

Supporting Information

Electroreduction of CO₂ on Au(310)@Cu High-index Facets

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Supporting information

EXPERIMENTAL DETAILS

Sample Preparation

Synthesis of Au truncated ditetragonal nanoprisms (DTPs)

A modified procedure based on the reported literature 1 was proposed to obtain uniformly Au DTPs: poly(diallyldimethylammonium chloride) aqueous solution (1 mL), H₂AuCl₄ (37.6 μ L, 0.5 M), AgNO₃ (4 μ L, 0.5 M), and PdCl₂ (125 μ L, 0.01 M) were mixed together in ethylene glycol (20 mL). The resulting solution was transferred to a Teflon-lined stainless-steel autoclave. The sealed vessel was then heated to 220°C for 2 h. It was magnetically stirred during the entire synthesis process. After the reaction was completed, the autoclave was let to naturally cool down to room temperature. The product was collected and washed with water and acetone for many times.

Cu electrodeposition

Polished glassy carbon working electrodes were 2-sided coated with 100 μ L catalyst ink, respectively (1.5 mg of Au samples in 1 mL ultrapure water), and the concentration of the catalyst ink was further confirmed by inductively coupled plasma optical emission spectrometry (ICP-OES). Cu was then electrodeposited on the glassy carbon electrodes in an aqueous solution of 1 mM CuSO₄ with 0.05 M H₂SO₄ by adjusting the applied potential of -0.2 V, -0.3 V and -0.4 V vs. V_{Ag/AgCl} for 1 minute under N₂ atmosphere to control the thickness of Cu layer deposition.

In addition, the Au NPs with the diameter of 300 nm were purchased from Alfa Aesar.

Characterizations

Electrochemical measurements

The CO₂ electrochemical reduction tests were carried out in an H-cell, which was separated by an anion exchange membrane, working in 0.1 M CO₂-saturated KHCO₃

solution. Polished glassy carbon, platinum mesh and Ag/AgCl electrode was used as working electrodes, counter electrode (CE), and reference electrode, respectively, measured with a Biologic SP 300 potentiostat. Before and during the electrochemical reaction the working compartment was purged continuously with CO₂ at a flow rate of 30 sccm (standard cubic centimeters per minute) from the bottom of the cell, and the gas atmosphere was controlled with mass-flow controller. All reported potentials were corrected for ohmic drop, determined by electrochemical impedance spectroscopy. EC-Lab software was used to automatically correct 50% of the ohmic drop, while the remaining 50% was corrected manually. For each measurement, fresh electrolyte was used to ensure that adsorbates from previous experiments did not influence the measurements. The volatile products were qualitatively analyzed by a Shimadzu gas chromatograph, while the non-volatile products were quantified by a Shimadzu gas chromatograph with a special evaporizer head and HPLC-MS (Agilent G6120AA).

CO oxidation experiments in 0.1 M KOH electrolyte

Rotating disk electrodes (RDE) were coated with 20 μ L catalyst ink, respectively (1.5 mg of Au samples in 1 mL ultrapure water). Cu was then electrodeposited on the RDE electrodes in an aqueous solution of 1 mM CuSO₄ with 0.05 M H₂SO₄ by adjusting the applied potential of -0.2 V, -0.3 V and -0.4 V vs. V_{Ag/AgCl} under N₂ atmosphere to control the thickness of Cu layer deposition. Then, the electrode was subjected to an electrochemical cleaning procedure by cycling the electrode in N₂ purged 0.1 M KOH for 10 cycles in a potential window of -0.21 to 0.72 V_{RHE} at a scan rate of 50 mV s⁻¹. Then, CO gas was bubbled in the electrolyte for 20 min while holding the electrode potential at -0.21 V to allow for the adsorption of CO molecules. Afterward, the voltammogram for CO stripping was recorded in a potential window of -0.21 to 0.72 V_{RHE} for 20 cycles at a scan rate of 50 mV s⁻¹. Finally, the electrolyte was bubbled with N₂ for 10 minutes.

Transmission electron microscopy (TEM) images were acquired using a JEOL 2100F

microscope operated at 200 kV and equipped with a retractable Centurio large-angle silicon drift detector. The microscope used for scanning transmission electron microscope (STEM)/X-EDS, high-angle annular dark-field (HAADF)/high-resolution STEM (HAADF-HRSTEM) measurements is a double-corrected (Cs-corrected for the illumination system and the imaging system) JEM-ARM300F operated at 300 kV using a cold field emission gun and equipped with a dual energy dispersive X-ray (EDX) analysis system with two 158 mm² detectors. In addition, STEM imaging using a secondary-electron detector (SE-STEM) combined with EDS mapping were performed on an aberration-corrected Hitachi HF5000 scanning transmission electron microscope operated at 200kV.

Scanning electron microscopy (SEM) images were obtained using a JEOL 7401F instrument (Tokyo, Japan) with an accelerating voltage of 10 kV. Corresponding EDX analysis was established by a Bruker XFLASH 4010 (Bruker, Billerica, MA, USA) at an accelerating voltage of 15 keV.

HR-Scanning electron microscopy (HR-SEM) images were obtained using a Hitachi SU8030 with CFE (cold field emission gun). Corresponding EDX analysis was established by a Ametek Inc., EDAX APEX2.5.

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Compositional analysis for the catalyst ink was performed using a 715-ES-ICP analysis system (Varian). The chosen wavelengths for concentration determination were 197.742 nm, 208.207 nm, 242.794 nm and 267.594 nm for Au.

X-ray photoelectron spectroscopy (XPS) measurements were acquired with a monochromatic X-ray source (Al K α , 1486.6 eV) with a spot size of around 650 μ m at an Escalab 250 by Thermo Fisher Scientific. All spectra were recorded with a pass energy of 10 eV and a step size of 0.05 eV using the “Large Area XL” lens mode. All

spectra with calibrated with respect to the Fermi edge of silver (0 eV), the Au 4f_{7/2} (84.0 eV), the Ag 3d_{5/2} (368.26 eV) and the Cu 2p_{3/2} emission line (932.67 eV) of sputter-cleaned metal surfaces. Atomic ratios were calculated by integrating the background-corrected peaks (using a Shirley background) and dividing the areas by Scofield photoionization cross-sections, the machine-specific transmission function and the kinetic energy of the photoelectrons raised to the power of 0.6 (E_{kin})^{0.6}.

Operando FTIR spectroscopy was carried out in a modified attenuated total reflection (ATR)-FTIR setup. The catalysts were dispersed in water, and the solution of catalysts was deposited directly onto the ATR prism, avoiding intensity loss due to the lack of a sputtered layer of a conducting material such as Au. The electrochemical connection was made via a carbon cloth material that provides a reservoir of electrolyte over the catalyst, minimizing mass transport limitations and polarization effects. The spectra were collected in a custom-made glass cell with a Bruker Vertex 70v FTIR spectrometer equipped with a Mercury-Cadmium-Telluride (MCT) detector cooled with liquid nitrogen. A platinum mesh was used as counter electrode and a RHE for reference fabricated by purging H₂ over a Pt-mesh. All in situ electrochemical measurements were controlled using a Metrohm Autolab PGSTAT204 potentiostat. An unpolarized beam was focused with a Pike Veemax II onto the sample spot of the cell. The spectral resolution was set to 4 cm⁻¹ and 100 to 107 interferograms were collected and averaged for each presented spectrum. Here, the reference spectrum RE1 was collected in the same electrolyte (0.1 M CO₂ saturated KHCO₃) immediately before the investigated potential scan at the respective start potential. A ZnSe hemisphere was used as the IR window and electrocatalyst sample was deposited on the prism on the IR beam ATR focus spot and contacted with Toray Paper 030 carbon cloth and a Pine glassy carbon rod fixating the carbon cloth. The complete beam pathway was under vacuum more than 24 hours prior to each measurement. The positions of the bands were determined by taking the band maximum, or, for bipolar bands, by taking the mean value of the maximum and the minimum. The potential was scanned from -100 to -1050 mV vs.

RHE and hold at -1050 mV for 10 minutes. The background spectrum was taken before applying any potential.

The thickness of Cu layer could be determined based on the measurement of their charge of deposition, assuming DTPs and NPs are spherical, the thickness (h) of Cu layers can be calculated by the following formula:

$$n_{\text{Cu}} = \frac{Q_{\text{Cu}}}{F} \times \frac{1}{2}; \quad m_{\text{Cu}} = n_{\text{Cu}} \times M_{\text{Cu}}; \quad \frac{V_{\text{Au}}}{V_{\text{Cu}}} = \frac{\frac{4}{3}\pi r_{\text{Au}}^3}{\frac{4}{3}\pi[(r_{\text{Au}}+h)^3 - r_{\text{Au}}^3]} = \frac{m_{\text{Au}/D_{\text{Au}}}}{m_{\text{Cu}/D_{\text{Cu}}}}$$

$$h = \left(\sqrt[3]{\frac{m_{\text{Cu}/D_{\text{Cu}}}}{m_{\text{Au}/D_{\text{Au}}}} + 1} - 1 \right) \times r_{\text{Au}}$$

n_{Cu} : the amount of Cu (mol);

Q_{Cu} : the charge of Cu (C);

F: the Faraday constant (96500 C mol⁻¹);

$\frac{1}{2}$: two electrons are required to reduce one Cu²⁺ to Cu;

m_{Cu} : the mass of Cu (g);

M_{Cu} : the molar mass of Cu (64 g mol⁻¹);

V_{Au} : the volume of Au (cm³);

V_{Cu} : the volume of Cu (cm³);

m_{Au} : the mass of Au (2.94 x 10⁻⁵ g);

D_{Cu} : the density of copper (8.96 g cm⁻³);

D_{Au} : the density of gold (19.30 g cm⁻³);

r_{Au} : the radius of Au (150 nm);

h: the thickness of Cu layer (nm).

Table S1. The thickness of Cu layers measured during electro-deposition process.

	Q_{Cu} (C)	m_{Cu} (x 10 ⁻⁶ g)	h (nm)
10 nm-thick Au@Cu DTPs	0.00857	2.84	9.76
7 nm-thick Au@Cu DTPs	0.00580	1.92	6.74
5 nm-thick Au@Cu DTPs	0.00382	1.25	4.50
10 nm-thick Au@Cu NPs	0.00977	3.24	11.03
7 nm-thick Au@Cu NPs	0.00589	1.95	6.84
5 nm-thick Au@Cu NPs	0.00393	1.30	4.63

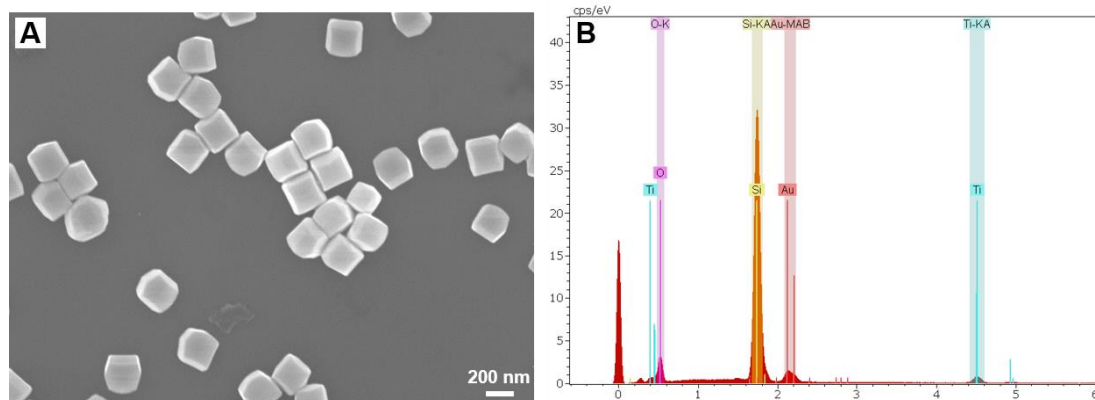


Figure S1. (A) SEM image and (B) the corresponding EDX spectrum for the Au DTPs.

SEM image for the Au DTPs showed a typical truncated ditetragonal prism (DTPs) morphology with average size of about 200-400 nm. EDX spectrum confirmed the purity of synthesized Au DTPs. (The presence of Ti, O, Si were attributed to the Ti coated Si substrate.)

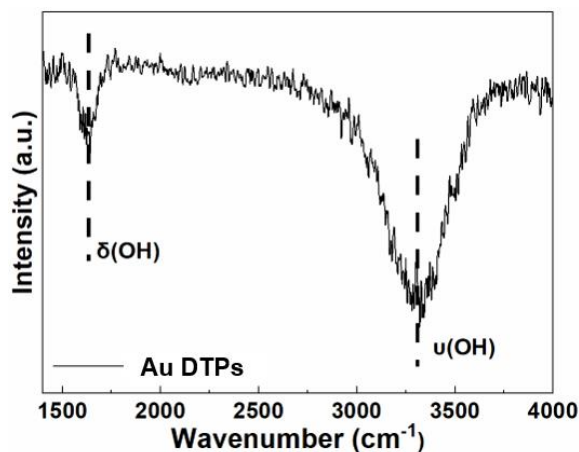


Figure S2. FTIR spectra for the Au DTPs.

FT-IR spectra of Au DTPs showed the band centered at 3310 and 1630 cm^{-1} could be attributed to the OH stretching and OH bending vibration of H_2O . No peaks at 2900 and 1465 cm^{-1} originated from the vibrations of $-\text{CH}_2$ and $-\text{CH}_3$ for poly(diallyldimethylammonium chloride) according to the literature²⁻⁴, respectively, indicating the removal of poly(diallyldimethylammonium chloride) from Au DTPs surface, and thus would not affect the subsequent Cu deposition process.

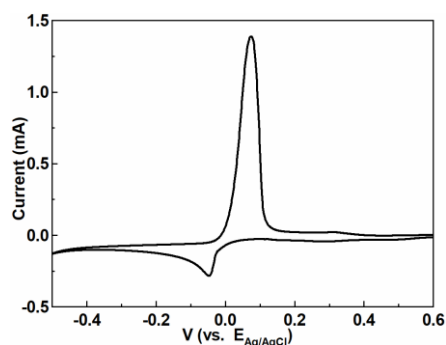


Figure S3. Cyclic voltammogram of 1 mM CuSO₄ in 0.05 M H₂SO₄ on Au DTPs coated - glassy carbon at a scan rate of 5 mV s⁻¹.

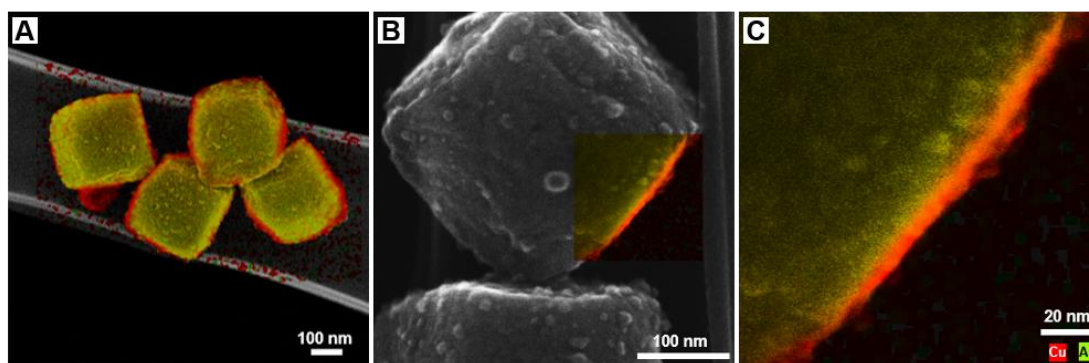


Fig. S4 (A) SE-STEM image, and (B) corresponding EDS mapping images of the 7 nm-thick Au@Cu DTPs.

SE-STEM imaging in combination with EDS mapping for the Au DTPs showed that Cu multilayers were deposited on top of Au DTPs, and the average thickness of the Cu layer was ~6.5 nm, which is consistent with the calculated charge thickness (6.74 nm). Surface roughness of the sample was caused by long-time exposure to air during transport for the measurement.

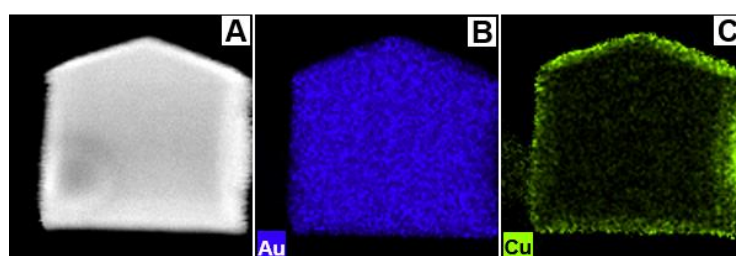


Figure S5 (A-C) EDX mapping images of an individual 7 nm-thick Au@Cu DTPs, indicating the homogeneous distribution of Cu and Au.

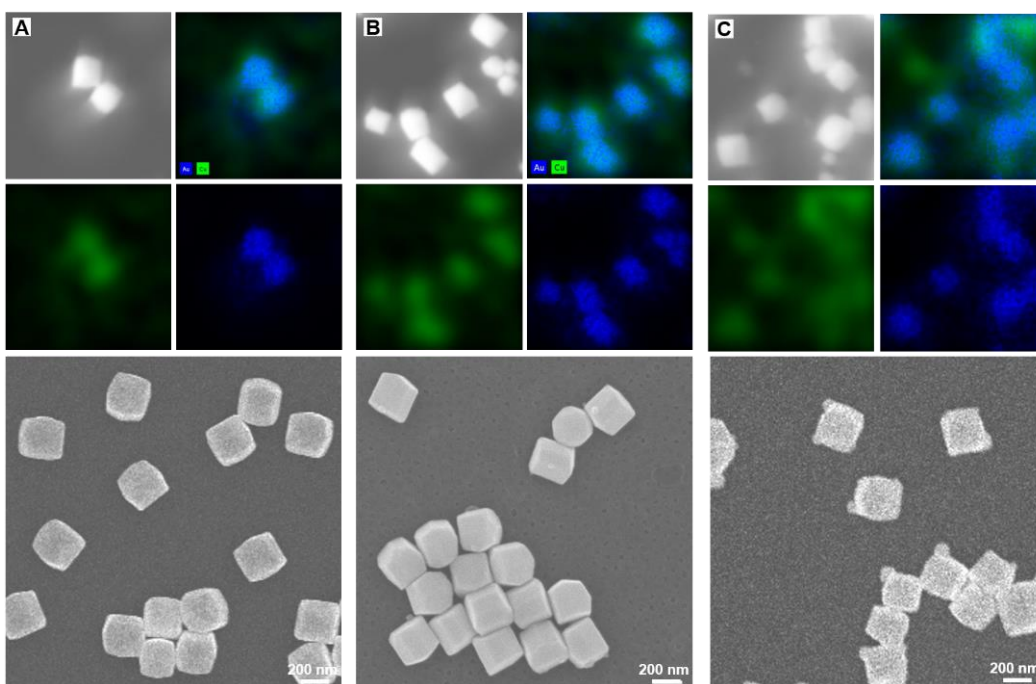


Figure S6 SEM image and the corresponding EDX mapping images for (A) the 5 nm-thick Au@Cu DTPs, (B) the 7 nm-thick Au@Cu DTPs, and (C) the 10 nm-thick Au@Cu DTPs, respectively.

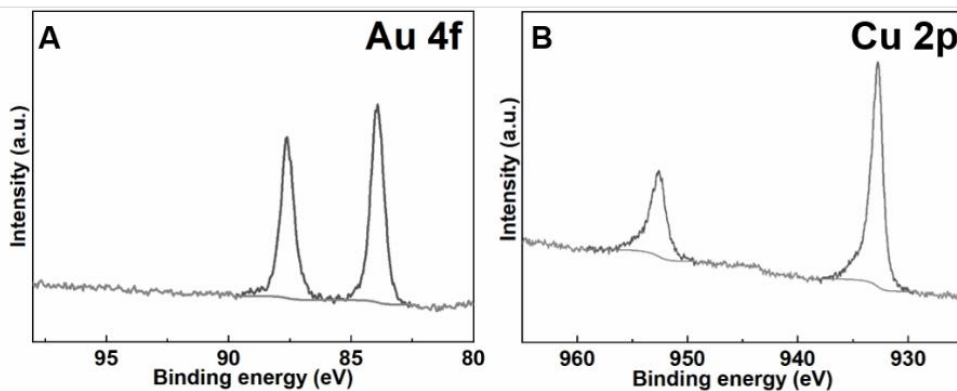


Figure S7. (A) Au 4f, (B) Cu 2p XPS spectra for the 7 nm-thick Au@Cu DTPs with the fitted Shirley background.

The atomic concentrations of Cu and Au for the 7 nm-thick Au@Cu DTPs showed 74% and 26%, respectively.

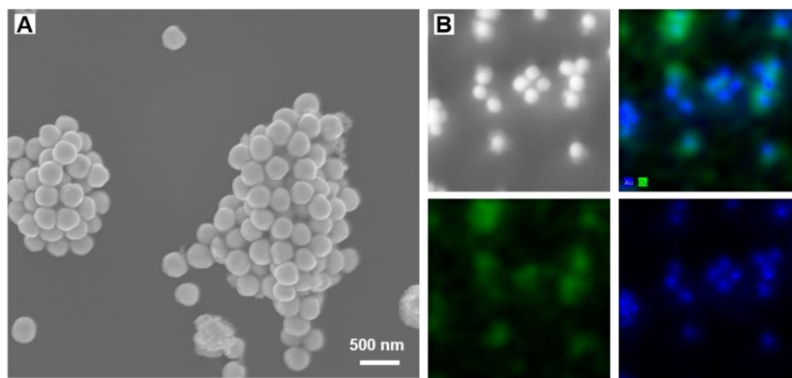


Figure S8. (A) SEM image and (B) the corresponding EDX mapping images for the 5 nm-thick Au@Cu NPs.

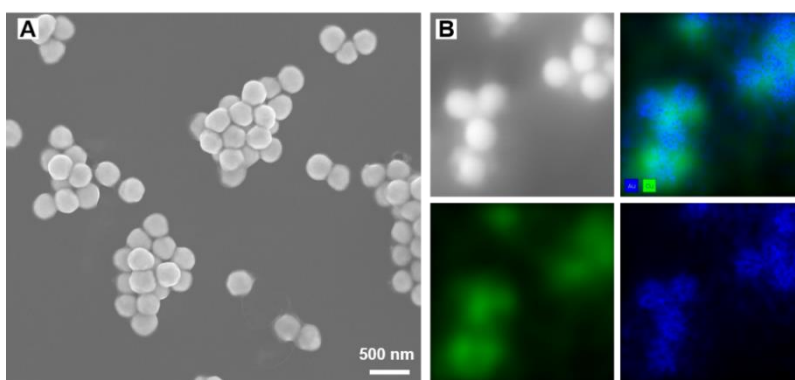


Figure S9. (A) SEM image and (B) the corresponding EDX mapping images for the 7 nm-thick Au@Cu NPs.

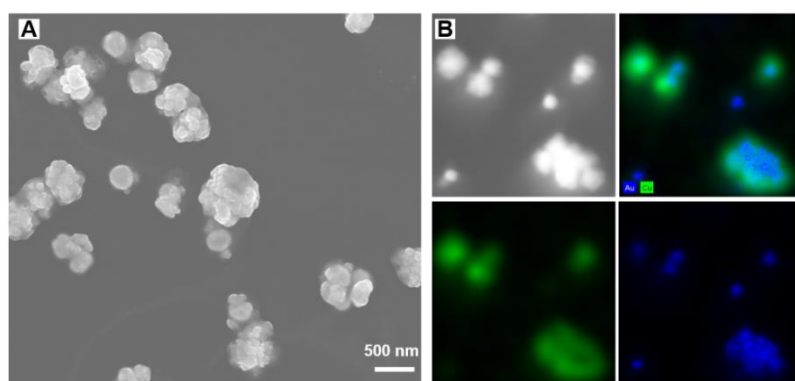


Figure S10. (A) SEM image and (B) the corresponding EDX mapping images for the 10 nm-thick Au@Cu NPs.

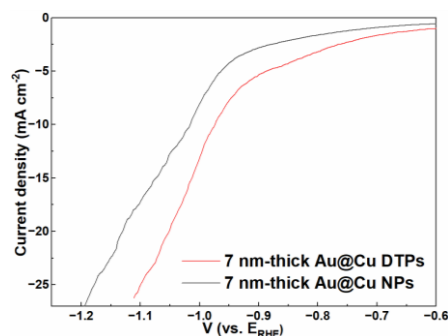
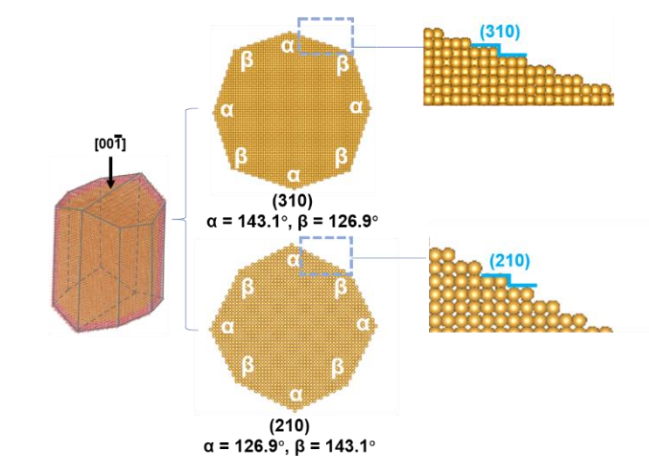


Figure S11. Linear sweep voltammetry curves of the 7 nm-Au@Cu DTPs and the 7 nm-Au@Cu NPs, respectively.



According to the projection angel,

$$\alpha = 2 \arctan \left(\frac{h}{k} \right), \beta = 270 - \alpha$$

So the theoretical angles for {310} is $\alpha = 2 \arctan 3 = 143.13^\circ$ and $\beta = 270 - \alpha = 126.87^\circ$.

Theoretical angles for {210} is $\alpha = 2 \arctan 2 = 126.87^\circ$ and $\beta = 270 - \alpha = 143.13^\circ$.

Figure S12. Model of Au@Cu DTPs bound by $\{hk0\}$ facets and projections along $[00\bar{1}]$ directions indicated with arrows.

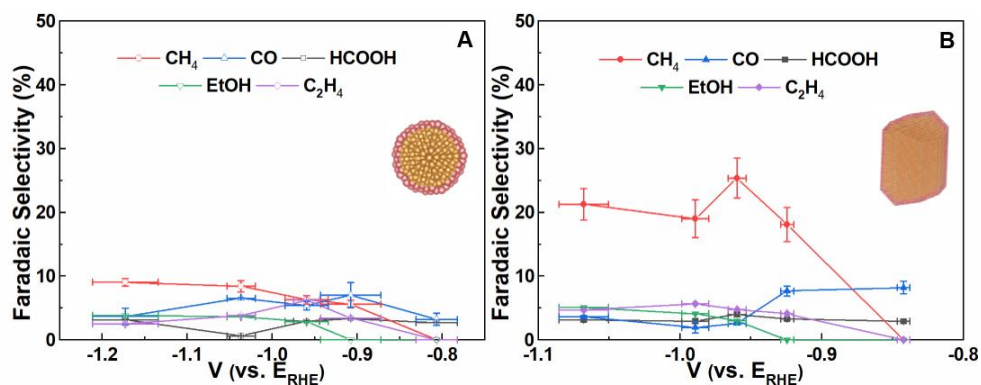


Figure S13. Faradaic selectivities for (A) the 7 nm-thick Au@Cu NPs and (B) the 7 nm-thick Au@Cu DTPs.

As shown in Figure S13, at ~ -0.96 V vs. RHE, for the 7 nm-thick Au@Cu NPs, methane, CO, formic acid, ethanol and ethylene were generated with faradaic selectivities of 6.27%, 5.36%, 2.93%, 2.81% and 6.21%, respectively.

For the 7 nm-thick Au@Cu DTPs at ~ -0.96 V vs. RHE, methane, CO, formic acid, ethanol and ethylene were generated with faradaic selectivities of 25.36%, 2.57%, 3.99%, 2.96% and 4.77%, respectively.

Reference

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