Supporting Information for

Electrochemical CO₂ Reduction Catalyzed by Atomically Precise Alkynyl-Protected Au₇Ag₈, Ag₉Cu₆, and Au₂Ag₈Cu₅ Nanoclusters: Probing the Effect of Multi-metal Core on Selectivity

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Experimental Procedures

I. Synthesis.

Materials and Reagent: Dichloromethane (DCM), ethanol (EtOH), methanol (MeOH), acetonitrile (MeCN), diethyl ether, and ethyl acetate (EA) were purchased from Caiyunfei Chemical Reagents (Tianjin, China). 3, 3-dimethyl-1-butyne (tBuC≡CH, 96%), triphenylphosphine (PPh₃, 98%), anhydrous dimethyl sulfide (Me₂S, 99.0%), anhydrous triethylamine (Et₃N, 99.5%), ammonium hydroxide (NH₃·H₂O: 28.0 ~ 30.0% NH₃), silver oxide (Ag₂O, 99.0%), sodium hexafluoroantimonate(V) (NaSbF₆, 99.0%), copper (I) chloride (CuCl, 98%), and hydrogen tetrachloroaurate (III) trihydrate (HAuCl₄·3H₂O, Au 50%) were acquired from Energy Chemicals (Shanghai, China). Sodium borohydride (NaBH₄, 98%) was obtained from Aladdin Industrial Corporation (Shanghai, China). The water with the resistivity of 18.3 MΩ·cm⁻¹ was supplied by a Barnstead Nanopure water system. All chemicals were used as received without further purification.

Synthesis of tert-butyl acetylene-protected trimetallic Au₂Ag₈Cu₅:

Me₂SAuCl, [Au₇Ag₈(C≡C-tBu)₁₂]SbF₆, and [Ag₉Cu₆(C≡C-tBu)₁₂]SbF₆ were prepared by following the method in our previous reports.¹⁻² For synthesizing Au₂Ag₈Cu₅ NCs, typically, 5 mg of [Ag₉Cu₆(C≡C-tBu)₁₂]SbF₆ was first dissolved in 6 mL mixed solvents of DCM and MeOH (VDCM: VMeOH = 2: 1) under the ultrasound condition at room temperature (160 W, 40 kHz). Under vigorous stirring (1000 rpm), freshly prepared DCM solution (1 mL) containing 2 equivalents of Me₂SAuCl was added dropwise to the above solution for ca. 1 min in the absence of light. During the addition process, the reaction system changed from blue solution to violet suspension and then to bright red solution. The reaction mixture was kept stirring at room temperature for 1 h in the absence of light. After that, the light red solution was evaporated to give a black solid, which was successively washed with excess ethyl acetate and MeOH to remove the byproducts and inorganic salt, followed by extraction by DCM. The solution was centrifuged for 5 mins at 10000 r·min⁻¹. The light red supernatant was subjected to evaporation in the dark at room temperature. Red block crystals were obtained after 1 week (yield: ca. 66.85% based on Cu). CCDC number is 2072663 for [Au₂Ag₈Cu₅(C≡C-tBu)₁₂]SbF₆.

II. Measurements and instrumentation.

The surface chemical composition and valence state were examined by X-ray photoelectron spectroscopy (XPS, Phi X-tool instrument). Scanning electron microscopic (SEM) images and energy-dispersive X-ray spectroscopy (EDS) were collected with a field-emission scanning electron microscope (FESEM, Merlin). UV-visible (UV-Vis) absorption spectra were recorded on a Shimadzu 2600/2700 spectrophotometer (Japan). The liquid products were analyzed by using a Bruker AVANCE III 400 MHz nuclear magnetic resonance (NMR) instrument and phenol was added into the deuterated water as an internal standard. The electrochemical performance of the catalysts was evaluated on a CHI 710C electrochemical workstation.

III. Electro spray ionization mass spectrometry (ESI-MS)

The ESI-MS spectra were acquired on a Bruker UlitMate3000 time-of-flight (TOF) system. ESI-MS instrumental parameters were maintained at the following values: Capillary voltage, -3.5 kV; Dry temp, 200 °C; Nebulizer, 0.6 bar; Dry gas, 6.01 mL·min⁻¹. The ESI sample was dissolved in dichloromethane (~1 mg·mL⁻¹). All the mass spectra were obtained with positive ion mode. Calibration was performed using CsI clusters.

IV. X-ray Crystallography

The diffraction data was collected on an Agilent Technologies SuperNova Single Crystal Diffractometer using Cu Kα radiation (λ = 1.54178 Å) at 100 K. Absorption corrections were applied by using the program CrysAlis (multi-scan). Structure solution was carried out using SHELXT and refinement with SHELXL, within the OLEX2 graphical interface. All non-hydrogen atoms were refined first isotropically and then anisotropically. All the hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. Detailed crystal data and
structure refinements for the three compounds are given in Table S5. CCDC 2072663 for [Au₂Ag₆Cu₅(C≡C-tBu)₁₂]SbF₆ contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

V. Computational details

All the spin-polarized density functional theory (DFT) calculations were implemented to investigate the electrocatalytic activity of M₁₅ nanoclusters for CO₂ reduction in the Vienna ab initio simulation package (VASP5.4.4). To save the computational cost, we simplified the -C≡C-tBu groups with -C≡C-CH₃ groups. These nanoclusters were placed in a cubic box with dimension of 22 Å × 22 Å × 22 Å, and their structures were optimized by the Perdew-Burke-Ernzerhof (PBE) function form of the generalized gradient approximation (GGA) to represent the interactions of electron exchange-correlation. The ion-electron interaction was described with the projector augmented wave (PAW) method, and the wave functions of all the computations were expanded via a plane-wave cutoff energy of 400 eV. The convergence criteria for energy and force was set as 10⁻⁵ eV and 0.02 eV·Å⁻¹ for maximal displacement, respectively. The Γ point only was used to sample the Brillouin zone, in addition, the van der Waals interactions between ligands were considered and described utilizing the empirical density functional dispersion (DFT-D3) method. All atoms were unconstraint and fully relaxed during the simulation.

Based on the computational hydrogen electrode (CHE) model, the change of Gibbs free energy for each CO₂RR elementary reaction can be calculated as:

\[
\Delta G = \Delta E + \Delta ZPE - T\Delta S
\]  

(S1)

Where ΔE is the difference in the DFT total energy, ΔZPE is the difference of zero-point energy calculated from the vibrational frequencies, and ΔS is the entropy difference between the products and the reactants at 298.15 K. The ΔE₄sol represents a solvation correction. For *COOH and *CO, the solvation correction is -0.25 eV and -0.1 eV, respectively. For the gas molecules, the entropy is taken from NIST database. The zero-point energy and entropy correction at 298.15 K for various gas-phase species are provided in the following table.

| Species  | ZPE (eV) | -T*S (eV) |
|----------|----------|-----------|
| CO₂      | 0.31     | -0.66     |
| CO       | 0.13     | -0.61     |
| formate  | 0.90     | -0.77     |
| H₂O      | 0.59     | -0.58     |
| H₂       | 0.27     | -0.40     |

For the adsorbed intermediates, only vibrational entropy is considered, which is calculated from the DFT calculated vibrational frequencies. In addition, due to the inaccurate description of CO₂ and CO molecules by PBE functional, we added correction of -0.34 eV for CO and +0.10 eV for CO₂ H₂O and HCOOH are formed in the liquid phase. However, it is often difficult to calculate the free energy of the liquid phase using the standard DFT method. Therefore, we have corrected the DFT-calculated free energy of the gas phase, which is based on the free energy difference between the liquid and gas phase formations obtained in the NIST database:

\[
G(H₂O,l) - G(H₂O,g) = -0.09 \text{ eV}
\]  

(S2)

\[
G(HCOOH,l) - G(HCOOH,g) = -0.12 \text{ eV}
\]  

(S3)
Therefore, we used a correction of -0.09 eV and -0.12 eV for H$_2$O and HCOOH, respectively.

VI. Electrochemical measurements

To prepare the catalyst sample, the as-prepared M$_{15}$ NC was loading on acidic multi-walled carbon (MWCNTs) with a mass ratio of 1 (5 mg NC and 5 mg MWCNTs). The catalyst ink was prepared by dispersing the sample in isopropyl alcohol (1.5 mg·mL$^{-1}$) under sonication for 5 mins. Then, 1 mL catalyst suspension and 5 μL Nafion (5 wt.%) were uniformly mixed as the final catalyst ink. Subsequently, 50 μL catalytic ink was dropwise cast onto the carbon paper (2 × 1.5 cm$^2$) and dried at room temperature as the working electrode. 1 M KOH solution (pH= 14.0) was used as the electrolyte.

The electrochemical performance of the catalysts was evaluated on a CHI 710C electrochemical workstation. Linear sweep voltammetry (LSV) was conducted at a scan rate of 10 mV·s$^{-1}$ from -0.39 to -1.19 V vs. RHE. The electrochemical performance of three catalysts on gas diffusion electrode (GDL, 2 × 1.5 cm$^2$) was carried out in a custom-designed flowcell reactor. The three NCS-coated carbon paper with a microporous layer (Sigracet 29 BCE, Fuel Cell Store) was applied as the GDL cathode. Ag/AgCl in 1.0 M KCl saturated aqueous electrolyte was employed as the reference electrode. The catholyte and anolyte chambers were separated by an anion exchange membrane (SELEMION, 2 × 1.5 cm$^2$). During the measurements, the flow rate of CO$_2$ into the cathode GDL was 20 mL·min$^{-1}$ and flow rate of the catholyte (1 M KOH) were controlled to be 65 rpm via a peristaltic pump (Cole-Parmer).

Electrode potentials measured on the Ag/AgCl scale ($E_{Ag/AgCl}$) were converted into the reversible hydrogen electrode (RHE) scale using the following equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.1976 + 0.0591 pH$$

(S3)

The output of the gas flow from the cathode chamber was directed into a gas chromatograph instrument (GC, Huaii 9560) for on-line identification and quantification of the gaseous products, which was purged for 30 mins prior to the test. The liquid products were analyzed by using a Bruker AVANCE III 400 MHz NMR instrument and phenol was added into the deuterated water as an internal standard.

The faradaic efficiency ($FE_X$) and partial current density ($j_X$) of X (X= CO or H$_2$ or formate) were calculated as below:

$$FE_X = \frac{Q_i}{Q_t} = \frac{I_i}{I_t} = \frac{(V_i \times v \times n \times F)}{I_t}$$

(S4)

$$FE_X = \frac{Q_i}{Q_t} = \frac{(N_i \times n \times F)}{Q_t}$$

(S5)

$$j_X = \frac{FE_X \times C}{t \times Area}$$

(S6)

where $Q_i$ stands for the total charge consumed, $Q_t$ represents the charge reducing a certain product, $I_i$ stands for the current value output from electrochemical workstation, $I_t$ represents the partial current reducing a certain product, $V_i$ is volume fraction of the product measured by GC, $v$ is the flow rate of CO$_2$, $N_i$ is the amount of moles of the product measured by NMR, $n$ is the number of electrons transferred in the elementary reaction (which is 2 for CO, H$_2$, and formate), and F denotes the Faradaic constant (96485 C·mol$^{-1}$), $C$ is total charge consumed in electrochemical reaction, $t$ is reaction time (s), Area is geometry area of the electrode (cm$^2$).
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Supporting Figures

Figure S1. ESI-MS spectra of [Au$_7$Ag$_8$(C≡C$\text{-}^t\text{Bu}$)$_{12}$]$^+$ (red), [Ag$_9$Cu$_6$(C≡C$\text{-}^t\text{Bu}$)$_{12}$]$^+$ (blue) and [Au$_2$Ag$_8$Cu$_5$(C≡C$\text{-}^t\text{Bu}$)$_{12}$]$^+$ (green) in positive mode. The experimental isotopic patterns and simulated (black) data of (a) Au$_7$Ag$_8$, (b) Ag$_9$Cu$_6$ and (c) Au$_2$Ag$_8$Cu$_5$ NCs. The local enlarged view of ESI-MS spectra of (d) Au$_7$Ag$_8$ (from 2950 to 3300 Da), (e) Ag$_9$Cu$_6$ (from 2220 to 2400 Da) and (f) Au$_2$Ag$_8$Cu$_5$ (from 2350 to 2550 Da). The asterisks (*) indicate the fragments of Au$_7$Ag$_8$ and Ag$_9$Cu$_6$ NCs, and the triangle (▲) indicates the product exchanged by one Au atom.
Figure S2. (a) XPS survey scan spectra of Au$_2$Ag$_8$Cu$_5$ NC. The core-level XPS spectra of the (b) Au 4f, (c) Ag 3d and (d) Cu 2p electrons in Au$_2$Ag$_8$Cu$_5$ NC. The binding energy was calibrated based on C 1s peak at 284.5 eV.

Figure S3. (a) SEM image and the corresponding elemental maps of the Au$_2$Ag$_8$Cu$_5$ crystal. (b) EDS spectrum of Au$_2$Ag$_8$Cu$_5$ and the inserted table displays the elemental percentage of Cu, Ag, Au, Sb, C, and F in Au$_2$Ag$_8$Cu$_5$ NCs.
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**Figure S10.** LSV curves recorded during the first (black), second (red) and third (blue) sweeps on (a) $\text{Au}_7\text{Ag}_8$/GDL, (b) $\text{Ag}_9\text{Cu}_6$/GDL, and (c) $\text{Au}_2\text{Ag}_8\text{Cu}_5$/GDL in 1.0 M KOH electrolyte at 50 mV·s$^{-1}$. 
**Figure S11.** The $^1$H-NMR spectra of the product in liquid phase for Ag$_9$Cu$_6$/GDL. Inset: Zoomed-in region is the $^1$H-NMR spectra, which confirms the formate production.

**Figure S12.** The $^1$H-NMR spectra of the product in liquid phase for Au$_2$Ag$_8$Cu$_5$/GDL. Inset: Zoomed-in region is the $^1$H-NMR spectra, which confirms the formate production.
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Figure S16. (a to f) Absorbance spectra of the Au$_2$Ag$_5$Cu$_5$/GDL before and after CO$_2$RR test at applied potentials, (g) the corresponding photos of the dichloromethane solution.
Figure S17. The detailed core-shell-shell configuration ($M_{\text{core}}@M_{\text{cube}}@M_{\text{octahedron}}$) of Au@AuAg$_4$Cu$_3$@Ag$_4$Cu$_2$ (-C≡C-CH$_3$ groups omitted for clarity).
Figure S18. Schematic presentation of adsorption structures of *COOH, *CO, *HCOO, and *H intermediates on (a) [Au7Ag9(C≡C-CH3)12]⁺, (b) [Ag9Cu6(C≡C-CH3)12]⁺, and (c) [Au2Ag9Cu5(C≡C-CH3)12]⁺ NCs, respectively. Color legend: Au, gold; Ag, blue; Cu, brick-red; C, gray; O, red; *H, green; other H, white.
Figure S19. The exposed 111-like surface (red dotted line) after releasing one \(-\text{C≡C-CH}_3\) ligand from (a) [\(\text{Au}_7\text{Ag}_8(\text{C≡C-CH}_3)_3\)]\(^+\), (b) [\(\text{Ag}_9\text{Cu}_6(\text{C≡C-CH}_3)_3\)]\(^+\), and (d) [\(\text{Au}_2\text{Ag}_8\text{Cu}_5(\text{C≡C-CH}_3)_3\)]\(^+\) NCs. (c) Highlight four unique ligand removal sites attached to the core of [\(\text{Au}_2\text{Ag}_8\text{Cu}_5\)]\(^+\), and the most favorable site for removal is circled in red. Color legend: Au, gold; Ag, blue; Cu, brick-red; C, gray; H, white.
**Figure S20.** Adsorption structure of *H intermediate on the (a) [Au$_7$Ag$_8$(C≡C-CH$_3$)$_{11}$]$^+$, (b) [Ag$_9$Cu$_6$(C≡C-CH$_3$)$_{11}$]$^+$, and (c) [Au$_2$Ag$_9$Cu$_5$(C≡C-CH$_3$)$_{11}$]$^+$ NCs. The Bader charge of the corresponding *H atom is given on the right. Color legend: Au, gold; Ag, blue; Cu, brick-red; C, gray; O, red; *H, green; other H, white.
Figure S21. Reaction scheme for CO₂ electroreduction on [Au₇Ag₈(C≡C-CH₃)₁₁]^+ to form CO. The calculated free energy difference (ΔG) for each elementary step is shown under each intermediate state. The most favorable reaction pathway is highlighted with the blue box. Of note, the first surface hydride transfer to produce COOH* is more difficult than direct protonation reduction, so subsequent reactions from COOH* to CO through hydride channel can be disregarded. The same case occurs for [Ag₉Cu₆(C≡C-CH₃)₁₁]^+ and [Au₂Ag₈Cu₅(C≡C-CH₃)₁₁]^+. 
**Figure S22.** Reaction scheme for CO$_2$ electroreduction on [Ag$_9$Cu$_6$(C≡C-CH$_3$)$_{11}$]$^+$ to form CO and formate. The most favorable reaction pathway is highlighted with the blue box; the first H* is marked in green and the second H* is marked in blue.
**Figure S23.** Reaction scheme for CO$_2$ electroreduction on [Au$_2$Ag$_8$Cu$_5$(C≡C-CH$_3$)$_{11}$]$^+$ to form CO and formate. The most favorable reaction pathway is highlighted with the blue box; the first H* is marked in green and the second H* is marked in blue.

**Figure S24.** The overall mechanism of CO formation from CO$_2$ reduction on [Au$_7$Ag$_8$(C≡C-CH$_3$)$_{11}$]$^+$ via the proton mechanism. Color legend: Au, gold; Ag, blue; Cu, brick-red; C, gray; O, red; H, white.
Figure S25. The overall mechanism of (a) CO formation via the proton mechanism and (b) formate formation via the hydride-proton mechanism from CO$_2$ reduction on [Ag$_9$Cu$_6$(C≡C-CH$_3$)$_{11}$]$^+$. Color legend: Au, gold; Ag, blue; Cu, brick-red; C, gray; O, red; H, white (mark the first H* in green and the second H* in blue).
Figure S26. The overall mechanism of (a) CO formation via the proton mechanism and (b) formate formation via the hydride-proton mechanism from CO$_2$ reduction on [Au$_2$Ag$_x$Cu$_y$(C≡C-CH$_3$)$_{11}$]$^+$. Color legend: Au, gold; Ag, blue; Cu, brick-red; C, gray; O, red; H, white (mark the first H* in green and the second H* in blue).
Figure S27. Schematic presentation of adsorption structures of *COOH, *CO and *H intermediates on (a) [Au₂Ag₆(C≡C-tBu)₁₂]⁺ and (b) [Au₇Ag₈(C≡C-tBu)₁₁]⁺ NCs, respectively. (c-d) Comparison of CO₂RR vs. HER on Au₇Ag₈ with -C≡C-tBu and -C≡C-CH₃ ligand protection. Color legend: Au, gold; Ag, blue; C, gray; O, red; *H, green; other H, white.
Supporting Tables

**Table S1.** The XPS data of Au$_2$Ag$_8$Cu$_5$ NCs.

| Sample     | Au 4f$_{5/2}$ (eV) | Au 4f$_{7/2}$ (eV) | Ag 3d$_{3/2}$ (eV) | Ag 3d$_{5/2}$ (eV) | Cu 2p$_{1/2}$ (eV) | Cu 2p$_{3/2}$ (eV) | Au/Ag/Cu ratio |
|------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|----------------|
| Au$_2$Ag$_8$Cu$_5$ | 88.04             | 84.43             | 374.87            | 368.87            | 953.31            | 933.40            | 1.85/8.12/5.30  |

**Table S2.** Molar absorption coefficients ($\varepsilon$) of Au$_2$Ag$_8$Cu$_5$ NC.

| Sample     | Molecular weight (M, g·mol$^{-1}$) | Wavelength ($\lambda_{\text{max}}$, nm) | Absorbance (A) | Concentration (c, M) | Absorption coefficient ($\varepsilon$, M$^{-1}$·cm$^{-1}$) |
|------------|-----------------------------------|----------------------------------------|----------------|----------------------|----------------------------------------------------------|
| Au$_2$Ag$_8$Cu$_5$ | 2784.02                          | 484                                    | 0.84           | 4.49 × 10$^{-5}$     | 1.88 × 10$^4$                                             |

**Table S3.** Summary of the calculated yields of Au$_2$Ag$_8$Cu$_5$ NC.

| Amount of reactants (mol) | Concentration of sample (M) | Amount of Au$_2$Ag$_8$Cu$_5$ in reaction (mol) | Yield |
|---------------------------|-----------------------------|-----------------------------------------------|-------|
| 1.95 × 10$^{-6}$ (Ag$_9$Cu$_6$ NC) | 4.25 × 10$^{-5}$ | 1.70 × 10$^{-6}$ | 66.85% (based on Cu) |

The calculation process of the yields of Au$_2$Ag$_8$Cu$_5$:

**Sample:**

$$c_{\text{AuAgCu5}} = \frac{0.80}{1.88 \times 10^4(M^{-1} \cdot \text{cm}^{-1}) \times 1(\text{cm})} = 4.25 \times 10^{-5} \ (M)$$

**Reaction solution:**

$$n_{\text{AuAgCu5}} = \frac{4.25 \times 10^{-5}(M) \times 4(\text{mL}) \times 10(\text{mL})}{1(\text{mL})} = 1.70 \times 10^{-6} (\text{mol})$$

**The yield of product based on Cu:**

$$Y_{\text{AuAgCu5}} = \frac{1.70 \times 10^{-6} (\text{mol}) \times 11.41\%}{1.95 \times 10^{-6} (\text{mol}) \times 14.88\%} \times 100\% = 66.85\%$$
Table S4. The mulliken charges analysis of Ag$_9$Cu$_6$.

| Atom | Mulliken charges | Atom | Mulliken charges | Atom | Mulliken charges |
|------|------------------|------|------------------|------|------------------|
| Ag(1) | 0.149            | C(30) | 0.122            | H(59) | 0.124            |
| Ag(2) | 0.161            | C(31) | -0.335           | H(60) | 0.123            |
| Ag(3) | 0.171            | C(32) | -0.326           | H(61) | 0.124            |
| Ag(4) | 0.172            | C(33) | 0.114            | H(62) | 0.125            |
| Ag(5) | 0.149            | C(34) | -0.097           | H(63) | 0.142            |
| Ag(6) | 0.159            | C(35) | -0.111           | H(64) | 0.125            |
| Ag(7) | 0.158            | C(36) | 0.111            | H(65) | 0.14             |
| Ag(8) | 0.163            | C(37) | -0.33            | H(66) | 0.125            |
| Ag(9) | **-0.004**       | C(38) | -0.324           | H(67) | 0.124            |
| Cu(10) | -0.352           | C(39) | 0.114            | H(68) | 0.144            |
| Cu(11) | -0.341           | C(40) | -0.113           | H(69) | 0.124            |
| Cu(12) | -0.35            | C(41) | -0.105           | H(70) | 0.14             |
| Cu(13) | -0.342           | C(42) | 0.119            | H(71) | 0.126            |
| Cu(14) | -0.347           | C(43) | -0.328           | H(72) | 0.129            |
| Cu(15) | -0.334           | C(44) | -0.336           | H(73) | 0.142            |
| C(16) | -0.109           | C(45) | 0.121            | H(74) | 0.125            |
| C(17) | -0.106           | C(46) | -0.111           | H(75) | 0.126            |
| C(18) | 0.112            | C(47) | -0.097           | H(76) | 0.125            |
| C(19) | -0.329           | C(48) | 0.117            | H(77) | 0.123            |
| C(20) | -0.337           | C(49) | -0.326           | H(78) | 0.143            |
| C(21) | 0.121            | C(50) | -0.326           | H(79) | 0.127            |
| C(22) | -0.099           | C(51) | 0.113            | H(80) | 0.137            |
| C(23) | -0.106           | H(52) | 0.125            | H(81) | 0.135            |
| C(24) | 0.112            | H(53) | 0.123            | H(82) | 0.139            |
| C(25) | -0.323           | H(54) | 0.143            | H(83) | 0.126            |
| C(26) | -0.326           | H(55) | 0.136            | H(84) | 0.134            |
| C(27) | 0.116            | H(56) | 0.127            | H(85) | 0.124            |
| C(28) | -0.108           | H(57) | 0.137            | H(86) | 0.143            |
| C(29) | -0.106           | H(58) | 0.141            | H(87) | 0.124            |
Table S5. The crystal structure parameters for \([\text{Au}_2\text{Ag}_8\text{Cu}_5(\text{C}≡\text{CBu}t)_{12}]\text{SbF}_6\).

| Identification code          | \([\text{Au}_2\text{Ag}_8\text{Cu}_5(\text{C}≡\text{CBu}t)_{12}]\text{SbF}_6\) |
|-----------------------------|-------------------------------------------------------------------------------------------------|
| Empirical formula           | \(\text{C}_{72}\text{H}_{108}\text{Au}_2\text{Ag}_8\text{Cu}_5\text{F}_6\text{Sb}_1\)            |
| Formula weight              | 2784.22                                                                                         |
| Temperature/K               | 149.99(10)                                                                                      |
| Crystal system              | Trigonal                                                                                        |
| Space group                 | \(R\)                                                                                           |
| \(a/Å\)                     | 16.1854(6)                                                                                      |
| \(b/Å\)                     | 16.1854(6)                                                                                      |
| \(c/Å\)                     | 28.7700(18)                                                                                     |
| \(α/°\)                     | 90                                                                                               |
| \(β/°\)                     | 120                                                                                              |
| \(γ/°\)                     | 90                                                                                               |
| Volume/Å³                   | 6527.1(6)                                                                                        |
| \(Z, \text{Calculated density}/\text{Mg/m}^3\) | 3.00006, 2.125                                   |
| Absorption coefficient/ mm\(^{-1}\) | 6.656                                                                                     |
| F(000)                      | 3972                                                                                             |
| Crystal size/mm\(^3\)      | 0.02 × 0.04 × 0.06                                                                              |
| Radiation                   | \(\text{CuK}_α (λ = 1.54184)\)                                                                  |
| \(2θ \text{ range for data collection}/°\) | 3.183 to 28.988                                   |
| Index ranges                | -19 ≤ \(h\) ≤ -22, -21 ≤ \(k\) ≤ 21, -39 ≤ \(l\) ≤ 36                                       |
| Reflections collected       | 18840                                                                                           |
| Independent reflections     | 3641 [\(R\text{(int)} = 0.0687\)]                                                                |
| Data/restraints/parameters  | 3641/55/149                                                                                     |
| Goodness-of-fit on \(F^2\)  | 1.051                                                                                           |
| Final R indexes [\(I≥2σ (I)\)] | \(R_1 = 0.0737, \text{wR}_2 = 0.1776\)                                                          |
| Final R indexes [all data]  | \(R_1 = 0.1468, \text{wR}_2 = 0.2231\)                                                          |
| Largest diff. peak/hole / e Å\(^{-3}\) | 3.145/-2.266                                  |
Table S6. A summary of $\sigma$(Cu/Ag-C) and $\pi$(Au/Ag/Cu-C) bond lengths in motif 1, 2, 3, 4 and 5 on the surface of Au$_2$Ag$_8$Cu$_5$ NC.

| Species   | The range length of $\sigma$ (M-C) bond (Å) | The average lengths of $\sigma$ (M-C) bond (Å) | The range length of $\pi$ (M-C) bond (Å) | The average lengths of $\pi$ (M-C) bond (Å) |
|-----------|-------------------------------------------|---------------------------------------------|------------------------------------------|------------------------------------------|
| Motif 1   | Ag1/Ag2-C                                  | Ag1-C                                      | Ag/ Cu-C                                  | Ag/ Cu-C                                  |
|           | 1.890 – 1.897                              | 1.894                                      | 2.387 ~ 2.397                             | 2.392                                      |
| Motif 2   | Ag3-C                                      | Ag3-C                                      | Au/ Ag/ Cu-C                              | Au/ Ag/ Cu-C                              |
|           | 1.891 – 1.896                              | 1.893                                      | 2.386 ~ 2.560                             | 2.395                                      |
| Motif 3   | Ag4-C                                      | Ag1-C                                      | Au/ Ag/ Cu-C                              | Au/ Ag/ Cu-C                              |
|           | 1.890 – 1.897                              | 1.894                                      | 2.387 ~ 2.559                             | 2.398                                      |
| Motif 4   | Cu1-C                                      | Cu1-C                                      | Au/ Ag/ Cu-C                              | Au/ Ag/ Cu-C                              |
|           | 1.858 – 1.888                              | 1.873                                      | 2.355 ~ 2.561                             | 2.394                                      |
| Motif 5   | Cu2-C                                      | Cu2-C                                      | Ag/ Cu-C                                  | Ag/ Cu-C                                  |
|           | 1.855 – 1.885                              | 1.870                                      | 2.385 ~ 2.393                             | 2.389                                      |

Table S7. A summary of $\sigma$ and $\pi$ bond lengths in motifs on the surface of Au$_7$Ag$_8$, Ag$_9$Cu$_6$ and Au$_2$Ag$_8$Cu$_5$ NCs.

| Species | The range length of $\sigma$ (M-C) bond (Å) | The average lengths of $\sigma$ (M-C) bond (Å) | The range length of $\pi$ (M-C) bond (Å) | The average lengths of $\pi$ (M-C) bond (Å) |
|---------|-------------------------------------------|---------------------------------------------|------------------------------------------|------------------------------------------|
| Au$_7$Ag$_8$ | Au-C                                      | Au-C                                      | Ag-C                                     | Ag-C                                     |
|         | 1.979 – 1.984                              | 1.982                                      | 2.490 ~ 2.564                             | 2.513                                      |
| Ag$_9$Cu$_6$ | Cu-C                                      | Cu-C                                      | Ag-C                                     | Ag-C                                     |
|         | 1.855 – 1.885                              | 1.870                                      | 2.355 ~ 2.400                             | 2.381                                      |
| Au$_2$Ag$_8$Cu$_5$ | Cu/ Ag-C                                | Cu/ Ag-C                                  | Au/ Ag/ Au-C                              | Au/ Ag/ Au-C                              |
|         | 1.855 – 1.897                              | 1.886                                      | 2.355 ~ 2.563                             | 2.394                                      |

Table S8. Lengths of bonds spread on different layer of M$_{\text{core}}$@M$_{\text{cube}}$@M$_{\text{octahedron}}$ structure in Au$_2$Ag$_8$Cu$_5$, Ag$_9$Cu$_6$, and Au$_7$Ag$_8$ NCs.

| NCs          | M$_{\text{core}}$-M$_{\text{cube}}$ (Å) | M$_{\text{core}}$-M$_{\text{octahedron}}$ (Å) | M$_{\text{cube}}$-M$_{\text{octahedron}}$ (Å) | M$_{\text{octahedron}}$-C$_{\text{ligand}}$ (Å) | M$_{\text{cube}}$-C$_{\text{ligand}}$ (Å) |
|--------------|----------------------------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|----------------------------------------|
| Au$_2$Ag$_8$Cu$_5$ | 2.957                                  | 3.297                                       | 3.414                                       | 2.890                                       | 1.886                                  | 2.394                                  |
| Ag$_9$Cu$_6$    | 2.886                                  | 3.171                                       | 3.333                                       | 2.796                                       | 1.870                                  | 2.381                                  |
| Au$_7$Ag$_8$    | 2.843                                  | 3.405                                       | 3.283                                       | 2.913                                       | 1.982                                  | 2.521                                  |
Table S9. Recovery of the Ag₉Cu₆ catalyst after CO₂RR test at applied potentials (the absorbance value of the original Ag₉Cu₆ catalyst was 0.385).

| Potential (V vs. RHE) | Absorbance after reaction (A) | Recycling amount of Ag₉Cu₆ (n, mol) | Recovery (%) |
|----------------------|-------------------------------|------------------------------------|--------------|
| -0.39                | 0.372                         | 4.77 × 10⁻⁵                        | 96.6%        |
| -0.49                | 0.361                         | 4.63 × 10⁻⁵                        | 93.7%        |
| -0.59                | 0.316                         | 4.05 × 10⁻⁵                        | 82.0%        |
| -0.79                | 0.142                         | 1.82 × 10⁻⁵                        | 36.8%        |
| -0.99                | 0.122                         | 1.56 × 10⁻⁵                        | 31.6%        |
| -1.19                | 0.117                         | 1.50 × 10⁻⁵                        | 30.4%        |

Table S10. Recovery of the Au₂Ag₈Cu₅ catalyst after CO₂RR test at applied potentials (the absorbance value of the original Au₂Ag₈Cu₅ catalyst was 0.862).

| Potential (V vs. RHE) | Absorbance after reaction (A) | Recycling amount of Ag₉Cu₆ NCs (n, mol) | Recovery (%) |
|----------------------|-------------------------------|----------------------------------------|--------------|
| -0.39                | 0.740                         | 3.94 × 10⁻⁵                           | 89.7%        |
| -0.49                | 0.738                         | 3.93 × 10⁻⁵                           | 89.5%        |
| -0.59                | 0.573                         | 3.05 × 10⁻⁵                           | 69.5%        |
| -0.79                | 0.283                         | 1.51 × 10⁻⁵                           | 34.4%        |
| -0.99                | 0.210                         | 1.12 × 10⁻⁵                           | 25.5%        |
| -1.19                | 0.173                         | 0.92 × 10⁻⁵                           | 21.0%        |

Table S11. The formate-selectivity comparison of recently reported atomically precise metal nanoclusters in CO₂RR.

| Catalyst               | Cell type | Electrolyte           | Potential (V_RHE) | FE_formate (%) | Ref. |
|------------------------|-----------|-----------------------|-------------------|----------------|------|
| [Ag₉Cu₆(C≡C-tBu)₁₂]⁺   | Flow-cell | 1.0 M KOH             | -1.19             | 47.0           |      |
| Au₂Ag₈Cu₅(C≡C-tBu)₁₂⁺  |           |                       | -0.99             | 28.3           | This work |
| Au₂₃Cd₃(PET)₁₈⁻¹       |           |                       | -0.30             | ~20.0          |      |
| (PET= 2-Phenylethanethiol) |       |                       | -0.30             | 14.0           |      |
| Au₂₃Cd₃(S-tol)₃⁻¹      | H-cell    | 1.0 M KHCO₃           | -0.50             | ~10.0          | 11   |
| (S-tol = p-toluenethiol) |         |                       | -0.30             | ~8.0           |      |
| Au₂₃Cd₃(d-MBT)₃₀⁻³     |           |                       | -0.30             | ~8.0           |      |
| (d-MBT= 3, 5-Dimethylthiophenol) |     |                       |                   |                |      |
| Cu₃justice[P(S₂P(OPr₂)₃)₁₂] | H-cell   | 0.1 M KHCO₃ and 0.4 M KCl | -0.53            | 89.0           | 12   |
Table S12. The CO-selectivity comparison of recently reported atomically precise metal nanoclusters in CO$_2$RR.

| Catalyst | Cell type | Electrolyte | Potential (V$_{RHE}$) | $F_{CO}$ (%) | $J_{CO}$ (mA·m$^{-2}$) | Ref. |
|----------|-----------|-------------|-----------------------|--------------|------------------------|-----|
| [Au$_7$Ag$_8$(C≡C-Bu)$_{12}$]$^{+}$ | Flow-cell | 1 M KOH | -0.49 | 98.1 | -156.5 | This work |
| [Ag$_5$Cu$_6$(C≡C-Bu)$_{12}$]$^{+}$ | Flow-cell | 1 M KOH | -0.49 | 94.2 | -41.8 |
| [Au$_2$Ag$_8$Cu$_4$(C≡C-Bu)$_{12}$]$^{+}$ | H-cell | 0.5 M KOH | -0.60 | 95.0 | 13.0 | 13 |
| [Ag$_{15}$(C≡C-tBu)$_{12}$]$^{+}$ | Flow-cell | 0.5 M KOH | -0.57 | 96.5 | N/A | 14 |
| [Au$_{28}$(Ph-form)]$_{12}^2+$ \(\text{Ph-form}= N, N’-Diphenylformamidine\) | H-cell | 0.1 M KHCO$_3$ | -0.57 | 95.0 | 13.0 | 15 |
| Au$_{25}$(PET)$_{18}$ \(\text{PET}= 2\text{Phenylethenanethiol}\) | H-cell | 1.0 M KHCO$_3$ | -0.50 | -63.0 | -2.3 | 11 |
| Au$_{25}$(PET)$_{18}^2+$ | H-cell | 0.5 M KHCO$_3$ | -0.80 | -100.0 | -33.0 | 16 |
| Au$_{25}$(PET)$_{18}$ \(\text{PET}= 2\text{Phenylethenanethiol}\) | H-cell | 0.5 M KHCO$_3$ | -0.80 | -100.0 | -28.0 | 16 |
| Au$_{25}$(S-Adm)$_{16}$ \(\text{S-Adm}= 1\text{-Adamantanethiolate}\) | Flow-cell | 3.0 M KOH | -0.30 | -90.0 | 59.0 |
| Au$_{25}$(S-Adm)$_{16}$ | H-cell | 0.5 M KHCO$_3$ | -0.60 | 65.0 | 25.0 | 18 |
| Au$_{25}$(S-Adm)$_{16}$ | H-cell | 0.5 M KHCO$_3$ | -0.90 | 95.0 | 45.0 | 19 |
| Au$_{25}$(TBBT)$_{31}$ \(\text{TBBT}= 4\text{-tert-butylenzenethiol}\) | H-cell | 0.5 M KHCO$_3$ | -0.57 | 96.0 | 3.2 | 19 |
| Au$_{44}$(TBBT)$_{28}$ | H-cell | 0.5 M KHCO$_3$ | -0.57 | 83.0 | -1.6 | 19 |
| [Au$_{28}$(S-Adm)$_{18}$]$^{+}$ \(\text{HS-Adm}= 1\text{-adamantanethiolate}\) | Cathode: EMIM- 
Anode: 0.5 M H$_2$SO$_4$ | -0.97 | 98.4 | 13.0 | 20 |
| [Ag$_{20}$(DMT)$_{18}$] \(\text{DMT}= 2,4\text{-dimethylbenzenethiol}\) | H-cell | BF$_4$/H$_2$ \((\text{V/V}=7/1);\) | -0.97 | -54.6 | -4.0 | 20 |
| Au$_{25}$(S-Adm)$_{16}$ | H-cell | 0.5 M KHCO$_3$ | -1.20 | -100.0 | 20.3 | 21 |
| Au$_{25}$(PET)$_{18}$ | H-cell | 0.1 M KHCO$_3$ | -0.90 | -100.0 | 19.0 | 21 |
| Au$_{25}$(PET)$_{18}$ | H-cell | 0.1 M KHCO$_3$ | -0.57 | 73.7 | 100.0 | 22 |
| Cu$_{33}$H$_{60}$L$_{12}$ \(\text{L}=S,P(O)Pr$_2$\) | H-cell | 0.1 M KHCO$_3$ and 0.4 M KCl | -0.63 | 3.0 | N/A | 12 |

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Table S13. Bader charges on the metal active atom bonded to *H.

|              | Au$_2$Ag$_8$ | Ag$_4$Cu$_6$ | Au$_2$Ag$_8$Cu$_6$ |
|--------------|--------------|--------------|--------------------|
| Bader charge (metal site)/|e|                  |                    |
| Au           | Au (0.18)    | Cu (0.46)    | Au (-0.15)         |
| Cu           | -0.14        | -0.29        | -0.08              |
| Bader charge (H*)/|e|                  |                    |
|              |              |              |                    |