Supporting information for

CuSnBi catalyst grown on copper foam by co-electrodeposition for efficient electrochemical reduction of CO_2 to formate

Hangxin Xie[1,2], Li Lv[2*], Yuan Sun[2], Chunlai Wang[2], Jialin Xu[1,2], Min Tang[1*]
1. School of Light Industry and Engineering, South China University of Technology, Guangzhou 510640, China;
2. State Key Laboratory of NBC Protection for Civilian, Beijing 100025, China

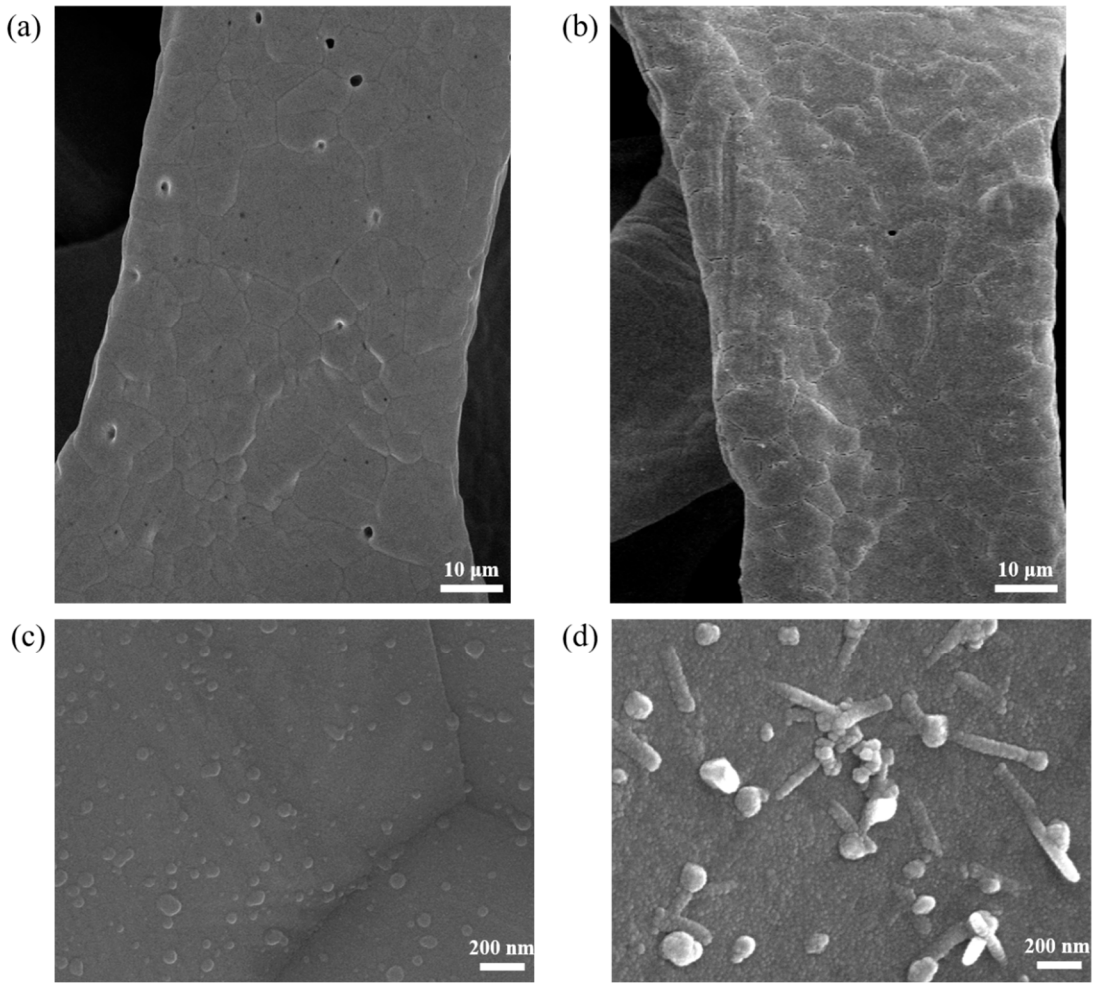

Figure S1. SEM image of (a) and (c) original Cu foam, (b) and (d) pretreated Cu foam

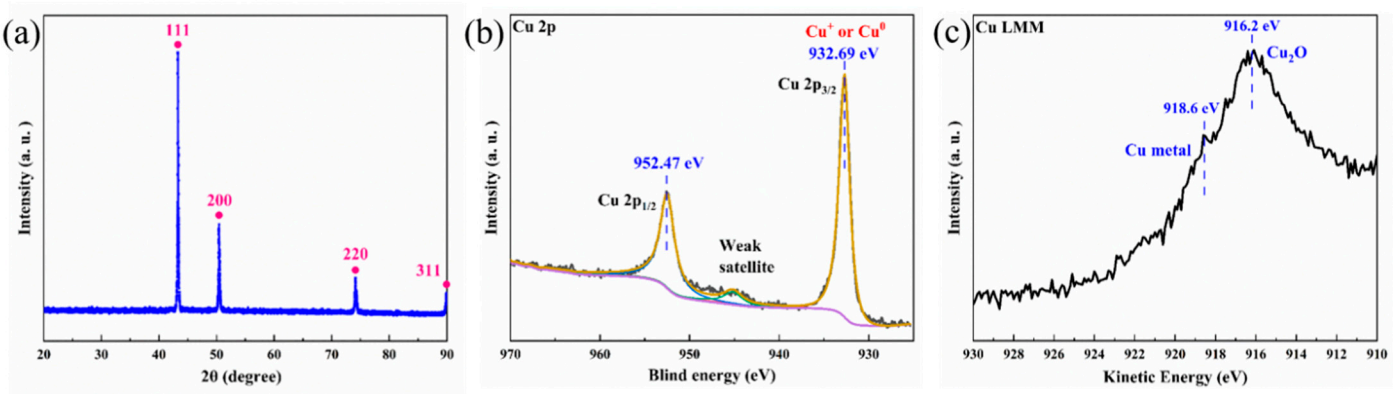

Figure S2. Spectrum of the derived Cu foam. (a) XRD patterns, (b) XPS fine spectra of Cu and (c) Auger spectra of Cu.

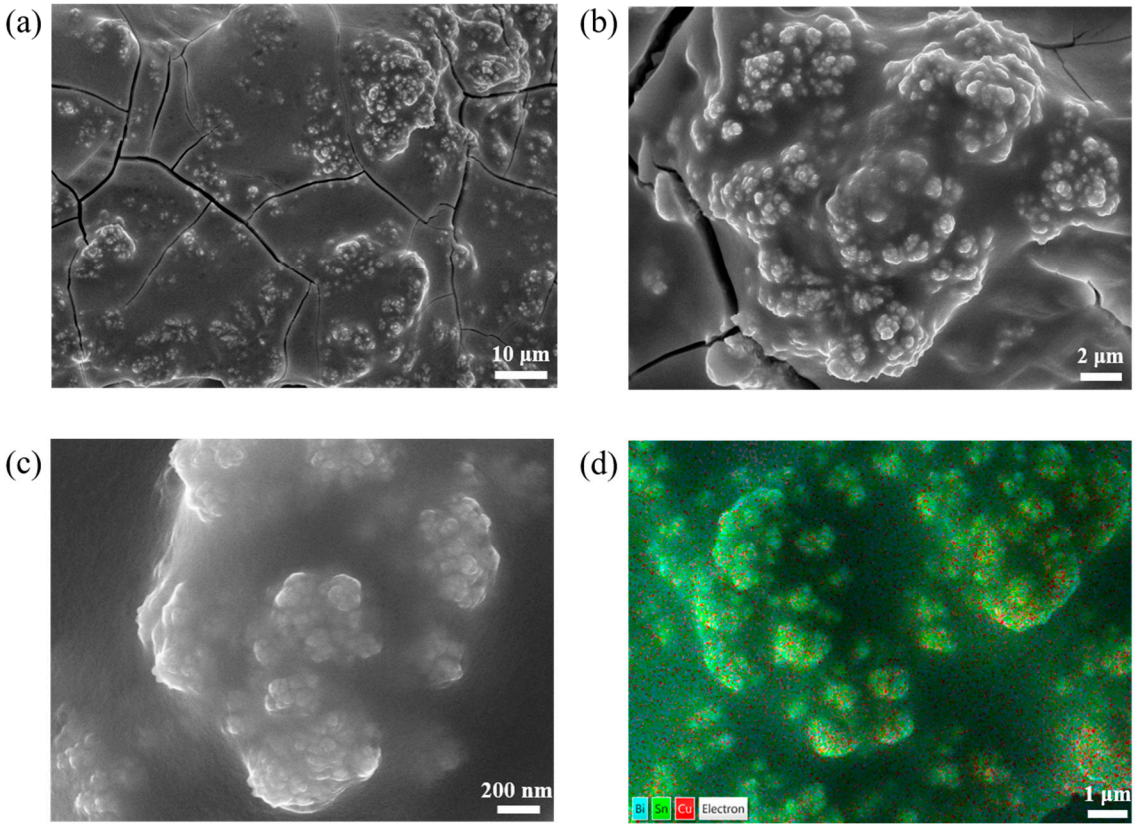

Figure S3. SEM images of the CuSnBi−1−pH7.5 electrode with scale bars of (a) 10 μm, (b) 2 μm, and (c) 200 nm. (d) Elemental map (Bi is blue, Sn is green, and Cu is red).

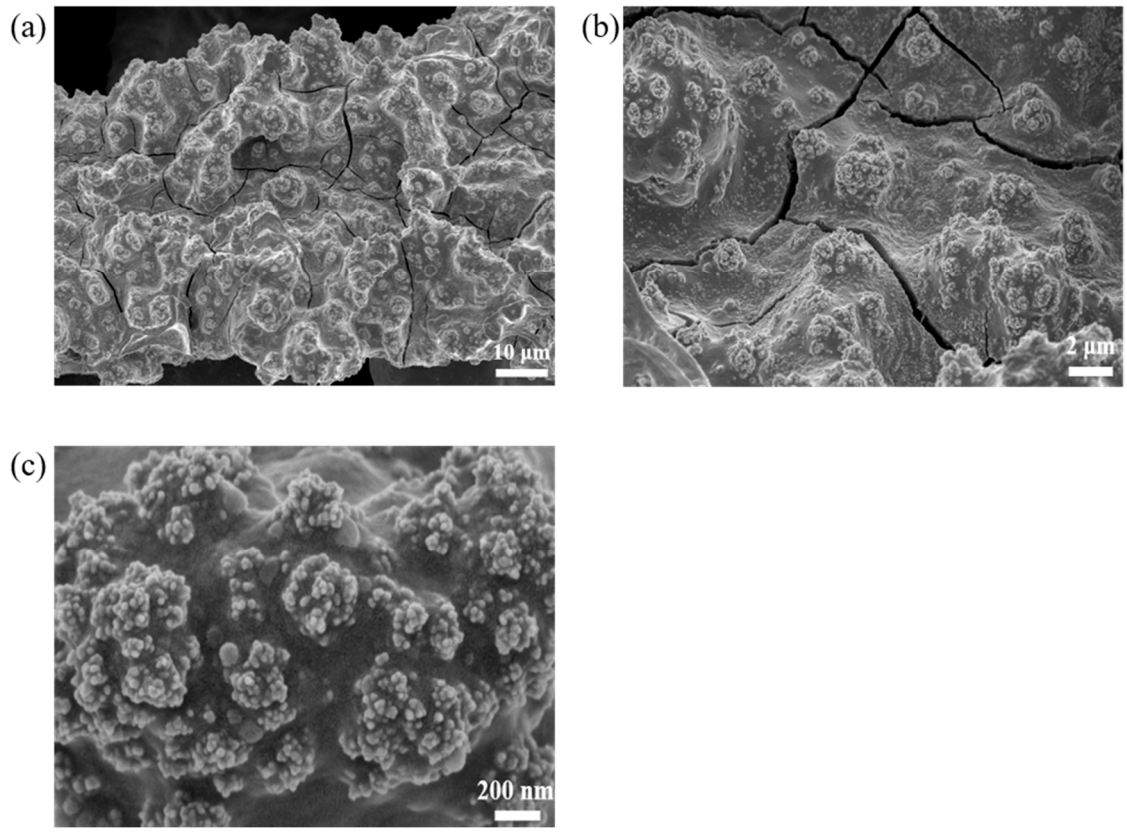

Figure S4. SEM images of the CuSnBi−1−pH8.0 electrode with scale bars of (a) 10 μm, (b) 2 μm, and (c) 200 nm.

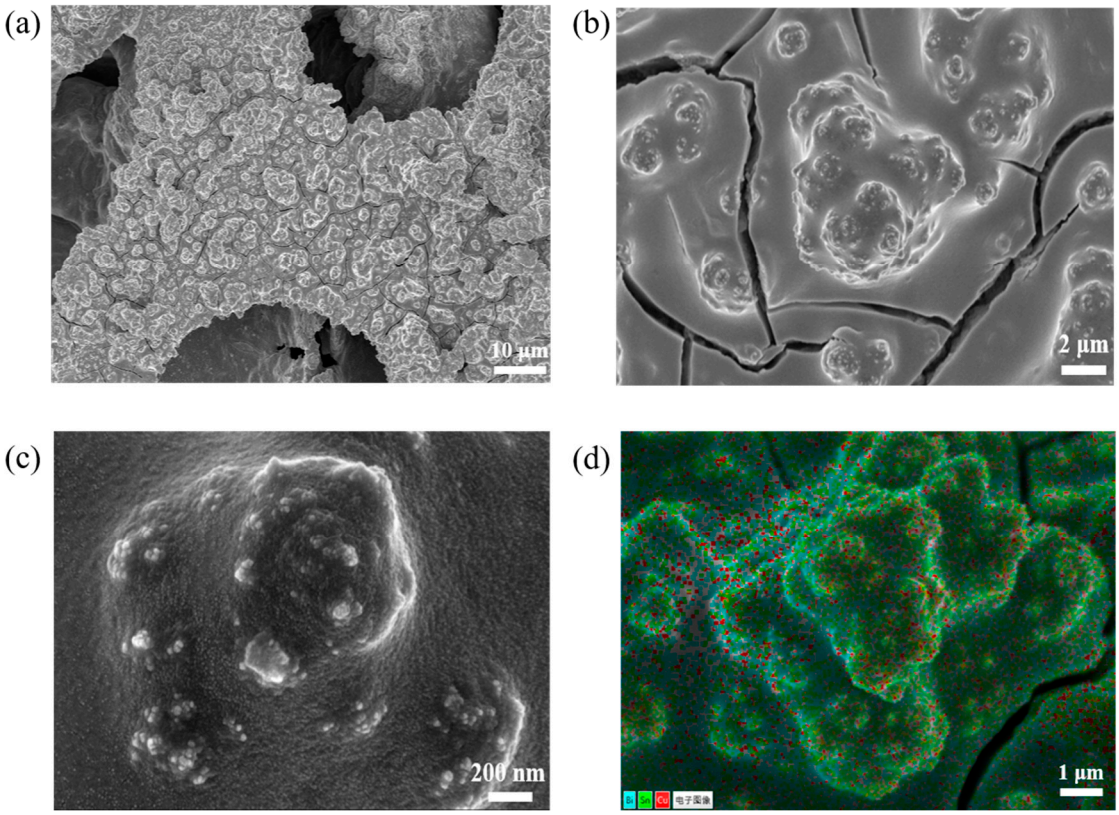

Figure S5. SEM images of the CuSnBi−1−pH9.0 electrode with scale bars of (a) 10 μm, (b) 2 μm, and (c) 200 nm. (d) Elemental map (Bi is blue, Sn is green, and Cu is red).

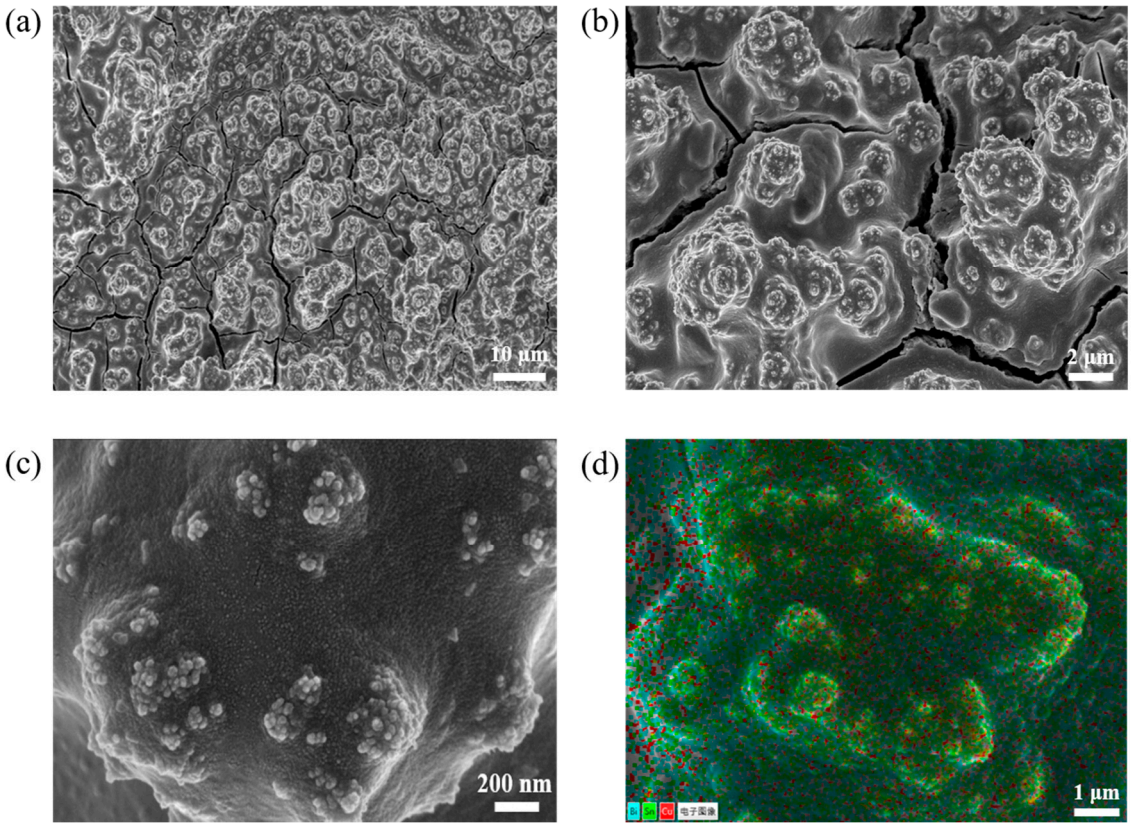

Figure S6. SEM images of the CuSnBi−1−pH9.5 electrode with scale bars of (a) 10 μm, (b) 2 μm, and (c) 200 nm. (d) Elemental map (Bi is blue, Sn is green, and Cu is red).

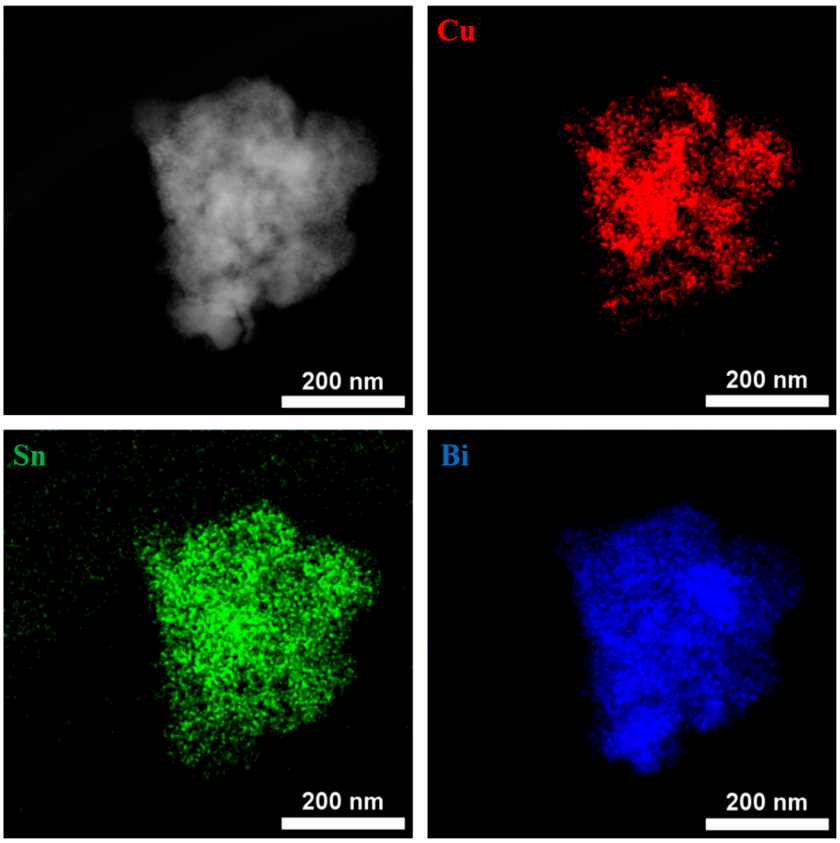

Figure S7. TEM-EDS mapping results of CuSnBi−1−pH8.5 electrode.

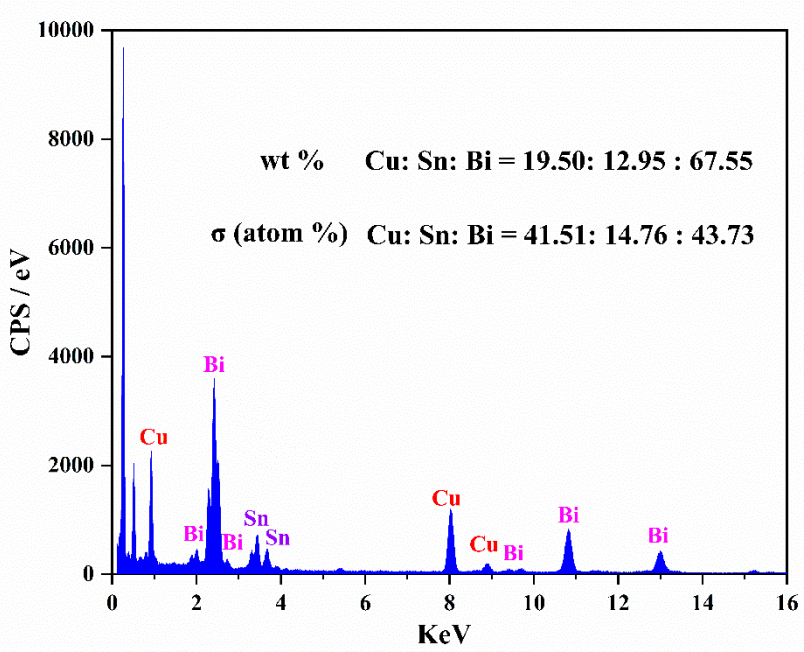

Figure S8. TEM-EDS spectrum of CuSnBi−1−pH8.5 electrode.

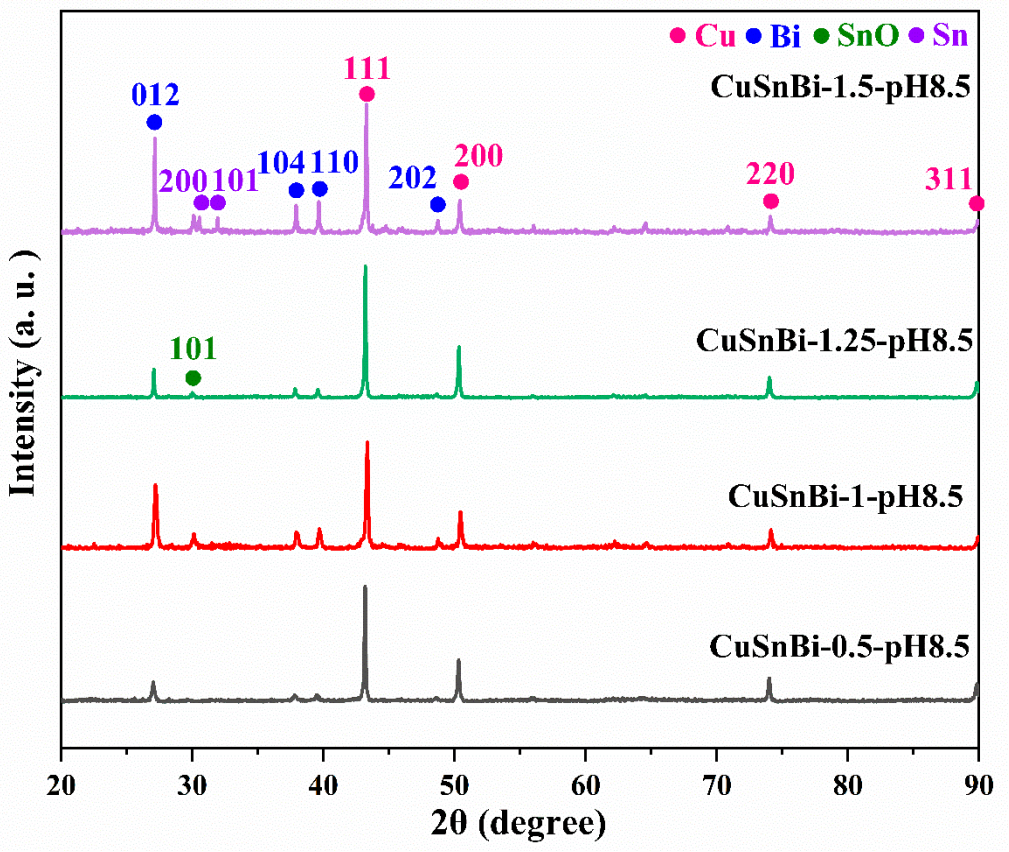

Figure S9. XRD patterns of the CuSnBi−x−pH8.5 electrodes prepared at different molar ratios of $Cu^{2+}/Sn^{2+}/Bi^{3+}$ in electrodeposition solution.

Table S1. Percentage of bismuth and tin species in CuSnBi−1−pHy electrodes prepared at different pH values

Electrode	CuSnBi−1−p H7.5	CuSnBi−1−p H8.0	CuSnBi−1−p H8.5	CuSnBi−1−p H9.0	CuSnBi−1−p H9.5
Sn^0 (%)	8.72	0	0	0	8.96
SnO_x (%)	29.53	37.19	31.74	34.06	45.65
Bi^0 (%)	12.01	8.04	6.33	7.04	13.56
Bi^{3+} (%)	49.74	54.77	62.03	58.9	31.83
Sn: Bi	1: 1.61	1: 1.69	1: 2.15	1: 1.94	1: 0.83

Table S2. Percentage of metal species in the CuSnBi−1−pH8.5 electrode before and after the stability test

Electrode	Cu^0 (%)	Cu^{2+} (%)	SnOx (%)	Bi^0 (%)	Bi^{3+} (%)
Before the reaction	0	0	31.74	6.33	62.03
After the reaction	20.68	35.79	9.42	1.66	32.45

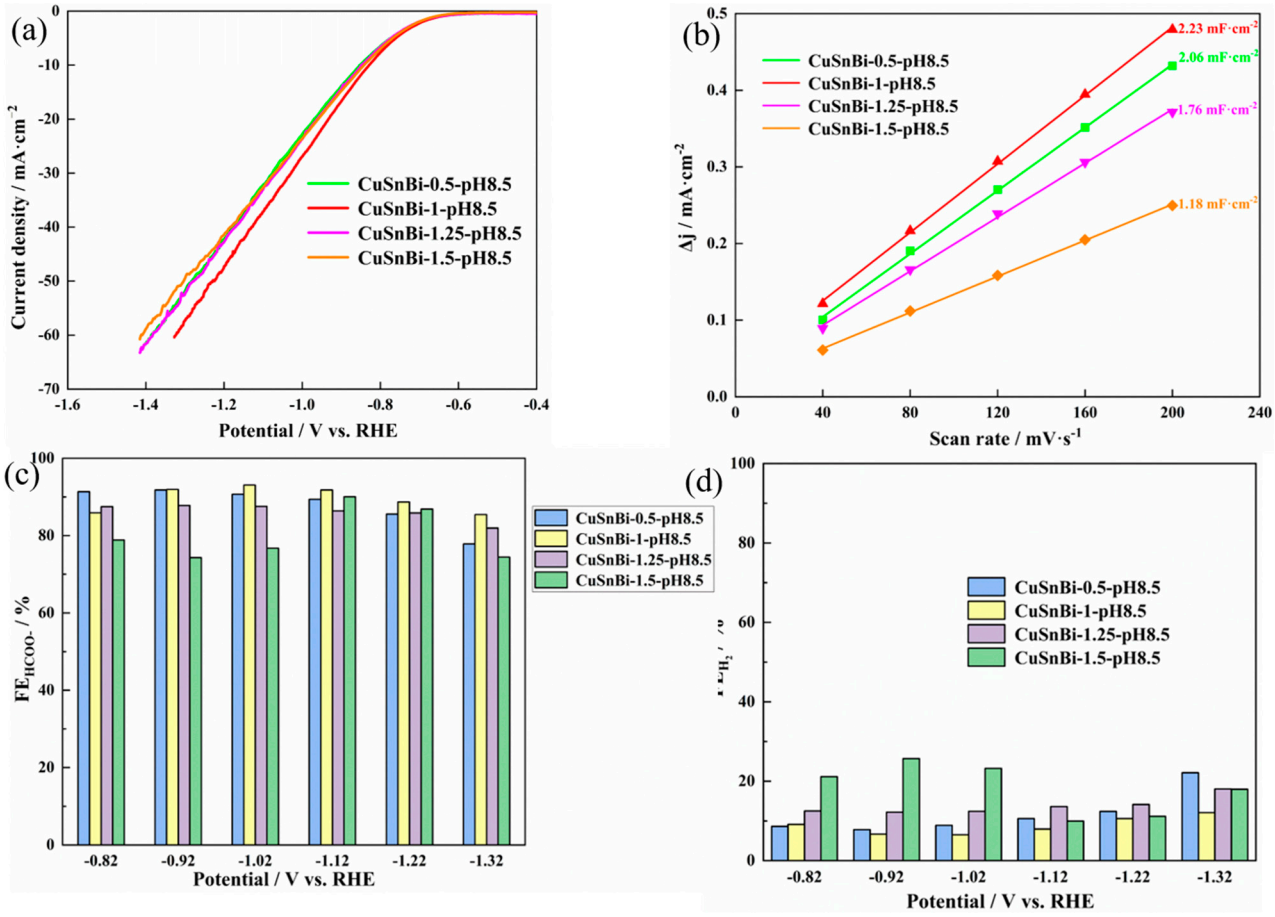

Figure S10. Electrochemical characterization of CuSnBi−x−pH8.5 electrodes prepared at different molar ratios of Cu^{2+}/Sn^{2+}/Bi^{3+}. (a) LSV, (b) Cdl, (c) FE_{HCOO-} and (d) FE_{H2}

Table S3. Fitting equivalent circuit parameters in CuSnBi−1−pHy electrodes prepared at different pH values

Electrode	CuSnBi−1−pH7.5	CuSnBi−1−pH8.0	CuSnBi−1−pH8.5	CuSnBi−1−pH9.0	CuSnBi−1−pH9.5
Ri / Ω	3.61	5.81	2.93	4.32	3.21
Rct / Ω	13.20	14.55	11.53	11.99	17.33

Table S4. Fitting equivalent circuit parameters in CuSnBi−x−pH8.5 electrodes prepared at different molar ratios of $Cu^{2+}/Sn^{2+}/Bi^{3+}$ in electrodeposition solution.

Electrode	CuSnBi−0.5−pH8.5	CuSnBi−1−pH8.0	CuSnBi−1.25−pH8.5	CuSnBi−1.5−pH9.0
Ri / Ω	3.72	2.93	3.72	3.51
Rct / Ω	16.41	11.53	15.70	13.68

Table S5 Performance summary of recent ternary metal catalysts for electrochemical reduction of carbon dioxide

Catalysts	Product	FE_{max} (%)	Current density ($mA \cdot cm^{-2}$)	Stability (h)	Ref
PbBiSn	Formate	30	30	-	[47]
PdSnPb	Formate	73	35	3	[48]
PdSnIn	Formate	38	35	3	[48]
BiSnPb	Formate	60	31	24	[49]
CuZnMo	Methanol	25	13	3	[50]
CuSnZn	Carbon monoxide	85	10	4	[51]
ZnAlCe	Carbon monoxide	89	24	5	[52]
CuZnAl	Carbon monoxide	25	15	-	[53]
This work	Formate	91.79	36.6	20	