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Supporting Information

Active-site stabilized Bi metal-organic framework-based catalyst for highly active and selective electroreduction of CO_2 to formate over a wide potential window

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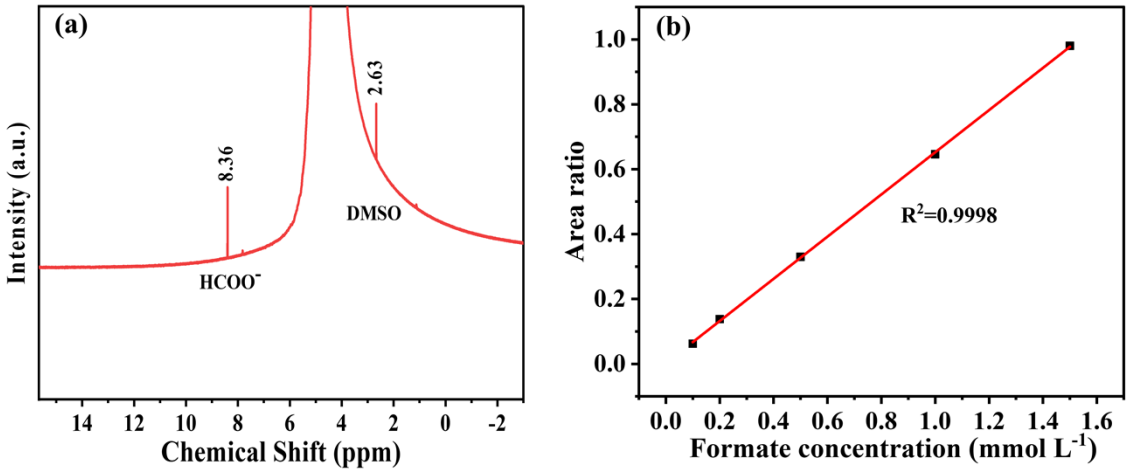

Fig. S1. (a) NMR trace of formate at -0.9 V potential for ECR by Bi-BDC-120 °C, (b) NMR standard curve of formate.

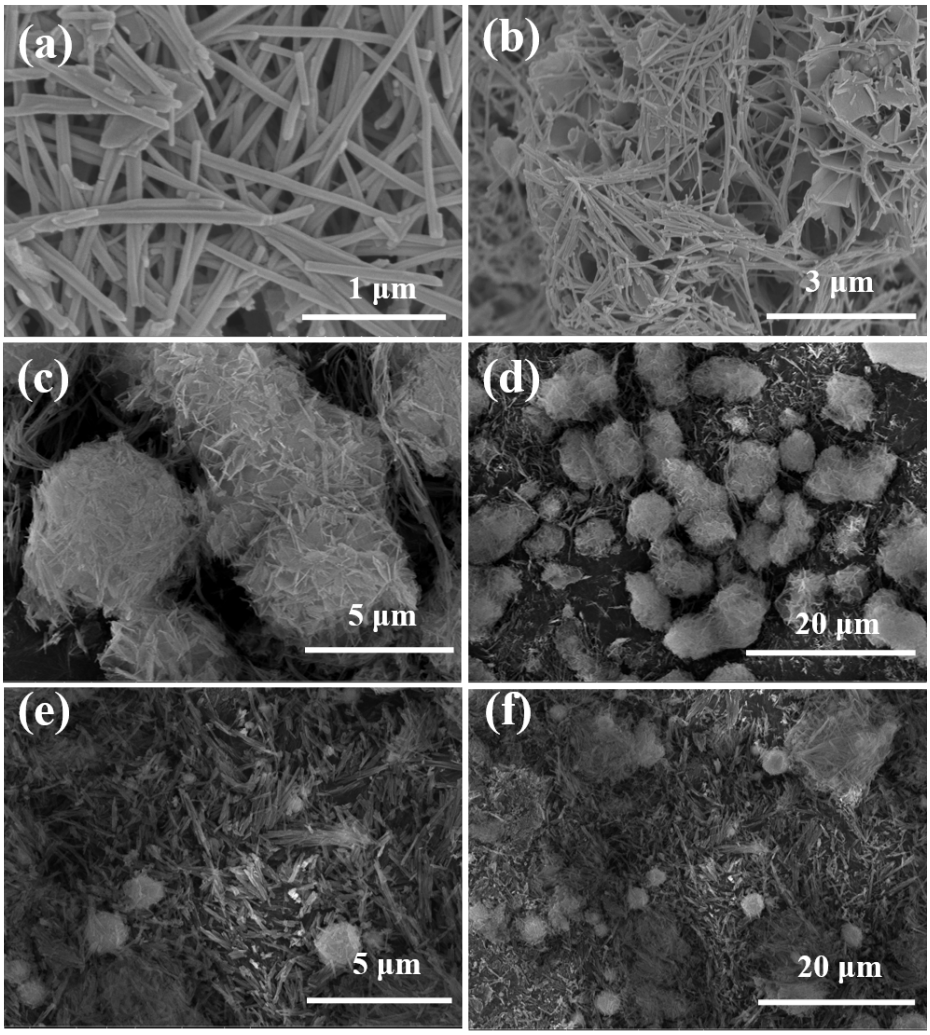

Fig. S2. (a-b) The SEM images of Bi-BDC-100 °C, (c-d) Bi-BDC-120 °C, and (e-f) Bi-BDC-140 °C.

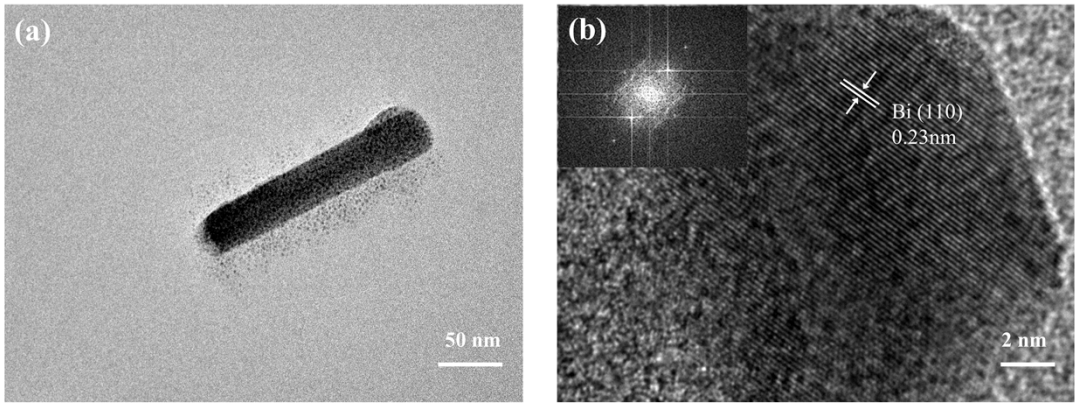

Fig. S3. (a) TEM and (b) HR-TEM image of the Bi-BDC-140 °C catalyst

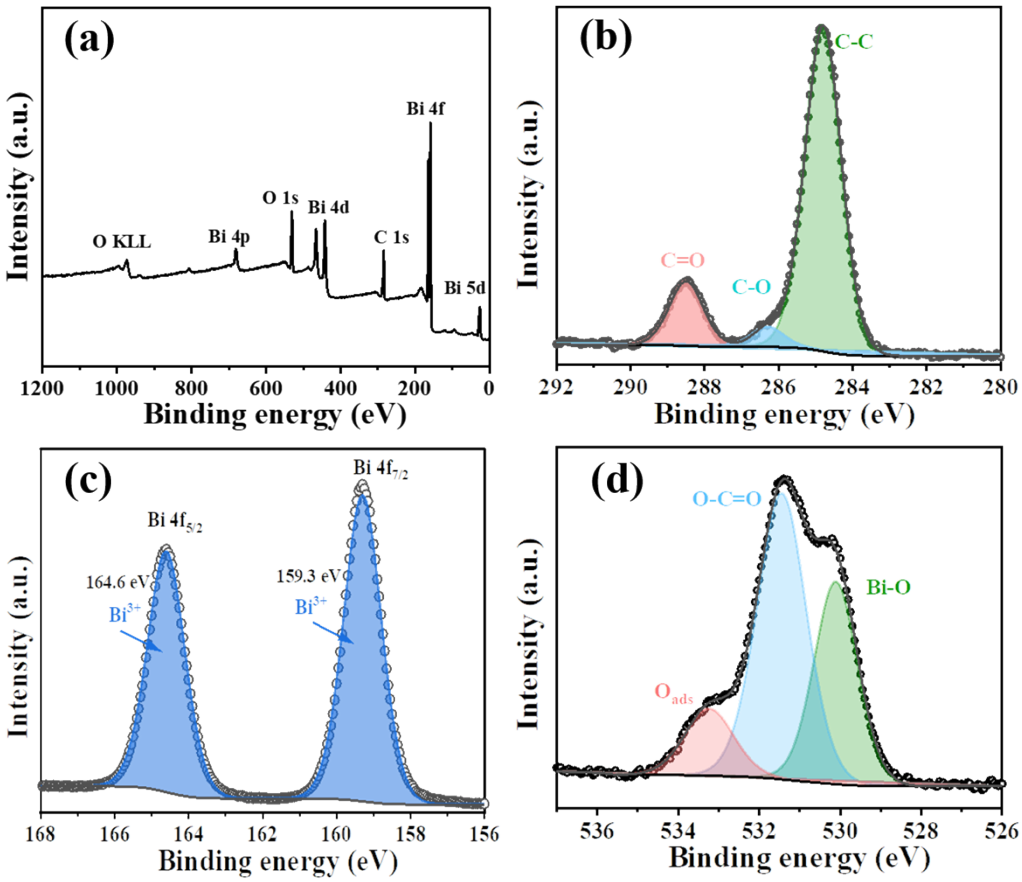

Fig. S4. XPS spectra of the Bi-BDC-140 °C: (a) survey scan, (b) C 1s, (c) Bi 4f, and (d) O 1s

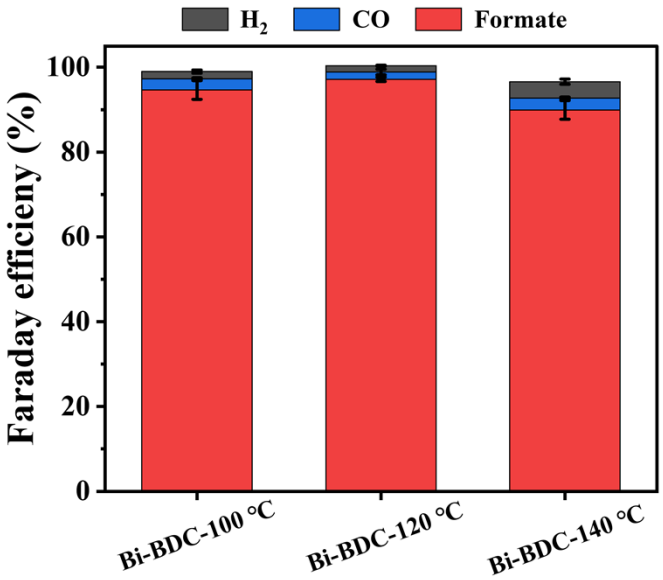

Fig. S5. Faraday efficiency (FE) of the products by Bi-BDC-T at -1.1 V vs RHE.

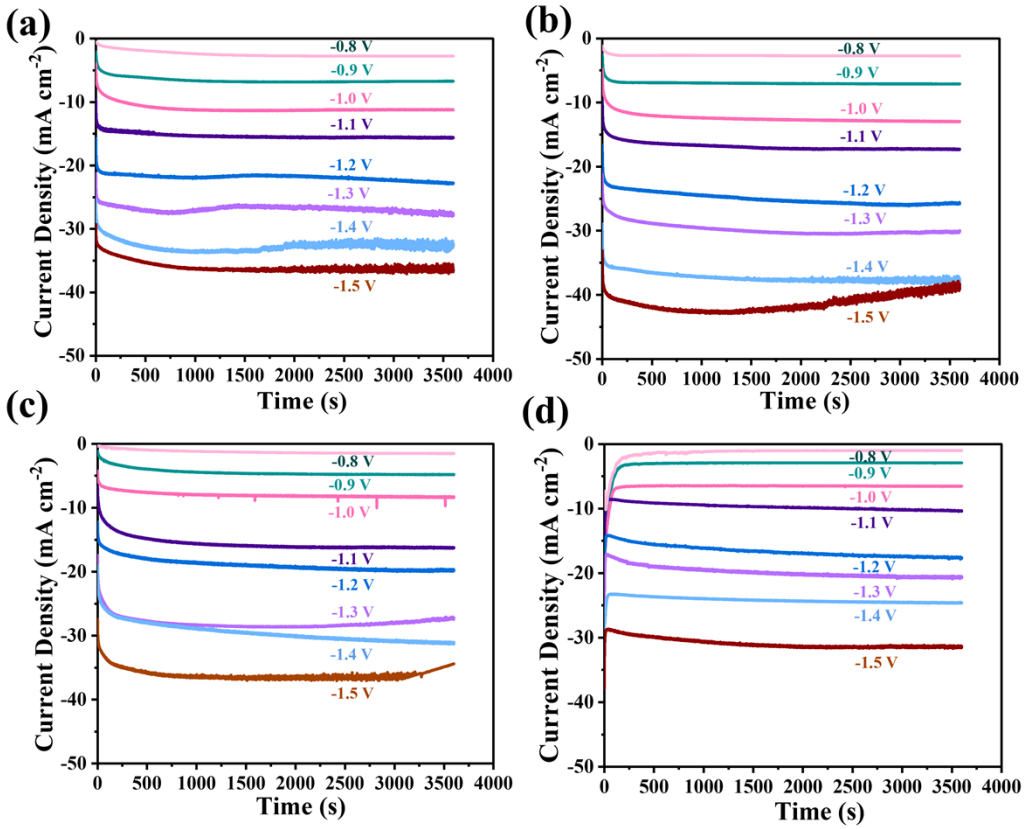

Fig. S6. Chronoamperometric responses at different working potentials in CO_2 saturated 0.1 mol L^{-1} $KHCO_3$ catalyzed by (a) Bi-BDC-100 °C, (b) Bi-BDC-120 °C, (c) Bi-BDC-140 °C and (d)commercial Bi_2O_3.

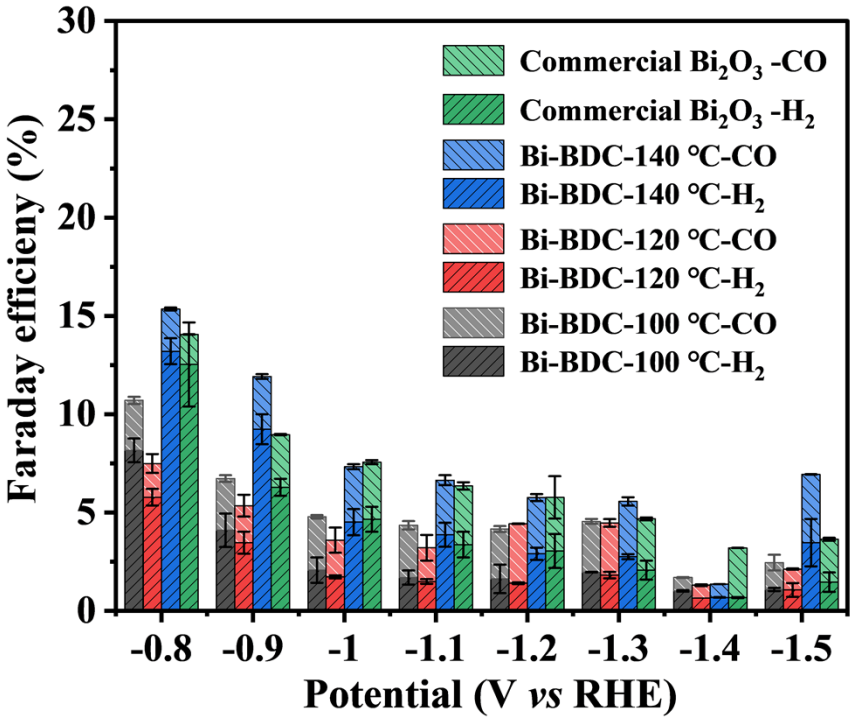

Fig. S7. Faraday efficiency (FE) of H_2 and CO at different working potentials.

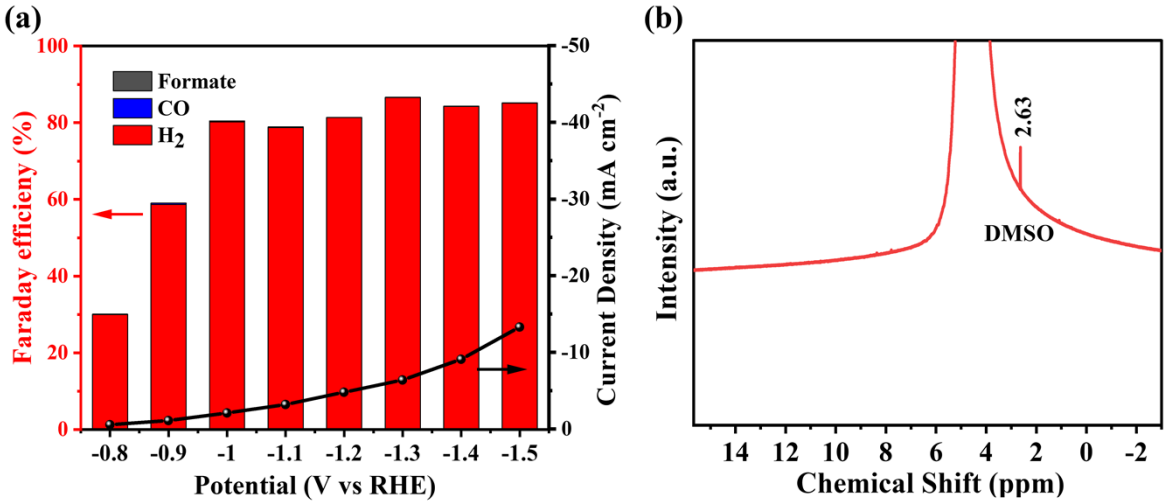

Fig. S8. (a) FE of products and current density at different working potentials in Ar-saturated electrolyte using Bi-BDC-120 °C as electrocatalyst. (b) NMR trace at -0.9 V potential in Ar-saturated electrolyte using Bi-BDC-120 °C as electrocatalyst.

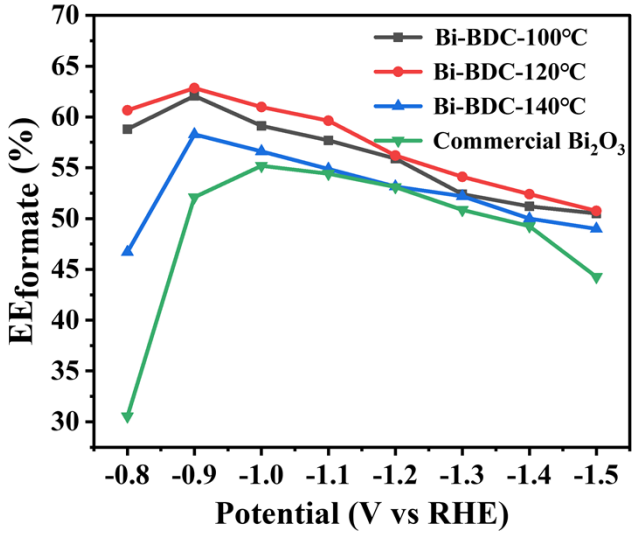

Fig. S9. Energy efficiencies (EE) of formate at different working potentials for ECR catalyzed by Bi-BDC-100 °C, 120 °C,140 °C, and commercial Bi_2O_3.

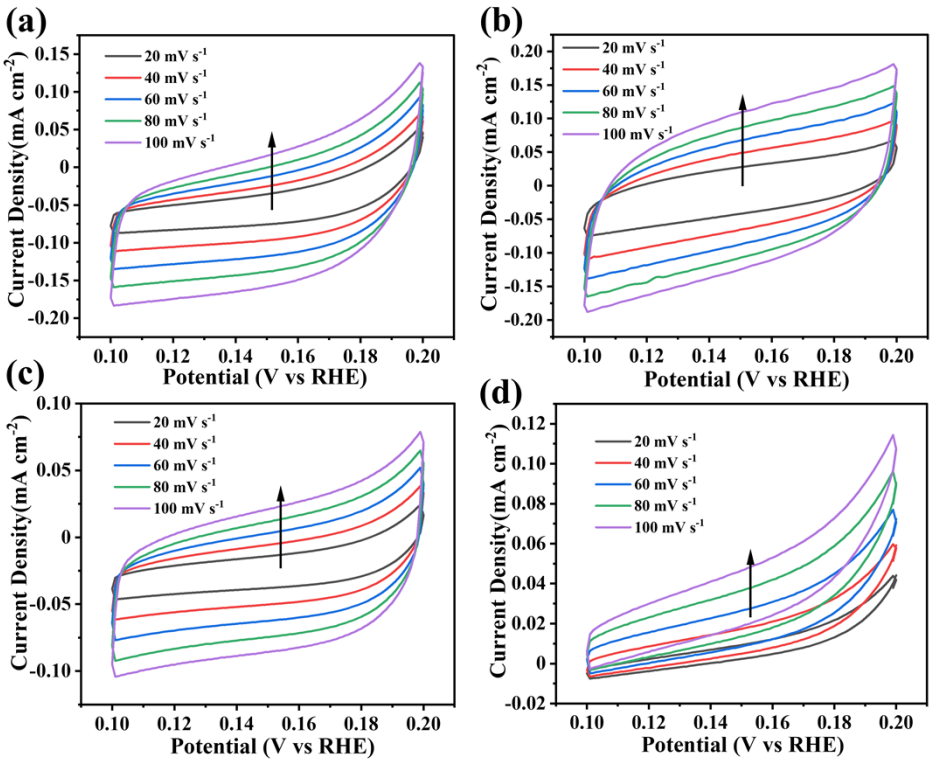

Fig. S10. Electrochemically surface area (ECSA) measurements. Cyclic voltammograms (CVs) of different catalysts at various sweep speeds (20–100 mV s-1) in the region of 0.10 to 0.20 V vs. RHE: (a) Bi-BDC-100 °C (b) Bi-BDC-120 °C (c) Bi-BDC-140 °C and (d) commercial Bi_2O_3.

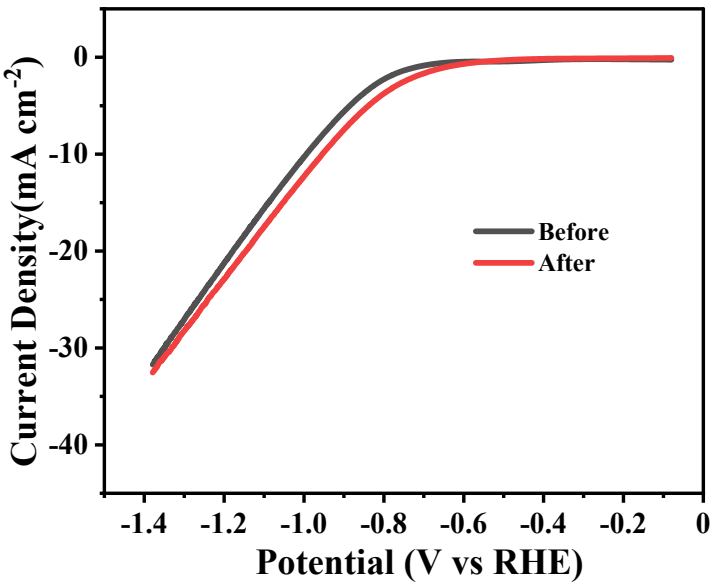

Fig. S11. Comparison of Linear Scanning Voltammogram (LSV) curves before and after the 36-hour stability test.

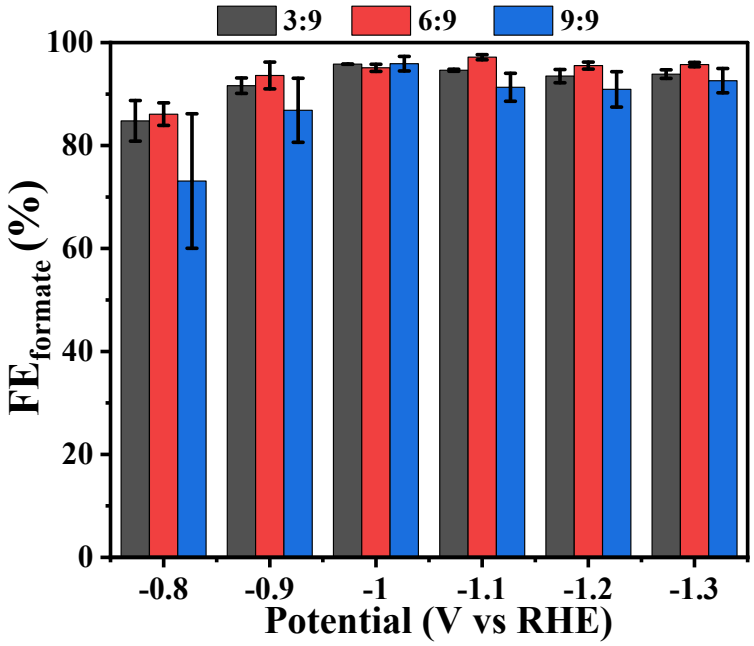

Fig. S12. FEsformate for catalysts synthesized with different molar ratios of $Bi(NO_3)_3 \cdot 5H_2O$ to H_2BDC.

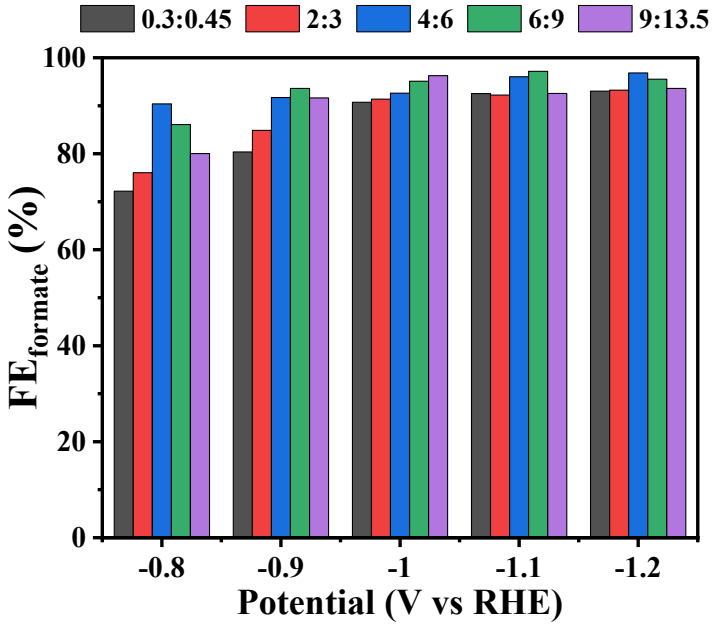

Fig.S13. FEsformate for catalysts synthesized with various stock concentrations but keeping the same molar ratios of $Bi(NO_3)_3{\cdot}5H_2O$ and H_2BDC (i.e., 0.3:0.45, 2:3, 4:6, 6:9, and 9:13.5).

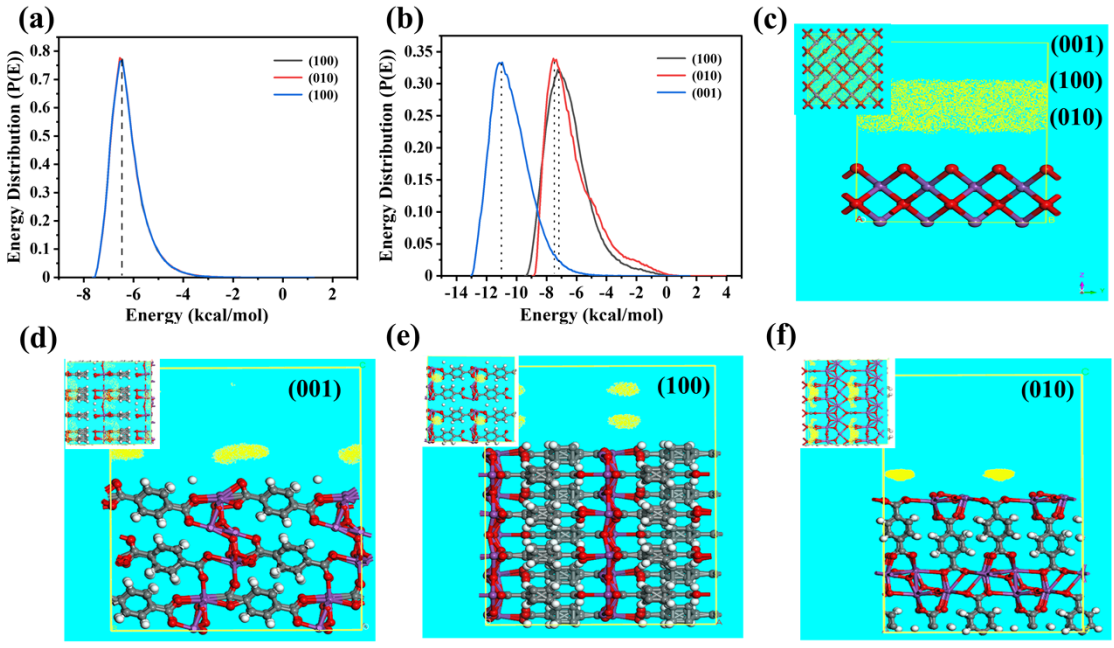

Fig. S14 Theoretical calculation of CO_2 adsorption on the surface of (a) Bi_2O_3 (b) Bi-BDC, and the crystal surface diagram of CO_2 adsorption by (c) Bi_2O_3 (d-f) Bi-BDC.

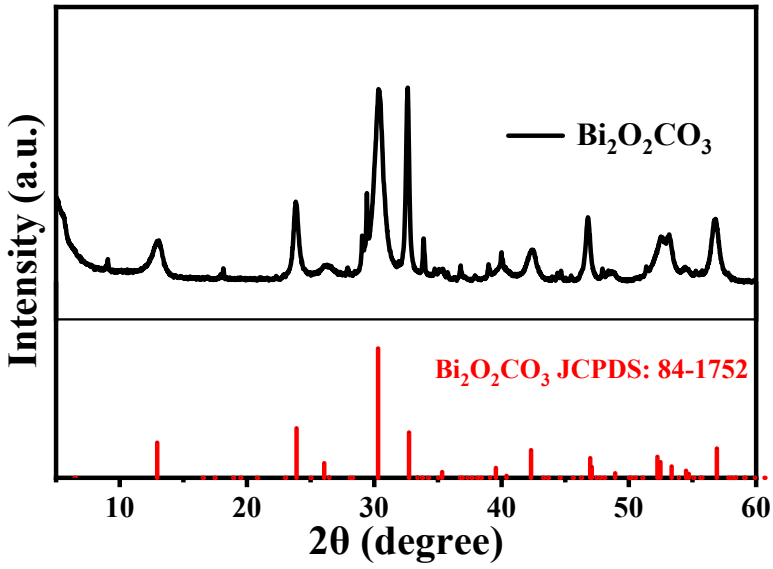

Fig.S15. XRD patterns of the synthesized $Bi_2O_2CO_3$.

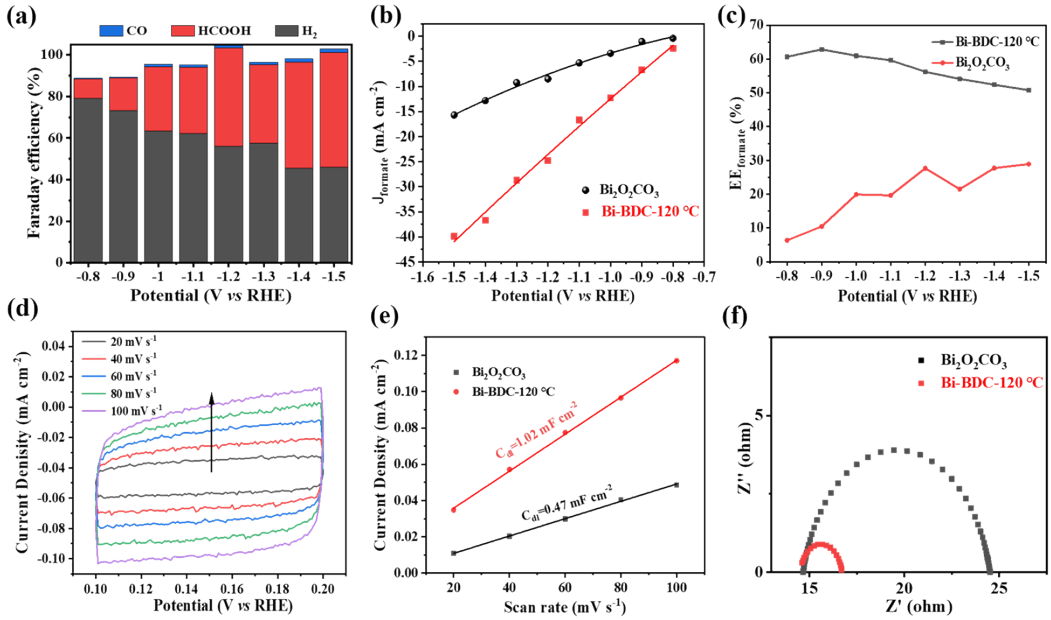

Fig.S16. (a) Faraday efficiency of formate at different working potentials catalyzed by the synthesized $Bi_2O_2CO_3$. (b) Comparison of the bias current densities and (c) Energy efficiencies (EE) of formate catalyzed with $Bi_2O_2CO_3$ and Bi-BDC-120 °C. (d) Cyclic voltammograms (CVs) of synthesized $Bi_2O_2CO_3$. (e) Comparison of ECSA measurement catalyzed with $Bi_2O_2CO_3$ and Bi-BDC-120 °C, and the charging current densities were plotted against the scan rates of CVs. (f) Nyquist plots for Bi-BDC-120 °C and synthesized $Bi_2O_2CO_3$ with the fitted circuit shown.

Table S1 Comparison of Bi-BDC-120 °C with the reported Bi-based catalysts for ECR conversion of CO_2 to formate.

Catalysts	Electrolyte	E (V *vs.* RHE)	$FE_{formate}$ (%)	$J_{formate}$ (mA cm^{-2})	Window (mV)	Stability	Ref.
Bi-BDC-120 °C	**0.1 M $KHCO_3$**	**-0.9**	**93.6**	**-6.6**	**700**	**36 h**	**This work**
		-1.1	**97.2**	**-16.7**			**This work**
Bi-MP	1 M KOH	-1.0	95	-180 (flow-cell)	600	10 h	[1]
Bi-BTC	0.1 M $KHCO_3$	-1.1	80	-8	400	30 h	[2]
Bi-BTC-D	0.5 M $KHCO_3$	-0.86	95.5	-11.2	400	12 h	[3]
Bi_2O_3@C	0.5 M $KHCO_3$	-0.9	93	-7.5	300	10 h	[4]
Bi/CeO*x*	0.2 M $NaSO_4$	-1.3	92	-137 (flow-cell)	500	30 h	[5]
Bi Ns	0.1 M $KHCO_3$	-1.1	92	-9	300	10 h	[6]
PNCB	0.5 M $KHCO_3$	-1.05	92.3	-22	400	No date	[7]
Bi-Sn	0.5 M $KHCO_3$	-1.14	94	-40.2	300	No date	[8]
Bi/Bi_2O_3-CP	0.5 M $KHCO_3$	-0.87	90.4	-38.8	200	17 h	[9]
Bi/CN	0.1 M $KHCO_3$	-1.3	98	-15.7	500	20 h	[10]
Bi_2O_3NSs@MCCM	0.1 M $KHCO_3$	-1.256	93.8	-15.1	400	12 h	[11]
$Bi_2O_2CO_3$	0.5 M $KHCO_3$	-0.669	96.1	-9.61	300	48 h	[12]
Cu NWs-Bi NSs	0.1 M $KHCO_3$	-0.86	87	-4.5	100	8 h	[13]

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