Electronic Supporting Information (ESI) for

Improvement of selectivity for CO_2 reduction by using Cu_2ZnSnS_4 electrodes modified with different buffer layers (CdS and In_2S_3) under visible light irradiation

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ESI. Fig. S1 Current-potential curves of bare CZTS electrode with various conditions.

ESI. Fig. S2 Current-potential curves for Pt/CZTS, Pt/CdS/CZTS and Pt/In_2S_3/CZTS.

ESI. Fig. S4 Mott–Schottky plots for the bare CZTS electrode.

ESI. Table S1 Photoelectrochemical CO_2 reduction by using various CZTS electrode.

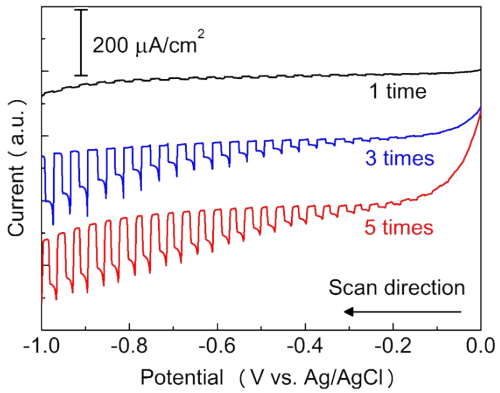

Figure S1. Dependence of the photocurrent response of the CZTS electrode on the number of times of spin-coating. The electrolyte was CO_2-purged 0.1 M $NaHCO_3$ solution, and light source was Xe lamp attached with cut-off filters ($420 < \lambda < 800$ nm, 100 mW/cm^2). More than 5 times spin-coating, a crack was appeared in bare CZTS electrode. Thereby, we concluded that 5 times spin-coating is the best for maximum efficiency of the photoelectrode.

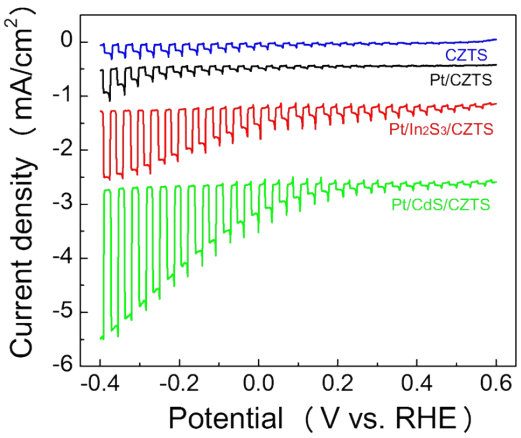

Figure S2. Current-potential curves for Pt/CZTS, Pt/CdS/CZTS and Pt/In_2S_3/CZTS in 0.1 M $NaHCO_3$ solution under chopped visible light irradiation ($420 < \lambda < 800$ nm, 100 mW/cm^2).

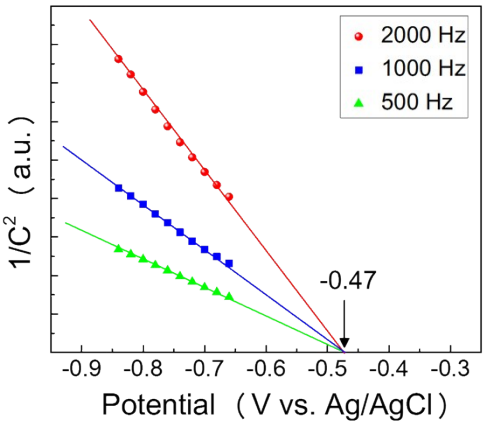

Figure S3. Mott–Schottky plots at 500 Hz, 1000 Hz and 2000 Hz measured under dark conditions by using the CZTS electrode in Na_2SO_4 + NaOH solution (pH 9.5).

Mott–Schottky analysis was carried out to clarify the band potential of CZTS electrode. Negative slopes were observed at all AC frequencies, suggesting that CZTS behaves as a p-type semiconductor. In the case of p-type semiconductors, E_{fb} is generally located near the VB, and it can be estimated from the intersection of a plot of $1/C^2$ against E by the following equation [19]:

$$\frac{1}{C^2} = \frac{2}{e\varepsilon\varepsilon_0 N}\left(E - E_{fb} - \frac{kT}{e}\right),$$

where C is capacitance, e is the electron charge, ε is the dielectric constant, ε_0 is permittivity of vacuum, N is an acceptor density, E is the electrode potential, E_{fb} is the flat band potential, k is the Boltzmann constant, and T is temperature. As shown in **Fig. S3**, the x-axis intersection was E = -0.47 V versus Ag/AgCl for all frequencies (500 Hz, 1000 Hz and 2000 Hz) and can be used to determine E_{fb} from the above equation $E = E_{fb} - kT/e$. This calculation showed that E_{fb} was approximately +0.06 V vs. Ag/AgCl at pH 0 by correcting the solution pH using the relation $E = E_0 - 0.059V(pH)$. This result indicated that the VB potential and CB potential of CZTS are approximately +0.26 V and –1.25 V vs. normal hydrogen electrode (NHE) at pH 0, respectively.

Table S1. Photoelectrochemical CO_2 reduction by using various CZTS electrode.[a]

Entry	Sample	CO_2	Coulomb /C	Products						Total /%
				H_2 /μmol	F. E. for H_2/%	CO /nmol	F. E. for CO/%	HCOOH /nmol	F. E. for HCOOH /%	
1	CZTS	○	0.8	3	72	59	1.4	110	2.7	76.1
2	CZTS	○	0.8	3	70	69	1.6	92	2.1	74.1
3	CZTS	○	1.0	4.9	81	57	0.9	139	2.3	84.2
4	CZTS	×[b]	0.4	1.3	63	n.d.	0	n.d.	0.0	63.0
5	CZTS	×[b]	0.7	2.3	60	n.d.	0	n.d.	0.0	60.0
6	CZTS	×[b]	0.5	1.7	65	n.d.	0	n.d.	0.0	65.0
7	CdS/CZTS	○	1.2	5.0	80	435	7.0	75	1.2	88.2
8	CdS/CZTS	○	2.0	7.4	72	810	7.8	110	1.1	80.6
9	CdS/CZTS	○	1.4	5.2	73	531	7.4	62	0.9	81.3
10	In_2S_3/CZTS	○	1.1	4.1	72	194	3.4	266	4.7	80.1
11	In_2S_3/CZTS	○	0.8	2.7	67	165	4.1	190	4.8	75.9
12	In_2S_3/CZTS	○	1.0	3.9	77	146	2.9	210	4.2	84.1
13	Pt/CdS/CZTS	○	6.9	20	56	trace	0	trace	0	56.0
14	Pt/CdS/CZTS	○	5.8	20	66.1	14	0.05	7.9	0.03	66.2
15	Pt/CdS/CZTS	○	5.4	22	79	4.3	0.01	24	0.09	79.1
16	Pt/In_2S_3/CZTS	○	5.8	23	77	trace	0	trace	0	77.0
17	Pt/In_2S_3/CZTS	○	5.4	21	81	1.9	0.009	61.7	0.27	81.3
18	Pt/In_2S_3/CZTS	○	6.9	22	62.2	34	0.09	264	0.74	63.0
19	CZTS	×[c]	0.3	1.3	69	n.d.	0.0	19	1.1	70.1
20	CdS/CZTS	×[c]	0.3	1.4	80	n.d.	0.0	n.d.	0	80.0
21	In_2S_3/CZTS	×[c]	0.4	1.7	77	n.d.	0	20	0.9	77.9

[a] Irradiated at visible light ($420 < \lambda < 800$ nm, 100 mW/cm^2) for 1 h in aqueous 0.1 M $NaHCO_3$ solution at -1.0 V vs. Ag/AgCl. [b] Under Ar-purged Na_2SO_4 aqueous solution. [c] Under N_2-purged $NaHCO_3$ aqueous solution.