Supporting Information

for

Compositional Gradient Au-Cu Bimetallic Heterostructures for

Electroreduction of CO₂ to Ethanal at Low Potential

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Contents

Details of characterization, electrode preparation, electrochemical measurements, product analysis, DFT Calculation and data analysis results, including SEM and TEM images, energy dispersive spectroscopy line scan elemental analysis, Elemental mapping images, HRTEM images, intensity profile across the particle of catalyst, PXRD patterns, optical extinction spectra, high-resolution XPS spectra, Cu LMM Auger spectra, Au/Cu atomic ratios value, product FE distributions, ¹H NMR patterns, CV curves, EIS plots, Tafel slope, proposed reaction pathways, peak parameters used to fit the high-resolution XPS spectra, the corresponding impedance values calculated by fitting, Cu^+/Cu^0 peak area ratio, charge density difference of key intermediates on catalysts surface, top and side views of the optimized structure for intermediates on catalysts surfaces, intermediates detected and their corresponding band positions in *in situ* ATR-FTIR during CO₂RR, and a comparison of electrocatalytic performance of typical catalysts in the electrochemical CO₂ reduction to alcohols.

Characterizations

The size and morphology of the nanoparticles were characterized by a transmission electron microscope (TEM, Philips Tecnai G2 20) operating at an accelerating voltage of 200 kV. The structure and composition of nanoparticles were further analyzed by high-angle annular dark field (HAADF) imaging and energy dispersive spectroscopy (EDX) element mapping, utilizing a Bruker Nano GmbH microscope (Berlin Germany). UV-vis spectra were recorded over the range of 400-1000 nm using UV-3600 spectrophotometer (Shimadzu, Japan). Samples for analysis were dispersed in ethanol and placed in quartz cuvettes. Powder X-ray Diffraction (PXRD) data were acquired using a Bruker axs D8 Discover (Cu K α = 1.5406 Å), with samples prepared by drop casting nanoparticles onto cover glasses. X-ray Photoelectron Spectroscopy (XPS) data were obtained on a VG Multilab 2000 photoelectron spectrometer equipped with a monochromatic Al Ka source. The content of gold and copper was quantified by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using an iCAP 7000 instrument (Thermo Fisher). The content of gold and copper was quantified by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using an iCAP 7000 instrument (Thermo Fisher). Standard curves were established using known concentrations of gold and copper solutions, and sample solutions were prepared by dissolving nanoparticles in aqua regia, followed by dilution with ultrapure water. In situ Raman spectra were collected by a Thermo Fisher DXR3 confocal Raman microscope equipped with a diode laser beam (532 nm) with a 50x magnification long working distance microscope objective. Prior to each Raman spectrum collection, a pre-applied potential was maintained for 3 minutes. Additionally, in-situ Fourier-transform infrared spectroscopy (FTIR, Thermo Nicolet iS50, USA) was employed to monitor the formation of intermediates and products during electrochemical CO₂ reduction reaction (CO_2RR) under varying potentials.

Preparation of electrodes

Glassy carbon plates (2 cm ×1 cm, SIGRACET GDL 29BC) loaded with electrocatalysts served as the working electrode. The Electrocatalyst ink were prepared by thoroughly mixing the nanoparticles (~1.5–6 mg) with a Nafion solution (1.5 mL, 0.25 wt%) diluted in isopropanol. The working electrode was then prepared by evenly depositing 200 μ L of the ink onto the carbon plates, followed by drying under infrared lamp irradiation for 30 seconds. A platinum mesh and an Ag/AgCl electrode (Gooss union-1038) served as the counter electrode and reference electrode, respectively.

Electrochemical measurements

All electrochemical measurements were performed using an Interface 1010E workstation (Gamry, America) at room temperature. A three-electrode system was employed for CO₂RR measurements in a custom airtight H cell, which was divided into anodic and cathodic compartments by a proton exchange membrane (Nafion 117). Each compartment was filled with 35 mL 0.1 M KHCO₃ aqueous solution, leaving approximately 30 mL of headspace. The H-cell was purged with CO₂ and N₂ of 30 mL/min for 15 minutes until the KHCO₃ was saturated. Subsequently, the CO₂ flow rate was adjusted to 20 mL/min before initiating the measurements. Linear sweep voltammetry (LSV) curves were measured in N₂ and CO₂ separately to assess the electrochemical CO₂ reduction activity of the samples, with a scan rate of 50 mV s⁻¹ over a potential range from 0 to -1.4 V versus the reversible hydrogen electrode (vs RHE; all potentials are referenced to RHE).

The cyclic voltammetry curves (CV) were used to determine the electrochemical surface area (ECSA) of the electrode at various scanning rates (10, 20, 40, 60, 80 and 100 mV s⁻¹) in the non-Faraday region. ECSA can be calculated by the following equation:

$$C_{dl} = \Delta j / v \tag{1}$$

$$S_{rf} = C_{dl \text{ sample}}/C_{dl \text{ blank}}$$
 (2)

$$ECSA = S_{rf} \times A_{geo}$$
 (3)

 C_{dl} was obtained from the linearly related slope of the changing current (Δj) and the sweep speed (v); S_{rf} represents the roughness factor; A_{geo} represents the geometric area of the electrode ($A_{geo} = 2 \text{ cm}^2$).

Electrochemical impedance spectroscopy (EIS) was conducted at -0.4 V vs RHE, with a frequency range from 10 to 10^5 Hz and an amplitude of 10 mV. The reduction of CO₂ was carried out at applied potentials of -0.4 V, -0.6 V, -0.8 V, -1.0 V, and -1.2 V relative to RHE for a duration of 40 minutes using chronoamperometry. All electrode potentials were converted according to the following equation by equal,

$$E (vs RHE) = E (vs Ag/AgCl) + 0.20 V + 0.0591 V*pH$$
 (4)

Product analysis

Liquid products (HCOOH, methanol, EtOH, and acetate) were analyzed via 1H nuclear magnetic resonance (NMR). The gas phase products (H₂, CO, CH₄, and C₂H₄) of CO_2RR were collected from the cathode compartments and directly introduced into a gas chromatography (GC9790II, Zhejiang Fuli Analyzing Instruments Co. Ltd.) before flowing through a drying tube. The gas product was injected into the GC every 11 minutes, using high-purity nitrogen (99.999%) as the carrier gas. The gas mixture was analyzed using a thermal conductivity detector (TCD) for hydrogen content and a flame ionization detector (FID) for carbon-containing compounds.

The FE of gas products was calculated by the following equation:

$$FE = \frac{n \cdot F \cdot G \cdot ppm \cdot P_0}{I \cdot R \cdot T} \tag{5}$$

Where n represents the number of electrons transferred during the CO₂RR (i.e., $n_{C0} = 2$, $n_{H_2} = 2$, $n_{C_2H_4} = 12$); F represents the Faraday constant (96485 C•mol⁻¹); G represents the flow rate of CO₂; I is the current under specific potential; P₀ = 1.01 × 10⁵ Pa; R = 8.314 J mol⁻¹ K⁻¹; T = 298.15 K.

Isotopic labeling study

For electroreduction of ${}^{13}CO_2$, the electrochemical cell was first completely sealed after both the electrolyte and headspace were purged with ${}^{13}CO_2$ at 50.00 cm³ min⁻¹ for 5 min. The electrolysis was then performed over AuCu-g at -0.4 V versus RHE for 5 h. The liquid-phase products were analyzed in the same way as in ${}^{12}CO_2$ electrolysis.

DFT calculation

The density functional theory (DFT) calculations were carried out with the VASP code.¹ The Perdew–Burke–Ernzerhof (PBE)² functional within generalized gradient approximation (GGA)³ was used to process the exchange–correlation, while the projectoraugmented-wave pseudopotential (PAW) was applied with a kinetic energy cut-off of 500 eV, which was utilized to describe the expansion of the electronic eigenfunctions. The vacuum thickness was set to be 15 Å to minimize interlayer interactions. The Brillouin-zone integration was sampled by a Γ -centered 7 × 7 × 1 Monkhorst–Pack k-point. All atomic positions were fully relaxed until energy and force reached a tolerance of 1 × 10⁻⁶ eV and 0.01 eV/Å, respectively. The dispersion corrected DFT-D method was employed to consider the long-range interactions.⁴ Considering the solvation environment, we constructed an explicit solvation model with one layer H₂O molecules in calculation models. Employing the climbing image nudged elastic band method (CI-NEB), we computed the minimum energy pathway of the reaction along with its corresponding activation barrier.

The Gibbs free energy change (ΔG) was calculated by computational hydrogen electrode (CHE) model as follows:

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S \qquad (6)$$

where ΔE is the reaction energy obtained by the total energy difference between the reactant and product molecules absorbed on the catalyst surface and ΔS is the change in entropy for each reaction, ΔZPE is the zero-point energy correction to the Gibbs free energy.

The differential charge density was computed under a -0.4 V vs RHE potential to simulate the electrochemical environment, considering the influence of applied bias on charge redistribution and electronic interactions at the interface.

Figures and tables



Figure S1. TEM images of (a) Au and (b) Au@Cu₂O NPs. (c) SEM image of Au@Cu₂O NPs.



Figure S2. (a) TEM and (b) High resolution TEM images of Cu@Cu₂O NPs. (c) Elemental mapping image and (d) Selected area electron diffraction pattern of Cu@Cu₂O NPs.



Figure S3. (a-b) Elemental mapping images and (c) dark field TEM image of AuCu-g NPs. (d) EDX line scan elemental analysis along the red dashed line in plane c.



Figure S4. Optical extinction spectra of samples.



Figure S5. (a) XPS profiles of Au 4f for Au NPs and (b) Cu 2p for Au@Cu₂O NPs.



Figure S6. The Au/Cu atomic ratios of the samples were calculated from XPS and ICP, respectively.



Figure S7. FE toward CO₂ reduction major products over Au NPs at different potentials.



Figure S8. The ¹H NMR patterns of EtOH produced from ${}^{12}CO_2$ or ${}^{13}CO_2$ electrocatalysis over AuCu-g NPs at -0.4 V versus RHE.



Figure S9. PXRD patterns of AuCu-1 and AuCu-2 NPs. The standard diffraction patterns for bulk Au (PDF # 04-0784) and Cu (PDF # 04-0836) are plotted for comparison.



Figure S10. The Au/Cu atomic ratios of the samples were calculated from XPS and ICP, respectively.



Figure S11. (a) TEM image of AuCu-1 NPs. (b) Dark field TEM image, (c) EDX line scan elemental analysis along the yellow dashed line in plane b, and (d) elemental mapping images of AuCu-1 NPs.



Figure S12. (a) TEM image of AuCu-2 NPs. (b) Dark field TEM image, (c) EDX line scan elemental analysis along the red dashed line in plane b, and (d) elemental mapping images of AuCu-2 NPs.



Figure S13. (a) High-resolution XPS spectra of the Cu 2p and (b) Cu LMM Auger spectrum of AuCu-1 NPs.



Figure S14. (a) High-resolution XPS spectra of the Cu 2p and (b) Cu LMM Auger spectrum of AuCu-2 NPs.



Figure S15. FE toward CO₂ reduction major products over AuCu-1 and AuCu-2 NPs at different potentials.



Figure S16. PXRD patterns of AuCu-a NPs. The standard diffraction patterns for bulk Au (PDF # 04-0784), Cu₂O (PDF # 34-1354) and Cu (PDF # 04-0836) are plotted for comparison.



Figure S17. XPS profiles of the (a) Au 4f and (b) Cu 2p for AuCu-a NPs.



Figure S18. Cu LMM Auger spectrum of AuCu-a NPs.



Figure S19. FE toward CO₂ reduction major products over AuCu-a NPs at different potentials.



Figure S20. Cu LMM Auger spectrum of Au@Cu₂O NPs.



Figure S21. FE toward CO₂ reduction major products over Au@Cu₂O NPs at different potentials.



Figure S22. PXRD pattern of Au@Cu NPs. The standard diffraction patterns for bulk Au (PDF # 04-0784), Cu₂O (PDF # 34-1354) and Cu (PDF # 04-0836) are plotted for comparison.



Figure S23. (a) TEM image of Au@Cu NPs. (b) Dark field TEM image, (c) EDX line scan elemental analysis along the purple dashed line in plane b, and (d) elemental mapping images of Au@Cu NPs.



Figure S24. High-resolution XPS spectra of Cu 2p and (b) Cu LMM Auger spectrum of Au@Cu NPs.



Figure S25. FE toward CO_2 reduction major products over Au@Cu NPs at different potentials.



Figure S26. High-resolution XPS spectra of the Cu 2p regions of AuCu-g NPs (after 75 h electrolysis).



Figure S27. Determination of double-layer capacitance. CV curves of (a) Blank, (b) Au, (c) $Au@Cu_2O$, (d) Au@Cu, (e) AuCu-a and AuCu-g in 0.1 M KHCO₃ at different sweep rates of 10, 20, 40, 60, 80 and 100 mV s⁻¹.



Figure S28. Current due to double-layer charging plotted against CV scan rate.



Figure S29. High-resolution XPS spectra of the Cu 2p regions and (b) Cu LMM Auger spectrum of AuCu-g NPs after stability test for different times.



Figure S30. (a) TEM image of AuCu-g NPs after electrolysis. (b) Dark field TEM image, and (c-f) elemental mapping images of AuCu-g NPs after electrolysis.



Figure S31. CV curves of AuCu-g NPs in 0.1 M KHCO₃ at a sweep rate of 50 mV s⁻¹.



Figure S32. Electrochemical impedance spectroscopy plots (inset is the corresponding fitting circuit) of different catalysts at -0.4 V versus RHE.



Figure S33. Tafel plots of the CO product.



Figure S34. In situ Raman spectra of (a) Au@Cu₂O, (b) Au@Cu and (c) AuCu-g NPs during CO_2 reduction.



Figure S35. In situ Raman spectra of Au@Cu₂O and Au@Cu NPs during CO₂ reduction.



Figure S36. In situ ATR-FTIRS spectra of AuCu-g electrode during CO_2 reduction.



Figure S37. Proposed reaction pathway for the CO_2RR to CH_3OH .



Figure S38. In situ ATR-FTIRS spectra of Au@Cu₂O electrode during CO₂ reduction.



Figure S39. In situ ATR-FTIRS spectra of Au@Cu electrode during CO2 reduction.



Figure S40. Proposed reaction pathways for the CO₂RR to EtOH.



Figure S41. Charge density difference of key intermediates *CO on (a) Cu (111), (b) Cu_2O (111), and (c) Au-Cu/Cu₂O.



Figure S42. Charge density difference of Au-Cu/Cu₂O interfaces at -0.4 V versus RHE. Yellow contours represent charge accumulations, and purple contours denote charge depressions. Cu: orange, Au: yellow, O: red.



Figure S43. Top and side views of the optimized structure for intermediates on the catalysts surface. Cu: orange, Au: yellow, C: grey, H: white, O: red.



Figure S44. Top and side views of the optimized structure for intermediates on the catalysts surface. Cu: orange, Au: yellow, C: grey, H: white, O: red.



Reaction coordinate

Figure S45. Energy profiles of the CO_2RR to *CO and *OCCO intermediates on surfaces of Cu (111), Cu₂O (111), and Au-Cu/Cu₂O.



Figure S46. Side views of the optimized structure for H* on catalysts surface. Cu: orange, Au: yellow, H: white, O: red.



Reaction coordinate

Figure S47. Energy profiles of *H on surfaces of Cu/Cu₂O and Au-Cu/Cu₂O.

Peak Catalyst	Au 4f 7/2 (eV)	Au 4f 5/2 (eV)	Cu 2p 3/2 (eV)	Satellite (eV)	Cu 2p 1/2 (eV)
Au	83.7	87.4	-	-	-
Au@Cu ₂ O	-	-	932.0 933.8	940.5 944.0	951.7 953.7
Au@Cu	-	-	932.4 934.2	942.2 944.0	952.2 954.0
AuCu-a	83.8	87.5	932.7 931.5	945.7	952.7 951.3
AuCu-g	84.1	87.8	931.9 933.8	941.1 943.5	951.7 953.6
AuCu-1	84.4	88.1	932.3 934.2	941.0 943.5	952.1 954.1
AuCu-2	84.2	87.9	932.2 934.2	941.5 943.8	951.9 953.8
AuCu-g (after 25h electrolysis)	84.8	88.5	932.9 934.6	941.1 944.1	952.8 954.4
AuCu-g (after 50h electrolysis)	84.8	88.4	933.1 934.8	942.3 944.5	952.9 954.9
AuCu-g (after 75h electrolysis)	84.6	88.3	932.9 934.8	942.2 944.2	952.8 954.9
AuCu-g (after 100h electrolysis)	84.5	88.1	932.6 934.4	942.1 944.5	954.8 952.5

Table S1. Peak parameters employed to analyze the XPS of samples.

Au	Overpotential (V)	FE(CO)	FE(H ₂)	_				
	0.4	29.3	70.7					
	0.6	88.8	11.2					
	0.8	91.2	8.8					
	1.0	81.1	18.9					
	1.2	51.7	48.3					
	Owner at antial (V)	EE(CO)	FF(II)	EE (E4OII)	EE(C II)			
Au@Cu	Overpotential (V)	18.0	FE (H ₂)	7 1	$\mathbf{FE}(\mathbf{C}_{2}\mathbf{\Pi}_{4})$			
	0.4	18.0	75.4	1.1	-			
	0.0	-	76.3	1.5	-			
	1.0	20.7	10.5	10.6	-			
	1.0	20.1	40.4	10.0	22.2			
	1.2	20.1	40.3	10.2	23.3			
Au@Cu ₂ O	Overpotential (V)	FE(CO)	FE(H ₂)	FE(EtOH)	FE(CH ₄)	$FE(C_2H_4)$		
	0.4	-	70.7	29.3	-	-		
	0.6	-	56.2	39.7	-	-		
	0.8	8.1	82.5	1.0	-	-		
	1.0	21.1	75.6	2.4	-	-		
	1.2	10.1	68.6	-	7.6	13.4		
AC		ER (GO)		EE (E. OVE		_		
Aucu-a	Overpotential (V)	FE(CO)	FE(H ₂)	FE(EtOH)	FE(CH ₃ OH)			
	0.4	27.5	55.9	11.3	5.3			
	0.6	9.7	69.1	15.8	1.4			
	0.8	22.4	59.1	12.9	1.2			
	1.0	60.3	35.7	-	-			
	1.2	43.3	49.9	2.3		_		
AuCu-g	Overpotential (V)	FE(CO)	FE(H ₂)	FE(EtOH)	FE(CH ₃ OH			
	0.4	-	-	84.6	14.1	-		
	0.6	-	71.7	19.7	6.8			
	0.8	13.8	79.7	3.4	3.8			
	1.0	20.0	74.9	3.1	2.0			
	1.2	20.7	72.3	2.7	3.6			
						_		
AuCu-1	Overpotential (V)	FE(CO)	FE(H ₂)	FE(EtOH)	FE(CH ₃ OH)	FE(HCOOH)	$FE(C_2H_4)$	FE(CH ₄)
	0.4	-	-	72.2	25.0	-	-	-
	0.6	15.6	52.1	26.2	6.0	3.7	-	-
	0.8	20.8	58.8	14.0	1.8	9.5	-	-
	1.0	57.3	25.3	6.9	-	9.0	4.7	-
	1.2	53.9	15.9	5.1	-	5.9	8.9	9.0
AuCu-2	Overpotential (V)	FE(CO)	FE(H.)	FE(EtOH)	FE(CH.OH	FE(HCOOH)	FE(C.H.)	-
15 - 017 (018 (018 (018 (017 (017 (018 (018 (018 (018 (018 (018 (018 (018	0.4	13.0		75.5	6.0	-		-
	0.6	36.0	-	54.3	4.1	3.7	-	
	0.8	24.7	63.2	10.5	1.1	9.5	-	
	1.0	41.9	36.7	6.9	0.4	9.0	5.6	
	1.2	41.3	37.0	4.2	0.6	5.9	8.5	
								-

Table S2. FE toward CO₂ reduction major products over samples at different potentials.

Samples	Cu ⁺ /Cu ⁰ peak area ratio
AuCu-g	1.71
Au@Cu	1.70
AuCu-1	1.28
AuCu-2	1.32
AuCu-g (after 25 h electrolysis)	1.64
AuCu-g (after 50 h electrolysis)	1.63
AuCu-g (after 75 h electrolysis)	1.51
AuCu-g (after 100 h electrolysis)	1.15

Table S3. Cu^+/Cu^0 peak area ratio summarization of samples.

Samples	ECSA (cm ²)
Au	5.56
Au@Cu ₂ O	4.93
Au@Cu	11.85
AuCu-a	15.90
AuCu-g	22.33

Table S4. ECSA summarization of samples.

Samples	$R_s(\Omega \text{ cm}^{-2})$	СРЕ-Т	CPE-P	$R_{ct}(\Omega \text{ cm}^{-2})$	W-R(Ω cm ⁻²)	W-T	W-P
Au	30.1	7.12×10 ⁻⁴	0.7314	56.18	1.39×10 ⁻⁶	0.953	0.60
Au@Cu ₂ O	30.49	4.42×10 ⁻⁴	0.8525	31.21	2.86×10 ⁻⁹	0.028	1.01
Au@Cu	32.99	6.57×10 ⁻⁴	0.7275	96.52	1.09×10 ⁻⁵	1.001	1.04
AuCu-a	35.17	1.05×10 ⁻³	0.7449	85.27	1.98×10 ⁻⁶	0.062	1.00
AuCu-g	23.35	1.07×10 ⁻³	0.7168	21.53	3.86×10 ⁻⁹	0.197	0.95

Table S5. The corresponding impedance values for different catalysts calculated by fitting.

Catalyst	Electrolyte	Max FE _{etOH} (%)	potential (V vs. RHE)	Geometric current density (mA/cm ²)	Stability	Refs.
Cu _x Zn	0.1 M KHCO ₃	29.1	1.05	8.2	5 h	5
Cu _{2-x} Se	0.5 M KHCO ₃	68.1	0.8	7.44	6h	6
K _{11.2%} -Cu ₂ Se	0.1 M KHCO ₃	70.3	0.8	35.8	130h	7
Cu/SnO _{2-x}	0.5 M KHCO3	39.8	1.05	17.04	N/A	8
Cu ₂ S _{1-x} HN	0.5 M KHCO ₃	73.3	0.19	N/A	8h	9
Cu-BDD	0.5 M KCl	42.4	1.0	N/A	2h	10
Bimetallic Ag/Cu	1 М КОН	41	0.67	250	2h	11
Multihollow Cu2O	2 M KOH	26.9	0.61	71.82	3h	12
Cu _x Au _y	0.1 M KHCO ₃	48	0.5	1	8h	13
Cu ₂ S–Cu-V	0.1 M KHCO ₃	15	0.95	4.8	16h	14
SnS ₂ /Sn ₁ -O3G	0.1 M KHCO ₃	82.5	0.9	17.8	100	15
Cu/C-0.4	0.1 M KHCO ₃	91	0.7	N/A	16h	16
dCu ₂ O/Ag _{2.3%}	1 М КОН	40.8	0.87	326.4	12h	17
Cu ₃ Ag ₁	0.5 M KHCO ₃	63	0.95	25	18h	18
Cu/Au heterojunctions	1 М КОН	60	0.75	500	90h	19
Cu/CNS	0.1 M KHCO ₃	63	1.2	1.19	6h	20
Cu GNC-VL	0.5 M KHCO ₃	70.5	0.87	10.4	12h	21

Table S6. Electrocatalytic performances of typical catalysts in the electrochemical CO_2 reduction to alcohols.

HMMP Cu ₅ Zn ₈	0.1 M KHCO ₃	46.6	0.8	2.01	11h	22
Nano-dendritic Cu	0.5 M KHCO ₃	24	1	2.71	6h	23
Fe ₂ P ₂ S ₆ Nanosheet	0.5 M KHCO ₃	23.1	0.2	~0.069	30h	24
Cu(Ag-20) ₂₀	0.1 M KHCO ₃	16.5	1.1	0.67	5h	25
Cu ₂ O nanoparticles	0.1 M KHCO ₃	~25	0.875	75	10h	26
34% N-C/Cu	1 М КОН	52	0.68	156	15h	27
Cu-Ag tandem catalyst	1 М КОН	<53	0.7	<160	1h	28
F-Cu catalyst	2.5 M KOH	~15	0.62	~36	40h	29
3.6um Copper(I) oxide films	0.1 M KHCO ₃	16.37	1	5.73	N/A	30
Cu ₂ O derived Cu with PdCl ₂	0.1 M KHCO ₃	11.1	1	2.16	N/A	31
Gradient AuCu	0.1 M KHCO ₃	84.62	0.4	~0.095	72h	This work

Notes: 0.1 M KHCO₃ (pH:8.3); 0.5 M KHCO₃ (pH:8.3); 1 M KOH (pH:14); 2.5 M KOH (pH:13.4); 0.5 M KCl (pH:7).

Band center (cm ⁻¹)	Assignment
~1100 and ~1352	*OC ₂ H ₅
~1185 and ~1550	*ОССОН
~1261 and ~1408	*СООН
~1321 and 1431	*ОССНО
~1600	*OCCO
~1720	*СНО
~2075	*CO

Table S7. Summary of detected intermediates and corresponding band positions of in situ ATR-FTIR in CO₂RR.

Samples	*C O	*0CC0	*СНО	TS(*CO-*OCCO)	TS(*CO-*CHO)
Cu	-0.13 eV	-0.32 eV	0.31 eV	1.36 eV	1.74 eV
Cu ₂ O	-0.29 eV	-0.56 eV	0.12 eV	1.14 eV	1.53 eV
Au-Cu/Cu ₂ O	-0.52 eV	-1.13 eV	-0.26 eV	0.85 eV	1.18 eV

Table S8. Free energy for hydrogenation of CO_2 to form *CO and the different pathways following *CO formation reduction on Cu, Cu₂O, and Au-Cu/Cu₂O interfaces.

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