SUPPORTING INFORMATION

Improvement of Carbon Dioxide Electroreduction by Crystal Surface Modification of ZIF-8

Ting Zhang[a,b†], Hong Liu[c†], Xu Han[a], Martí Biset-Peiró[b], Yunhui Yang[a], Inhar Imaz[a], Daniel Maspoch[a,d], Bo Yang[c]*, Joan Ramon Morante[b,e], Jordi Arbiol[a,d]*

[a]Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Bellaterra, 08193, Barcelona, Catalonia, Spain

[b]Catalonia Institute for Energy Research (IREC), Jardins de les Dones de Negre 1, Sant Adrià del Besòs, Barcelona 08930, Catalonia, Spain

[c]School of Physical Science and Technology, ShanghaiTech University, 393 Middle Huaxia Road, Shanghai 201210, China

[d]ICREA, Pg. Lluís Companys 23, 08010, Barcelona, Catalonia, Spain

[e]Department of Physics, Universitat de Barcelona, 08028, Barcelona, Catalonia, Spain

*Corresponding author:

E-mail: yangbo1@shanghaitech.edu.cn, arbiol@icrea.cat

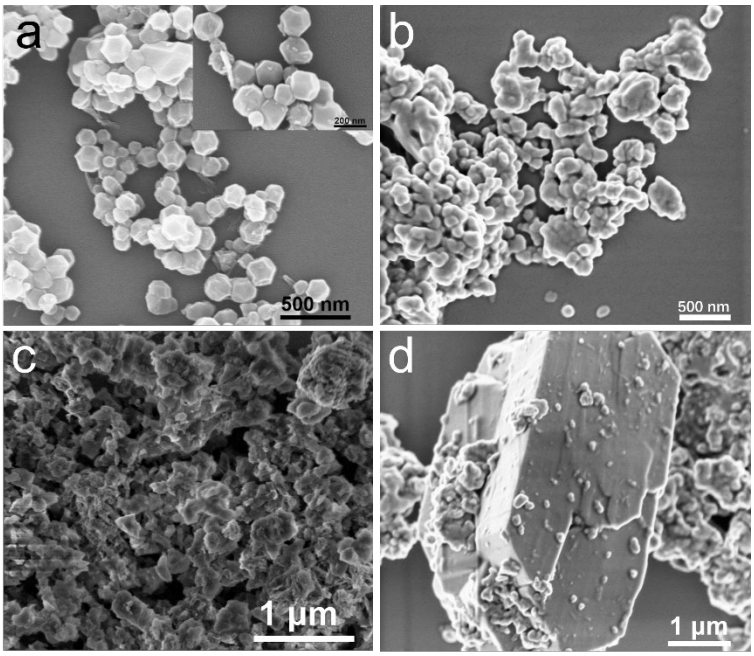

Fig. S1. FE-SEM images of (a) ZIF-8-1.7% (b) ZIF-8-10%, (c) ZIF-8-17% and (d) ZIF-8-33%.

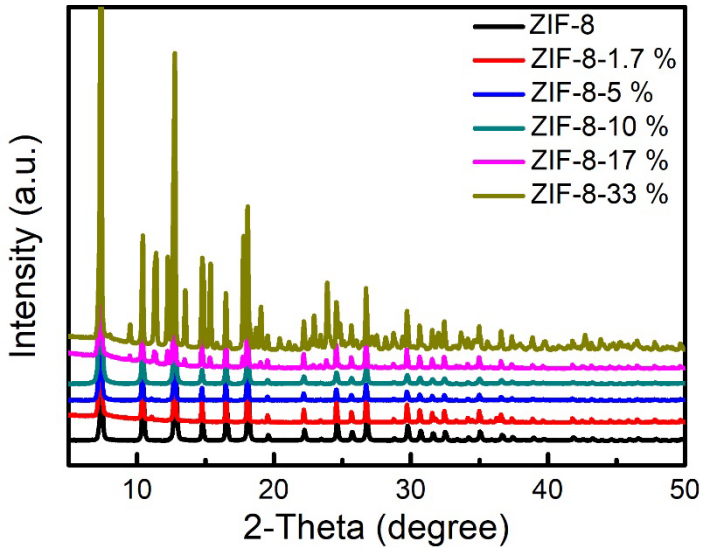

Fig. S2. Experimental XRD patterns of ZIF-8 and ZIF-8-x with different DOBDC modification ratios.

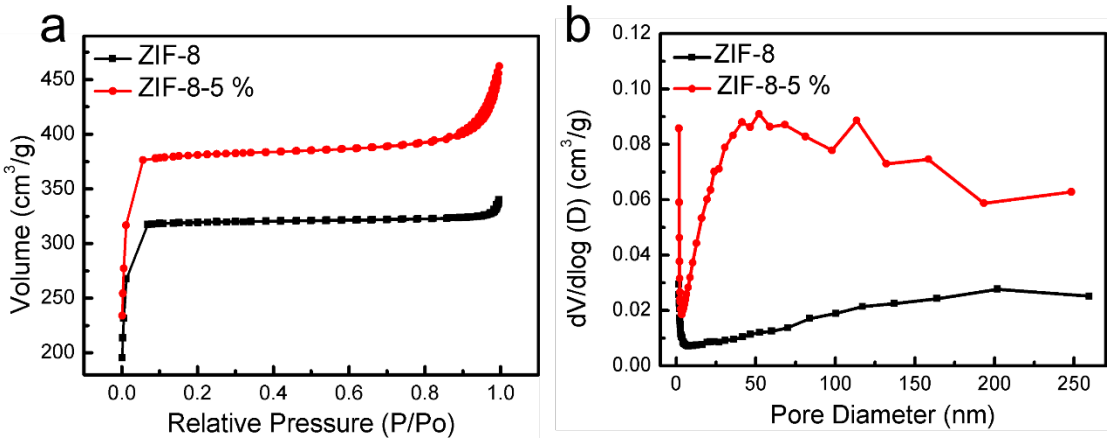

Fig. S3. (a) N_2 adsorption-desorption isotherms and (b) corresponding pore size distributions of ZIF-8 and ZIF-8-5% samples.

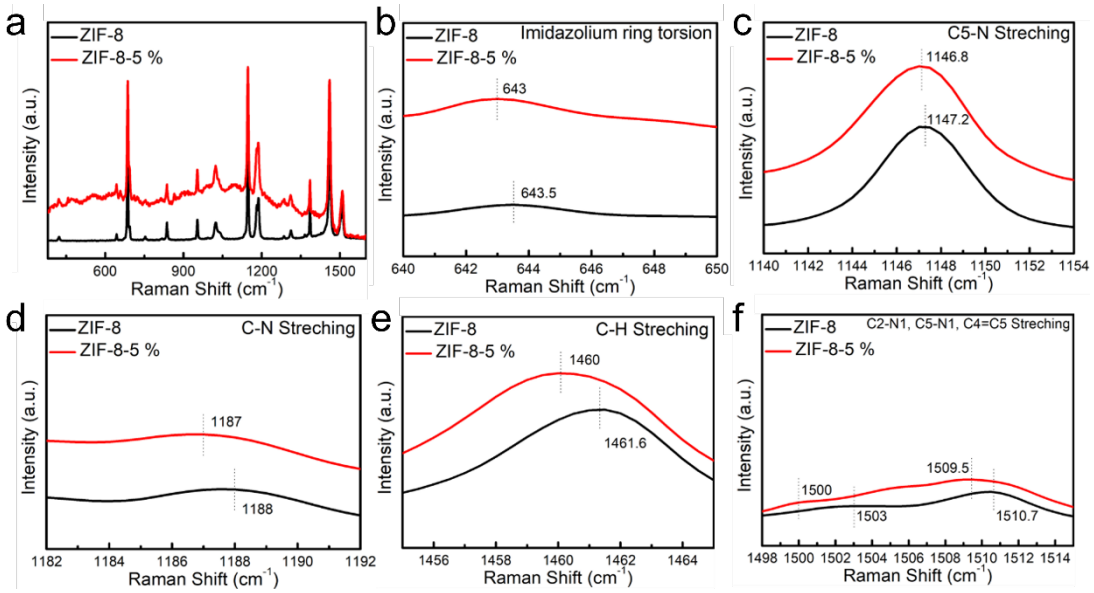

Fig. S4. Raman spectra of the ZIF-8 and ZIF-8-5%.

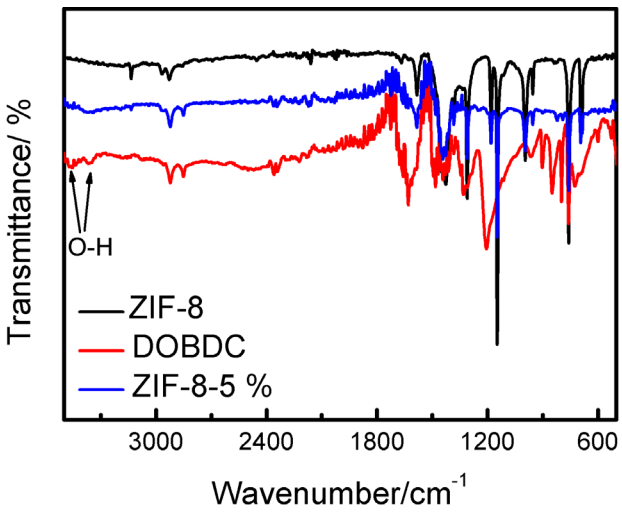

Fig. S5. FTIR spectra of the ZIF-8, DOBDC and ZIF-8-5%.

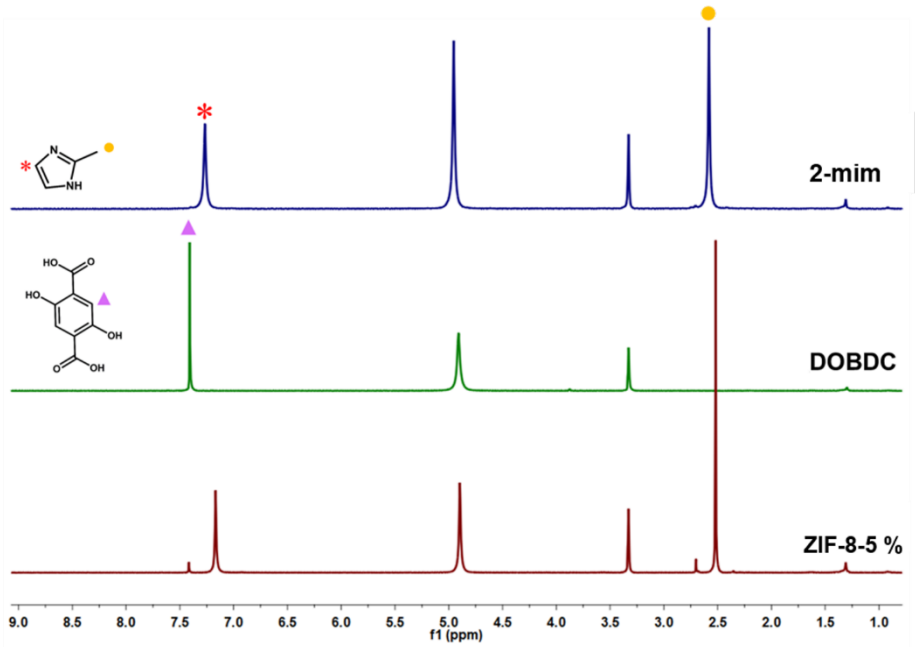

Fig. S6. ^{1}H-NMR spectra of ZIF-8-5 %.

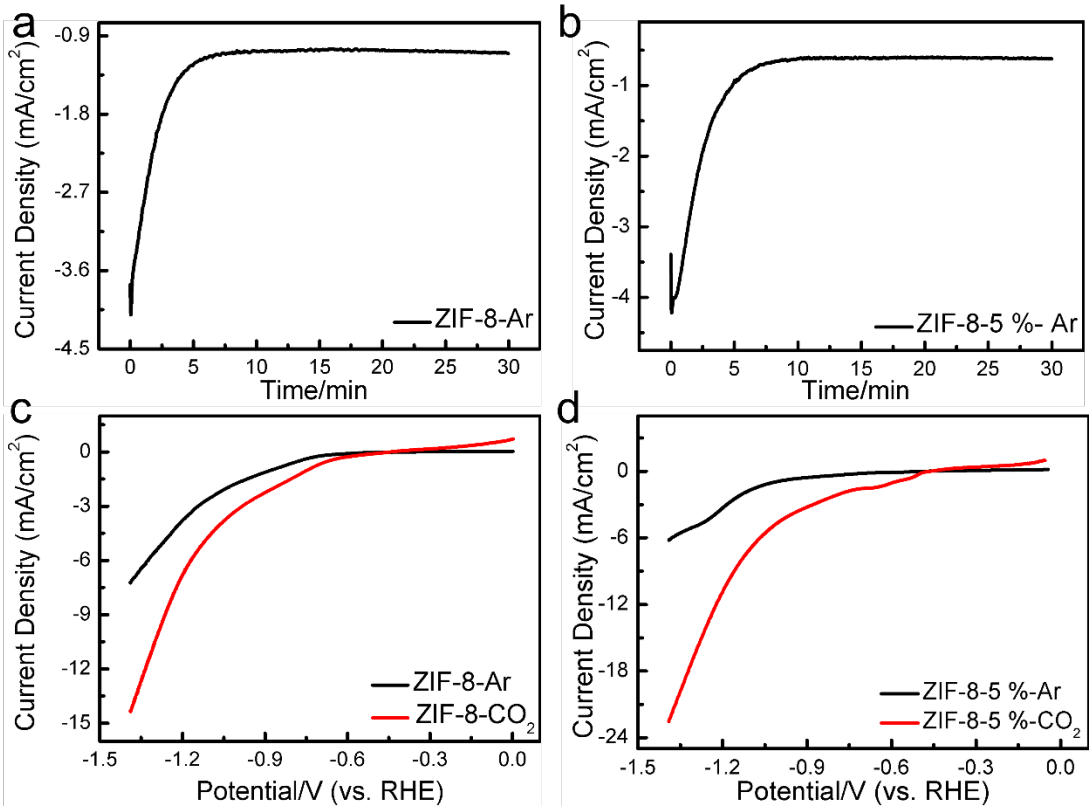

Fig. S7. (a and b) Electrode current recorded during reduction of ZIF-8 and ZIF-8-5% at −0.90 V vs. RHE in 0.5 M $NaHCO_3$ purged with Ar; (c and d) LSV curves of ZIF-8 and ZIF-8-5% in Ar- and CO_2-saturated 0.5 M $NaHCO_3$ solution (scan rate: 20 mV/s).

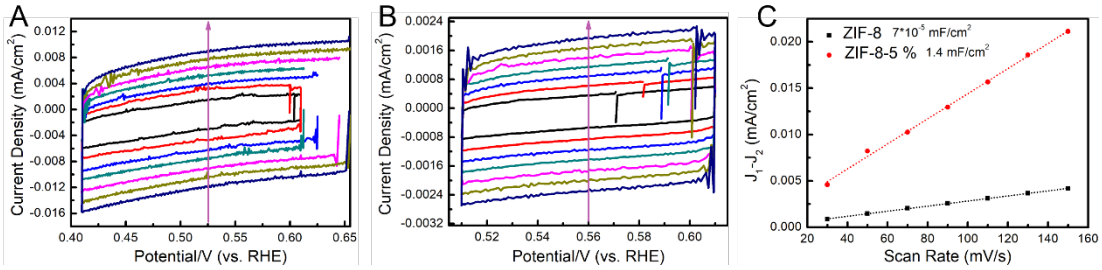

Fig. S8. Cyclic voltammograms curves for (a) ZIF-8 and (b) ZIF-8-5%. (c) Plots of the current density vs. scan rate for ZIF-8 and ZIF-8-5% electrodes.

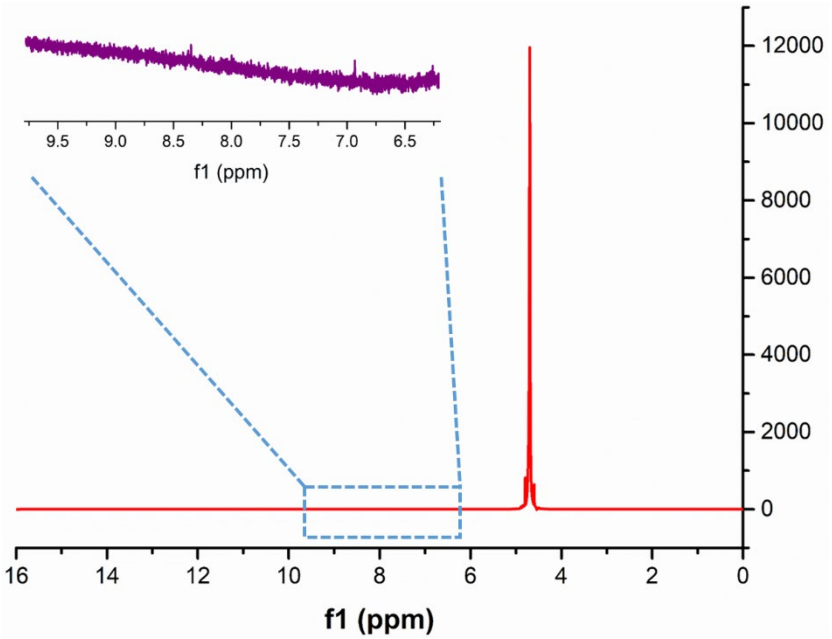

Fig. S9. The representative ^{1}H-NMR spectra of the electrolyte after electrolysis of −1.20 V for ZIF-8-5% in CO_2-saturated 0.5 M $NaHCO_3$ electrolyte for 12 h.

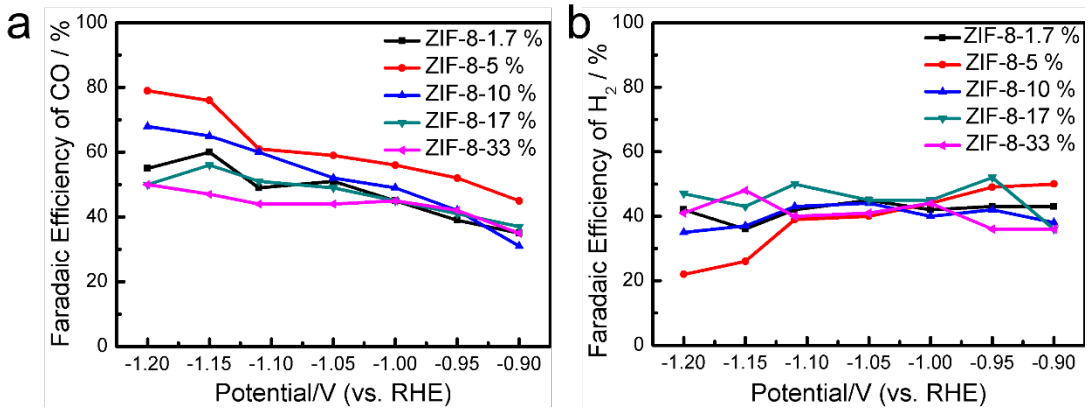

Fig. S10. Corresponding FE of (a) CO and (b) H_2 on ZIF-8-x samples with different modifying ratio.

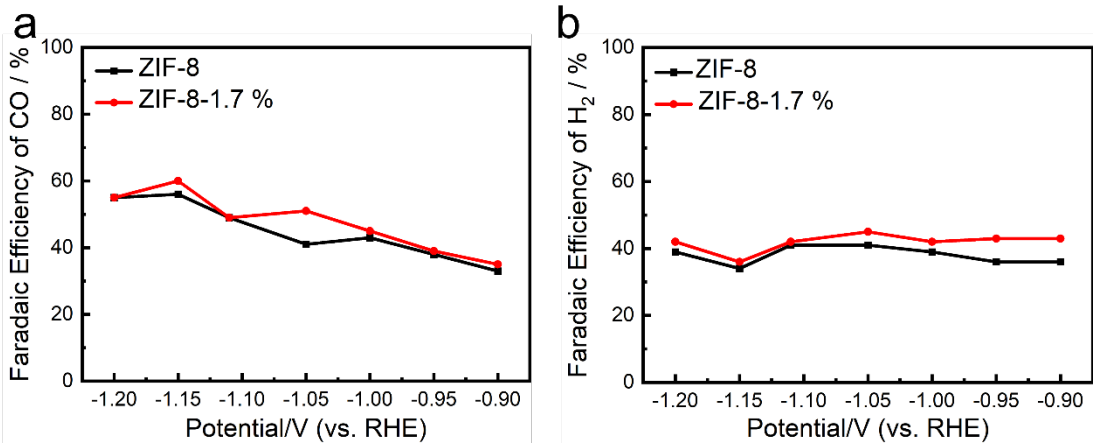

Fig. S11. Corresponding FE of (a) CO and (b) H_2 on ZIF-8 and ZIF-8-1.7% samples with different modifying ratio.

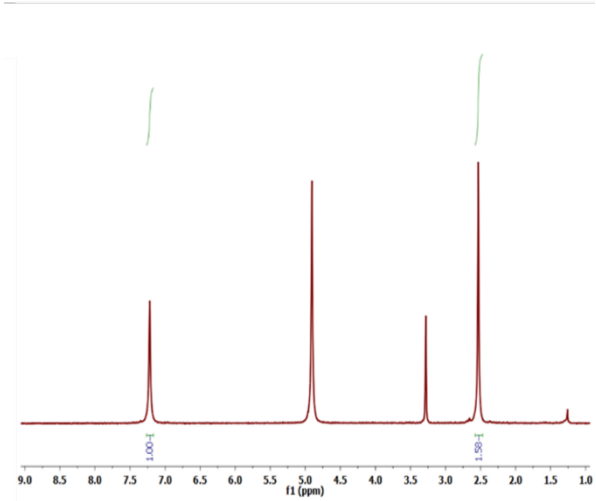

Fig. S12. ^{1}H-NMR spectra of ZIF-8-1.7%.

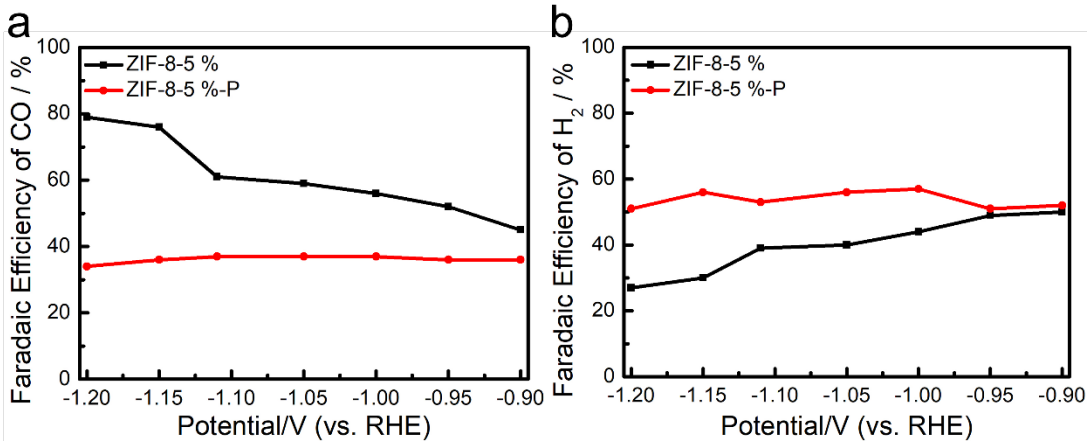

Fig. S13. FE of (a) CO and (b) H_2 on ZIF-8-5% and ZIF-8-5%-P electrodes.

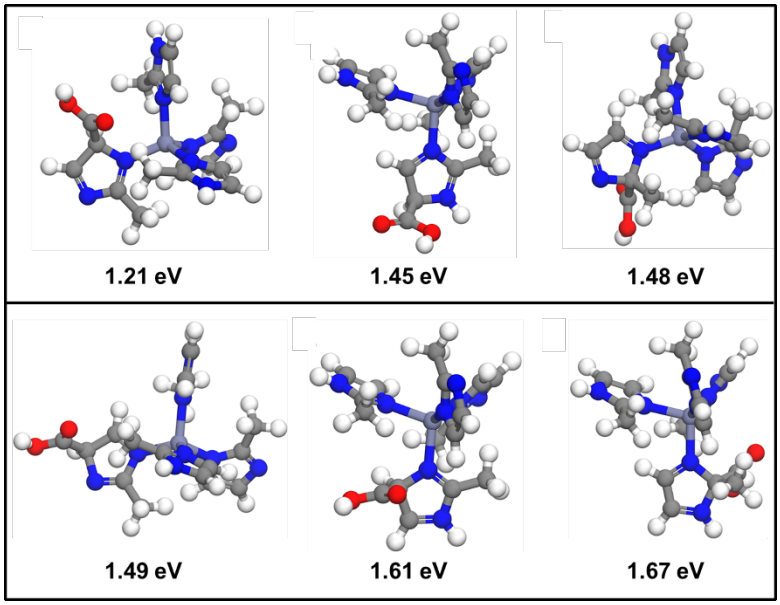

Fig. S14. Optimized models of adsorption structure of COOH* and free-energy (CO_2 → COOH*) on different sites on ZIF-8 (Zn, C, N, O atoms are represented in purple, grey, blue, and red, respectively).

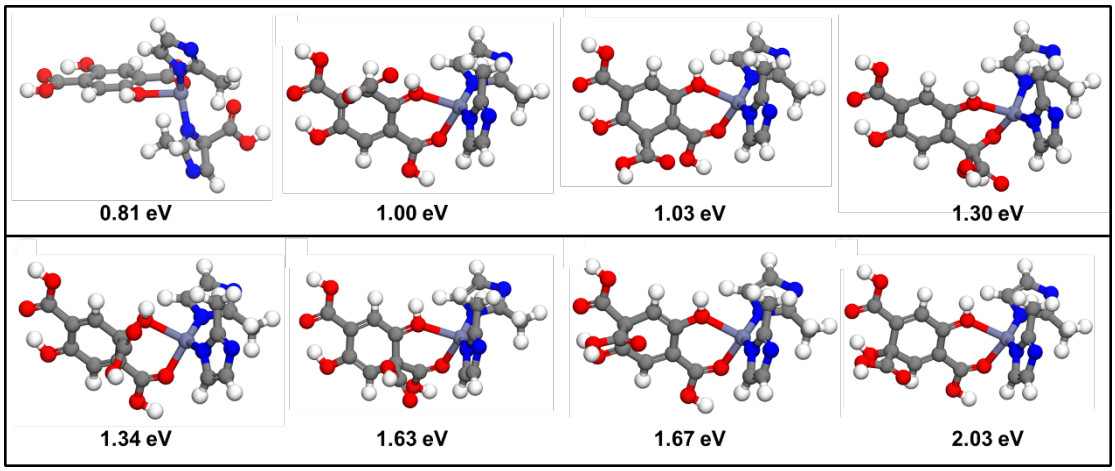

Fig. S15. Optimized models of adsorption structure of COOH* free-energy (CO_2 → COOH*) on different sites on ZIF-8-5% (Zn, C, N, O atoms are represented in purple, grey, blue, and red, respectively).

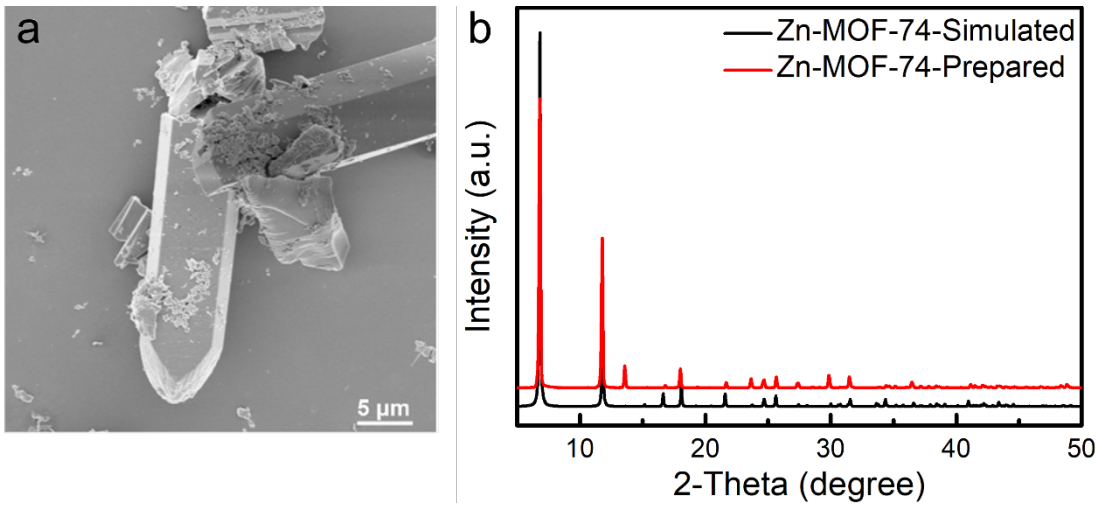

Fig. S16. (a) SEM, (b) XRD images of Zn-MOF-74.

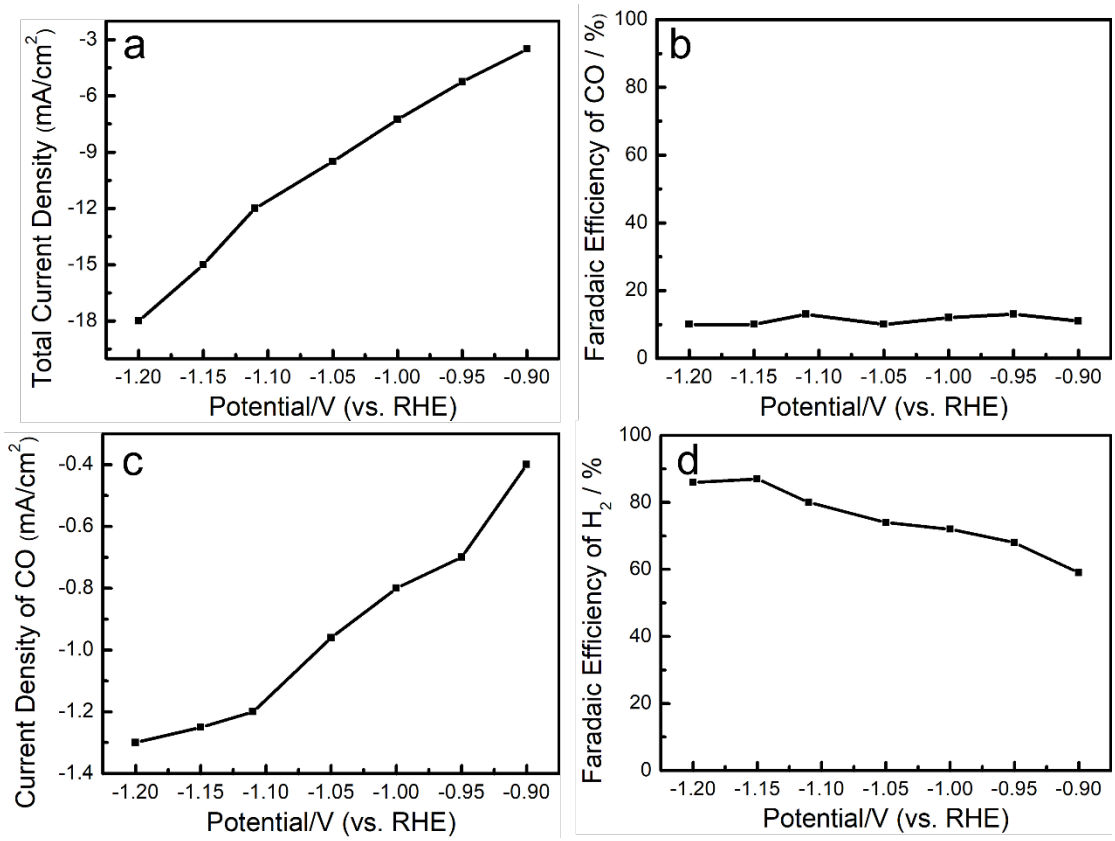

Fig. S17. (a) Total current densities for Zn-MOF-74 sample coated on carbon paper in CO_2-saturated 0.5 M $NaHCO_3$ solution at different applied potentials. (b) Corresponding FE for CO. (c) Partial current densities of CO. (d) Corresponding FE for H_2.

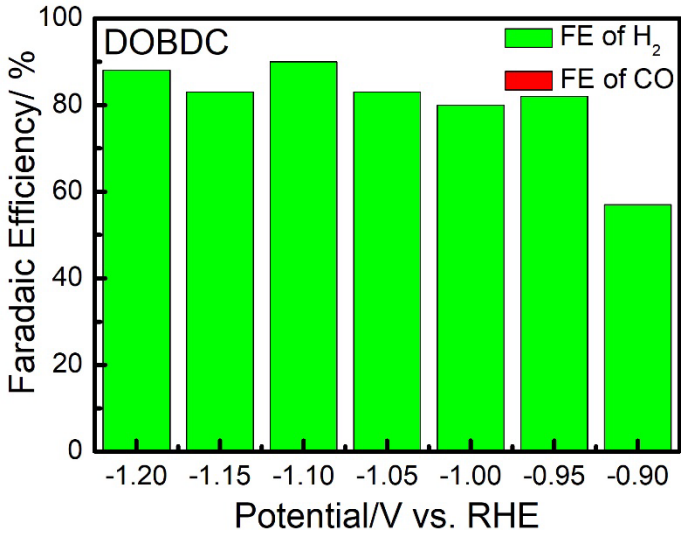

Fig. S18. FE of CO and H_2 on pure DOBDC ligand.

Table S1. Faradaic Efficiency of the reported MOFs-based electrocatalysts for CO_2 electroreduction

Catalyst	Electrolyte	Product	FE	Current Density (CO)	Potential	Reference
ZIF-8	0.5 M $KHCO_3$	CO	65%	−1.75 mA/cm^2	−1.8 V vs. SCE	[1]
ZIF-8	0.25 M K_2SO_4	CO	81%	−7 mA/cm^2	−1.1 V vs. RHE	[2]
HKUST-1	0.5 M $KHCO_3$	CH_3OH	5.6%	−10 mA/cm^2	−1.0 V vs.Ag/AgCl	[3]
HKUST-1	0.5 M $KHCO_3$	C_2H_5OH	10.3%	−10 mA/cm^2	−1.0 V vs.Ag/AgCl	[3]
HKUST-1	1 M KOH	C_2H_4	45%	262 mA/cm^2	−1.07 V vs. RHE	[4]
$Al_2(OH)_2$ TCPP-Co	0.5 M K_2CO_3	CO	76%	−1 mA/cm^2	−0.7 V vs. RHE	[5]
ZIF-A-LD	0.1 M $KHCO_3$	CO	73%	−5 mA/cm^2	−1.1 V vs. RHE	[6]
ZIF-A-LD/CB	0.1 M $KHCO_3$	CO	91%	−7 mA/cm^2	−1.1 V vs. RHE	[6]
Copper rubeanate MOF	0.5 M $KHCO_3$	HCOOH	30%	None	−1.2 V vs. SHE	[7]
Zn-BTC	Ionic liquid	CH_4	88.3%	0.5 mA/cm^2	−2.2 V vs.Ag/AgCl	[8]
Cu installed NU-1000	0.1 M $NaClO_4$	HCOOH	31%	−1.2 mA/cm^2	−0.82 V vs. RHE	[9]
MOF-1992	0.1 M $KHCO_3$	CO	80 %	−16.5 mA/cm^2	−0.63 V vs. RHE	[10]
Fe/ZIF-8	0.1 M $KHCO_3$	CO	89.1%	−1.8 mA/cm^2	−0.33 V vs. RHE	[11]
ZIF-8-5 %	**0.5 M $NaHCO_3$**	**CO**	**79%**	**−10 mA/cm^2**	**−1.2 V vs. RHE**	**This work**

References

1. Y. Wang, P. Hou, Z. Wang and P. Kang, *ChemPhysChem*, 2017, **18**, 3142-3147.
2. X. Jiang, H. Li, J. Xiao, D. Gao, R. Si, F. Yang, Y. Li, G. Wang and X. Bao, *Nano Energy*, 2018, **52**, 345-350.
3. J. Albo, D. Vallejo, G. Beobide, O. Castillo, P. Castaño and A. Irabien, *ChemSusChem*, 2017, **10**, 1100-1109.
4. D.-H. Nam, O. S. Bushuyev, J. Li, P. De Luna, A. Seifitokaldani, C.-T. Dinh, F. P. García de Arquer, Y. Wang, Z. Liang, A. H. Proppe, C. S. Tan, P. Todorović, O. Shekhah, C. M. Gabardo, J. W. Jo, J. Choi, M.-J. Choi, S.-W. Baek, J. Kim, D. Sinton, S. O. Kelley, M. Eddaoudi and E. H. Sargent, *J. Am. Chem. Soc.*, 2018, **140**, 11378-11386.
5. N. Kornienko, Y. Zhao, C. S. Kley, C. Zhu, D. Kim, S. Lin, C. J. Chang, O. M. Yaghi and P. Yang, *J. Am. Chem. Soc.*, 2015, **137**, 14129-14135.
6. S. Dou, J. Song, S. Xi, Y. Du, J. Wang, Z.-F. Huang, Z. J. Xu and X. Wang, *Angew. Chem. Int. Ed.*, 2019, **58**, 4041-4045.
7. R. Hinogami, S. Yotsuhashi, M. Deguchi, Y. Zenitani, H. Hashiba and Y. Yamada, *ECS Electrochem. Lett.*, 2012, **1**, H17-H19.
8. X. Kang, Q. Zhu, X. Sun, J. Hu, J. Zhang, Z. Liu and B. Han, *Chem. Sci.*, 2016, **7**, 266-273.
9. C.-W. Kung, C. O. Audu, A. W. Peters, H. Noh, O. K. Farha and J. T. Hupp, *ACS Energy Lett.*, 2017, **2**, 2394-2401.
10. R. Matheu, E. Gutierrez-Puebla, M. Á. Monge, C. S. Diercks, J. Kang, M. S. Prévot, X. Pei, N. Hanikel, B. Zhang, P. Yang and O. M. Yaghi, *J. Am. Chem. Soc.*, 2019, **141**, 17081-17085.
11. Y. Ye, F. Cai, H. Li, H. Wu, G. Wang, Y. Li, S. Miao, S. Xie, R. Si, J. Wang and X. Bao, *Nano Energy*, 2017, **38**, 281-289.