

Table S1. Summary of catalysts for direct electrochemical CO₂/CO-to-C₃₊ conversion.

Category	Catalyst ^a	Feed	Electrolyte	pH ^b	Major C ₃₊ product(s) ^c	Reference electrode	Potential (V) ^d	<i>j</i> _{C3+} (mA cm ⁻²) ^e	Optimal FE (%) ^e	Ref.
Single-crystal Cu	Cu(111)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.55	0.07	1.3	1
	Cu(11 9 9)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.48	0.09	1.8	1
	Cu(755)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.43	0.13	2.5	1
	Cu(533)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.42	0.08	1.6	1
	Cu(211)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.38	0.20	4.0	1
	Cu(311)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.37	0.21	4.2	1
	Cu(511)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.36	0.40	7.9	1
	Cu(711)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.34	0.60	12.0	1
	Cu(911)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.36	0.47	9.4	1
	Cu(11 1 1)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.37	0.33	6.6	1
	Cu(100)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.40	0.26	5.1	1
	Cu(810)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.38	0.20	3.9	1
	Cu(610)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.37	0.23	4.5	1
	Cu(510)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.38	0.30	6.0	1
	Cu(310)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.42	0.27	5.4	1
	Cu(210)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.52	0.07	1.3	1
	Cu(332)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.51	0.04	0.70	1
	Cu(331)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.55	0.05	0.90	1
	Cu(110)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.58	0.07	1.34	1
	Cu(650)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.59	0.04	0.86	1
Cu(320)	CO ₂	0.1 M KHCO ₃	6.8	PrD+AlOH+1-PrOH	SHE	-1.52	0.07	1.3	1	
Nanostructured Cu or OD-Cu	Cu NPs < 100 nm	CO ₂	1 M KHCO ₃	7.8	AcO+AlOH+1-PrOH	Ag/AgCl	-1.50	~7	~7	2

Cu NPs < 100 nm	CO	1 M KHCO ₃	8.3	AcO+AlOH+1-PrOH	Ag/AgCl	-1.50	~31	~28	2
Cu 5 μm	CO ₂	1 M KHCO ₃	7.8	AcO+AlOH+1-PrOH	Ag/AgCl	-1.30	~3	~4	2
Cu 5 μm	CO	1 M KHCO ₃	8.3	AcO+AlOH+1-PrOH	Ag/AgCl	-1.30	~7	~7	2
trans-CuEn	CO ₂	0.1 M CsHCO ₃	6.8	1-PrOH	RHE	-0.75	0.80	~4	3
BCF-Cu ₂ O	CO	1 M KOH	14	1-PrOH	RHE	-0.45	0.85	19.3	4
Cu/Cu ₂ O@NG	CO ₂	0.2 M KI	5.17	1-PrOH	RHE	-1.90	~1.60	~10	5
Cu nanocavity	CO	1 M KOH	14	1-PrOH	RHE	-0.56	7.8 ± 0.5	21 ± 1	6
3-shell	CO ₂	0.5 M KHCO ₃	7.5	1-PrOH	RHE	-0.65	11	~15	7
HoMSs									
2-shell	CO	1 M KOH	14	1-PrOH	Hg/HgO	-1.90	11	22	8
YSNPs									
OD-Cu NCs	CO ₂	0.1 M KHCO ₃	6.8	1-PrOH	RHE	-0.95	1.74	8.8	9
HF-Cu	CO	1 M KOH	14	1-PrOH	RHE	-0.45	8.5	20	10
Cu AD	CO	1 M KOH	14	1-PrOH	RHE	-0.47	11	23	11
Cu(OH) ₂ -D	CO ₂	0.1 M KHCO ₃	6.8	1-PrOH	RHE	-0.98	~4	11	12
Cu(OH) ₂ -D	CO ₂	1 M KOH	14	1-PrOH	RHE	-0.54	~17.5	7	12
CuOD-Cu	CO ₂	0.1 M KHCO ₃	6.8	1-PrOH	RHE	-0.94	4.61	17.9	13
CuOD-Cu	CO ₂	1 M KHCO ₃	7.8	1-PrOH	RHE	-0.94	8.51	6.96	13
R-Cu/Au	CO	1 M KOH	14	1-PrOH	RHE	-0.58	21.5	48.0	14
Cu ₂ S-Cu-V	CO ₂	0.1 M KHCO ₃	6.8	1-PrOH	RHE	-0.95	2.5 ± 0.1	8 ± 0.7	15
DSV-rich	CO ₂	0.1 M KHCO ₃	6.8	1-PrOH	RHE	-1.05	3.10	15.4	16
CuS _x									
Cu ₂ O-Cl	CO ₂	0.1 M KCl	3.98	1-PrOH	RHE	-1.6	0.96	8.7	17
O-plasma Cu	CO ₂	0.1 M KHCO ₃	6.8	1-PrOH	RHE	-1.00	~3.2	~9	17
Cu ₂ O-I	CO	1 M KOH	14	C ₃ -C ₆ AcE	RHE	-0.72	55	22	18

Doped or alloyed Cu	Cu ₉₁ Pd ₉	CO ₂	0.5 M KHCO ₃	7.5	1-PrOH	RHE	-0.65	1.15	13.7	19
	Cu ₉₈ Au ₂	CO ₂	1 M KOH	14	1-PrOH	RHE	-0.41	12.7	18.2	20
	Cu ₉₆ Ag ₄	CO	1 M KOH	14	1-PrOH	RHE	-0.46	4.5	33	21
	Cu ₉₅ Ag ₄ Ru ₁	CO	1 M KOH	14	1-PrOH	RHE	-0.46	111	37	22
	CuAg _{5%} N _{20h}	CO	1 M CsOH	14	1-PrOH	RHE	-1.00	67.5	45	23
	Cu ₉₄ Ag ₆	CO ₂	1 M CsHCO ₃ + 0.3 M CO ₂	5.4 ± 0.4	2-PrOH	RHE	-0.73	12.0	39.6	24
	Cu ₉₄ Ag ₆	CO ₂	1 M CsHCO ₃ + 3 M CO ₂		2-PrOH	RHE	-0.70	59.3	56.7	24
CuSA	Pb-Cu	CO	1 M KOH	14	1-PrOH	RHE	-0.68	38	47	25
	Cu-SA/NPC	CO ₂	0.1 M KHCO ₃	6.8	AcO	RHE	-0.36	2.35	36.7	26
Non-Cu	MoS ₂	CO ₂	0.1 M Na ₂ CO ₃	6.8	1-PrOH	RHE	-0.59	0.25	3.5	27
	Ni ₃ Al	CO ₂	0.1 M K ₂ SO ₄	4.5	1-PrOH	Ag/AgCl	-1.38	0.04	1.9	28
	PD-Ni	CO ₂	0.1 M KHCO ₃	6.8	C ₃ to C ₆ HCs	RHE	-1.20	0.91	6.5	29
	NiP ₂	CO ₂	0.5 M KHCO ₃	7.5	methylglyoxal	RHE	-0.10	0.39	84	30
	Ni ₂ P	CO ₂	0.5 M KHCO ₃	7.5	2,3-furandiol	RHE	0.00	0.02	71	30
	ImF-Mo ₃ P	CO ₂	1 M KOH	14	C ₃ H ₈	RHE	-0.80	359	91	31

- a. Some abbreviations for catalysts: NPs, nanoparticles; trans-CuEn, transformed Cu-NP ensemble; BCF, branching cubic framework; NG, nitrogen-doped graphene; HoMSs, hollow multi-shell structures; YSNPs, yolk-shell nanoparticles; OD-Cu, oxide-derived Cu; NCs, nanocrystals; HF-Cu, highly fragmented Cu; Cu AD, Cu adparticle; Cu(OH)₂-D, Cu(OH)₂-derived Cu; CuOD-Cu, CuO-derived Cu; R-Cu/Au, reconstructed Cu assisted with Au NPs; Cu₂S-Cu-V, core-shell Cu₂S-Cu with Cu vacancy; DSV, double sulfur vacancies; Cu₂O-Cl, chlorine-induced bi-phasic Cu₂O-Cu; Cu₂O-I, iodine-modified Cu₂O; CuAg_{5%}N_{20h}, nitride-derived Cu with 5 mol% Ag and 20-h nitridation duration; Cu-SA/NPC, single-atom Cu encapsulated on nitrogen-doped porous carbon; PD-Ni, phosphate-derived Ni; ImF-Mo₃P, imidazolium-functionalized Mo₃P.
- b. The values of pH were either directly adopted from the original study or estimated based on Ref.32.
- c. Abbreviations for products: PrD, propionaldehyde; ALOH, allyl alcohol; 1-PrOH, 1-propanol; AcO, acetone; AcE, acetate ester; 2-PrOH, 2-propanol; HCs,

hydrocarbons; C₃H₈, propane.

- d. The values of potential were directly adopted from the original study, and some of these values were not subjected to *i*R-correction.
- e. $j_{C_3^+}$, partial current density of C₃⁺; FE, Faradaic efficiency.

Reference

- 1 Y. Hori, I. Takahashi, O. Koga and N. Hoshi, *J. Mol. Catal. A: Chem.*, 2003, **199**, 39–47.
- 2 N. S. Romero Cuellar, K. Wiesner-Fleischer, M. Fleischer, A. Rucki and O. Hinrichsen, *Electrochim. Acta*, 2019, **307**, 164–175.
- 3 D. Kim, C. S. Kley, Y. Li and P. Yang, *Proc. Natl. Acad. Sci.*, 2017, **114**, 10560–10565.
- 4 J. Liu, F. You, B. He, Y. Wu, D. Wang, W. Zhou, C. Qian, G. Yang, G. Liu, H. Wang, Y. Guo, L. Gu, L. Feng, S. Li and Y. Zhao, *J. Am. Chem. Soc.*, 2022, **144**, 12410–12420.
- 5 W.-Y. Zhi, Y.-T. Liu, S.-L. Shan, C.-J. Jiang, H. Wang and J.-X. Lu, *J. CO₂ Util.*, 2021, **50**, 101594.
- 6 T.-T. Zhuang, Y. Pang, Z.-Q. Liang, Z. Wang, Y. Li, C.-S. Tan, J. Li, C. T. Dinh, P. De Luna, P.-L. Hsieh, T. Burdyny, H.-H. Li, M. Liu, Y. Wang, F. Li, A. Proppe, A. Johnston, D.-H. Nam, Z.-Y. Wu, Y.-R. Zheng, A. H. Ip, H. Tan, L.-J. Chen, S.-H. Yu, S. O. Kelley, D. Sinton and E. H. Sargent, *Nat. Catal.*, 2018, **1**, 946–951.
- 7 C. Liu, M. Zhang, J. Li, W. Xue, T. Zheng, C. Xia and J. Zeng, *Angew. Chem., Int. Ed.*, 2022, **61**, e202113498.
- 8 H. Du, L.-X. Liu, P. Li, Q. Min, S. Guo and W. Zhu, *ACS Nano*, 2023, **17**, 8663–8670.
- 9 D. Ren, N. T. Wong, A. D. Handoko, Y. Huang and B. S. Yeo, *J. Phys. Chem. Lett.*, 2016, **7**, 20–24.
- 10 Y. Pang, J. Li, Z. Wang, C.-S. Tan, P.-L. Hsieh, T.-T. Zhuang, Z.-Q. Liang, C. Zou, X. Wang, P. De Luna, J. P. Edwards, Y. Xu, F. Li, C.-T. Dinh, M. Zhong, Y. Lou, D. Wu, L.-J. Chen, E. H. Sargent and D. Sinton, *Nat. Catal.*, 2019, **2**, 251–258.
- 11 J. Li, F. Che, Y. Pang, C. Zou, J. Y. Howe, T. Burdyny, J. P. Edwards, Y. Wang, F. Li, Z. Wang, P. De Luna, C.-T. Dinh, T.-T. Zhuang, M. I. Saidaminov, S. Cheng, T. Wu, Y. Z. Finfrock, L. Ma, S.-H. Hsieh, Y.-S. Liu, G. A. Botton, W.-F. Pong, X. Du, J. Guo, T.-K. Sham, E. H. Sargent and D. Sinton, *Nat. Commun.*, 2018, **9**, 4614.
- 12 D. Zhong, Z.-J. Zhao, Q. Zhao, D. Cheng, B. Liu, G. Zhang, W. Deng, H. Dong, L. Zhang, J. Li, J. Li and J. Gong, *Angew. Chem., Int. Ed.*, 2021, **60**, 4879–4885.
- 13 C. Long, X. Liu, K. Wan, Y. Jiang, P. An, C. Yang, G. Wu, W. Wang, J. Guo, L. Li, K. Pang, Q. Li, C. Cui, S. Liu, T. Tan and Z. Tang, *Sci.*

- Adv.*, 2023, **9**, eadi6119.
- 14C. Long, K. Wan, Y. Chen, L. Li, Y. Jiang, C. Yang, Q. Wu, G. Wu, P. Xu, J. Li, X. Shi, Z. Tang and C. Cui, *J. Am. Chem. Soc.*, 2024, **146**, 4632–4641.
- 15T.-T. Zhuang, Z.-Q. Liang, A. Seifitokaldani, Y. Li, P. De Luna, T. Burdyny, F. Che, F. Meng, Y. Min, R. Quintero-Bermudez, C. T. Dinh, Y. Pang, M. Zhong, B. Zhang, J. Li, P.-N. Chen, X.-L. Zheng, H. Liang, W.-N. Ge, B.-J. Ye, D. Sinton, S.-H. Yu and E. H. Sargent, *Nat. Catal.*, 2018, **1**, 421–428.
- 16C. Peng, G. Luo, J. Zhang, M. Chen, Z. Wang, T.-K. Sham, L. Zhang, Y. Li and G. Zheng, *Nat. Commun.*, 2021, **12**, 1580.
- 17S. Lee, D. Kim and J. Lee, *Angew. Chem., Int. Ed.*, 2015, **54**, 14701–14705.
- 18Y. Zhou, R. Ganganahalli, S. Verma, H. R. Tan and B. S. Yeo, *Angew. Chem., Int. Ed.*, 2022, **61**, e202202859.
- 19M. Rahaman, K. Kiran, I. Z. Montiel, V. Grozovski, A. Dutta and P. Broekmann, *Green Chem.*, 2020, **22**, 6497–6509.
- 20S. Jeong, C. Huang, Z. Levell, R. X. Skalla, W. Hong, N. J. Escorcía, Y. Losovyj, B. Zhu, A. N. Butrum-Griffith, Y. Liu, C. W. Li, D. Reifsnnyder Hickey, Y. Liu and X. Ye, *J. Am. Chem. Soc.*, 2024, **146**, 4508–4520.
- 21X. Wang, Z. Wang, T.-T. Zhuang, C.-T. Dinh, J. Li, D.-H. Nam, F. Li, C.-W. Huang, C.-S. Tan, Z. Chen, M. Chi, C. M. Gabardo, A. Seifitokaldani, P. Todorović, A. Proppe, Y. Pang, A. R. Kirmani, Y. Wang, A. H. Ip, L. J. Richter, B. Scheffel, A. Xu, S.-C. Lo, S. O. Kelley, D. Sinton and E. H. Sargent, *Nat. Commun.*, 2019, **10**, 5186.
- 22X. Wang, P. Ou, A. Ozden, S.-F. Hung, J. Tam, C. M. Gabardo, J. Y. Howe, J. Sisler, K. Bertens, F. P. García de Arquer, R. K. Miao, C. P. O'Brien, Z. Wang, J. Abed, A. S. Rasouli, M. Sun, A. H. Ip, D. Sinton and E. H. Sargent, *Nat. Energy*, 2022, **7**, 170–176.
- 23H. Phong Duong, J. G. Rivera de la Cruz, N.-H. Tran, J. Louis, S. Zanna, D. Portehault, A. Zitolo, M. Walls, D. V. Peron, M. W. Schreiber, N. Menguy and M. Fontecave, *Angew. Chem., Int. Ed.*, 2023, **62**, e202310788.
- 24K. Qi, Y. Zhang, N. Onofrio, E. Petit, X. Cui, J. Ma, J. Fan, H. Wu, W. Wang, J. Li, J. Liu, Y. Zhang, Y. Wang, G. Jia, J. Wu, L. Lajaunie, C. Salameh and D. Voiry, *Nat. Catal.*, 2023, **6**, 319–331.
- 25W. Niu, Z. Chen, W. Guo, W. Mao, Y. Liu, Y. Guo, J. Chen, R. Huang, L. Kang, Y. Ma, Q. Yan, J. Ye, C. Cui, L. Zhang, P. Wang, X. Xu and B. Zhang, *Nat. Commun.*, 2023, **14**, 4882.
- 26K. Zhao, X. Nie, H. Wang, S. Chen, X. Quan, H. Yu, W. Choi, G. Zhang, B. Kim and J. G. Chen, *Nat. Commun.*, 2020, **11**, 2455.
- 27S. A. Francis, J. M. Velazquez, I. M. Ferrer, D. A. Torelli, D. Guevarra, M. T. McDowell, K. Sun, X. Zhou, F. H. Saadi, J. John, M. H. Richter, F. P. Hyler, K. M. Papadantonakis, B. S. Brunshwig and N. S. Lewis, *Chem. Mater.*, 2018, **30**, 4902–4908.

- 28 A. R. Paris and A. B. Bocarsly, *ACS Catal.*, 2017, **7**, 6815–6820.
- 29 Y. Zhou, A. J. Martín, F. Dattila, S. Xi, N. López, J. Pérez-Ramírez and B. S. Yeo, *Nat. Catal.*, 2022, **5**, 545–554.
- 30 K. U. D. Calvino, A. B. Laursen, K. M. K. Yap, T. A. Goetjen, S. Hwang, N. Murali, B. Mejia-Sosa, A. Lubarski, K. M. Teeluck, E. S. Hall, E. Garfunkel, M. Greenblatt and G. C. Dismukes, *Energy Environ. Sci.*, 2018, **11**, 2550–2559.
- 31 M. Esmacilrad, Z. Jiang, A. M. Harzandi, A. Kondori, M. Tamadoni Saray, C. U. Segre, R. Shahbazian-Yassar, A. M. Rappe and M. Asadi, *Nat. Energy*, 2023, **8**, 891–900.
- 32 H. Zhong, K. Fujii, Y. Nakano and F. Jin, *J. Phys. Chem. C*, 2015, **119**, 55–61.