Supporting Information for

Enhanced Electrochemical CO₂ Reduction to C₂₊ Products on Porous CuCo Bimetallic Electrodes via Prereduction in Alkaline Solution

Xiaofan Hou^a, Feifei You^b, Minghui Zhao^a, Mingming Peng^a, Na Lyu^a, Kenji Kamiya^a, Eika W. Qian^{a*}

^aGraduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Nakacho 2-24-16, Koganei, Tokyo 184-8588, Japan

^bCollege of Textile and Clothing, Yancheng Institute of Technology, Yancheng 224051, P.R. China

^{*}Corresponding author. Tel: +81-0423887410. Fax: ++81-0423887410.

E-mail address: whqian@cc.tuat.ac.jp (E.W. Qian).

Chemicals and materials. Chemicals used in this work containing trisodium citrate dihydrate (Na₃C₆H₅O₇·2H₂O), nitric acid (HNO₃), urea (CH₄N₂O), cobaltous nitrate hexahydrate (Co (NO₃)₂·6H₂O) and copper(ii) nitrate hydrate (Cu (NO₃)₂·3H₂O) were all bought from FUJIFILM Wako pure Chemical Corporation and KISHIDA CHEMICAL Co., Ltd. (Japan). Above reagents were all analytical reagents and without further purified.

Characterizations and product analysis. Scanning electron microscope (SEM; JSM-6510, Japan) was applied to explore the prepared electrodes' morphology. Transmission electron microscope (TEM; JEOL ARM-200F) was conducted to characterize the particles exfoliated from the electrode surface. X-ray diffraction (XRD; RINT2100VPC/N, Japan) with Cu-Ka radiation was used to determine the chemical information. The outmost surface composition was determined by X-ray photoelectron spectroscopy (XPS) measurements (Thermo-VG Scientific, USA). The surface roughness and related data were detected via atomic force microscope (AFM; SPM-9700HT, Japan). Fourier transform infrared (FTIR) measurements were conducted via a Bruker Vertex 70 FTIR spectrometer which equipped KBr pellet technique.

All electrochemical reduction reactions were measured in a typical H-cell with threeelectrode configuration via electrochemical workstation (CHI760E). The saturated silver chloride reference electrode (Ag/AgCl) worked as reference electrode, the platinum wire played the role as counter electrode, and CuCo-related electrodes were used as working electrodes. The cathode and anode section were separated by a proton exchange membrane (Nafion®212) so that only H⁺ could be transferred between 2 compartment and products were prevented to shift to and oxidized in anode compartments. After the KHCO₃ solution was purged with N₂ for at least 30 mins to achieve N₂ saturation, CV was performed in the N₂-saturated electrolyte at a scan rate of 50 mV s⁻¹. Prior to recording the CV data, the CV was cycled for at least 30 mins and over 30 cycles until the CV curves of consecutive scans completely overlapped. Subsequently, LSV measurements were conducted at a scan rate of 5 mV s⁻¹. Similarly, CO₂ was introduced to replace N₂ and bubbled into the cathode, and both CV and LSV measurements were carried out under CO2-saturated conditions. Again, before recording the CV and LSV data, the CV was cycled for at least 30 mins and over 30 cycles until the consecutive CV curves fully overlapped. After conducting CV and LSV under CO₂-saturated conditions, we performed electrolysis of CO₂ at different potentials, with each electrolysis process lasting for one hour. Electrochemical specific active surface area (ECSA) of E-CuCo and CuCo in this work was determined and calculated via CV test under different scan rates and electrochemical double-layer capacitance in the non-Faradaic area. The electrodes performance was also characterized by electrochemical impedance spectroscopy (EIS) in the mode of AC impedance at electrolysis voltage with the frequency from 0.1 M Hz to 0.01 Hz. ECR electrolysis at different potentials was measured to determine the potential effect and electrode performance. After electrolysis, both gaseous and liquid products were collected from the top of gas-tight cell and electrolyte, respectively and then investigated by GC, LC or NMR.

The Faradaic efficiency (*FE*) was calculated against calibration curve and using Eq. (1):[1]

$$FE = \frac{mnF}{Q}$$
(1)

Where m means the electrons needed when CO_2 reduced to a certain product of 1 mol, *n* is the product amount (mol) generated from ECR in 1 h, *F* is Faraday constant (*F* = 96485 C mol⁻¹), *Q* is the quantity of electric charge consumed from a certain time of ECR.



Fig. S1. SEM mapping images of CuCo for Co (yellow), Cu (blue) and O (white).



Fig. S2. AFM images of E-CuCo.



Fig. S3. Cu LMM of CuCo and E-CuCo.



Fig. S4. HRTEM images of E-CuCo.



Fig. S5. TEM mapping, Co (green) and Cu (red) of CuCo.



Fig. S6. I-t curves of (a) CuCo and (b) E-CuCo at different potentials.



Fig. S7. H_2 , C_1 and C_{2+} products selectivity of (a) CuCo and (b) E-CuCo.



Fig. S8. ECR product analysis of CuCo in CO₂-saturated KHCO₃ at different potentials.



Fig. S9. (a) LSV curves under CO_2 and N_2 conditions and (b) HER selectivity of E-Cu.



Fig. S10. Stability and (a) i-t curve, (b) SEM, (c-d) XPS and (e) Cu LMM spectrum of E-CuCo after long-term electrolysis during ECR.



Fig. S11. Potential-dependent ATR-SEIRAS spectra recorded during ECR on (a) CuCo, (b) E-CuCo electrode in a CO_2 -sturated 0.5 M KHCO₃ solution ranging from 1000 to 4000 cm⁻¹.



Fig. S12. ATR-SEIRAS study of CO intermediates produced in CO_2 -purged 0.5 M KHCO₃ electrolyte in real time for (a) CuCo and (b) E-CuCo.



Fig. S13. *In situ* ATR-SEIRAS spectra of O-H stretching vibration at applied potentials from 0 to -1.6 V vs. Ag/AgCl in CO₂-saturated KHCO₃ solution on (a) CuCo and (b) E-CuCo.



Fig. S14. Schematic illustration of E-CuCo for ECR to C_{2^+} products.

	Ra[nm]	Rz[nm]	Rzjis [nm]	Rq[nm]	Rp[nm]	Rv[nm]
CuCo	167.299	749.654	371.513	191.354	284.452	465.202
E-CuCo	213.861	938.838	450.148	243.247	421.861	516.977

Table S1. Roughness parameters of CuCo and E-CuCo.

	Co 2p				
	Binding energy (eV)	Full width high maximum (eV)	Area (cps, eV)	Content	
$Co^0 2p_{3/2}$	778.69	1.7	291.45	42.26%	
$Co^0 2p_{1/2}$	793.65	1.71	149.84		
$Co^{2+}2p_{3/2}$	780.12	3.01	397.67	57.74%	
$Co^{2+} 2p_{1/2}$	795.66	3.01	204.70		
	С	u 2p			
	Binding energy (eV)	Full width high maximum (eV)	Area (cps, eV)	Content	
$Cu^{+}2p_{3/2}$	932.56	2.39	1738.94	55.68%	
$Cu^{+}2p_{1/2}$	952.45	2.39	950.38		
$Cu^{2+}2p_{3/2}$	934.13	2.51	1381.33	44.32%	
$Cu^{2+}2p_{1/2}$	954.38	2.51	583.31	_	

Table S2. A summary of peak area ration and the full width at half maximum of eachpeak for CuCo according to XPS peaks fitting results.

		Co 2p		
	Binding energy (eV)	Full width high maximum (eV)	Area (cps, eV)	Content
$Co^0 2p_{3/2}$	780.08	2	291.45	55.4%
$Co^0 2p_{1/2}$	795.85	2	149.84	
$Co^{2+} 2p_{3/2}$	781.66	2	397.67	44.6%
$Co^{2+} 2p_{1/2}$	797.45	2	204.70	
		Cu 2p		
	Binding energy (eV)	Full width high maximum (eV)	Area (cps, eV)	Content
$Cu^+ 2p_{3/2}$	932.21	1.43	3029.04	100%
$Cu^+ 2p_{1/2}$	951.95	1.57	2291.56	

Table S3. A summary of peak area ration and the full width at half maximum of each peak for E-CuCo according to XPS peaks fitting results.

Electrodes	Applied potential	FE (%)	Reference	
E-CuCo	-0.65 V vs RHE	C ₂₊ , 35.12% n-propanol, 6.92%	This work	
E-CuCo	-0.85 V vs RHE	C ₂₊ , 29.89% n-propanol, 10.50%	This work	
Cu ₂ S-Cu-V	-0.95 V vs RHE	$C_{2+},32\pm1\%$ n-propanol, $8\pm0.7\%$	[2]	
Cu-B	-1.15 V vs RHE	C ₂₊ , 53.5% n-propanol, 7.1%	[3]	
Cu-P	-1.15 V vs RHE	C ₂₊ , 50.3% n-propanol, 5.1%	[3]	
trans-CuEn	-0.86 V vs RHE	C ₂₊ , 55.2% n-propanol, 3.5%	[4]	
trans-CuEn 2	-0.75 V vs RHE	C ₂₊ , 50.3% n-propanol, 3.5%	[4]	
Cu nanocrystals-20	-0.85 V vs RHE	C ₂₊ , 38.3% n-propanol, 10.6%	[5]	
Plasma-Activated Copper Nanocube	-1.0 V vs RHE	C ₂₊ , 73% n-propanol, 9%	[6]	
Cu ₂ O-Derived Cu Catalysts	-0.98 V vs RHE	C ₂₊ , 59.8% n-propanol, 5.4%	[7]	
Cu (100) electrode	-1.0 V vs RHE	C ₂₊ , 76% n-propanol, 5.5%	[8]	
Cu foil KF cycled	-1.0 V vs RHE	C ₂₊ , 28% n-propanol, 3.08%	[9]	
Cu ₂ O-derived Cu with PdCl ₂	-0.9 V vs RHE	C ₂₊ , 37.7% n-propanol, 6.1%	[10]	
Cu ₄ Zn	-1.05 V vs RHE	C ₂₊ , 51.39% n-propanol, 4.39%	[11]	

Table S4. Comparison of the performances of ECR to n-propanol and C_{2^+} products performances of Cu-based electrodes.

Electrodes	Applied potential	FE (%)	Reference
CoP ₂ O ₆ /HCS-Cu	-0.66 V vs RHE	Formate, 89.9%	[12]
CoCu-N-C	-0.68 V vs RHE	CO, 76.5%	[13]
CoCu(1:3)-N-C-900	-0.53 V vs. RHE	CH ₄ , 21% CO, 35% H ₂ , 30%	[14]
Co ₃ Cu/CFs	-0.8 V vs. RHE	CO, 68 HCOOH, 29%	[15]
Co ₃ O ₄ /Cu HNT	-0.4 V vs RHE	CO, 98%	[16]
Sn-Co/Cu foam	-1.36 V vs RHE	Formate, 72.2%	[17]
Cu-Co bimetallic nanoparticles	-2.1 V vs. Ag/Ag ⁺	CO, 97.4%	[18]
Cobalt-decorated copper thin films	-0.65 V vs RHE	Formate, 80%	[19]
Copper Cobalt Selenide	-0.9 V vs RHE	Formate, 24.18% Ethanol, 23.63% Acetate, 27.82% Methanol, 15.65%	[20]
Copper Cobalt Selenide	-0.25 V vs RHE	Acetate, 98.13%	[20]
Copper Cobalt Selenide	-0.1 V vs RHE	Ethanol, 27.62% Acetate, 65.92%	[20]

Table S5. Comparison of the performances of ECR on Cu and Co-based electrodes.

-

Reference

[1] J.J. Wu, F. Risalvato, X.D. Zhou, Effects of the Electrolyte on Electrochemical Reduction of CO_2 on Sn Electrode, Ecs Transactions, 41 (2012) 49-60.

[2] Z.-Q.L. Tao-Tao Zhuang, Ali Seifitokaldani, Yi Li, Phil De Luna, Thomas Burdyny, Fanglin Che, Fei Meng, Yimeng Min, Rafael Quintero-Bermudez, Cao Thang Dinh, Yuanjie Pang, Miao Zhong, Bo Zhang, Jun Li, Pei-Ning Chen, Xue-Li Zheng, Hongyan Liang, Wen-Na Ge, Bang-Jiao Ye, David Sinton, Shu-Hong Yu & Edward H. Sargent, Steering post-C–C coupling selectivity enables high efficiency electroreduction of carbon dioxide to multi-carbon alcohols, Nature Catalysis, 1 (2018) 421-428.

[3] H. Li, X. Qin, T. Jiang, X.Y. Ma, K. Jiang, W.B. Cai, Changing the Product Selectivity for Electrocatalysis of CO₂ Reduction Reaction on Plated Cu Electrodes, ChemCatChem, 11 (2019) 6139-6146.

[4] D. Kim, C.S. Kley, Y. Li, P. Yang, Copper nanoparticle ensembles for selective electroreduction of CO_2 to C_2 - C_3 products, Proc Natl Acad Sci USA, 114 (2017) 10560-10565.

[5] N.T.W. Dan Ren, Albertus Denny Handoko, Yun Huang, and Boon Siang Yeo, Mechanistic Insights into the Enhanced Activity and Stability of Agglomerated Cu Nanocrystals for the Electrochemical Reduction of Carbon Dioxide to n-Propanol, The Journal of Physical Chemistry Letters, 7 (2015) 20-24.

[6] I.Z. Dunfeng Gao, Nuria J. Divins, Fabian Scholten, Ilya Sinev, Philipp Grosse, and Beatriz Roldan Cuenya, Plasma-activated copper nanocube catalysts for efficient carbon dioxide electroreduction to hydrocarbons and alcohols, ACS Nano, 11 (5) (2017) 4825–4831.

[7] A.D. Handoko, C.W. Ong, Y. Huang, Z.G. Lee, L. Lin, G.B. Panetti, B.S. Yeo, Mechanistic Insights into the Selective Electroreduction of Carbon Dioxide to Ethylene on Cu_2O -Derived Copper Catalysts, The Journal of Physical Chemistry C, 120 (2016) 20058-20067.

[8] R.M. Arán-Ais, F. Scholten, S. Kunze, R. Rizo, B. Roldan Cuenya, The role of in situ generated morphological motifs and Cu(i) species in C_{2+} product selectivity during CO_2 pulsed electroreduction, Nature Energy, 5 (2020) 317-325.

[9] Y. Kwon, Y. Lum, E.L. Clark, J.W. Ager, A.T. Bell, CO₂ Electroreduction with Enhanced Ethylene and Ethanol Selectivity by Nanostructuring Polycrystalline Copper, ChemElectroChem, 3 (2016) 1012-1019.

[10] C.S. Chen, J.H. Wan, B.S. Yeo, Electrochemical Reduction of Carbon Dioxide to Ethane Using Nanostructured Cu₂O-Derived Copper Catalyst and Palladium(II) Chloride, The Journal of Physical Chemistry C, 119 (2015) 26875-26882.

[11] D. Ren, B.S.-H. Ang, B.S. Yeo, Tuning the Selectivity of Carbon Dioxide Electroreduction toward Ethanol on Oxide-Derived CuxZn Catalysts, ACS Catal., 6 (2016) 8239-8247.

[12] J. Du, Y. Han, H. Zhang, X. Gao, J. Guan, A. Chen, CoP₂O₆-Assisted Copper/Carbon Catalyst for Electrocatalytic Reduction of CO₂ to Formate, ACS Nano, 17 (2023) 10055-10064.

[13] S. Yin, J. Zhao, S. Wu, X. Wang, Y. Quan, J. Ren, Electrochemical reduction of CO₂ to CO on bimetallic CoCu–N–C catalyst, Journal of Cleaner Production, 371 (2022).

[14] R. Ke, F. Zhang, D. Chen, W. Ming, X. Zhang, Y. Wang, Y. Wang, Copper and cobalt loading carbon as an efficient catalyst for the electroreduction CO_2 to CO and hydrocarbons, Surfaces and Interfaces, 31 (2022).

[15] C. He, S. Wang, X. Jiang, Q. Hu, H. Yang, C. He, Bimetallic Cobalt-Copper Nanoparticle-Decorated Hollow Carbon Nanofibers for Efficient CO₂ Electroreduction, Front Chem, 10 (2022) 904241.

[16] Z. Cheng, X. Wang, H. Yang, X. Yu, Q. Lin, Q. Hu, C. He, Construction of cobaltcopper bimetallic oxide heterogeneous nanotubes for high-efficient and low-overpotential electrochemical CO₂ reduction, Journal of Energy Chemistry, 54 (2021) 1-6.

[17] Q. Hu, M. Xu, S. Hu, P.-L. Tremblay, T. Zhang, Selective electrocatalytic reduction of carbon dioxide to formate by a trimetallic Sn-Co/Cu foam electrode, J. Electroanal. Chem., 877 (2020).

[18] W. Guo, J. Bi, Q. Zhu, J. Ma, G. Yang, H. Wu, X. Sun, B. Han, Highly Selective CO₂ Electroreduction to CO on Cu–Co Bimetallic Catalysts, ACS Sustainable Chemistry & Engineering, 8 (2020) 12561-12567.

[19] C. Dai, L. Sun, J. Song, H. Liao, A.C. Fisher, Z.J. Xu, Selective Electroreduction of Carbon Dioxide to Formic Acid on Cobalt-Decorated Copper Thin Films, Small Methods, 3 (2019).

[20] A. Saxena, S. Kapila, J.E. Medvedeva, M. Nath, Copper Cobalt Selenide as a Bifunctional Electrocatalyst for the Selective Reduction of CO₂ to Carbon-Rich Products and Alcohol Oxidation, ACS Appl Mater Interfaces, (2023).