Supplementary Materials: Tuning Sn-Cu Catalysis for Electrochemical Reduction of CO_2 on Partially Reduced Oxides SnOx-CuOx-Modified Cu Electrodes

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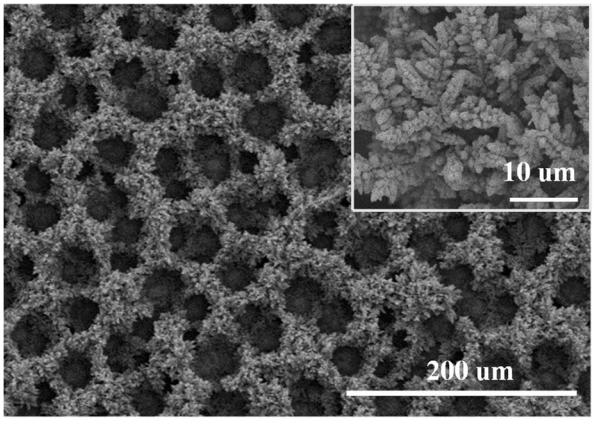


Figure S1. The SEM image of Cu foam.

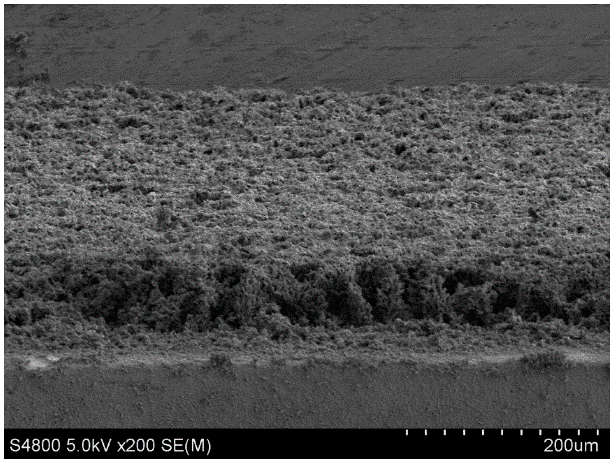
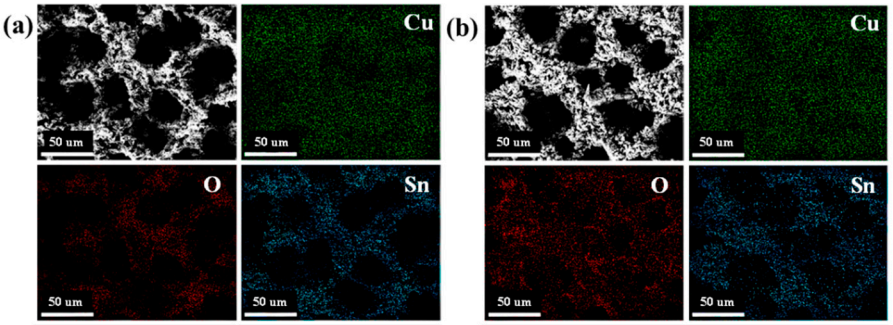


Figure S2. The cross-sectional views of Cu/SnO_2.



Element	Atomic%
Cu	60.0
Sn	40.0

Element	Atomic%
Cu	74.0
Sn	26.0

Figure S3. SEM elemental mapping for (**a**) Cu/SnO_2 and (**b**) A-Cu/SnO_2 before pre-reduction. The table is EDX analysis identifying.

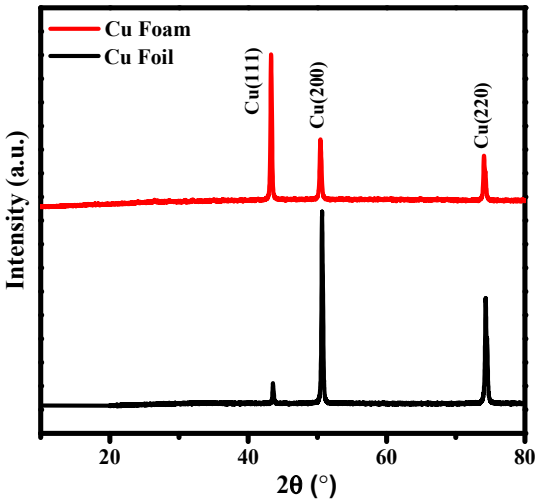


Figure S4. XRD patterns of Cu Foil and Cu foam.

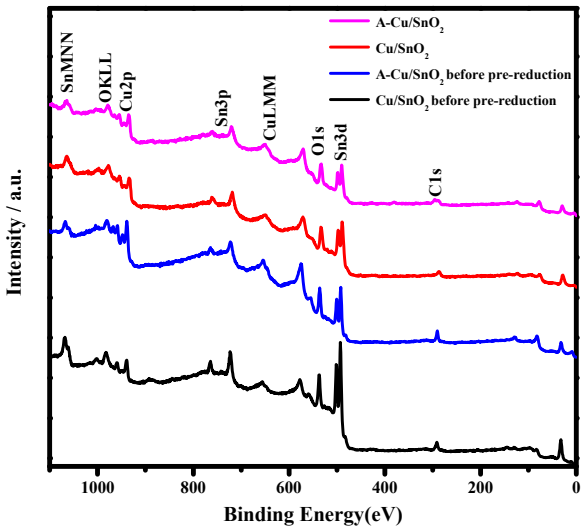


Figure S5. XPS survey spectra of Cu/SnO_2, A-Cu/SnO_2 before and after pre-reduction.

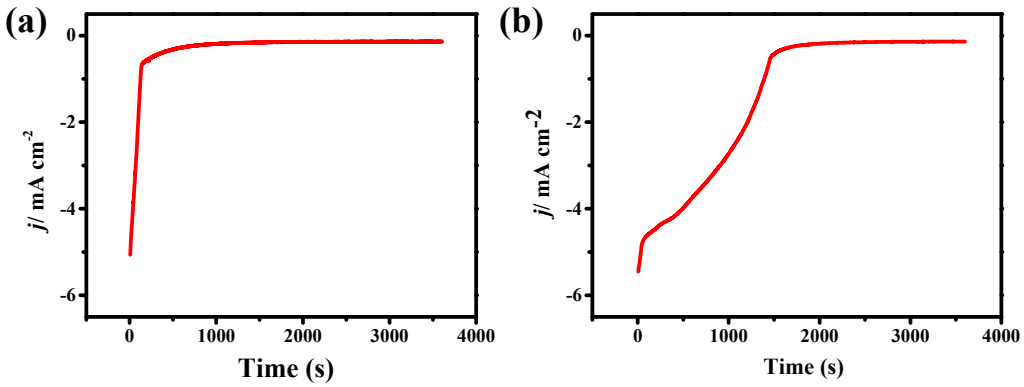


Figure S6. The I-t curves of pre-reduction of for (a) Cu/SnO_2 and (b) A-Cu/SnO_2 at -0.5 V vs. RHE in 0.1M $KHCO_3$ purged with CO_2 gas.

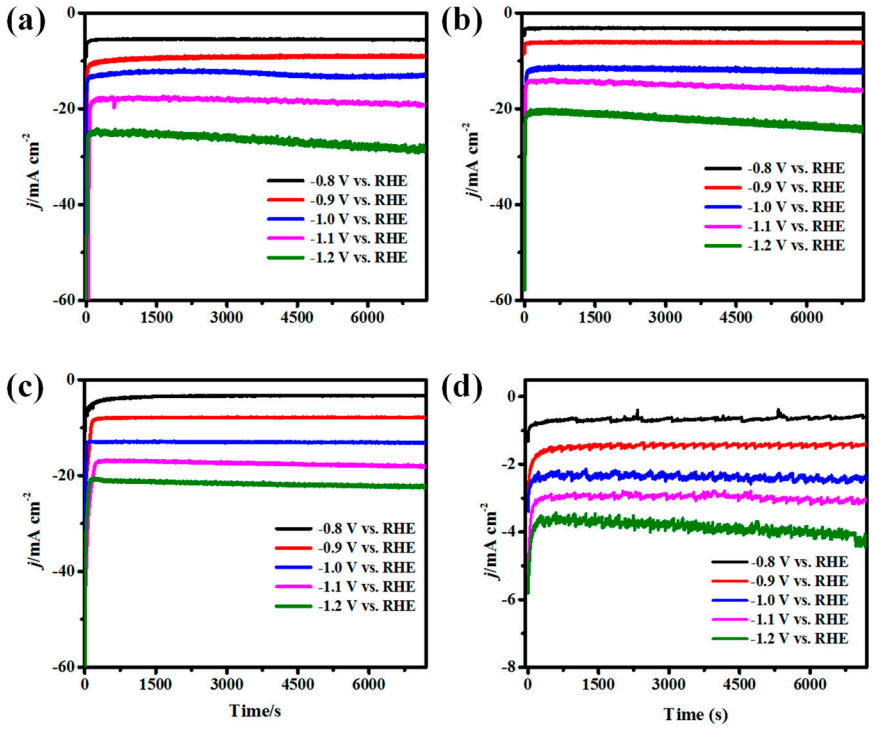


Figure S7. The I-t curves during CO_2 electroreduction of (**a**) Cu foam, (**b**) Cu/SnO_2, (**c**) A-Cu/SnO_2, (**d**) Sn plate at different voltages in 0.1 M $KHCO_3$ purged with CO_2 gas.

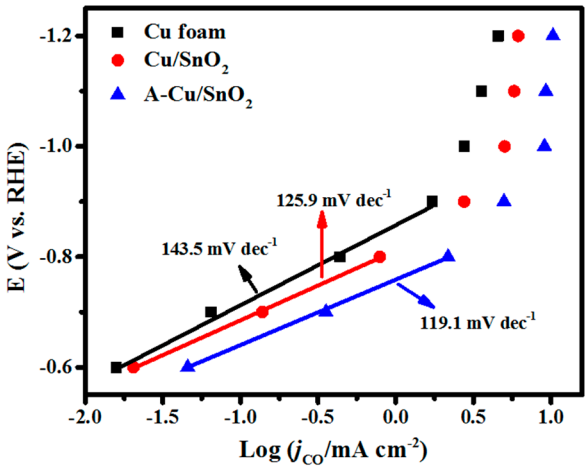


Figure S8. CO partial current density Tafel plots for Cu foam, Cu/SnO_2 and A-Cu/SnO_2.

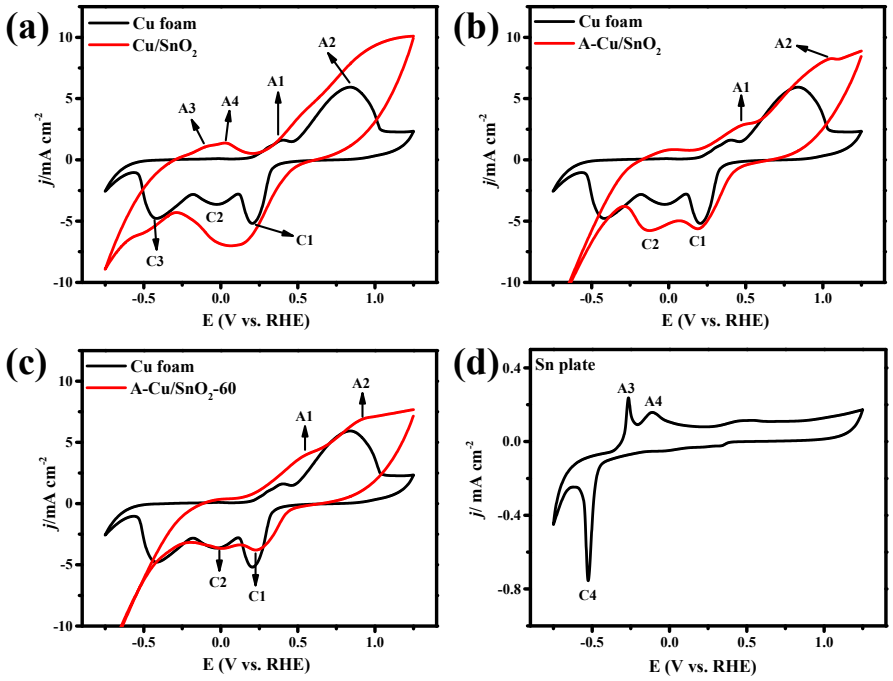


Figure S9. CV curves of Cu foam and (**a**) Cu/SnO_2, (**b**) A-Cu/SnO_2, (**c**) A-Cu/SnO_2-60 (SnO_2 deposition time: 60 min) and (**d**) Sn plate in N_2-saturated 0.1 M $KHCO_3$ solution, scan rate = 10 mV/s.

The surface redox potentials of the electrodes were studied by CVs from −0.75 to +1.25 V vs RHE in the N_2-saturated 0.1 M $KHCO_3$ (Figure S7). Cu foam shows two anodic peak at −0.39 V and −0.83 V vs RHE due to the oxidation of Cu to Cu_2O and CuO, and the three cathodic peaks are attributed to CuO reduction to Cu_2O (0.19 V), Cu_2O reduction to Cu (−0.04 V) and $HCuO_2^-$ reduction (−0.42 V) [1]. $HCuO_2^-$ could be observed when the most positive limit of the potential scan is high enough [2]. As shown in Figure S6(d) is CV of Sn plate, Two anodic peaks correspond to the oxidation of Sn to SnO (−0.26 V) and SnO to SnO_2 (−0.11 V) and the cathodic peak which involves a larger peak current than two anodic peaks are from the combination of two processes: reduction of SnO_2 to SnO and also the reduction of SnO to Sn (−0.52 V) [3]. For Cu/SnO_2, the apparent anodic peak at −0.1 V correspond to the oxidation of Sn to SnO_2, and the peaks correspond to the oxidation of Cu to CuO was not observed. However, for A-Cu/SnO_2,

the redox feature of Sn is much reduced and of Cu is observed. It indicated Cu atoms diffuse out and replace the SnO_2 surface [3]. In addition, when SnO_2 deposition time was prolonged to 60 min, the redox feature of Cu was still observable but reduced, attesting to Cu atoms exposed to electrode decreased with the increase of SnO_2 amount.

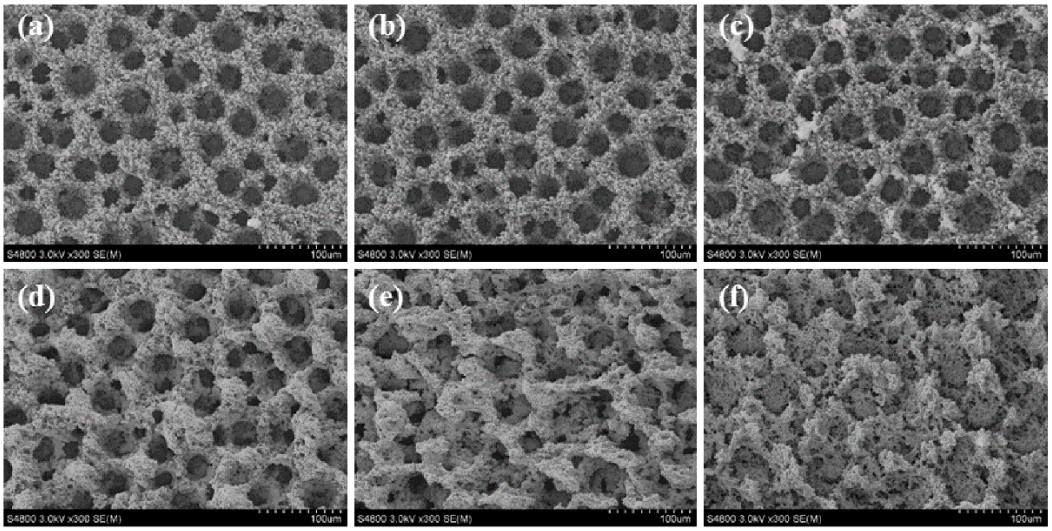


Figure S10. The SEM images of Cu/SnO_2 with different SnO_2 deposition time, (**a**) 0 min, (**b**) 5 min, (**c**) 15 min, (**d**) 30 min, (**e**) 45 min, (**f**) 60 min.

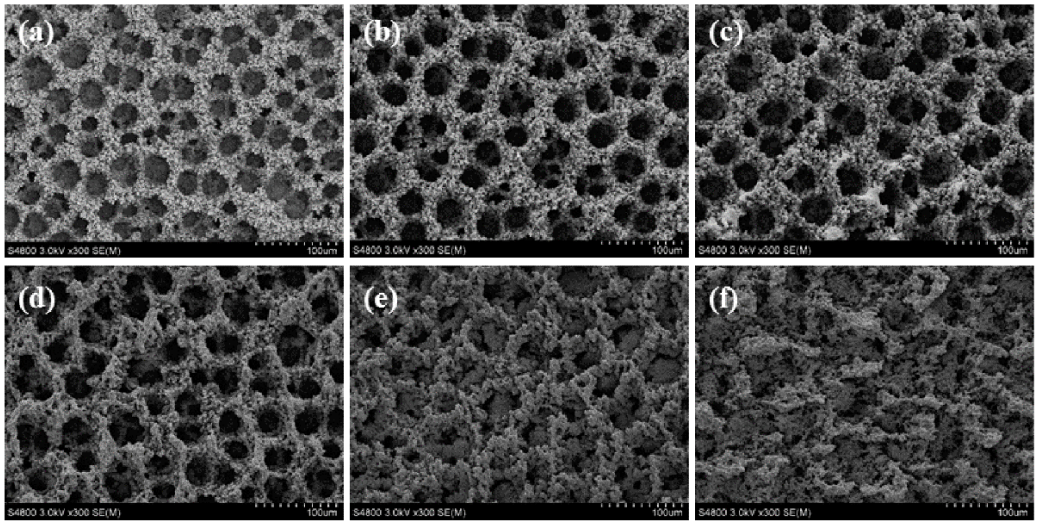


Figure S11. The SEM images of A-Cu/SnO_2 with different SnO_2 deposition time, (a)0 min, (b) 5 min, (**c**) 15 min, (**d**) 30 min, (**e**) 45 min, (**f**) 60 min.

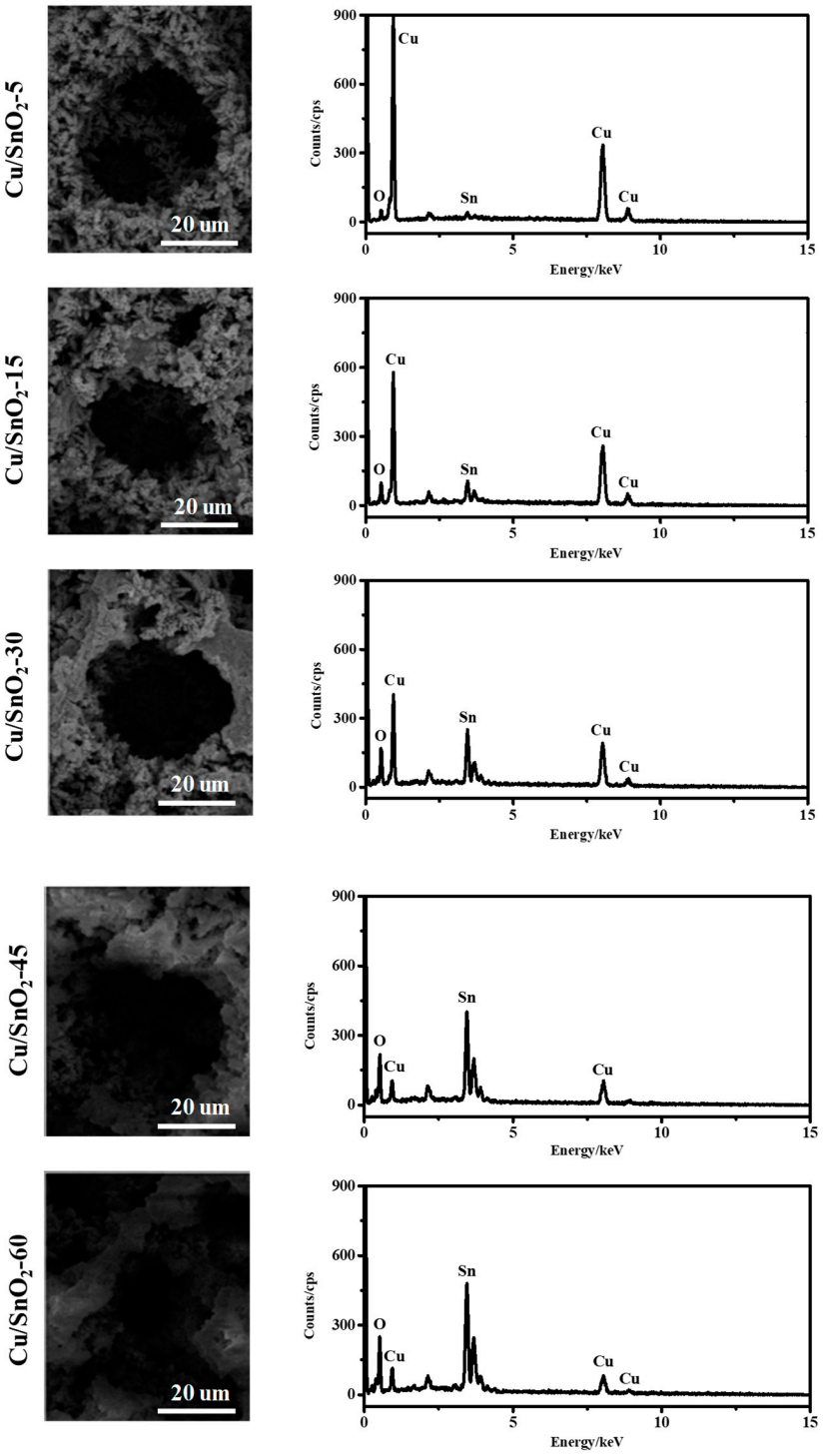


Figure S12. The EDS spectra of Cu/SnO_2-T (T represents the deposition time of SnO_2).

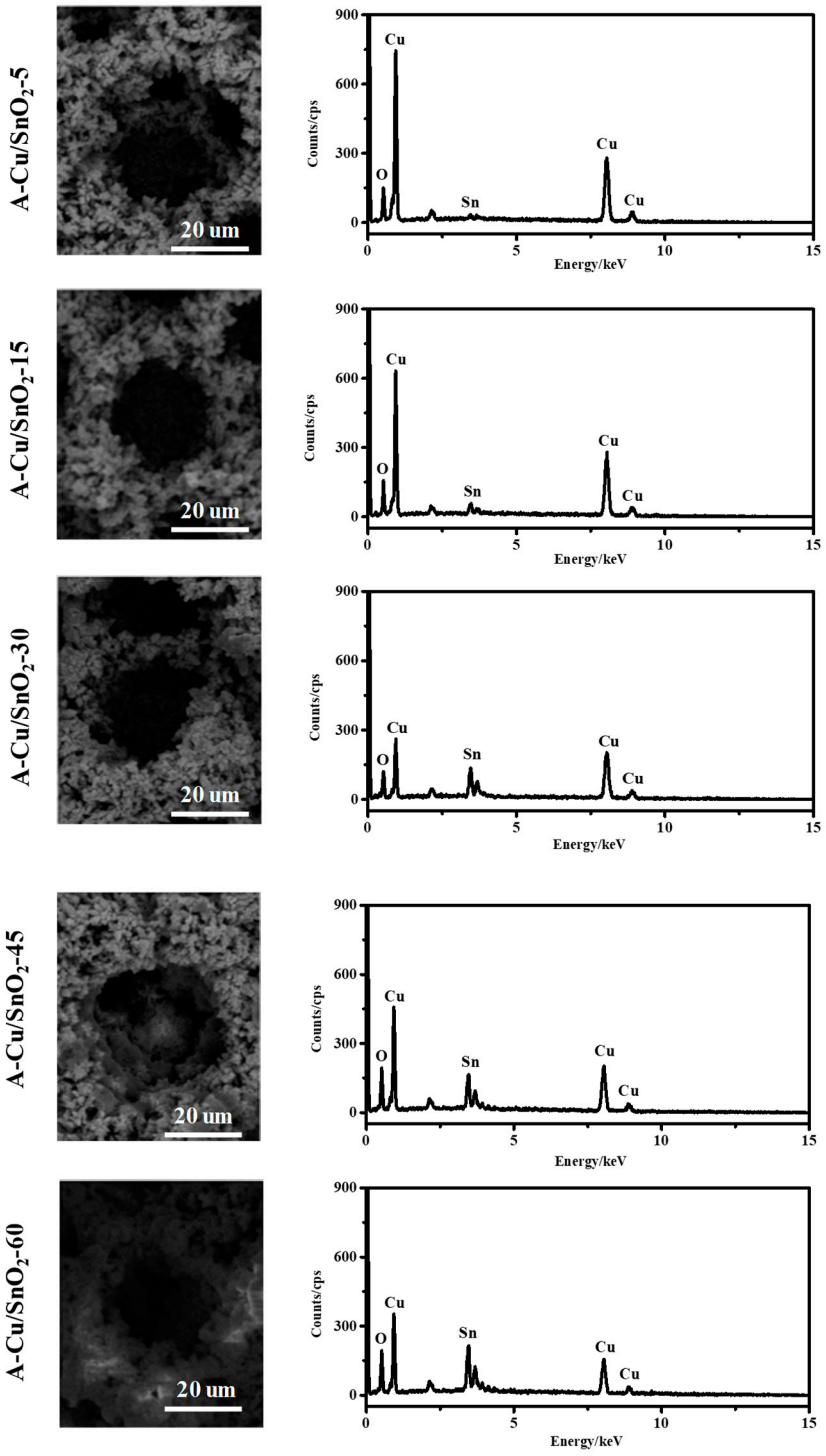


Figure S13. The EDS spectra of A-Cu/SnO_2-T (T represents the deposition time of SnO_2).

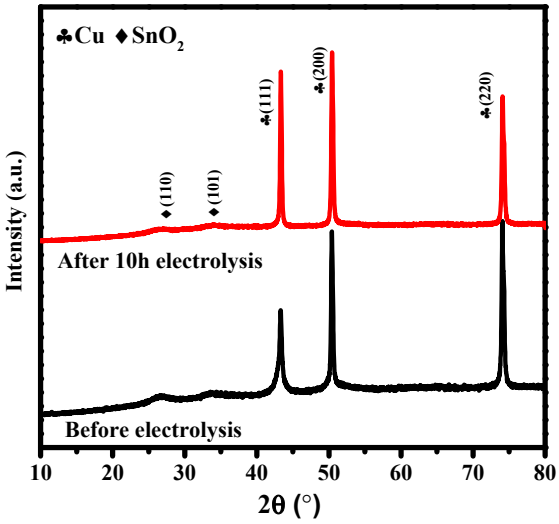


Figure S14. XRD patterns of A-Cu/SnO_2 before and after 10 h of CO_2 reduction -1.0 V vs RHE in CO_2-saturated 0.1 M $KHCO_3$ solution.

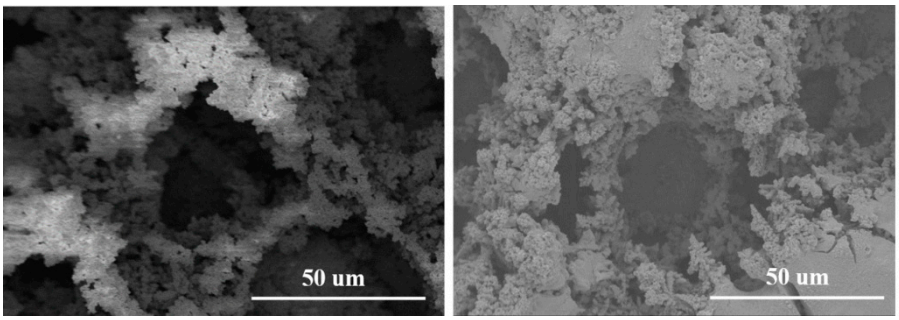


Figure S15. SEM images of (a) A-Cu/SnO_2 before CO_2 reduction, (b) A-Cu/SnO_2 after CO_2 reduction for 10 h at −1.0 V vs RHE.

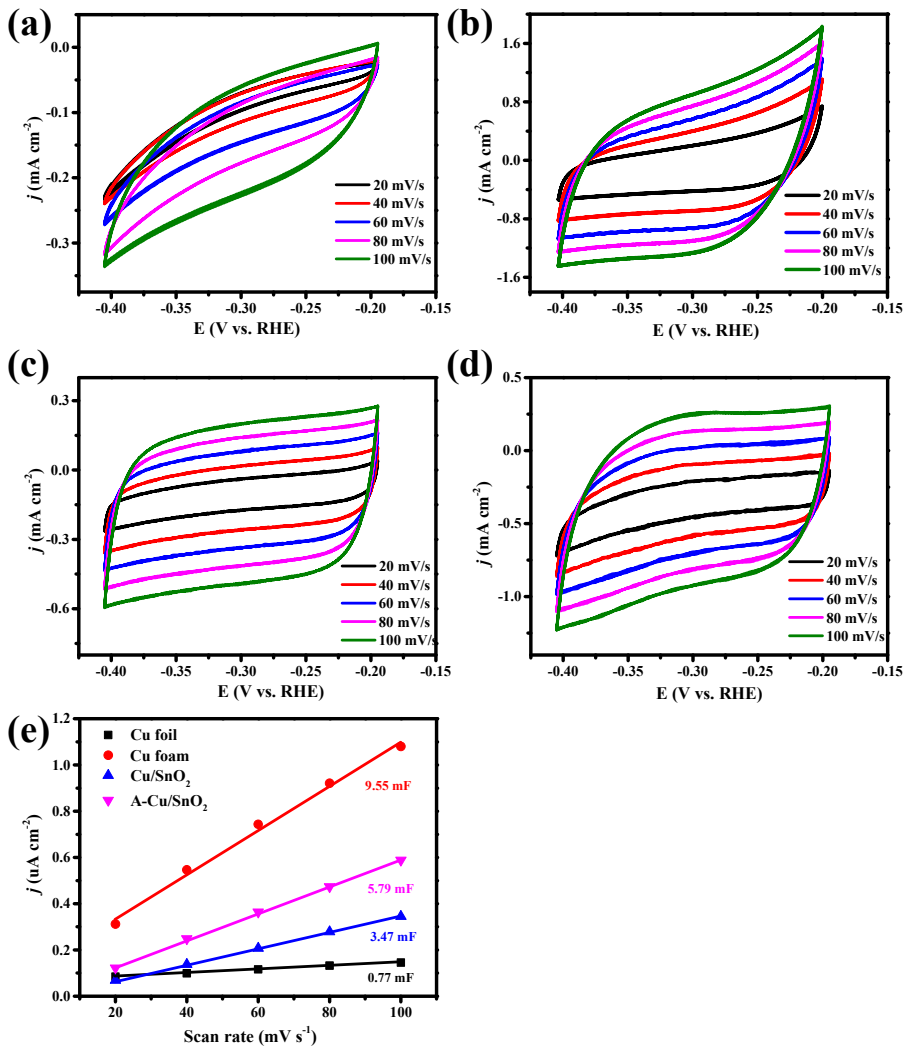


Figure S16. Double layer capacitance (C_{dl}) obtained from CV measurements. CV curves of (a) Cu foil, (b) Cu foam, (c) Cu/SnO_2, (d) $A\text{-}Cu/SnO_2$ in CO_2 saturated 0.1 M $KHCO_3$ electrolyte between -0.2 V and -0.4 V vs RHE. (e) Current density difference between cathodic and anodic sweeps at -0.3 V vs RHE against scan rate (20 mV s^{-1} to 40 mV s^{-1}). The C_{dl} was calculated by plotting the $\Delta j/2$ against scan rates, in which the slope was C_{dl}. The Δj is the difference between j_a and j_c, where j_a and j_c are the anodic and cathodic current density at the midpoint of applied potential range, respectively [4].

The electrochemical surface area (ECSA) of the catalyst can be determined by Equation (1).

$$ECSA = R_f S \quad (1)$$

Where S is the geometric area of the smooth metal electrode, R_f is the roughness factor, which is calculated from the ratio C_{dl} for the working electrode and the corresponding smooth metal electrode. Therefore, the ECSAs of Cu foam, Cu/SnO_2 and $A\text{-}Cu/SnO_2$ are calculated to be 12.4 cm^{-2}, 4.5 cm^{-2} and 7.5 cm^{-2}, respectively. It indicates that the introduction of SnO_2 reduces the ECSA and the annealing treatment increases the ECSA, which affects the steady-state current density of electrodes (Figure S13).

Table S1. The content of Cu and Sn of Cu/SnO_2 and $A\text{-}Cu/SnO_2$ obtained from ICP-AES.

Catalysts	Cu (wt%)	Sn (wt%)
Cu/SnO_2	56.54	1.79
$A\text{-}Cu/SnO_2$	59.19	1.88

The inductively coupled atomic emission spectroscopy (ICP-AES) were taken using a Varian VISTA-MPX equipped with a charge coupled device (CCD) detector. Samples were dissolved in aqua regia (the volume ratio of concentrated HNO3 to concentrated HCl is 1:3). Then samples were diluted with deionized water and adjusted pH to 5~6 with 0.1 M NaOH aqueous solution prior to measurements. Cu standard solution (100 ppm) and Sn standard solution (100 ppm) were used and diluted for calibration measurement.

Table S2. Summary of atomic percent of Cu/SnO_2 and $A\text{-}Cu/SnO_2$ before and after pre-reduction obtained from XPS and SEM-EDX elemental mapping.

Samples		**XPS**	**SEM-EDX**
Cu/SnO_2 before pre-reduction	Cu	10.1	47.3
	Sn	32.1	31.5
	O	57.8	21.2
Cu/SnO_2	Cu	17.1	57.9
	Sn	23.8	27.7
	O	59.1	14.4
$A\text{-}Cu/SnO_2$ before pre-reduction	Cu	25.8	59.0
	Sn	18.5	20.7
	O	55.7	20.3
$A\text{-}Cu/SnO_2$	Cu	26.0	74.1
	Sn	10.1	18.6
	O	63.9	7.3

Table S3. The current density at different potentials obtained from Figure S13 on (**a**) Cu foam, (**b**) Cu/SnO_2, (**c**) A-Cu/SnO_2 and (**d**) Sn plate.

Current density (j/mA cm^{-2})	Cu foam	Cu/SnO_2	A-Cu/SnO_2	Sn plate
−0.8 V vs. RHE	−5.7	−3.3	−3.7	−0.7
−0.9 V vs. RHE	−10.7	−6.3	−7.9	−1.4
−1.0 V vs. RHE	−13.4	−11.9	−12.9	−2.3
−1.1 V vs. RHE	−18.8	−14.4	−16.9	−2.9
−1.2 V vs. RHE	−25.3	−19.8	−21.0	−3.7

Table S4. Mass fraction and atomic fraction of Cu, Sn, O on the surface of the electrode with different deposition time of SnO_2 detected by SEM-EDS.

Catalysts	Deposition time	Wt. %			Atom %			Atom ratio of Sn:Cu
		Cu	Sn	O	Cu	Sn	O	
Cu/SnO_2	5	89.52	6.31	4.17	81.78	3.09	15.13	0.04
	15	68.46	22.04	9.5	58.02	10.01	31.97	0.17
	30	44.37	39.38	16.25	34.13	16.23	49.64	0.48
	45	13.35	62.08	24.57	9.26	23.07	67.67	2.49
	60	12.35	63.94	23.71	8.77	24.34	66.89	2.78
A-Cu/SnO_2	5	81.91	5.18	12.9	60.27	2.04	37.69	0.03
	15	73.77	12.61	13.62	54.80	5.02	40.18	0.09
	30	52.62	30.24	17.17	38.41	11.82	49.77	0.31
	45	45.82	35.86	18.31	33.26	13.95	52.79	0.42
	60	37.91	41.8	20.29	26.91	15.90	57.19	0.59

References

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3. Li, Q.; Fu, J.; Zhu, W.; Chen, Z.; Shen, B.; Wu, L.; Xi, Z.; Wang, T.; Lu, G.; Zhu, J.; Sun, S. Tuning Sn-catalysis for electrochemical reduction of CO_2 to CO via the core/shell Cu/SnO_2 structure. *J. Am. Chem. Soc.* **2017**, *139*, 4290-4293.

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