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Photocatalytic CO_2 reduction using water as an electron donor by a powdered Z-scheme system consisting of metal sulfide and an RGO–TiO_2 composite†

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$CuGaS_2$, $(AgInS_2)_x$–$(ZnS)_{2-2x}$, Ag_2ZnGeS_4, Ni- or Pb-doped ZnS, $(ZnS)_{0.9}$–$(CuCl)_{0.1}$, and $ZnGa_{0.5}In_{1.5}S_4$ showed activities for CO_2 reduction to form CO and/or HCOOH in an aqueous solution containing K_2SO_3 and Na_2S as electron donors under visible light irradiation. Among them, $CuGaS_2$ and Ni-doped ZnS photocatalysts showed relatively high activities for CO and HCOOH formation, respectively. $CuGaS_2$ was applied in a powdered Z-scheme system combining with reduced graphene oxide (RGO)-incorporated TiO_2 as an O_2-evolving photocatalyst. The powdered Z-scheme system produced CO from CO_2 in addition to H_2 and O_2 due to water splitting. Oxygen evolution with an almost stoichiometric amount indicates that water was consumed as an electron donor in the Z-schematic CO_2 reduction. Thus, we successfully demonstrated CO_2 reduction of artificial photosynthesis using a simple Z-scheme system in which two kinds of photocatalyst powders ($CuGaS_2$ and an RGO–TiO_2 composite) were only dispersed in water under 1 atm of CO_2.

Introduction

Photocatalytic CO_2 reduction using water as an electron donor can be called artificial photosynthesis, converting photon energy to chemical energy with a positive change in the Gibbs free energy (an uphill reaction). The reaction also contributes to CO_2 fixation to produce raw materials such as CO for C1 chemistry. A powder-based photocatalyst system has an advantage in a practical large-scale application because of its simplicity. CO_2 reduction over various powdered photocatalysts has been investigated.[1–7] In photocatalytic CO_2 reduction,

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stoichiometric O_2 evolution as an oxidation product of water is necessary to show that the water is consumed as an electron source. Sayama *et al.* reported that a pristine ZrO_2 photocatalyst reduced CO_2 to CO with stoichiometric O_2 evolution and that the loading of a Cu cocatalyst on the ZrO_2 improved the selectivity of the CO formation.[8] We also reported that Ag-loaded $BaLa_4Ti_4O_{15}$ (ref. 9) (denoted as $Ag/BaLa_4Ti_4O_{15}$), $Ag/NaTaO_3$:Ba,[10] and $Ag/KCaSrTa_5O_{15}$ (ref. 11 and 12) showed activity for CO_2 reduction using water as an electron donor. In our works, metallic Ag nanoparticles were found to be the most efficient cocatalyst for photocatalytic CO_2 reduction to form CO at the present stage. Moreover, Teramura and Yoshida *et al.* also applied a Ag cocatalyst to CO_2 reduction using metal oxide photocatalysts which were active for water splitting, resulting in that $Ag/La_2Ti_2O_7$,[13] $Ag/CaTiO_3$,[14] $Ag/ZnTa_2O_6$,[15] Ag/Ta_2O_5 modified with SrO,[16] and $Ag/ZnGa_2O_4/Ga_2O_3$ (ref. 17) were found to be active photocatalysts for CO_2 reduction.

Many metal sulfide photocatalysts show activity for hydrogen evolution under visible light irradiation in the presence of a sacrificial electron donor.[18,19] CdS nanoparticles of a well-known efficient photocatalyst for hydrogen evolution[20,21] are also active for CO_2 reduction.[22] Thus, metal sulfides have the possibility to reduce CO_2 under visible light irradiation in the presence of electron donors. However, self-oxidation by photogenerated holes, photocorrosion, still remains as an issue for metal sulfides in CO_2 reduction using water as an electron donor. Recently, we have successfully applied metal sulfides as an H_2-evolving photocatalyst in a Z-scheme system for water splitting into H_2 and O_2 upon employing a reduced graphene oxide (RGO) as a solid-state electron mediator and Co-complexes as ionic electron mediators.[23,24] The system using RGO as the solid-state electron mediator can be successfully applied to powdered Z-schematic CO_2 reduction with certain O_2 evolution upon combining $CuGaS_2$ as a CO_2-reducing photocatalyst, with an $RGO–CoO_x/BiVO_4$ composite as an O_2-evolving photocatalyst.[25] Although CO_2 reduction proceeds even under visible light irradiation, the number of combinations of metal sulfide photocatalysts and $CoO_x/BiVO_4$ for the Z-scheme system is limited at the present stage because of the relatively low reduction power of $BiVO_4$, for example, compared with TiO_2. Consequently, various metal sulfides such as $CuGaS_2$, $CuInS_2$, Cu_2ZnGeS_4, and Cu_2ZnSnS_4 can be used as an H_2-evolving photocatalyst when $RGO–TiO_2$ is used as an O_2-evolving photocatalyst.[24] Therefore, TiO_2 is a suitable O_2-evolving photocatalyst for surveying metal sulfide-based Z-scheme photocatalyst systems employing an RGO solid-state electron mediator. Activity for Z-schematic water splitting strongly depends on the reaction conditions such as the amounts of H_2- and O_2-evolving photocatalysts and electron mediator used, and pH values of the reactant solution.[26,27] Accordingly, it is also important to clarify the factors affecting activity for Z-schematic CO_2 reduction to construct highly efficient systems.

In the present study, we developed metal sulfide photocatalysts that were active for CO_2 reduction under visible light irradiation in an aqueous solution containing sacrificial reagents based on our library of metal sulfide photocatalysts for solar hydrogen production.[18,28–37] The developed metal sulfides were applied to a powdered Z-scheme system to achieve CO_2 reduction using water as an electron donor upon combining with RGO-incorporated TiO_2 as an O_2-evolving photocatalyst.

Experimental

Preparation of metal sulfide photocatalysts

$CuGaS_2$,[35] Cu_2ZnGeS_4,[32] $CuGa_5S_8$,[34] $CuGa_2In_3S_8$,[33] $AgGaS_2$,[31,36] $(AgInS_2)_x–(ZnS)_{2−2x}$ ($x = 0.1$ and 0.22),[30] Ag_2ZnGeS_4,[32] Ni- or Pb-doped ZnS,[28,29] $Zn_{1−x}Cu_xGa_2S_{4−x/2}$,[34] Cu_3NbS_4,[37] Cu_3TaS_4,[37] $(ZnS)_{0.9}–(CuCl)_{0.1}$,[37] $BaLaCuS_3$,[37] $ZnIn_2S_4$,[37] $ZnGa_{0.5}In_{1.5}S_4$,[37] and $MnGaInS_4$ (ref. 37) were prepared by solid-state reaction and precipitation methods according to previous reports. Obtained samples were identified by X-ray diffraction (Rigaku; MiniFlex, Cu Kα). Diffuse reflectance spectra were obtained by a UV-vis-NIR spectrometer (JASCO, V-570) equipped with an integrating sphere and were converted to absorbance by the Kubelka–Munk method.

Preparation of an RGO–TiO$_2$ composite

An RGO-incorporated TiO_2 photocatalyst (denoted as RGO–TiO_2 composite) was prepared by photocatalytic reduction of graphene oxide using TiO_2 according to a previous report.[24] The powders of GO prepared by Hummers' method[38] and rutile TiO_2 (Kojundo; 99.99%) were dispersed in an aqueous methanol (Kanto; 99.8%) solution (50 vol%). The suspension was irradiated with UV light from a 300 W Xe-lamp (PerkinElmer; CERMAX PE300BF) under 1 atm of N_2 atmosphere to obtain an RGO–TiO_2 composite. The methanol was carefully removed by washing with water. The RGO–TiO_2 composite was collected by filtration and was dried at room temperature in air.

Sacrificial CO$_2$ reduction

CO_2 reduction using sacrificial reagents was conducted using a batch-type top-irradiation cell with a Pyrex window under 1 atm of CO_2 gas (99.995%). Metal sulfide photocatalysts were dispersed in an aqueous solution containing sacrificial reagents of $0.05–0.1$ mol L^{-1} Na_2S (Kanto; 98%) and 0.1 mol L^{-1} K_2SO_3 (Kanto; 95%). A 300 W Xe-lamp was employed as a light source. The wavelength of the irradiation light was controlled to visible light using a cut-off filter ($\lambda > 420$ nm). Products in gas and liquid phases were analyzed using a gas-chromatograph (Shimadzu; GC-8A, MS-5A, TCD, Ar carrier for H_2 and O_2; GC-8A, MS-13X, FID with a methanizer, N_2 carrier for CO) and a high performance liquid chromatograph (Shimadzu), respectively.

Z-schematic CO$_2$ reduction

Z-schematic CO_2 reduction was conducted using a gas-flow system with a top-irradiation cell with a Pyrex window. $CuGaS_2$ and an RGO–TiO_2 composite were dispersed in 120 mL of water without any sacrificial reagents. CO_2 gas was bubbled into the suspension at about 20 mL min^{-1} flow rate. The light source was a 300 W Xe-lamp without any cut-off filters ($\lambda > 330$ nm). Products in gas and liquid phases were analyzed using a gas-chromatograph and an ion-chromatograph, respectively. An isotope experiment for CO_2 reduction was conducted using $^{13}CO_2$ (99.5 atom%). The obtained CO was analyzed using a GC-MS (Shimadzu; GCMS-QP2010 Plus, RESTEK; RT-Msieve 5A).

Results and discussion

Sacrificial CO_2 reduction over metal sulfide photocatalysts under visible light irradiation

The CO_2 reduction abilities of metal sulfide photocatalysts showing activity for sacrificial H_2 production[28–37] were evaluated under visible light irradiation in an aqueous solution containing Na_2S and/or K_2SO_3 as electron donors in the absence of cocatalysts, as shown in Table 1. When $CuGaS_2$, $(AgInS_2)_x$–$(ZnS)_{2-2x}$, Ag_2ZnGeS_4, Ni- or Pb-doped ZnS, $ZnGa_{0.5}In_{1.5}S_4$, and $(ZnS)_{0.9}$–$(CuCl)_{0.1}$ were used, CO and/or HCOOH were obtained as reduction products of CO_2 in addition to H_2. Others did not show any activities for CO_2 reduction under the present reaction conditions.

$CuGaS_2$ was the most active photocatalyst for CO formation (Table 1, entry 1). CO and H_2 continuously evolved under visible light irradiation over $CuGaS_2$ in the presence of K_2SO_3, as shown in Fig. 1. The turnover number of reacted electrons

Table 1 CO_2 reduction under visible light irradiation on various metal sulfide photocatalysts in the presence of electron donors[a]

Entry	Photocatalyst	BG and EG/eV	Electron donor	Activity/μmol h^{-1}		
				H_2	CO	HCOOH
1	$CuGaS_2$	2.3	K_2SO_3	11	0.25	Trace
2	Cu_2ZnGeS_4	2.2	K_2SO_3	Trace	0	0
3	Cu_2ZnGeS_4	2.2	Na_2S	0.1	0	0
4	$CuGa_5S_8$	2.5	K_2SO_3	2.5	0	0
5	$CuGa_2In_3S_8$	1.9	Na_2S	11.2	0	Trace
6	Cu_3NbS_4	2.5	K_2SO_3	0.2	0	0
7	Cu_3TaS_4	2.8	$Na_2S + K_2SO_3$	2.1	0	0
8	$AgGaS_2$	2.6	K_2SO_3	18	0	0
9	$(AgInS_2)_{0.22}$–$(ZnS)_{1.56}$	2.3	K_2SO_3	0.1	0	0
10	$(AgInS_2)_{0.22}$–$(ZnS)_{1.56}$	2.3	$Na_2S + K_2SO_3$	16	0.01	0
11	$(AgInS_2)_{0.1}$–$(ZnS)_{1.8}$	2.6	Na_2S	23	0.06	0.10
12	$(AgInS_2)_{0.1}$–$(ZnS)_{1.8}$	2.6	K_2SO_3	0.02	Trace	0
13	Ag_2ZnGeS_4	2.5	Na_2S	38	0	0.14
14	Ag_2ZnGeS_4	2.5	K_2SO_3	1	0	0
15	ZnS	3.5	Na_2S	Trace	Trace	0
16	ZnS:Ni (0.1%)	2.3	Na_2S	22	Trace	4.0
17	ZnS:Pb (1.0%)	2.4	Na_2S	47	0.02	0.96
18	$(ZnS)_{0.9}$–$(CuCl)_{0.1}$	2.9	$Na_2S + K_2SO_3$	37	Trace	0
19	$(ZnS)_{0.9}$–$(CuCl)_{0.1}$	2.9	Na_2S	140	0.01	0
20	$Cu_{0.045}Zn_{0.955}Ga_2S_{3.9775}$	2.9	Na_2S	0.4	0	0
21	$Cu_{0.12}Zn_{0.88}Ga_2S_{3.94}$	2.8	Na_2S	0.4	0	0
22	$Cu_{0.15}Zn_{0.85}Ga_2S_{3.925}$	2.7	Na_2S	1	0	0
23	$ZnIn_2S_4$	2.4	Na_2S	2	0	0
24	$ZnGa_{0.5}In_{1.5}S_4$	2.7	$Na_2S + K_2SO_3$	2	Trace	0
25	$ZnGa_{0.5}In_{1.5}S_4$	2.7	Na_2S	14	0.01	0
26	$MnGaInS_4$	2.1	Na_2S	0.05	0	0
27	$BaLaCuS_3$	2.0	Na_2S	0.6	Trace	0

[a] Catalyst: 0.2–0.3 g, reactant solution: 120–150 mL of an aqueous solution containing Na_2S (0.05–0.1 mol L^{-1}) or/and K_2SO_3 (0.1 mol L^{-1}) under 1 atm of CO_2, reactor: a batch-type top-irradiation cell made of Pyrex, light source: a 300 W Xe-lamp with a cut-off filter ($\lambda > 420$ nm). BG: band gap, EG: energy gap.
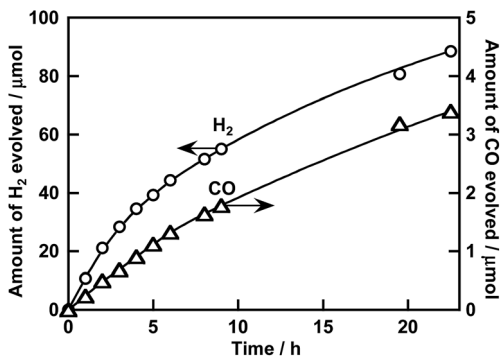
Fig. 1 CO_2 reduction over $CuGaS_2$ from an aqueous solution containing K_2SO_3 as a sacrificial reagent under visible light irradiation. Catalyst: 0.3 g, reactor: a batch-type top-irradiation cell with a Pyrex window, light source: a 300 W Xe-lamp with a cut-off filter ($\lambda >$ 420 nm), reactant solution: 150 mL of an aqueous solution containing 0.1 mol L^{-1} K_2SO_3 under 1 atm of CO_2 atmosphere.

used for CO and H_2 formation to S atoms at the surface of $CuGaS_2$ was calculated to be 32 at 22.5 h. The turnover number larger than unity indicates that this reaction proceeded photocatalytically.

HCOOH was also obtained as a reduction product of CO_2 under visible light irradiation in an aqueous solution containing Na_2S as an electron donor, when an $(AgInS_2)_{0.1}$–$(ZnS)_{1.8}$ solid solution, Ag_2ZnGeS_4, and Ni- or Pb-doped ZnS were used, as shown in Table 1. All photocatalysts that produced HCOOH from CO_2 contained Zn as a component. The Ni-doped ZnS photocatalyst was reported to be active for CO_2 reduction to form $HCOOCH_3$ in methanol as a nonaqueous solution.[39] Additionally, it has also been reported that a non-doped ZnS photocatalyst without loading of a cocatalyst is active for CO_2 reduction to form HCOOH in an aqueous solution containing an electron donor under UV light irradiation.[40]
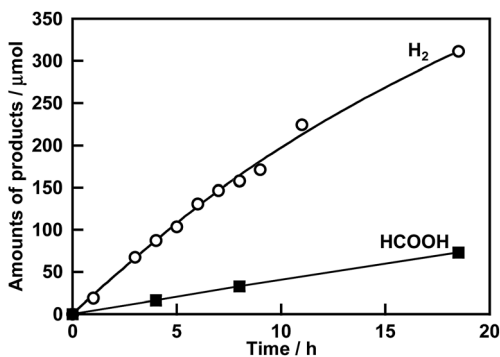

Fig. 2 CO_2 reduction over Ni (0.1%)-doped ZnS from an aqueous solution containing Na_2S as a sacrificial reagent under visible light irradiation. Catalyst: 0.2 g, reactor: a batch-type top-irradiation cell with a Pyrex window, light source: a 300 W Xe-lamp with a cut-off filter ($\lambda >$ 420 nm), reactant solution: 150 mL of an aqueous solution containing 0.05 mol L^{-1} Na_2S under 1 atm of CO_2 atmosphere.

Table 2 CO_2 reduction using water as an electron donor and the control experiment on $CuGaS_2$–(RGO–TiO_2) of a Z-scheme photocatalyst system[a]

Entry	CO₂-photocatalyst Metal sulfide	O₂-photocatalyst Metal oxide	Gas	Activity/μmol h⁻¹			
				H_2	O_2	CO	e^-/h^+
1	$CuGaS_2$	RGO–TiO_2	CO_2	28.8	11.2	0.15	1.29
2	$CuGaS_2$	TiO_2	CO_2	8.4	0	0.02	—
3[b]	$CuGaS_2$	RGO–TiO_2	Ar	18.8	4.1	0.05	2.30
4	None	RGO–TiO_2	CO_2	0.1	0.2	0.02	—
5[b]	None	RGO–TiO_2	Ar	0	0	0.01	—
6[b]	None	TiO_2	Ar	0	0	0	—

[a] Catalyst: 0.1 g each, reactant solution: 120 mL of water under 1 atm of CO_2 and Ar, reactor: a gas flow system using a top-irradiation cell made of Pyrex, light source: a 300 W Xe-lamp (λ > 330 nm). [b] pH was adjusted to about 4 with H_2SO_4.

These results suggest that contributions of Zn to the formation of a suitable conduction band and an active site for CO_2 reduction cause the formation of HCOOH. Ni-doped and Pb-doped ZnS, of which the conduction band levels should be similar to that of non-doped ZnS, showed relatively high activities.[41] The Ni-doped ZnS was the most active photocatalyst for HCOOH formation (Table 1, entry 16). HCOOH and H_2 continuously evolved under visible light irradiation in the presence of Na_2S, while CO evolution was negligible, as shown in Fig. 2. The turnover number of reacted electrons used for HCOOH formation of doped Ni atoms in Ni-doped ZnS was calculated to be 71 at 18.5 h. The turnover number larger than unity indicates that the CO_2 reduction to form HCOOH proceeded photocatalytically. Moreover, we have confirmed that non-doped ZnS did not show photocatalytic activity for CO_2 reduction under visible light irradiation (Table 1, entry 15). This indicates that the photocatalytic HCOOH formation from CO_2 proceeded by the photo-excitation of electrons from impurity levels formed with Ni 3d orbitals to a conduction band formed with Zn 4s4p orbitals.[28]
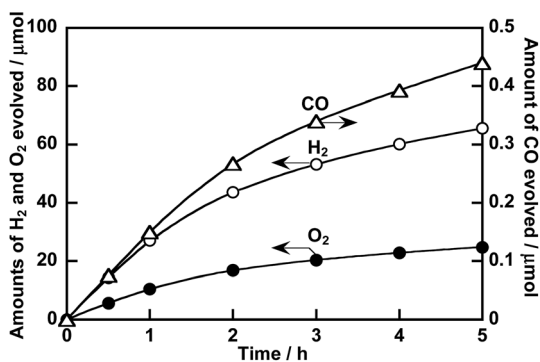

Fig. 3 CO_2 reduction using water as an electron donor over a Z-schematic photocatalyst system consisting of $CuGaS_2$ and RGO–TiO_2. Catalyst: 0.1 g each, reactant solution: 120 mL of water under 1 atm of CO_2, reactor: a gas flow system using a top-irradiation cell with a Pyrex window, light source: a 300 W Xe-lamp (λ > 330 nm).
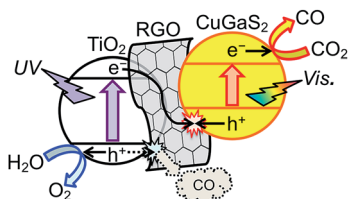
Fig. 4 Reaction scheme of CO_2 reduction on the Z-scheme photocatalyst system consisting of $CuGaS_2$ and $RGO-TiO_2$ using water as an electron donor.

Thus, band engineering including doping of metal ions, formation of solid solutions, and substitution of metal cations is a useful strategy not only for water reduction to form hydrogen, but also for CO_2 reduction to form CO and HCOOH under visible light irradiation.

Z-schematic CO_2 reduction using water as an electron donor

Various metal sulfide photocatalysts for CO_2 reduction under visible light irradiation in the presence of Na_2S and K_2SO_3 as electron donors have been developed in the present study as mentioned above. Among them, $CuGaS_2$ and Ni-doped ZnS showed high activities for CO and HCOOH formation, respectively. However, sulfide and/or sulfite ions were used as electron donors for the CO_2 reduction, because the metal sulfides cannot oxidize water to O_2. We have previously reported a Z-scheme photocatalyst system composed of a metal sulfide photocatalyst with a p-type semiconductor character and a reduced graphene oxide (RGO)–TiO_2 and RGO–CoO_x/$BiVO_4$ composites.[24,25] In this system, electrons are supplied to the metal sulfide photocatalyst from not a sacrificial reagent but by the RGO–TiO_2 and RGO–CoO_x/$BiVO_4$ composites on which electrons are extracted from water accompanied by O_2 evolution. TiO_2 is a suitable O_2-evolving
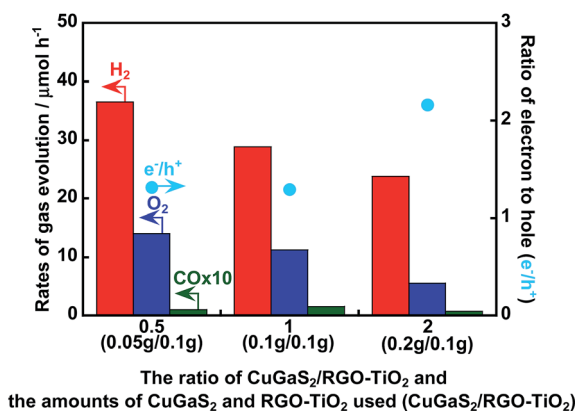

Fig. 5 Dependence of photocatalytic activity on the ratio of the amount of $CuGaS_2$ to that of RGO–TiO_2. Reactant solution: 120 mL of water under 1 atm of CO_2, reactor: a gas flow system using a top-irradiation cell with a Pyrex window, light source: a 300 W Xe-lamp ($\lambda >$ 330 nm).

photocatalyst for surveying metal sulfide-based Z-scheme photocatalyst systems employing an RGO solid-state electron mediator, because TiO_2 possesses higher reduction power than $BiVO_4$.[24,25] Here, the $CuGaS_2$ photocatalyst possesses a p-type character and CO_2 reduction activity, as shown in Table 1. Therefore, it is expected that a Z-scheme photocatalyst system composed of $CuGaS_2$ and RGO–TiO_2 is active for CO_2 reduction using water as an electron donor without any sacrificial reagents. Actually, CO_2 reduction to form CO proceeded with water splitting by employing the powdered Z-scheme system composed of $CuGaS_2$ and RGO–TiO_2 photocatalysts, as shown in Table 2 (entry 1) and Fig. 3. It is noteworthy that O_2 evolution was observed indicating that water was consumed as an electron donor. However, the photocatalytic activity decreased with the reaction time and the ratio of e^-/h^+ calculated by the eqn (1) was about 1.3 being beyond unity.

$$e^-/h^+ = \text{(the numbers of electrons consumed for } H_2 \text{ and CO formation)/(the numbers of holes consumed for } O_2 \text{ formation)} \tag{1}$$

This is due to partial photocorrosion and hydrolysis of the $CuGaS_2$ photo-catalyst, and detachment of RGO from TiO_2 as have been discussed in previous paper.[24] Therefore, the initial activity in the time course should be an intrinsic ability. The combination of $CuGaS_2$ and TiO_2 without RGO gave small amounts of H_2 and CO formed without O_2 evolution due to photocorrosion (Table 2, entry 2), indicating that RGO was necessary for smooth electron transfer from TiO_2 to $CuGaS_2$ photocatalysts.

$^{13}CO_2$ was employed to see the carbon source of produced CO. ^{12}CO and ^{13}CO were unexpectedly detected as a reduction product even in an atmosphere of $^{13}CO_2$ (Fig. S1†). The ^{12}CO is thought to come from RGO oxidation by the TiO_2 photocatalyst judging from control experiments as shown in Table 2 (entries 3–6). Even under Ar condition, a small amount of CO was detected with water splitting (Table 2, entry 3). The rate of CO evolution under Ar was smaller than that under CO_2. Small amounts of CO were detected only for RGO–TiO_2 under Ar and CO_2, but not for TiO_2 under Ar (Table 2, entries 4–6). Although RGO is partially oxidized to form CO by the strong oxidation power of the TiO_2 photocatalyst, CO was also produced from CO_2 molecules over $CuGaS_2$ as a CO_2-reducing photocatalyst in the present Z-scheme system. These results derive the scheme as shown in Fig. 4. Z-schematic CO_2 reduction proceeds by electron transfer to $CuGaS_2$ of a CO_2-reducing photocatalyst from TiO_2 of an O_2-evolving photocatalyst through RGO of a solid-state electron mediator using water as an electron donor accompanied by O_2 evolution as a main reaction. However, a part of photogenerated holes in TiO_2 oxidizes RGO to form CO.

Here, cocatalysts usually enhance photocatalytic reactions. For instance, an Ag cocatalyst is highly active for CO_2 reduction to CO over metal oxide photocatalysts with wide band gaps.[9–17] Therefore, Pt, Ru, Rh, and Ag-cocatalyst materials were loaded on $CuGaS_2$ (Table S1,† entries 2–5). Unfortunately, no effective cocatalysts were found for CO_2 reduction in the present Z-scheme system. The Ag cocatalyst was not effective, probably due to sulfurization of the Ag surface. When Pt and Ru were loaded, water splitting was enhanced[24] even under CO_2 whereas CO_2 reduction was suppressed.

In a Z-scheme system, the ratio of reduction- and oxidation-photocatalysts is an important factor that affects the photocatalytic activity. The photocatalytic activity of the present Z-scheme system also depended on the ratio of the amount of $CuGaS_2$ to that of RGO–TiO_2, as shown in Fig. 5. The ratio affects the frequency of collision between particles of $CuGaS_2$ and RGO–TiO_2, and photon absorption by each particle. $CuGaS_2$ can absorb a wider spectrum including visible light than RGO–TiO_2 (Fig. S2†). When the ratio of $CuGaS_2$/RGO–TiO_2 is 2, the ratio of e^-/h^+ largely deviates from unity. This is probably due to photocorrosion of $CuGaS_2$. $CuGaS_2$ mainly absorbs incident light, and hence shields incident light toward RGO–TiO_2, resulting in inefficient electron supply from RGO–TiO_2 to $CuGaS_2$. When the ratios were 1 and 0.5, the activities of water splitting and CO_2 reduction became higher than those in the case of 2 of the ratio. Thus, sufficient electron supply from an O_2-evolving photocatalyst is important for the Z-scheme system using a photocorrosive metal sulfide photocatalyst.

Conclusions

A survey of metal sulfide photocatalysts revealed that cocatalyst-unloaded $CuGaS_2$, $(AgInS_2)_x$–$(ZnS)_{2-2x}$, Ag_2ZnGeS_4, Ni- or Pb-doped ZnS, $(ZnS)_{0.9}$–$(CuCl)_{0.1}$, and $ZnGa_{0.5}In_{1.5}S_4$ have abilities for CO_2 reduction under visible light irradiation in aqueous solutions containing electron donors. Among them, $CuGaS_2$ was the most active photocatalyst for CO formation. Ni-doped ZnS was the most active photocatalyst for HCOOH production. This is due to the character of Zn contributing to the formation of a suitable conduction band and the active site for CO_2 reduction as seen for a non-doped ZnS photocatalyst. The CO_2 reduction using sacrificial reagents is regarded as a half reaction of CO_2 reduction using water as an electron donor. When the half reaction system was combined with an RGO–TiO_2 composite as an O_2-evolving system, Z-schematic CO_2 reduction proceeded using water as an electron donor accompanied by O_2 evolution in a simple suspension system. A tracer experiment using $^{13}CO_2$ revealed that a part of the CO was formed by oxidation of RGO by a TiO_2 photocatalyst with strong oxidation power. A Z-scheme photocatalyst system is able to employ various kinds of powdered photocatalysts including metal sulfide photocatalysts with visible light response. The present work shows the possibility to develop efficient CO_2 reduction systems for artificial photosynthesis using powdered photocatalyst materials with water as an electron donor.

Acknowledgements

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