solid solution of CuGaS<sub>2</sub> and ZnS ((CuGa)<sub>1-x</sub>Zn<sub>2x</sub>S<sub>2</sub>)<sup>32</sup> was selected as the semiconductor for the hybrid photocatalyst because their BG and band position, particularly  $E_{\text{CBM}}$ , 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)<sub>1-x</sub>Zn<sub>2x</sub>S<sub>2</sub> synthesized by a solid-state reaction<sup>32</sup> revealed that a single chalcopyrite phase ( $x \leq 0.2$ ) or zincblende structure ( $x \geq 0.5$ ) was obtained (Fig. S1 and Table S1, ESI<sup>†</sup>). The BG of CuGaS<sub>2</sub> and (CuGa)<sub>1-x</sub>Zn<sub>2x</sub>S<sub>2</sub> ( $x < 1.0$ ) was within the range of 2.24–2.54 eV, which enables absorption of visible light (Fig. S2 and Table S1, ESI<sup>†</sup>). Hybrid catalysts of 0.03–0.08 wt% [Ru(dpbpy)] with the phosphonate ligand (CO<sub>2</sub> reduction potential of *ca.* -1.0 V vs. NHE)<sup>30</sup> linked with (CuGa)<sub>1-x</sub>Zn<sub>2x</sub>S<sub>2</sub> were prepared using an adsorption method<sup>30</sup> (Table S2, ESI<sup>†</sup>).

Typical Z-schematic CO<sub>2</sub> reduction was performed by using [Ru(dpbpy)]/(CuGa)<sub>1-x</sub>Zn<sub>2x</sub>S<sub>2</sub> and BiVO<sub>4</sub> in a test tube filled with [Co(tpy)]<sub>2</sub><sup>2+</sup> containing aqueous NaHCO<sub>3</sub> solution saturated with CO<sub>2</sub> under visible light irradiation for 16 h. This method is useful to measure the tendency of the sample-dependent product for multiple runs.<sup>33</sup> Fig. 2(a) shows that the CO<sub>2</sub> reduction activity was significantly dependent on the composition of (CuGa)<sub>1-x</sub>Zn<sub>2x</sub>S<sub>2</sub>. For bare (CuGa)<sub>1-x</sub>Zn<sub>2x</sub>S<sub>2</sub>, the amount of CO produced increased with  $x$  within the range of  $0.0 \leq x \leq 0.5$ , which could be explained by the more negative  $E_{\text{CBM}}$  and narrower BG (Fig. 2(b) and Fig. S2, ESI<sup>†</sup>), which led to a more efficient electron transfer toward a higher CO<sub>2</sub> reduction rate. Further increase in  $x$  ( $x \geq 0.7$ ) decreased CO evolution due to a reduced amount of absorbed photons with a wider BG ( $\geq 2.36$  eV). H<sub>2</sub> evolution induced by the competitive proton reduction increased with  $x$  within the range of  $0.5 \leq x \leq 0.7$ . Replacement of the bare (CuGa)<sub>1-x</sub>Zn<sub>2x</sub>S<sub>2</sub> with the [Ru(dpbpy)]/(CuGa)<sub>1-x</sub>Zn<sub>2x</sub>S<sub>2</sub> 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.<sup>30,34</sup> [Ru(dpbpy)]/(CuGa)<sub>1-x</sub>Zn<sub>2x</sub>S<sub>2</sub> at  $x = 0.7$  showed the highest CO<sub>2</sub> reduction activity for CO and HCOO<sup>-</sup> 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)<sub>1-x</sub>Zn<sub>2x</sub>S<sub>2</sub> for H<sub>2</sub> generation, CoO<sub>x</sub>-loaded BiVO<sub>4</sub> for water oxidation and [Co(tpy)]<sub>2</sub><sup>2+/3+</sup> for electron mediation, the highest water splitting rate was reported at  $x = 0.2$ .<sup>32</sup> In contrast, [Ru(dpbpy)]/(CuGa)<sub>0.8</sub>Zn<sub>0.4</sub>S<sub>2</sub> ( $x = 0.2$ ) showed a negligibly small CO<sub>2</sub> reduction activity. These results suggest that more negative  $E_{\text{CBM}}$  (with greater  $x$ ) improves the electron transfer rate for CO<sub>2</sub> reduction at [Ru(dpbpy)].<sup>16,17,23,30</sup> The CO<sub>2</sub> reduction activity of the hybrid catalyst is in a trade-off relationship between



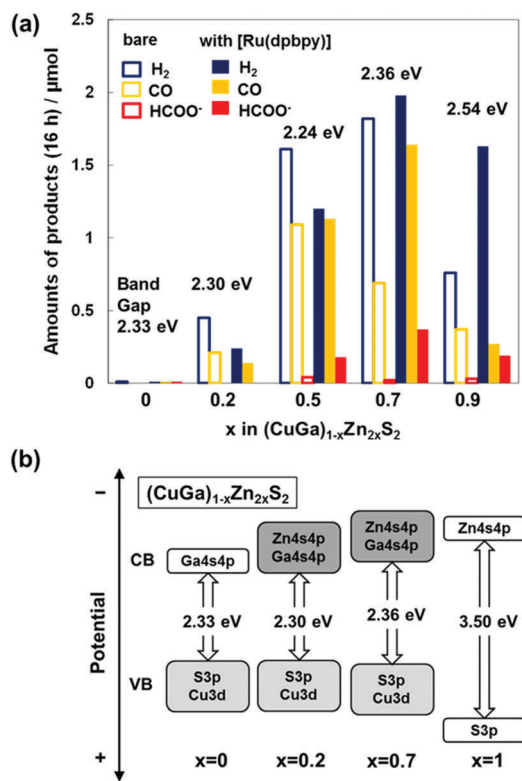


Fig. 2 (a) Z-Schematic CO<sub>2</sub> reduction using the (CuGa)<sub>1-x</sub>Zn<sub>2x</sub>S<sub>2</sub> or ([Ru(dpbpy)]/(CuGa)<sub>1-x</sub>Zn<sub>2x</sub>S<sub>2</sub>)-([Co(tpy)<sub>2</sub>]<sup>3+/2+</sup>)-(BiVO<sub>4</sub>)) systems under visible-light irradiation using the test tube method. Conditions: 8 mg of each photocatalyst; 0.02 mM [Co(tpy)<sub>2</sub>]<sup>2+</sup> containing 0.1 M NaHCO<sub>3</sub> aqueous solution (4 mL); visible-light (390 < λ ≤ 750 nm) for 16 h. (b) Estimated band structures of (CuGa)<sub>1-x</sub>Zn<sub>2x</sub>S<sub>2</sub>.

the negative  $E_{\text{CBM}}$  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)<sub>1-x</sub>Zn<sub>2x</sub>S<sub>2</sub>)-([Co(tpy)<sub>2</sub>]<sup>3+/2+</sup>)-(BiVO<sub>4</sub>) system.

Experimental data used to determine the effective components for the Z-schematic CO<sub>2</sub> reduction are summarized in Table 1. A mixture of BiVO<sub>4</sub> and [Co(tpy)<sub>2</sub>]<sup>2+</sup> produced neither H<sub>2</sub>,

nor CO, nor HCOO<sup>-</sup> due to the unfavorably deep  $E_{\text{CBM}}$  position (entry 1). The addition of (CuGa)<sub>0.3</sub>Zn<sub>1.4</sub>S<sub>2</sub> produced H<sub>2</sub> and CO (entry 2), and [Ru(dpbpy)] modification of (CuGa)<sub>0.3</sub>Zn<sub>1.4</sub>S<sub>2</sub> induced HCOO<sup>-</sup> formation and further improved CO production by the effect of [Ru(dpbpy)] (entry 3, Fig. S3, ESI<sup>†</sup>). The absence of [Co(tpy)<sub>2</sub>]<sup>2+</sup> largely decreased CO and HCOO<sup>-</sup> generation (entry 4), and removal of BiVO<sub>4</sub> resulted in the termination of both CO and HCOO<sup>-</sup> formation (entry 5, Fig. S4, ESI<sup>†</sup>). These results indicate that BiVO<sub>4</sub> is necessary for high CO<sub>2</sub> reduction activity, and the presence of [Co(tpy)<sub>2</sub>]<sup>2+</sup> is essential for a high CO and HCOO<sup>-</sup> formation rate. The absence of NaHCO<sub>3</sub> decreased the formation of both CO and HCOO<sup>-</sup> (entry 6), and the formation of CO and HCOO<sup>-</sup> was negligible in the absence of [Co(tpy)<sub>2</sub>]<sup>2+</sup> (entry 7). Among the aqueous electrolyte and Co-complexes, NaHCO<sub>3</sub> and [Co(tpy)<sub>2</sub>]<sup>2+</sup> were evaluated to be the best for the CO<sub>2</sub> reduction selectivity and production rate, respectively (Tables S3 and S4, ESI<sup>†</sup>). It was also confirmed that no reaction occurred without irradiation (entry 8), and that the formation of CO and HCOO<sup>-</sup> was negligibly small when Ar was bubbled in the solution (entry 9).

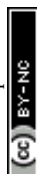
[Co(tpy)<sub>2</sub>]<sup>2+</sup> was reported to act as a [Co(tpy)<sub>2</sub>]<sup>3+/2+</sup> redox shuttle electron mediator connecting two semiconductors for H<sub>2</sub> and O<sub>2</sub> generation in Z-scheme water splitting.<sup>32</sup> As inferred from the mechanism of the IO<sub>3</sub><sup>-</sup>/I<sup>-</sup> shuttle redox mediator system,<sup>35,36</sup> it is speculated that [Co(tpy)<sub>2</sub>]<sup>3+</sup> may favorably adsorb onto BiVO<sub>4</sub>, while [Co(tpy)<sub>2</sub>]<sup>2+</sup> adsorbs onto (CuGa)<sub>0.3</sub>Zn<sub>1.4</sub>S<sub>2</sub>, mediating electrons between them as a redox shuttle. [Co(tpy)<sub>2</sub>]<sup>2+</sup> was reported to be an electrocatalyst for the reduction of CO<sub>2</sub> to CO in dimethylformamide/H<sub>2</sub>O (90/10 v/v) when one terpyridine ligand was eliminated.<sup>37,38</sup> However, the intrinsic potential for the reaction is too negative (-2.0 V vs. Fc/Fc<sup>+</sup>) compared to the  $E_{\text{CBM}}$  of (CuGa)<sub>0.3</sub>Zn<sub>1.4</sub>S<sub>2</sub>; therefore, [Co(tpy)<sub>2</sub>]<sup>2+</sup> is not a catalyst in the present case. [Co(tpy)<sub>2</sub>]<sup>2+</sup> did not catalyze CO<sub>2</sub> reduction in an aqueous solution when electrically biased in the  $E_{\text{CBM}}$  region under visible light irradiation.

Isotope tracer analyses using <sup>13</sup>CO<sub>2</sub> confirmed that the carbon source of evolved CO and HCOO<sup>-</sup> was dissolved CO<sub>2</sub> (Fig. S5 and S6, ESI<sup>†</sup>). O<sub>2</sub> was also confirmed to originate from water using H<sub>2</sub><sup>18</sup>O (Fig. S7, ESI<sup>†</sup>), in which the total amount of <sup>18</sup>O<sub>2</sub> and <sup>16</sup>O<sup>18</sup>O was more than 85% of the total dioxygen detected.

Table 1 Z-Schematic CO<sub>2</sub> reduction activity of the ([Ru(dpbpy)]/(CuGa)<sub>0.3</sub>Zn<sub>1.4</sub>S<sub>2</sub>)-([Co(tpy)<sub>2</sub>]<sup>3+/2+</sup>)-(BiVO<sub>4</sub>) system under visible-light irradiation for 16 h<sup>a</sup>

| Entry | CO <sub>2</sub> reduction photocatalyst                |             | Mediator                              | O <sub>2</sub> evolution photocatalyst |  | Salt               | Gas             | hν | Amount of products (μmol) |      |                   |
|-------|--------------------------------------------------------|-------------|---------------------------------------|----------------------------------------|--|--------------------|-----------------|----|---------------------------|------|-------------------|
|       | (CuGa) <sub>0.3</sub> Zn <sub>1.4</sub> S <sub>2</sub> | [Ru(dpbpy)] | [Co(tpy) <sub>2</sub> ] <sup>2+</sup> | BiVO <sub>4</sub>                      |  | NaHCO <sub>3</sub> |                 |    | H <sub>2</sub>            | CO   | HCOO <sup>-</sup> |
| 1     |                                                        |             | ✓                                     | ✓                                      |  | ✓                  | CO <sub>2</sub> | ✓  | 0.00                      | 0.00 | 0.00              |
| 2     | ✓                                                      |             | ✓                                     | ✓                                      |  | ✓                  | CO <sub>2</sub> | ✓  | 1.82                      | 0.69 | 0.02              |
| 3     | ✓                                                      | ✓           | ✓                                     | ✓                                      |  | ✓                  | CO <sub>2</sub> | ✓  | 1.98                      | 1.64 | 0.37              |
| 4     | ✓                                                      | ✓           | ✓                                     | ✓                                      |  | ✓                  | CO <sub>2</sub> | ✓  | 1.53                      | 0.10 | 0.10              |
| 5     | ✓                                                      | ✓           | ✓                                     | ✓                                      |  | ✓                  | CO <sub>2</sub> | ✓  | 1.06                      | 0.79 | 0.28              |
| 6     | ✓                                                      | ✓           | ✓                                     | ✓                                      |  | ✓                  | CO <sub>2</sub> | ✓  | 3.59                      | 0.56 | 0.18              |
| 7     | ✓                                                      | ✓           | ✓                                     | ✓                                      |  | ✓                  | CO <sub>2</sub> | ✓  | 2.42                      | 0.01 | 0.02              |
| 8     | ✓                                                      | ✓           | ✓                                     | ✓                                      |  | ✓                  | CO <sub>2</sub> | ✓  | 0.00                      | 0.00 | 0.00              |
| 9     | ✓                                                      | ✓           | ✓                                     | ✓                                      |  | ✓                  | Ar              | ✓  | 0.96                      | 0.01 | 0.01              |

<sup>a</sup> Conditions: 8 mg of each photocatalyst; 0.02 mM [Co(tpy)<sub>2</sub>]<sup>2+</sup> containing 0.1 M NaHCO<sub>3</sub> aqueous solution (4 mL); visible-light (390 < λ ≤ 750 nm) for 16 h; Pyrex test tube.





These results explained that  $\text{CO}_2$  was reduced to CO and  $\text{HCOO}^-$  using electrons extracted from  $\text{H}_2\text{O}$  molecules. The TON for  $\text{O}_2$  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  $\text{O}_2$  evolution (4-electron reaction) compared with half of the total of  $\text{CO} + \text{HCOO}^- + \text{H}_2$  (2-electron reactions) in Fig. 1(b) was similarly observed in all-inorganic Z-scheme systems for  $\text{CO}_2$  reduction.<sup>8,9</sup> Self-photooxidation of  $(\text{CuGa})_{1-x}\text{Zn}_{2x}\text{S}_2$  could partially supply electrons for the  $\text{CO}_2$  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  $[\text{Ru}(\text{dpbpy})]$  was eliminated from the  $(\text{CuGa})_{1-x}\text{Zn}_{2x}\text{S}_2$  surface according to the change in the Ru/S and Ru/Zn ratios (Table S5, ESI†).

In conclusion, a visible-light-driven Z-schematic  $\text{CO}_2$  reduction to CO and  $\text{HCOO}^-$  in an aqueous particulate suspension system was achieved using a simple mixture of  $[\text{Ru}(\text{dpbpy})]/(\text{CuGa})_{1-x}\text{Zn}_{2x}\text{S}_2$  hybrid,  $[\text{Co}(\text{tpy})_2]^{2+}$  and  $\text{BiVO}_4$ . Adjustment of band alignment is essential to the Z-schematic  $\text{CO}_2$  reduction reaction accompanying  $\text{O}_2$  generation. The very high  $\text{CO}_2$  reduction selectivity beyond 60% against competing  $\text{H}_2$  generation strongly suggests that the particulate Z-schematic system is feasible to construct selective and efficient photocatalysts for  $\text{CO}_2$  fixation and solar fuel generation.

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## Conflicts of interest

There are no conflicts to declare.

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