

# Water Splitting and CO<sub>2</sub> Reduction under Visible Light Irradiation Using Z-Scheme Systems Consisting of Metal Sulfides, CoOx-Loaded BiVO<sub>4</sub>, and a Reduced Graphene Oxide Electron Mediator

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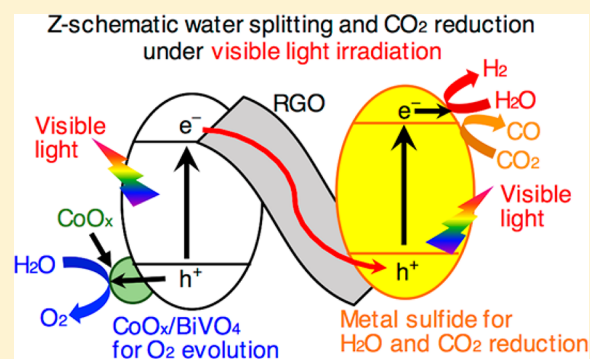
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## Supporting Information

**ABSTRACT:** Metal sulfides are highly active photocatalysts for water reduction to form H<sub>2</sub> under visible light irradiation, whereas they are unfavorable for water oxidation to form O<sub>2</sub> because of severe self-photooxidation (i.e., photocorrosion). Construction of a Z-scheme system is a useful strategy to split water into H<sub>2</sub> and O<sub>2</sub> using such photocorrosive metal sulfides because the photogenerated holes in metal sulfides are efficiently transported away. Here, we demonstrate powdered Z-schematic water splitting under visible light and simulated sunlight irradiation by combining metal sulfides as an H<sub>2</sub>-evolving photocatalyst, reduced graphene oxide (RGO) as an electron mediator, and a visible-light-driven BiVO<sub>4</sub> as an O<sub>2</sub>-evolving photocatalyst. This Z-schematic photocatalyst composite is also active in CO<sub>2</sub> reduction using water as the sole electron donor under visible light.



## INTRODUCTION

Solar water splitting and CO<sub>2</sub> reduction will be the ultimate reactions to convert renewable energy to chemical fuel and products, in which the reactions are generally grouped as artificial photosynthesis. Design of visible-light-driven photocatalyst systems is indispensable to realize such reactions utilizing sunlight. Many photocatalysts have been reported since the discovery of the Honda–Fujishima effect.<sup>1</sup> Among them, metal sulfides are a promising material group for harvesting a wide range of visible light.<sup>2,3</sup> Although many metal sulfide photocatalysts show high activities for water reduction to form H<sub>2</sub>, they are suffering from severe self-photooxidation (photocorrosion) and are hence unfavorable for water oxidation to form O<sub>2</sub>. Therefore, metal sulfides were considered not suitable for water splitting in powdered systems.

Against such a background, we achieved water splitting into a stoichiometric amount of H<sub>2</sub> and O<sub>2</sub> upon using metal sulfide materials as an H<sub>2</sub>-evolving photocatalyst in two-photon excitation (Z-scheme) systems.<sup>4,5</sup> The Z-scheme system is typically constructed of three components: an H<sub>2</sub>-evolving photocatalyst, an electron mediator, and an O<sub>2</sub>-evolving photocatalyst.<sup>2,6–8</sup> We reported that the first successful example of the use of such a photocorrosive metal sulfide was

demonstrated using a Co-complex ionic mediator to relay photogenerated electrons from a metal oxide O<sub>2</sub>-evolving photocatalyst to a metal sulfide H<sub>2</sub>-evolving photocatalyst.<sup>4</sup> Other than Co-complex ionic mediator, however, the metal ion redox couples are not usable as an electron mediator in a Z-scheme system with a metal sulfide as the H<sub>2</sub>-evolving photocatalyst at the present stage. This is probably because the metal ions strongly adsorb on the surface of a metal sulfide photocatalyst due to small solubility product constants (*K<sub>sp</sub>*). Moreover, (CuGa)<sub>0.8</sub>Zn<sub>0.4</sub>S<sub>2</sub> was the only available metal sulfide with demonstrated ability to split water in the Z-scheme system at the present stage. In a separate work, in replace of ionic mediators, reduced graphene oxide (RGO) was found effective as a solid-state electron mediator in transporting the photo-excited charges between Ru-loaded SrTiO<sub>3</sub> doped with Rh of an H<sub>2</sub>-evolving photocatalyst and BiVO<sub>4</sub> of an O<sub>2</sub>-evolving photocatalyst.<sup>5</sup> The use of RGO contributes to expanding the variety of usable metal sulfide photocatalysts such as Pt-loaded CuGaS<sub>2</sub>, CuInS<sub>2</sub>, Cu<sub>2</sub>ZnGeS<sub>4</sub>, and Cu<sub>2</sub>ZnSnS<sub>4</sub> in the Z-scheme system as an H<sub>2</sub>-evolving photocatalyst.<sup>9</sup> However, in that

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particular previous work employing RGO and the metal sulfide photocatalysts,  $\text{TiO}_2$  (bandgap energy 3.0 eV) was used as the  $\text{O}_2$ -evolving photocatalyst. Consequently, the Z-scheme with RGO functions only under UV irradiation. Therefore, a careful selection of a visible-light-driven  $\text{O}_2$ -evolving photocatalyst is required in the RGO-bridged Z-scheme system with a metal sulfide  $\text{H}_2$ -evolving photocatalyst.

Here, we demonstrate Z-schematic water splitting under visible light irradiation upon combining metal sulfides as an  $\text{H}_2$ -evolving photocatalyst, RGO electron mediator, and a visible-light-driven CoOx-loaded  $\text{BiVO}_4$  (bandgap energy 2.4 eV)<sup>10</sup> as an  $\text{O}_2$ -evolving photocatalyst instead of  $\text{TiO}_2$ . The role of the CoOx-cocatalyst in the developed Z-scheme system was investigated and determined to be the key factor regulating the overall activities. We also demonstrated  $\text{CO}_2$  reduction using water as the sole electron donor under visible light irradiation using the developed Z-scheme photocatalyst in a simple suspension system.

## EXPERIMENTAL SECTION

**Preparation of Photocatalysts and Characterization.**  $\text{CuGaS}_2$ ,  $\text{CuInS}_2$ ,  $\text{Cu}_2\text{ZnGeS}_4$ , and  $\text{Cu}_2\text{ZnSnS}_4$  were prepared at 873, 1073, 923, and 973 K under vacuum by a solid-state reaction for 10 h, respectively, according to previous reports.<sup>11–13</sup> All of the starting materials of metal sulfides,  $\text{Cu}_2\text{S}$  (99%),  $\text{Ga}_2\text{S}_3$  (99.99%),  $\text{In}_2\text{S}_3$  (99.99%),  $\text{ZnS}$  (99.999%),  $\text{GeS}_2$  (99.99%), and  $\text{SnS}_2$  (99.9%), were purchased from Kojundo Chemical. They were mixed in an agate mortar with 20% excess Ga for  $\text{CuGaS}_2$ , 10% excess In for  $\text{CuInS}_2$ , 15% excess Zn and Ge for  $\text{Cu}_2\text{ZnGeS}_4$ , and 15% excess Sn for  $\text{Cu}_2\text{ZnSnS}_4$ . A Pt-cocatalyst was adsorbed on metal sulfides by stirring metal sulfides (0.3 g) in a  $46 \mu\text{mol L}^{-1}$  aqueous  $\text{H}_2\text{PtCl}_6$  solution (100 mL) for 1 h.

$\text{BiVO}_4$  was prepared by a liquid–solid-state reaction at room temperature, according to the previous report.<sup>5,14</sup> A CoOx-cocatalyst was loaded on the  $\text{BiVO}_4$  by an impregnation with an aqueous solution of  $\text{Co}(\text{NO}_3)_2$  (Wako, 99.5%). The  $\text{BiVO}_4$  powder (0.5 g) and a  $80 \text{ mmol L}^{-1}$  aqueous  $\text{Co}(\text{NO}_3)_2$  solution (0.53 mL) were placed in a porcelain crucible and dried. The impregnated powder was calcined in air at 673 K for 2 h to obtain  $\text{CoOx}/\text{BiVO}_4$ . The RGO-CoOx/ $\text{BiVO}_4$  composite was prepared by photocatalytic reduction of graphene oxide over  $\text{CoOx}/\text{BiVO}_4$  under visible light irradiation. A certain amount of graphene oxide powder and 0.2 g of  $\text{CoOx}/\text{BiVO}_4$  powder were dispersed in a 50 vol % of aqueous methanol solution (40 mL). The suspensions were stirred and bubbled with Ar gas during visible light irradiation for 3 h.

The crystal phases of the obtained powders were confirmed by X-ray diffraction (Rigaku, MiniFlex 600). The oxidation states of graphene oxide and reduced graphene oxide were studied using X-ray photoelectron spectroscopy (Kratos Analytical, ESCA-3400).

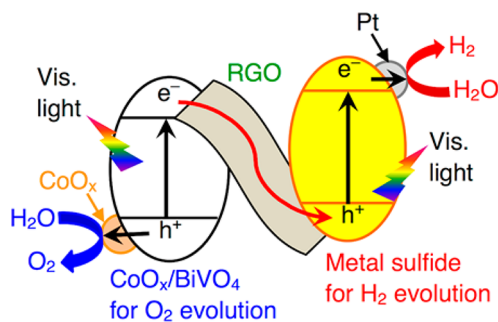
**Photocatalytic Reactions.** Photocatalytic water splitting and  $\text{CO}_2$  reduction were carried out under 1 atm of Ar and  $\text{CO}_2$  gas flow, respectively. Pt-loaded metal sulfides (0.05 g) and an RGO-CoOx/ $\text{BiVO}_4$  composite (0.05 g) were dispersed in water (120 mL) in a top-irradiation cell with a Pyrex window. A 300 W Xe arc lamp (PerkinElmer; CERMAX PE300BF) with a long-pass filter ( $\lambda > 420 \text{ nm}$ ) and a solar simulator (Yamashita Denso; YSS-80QA,  $100 \text{ mW cm}^{-2}$ ) was employed as a light source. Amounts of evolved hydrogen and oxygen were determined using an online gas chromatograph (Shimadzu; GC-8A, MS-5A column, TCD, Ar carrier).

**Photoelectrochemical Measurements.** Metal sulfides and  $\text{BiVO}_4$  photoelectrodes were prepared by a drop-casting method. Photocatalyst powders were dispersed in ethanol ( $1 \text{ mg mL}^{-1}$ ) by sonication. The suspension was drop-cast onto an FTO substrate (Asahi Glass) to obtain  $1 \text{ mg cm}^{-2}$  of the photocatalyst on the FTO. The metal sulfide- and  $\text{BiVO}_4$ -loaded FTO substrates were calcined at 573 and 673 K for 2 h in  $\text{N}_2$  and air, respectively.

Photoelectrochemical properties were evaluated with a three-electrode system consisting of working, Ag/AgCl reference, and Pt counter electrodes using a potentiostat (Hokuto Denko; HZ-7000). The electrolyte used was  $0.1 \text{ mol L}^{-1} \text{ K}_2\text{SO}_4 + 0.025 \text{ mol L}^{-1} \text{ KH}_2\text{PO}_4 + 0.025 \text{ mol L}^{-1} \text{ Na}_2\text{HPO}_4$ . A 300 W Xe arc lamp (PerkinElmer; CERMAX PE300BF) with a long-pass filter ( $\lambda > 420 \text{ nm}$ ) was employed as a light source.

## RESULTS AND DISCUSSION

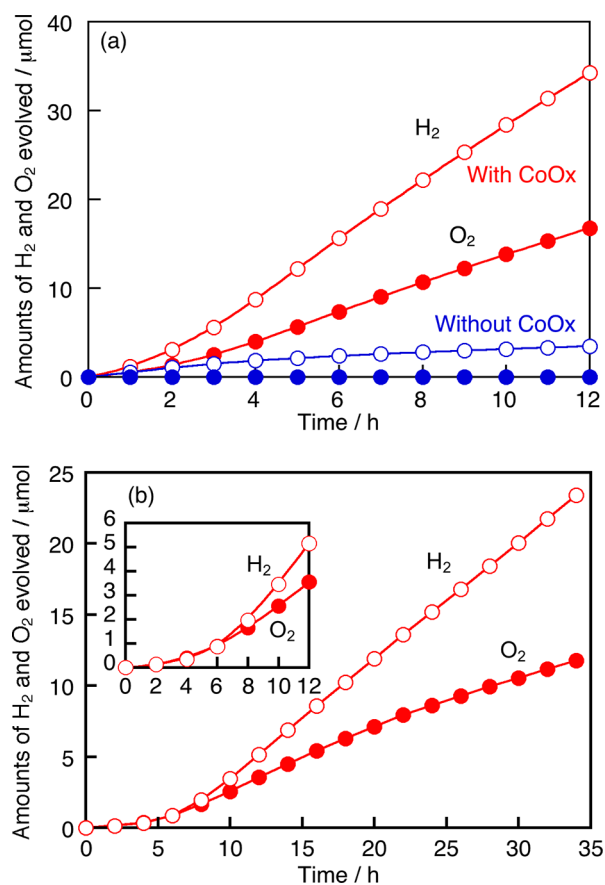
**Construction of Visible-Light-Driven Z-Scheme Systems for Water Splitting Using Metal Sulfide and  $\text{BiVO}_4$  Photocatalysts.** A cobalt oxide (CoOx) as a well-known cocatalyst for  $\text{O}_2$  evolution was impregnated on  $\text{BiVO}_4$  photocatalyst to prepare  $\text{CoOx}(0.5 \text{ wt } \% \text{ as Co})/\text{BiVO}_4$ . The RGO(5 wt % to  $\text{CoOx}/\text{BiVO}_4$ ) was incorporated with  $\text{CoOx}/\text{BiVO}_4$  in consideration of facilitating the electron flow from an  $\text{O}_2$ -evolving photocatalyst to an  $\text{H}_2$ -evolving photocatalyst in the Z-scheme system (Figure 1), according to previous



**Figure 1.** Z-scheme system for water splitting consisting of a Pt-loaded metal sulfide photocatalyst and an RGO-CoOx/ $\text{BiVO}_4$  composite photocatalyst.

works.<sup>5,9</sup> In more detail, graphene oxide prepared by Hummers' method<sup>15</sup> was photocatalytically reduced on  $\text{BiVO}_4$  to form an RGO-CoOx/ $\text{BiVO}_4$  composite. Photocatalytic reduction of graphene oxide to form RGO was confirmed by a significant decrease in intensity of oxygenated carbon peaks in a XPS spectrum (Figure S1).<sup>5,14</sup>

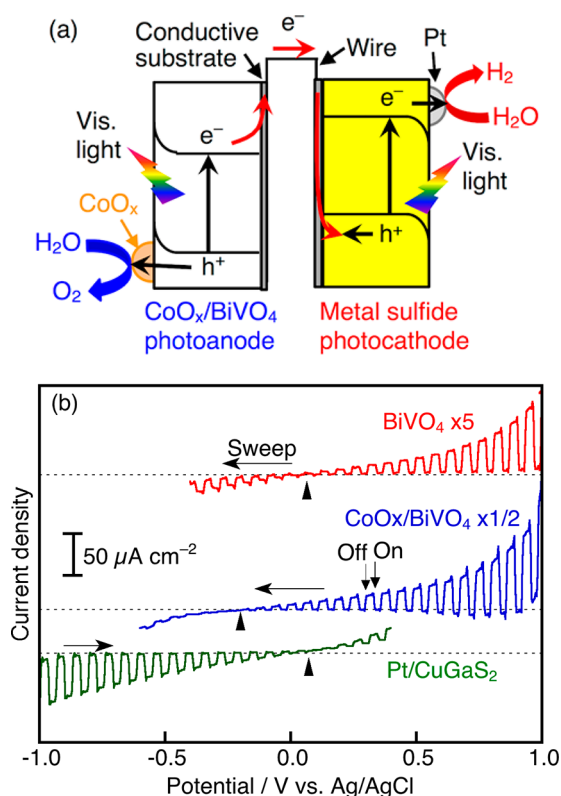
The RGO-CoOx/ $\text{BiVO}_4$  composite was dispersed with Pt-loaded  $\text{CuGaS}_2$  (Pt/ $\text{CuGaS}_2$ ) as an  $\text{H}_2$ -evolving photocatalyst in water to construct a Z-scheme system as shown in Figure 1. Upon irradiating visible light,  $\text{H}_2$  and  $\text{O}_2$  evolved steadily with a stoichiometric amount, as shown in Figure 2a. In contrast, only a small amount of  $\text{H}_2$  was obtained due to photocorrosion in the absence of the CoOx cocatalyst. This clearly indicates that the key factor for the present Z-scheme system lies in the presence of the CoOx-cocatalyst on the  $\text{BiVO}_4$  photocatalyst. The turnover numbers of the number of reacted electrons (holes) for water splitting to Co atoms and to atoms at the surface of  $\text{BiVO}_4$  and  $\text{CuGaS}_2$  were calculated to be 16, 17, and 18 at 12 h, respectively. The activity was still steadily at the time. To calculate the turnover number to carbon atoms in RGO, the RGO(1 wt %)-CoOx/ $\text{BiVO}_4$  was employed, and the turnover number was 1.9 at 15 h (Figure S2). Moreover, no water splitting proceeded when Pt/ $\text{CuGaS}_2$  or RGO-CoOx/ $\text{BiVO}_4$  alone was used (Table S1). Additionally, the combination of Pt/ $\text{CuGaS}_2$  and  $\text{CoOx}/\text{BiVO}_4$  in the absence of RGO did not show activity for water splitting (Table S1). These control experiments and the turnover numbers for each component greater than one indicate that the Z-schematic water splitting photocatalytically proceeded. The present Z-



**Figure 2.** Z-schematic water splitting using Pt/CuGaS<sub>2</sub> and an RGO (5 wt%)-BiVO<sub>4</sub> composite with and without a CoOx-cocatalyst under (a) visible light ( $\lambda > 420$  nm) and (b) simulated sunlight (AM 1.5) irradiation. Photocatalyst: 0.05 g each, solution: water without pH adjustment (120 mL), cell: top-irradiation cell with a Pyrex window.

scheme system consisting of the Pt/CuGaS<sub>2</sub> and the RGO-CoOx/BiVO<sub>4</sub> composite steadily split water even under simulated sunlight irradiation after 6 h with an obvious induction period as shown in the inset in Figure 2b, as shown in Figure 2b. In the induction period, a small amount of excess O<sub>2</sub> evolved mainly due to the further reduction of RGO. In fact, O<sub>2</sub> evolution over CoOx/BiVO<sub>4</sub> accompanied by reduction of GO was confirmed under visible light and simulated sunlight irradiation, when GO and CoOx/BiVO<sub>4</sub> were dispersed in water.

To clarify the role of CoOx in the present Z-scheme system, photoelectrochemical measurements were carried out. We have suggested that the combination of photocatalysts having p-type and n-type semiconductor properties is indispensable for the Z-scheme system with an RGO electron mediator,<sup>9</sup> because an electron flow in the Z-scheme system is similar to that in a photoelectrode system in terms of migration of electrons photogenerated in an O<sub>2</sub>-evolving side to an H<sub>2</sub>-evolving side, as explained in Figure 1 and Figure 3a. Figure 3b shows *I*-*V* curves of Pt/CuGaS<sub>2</sub> and BiVO<sub>4</sub> which are respectively well-known as p-type and n-type semiconductors. Pt/CuGaS<sub>2</sub> and BiVO<sub>4</sub> demonstrated cathodic and anodic photocurrents, respectively, as previously reported.<sup>11,16–21</sup> There is no overlapped range between the potentials for the cathodic photocurrent of the Pt/CuGaS<sub>2</sub> and the anodic photocurrent of the pristine BiVO<sub>4</sub>, because both of their onset potentials are around 0.1 V vs Ag/AgCl at pH 7. In contrast, the onset



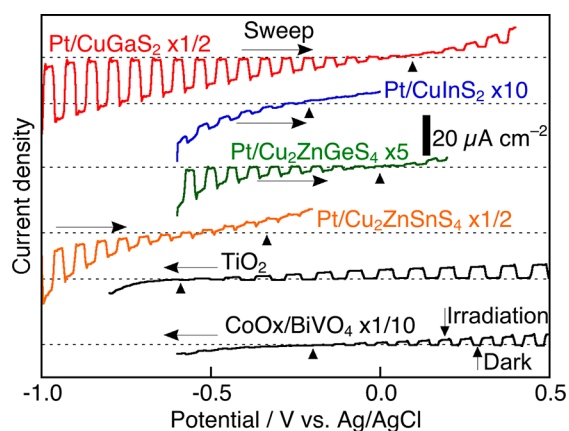
**Figure 3.** (a) Photoelectrochemical system consisting of a metal sulfide photocatalyst electrode with a p-type semiconductor character and a CoOx/BiVO<sub>4</sub> photoelectrode for water splitting without an external bias. (b) Current–potential curves of BiVO<sub>4</sub>, CoOx/BiVO<sub>4</sub>, and Pt/CuGaS<sub>2</sub> under visible light irradiation. Electrolyte: 0.1 mol L<sup>-1</sup> K<sub>2</sub>SO<sub>4</sub> + 0.025 mol L<sup>-1</sup> KH<sub>2</sub>PO<sub>4</sub> + 0.025 mol L<sup>-1</sup> Na<sub>2</sub>HPO<sub>4</sub>, light source: 300 W Xe-arc lamp ( $\lambda > 420$  nm).

potential of BiVO<sub>4</sub> shifted to negative direction upon loading of CoOx due to the promotion of water oxidation,<sup>17,18</sup> and hence overlapped potential range appeared. This clearly means that photogenerated electrons in the CoOx-loaded BiVO<sub>4</sub> can migrate to Pt/CuGaS<sub>2</sub> through RGO without assistance of external bias, as shown in Figure 1. Thus, promotion of water oxidation over the BiVO<sub>4</sub> by loading CoOx induced enhancement of an electron injection from BiVO<sub>4</sub> to CuGaS<sub>2</sub> through RGO, resulting in achievement of the Z-schematic water splitting. We previously employed CuInS<sub>2</sub>, Cu<sub>2</sub>ZnGeS<sub>4</sub>, and Cu<sub>2</sub>ZnSnS<sub>4</sub> which function as an H<sub>2</sub>-evolving photocatalyst in a Z-scheme system using RGO-TiO<sub>2</sub> composite as an O<sub>2</sub>-evolving photocatalyst under UV illumination.<sup>9</sup> In this work, stoichiometric H<sub>2</sub> and O<sub>2</sub> evolution were observed under visible light irradiation, when Pt/Cu<sub>2</sub>ZnGeS<sub>4</sub> and Pt/CuGaS<sub>2</sub> were used together with RGO-CoOx/BiVO<sub>4</sub> (entries 1 and 3 in Table 1). In contrast, no water splitting proceeded when Pt/CuInS<sub>2</sub> and Pt/Cu<sub>2</sub>ZnSnS<sub>4</sub> were used (entries 2 and 4 in Table 1). Thus, CuGaS<sub>2</sub> and Cu<sub>2</sub>ZnGeS<sub>4</sub> function as an H<sub>2</sub>-evolving photocatalyst in the Z-scheme system with both RGO-TiO<sub>2</sub> and RGO-CoOx/BiVO<sub>4</sub>, while CuInS<sub>2</sub> and Cu<sub>2</sub>ZnSnS<sub>4</sub> function with only RGO-TiO<sub>2</sub>. This can also be explained from the point of view of photoelectrochemical properties, as shown in Figure 4. The onset potentials of CuGaS<sub>2</sub>, CuInS<sub>2</sub>, Cu<sub>2</sub>ZnGeS<sub>4</sub>, and Cu<sub>2</sub>ZnSnS<sub>4</sub> were found to be around 0.1, -0.2, 0, and -0.3 V vs Ag/AgCl at pH 7, respectively. Therefore, the CoOx/BiVO<sub>4</sub> (-0.2 V vs Ag/AgCl at pH 7) possessed overlapped potential range with CuGaS<sub>2</sub> and Cu<sub>2</sub>ZnGeS<sub>4</sub>. In

**Table 1. Z-Schematic Water Splitting under Visible Light Irradiation Using Z-Scheme Systems Consisting of Various Metal Sulfides of an H<sub>2</sub>-Evolving Photocatalyst and RGO-CoOx/BiVO<sub>4</sub> of an O<sub>2</sub>-Evolving Photocatalyst<sup>a</sup>**

entry	H <sub>2</sub> -photocatalyst (metal sulfide)	activity/ $\mu\text{mol h}^{-1}$	
		H <sub>2</sub>	O <sub>2</sub>
1	Pt/CuGaS <sub>2</sub>	3.5	1.7
2	Pt/CuInS <sub>2</sub>	0.1	trace
3	Pt/Cu <sub>2</sub> ZnGeS <sub>4</sub>	1.1	0.7
4	Pt/Cu <sub>2</sub> ZnSnS <sub>4</sub>	0	0

<sup>a</sup>Photocatalyst: 0.05 g each, solution: water without pH adjustment (120 mL), light source: 300 W Xe-lamp with a cutoff filter ( $\lambda > 420$  nm), cell: top-irradiation cell with a Pyrex window.

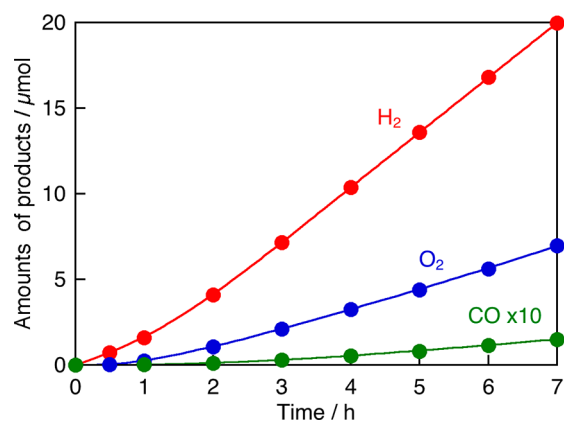


**Figure 4.** Current–potential curves of Pt/CuGaS<sub>2</sub>, Pt/CuInS<sub>2</sub>, Pt/Cu<sub>2</sub>ZnGeS<sub>4</sub>, Pt/Cu<sub>2</sub>ZnSnS<sub>4</sub>, TiO<sub>2</sub>, and CoOx/BiVO<sub>4</sub>. Electrolyte: 0.1 mol L<sup>-1</sup> K<sub>2</sub>SO<sub>4</sub> + 0.025 mol L<sup>-1</sup> KH<sub>2</sub>PO<sub>4</sub> + 0.025 mol L<sup>-1</sup> Na<sub>2</sub>HPO<sub>4</sub>, light source: 300 W Xe-arc lamp ( $\lambda > 300$  nm for TiO<sub>2</sub> and  $\lambda > 420$  nm for others).

contrast, the TiO<sub>2</sub> possessed more negative onset potential (around -0.6 V vs Ag/AgCl at pH 7) than CoOx/BiVO<sub>4</sub> (-0.2 V vs Ag/AgCl at pH 7), resulting in the presence of overlapped potential range with all of the metal sulfides. Thus, a strong relation between the present Z-scheme system with an RGO electron mediator and photoelectrochemical properties was confirmed.

**CO<sub>2</sub> Reduction under Visible Light Irradiation Using the Z-Scheme System with CuGaS<sub>2</sub> and CoOx-Loaded BiVO<sub>4</sub> Photocatalysts.** The CuGaS<sub>2</sub> possesses a conduction band which is thermodynamically sufficient for CO<sub>2</sub> reduction.<sup>22,23</sup> Therefore, it is expected that the CuGaS<sub>2</sub> can be employed not only for H<sub>2</sub>O reduction but also for CO<sub>2</sub> reduction. In fact, we preliminarily reported that the CuGaS<sub>2</sub> is active for CO<sub>2</sub> reduction to form CO under visible light irradiation in an aqueous solution containing K<sub>2</sub>SO<sub>3</sub> as an electron donor.<sup>24</sup> Accordingly, we tried to apply the developed Z-scheme system to CO<sub>2</sub> reduction under visible light irradiation using water as an electron donor. Because a Pt-cocatalyst does not work as active sites for photocatalytic CO<sub>2</sub> reduction at the present stage,<sup>25</sup> first, pristine CuGaS<sub>2</sub> was used as an H<sub>2</sub>-evolving photocatalyst for Z-schematic water splitting as a preliminary experiment. A Z-scheme system using the pristine CuGaS<sub>2</sub> and RGO-CoOx/BiVO<sub>4</sub> split water under visible light irradiation (Figure S3). This is reasonable because photoelectrochemical water splitting using a nonloaded CuGaS<sub>2</sub> photocathode and a CoOx/BiVO<sub>4</sub> photoanode

without any external bias has been reported.<sup>21</sup> However, the activity was lower than that in the presence of the Pt-cocatalyst on CuGaS<sub>2</sub>. Next, the pristine CuGaS<sub>2</sub> was employed as a CO<sub>2</sub>-reducing photocatalyst. The pristine CuGaS<sub>2</sub> and RGO-CoOx/BiVO<sub>4</sub> were dispersed in water and were irradiated with visible light in an atmosphere of CO<sub>2</sub>. As the result, a certain amount of CO evolved in addition to H<sub>2</sub> and O<sub>2</sub> due to water splitting, as shown in Figure 5. In the absence of CO<sub>2</sub>, H<sub>2</sub> and O<sub>2</sub> but no



**Figure 5.** Z-schematic CO<sub>2</sub> reduction using CuGaS<sub>2</sub> and an RGO(5 wt %)-CoOx/BiVO<sub>4</sub> composite under visible light irradiation. Photocatalyst: 0.05 g each, solution: water without pH adjustment (120 mL), light source: 300 W Xe-arc lamp ( $\lambda > 420$  nm), cell: top-irradiation cell with a Pyrex window.

CO were observed. Thus, we rule out the possibility that the CO formation was originated from other contamination and/or RGO. Slightly higher amount of evolved H<sub>2</sub> than a stoichiometric amount will be probably due to the fact that the H<sub>2</sub>S (S<sup>2-</sup>) generated by hydrolysis of CuGaS<sub>2</sub> in an acidic condition worked as an electron donor. Although the selectivity of CO<sub>2</sub> reduction is not very high, achievement of the Z-schematic CO<sub>2</sub> reduction under visible light irradiation has great significance in terms of expanding the possibility of powdered photocatalysis systems.

## CONCLUSIONS

We have demonstrated that the visible-light-responsive BiVO<sub>4</sub> can be used as an O<sub>2</sub> evolving photocatalyst upon CoOx-loading for a Z-scheme water-splitting system with metal sulfides as an H<sub>2</sub>-evolving photocatalyst bridged by RGO electron mediator. The CoOx played an important role in the present Z-scheme system to promote water oxidation on BiVO<sub>4</sub>, resulting in the enhancement of the electron injection from BiVO<sub>4</sub> to CuGaS<sub>2</sub> through RGO. We have also confirmed a strong relation between the present Z-scheme system with an RGO electron mediator and photoelectrochemical properties. In more detail, the combination of p-type and n-type photocatalysts for H<sub>2</sub> evolution and O<sub>2</sub> evolution, respectively, and the presence of overlapped potential are indispensable for the Z-scheme system with RGO. Thus, we successfully achieve Z-schematic water splitting and CO<sub>2</sub> reduction under visible light irradiation of artificial photosynthesis using photocorrosive metal sulfide materials and found guidelines for construction of such Z-scheme systems. Our finding will contribute to develop metal sulfide-based artificial photosynthetic systems.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/jacs.6b05304](https://doi.org/10.1021/jacs.6b05304).

XPS spectra;  $I$ - $V$  curves; control experiments (PDF)

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### Notes

The authors declare no competing financial interest.

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