Supporting Information for

Electrocatalytic Conversion of Carbon Dioxide to Formic Acid over Nanosized Cu_6Sn_5 Intermetallic Compounds with a SnO_2 Shell Layer

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Supporting Table and Figures

Table S1 Summarized XPS analysis

Entry	Sn (%)	Cu (%)
Cu_6Sn_5 /CB (Without etching)	80.1	19.9
Cu_6Sn_5 /CB (Etching time : 6s)	52.8	47.2
Cu_6Sn_5 /CB (Etching time : 16s)	54.7	45.3

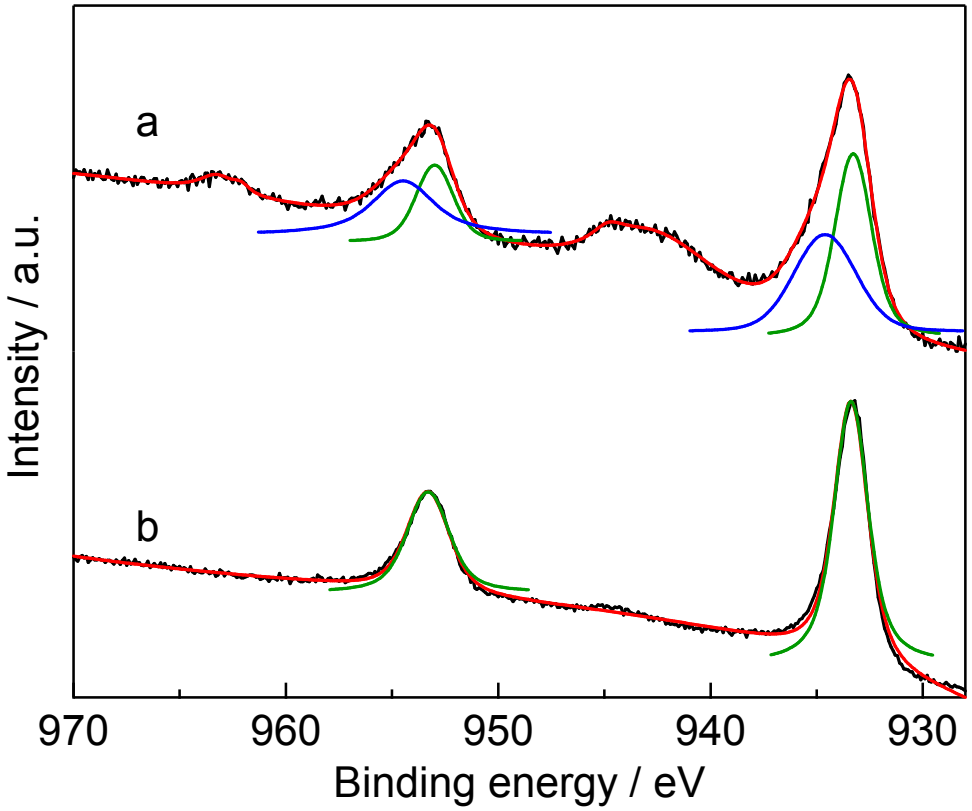

Figure S1 XPS profile for Cu6Sn5 NPs/CB in the Cu 2p region (a) before and (b) after 6s etching treatment.

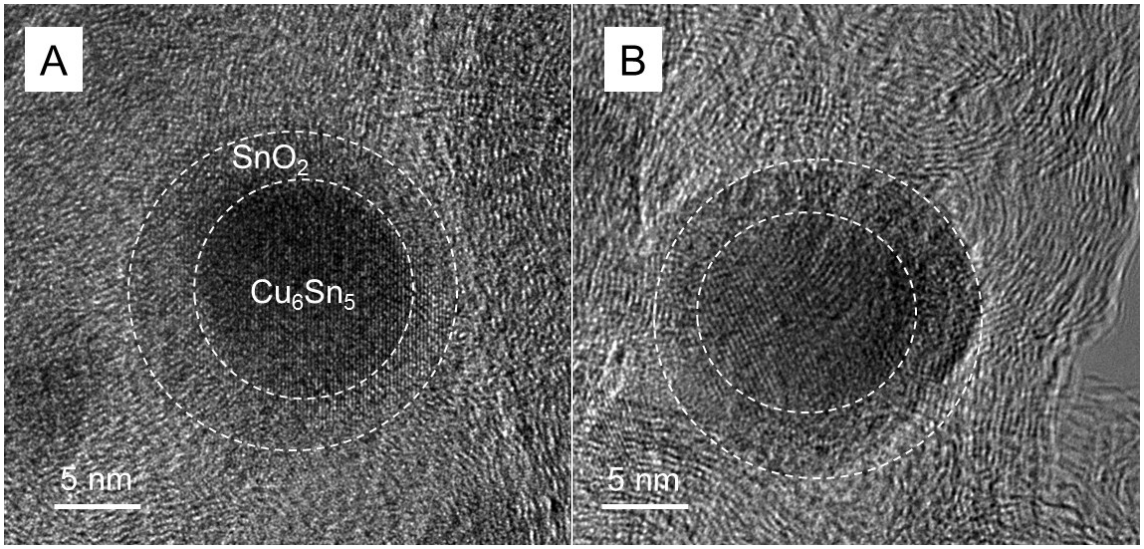

Figure S2. (A, B) High-magnification TEM images of Cu6Sn5 NP/CB sample. These images were captured in different area.

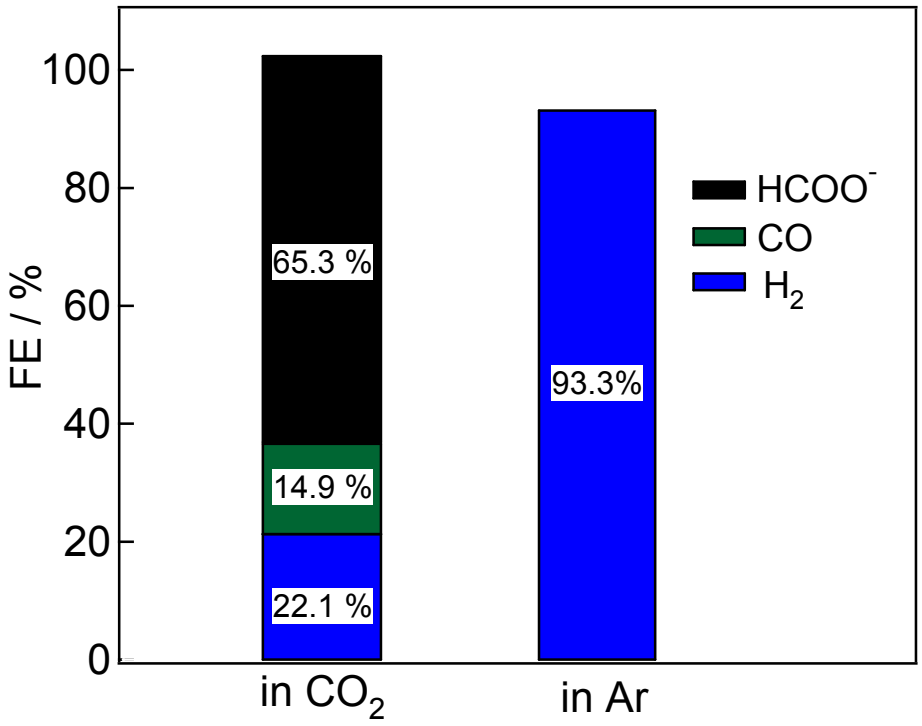

Figure S3 Faradaic efficiencies for $HCOO^-$, CO and H_2 produced over Cu_6Sn_5 NP/CB at −0.6 V vs RHE in Ar- and CO_2-saturated 0.1 M $KHCO_3$ aqueous solution.

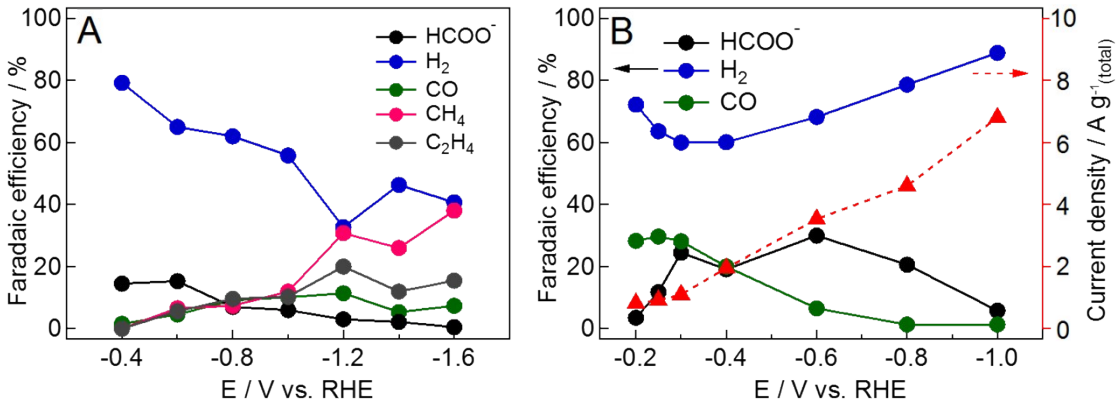

Figure S4 Potential dependence on Faradaic efficiency (left) and current density (right) towards electrochemical reduction of CO_2 over (A) Cu plate and (B) Cu NPs/CB.

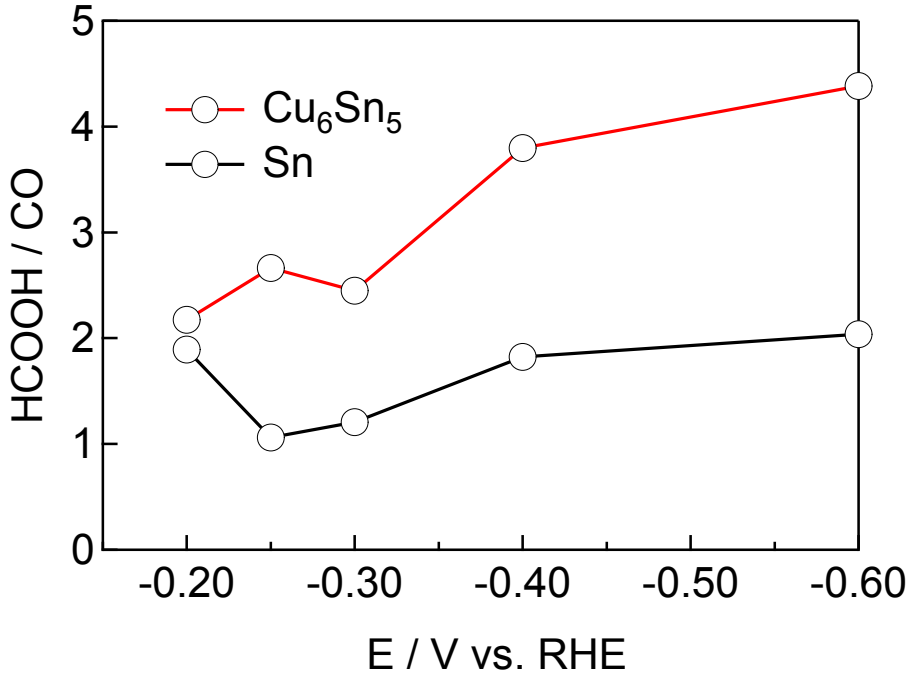

Figure S5 Potential dependence on production ratio over Sn NPs/CB and Cu_6Sn_5 NPs/CB.

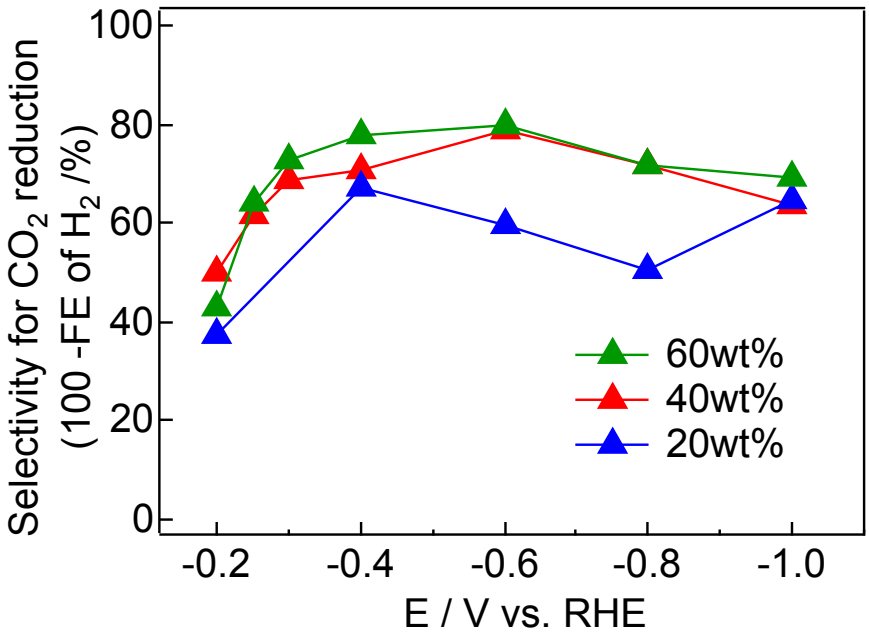

Figure S6 Electrocatalytic selectivity (100 % - FE of H_2) over Cu_6Sn_5 NP/CB with various loading weight % of metal.

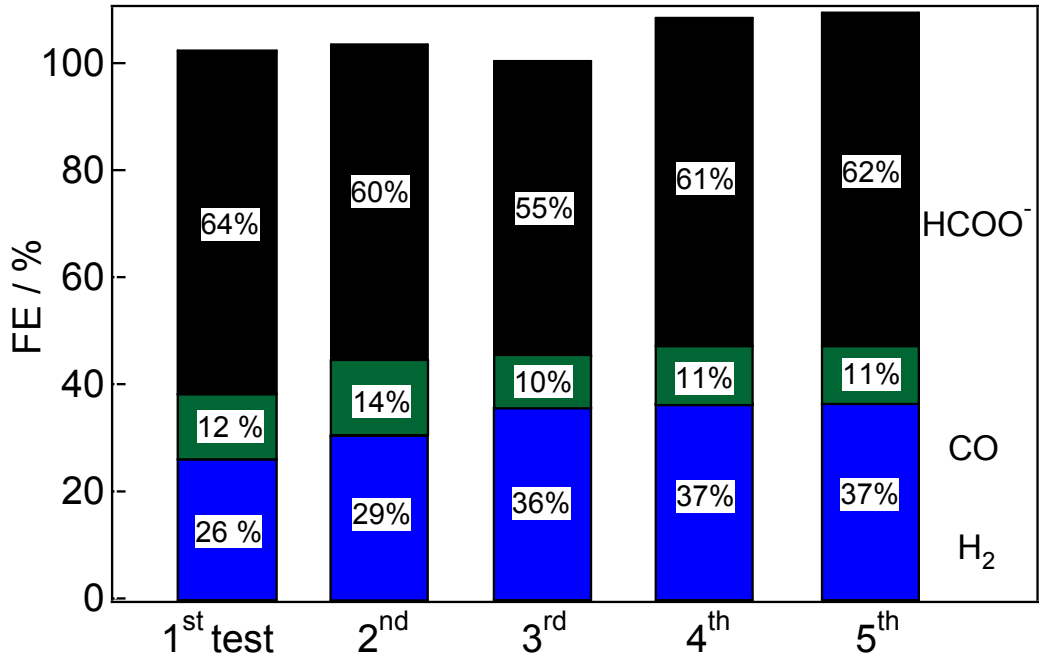

Figure S7 Stability test in the faradaic efficiencies for HCOO-, CO, and H_2 produced over Cu_6Sn_5 NP/CB at -0.6 V over five cycles.

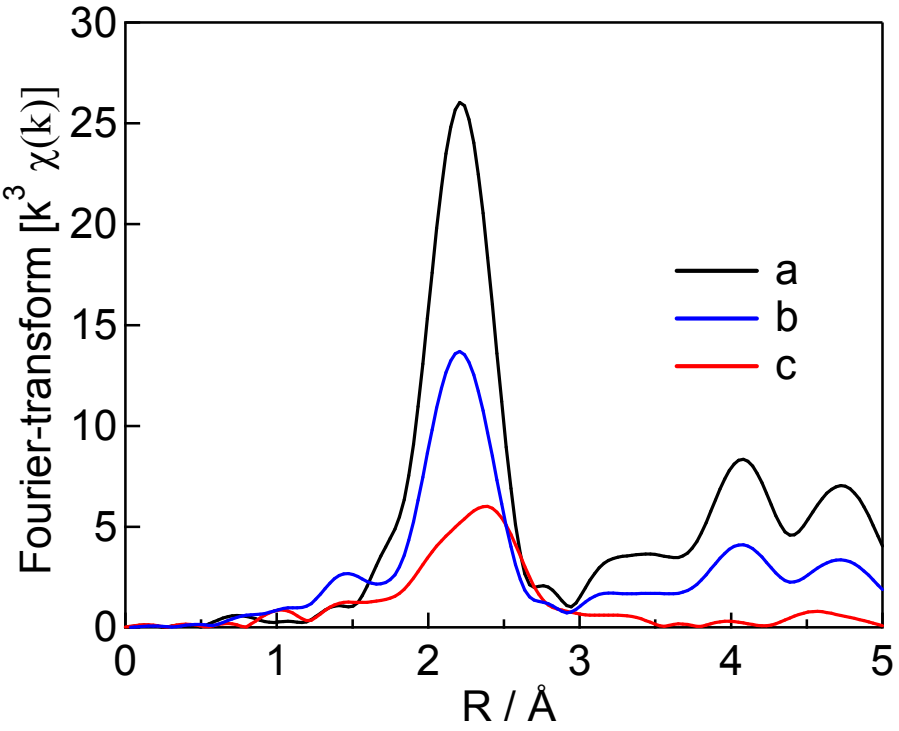

Figure S8 The k3-weighted Fourier-transform from Cu K-edge EXAFS spectra for (a) Cu foil, (b) Cu NPs/CB and (c) Cu_6Sn_5 NPs/CB.

Table S2 Summarized bond type, and distance between the nearest neighbors (R) estimated from the Cu K EXAFS analysis.

	Bond	R (ref.) / Å	R (expt.) / Å	R-factor[a]
Cu foil	Cu- Cu	2.56	2.54	0.0057
Cu_6Sn_5 NPs/CB	Cu – Cu	2.56	2.49	0.0076
	Cu – Cu	2.61	2.53	
	Cu – Sn	2.69	2.55	
	Cu – Sn	2.74	2.73	
	Cu – Sn	2.82	2.68	
Cu NPs/CB (Cu metal)	Cu – Cu	2.56	2.53	0.059[b]
Cu NPs/CB (Cu metal and oxide)	Cu – Cu	2.56	2.54	0.0074[c]
	Cu – O	1.96	1.86	
	Cu – Cu (oxide)	2.94	2.98	

a, The R-factor represents the quality of fitting. b was fitted using Cu metal. c was fitted using Cu metal and Cu oxide.