Supporting Information

Metal-organic Framework-derived Cupric Oxide Polycrystalline Nanowires for Fast Carbon Dioxide Electroreduction to C2 Valuables

Fan Yang [a], *PeiLin Deng* [a], *Qingyong Wang* [a], *Jiexin Zhu* [b], *Ya Yan* [c], *Liang Zhou* [b] *Kai Qi* [a], *Hongfang Liu* [a], *Ho Seok Park* [d*], and *Bao Yu Xia* [a]*

[a] *Key Laboratory of Material Chemistry for Energy Conversion and Storage (Ministry of Education), Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology (HUST), 1037 Luoyu Road, Wuhan 430074, PR China*

[b] *State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, International School of Materials Science and Engineering, Wuhan University of Technology, Wuhan, 430070, PR China*

[c] *School of Materials Science and Engineering, University of Shanghai for Science and Technology, 516 Jungong Road, Shanghai, 200093, PR China*

d Department of Health Sciences and Technology, Samsung Advanced Institute for Health Sciences and Technology (SAIHST), SKKU Advanced Institute of NanoTechnology (SAINT), School of Chemical Engineering Sungkyunkwan University

Corresponding authors: byxia@hust.edu.cn (B.Y. Xia); phs0727@skku.edu (H. S. Park)

Preparation

Cu aspartic acid MOFs (Cu-ASP MOFs) nanofibers were prepared with aqueous/organic interfacial method according to previous literature.[1] A series of CuO precursors are obtained by annealing Cu-ASP at 300 ^{o}C 1 h, 300 ^{o}C 3 h, 400 ^{o}C 1 h, 500 ^{o}C 1 h and 600 ^{o}C 1 h, respectively, accordingly the OD-Cu-1~5 were in-situ formed during electrolysis. The copper succinic acid MOFs (Cu-SUC) was prepared by the same way of Cu-ASP MOFs, and the CuO-SUC was achieved by annealing the Cu-SUC MOFs at 400 ^{o}C with 1 h. Accordingly the OD-Cu- SUC was in-situ formed during electrolysis.

Characterization

The crystalline structures of series catalysts were identified by X-ray diffraction (XRD) measurements performed on x'pert3 powder diffractometer equipped Cu Kα (λ = 1.54056 Å) radiation (60 kV, 60 mA) from the 2θ = 5 to 80° or 20 to 80°. The scanning electron microscopy (SEM) images were conducted on Sirion 200 microscopy to acquire the morphology of CuO and OD-Cu catalysts. The transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) images and selected area electron diffraction (SAED) patterns were performed on Talos F200X microscopy (200 KV). The X-ray photoelectron spectroscopy (XPS) were collected by AXIS-ULTRA DLD-600W spectrometer with the dual chromicized Al and Mg as excitation sources to confirm the valence state of copper on CuO and OD-Cu surface.

H-cell measurement

5 mg catalyst was dispersed into 500 μL ethanol and 25 μL Nafion solution (5 wt%), a homogenous catalyst ink was obtained by sonicating for 15 min. 10 μL of the catalyst ink was dropped on to the glass carbon electrode and dried under room temperature. The CO_2 electrochemical reduction experiment were tested in a sealed H-type cell which separated by Nafion-117 proton exchange membrane. Each cell was injected into 12 mL electrolyte. The electrolyte was CO_2-saturated 0.1 M potassium bicarbonate ($KHCO_3$) solution (pH 6.8).

Flow cell measurement

10 mg catalyst was dispersed into 1 mL ethanol and 50 μL Nafion solution (5 wt%), a homogenous catalyst ink was obtained by sonicating for 30 min. 300 μL of the catalyst ink was dropped on to the carbon paper electrode and dried under room temperature. The CO_2 electrochemical reduction experiment were tested in a sealed flow cell which separated by an anion exchange membrane. The electrolyte was 1.0 M potassium hydroxide (KOH) solution, which was flowed in the cathode and anode chambers separately. The working electrode was glass carbon and carbon paper electrode with catalyst ink, and Ag/AgCl (saturated KCl) electrode and Pt electrode were used as the reference electrode and counter electrode, respectively. The conversion equation: E (vs. RHE) = E (vs. Ag/AgCl) + 0.21 V + 0.0591 × pH. And all tests were carried out at the room temperature (25 ℃). CO_2 gas was flowed with a flow rate of 20 sccm. Chronoamperometry was performed using an electrochemical station and each potential among -1.0 V to -1.4 V vs. RHE was tested for 1 hour. The cathode cell was linked to a GC, after applying potentials, the online gas chromatograph (Shimadzu GC-2014) detected the gaseous products every 13 minutes, which equipped with two flame ionization detectors (FID) and thermal conductivity detector (TCD). TCD detect H_2, FID 1 detects CO and CH_4, FID 2 detects hydrocarbons. And the liquid products were quantified by a nuclear magnetic resonance (NMR) spectrometer (400 MHz). Linear scan voltammetry (LSV) measurements were performed among 0 V to -1.4 V vs. RHE in Ar or CO_2-saturated 0.1 M $KHCO_3$ or 1.0 M KOH solution with a scan rate of 10 mV s^{-1}. The cyclic voltammetry measurements were measured from 0.1 to 0 V vs. RHE under CO_2 saturated 0.1 M $KHCO_3$ solution with various scan rates (10, 20, 30, 40, and 50 mV s^{-1}). And all the electrochemical data in this paper were not applied IR compensation.

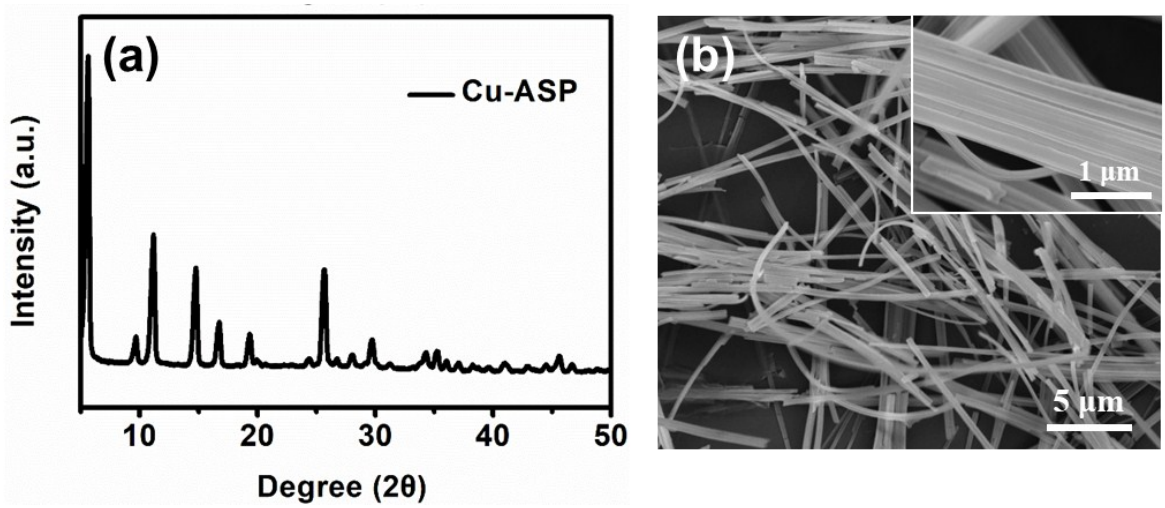

Figure S1. (a) XRD pattern and (b) SEM image of Cu-ASP MOFs.

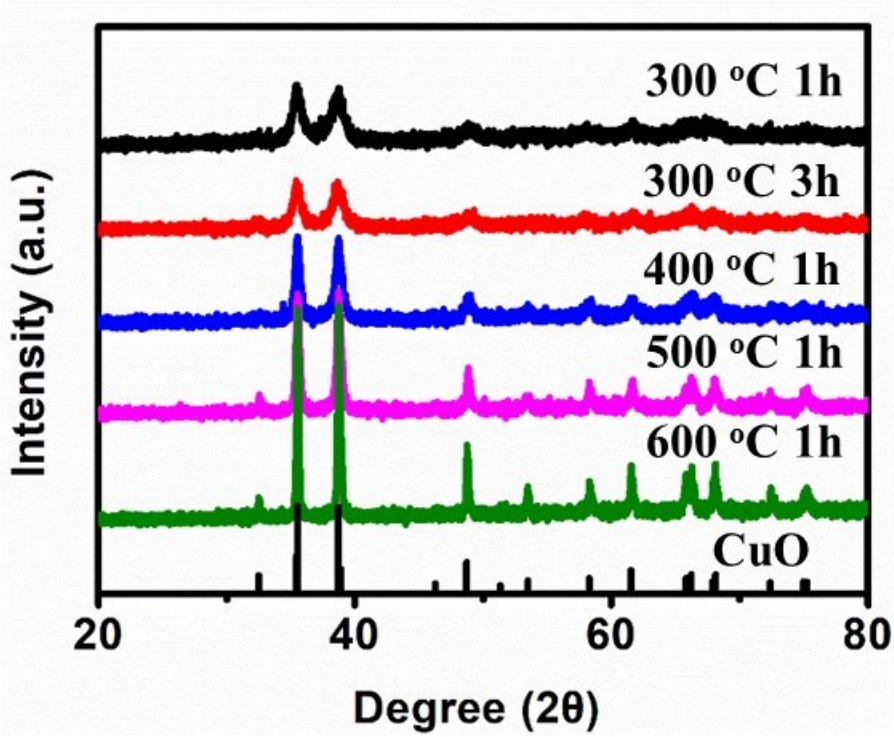

Figure S2. XRD pattern of series CuO nanowires.

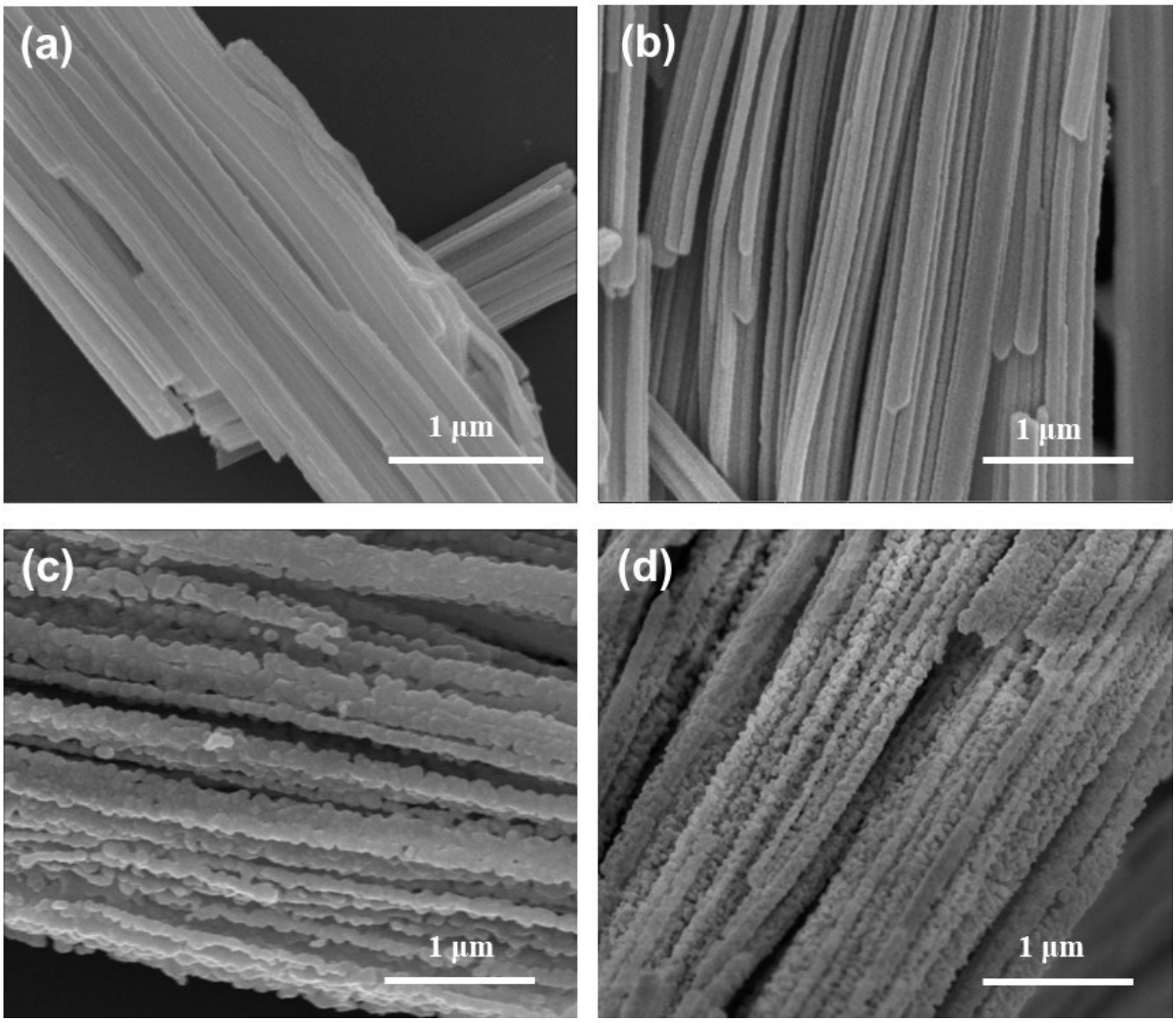

Figure S3. SEM images of series CuO nanowires. (a) 300 ^{o}C 1h. (b) 300 ^{o}C 3h. (c) 500 ^{o}C 1h. (d) 600 ^{o}C 1h.

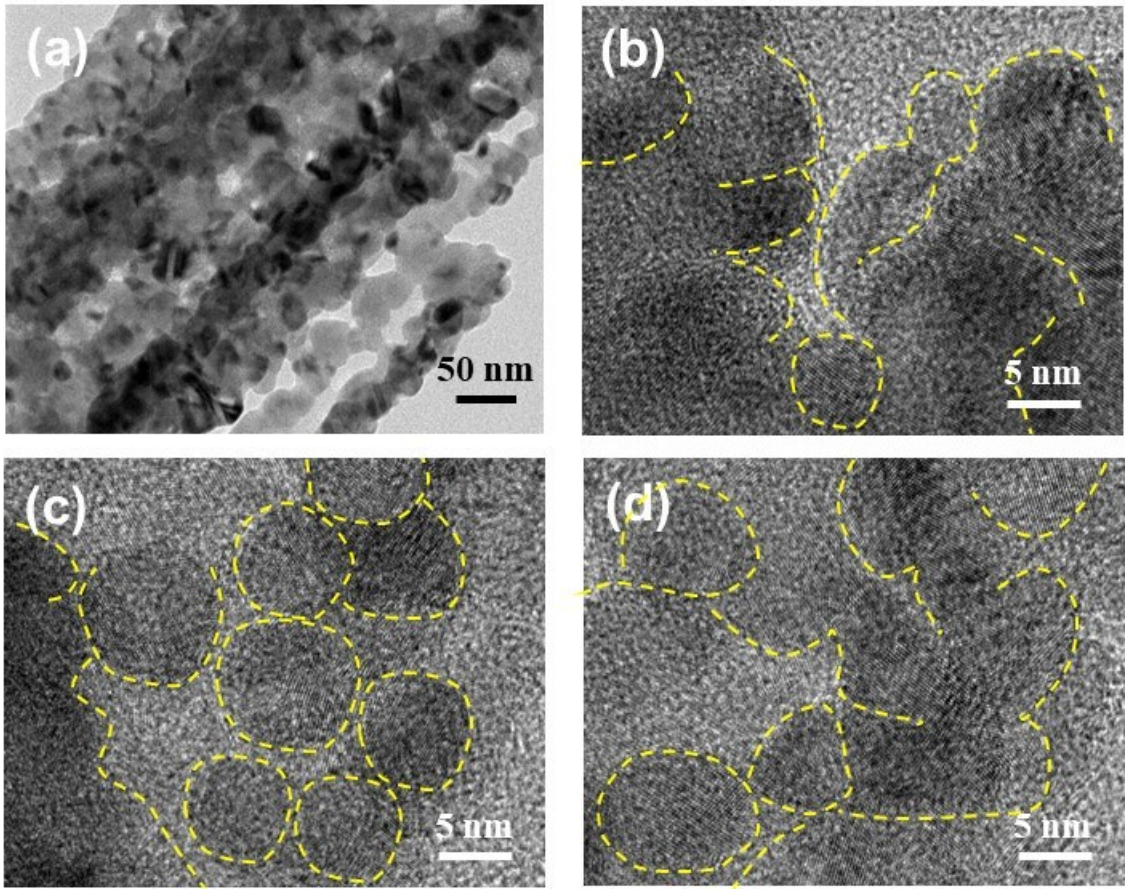

Figure S4. (a) TEM, (b, c, d) High-resolution TEM images of CuO nanowires.

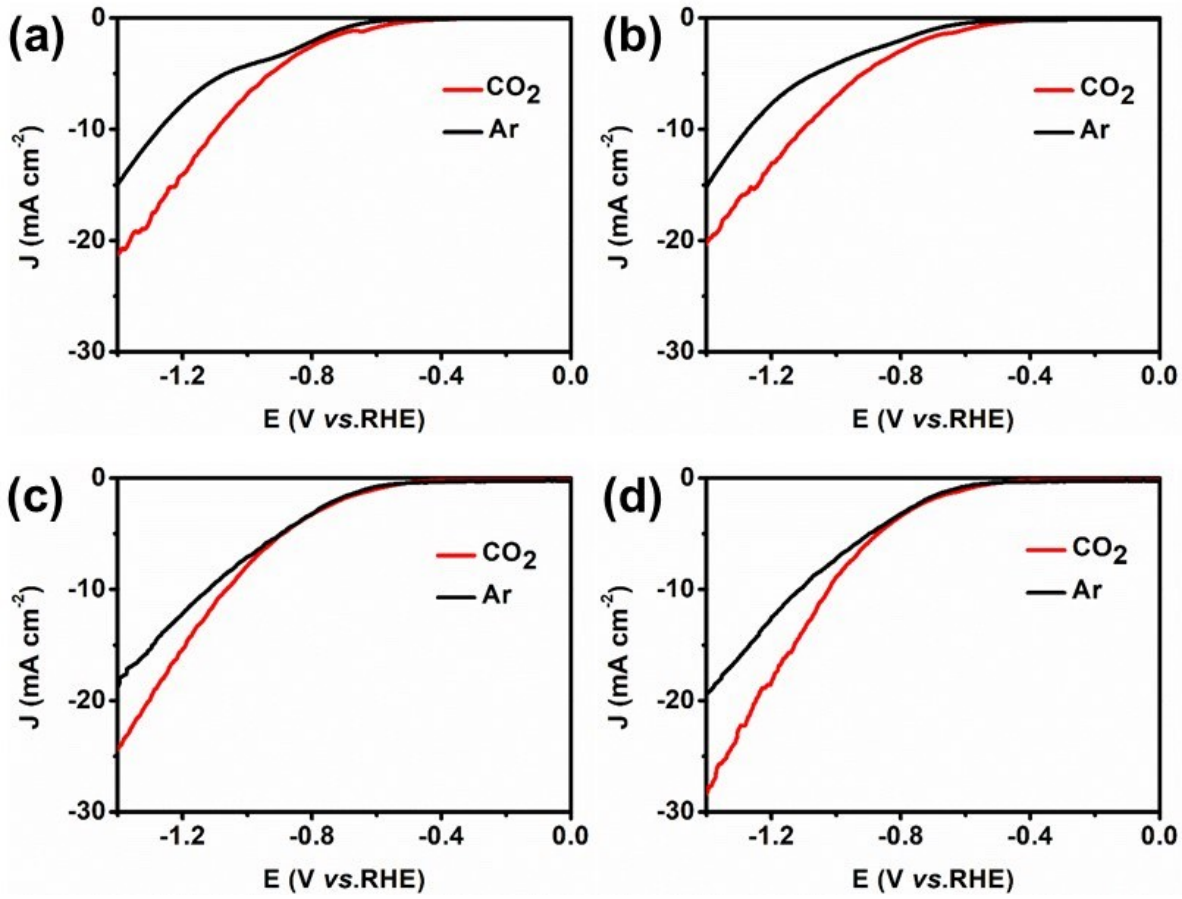

Figure S5. LSV curves in Ar-/CO_2-saturated 0.1 M $KHCO_3$ solution. (a) OD-Cu-1. (b) OD-Cu-2. (c) OD-Cu-4. (d) OD-Cu-5.

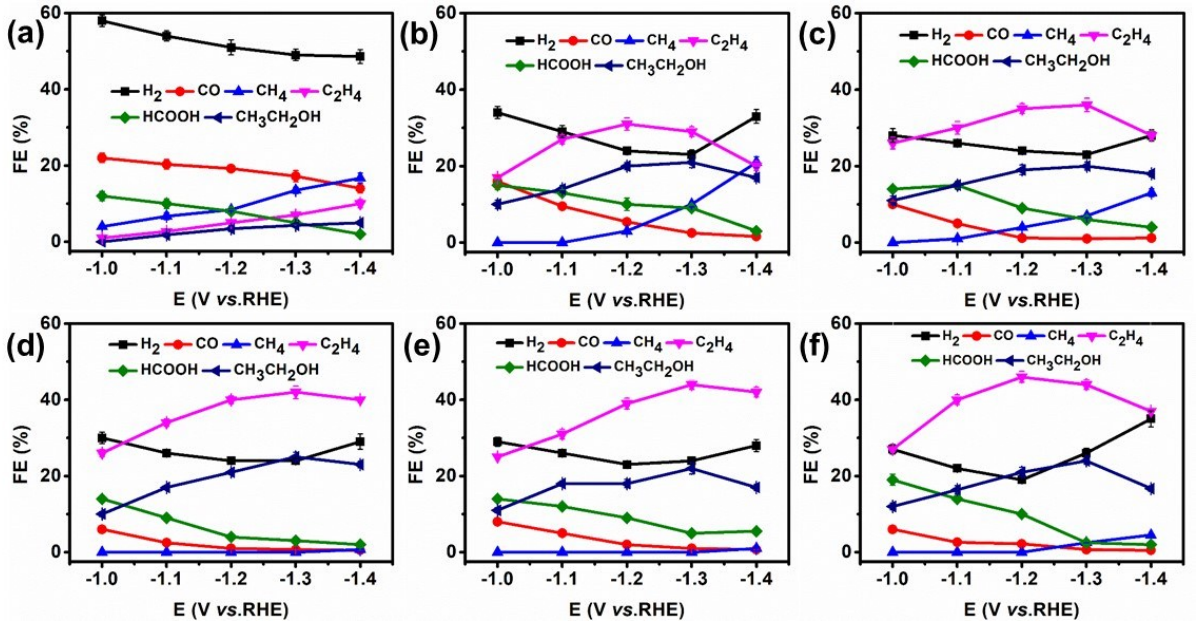

Figure S6. Product distribution analysis of (a) Cu foil, (b) OD-Cu-1, (c) OD-Cu-2, (d) OD-Cu-3, (e) OD-Cu-4, (f) OD-Cu-5.

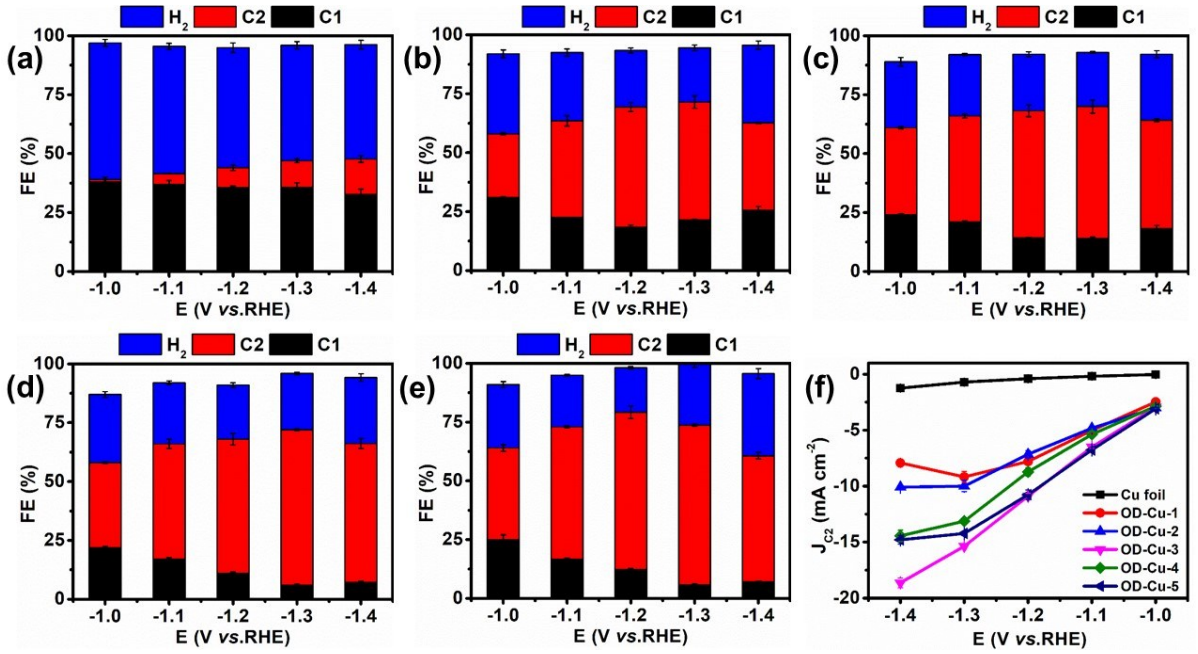

Figure S7. FE of C2, C1 and H_2 products for (a) Cu foil, (b) OD-Cu-1, (c) OD-Cu-2, (d) OD-Cu-4, (e) OD-Cu-5, and (f) partial current density of C2 (C_2H_4 and CH_3CH_2OH) products.

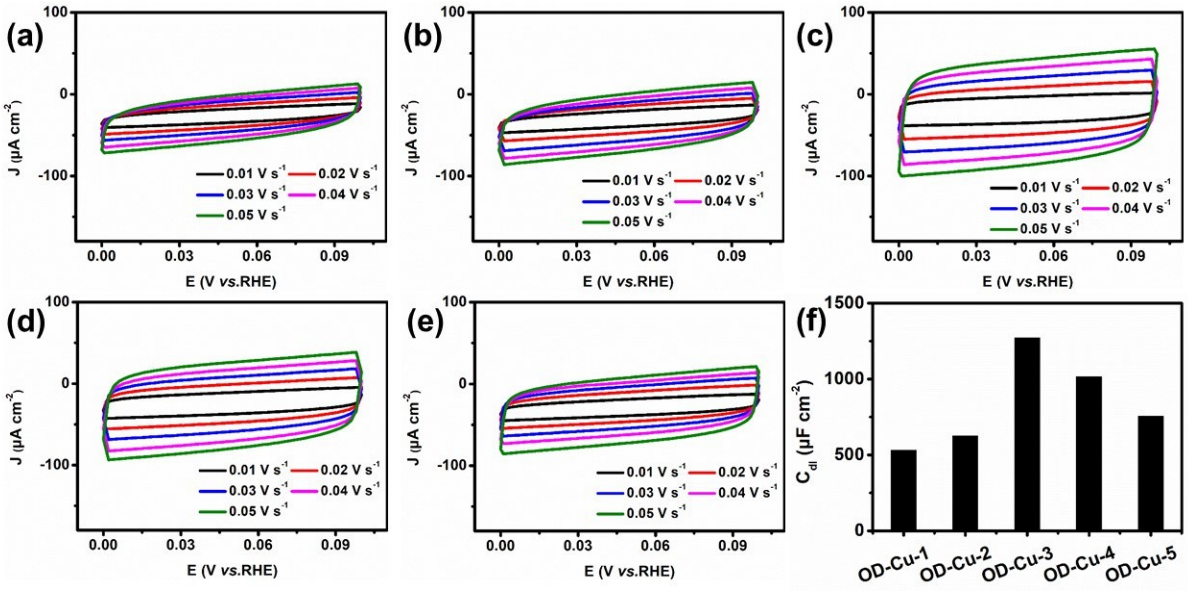

Figure S8. Capacitive behaviors of (a) OD-Cu-1, (b) OD-Cu-2, (c) OD-Cu-3, (d) OD-Cu-4, (e) OD-Cu-5, and (f) C_{dl} of series OD-Cu catalysts.

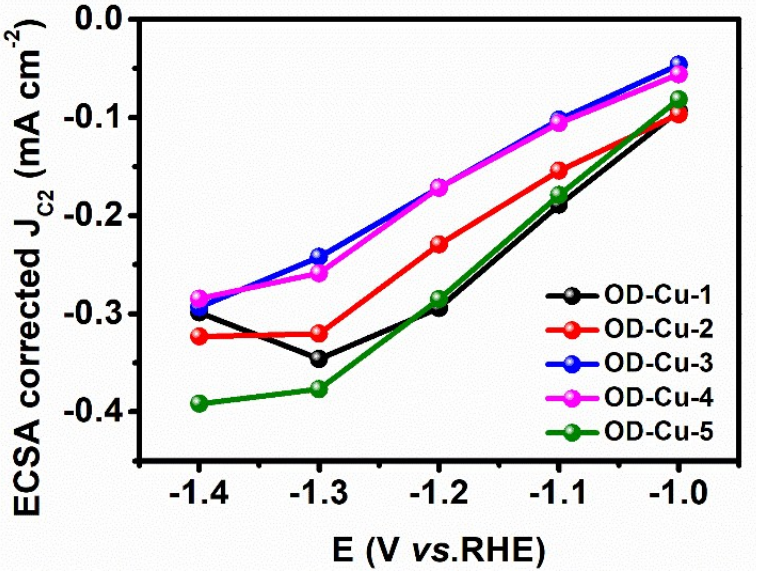

Figure. S9 ECSA corrected partial current density for C2 products.

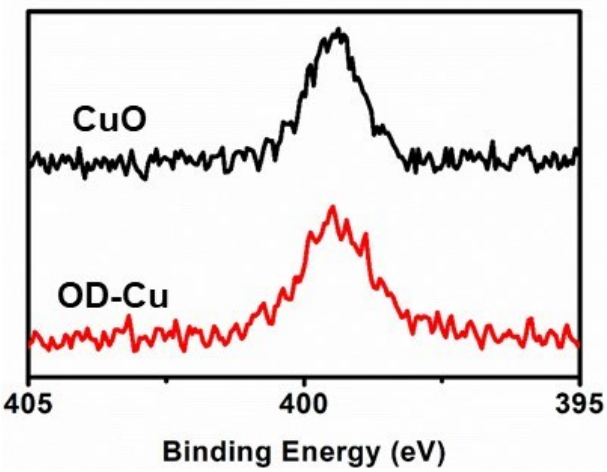

Figure S10. N 1s XPS spectra of CuO and OD-Cu.

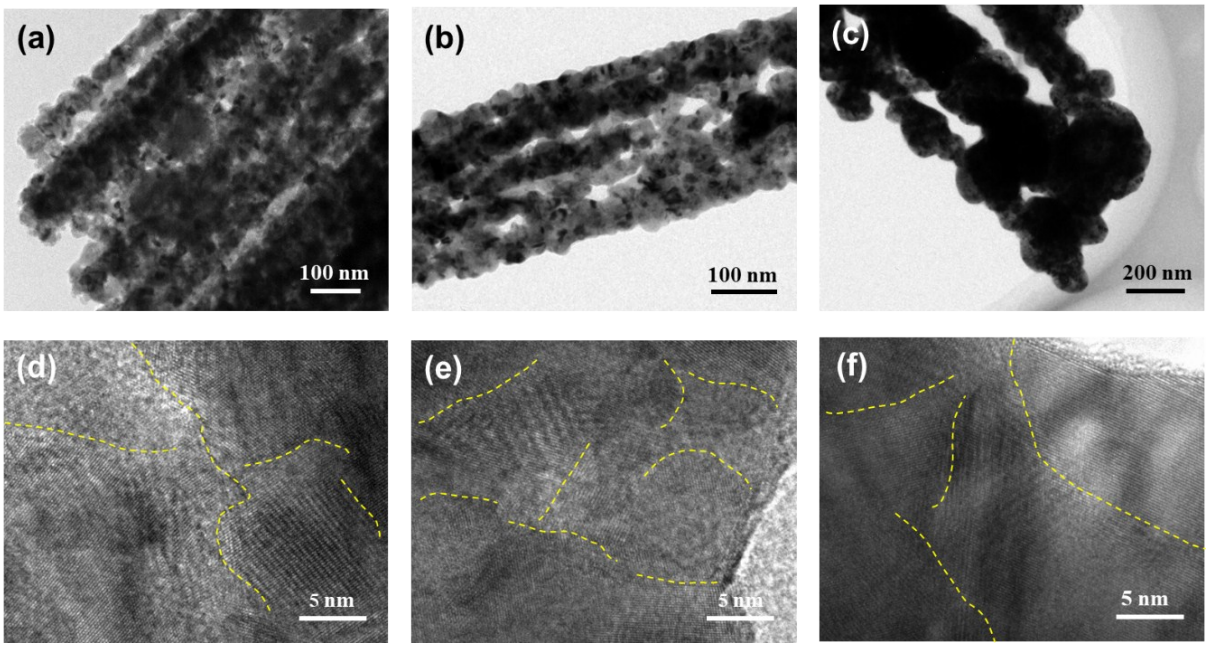

Figure S11. TEM and HRTEM images of (a, d) OD-Cu-3, (b, e) OD-Cu-4 and (c, f) OD-Cu-5.

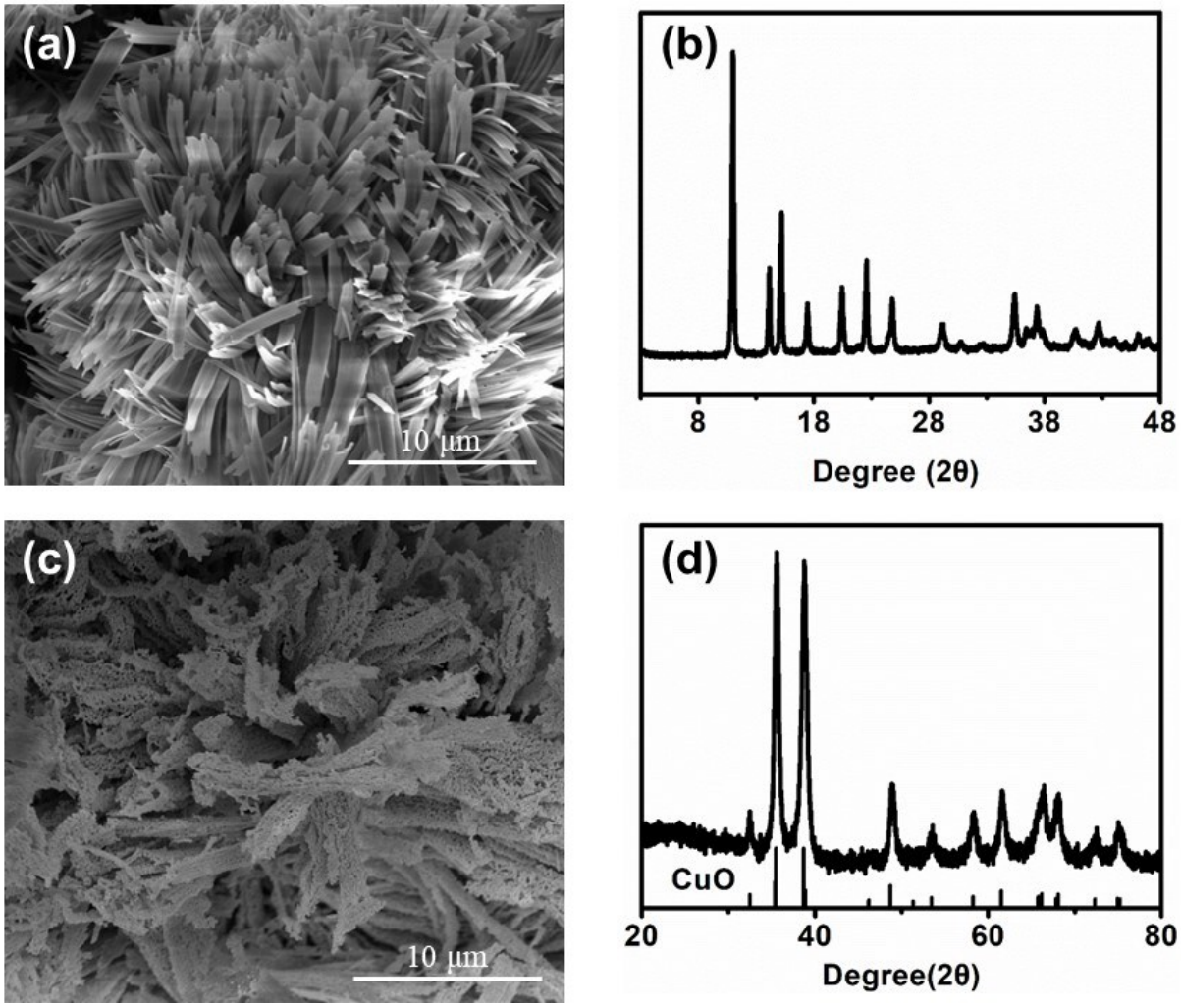

Figure S12. (a, c) SEM images and (b, d) XRD pattern of Cu-SUC MOFs (a, b) and its derived CuO-SUC (c, d)**.**

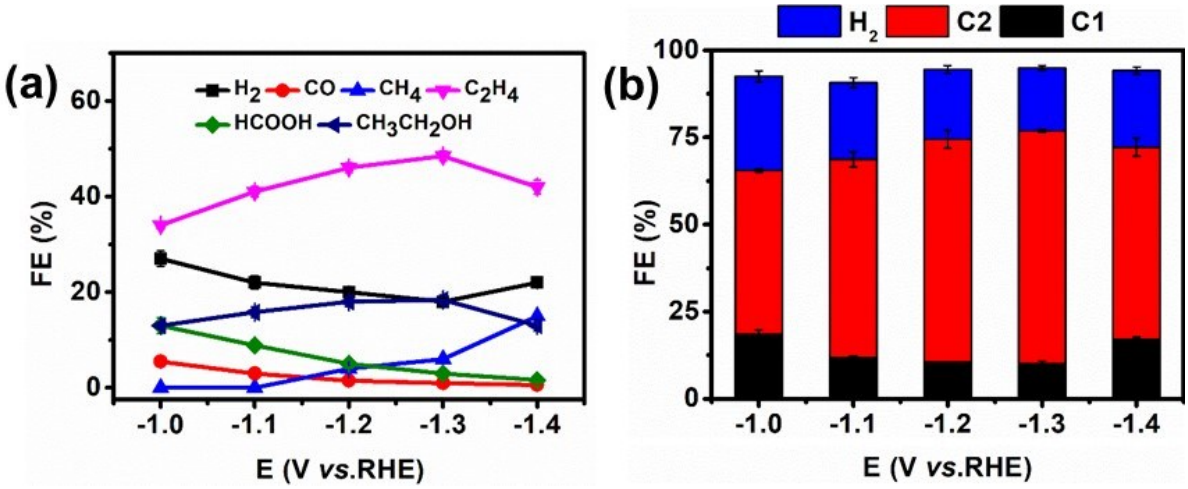

Figure S13. (a) Product distribution analysis and (b) H_2, C1, C2 products on OD-Cu-SUC at various applied potentials in 0.1 M $KHCO_3$ solution.

Table S1. Summary of recent reported Cu-based catalysts for CO_2 reduction toward C_2H_4 and C2 products.

Catalyst	cell	Electrolyte	FE of C2 (%)	FE (C_2H_4) (%)	J (C_2H_4) (mA cm^{-2})	Ref.
Cu nanocubes	H-cell	0.1 M $KHCO_3$	46	41	3.6	[2]
Cu_2O derived Cu	H-cell	0.1 M $KHCO_3$	54.4	42.6	13.3	[3]
Cu_2O derived Cu	H-cell	0.1 M $KHCO_3$	51	35	12.3	[4]
Plasma treated Cu foil	H-cell	0.1 M $KHCO_3$	60	60	14	[5]
anodized copper (AN-Cu) $Cu(OH)_2$ catalysts	H-cell	0.1 M $KHCO_3$	40	40	7	[6]
Carbon-Supported Cu Nanoparticles	H-cell	0.1 M $KHCO_3$	45	45	~11	[7]
Molecular Cu	H-cell	0.5 M $KHCO_3$	15	~15	8.4	[8]
OD-Cu/ Carbons fabricated from HKUST-1	H-cell	0.1 M $KHCO_3$	35	0	0	[9]
Cu_2O@Cu-MOF	H-cell	0.1 M $KHCO_3$	21	~18	~3.2	[10]
Cathodized copper-organic frameworks	H-cell	0.1 M $KHCO_3$	45	45	8.5	[11]
copper (II) phthalocyanine (CuPc)	H-cell	0.5 M $KHCO_3$	15	~15	~2	[12]
CuO nanowire derived Cu	H-cell	0.1 M $KHCO_3$	~25	~10	/	[13]
CuO nanowire derived Cu	H-cell	0.1 M $KHCO_3$	/	~21	/	[14]
CuO nanowire derived Cu arrays	H-cell	0.1 M $KHCO_3$	23	17	0.9	[15]
copper-chloride derived catalyst	H-cell	0.1 M $KHCO_3$	73	56	9.5	[16]
CuO nanowire derivates	H-cell	0.1 M $KHCO_3$	**70**	**45**	**18.5**	**This work**

Table S2. Summary of recent reported Cu-based catalysts for CO_2 reduction in flow cell.

Catalyst	**cell**	**Electrolyte**	**FE of C2 (%)**	**FE (C_2H_4) (%)**	**J (C_2H_4) (mA cm^{-2})**	**Ref.**
Cu wire	Flow cell	1.0 M KOH	64	39	75	[17]
Nanoporous copper	Flow cell	1.0 M KOH	65	40	76	[18]
Abrupt Cu interface	Flow cell	7.0 M KOH	84	70	175	[19]
Cu_4O_3	Flow cell	2.5 M KOH	~60	~40	120	[20]
Cu nanoparticles	Flow cell	1.0 M KOH	46	35	150	[21]
Copper nanodendrites	Flow cell	0.1 M $KHCO_3$	57	57	96.9	[22]
Copper	Flow cell	5.0 M KOH	/	72	800	[23]
Cu_2O	Flow cell	1.0 M $KHCO_3$	~75.5	~38	114	[24]
HKUST-1 derived Cu clusters	Flow cell	1.0 M KOH	/	~45	118	[25]
CuO nanowire derivates	Flow cell	1.0 M KOH	/	**37**	**141**	**This work**

Reference:

[1] I. Imaz, M. Rubio-Martínez, W. J. Saletra, D. B. Amabilino, D. Maspoch, *J. Am. Chem. Soc.* **2009**, *131*, 18222.

[2] A. Loiudice, P. Lobaccaro, E. A. Kamali, T. Thao, B. H. Huang, J. W. Ager, R. Buonsanti, *Angew. Chem. Int. Ed.* **2016**, *55*, 5789.

[3] A. D. Handoko, C. W. Ong, Y. Huang, Z. G. Lee, L. Lin, G. B. Panetti, B. S. Yeo, *J. Phys. Chem. C* **2016**, *120*, 20058.

[4] D. Ren, Y. Deng, A. D. Handoko, C. S. Chen, S. Malkhandi, B. S. Yeo, *ACS Catal.* **2015**, *5*, 2814.

[5] H. Mistry, A. S. Varela, C. S. Bonifacio, I. Zegkinoglou, I. Sinev, Y.-W. Choi, K. Kisslinger, E. A. Stach, J. C. Yang, P. Strasser, *Nat. Commun.* **2016**, *7*, 12123.

[6] S. Y. Lee, H. Jung, N.-K. Kim, H.-S. Oh, B. K. Min, Y. J. Hwang, *J. Am. Chem. Soc.* **2018**, *140*, 8681.

[7] O. A. Baturina, Q. Lu, M. A. Padilla, L. Xin, W. Li, A. Serov, K. Artyushkova, P. Atanassov, F. Xu, A. Epshteyn, *ACS Catal.* **2014**, *4*, 3682.

[8] Z. Weng, J. Jiang, Y. Wu, Z. Wu, X. Guo, K. L. Materna, W. Liu, V. S. Batista, G. W. Brudvig, H. Wang, *J. Am. Chem. Soc.* **2016**, *138*, 8076.

[9] K. Zhao, Y. Liu, X. Quan, S. Chen, H. Yu, *ACS Appl. Mater. Interfaces* **2017**, *9*, 5302.

[10] X. Tan, C. Yu, C. Zhao, H. Huang, X. Yao, X. Han, W. Guo, S. Cui, H. Huang, J. Qiu, *ACS Appl. Mater. Inter.* **2019**, *11*, 9904.

[11] F. Yang, A. Chen, P. L. Deng, Y. Zhou, Z. Shahid, H. Liu, B. Y. Xia, *Chem. Sci.* **2019**, *10*, 7975.

[12] Z. Weng, Y. Wu, M. Wang, J. Jiang, K. Yang, S. Huo, X.-F. Wang, Q. Ma, G. W. Brudvig, V. S. Batista, *Nat. Commun.* **2018**, *9*, 415.

[13] D. Raciti, K. J. Livi, C. Wang, *Nano Letters* **2015**, *15*, 6829.

[14] D. Raciti, M. Mao, J. H. Park, C. Wang, *Catal. Sci. & Technol.* **2018**, *8*, 2364.

[15] M. Ma, K. Djanashvili, W. A. Smith, *Angew. Chem. Int. Ed.* **2016**, *55*, 6680.

[16] M. G. Kibria, C.-T. Dinh, A. Seifitokaldani, P. De Luna, T. Burdyny, R. Quintero-Bermudez, M. B. Ross, O. S. Bushuyev, F. P. García de Arquer, P. Yang, D. Sinton, E. H. Sargent, *Adv. Mater.* **2018**, *30*, 1804867.

[17] T. T. H. Hoang, S. Verma, S. Ma, T. T. Fister, J. Timoshenko, A. I. Frenkel, P. J. A. Kenis, A. A. Gewirth, *J. Am. Chem. Soc.* **2018**, *140*, 5791.

[18] T. T. H. Hoang, S. Ma, J. I. Gold, P. J. A. Kenis, A. A. Gewirth, *ACS Catal.* **2017**, *7*, 3313.

[19] C.-T. Dinh, T. Burdyny, M. G. Kibria, A. Seifitokaldani, C. M. Gabardo, F. P. García de Arquer, A. Kiani, J. P. Edwards, P. De Luna, O. S. Bushuyev, C. Zou, R. Quintero-Bermudez, Y. Pang, D. Sinton, E. H. Sargent, *Science* **2018**, *360*, 783.

[20] N. Martić, C. Reller, C. Macauley, M. Löffler, B. Schmid, D. Reinisch, E. Volkova, A. Maltenberger, A. Rucki, K. J. J. Mayrhofer, G. Schmid, *Adv. Energy Mater.* **2019**, *9*, 1901228.

[21] S. Ma, M. Sadakiyo, R. Luo, M. Heima, M. Yamauchi, P. J. A. Kenis, *J. Power Sources* **2016**, *301*, 219.

[22] C. Reller, R. Krause, E. Volkova, B. Schmid, S. Neubauer, A. Rucki, M. Schuster, G. Schmid, *Adv. Energy Mater.* **2017**, *7*, 1602114.

[23] J. Li, Z. Wang, C. McCallum, Y. Xu, F. Li, Y. Wang, C. M. Gabardo, C.-T. Dinh, T.-T. Zhuang, L. Wang, J. Y. Howe, Y. Ren, E. H. Sargent, D. Sinton, *Nat. Catal.* **2019**, *2*, 1124.

[24] Y. C. Tan, K. B. Lee, H. Song, J. Oh, *Joule* **2020**.

[25] 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, E. H. Sargent, *J. Am. Chem. Soc.* **2018**, *140*, 11378.