Electronic Supplementary Material

Intimate atomic Cu-Ag interfaces for high CO_2RR selectivity towards CH_4 at low over potential

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Materials and Methods

Chemicals

Copper(II) chloride dihydrate ($CuCl_2{\cdot}2H_2O$, 99.999%), Silver acetate(99.99%), Imidazole ($\geq$99%), D-(+)-Glucose (> 99.5%), Hexadecylamine (HDA) (> 98 %), Ethanol (200 proof), were all purchased from Sigma-Aldrich. Ultra-pure purification system (Aqua Solutions) purified the deionized (DI) water (18.2 MΩ/cm) used in aqueous solutions.

Preparation of CuAg nanowires (CuAgNWs) catalyst

To synthesize CuAgNWs catalyst, we use a two-steps process. First, 22 mg $CuCl_2{\cdot}2H_2O$, 50 mg D-(+)-Glucose, 180 mg HDA were mixed in 10 ml DI water containing in 30 ml vial. The mixtures were sonication for 15 min. The mixture was then transferred to an oil bath and was heated to 100 °C with stirring for 8 hr. The synthesized CuNWs was naturally cooled down to room temperature for 12 hr. Second, 9.72 mg Ag acetate and 6.7 mg Imidazole were mixed in 8 ml DI water, 1 ml of the mixture was added in the CuNWs solutions, and kept at 50 °C without stirring for 25 min or 60 min. The synthesized CuAgNWs were thoroughly washed with hexane/ethanol solvents and were collected by centrifuge at 9500 rpm.

Materials characterizations

After the synthesized CuAgNWs were washed, the CuAgNWs dispersed in hexane were dropped and dried onto carbon-coated copper TEM grids (Ted Pella, Redding, CA) under room temperature for TEM analysis. To get transmission electron microscopy (TEM) images, a FEI CM120 transmission electron microscope was operated at 120 kV. A 300 kV FEI Titan transmission electron microscope was used for high-resolution TEM images (HRTEM). JEM-ARM300F Grand ARM TEM with 300 kV was used for high resolution dark field images and Energy-dispersive X-ray spectroscopy (EDX). We measured the size of CuNWs by the longest width within the CuAgNWs. Powder X-ray diffraction (PXRD) patterns were taken from a Panalytical X'Pert Pro X-ray Powder Diffractometer with Cu-Kα radiation. The concentration of catalysts was analyzed by inductively coupled plasma atomic emission spectroscopy (TJA RADIAL IRIS 1000 ICP-AES) and Kratos X-ray photoelectron spectroscopy (XPS).

Electrochemical Measurements

To measure current densities, a three-electrode cell was used. We used a glassy-carbon rotating disk electrode (RDE) working electrode (diameter: 5 mm, area: 0.196 cm^2) purchased from Pine Instruments. The current densities were measured by CV scanning at a rate of 50 mV/s in CO_2-saturated 0.1 M $KHCO_3$ electrolyte. To calculate Faradaic efficiency (FE), we used a gas-tight electrolysis H-cell (WizMac) separated with a cation exchange membrane (Sigma Aldrich). Consumed charges were collected to calculate FE from Princeton Applied Research VersaSTAT 4 workstation. Working, reference, and counter electrodes were 1 cm diameter glassy-carbon electrode, Ag/AgCl (4 M KCl) electrode, and Pt wire, respectively. CO_2 (Air gas, 99.99%) was bubbled to 0.1 M $KHCO_3$ electrolyte solution for 30 minutes and kept purging into the cathodic compartment at 15 sccm. All discussed potentials were converted to those against vs RHE after iR correction.

Product analysis

Gas products were analyzed by gas chromatography equipped with a barrier ionization discharge detector (GC-BID) (Shimadzu Tracera GC-BID 2010 Plus) and a Restek Micropacked GC column. GC-BID was calibrated by five standard gases. Helium (Air gas, 99.9999 %) was the carrier gas. An outlet gas line of gas-tight H-cell was directly routed to a p-type Hastelloy 6 port with a

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sampling loop (1.5 ml). 1.5 ml effluence gas was analyzed at every 45 ± 1 min. The FE was calculated as below:[1]

$$FE_j = \frac{nFv_jGp_0}{RTi_{total}} \times 100\%$$

where:

n = the number of electrons for a given product.

v_j(vol.%) = The volume concentration of gas products (CO, H_2, CH_4, and C_2H_4) in the effluence gas from the electrochemical cell (GC data)

G (ml/min at room temperature and ambient pressure) = Gas flow rate measured by a ProFlow 6000 electronic flow meter (Restek) at the exit of the electrochemical cell

i_{total}(mA) = steady-state cell current

p_0 = 1.01 x 105 Pa, T= 298.15 K, F = 96485 $C \cdot mol^{-1}$, R = 8.314 $J \cdot mol^{-1} \cdot K^{-1}$

Quantitative NMR (Bruker AV-600) was conducted to analyze the liquid product. Specifically, 0.3 mL of D_2O was added to 0.65 mL of the reacted electrolyte, and 50 μL of dimethyl sulfoxide (0.512 μM/mL) was mixed as an internal standard. The 1D 1H spectrum was measured with a pre-water saturation method.

Supplementary Figures and Tables

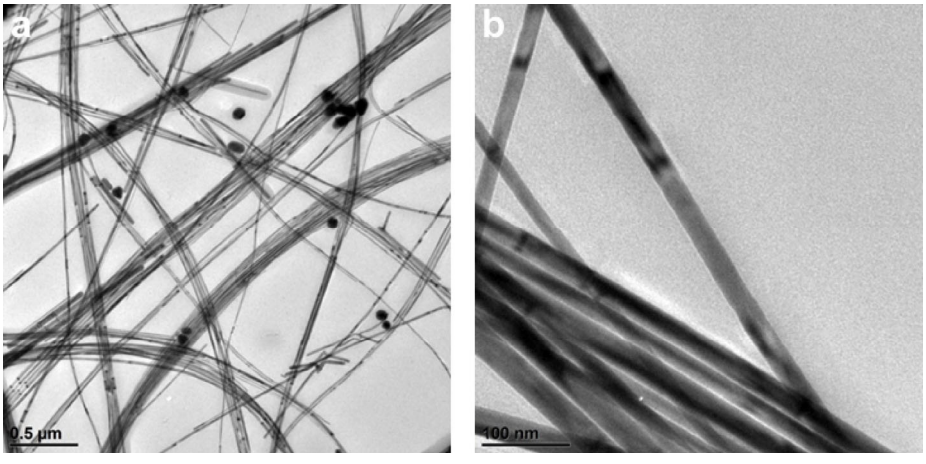

Figure S1 TEM characterizations of the CuNWs. (a, b) Low magnification TEM image of CuNWs. The d = 25 ± 7.7 nm width was determined by averaging more than 100 NWs.

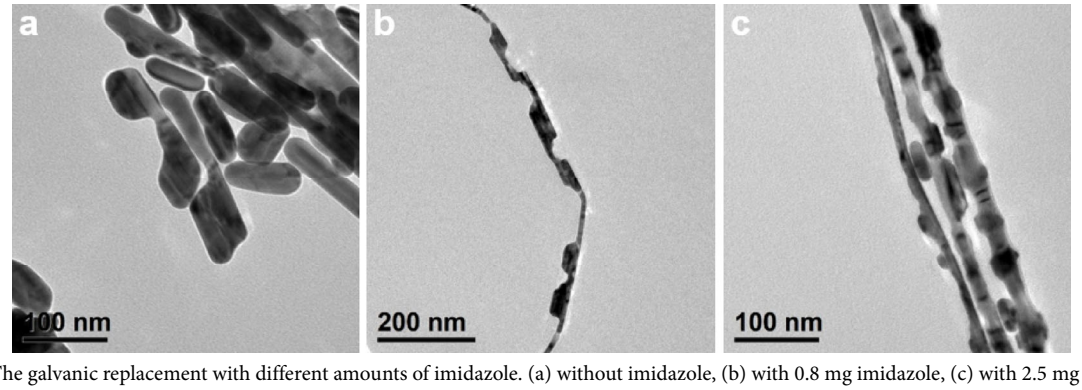

Figure S2 The galvanic replacement with different amounts of imidazole. (a) without imidazole, (b) with 0.8 mg imidazole, (c) with 2.5 mg imidazole.

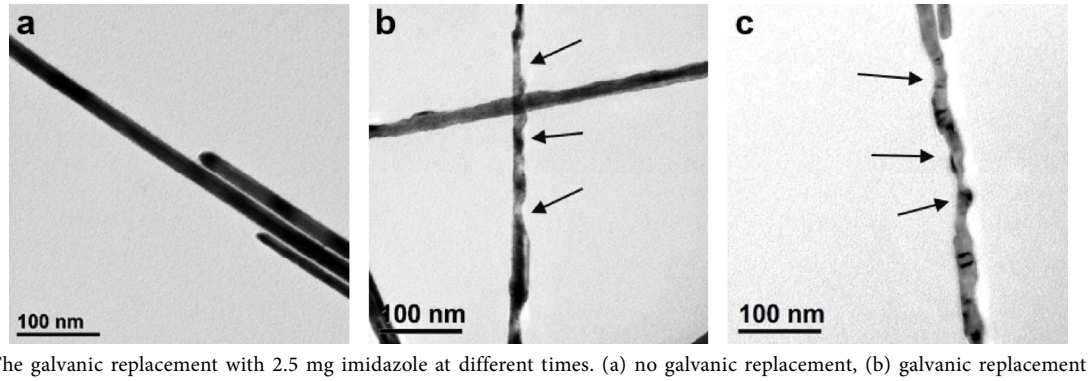

Figure S3 The galvanic replacement with 2.5 mg imidazole at different times. (a) no galvanic replacement, (b) galvanic replacement for 25 min, (c) galvanic replacement for 60 min.

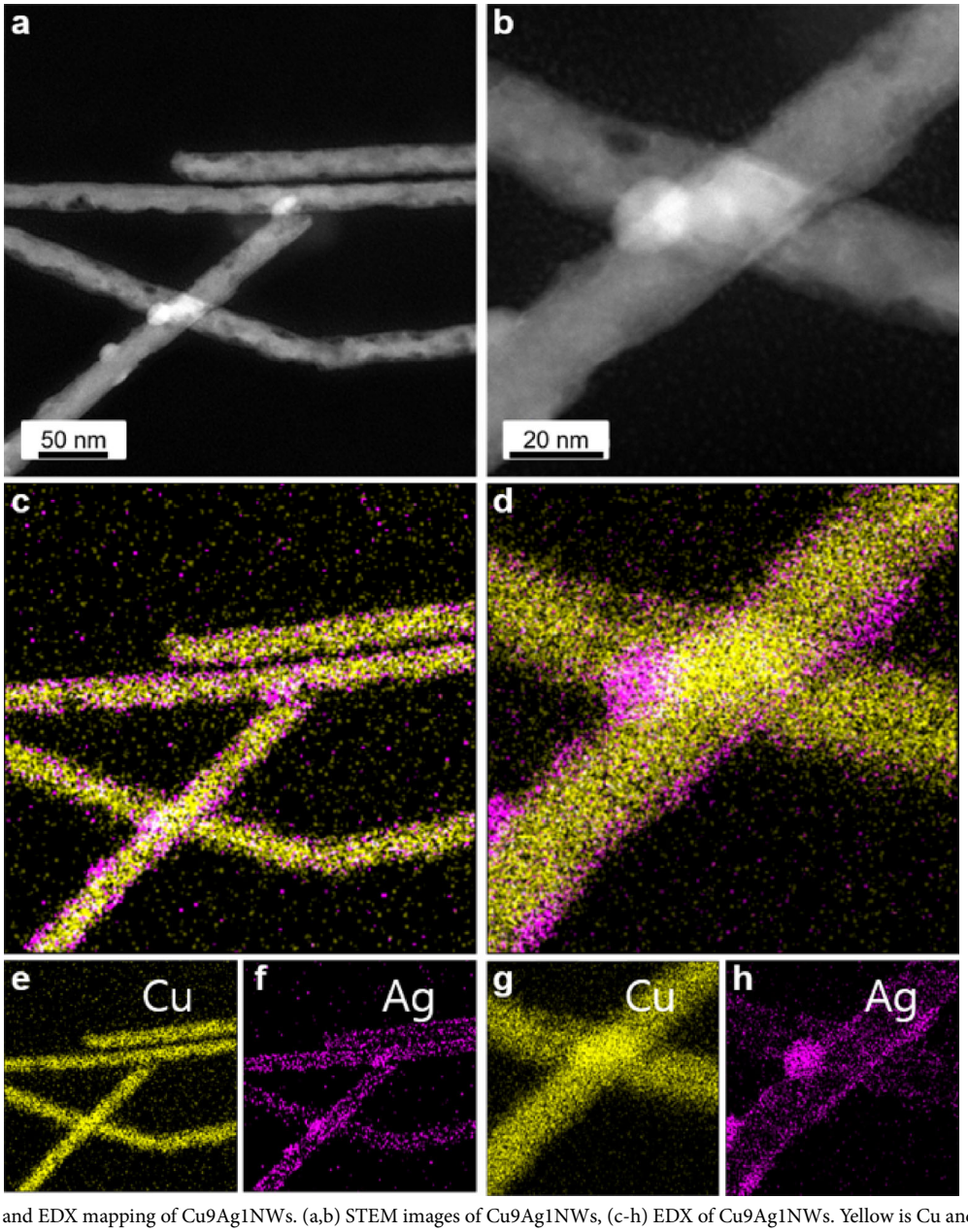

Figure S4 STEM and EDX mapping of Cu9Ag1NWs. (a,b) STEM images of Cu9Ag1NWs, (c-h) EDX of Cu9Ag1NWs. Yellow is Cu and purple is Ag.

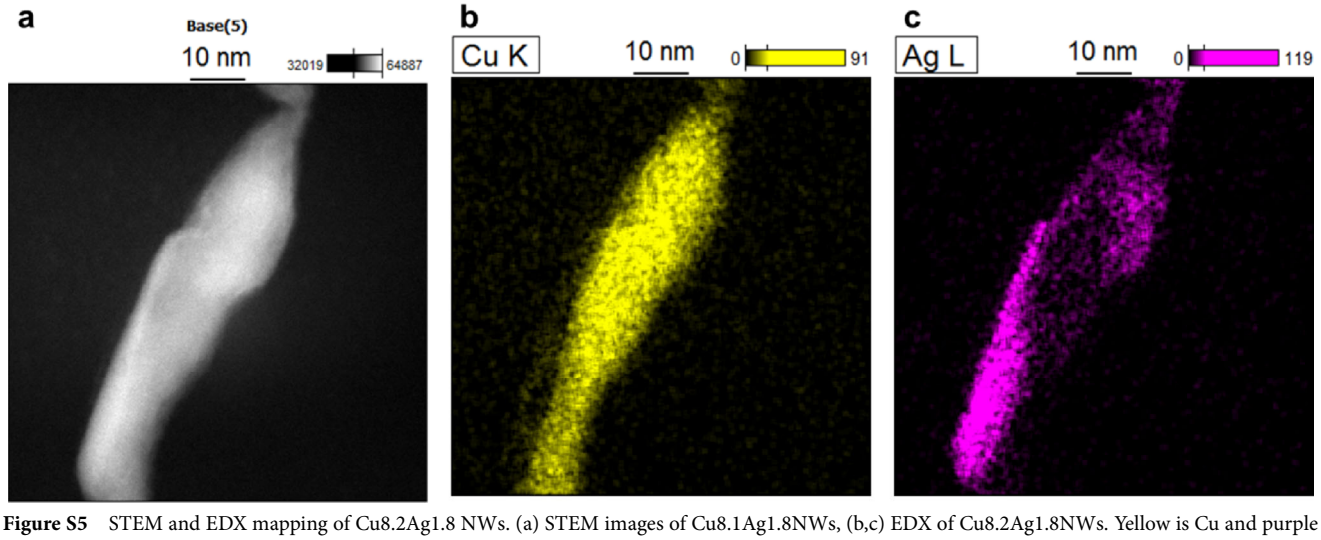

Figure S5 STEM and EDX mapping of Cu8.2Ag1.8 NWs. (a) STEM images of Cu8.1Ag1.8NWs, (b,c) EDX of Cu8.2Ag1.8NWs. Yellow is Cu and purple is Ag.

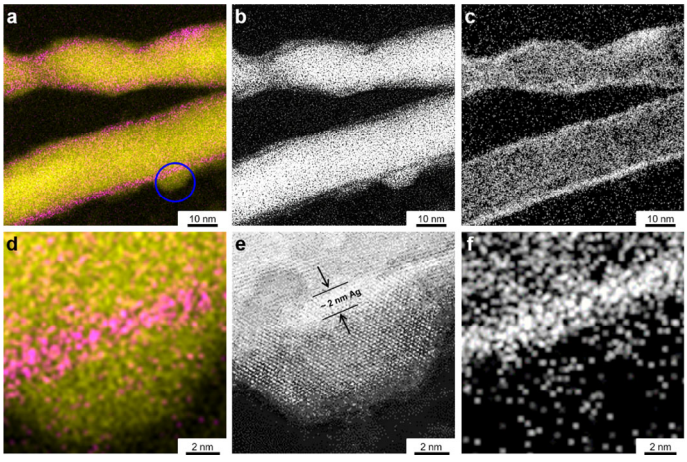

Figure S6 STEM and EDX mapping of Cu9Ag1NWs after CO_2RR at -1.05 V (vs RHE) for 2 h. (a) EDX of Cu9Ag1NWs, (b) Cu component in the STEM images of Cu9Ag1NWs, (c) Ag component in the STEM images of Cu9Ag1NWs. (d) EDX of ensembles of Cu K and Ag L on the surface of Cu9Ag1NWs (Zoom in the blue circle in Fig. S6a), yellow is Cu and purple is Ag (e) Cu component in the STEM images of Cu and Ag ensemble on the surface of Cu9Ag1NWs, (f) Ag component in the STEM images of the Cu ensemble with Ag on the surface of Cu9Ag1NWs.

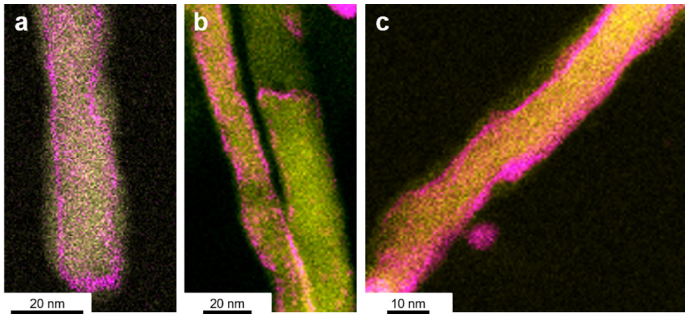

Figure S7 EDX mapping of Cu9Ag1NWs after activations with H_2, CO_2, and CO at -1.05 V (vs RHE) for 30 min. (a) Purging with H_2, (b) Purging with CO_2, (c) Purging with CO. Yellow is Cu and purple is Ag.

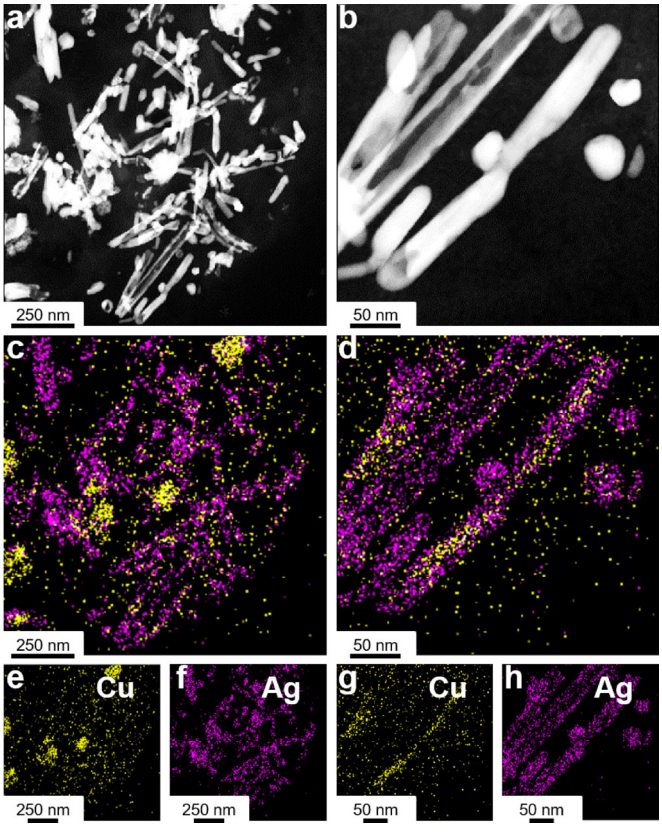

Figure S8 STEM and EDX mapping of Cu8.2Ag1.8NWs after CO_2RR at -1.05 V (vs RHE) for 2 hr. (a,b) STEM images of Cu8.2Ag1.8NWs, (e,f,c,d,g,h) EDX of Cu8.2Ag1.8 NWs. Yellow is Cu and purple is Ag.

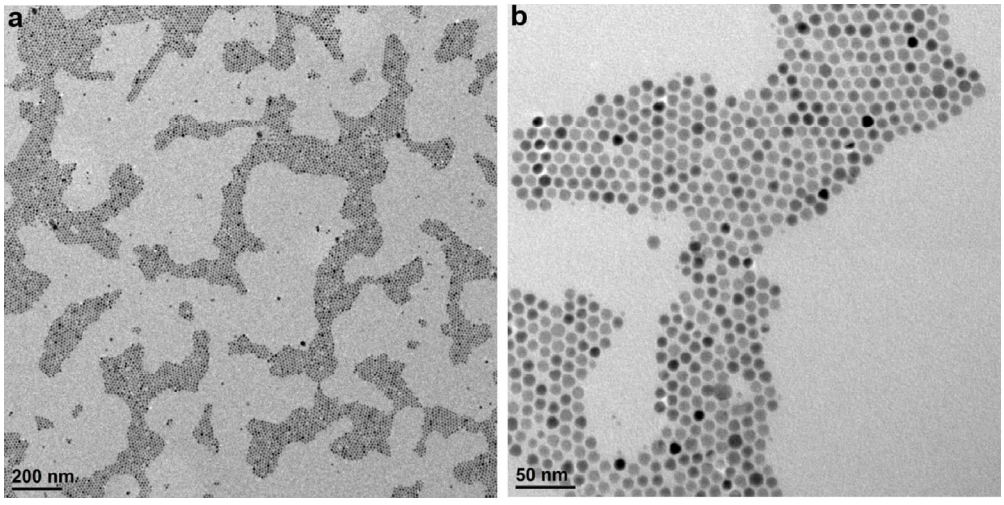

Figure S9 AgNPs. (a,b) Low magnification TEM image of AgNPs.

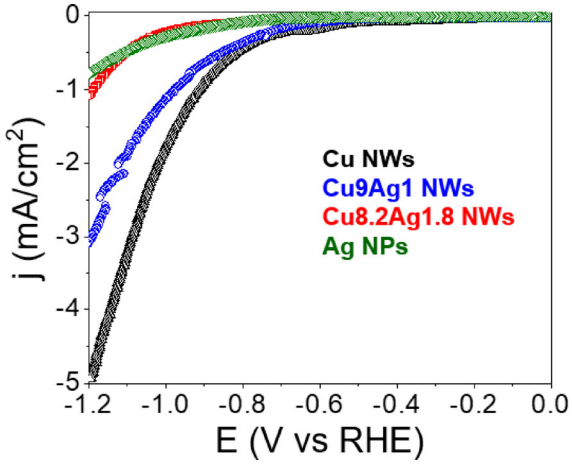

Figure S10 The electrochemically active surface area (ECSA) normalized current density. The ECSA was calculated by the double-layer capacitance of the electrode–electrolyte interface in CO_2-saturated 0.1 M $KHCO_3$ solution at room temperature.

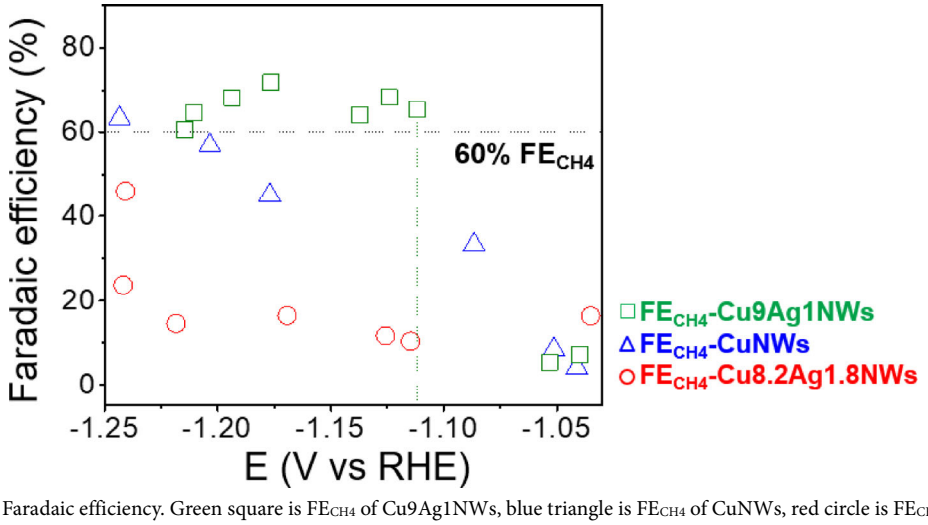

Figure S11 Methane Faradaic efficiency. Green square is FE_{CH4} of Cu9Ag1NWs, blue triangle is FE_{CH4} of CuNWs, red circle is FE_{CH4} of Cu8.2Ag1.8NWs.

Table S1 FE of Cu9Ag1 NWs

V (vs RHE)	H_2%	CO%	CH_4%	C_2H_4%	Ethanol%	Acetate%	Formate%	Total%
-1.05±0.01	14.73±3.56	55.08±0.11	6.25±0.88	17.34±4.06	1.93	0.61	0.15	96.10±8.39
-1.12±0.01	16.79±4.98	3.16±0.54	63.29±4.85	21.51±1.22	1.53	0.34	0.10	106.72±4.17
-1.20±0.02	24.66±8.11	2.30±0.52	66.36±4.18	8.89±4.46	1.17	0.22	0.11	103.72±5.01

Table S2 FE of Cu8.2Ag1.8NWs

V (vs RHE)	H_2%	CO%	CH_4%	C_2H_4%	Ethanol%	Acetate%	Formate%	Total%
-1.04	16.36	82.03	0.05	2.1	5.09	1.87	0.61	108.14
-1.13±0.02	12.80±2.63	53.21±20.00	10.55±9.15	19.50±7.42	3.07	1.15	1.34	101.62±2.12
-1.23±0.01	28.07±16.16	25.58±1.55	33.75±7.27	11.21±4.44	2.43	0.47	2.09	103.61±10.92

Table S3 FE of CuNWs

V (vs RHE)	H_2%	CO%	CH_4%	C_2H_4%	Ethanol%	Acetate%	Formate%	Total%
-1.06±0.02	25.70±5.35	1.49±1.26	15.19±12.87	60.37±4.46	5.17	0.54	0.55	109.02±2.92
-1.23±0.028	17.76±3.88	2.05±1.20	55.01±7.58	28.04±12.89	6.78	0	0.48	110.13±7.11

References

[1] Zhu, W. et al. Monodisperse Au nanoparticles for selective electrocatalytic reduction of CO2 to CO. *Journal of the American Chemical Society*, 135, 16833-16836, (2013).

[2] Huang, Jianfeng, et al. Structural sensitivities in bimetallic catalysts for electrochemical CO2 reduction revealed by Ag–Cu nanodimers. *Journal of the American Chemical Society*, 141, 2490-2499, (2019).