Supplementary Information (SI) for New Journal of Chemistry.

Supporting Information

In situ transformation of a Bi-based MOF to highly active catalyst for CO_2 reduction

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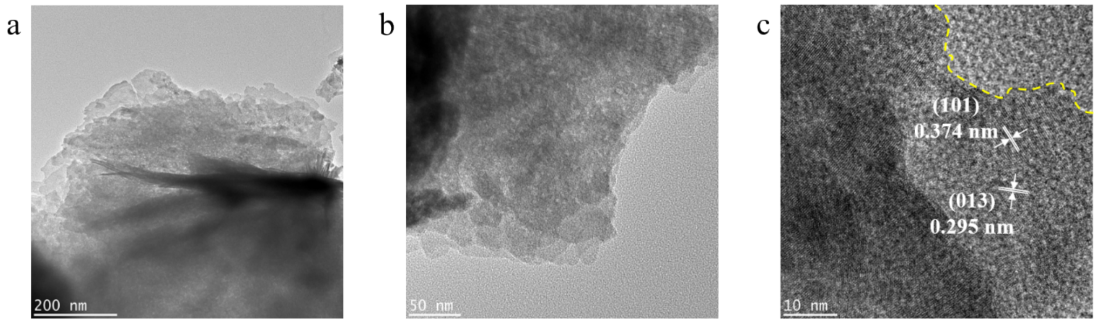

Fig. S1 a, b) TEM images and c) HR-TEM of Bi-TATB soaked in CO_2-saturated $KHCO_3$ electrolyte.

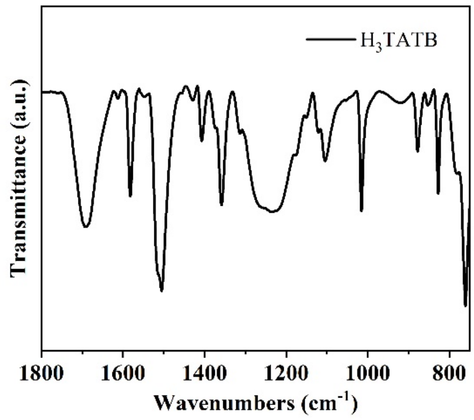

Fig. S2 FTIR spectra of H_3TATB.

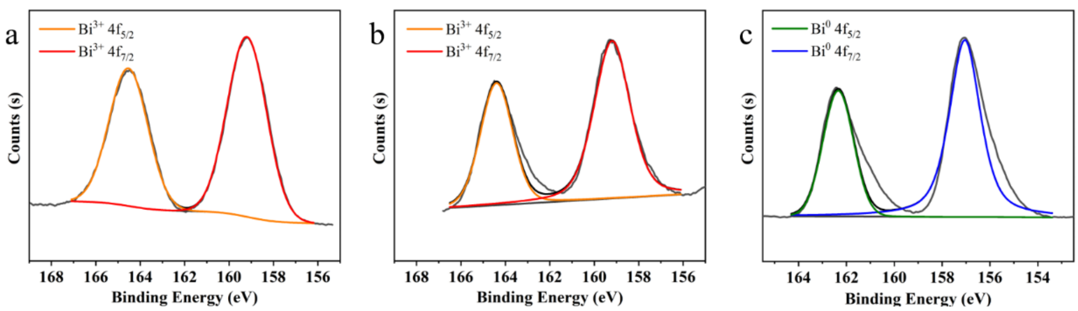

Fig. S3 a-c) High-resolution XPS spectra centered in the binding energy regions of Bi 4f for Bi-TATB, Bi-TATB soaked in $KHCO_3$ electrolyte and Bi-TATB after electrochemical activation.

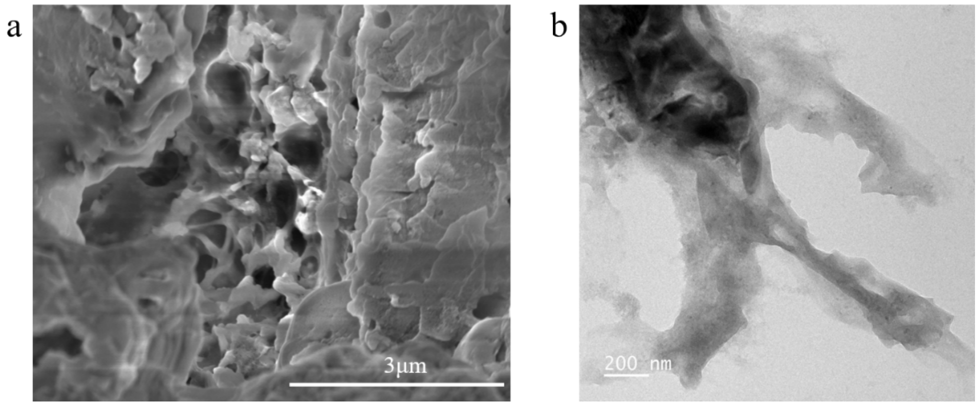

Fig. S4 a) SEM image of Bi-TATB on a carbon paper using Nafion as binder after activation. b) TEM image of Bi-TATB after activation.

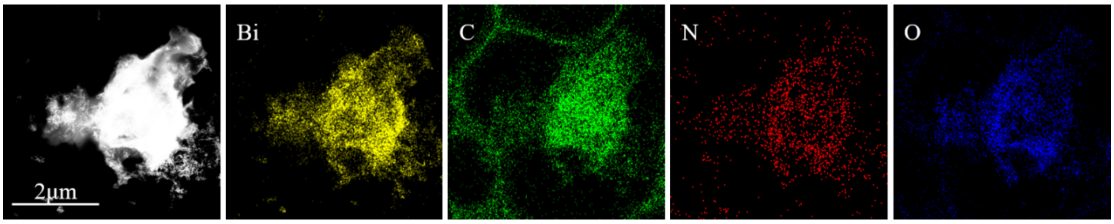

Fig. S5 HAADF-STEM and EDX mapping images of Bi-TATB after activation.

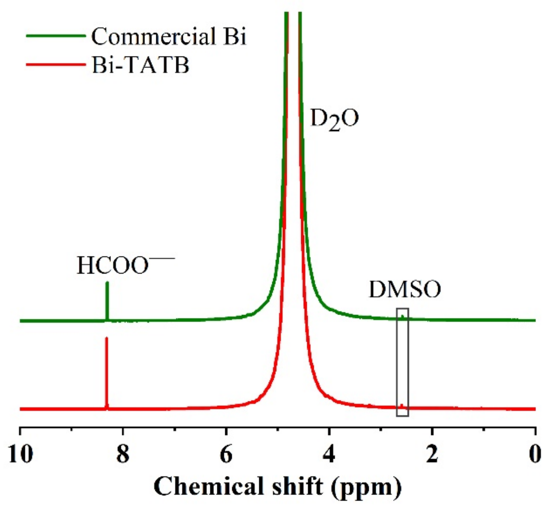

Fig. S6 NMR hydrogen spectrum of liquid products of commercial Bi and Bi-TATB after electrolysis at -1.08 V vs RHE for 2 hours.

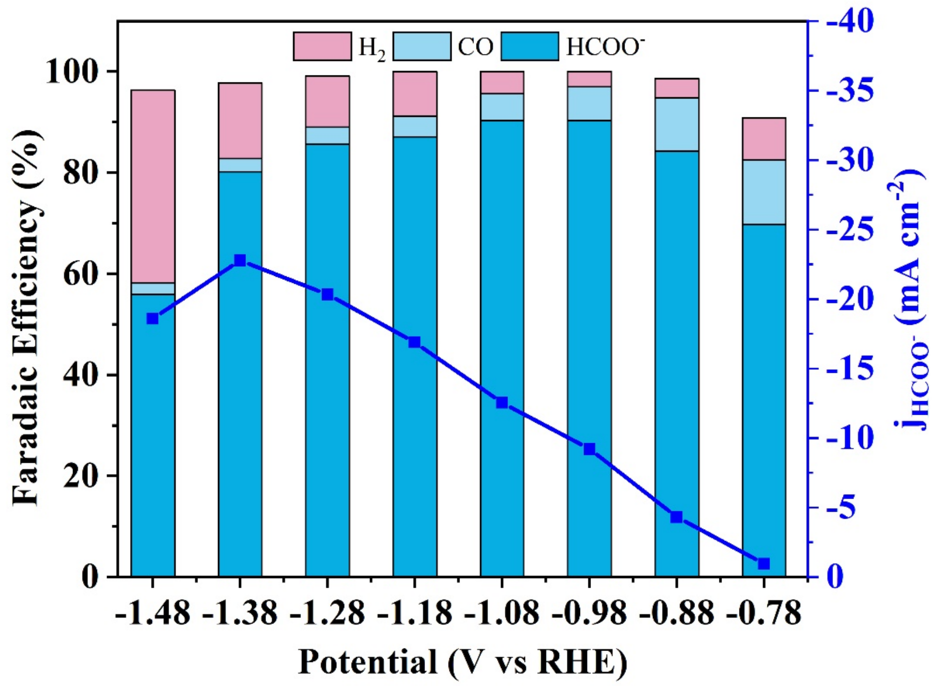

Fig. S7 Potential-dependent Faradaic efficiencies and partial current densities of $HCOO^-$ for commercial Bi in CO_2-saturated 0.5 M $KHCO_3$.

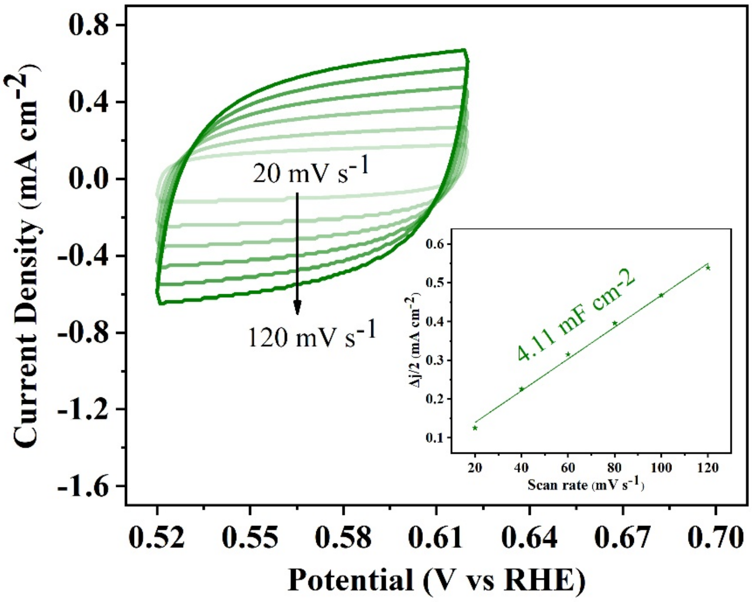

Fig. S8 C_{dl} measurement of commercial Bi.

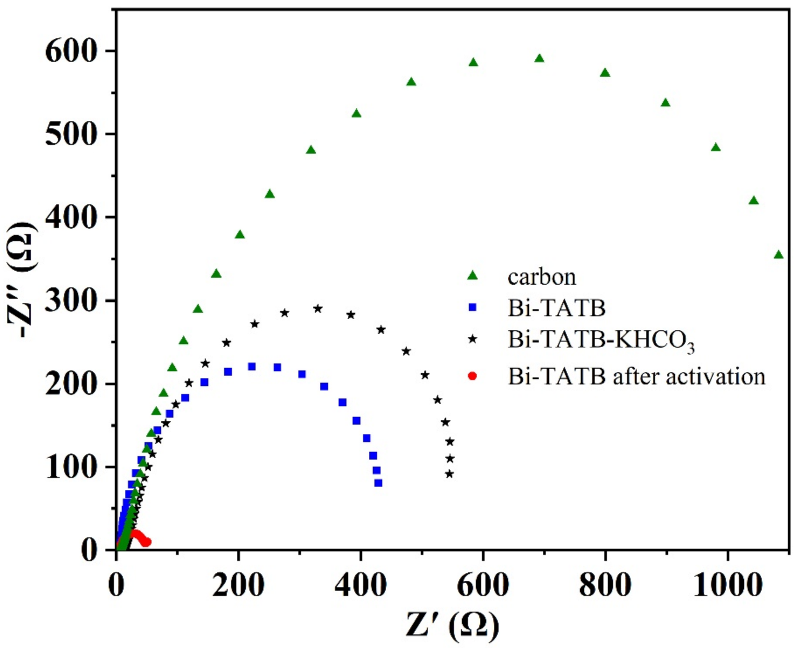

Fig. S9 EIS of different samples.

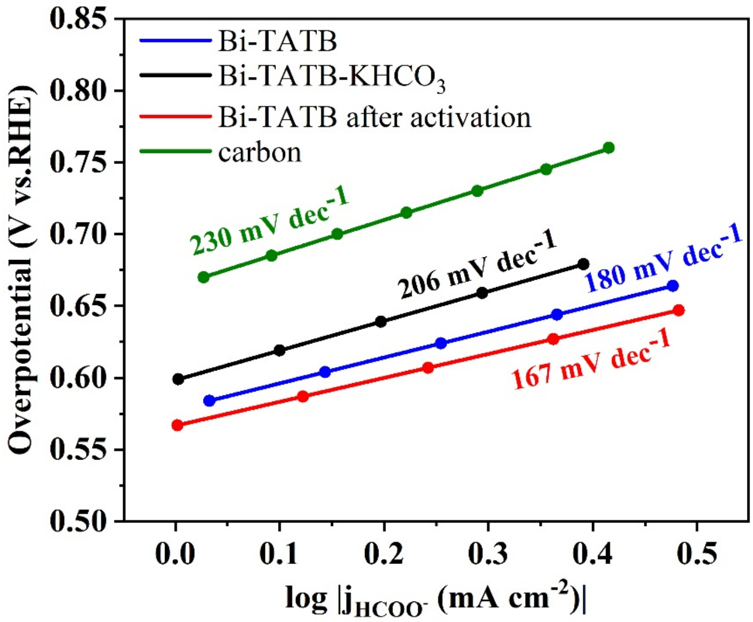

Fig. S10 Tafel slope of different samples.

Table S1. Electrocatalytic performance comparisons of the Bi-TATB with previously reported Bi-based electrocatalysts for CO_2-to-formate.

Catalyst	Electrolyte	Potential (V vs.RHE)	$FE_{formate}$	$\lvert j_{formate} \rvert$ (mA cm^{-2})	Stability (h)
this work	0.5 M $KHCO_3$	-1.08	94.3%	20.0	14.5
CAU-17[1]	0.1 M $KHCO_3$	-0.9	92.2%	15.0	30
Bi-ZMOF[2]	0.1 M $KHCO_3$	-1.1	91%	-	12
MFM-220[3]	0.1 M $KHCO_3$	-1.1	90.4%	20.8	-
$Bi_2O_2CO_3$ derived Bi[4]	0.1 M $KHCO_3$	-1.0	90%	4.8	-
$BiPO_4$ derived Bi[5]	0.5 M $KHCO_3$	-0.9	91.4%	7.2	15
Bi_2S_3 derived Bi[6]	0.5 M $NaHCO_3$	-0.75	84%	4.2	24
Bi-NFs[7]	0.1 M $KHCO_3$	-0.9	92.3%	11.4	12
Bi@C nanotubes[8]	0.1 M $KHCO_3$	-0.9	90.9%	6.0	24
Bi nanosheets[9]	0.1 M $KHCO_3$	-1.1	86%	16.5	10
α-Bi_2O_3[10]	0.5 M $KHCO_3$	-1.58	93%	-	-
f-Bi_2O_3[11]	0.1 M $KHCO_3$	-1.2	87%	20.9	-

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