Supplementary Information

Electronic structure modulation of bismuth catalysts induced by sulfur and oxygen co-doping for promoting CO_2 electroreduction

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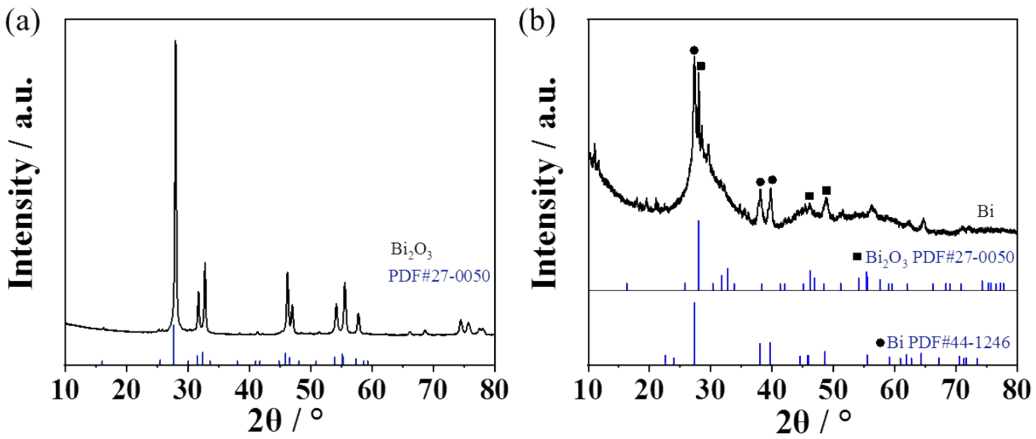

Fig. S1 XRD patterns of (a) Bi_2O_3 and (b) Bi.

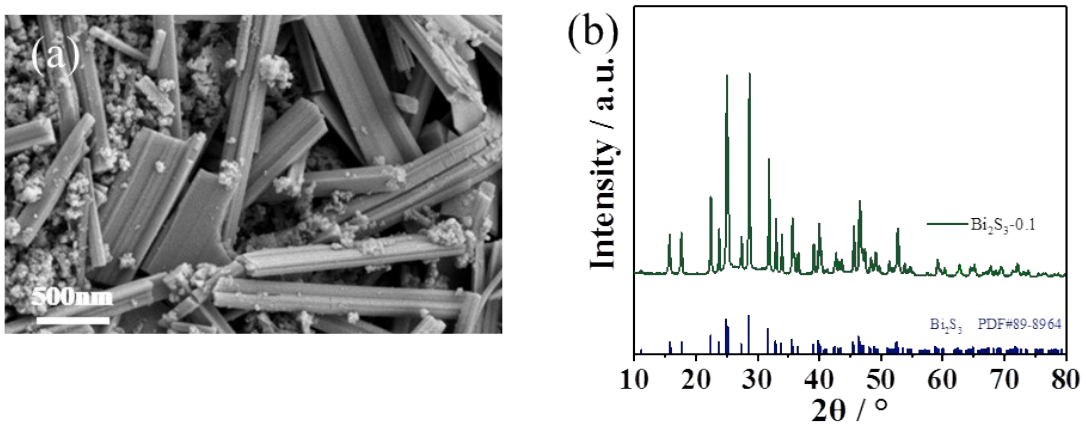

Fig. S2 (a) SEM image and (b) XRD pattern of Bi_2S_3-0.1.

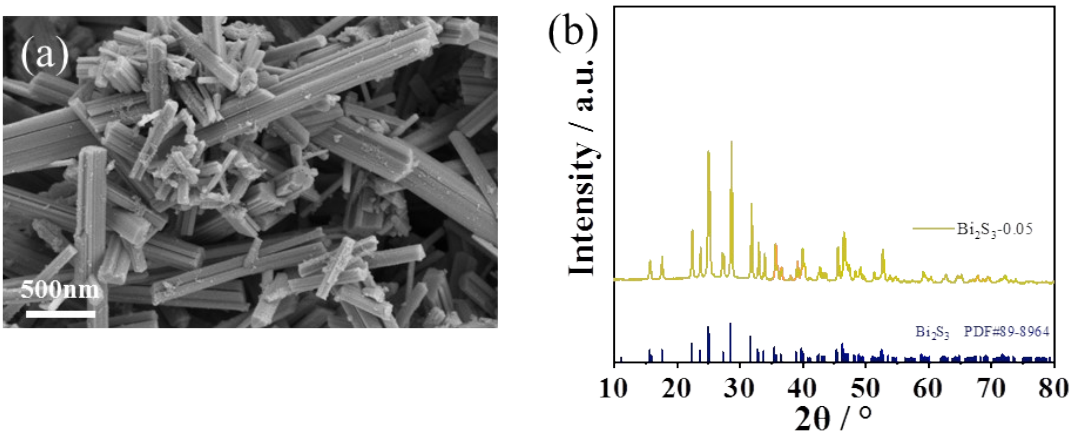

Fig. S3 (a) SEM image and (b) XRD pattern of Bi_2S_3-0.05.

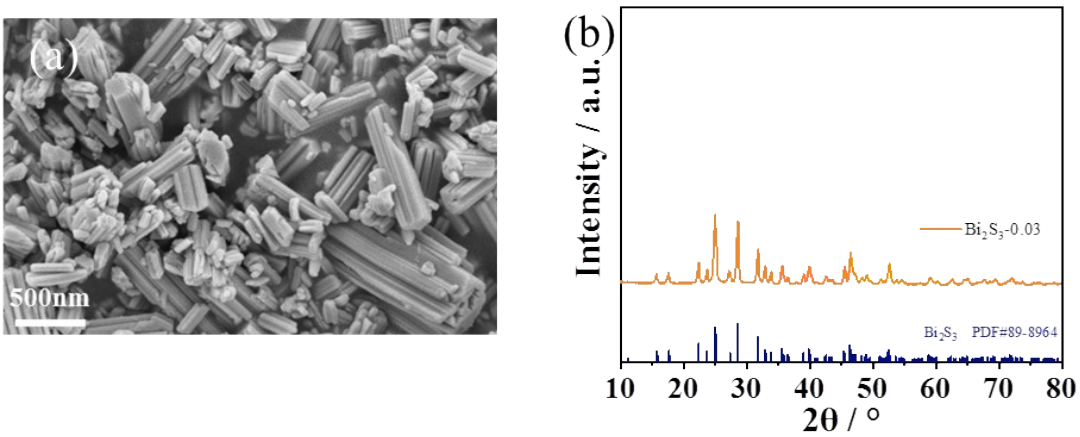

Fig. S4 (a) SEM image and (b) XRD pattern of Bi_2S_3-0.03.

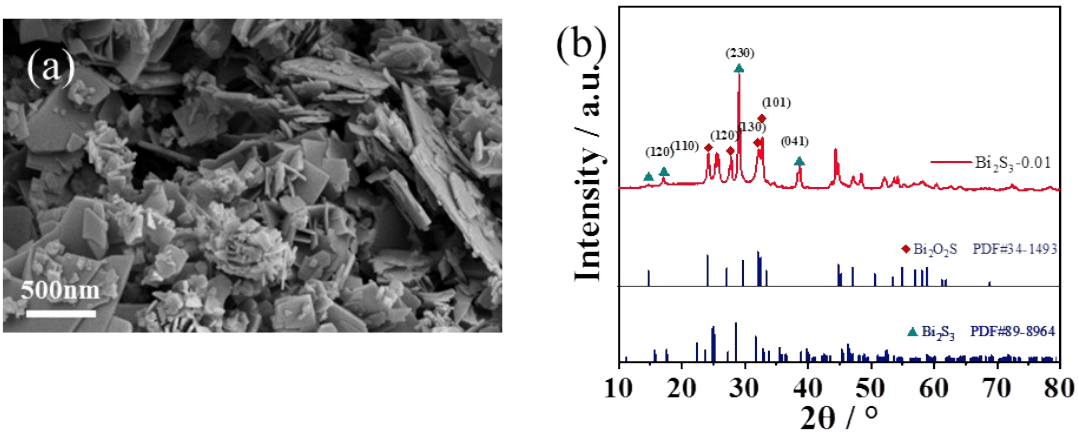

Fig. S5 (a) SEM image and (b) XRD pattern of Bi_2S_3-0.01.

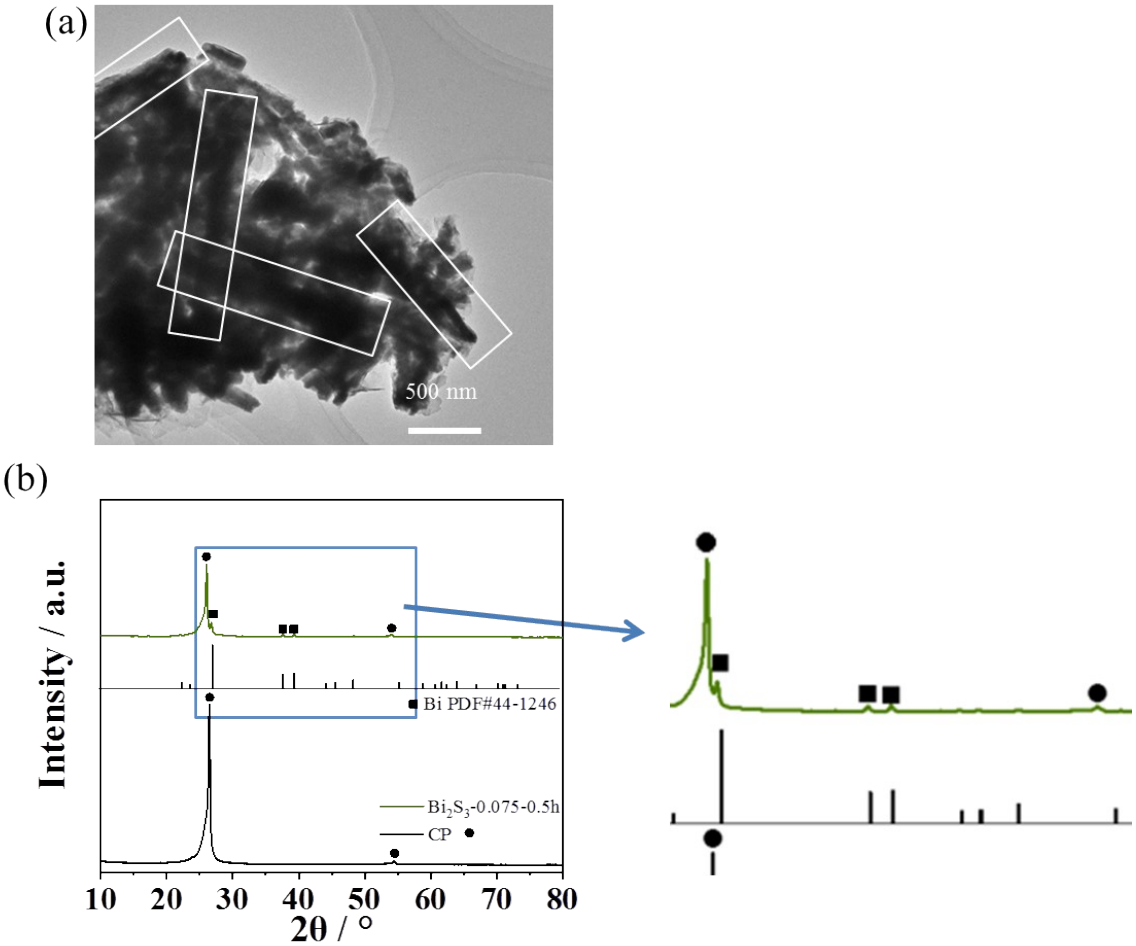

Fig. S6 (a) TEM image of Bi_2S_3-0.075-D-0.5h, (b) XRD patterns of Bi_2S_3-0.075-D-0.5h and CP.

In Fig. S6(a), because the material was scraped off the carbon paper after the reaction, some carbon paper debris was mixed.

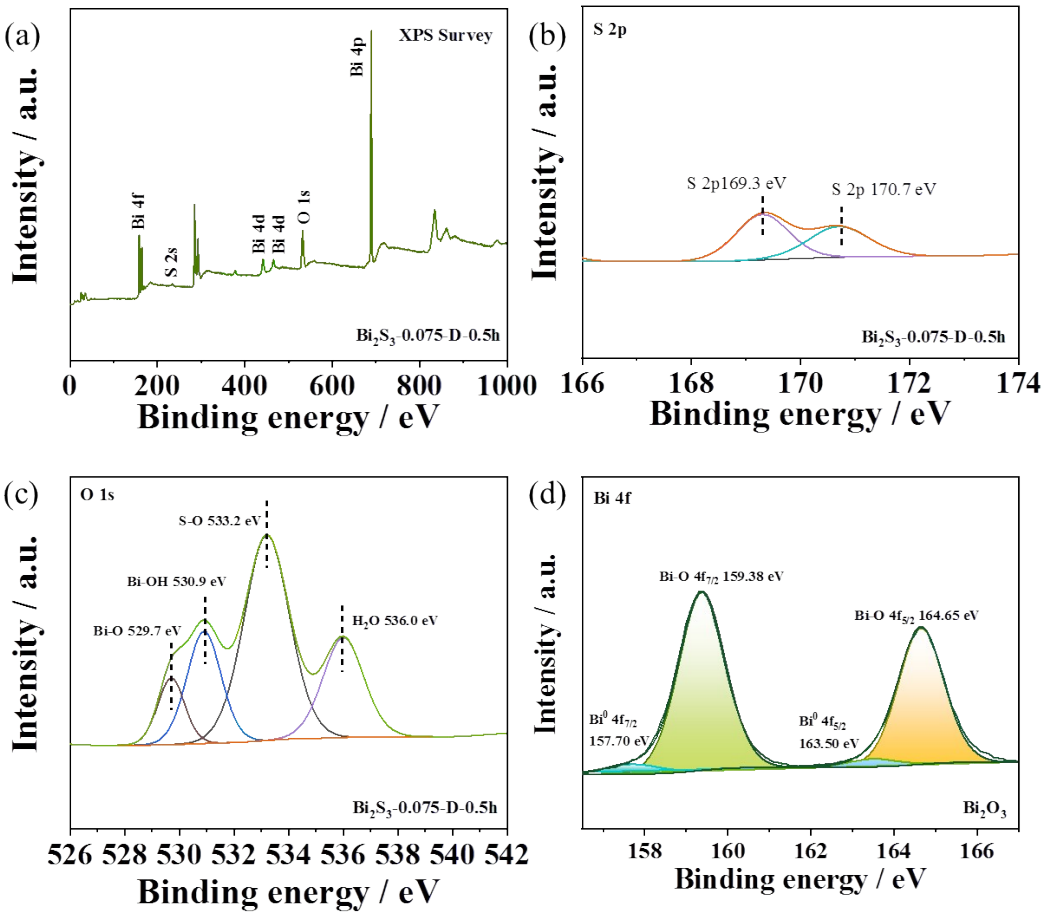

Fig. S7 XPS survey spectra of (a) Bi_2S_3-0.075-D-0.5h, (b) S 2p, (c) O 1s of Bi_2S_3-0.075-D-0.5h electrode and (d) Bi 4f of Bi_2O_3 derived electrode.

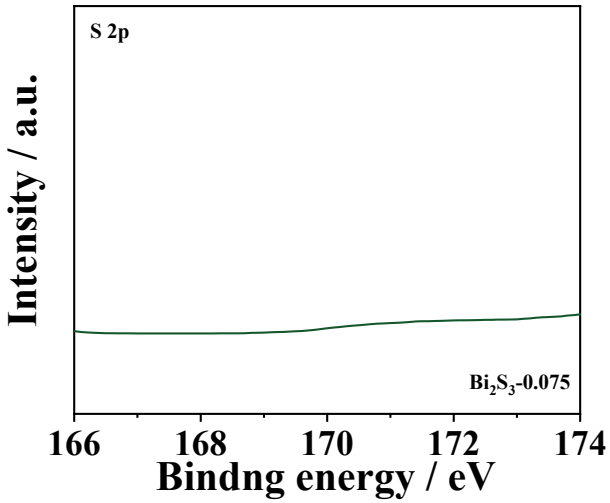

Fig. S8 XPS survey spectra of S 2p of Bi_2S_3-0.075 electrode.

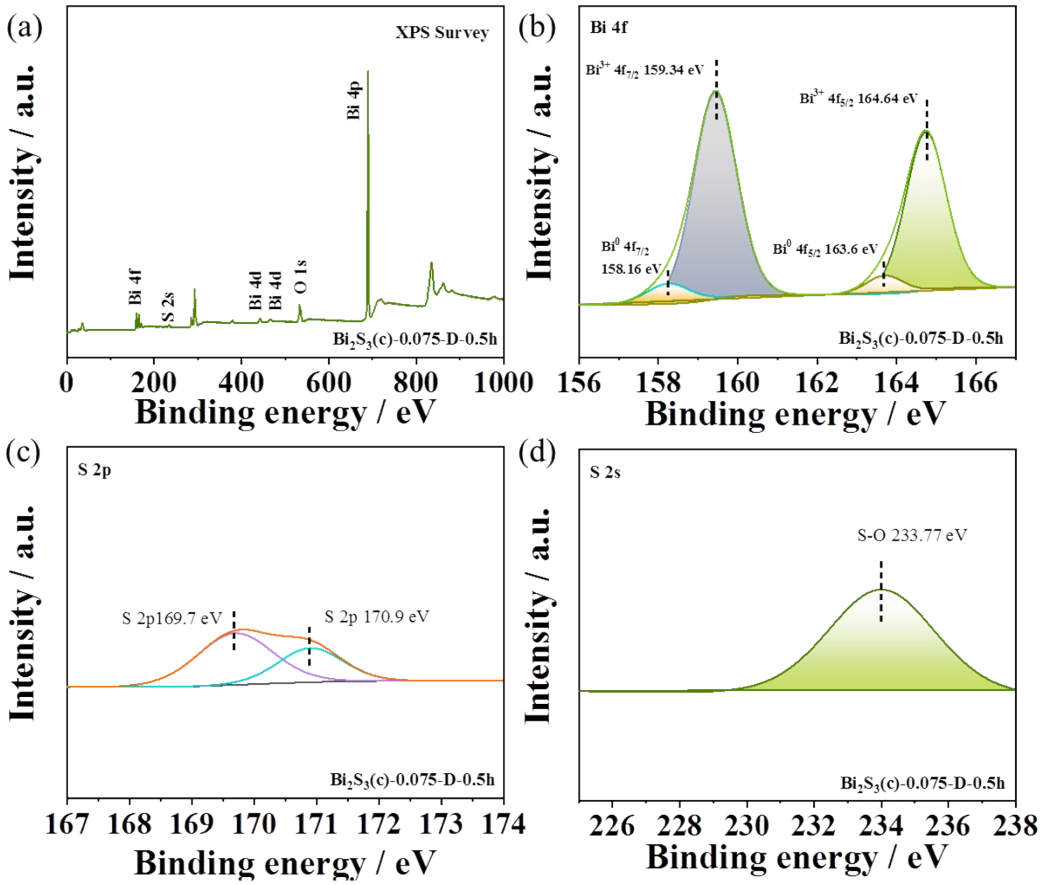

Fig. S9 XPS survey spectra of (a) Bi_2S_3(c)-0.075-D-0.5h and (b) Bi 4f, (c) S 2p and (d) S 2s of Bi_2S_3(c)-0.075-D-0.5h electrode.

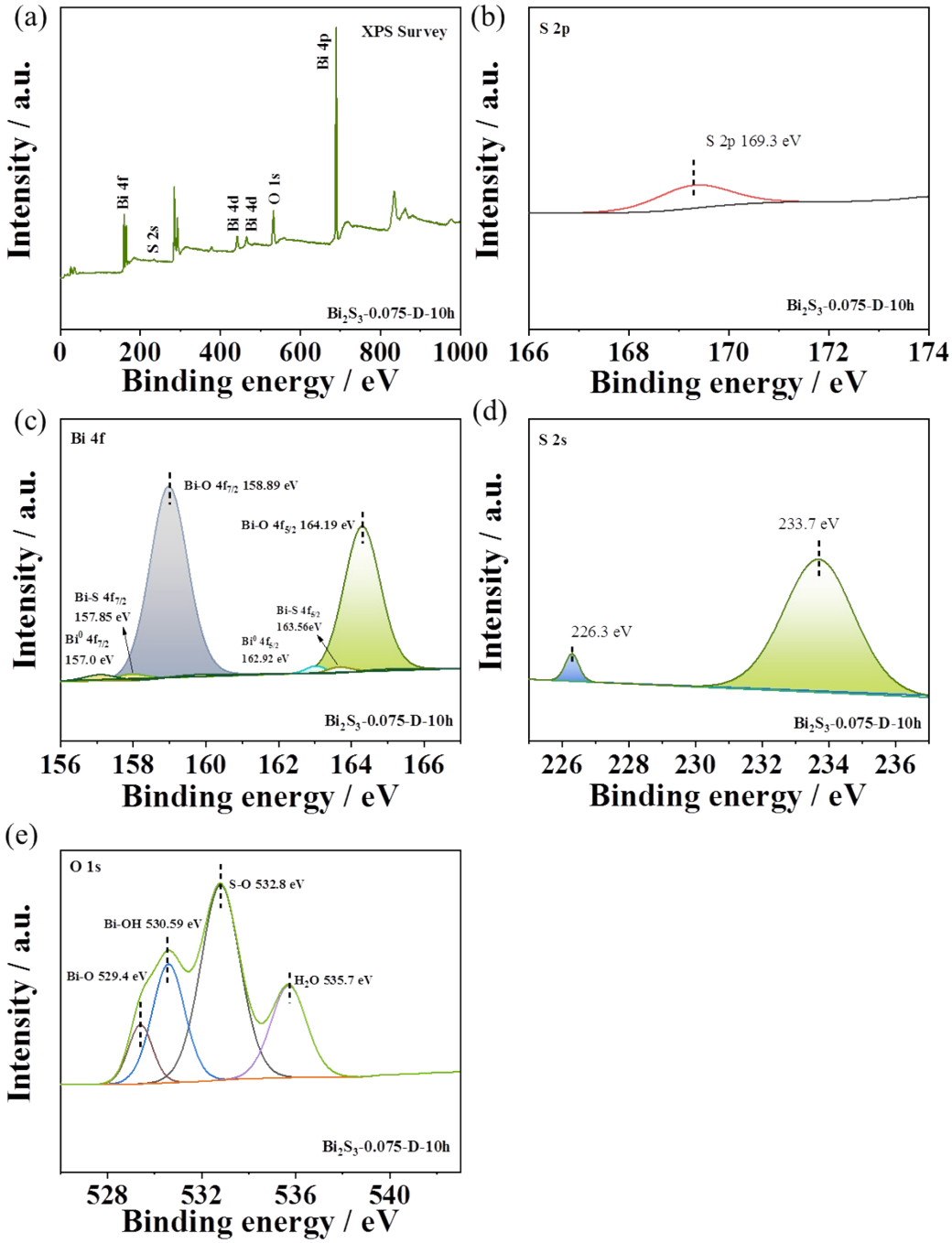

Fig. S10 XPS survey spectra of (a) Bi_2S_3-0.075-D-10h and (b) Bi 4f, (c) S 2p, (d) S 2s and (e) O 1s of Bi_2S_3-0.075-D-10h electrode.

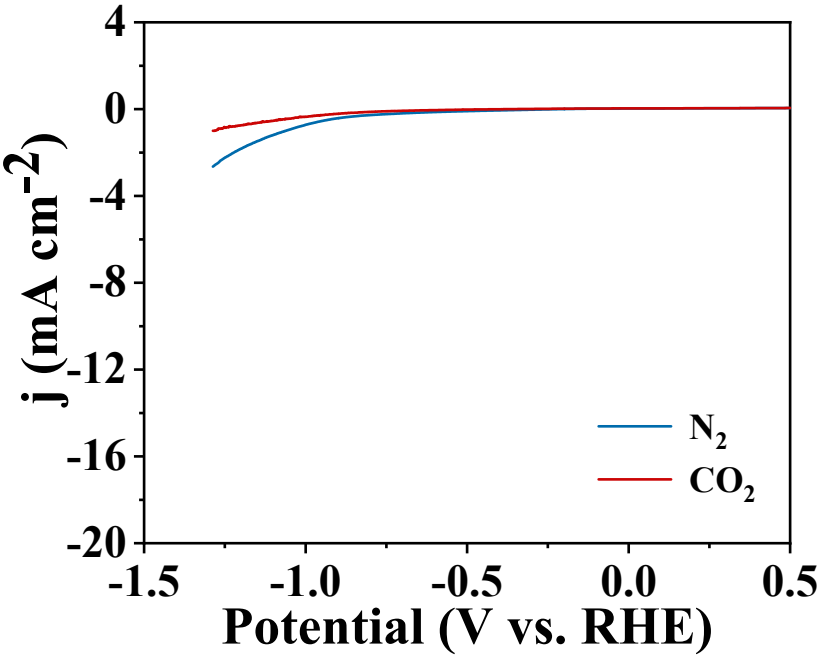

Fig. S11 LSV curves of CP in N_2 and CO_2 atmosphere in 0.1 M $KHCO_3$ at 50 mV s^{-2}.

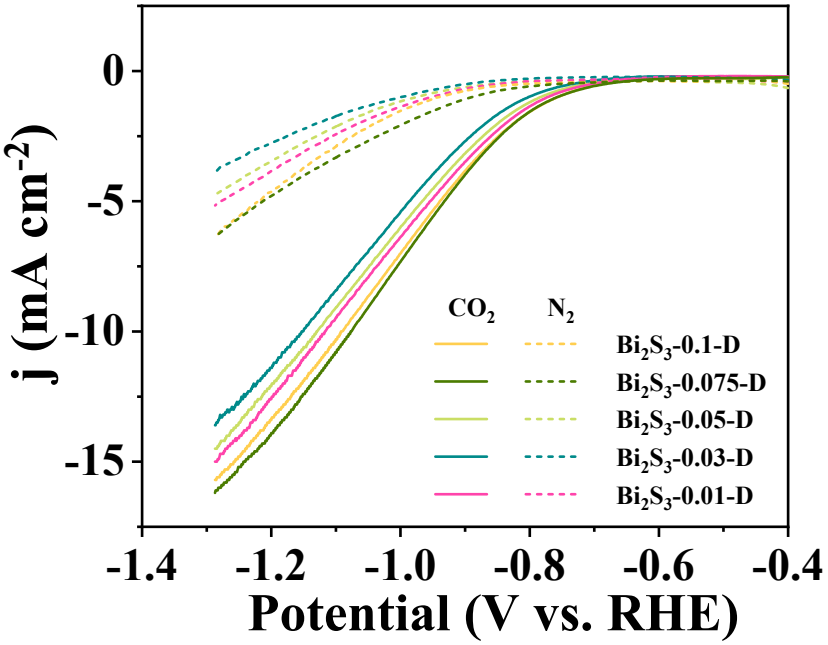

Fig. S12 LSV curves of Bi_2S_3-0.1-D, Bi_2S_3-0.075-D, Bi_2S_3-0.05-D, Bi_2S_3-0.03-D to Bi_2S_3-0.01-D in N_2-saturated and CO_2-saturated 0.1 M $KHCO_3$ at 50 mV s^{-2}.

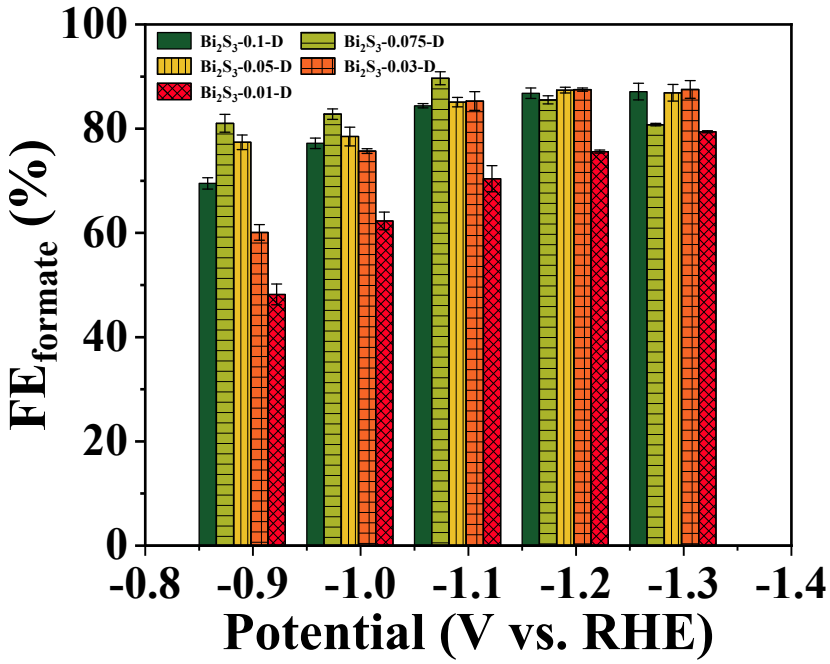

Fig. S13 The $FE_{formate}$ of Bi_2S_3-0.1-D, Bi_2S_3-0.075-D, Bi_2S_3-0.05-D, Bi_2S_3-0.03-D and Bi_2S_3-0.01-D electrodes at different applied potential.

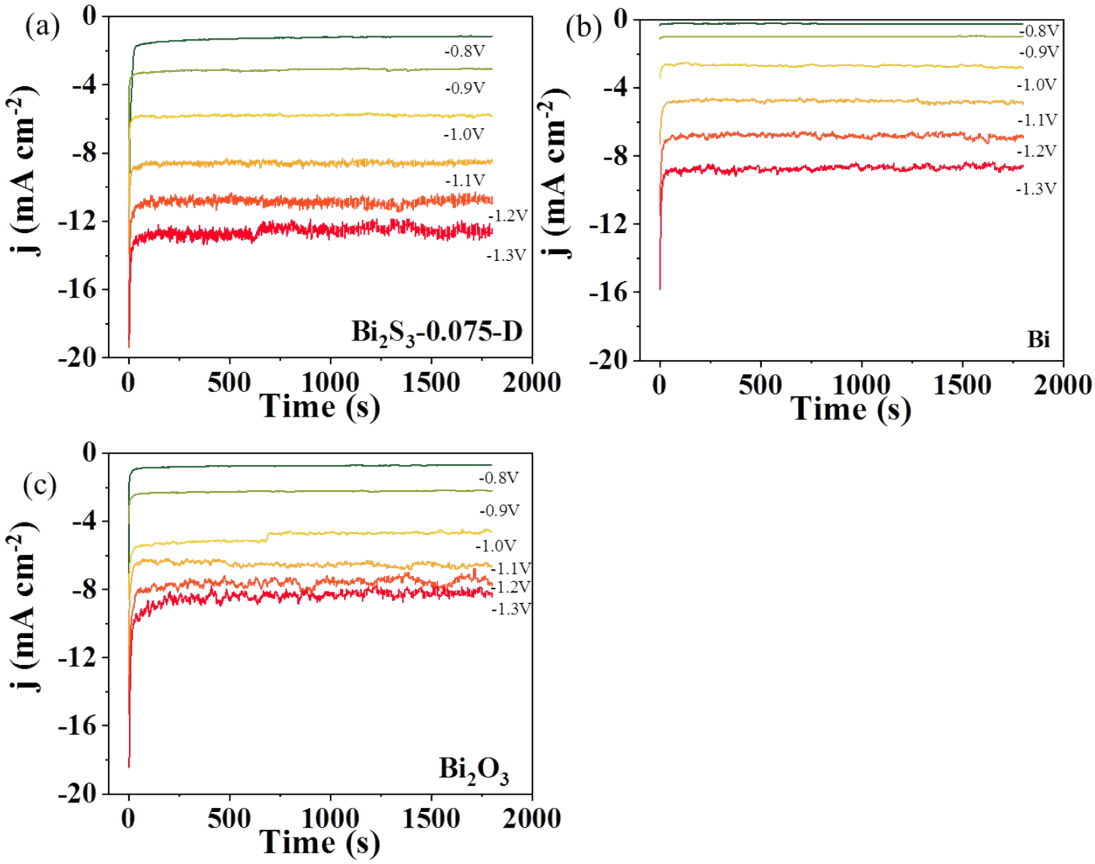

Fig. S14 I-t curves of $ERCO_2$ over (a) Bi_2S_3-0.075-D, (b) Bi and (d) Bi_2O_3 at different potential within 1800 s.

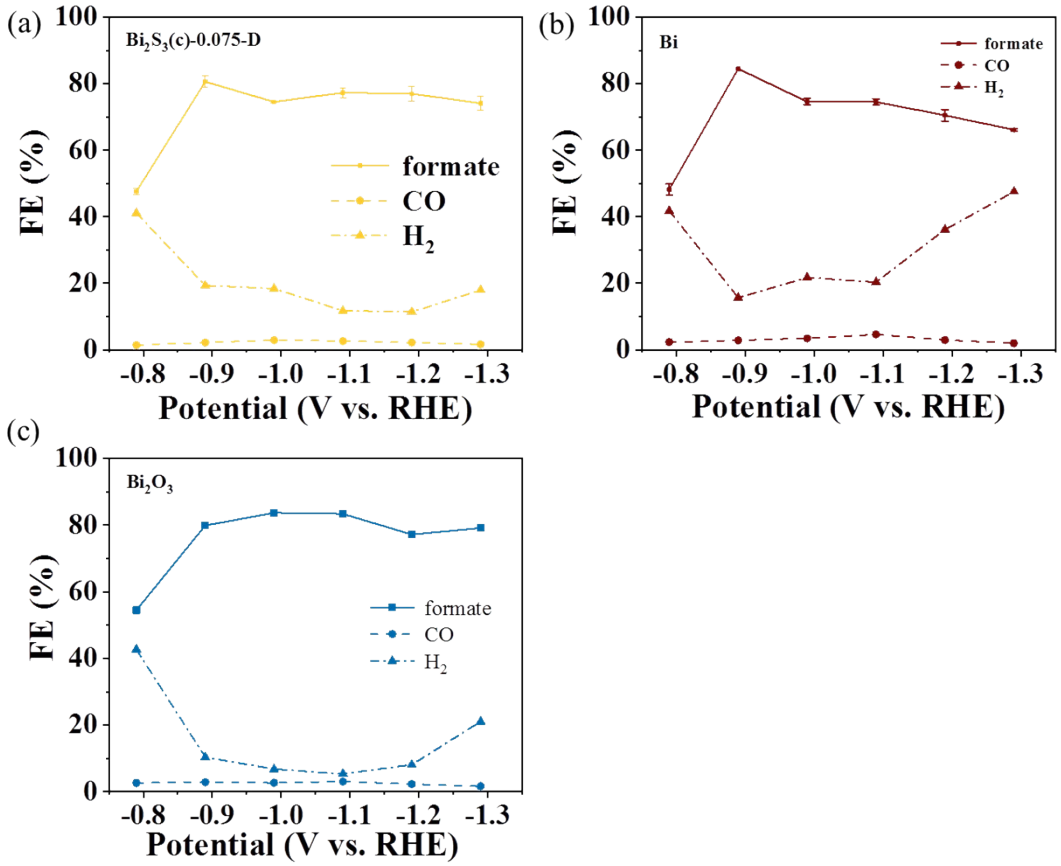

Fig. S15 FE of formate, CO and H_2 over (a) Bi_2S_3(c)-0.075-D, (b) Bi and (c) Bi_2O_3 electrodes.

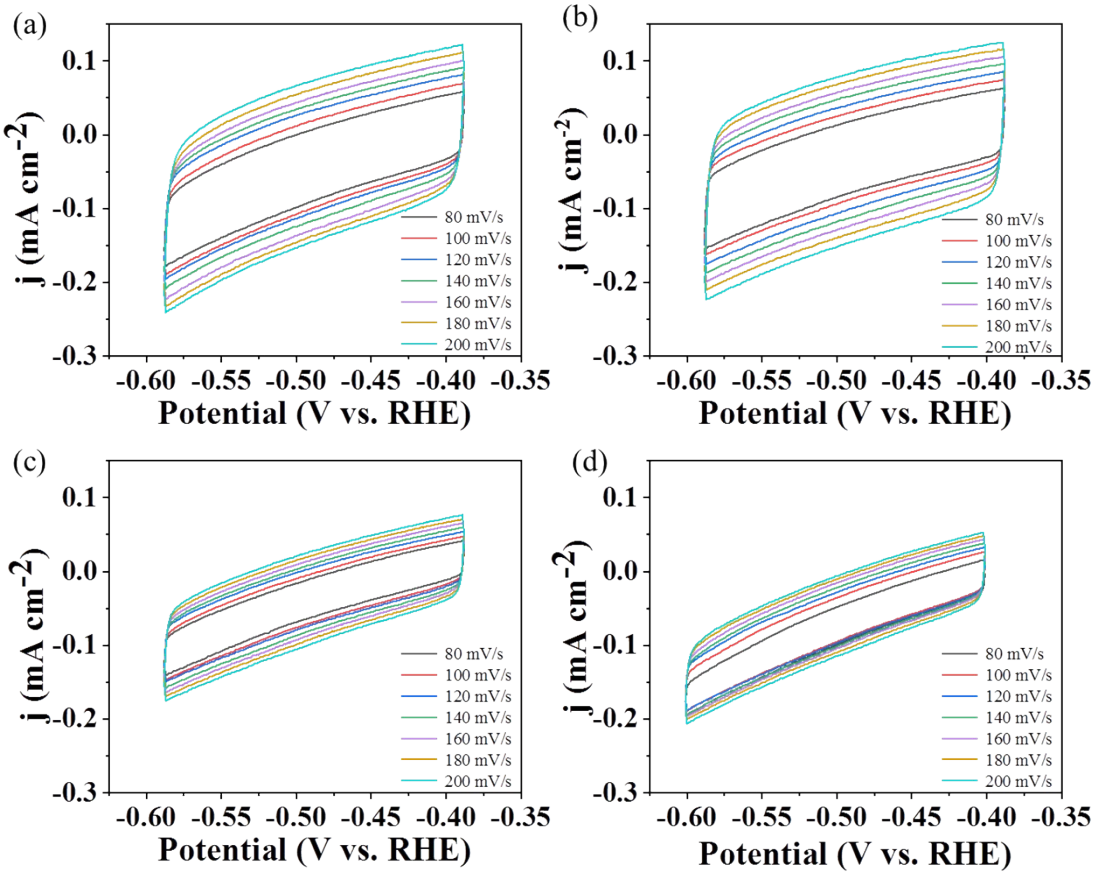

Fig. S16 CV curves of (a) Bi_2S_3-0.1-D, (b) Bi_2S_3-0.075-D, (c) Bi_2S_3-0.05-D and (d) Bi_2S_3-0.03-D at the range of −0.4 to −0.6 V with different scan rates in N_2-saturated 0.1 M $KHCO_3$ solution.

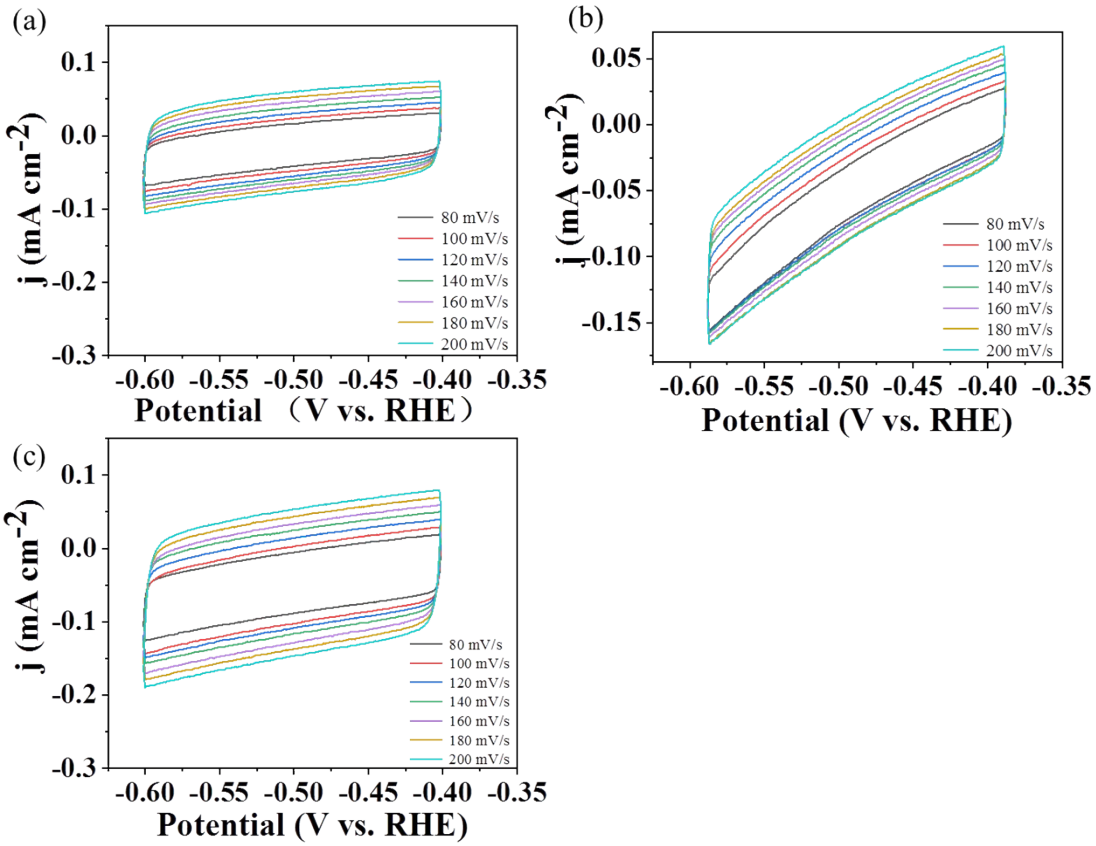

Fig. S17 CV curves of (a) Bi, (b) Bi_2S_3(c)-0.075-D and (c) Bi_2O_3 at the range of −0.4 to −0.6 V with different scan rates in N_2-saturated 0.1 M $KHCO_3$ solution.

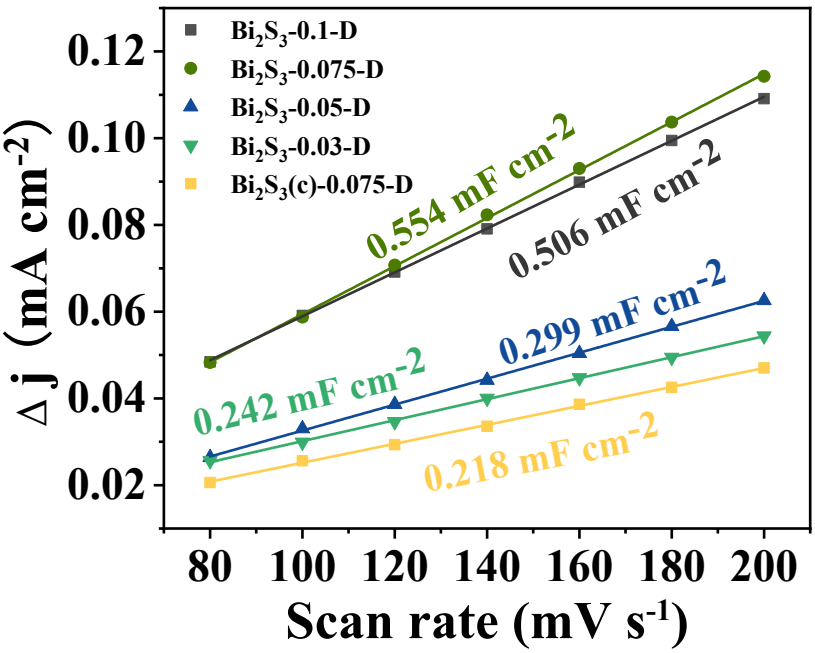

Fig. S18 Comparison of corresponding Cdl of Bi_2S_3-0.1-D, Bi_2S_3-0.075-D, Bi_2S_3-0.05-D and Bi_2S_3-0.03-D samples.

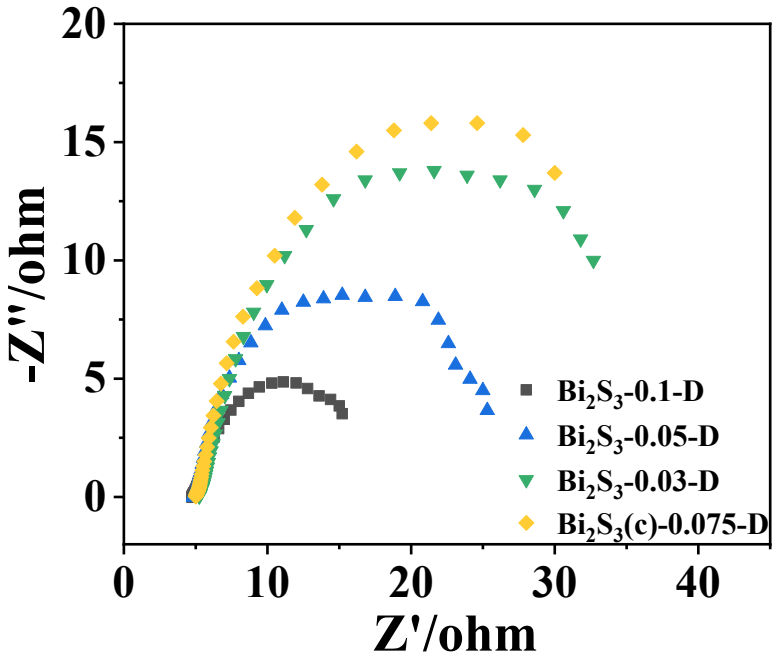

Fig. S19 EIS measurements of Bi_2S_3-0.1-D, Bi_2S_3-0.075-D, Bi_2S_3-0.05-D and Bi_2S_3-0.03-D samples at the potential of $-1.09V_{RHE}$.

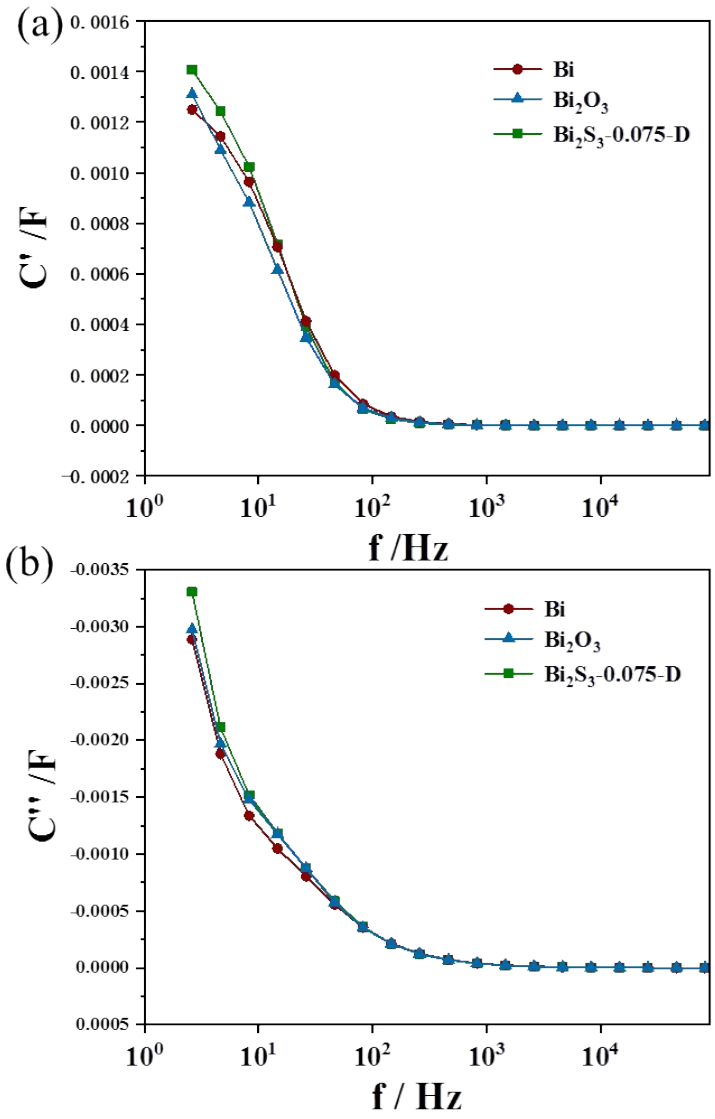

Fig. S20 Bode plots of (a) real part and (h) imaginary part of complex capacitance with respect to frequency of Bi_2S_3-0.075-D, Bi_2O_3 and Bi samples.

Sample	Bi : S: O (atomic rate)
Bi_2S_3	1:1.47
Bi_2S_3-0.075-D-0.5h	1:10.24:11.28
Bi_2S_3(c)-0.075-D-0.5h	1:20.87:6.76
Bi_2S_3-0.075-D-10h	1:10.09:10.35

Table S1 Atomic ratio of Bi to S in different materials.

Catalysts	Bi_2S_3	Bi_2S_3-0.075-D-0.5h	Bi_2S_3(c)-0.075-D-0.5h	Bi_2S_3-0.075-D-10h	Bi_2O_3-D
A Bi3+ 4f7/2(Bi2S3)	574912.88	2536.52	-	1466.67	-
A Bi3+ 4f5/2(Bi2S3)	424810.24	1903.91	-	1052.90	-
A Bi3+ 4f7/2(Bi2O3)	-	19328.47	30788.72	54715.12	65338.93
A Bi3+ 4f5/2(Bi2O3)	-	14291.91	22414.77	40026.79	48735.22
A Bi0 4f7/2	-	2119.97	3091.30	1582.9	4331.67
A Bi0 4f5/2	-	1571.28	2373.81	1194.17	3124.51

Table S2 Peak area parameters of XPS spectrum for Bi 4f of different catalysts.

Catalysts	ECSA(cm^2)
Bi_2S_3-0.075	6.925
Bi	4.06
Bi_2O_3	6.05

Table S3 The electrochemical active surface area of different catalysts.

Catalyst	Electrolyte	Potential (V vs. RHE)	J (mA cm^{-2})	$FE_{formate}$ (%)	Ref.
Defect-rich Bi (derived from Bi_2S_3)	0.5 M $NaHCO_3$	−0.75	5	84	[1]
Bi with rich Bi-O bond (derived from Bi_2S_3)	0.5 M $KHCO_3$	−1.0	6.6	80	[2]
Bi_2S_3-Bi_2O_3@rGO	0.1 M $KHCO_3$	−0.9	4	90.1	[3]
S doped BiOC	0.5 M $KHCO_3$	−0.9	30	96.7	[4]
Bi nanoparticles	0.5 M $KHCO_3$	−0.83	55	86	[5]
β-Bi_2O_3	0.1 M $KHCO_3$	−1.2	20.9	87	[6]
Bi nanosheets	0.1 M $KHCO_3$ (flow cell)	−1.36	210	88.1	[7]
Bi/Bi_2O_3 nanoparticles	0.5 M $KHCO_3$	−0.9	18	85	[8]
Bi Dendrite	0.5 M $KHCO_3$	−0.74	3.2	89	[9]
Bi nanosheets	0.1 M $KHCO_3$	−1.1	17	86.0	[10]
S and O co-doping Bi	0.1 M $KHCO_3$	−1.09	9	89.7	This work

Table S4 The performance of CO_2 electroreduction to formate over Bi-based catalysts reported recently.

References

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