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Electronic Supporting Information (ESI) for

Improvement of selectivity for CO₂ reduction by using Cu₂ZnSnS₄ electrodes modified with different buffer layers (CdS and In₂S₃) under visible light irradiation

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< Contents >

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/In₂S₃/CZTS.

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

ESI. Table S1 Photoelectrochemical CO₂ reduction by using various CZTS electrode.

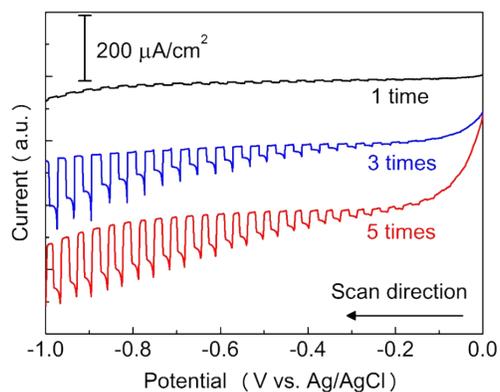


Figure S1. Dependence of the photocurrent response of the CZTS electrode on the number of times of spin-coating. The electrolyte was CO_2 -purged 0.1 M NaHCO_3 solution, and light source was Xe lamp attached with cut-off filters ($420 < \lambda < 800$ nm, $100 \text{ mW}/\text{cm}^2$). More than 5 times 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.

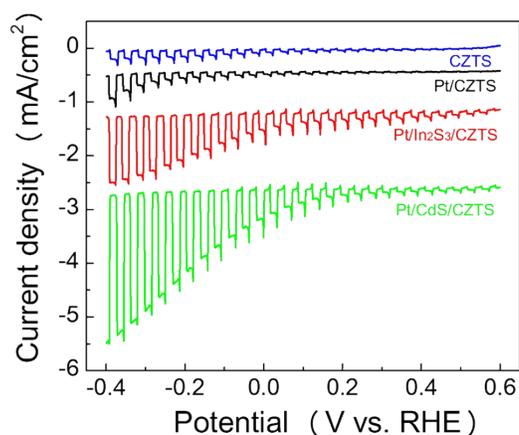


Figure S2. Current-potential curves for Pt/CZTS, Pt/CdS/CZTS and Pt/ In_2S_3 /CZTS in 0.1 M NaHCO_3 solution under chopped visible light irradiation ($420 < \lambda < 800$ nm, $100 \text{ mW}/\text{cm}^2$).

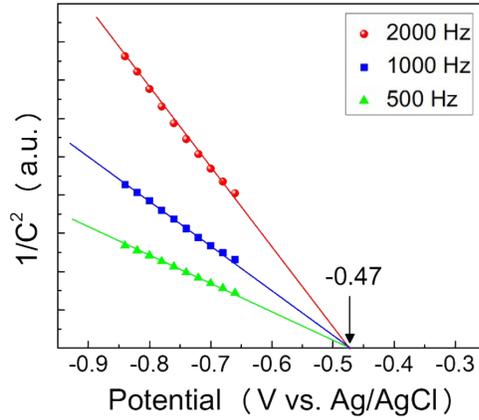


Figure S3. Mott–Schottky plots at 500 Hz, 1000 Hz and 2000 Hz measured under dark conditions by using the CZTS electrode in $\text{Na}_2\text{SO}_4 + \text{NaOH}$ solution (pH 9.5).

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]:

$$\frac{1}{C^2} = \frac{2}{e\epsilon\epsilon_0 N} \left(E - E_{fb} - \frac{kT}{e} \right),$$

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 $E = E_0 - 0.059V(\text{pH})$. 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 CO₂ reduction by using various CZTS electrode.^a

Entry	Sample	CO ₂	Coulomb /C	Products						Total /%
				H ₂ / μ mol	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 ₂ S ₃ /CZTS	○	1.1	4.1	72	194	3.4	266	4.7	80.1
11	In ₂ S ₃ /CZTS	○	0.8	2.7	67	165	4.1	190	4.8	75.9
12	In ₂ S 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 ₂ S ₃ /CZTS	○	5.8	23	77	trace	0	trace	0	77.0
17	Pt/In ₂ S ₃ /CZTS	○	5.4	21	81	1.9	0.009	61.7	0.27	81.3
18	Pt/In ₂ S 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 ₂ S 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/cm²) for 1 h in aqueous 0.1 M NaHCO₃ solution at -1.0 V vs. Ag/AgCl. ^b Under Ar-purged Na₂SO₄ aqueous solution. ^c Under N₂-purged NaHCO₃ aqueous solution.