Supporting information

Enhancement of electrocatalytic CO$_2$ performance by different components of Cu-based bimetallic MOFs

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School of Chemistry & Chemical Engineering, Chongqing University of Technology, Chongqing 400054, P. R. China
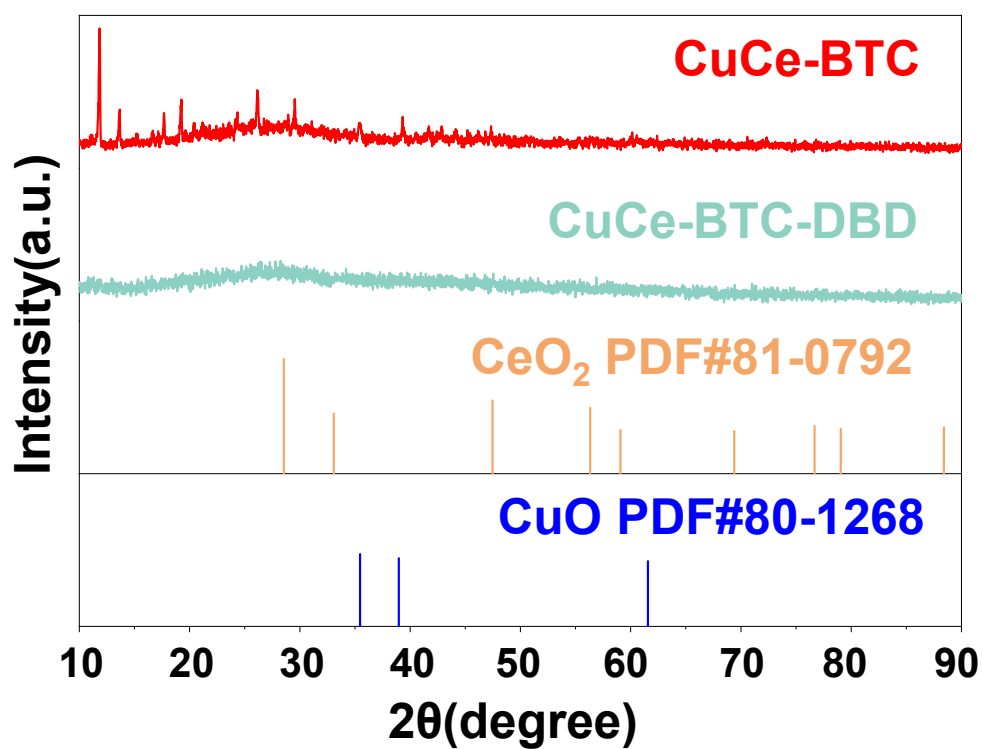
E-mail: zqiang@cqut.edu.cn

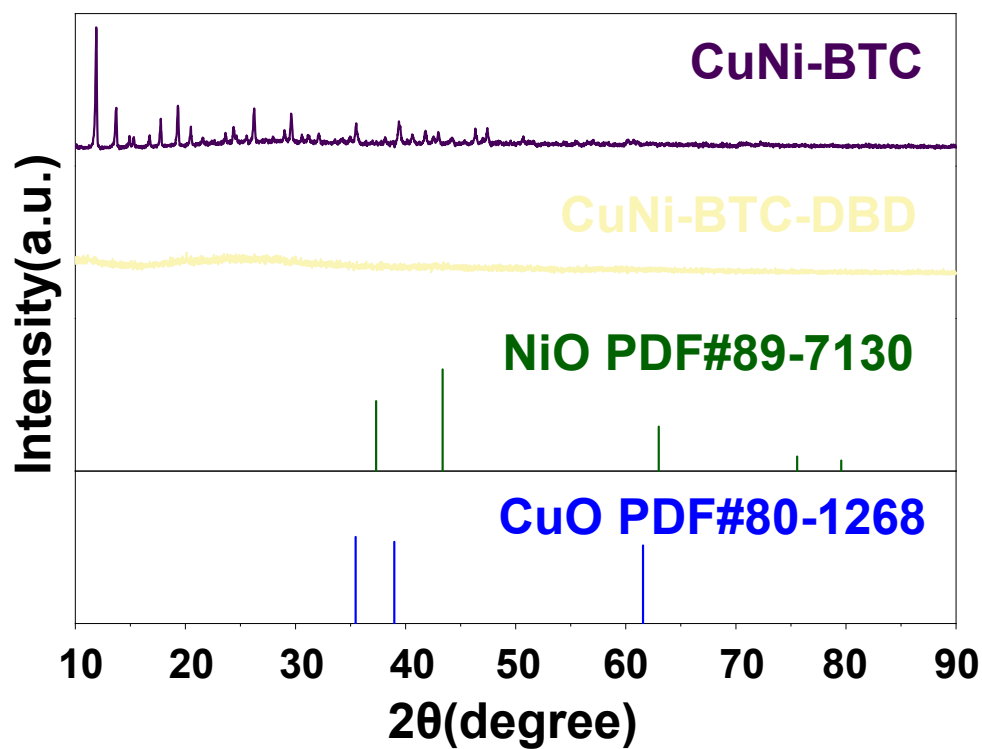Figure S1. XRD patterns of CuCe-BTC catalysts before and after O_2-DBD treatment

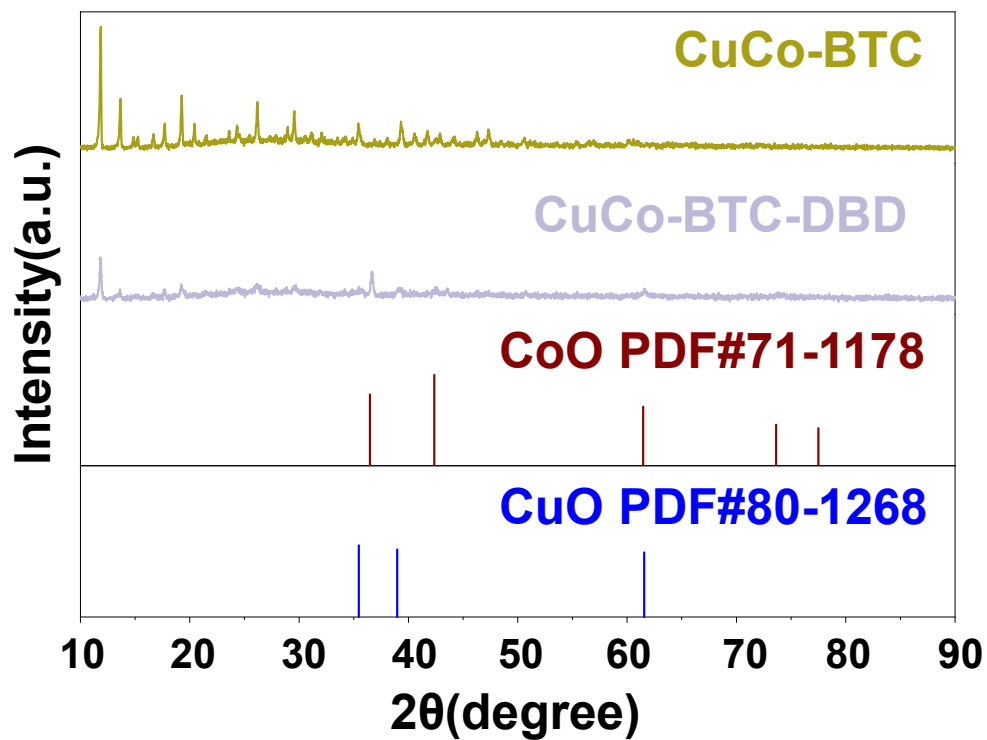Figure S2. XRD patterns of CuNi-BTC catalysts before and after O_2-DBD treatment

Figure S3. XRD patterns of CuCo-BTC catalysts before and after O_2-DBD treatment

Figure S4. XRD patterns of CuMg-BTC catalysts before and after O_2-DBD treatment

Figure S5. XRD patterns of CuBi-BTC catalysts before and after O_2-DBD treatment

Figure S6. XRD patterns of CuZn-BTC catalysts before and after O_2-DBD treatment

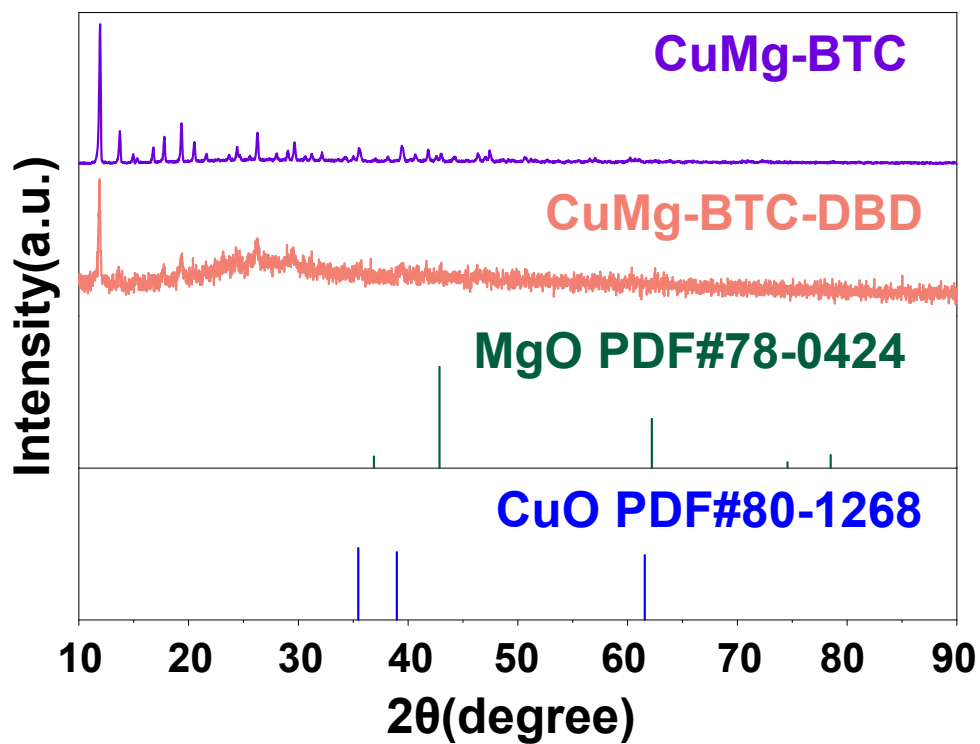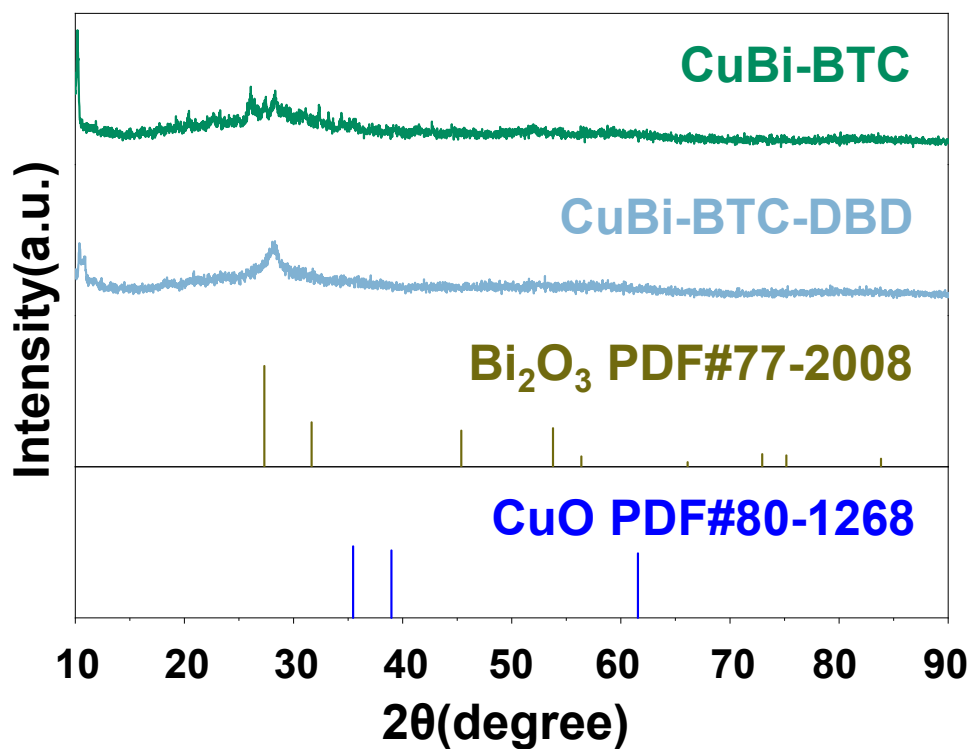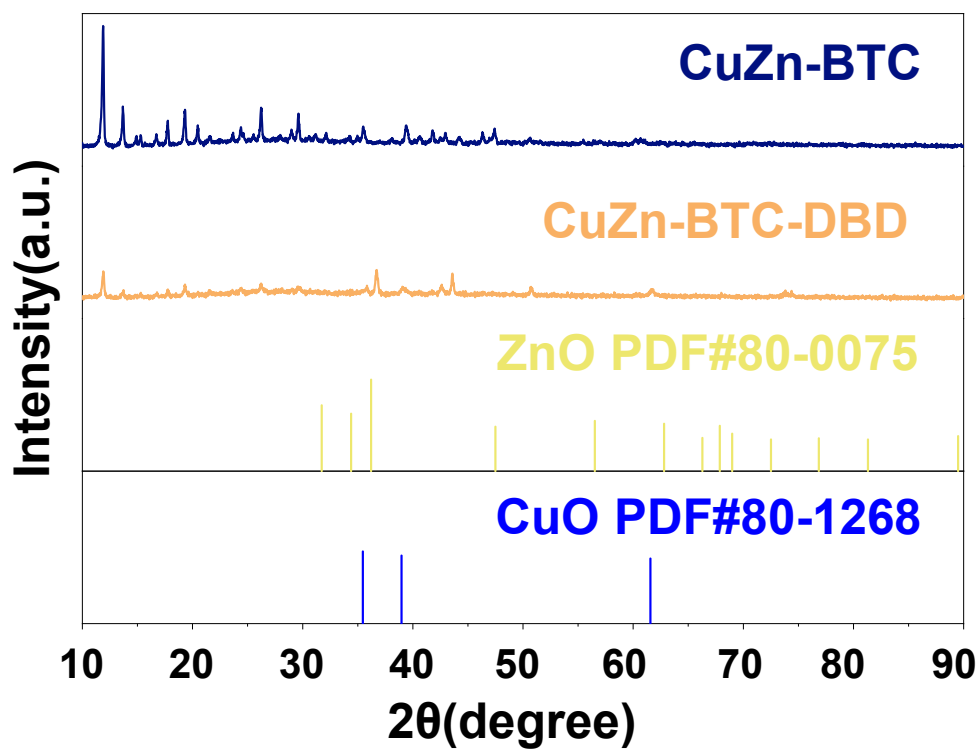Figure S7. XRD patterns of CuFe-BTC catalysts before and after O_2-DBD treatment
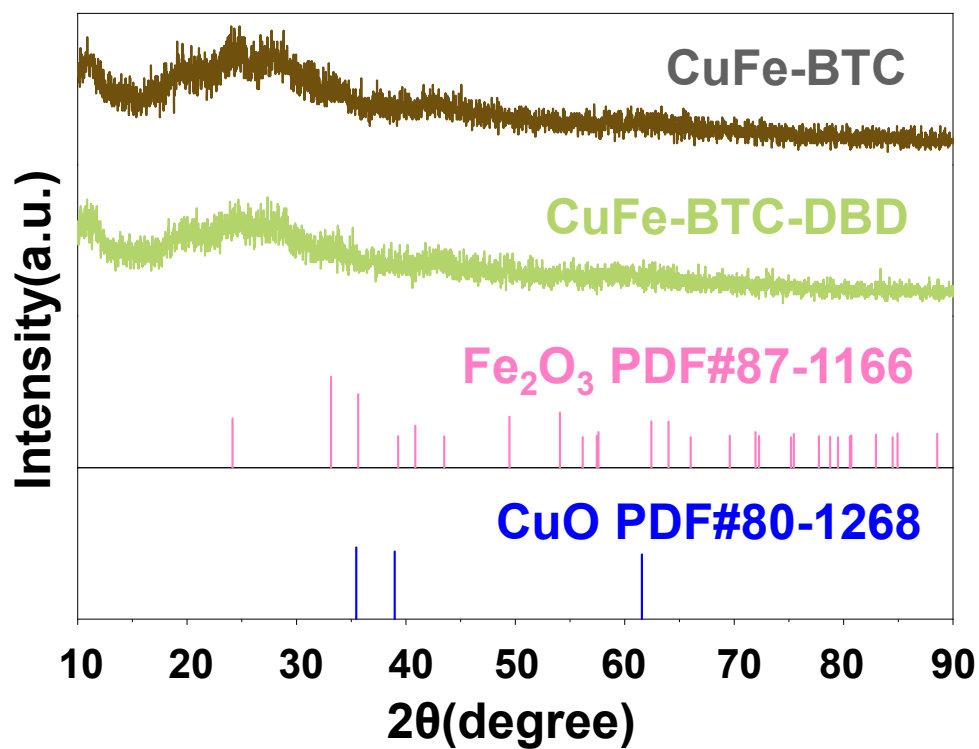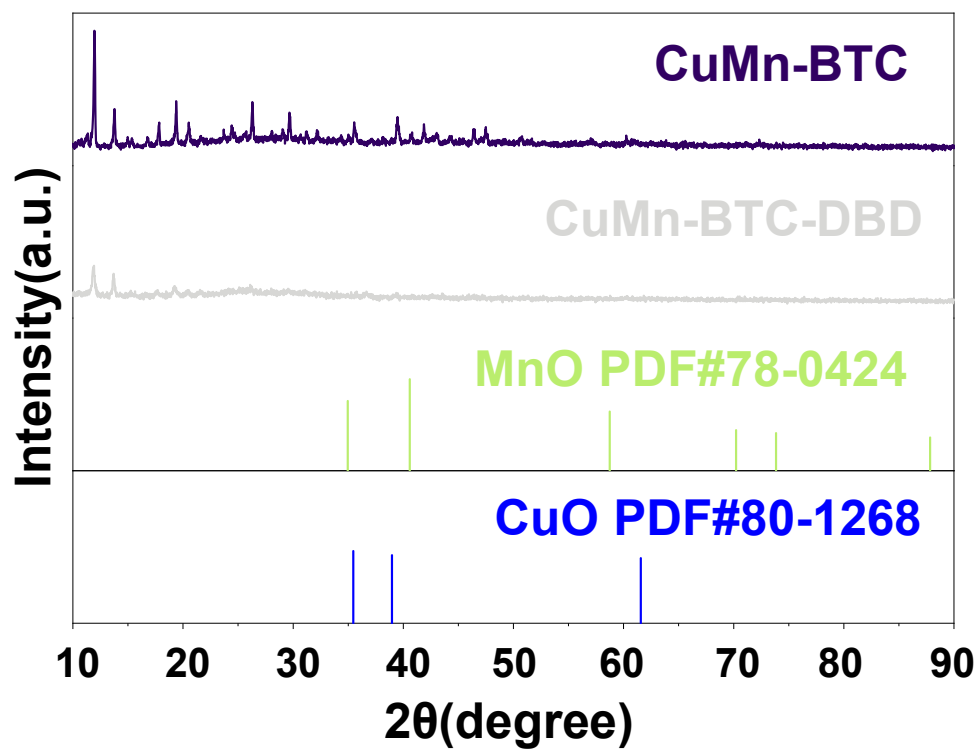

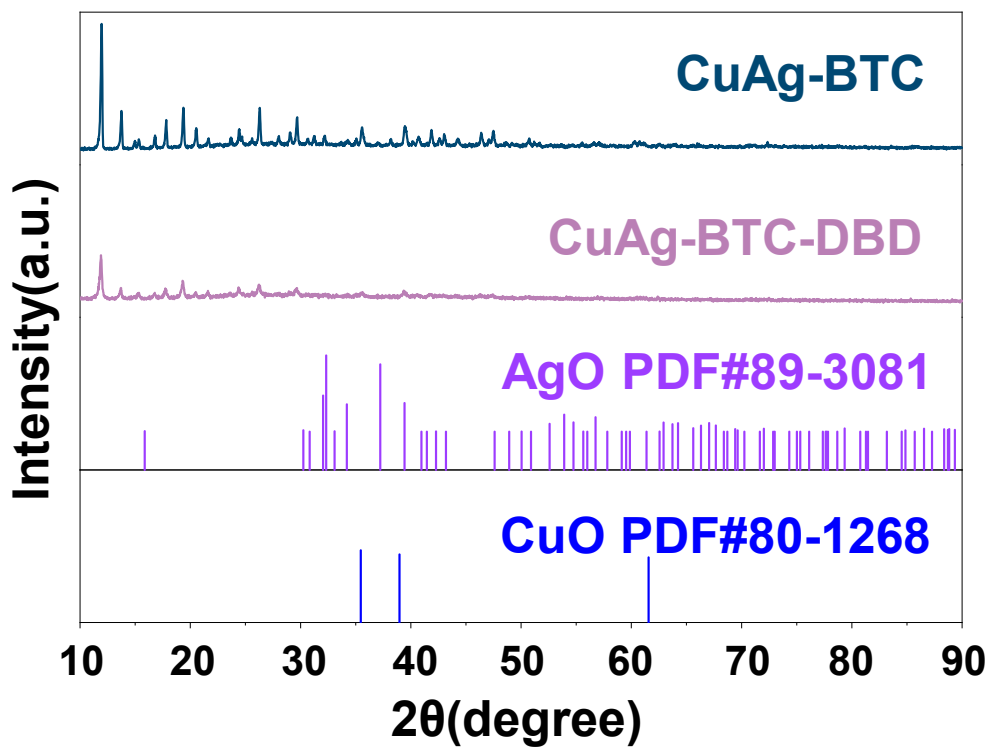Figure S8. XRD patterns of CuMn-BTC catalysts before and after O_2-DBD treatment

Figure S9. XRD patterns of CuAg-BTC catalysts before and after O_2-DBD treatment
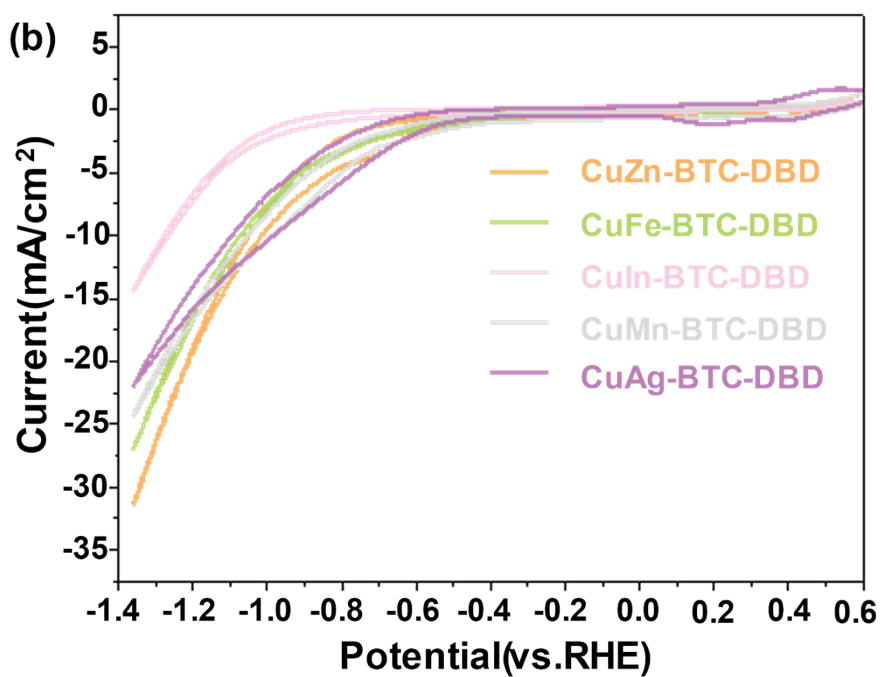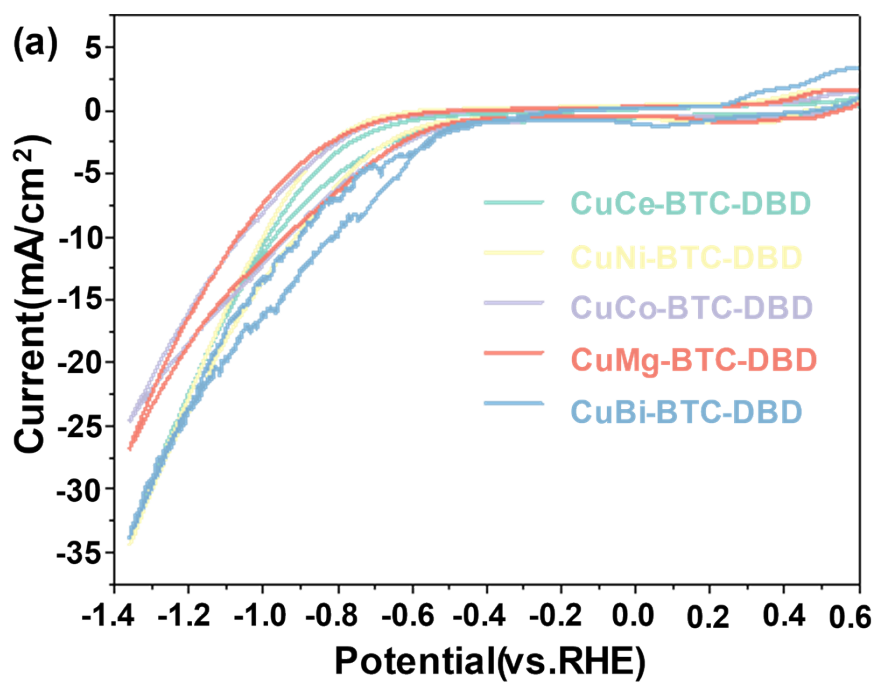
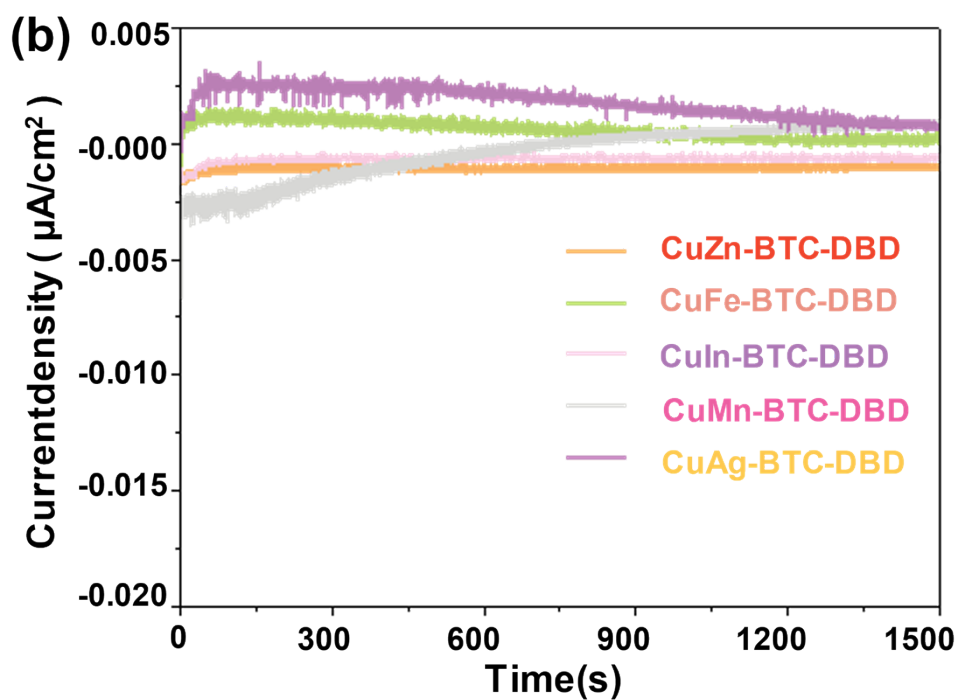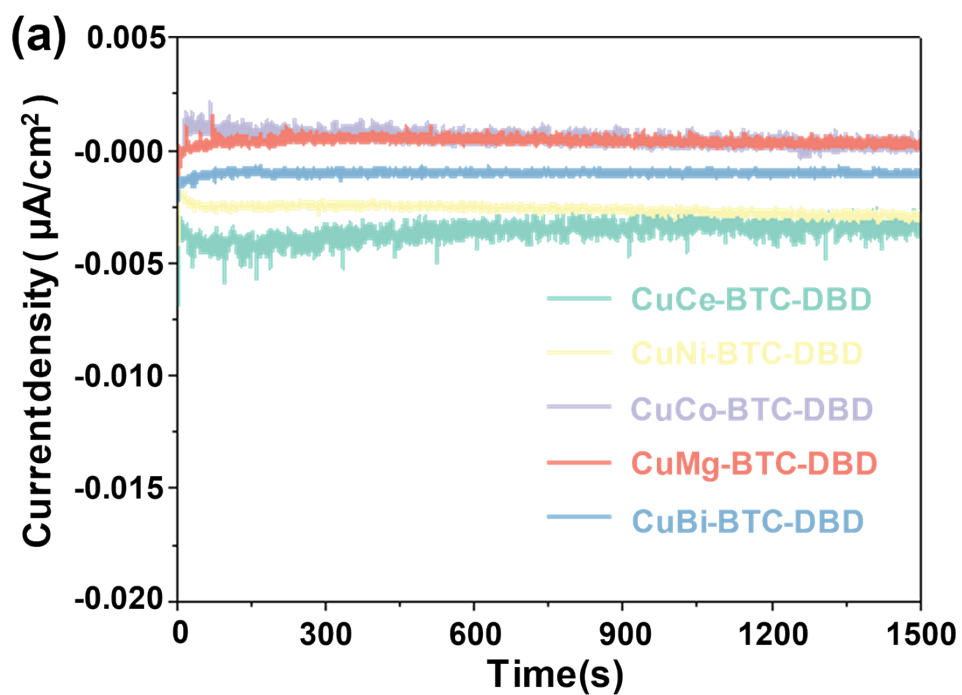Figure S10. (a)-(b) Cyclic voltammetry curves (CV) of different catalysts after O_2-DBD treatment.

Figure S11. (a)-(b) Stability test (it) of different catalysts after O_2-DBD treatment.

BD treatment.

Table S1. Comparison of the performance of Cu-based and Cu-based MOF-derived

catalysts for the electrocatalytic reduction of CO_2 to ethanol.

Catalysts	Oneset potential (V vs.RHE)	$J_{ethanol}$ (mA/cm^2)	$FE_{ethanol}(\%)$	Stability (h)	C_{dl}(mF/cm^2)	Refs.
CuIn-BTC-DBD	-0.2	36	87			This work
Cu/BNC-1	-1	20.4	58.64	24	45	S1
V_{Se}-$Cu_{2-x}Se$	-0.8	10.96	68.1	6	7.88	S2
Cu^+/hf-Cu	-0.8	0.23	43	6		S3[0]
LNCCs	-1	8.66	82.5	10	2.81	S4
$dCu_2O/Ag_{2.3\%}$	-0.87	326.4	40.8	12		S5
SnS_2/Sn_1-O_3G	-0.7	17.8	82.5	100		S6
CuAg-0.75%	-0.71	214	20	60		S7
PGA-2	-0.8	4.7	48.7	70	28	S8
Ag-Cu 5 %	-0.3	320	52.6	60	6.27	S9
$K_{11.2\%}$- Cu_2Se	-0.6	35.8	70.3	130	37.1	S10
CuOx@C	-1	164	45	56	10.03	S11
Cu-N-G	-0.4	21	33.1			S12
Cu/CuNC	-0.2	1	55	6		S13
Cu_2-CuN_3	-0.7	14.4	51	10		S14
$Cu_{1.22}V_{0.19}Se$	-0.4	21.3	70.5	138	41.4	S15
Cu/Bi	-0.21	20	28.3	5		S16
H-Ru10	-1	20	47.2	1		S17

S1.   B. Shao, D. Huang, R. K. Huang, X. L. He, Y. Luo, Y. L. Xiang, L. B. Jiang, M. Dong, S. Li, Z. Zhang and J. Huang, Metal-Organic Framework Supported Low-Nuclearity Cluster Catalysts for Highly Selective Carbon Dioxide Electroreduction to Ethanol, *Angew. Chem., Int. Ed.*, 2024, DOI: 10.1002/anie.202409270.

S2.   Y. Zang, T. Liu, P. Wei, H. Li, Q. Wang, G. Wang and X. Bao, Selective CO_2 Electroreduction to Ethanol over a Carbon-Coated CuO_x Catalyst, *Angew. Chem., Int. Ed.*, 2022, **61**, e202209629.

S3.   Y. Zhao, Q. Yuan, R. Xu, C. Zhang, K. Sun, A. Wang, A. Zhang, Z. Wang, J. Jiang and M. Fan, Boosting electrochemical conversion of CO_2 to ethanol through the confinement of pyridinic N-B layer on copper nanoparticles, *Appl. Catal., B*, 2024, **355**.124168

S4.   H. Wang, X. Bi, Y. Yan, Y. Zhao, Z. Yang, H. Ning and M. Wu, Efficient Electrocatalytic Reduction of CO_2 to Ethanol Enhanced by Spacing Effect of Cu-Cu in $Cu_{2-x}Se$ Nanosheets, *Adv. Funct. Mater.*, 2023, **33**.2214946

S5.   J. Y. Kim, G. Kim, H. Won, I. Gereige, W. B. Jung and H. T. Jung, Synergistic Effect of Cu_2O Mesh Pattern on High-Facet Cu Surface for Selective CO_2 Electroreduction to Ethanol, *Adv. Mater.*, 2022, **34**, e2106028.

S6.   J. Ding, H. Bin Yang, X.-L. Ma, S. Liu, W. Liu, Q. Mao, Y. Huang, J. Li, T. Zhang and B. Liu, A tin-based tandem electrocatalyst for CO2 reduction to ethanol with 80% selectivity, *Nat. Energy*, 2023, **8**, 1386-1394.

S7.   F. Yang, C. Liang, H. Yu, Z. Zeng, Y. M. Lam, S. Deng and J. Wang, Phosphorus-Doped Graphene Aerogel as Self-Supported Electrocatalyst for CO_2 -to-Ethanol Conversion, *Adv. Sci.*, 2022, **9**, e2202006.

S8.   W. Sun, P. Wang, Y. Jiang, Z. Jiang, R. Long, Z. Chen, P. Song, T. Sheng, Z. Wu and Y. Xiong, V-Doped Cu_2Se Hierarchical Nanotubes Enabling Flow-Cell CO_2 Electroreduction to Ethanol with High Efficiency and Selectivity, *Adv. Mater.*, 2022, **34**, e2207691.

S9.   P. Wang, H. Yang, C. Tang, Y. Wu, Y. Zheng, T. Cheng, K. Davey, X. Huang and S. Z. Qiao, Boosting electrocatalytic CO_2-to-ethanol production via asymmetric C-C coupling, *Nat. Commun*, 2022, **13**, 3754.

S10.   H. Tang, Y. Liu, Y. Zhou, Y. Qian and B.-L. Lin, Boosting the Electroreduction of CO_2 to Ethanol via the Synergistic Effect of Cu-Ag Bimetallic Catalysts, *ACS Appl. Energy Mater.*, 2022, **5**, 14045-14052.

S11.   Z. Cai, N. Cao, F. Zhang, X. Lv, K. Wang, Y. He, Y. Shi, H. Bin Wu and P. Xie, Hierarchical Ag-Cu interfaces promote C-C coupling in tandem CO_2 electroreduction, *Appl. Catal., B*, 2023, **325**.122310

S12.   L. Ding, N. Zhu, Y. Hu, Z. Chen, P. Song, T. Sheng, Z. Wu and Y. Xiong, Over 70 % Faradaic Efficiency for CO_2 Electroreduction to Ethanol Enabled by Potassium Dopant-Tuned Interaction between Copper Sites and Intermediates, *Angew. Chem., Int. Ed.*, 2022, **61**, e202209268.

S13.   D. Zang, X. J. Gao, L. Li, Y. Wei and H. Wang, Confined interface engineering of self-supported Cu@N-doped graphene for electrocatalytic CO_2 reduction

with enhanced selectivity towards ethanol, *Nano Res.*, 2022, **15**, 8872-8879.

S14. Y. Yang, J. Fu, Y. Ouyang, T. Tang, Y. Zhang, L. R. Zheng, Q. H. Zhang, X. Z. Liu, J. Wang and J. S. Hu, In-situ constructed Cu/CuNC interfaces for low-overpotential reduction of CO_2 to ethanol, *Natl. Sci. Rev.*, 2023, **10**, nwac248.

S15. X. Su, Z. Jiang, J. Zhou, H. Liu, D. Zhou, H. Shang, X. Ni, Z. Peng, F. Yang, W. Chen, Z. Qi, D. Wang and Y. Wang, Complementary Operando Spectroscopy identification of in-situ generated metastable charge-asymmetry Cu_2-CuN_3 clusters for CO_2 reduction to ethanol, *Nat. Commun*, 2022, **13**, 1322.

S16. J. Albo, M. Perfecto-Irigaray, G. Beobide and A. Irabien, Cu/Bi metal-organic framework-based systems for an enhanced electrochemical transformation of CO_2 to alcohols, *J. CO_2 Util.*, 2019, **33**, 157-165.

S17. M. Perfecto-Irigaray, J. Albo, G. Beobide, O. Castillo, A. Irabien and S. Perez-Yanez, Synthesis of heterometallic metal-organic frameworks and their performance as electrocatalyst for CO_2 reduction, *RSC Adv.*, 2018, **8**, 21092-21099.