Supporting Information

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

Tomoaki Takayama,[1] Ko Sato,[1] Takehiro Fujimura,[1] Yuki Kojima,[1] Akihide Iwase,[1, 2] Akihiko Kudo*[1, 2]

[1]Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo, 162-8601, Japan; [2]Photocatalysis International Research Center, Research Institute for Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda-shi, Chiba, 278-8510, Japan

**Corresponding author, Fax: +81-3-5261-4631, E-mail: a-kudo@rs.kagu.tus.ac.jp*

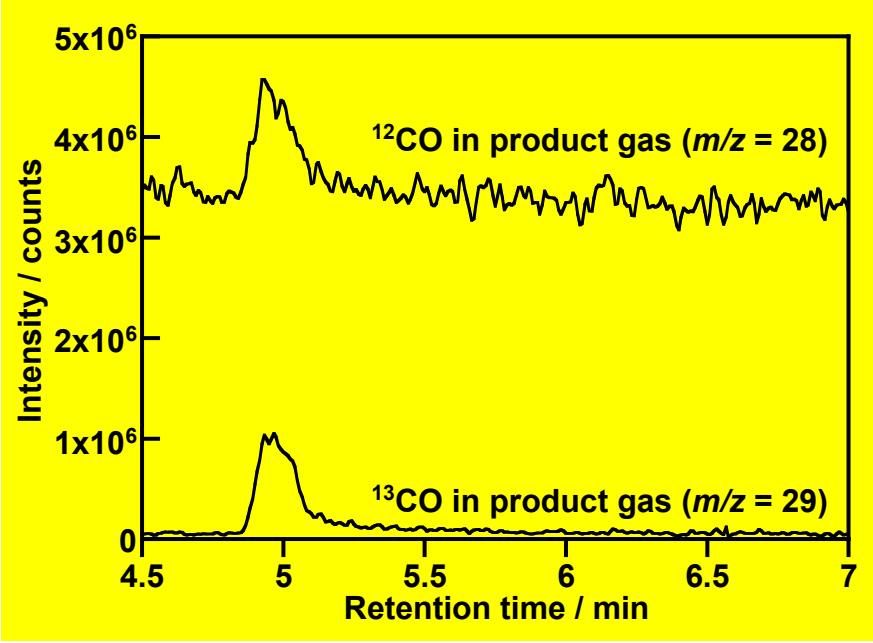

Figure S1. Analysis of products for $^{13}CO_2$ reduction over a Z-schematic photocatalyst system consisting of $CuGaS_2$ and RGO-TiO_2.
Catalyst: 0.2 ($CuGaS_2$) and 0.4 (RGO-TiO_2) g, reactant solution: 360 mL of water under 1 atm of $^{13}CO_2$ atmosphere, reactor: a gas flow system using an inner irradiation cell made of Pyrex, light source: a 400 W high-pressure mercury lamp. The elevated background for ^{12}CO is due to N_2 of an impurity in a carrier gas.

Table S1 Effect of loading cocatalyst on CO_2 reduction using water as an electron donor on $CuGaS_2$-(RGO-TiO_2) of a Z-scheme photocatalyst system.

Entry	CO_2-photocatalyst		O_2-photocatalyst	Gas	Activity / μmol h^{-1}			e^-/h^+
	Cocatalyst	Metal sulfide	Metal oxide		H_2	O_2	CO	
1	None	$CuGaS_2$	RGO-TiO_2	CO_2	28.8	11.2	0.15	1.29
2	Pt[a)]	$CuGaS_2$	RGO-TiO_2	CO_2	33.1	14.1	0.09	1.18
3	Ru[b)]	$CuGaS_2$	RGO-TiO_2	CO_2	32.0	13.1	0.04	1.22
4	Rh[b)]	$CuGaS_2$	RGO-TiO_2	CO_2	17.7	6.9	0.04	1.29
5	Ag[a)]	$CuGaS_2$	RGO-TiO_2	CO_2	17.2	4.4	0.11	1.97

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 made of Pyrex, light source: a 300 W Xe-lamp (λ > 330 nm). Loading method: [a)] adsorption, [b)] photodeposition.

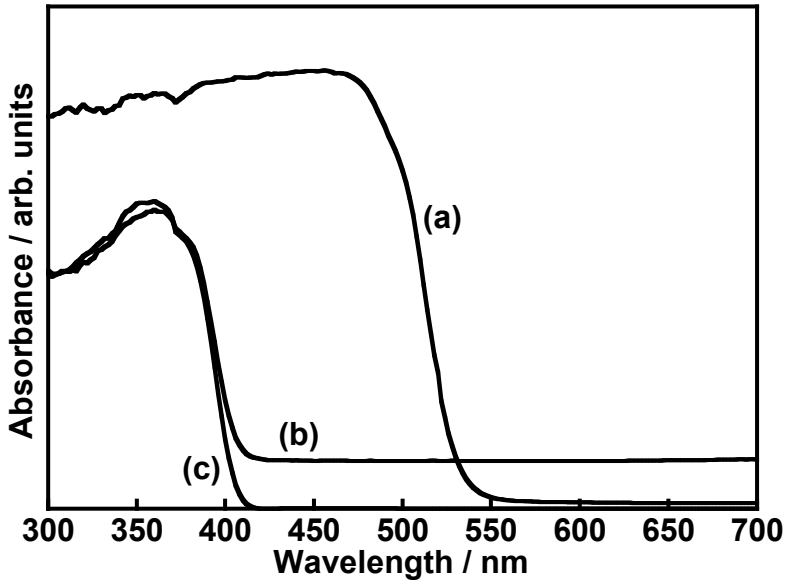

Figure S2. Diffuse reflectance spectra of (a) $CuGaS_2$, (b) RGO(5 wt%)-incorporated TiO_2 (rutile), and (c) pristine TiO_2 (rutile).