

Supporting Information

**Formation of Enriched Vacancies for Enhanced CO₂
Electrocatalytic Reduction over AuCu Alloys**

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Experimental Section

Chemicals and Materials: sodium borohydride (NaBH_4), cetyl trimethyl ammonium bromide (CTAB, Aladdin Co. Ltd, 99.0%), ascorbic acid (Energy Chemical Co. Ltd, AR), Potassium bicarbonate (KHCO_3 , J&K Scientific Co. Ltd, 99.5%), gold chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, Energy Chemical Co. Ltd, 98.0%), copper acetylacetonate ($\text{Cu}(\text{acac})_2$, Heowns Co. Ltd, 98.0%), 1-dodecanethiol (DDT, Aladdin Co. Ltd, 98.0%), diphenyl ether (DPE, Energy Chemical Co. Ltd, 99.0%), 1-adamantanecarboxylic acid (ACA, Energy Chemical Co. Ltd, 98.0%), 1,2-hexadecanediol (HDD, Aladdin Co. Ltd, 98.0%), 1-hexadecylamine (HDA, Tokyo Chemical Industry Co. Ltd, > 90.0%), acetic acid (Alfa Aesar, AR), nitric acid (Aladdin Co. Ltd, AR), chloroform (Aladdin Co. Ltd, AR), ethanol (Aladdin Co. Ltd, AR), VULCAN[®] XC72 (Cabot Co. Ltd), Nafion solution (Sigma-Aldrich, 5 wt%) were all used as received. Ultrapure (UP) water ($18.2 \text{ M}\Omega \cdot \text{cm}$) were used as the solvent.

Preparation of Au_3Cu nanocubes: The solution of 85 mg $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 65 mg $\text{Cu}(\text{acac})_2$, 270 mg ACA, 1.6 g HDD, 2.0 g HDA, 0.5 ml DDT and 10.0 ml DPE were mixed in a 25mL round bottom flask. The mixture was firstly stirred and heated at 60°C for 10 mins to obtain the transparent solution. Then it was heated to 160°C for 5 hrs. The final solution was collected by centrifugation with chloroform at 10000 rpm three times and finally dispersed in ethanol.

Preparation of Dealloyed Au_3Cu nanocubes: The product dispersed in ethanol was firstly precipitated via centrifugation, and then immersed in acetic acid at 60°C for 30mins (Au_3Cu -0) or 5hrs (Au_3Cu -1), in dilute nitric acid at room temperature for 30mins (Au_3Cu -2).

Preparation of Au nanocubes: Au seeds were prepared by adding aqueous NaBH_4 solution (0.01 M, 0.6 mL) into an aqueous solution including $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.01 M, 0.25 mL) and CTAB (0.1 M, 7.5 mL). After 2 mins rigorous stirring, the seed solution was kept at room temperature for 1

h. Then the CTAB-stabilized seed solution was diluted 10 times with water. The growth solution was prepared by the sequential addition of CTAB (0.1 M, 6.4 mL), $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.01 M, 0.8 mL), and ascorbic acid (0.1 M, 3.8 mL) into water (32 mL). The diluted seed solution (0.02 mL) was then added into the growth solution. Finally, the mixture was mildly stirred for 10 s and then left undisturbed for 2hrs¹.

Electrode Preparation: Catalysts and Nafion solution were mixed and sonicated together for 30 mins. Among them, the volume ratio of Nafion solution : solvent = 1 : 20. Meanwhile, the glassy carbon electrode with 8 mm diameter was carefully polished and washed with ethanol before every experiment. Subsequently, certain volume of the suspension containing 0.05 mg catalysts was dropped onto the surface of glassy carbon electrode with a geometric area of 0.5027 cm^2 and later dried up in an oven at 50°C for 15 mins.

Electrochemical Test: Electrochemical CO_2 reduction reaction (CO_2ER) measurements were carried out in a gas-tight two-compartment electrochemical cell separated by a piece of Nafion-115 proton exchange membrane. Before the reaction, the cathode and anode compartment were filled with 100 mL of the electrolyte. The electrode chambers were connected to a gas circulation system with a ten-port valve (VICI) for on-line sampling to a gas chromatograph (Ruimin GC 2060, Shanghai). The gas circulation system was primarily made of stainless steel tubing and a home-made gas pump for the gas circulation. A mechanical pump was connected into the system to exhaust the carrier gas of the gas chromatograph when switching back the ten-port valve. A pressure gauge was also connected into the system to monitor the gas pressure. The total volume of gas in the circulation system after filling the reactor with electrolyte was 140 mL. Before starting the reaction, both electrolyte and circulation system were purged with CO_2 ($\geq 99.995\%$) for 20 min to achieve CO_2 saturation and to remove

air. Then the system was sealed and the initial CO₂ pressure was kept atmospheric. There was no more CO₂ purged into the closed system during the reaction. The gases in the closed circulation system were continuously circulated through the electrolyte for the entire reaction period.

A saturated Ag/AgCl and a platinum foil (2×2 cm²) were used as the reference electrode and the counter electrode, respectively. All potentials were measured against an Ag/AgCl reference electrode and converted to the RHE reference scale using $E \text{ (vs. RHE)} = E \text{ (vs. Ag/AgCl)} + 0.21 \text{ V} + 0.0591 \times \text{pH}$.

Material Characterization: The morphology of products were characterized by transmission electron microscopy (TEM, JEM-2100). The HAADF-STEM-EDS was performed on the Tecnai G2 F20 microscope operated at 200 kV. Elemental content was detected by ICP-MS (7700x, Agilent). Electrochemical experiments were carried out using B51758, IVIUM Technologies. The bulk structure was investigated by X-ray diffraction (XRD, RigakuC/max-2500 $\lambda = 1.5406 \text{ \AA}$). XPS was performed under ultrahigh vacuum ($<10^{-6} \text{ Pa}$) on a Kratos XSAM 800 spectrometer with Mg Ka X-ray source ($E = 1253.6 \text{ eV}$). Raman was performed on inVia reflex, RENISHAW.

Computational details:

Periodic DFT calculations were carried out with the Vienna Ab initio Simulation Package². The calculations employed the generalized-gradient approximation (GGA) in the form of the Bayesian error estimation functional with van der Waals corrections³⁻⁴. The interactions between the atomic cores and electrons were described by the projector augmented wave method⁵. The valence wave functions were expanded by a plane wave with a cutoff energy of 400 eV. The thickness of the employed slabs is five layers with top three layers relaxed on each surface. Optimized geometries were found when the force on each relaxed atom was less than 0.02 eV/ \AA . A k-point mesh of $5 \times 5 \times 1$ was used in a $2\sqrt{2} \times 2\sqrt{2}$ unit cell of each model slab.

The adsorption energy of an adsorbate, E_{ads} , was calculated as follows:

$$E_{\text{ads}} = E_{\text{total}} - E_{\text{adsorbate}} - E_{\text{surface}}$$

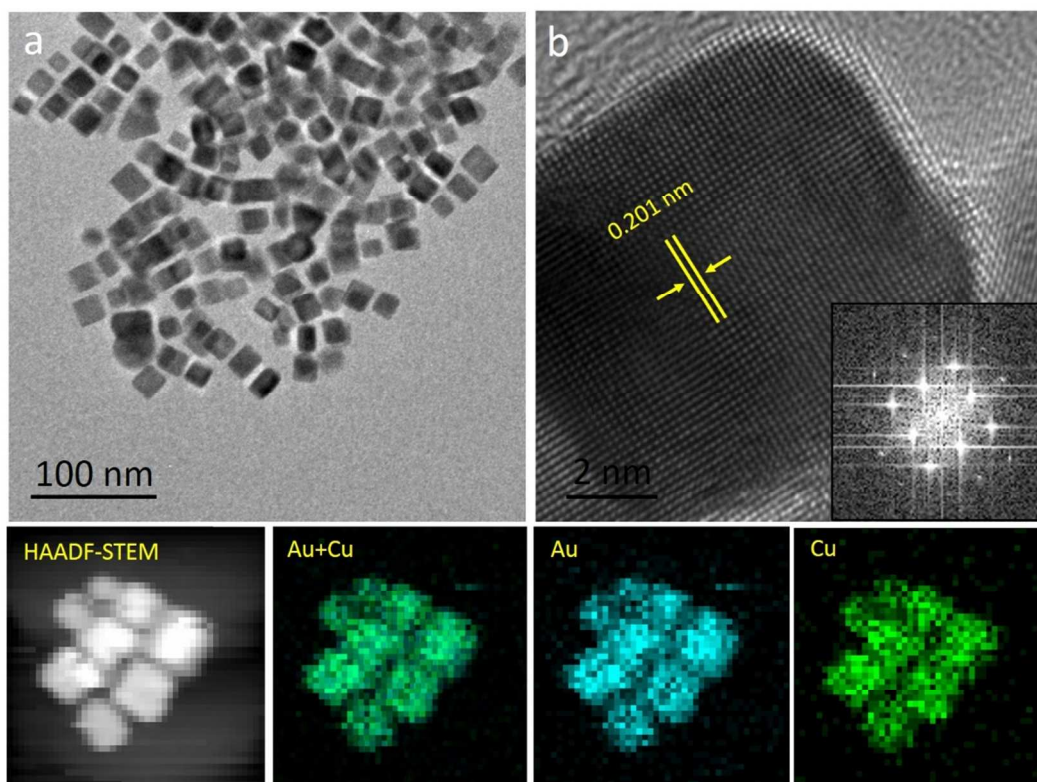


Figure S1. (a) TEM, (b) HRTEM and FFT of Au₃Cu nanocubes. The second row: HAADF-STEM and elemental mapping of Au₃Cu nanocubes.

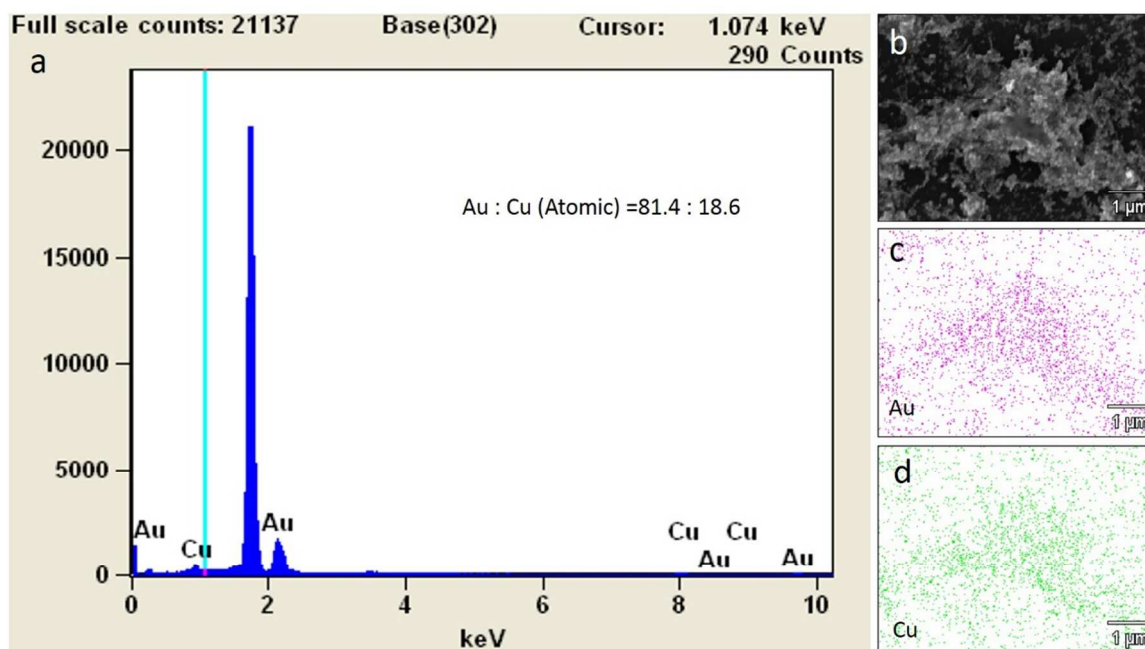


Figure S2. (a) Atomic ratios, (b) SEM images, (c) Elemental Au distribution, (d) Elemental Cu distribution of dealloyed Au_3Cu nanocubes.

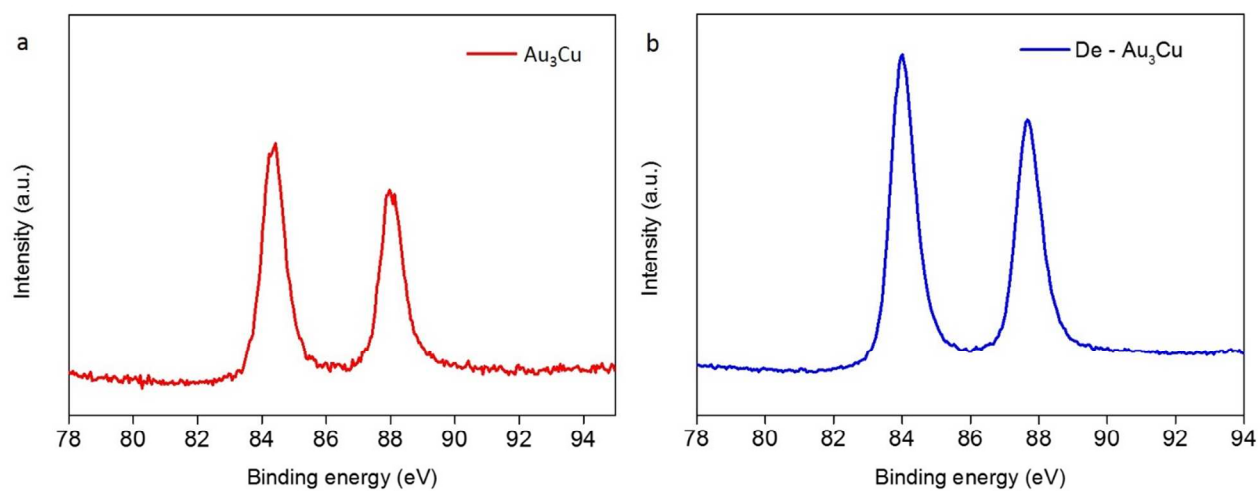


Figure S3. Au 4f XPS spectra of (a) Au_3Cu and (b) dealloyed Au_3Cu .

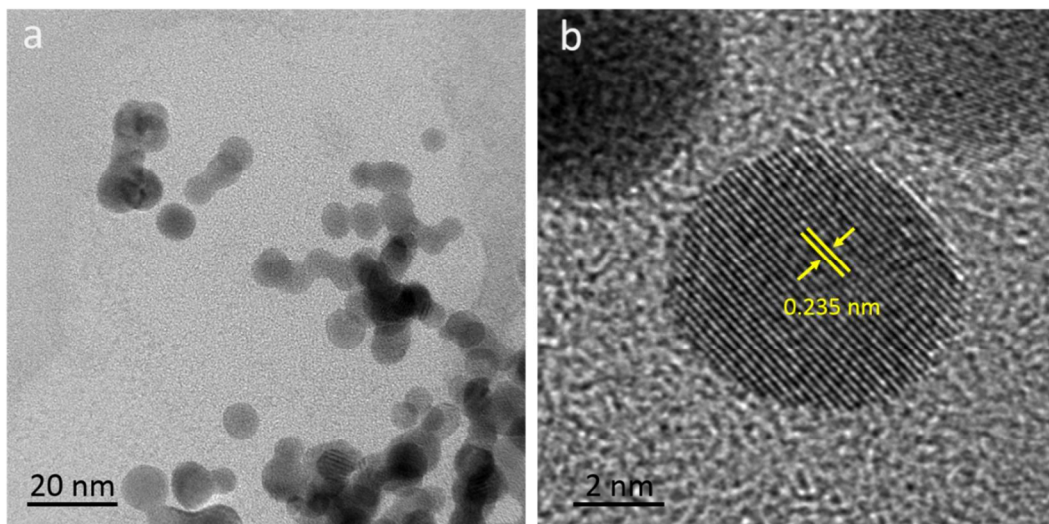


Figure S4. (a) TEM images and (b) HRTEM images of dealloyed Au_3Cu cubes with 30 mins nitric acid treatment.

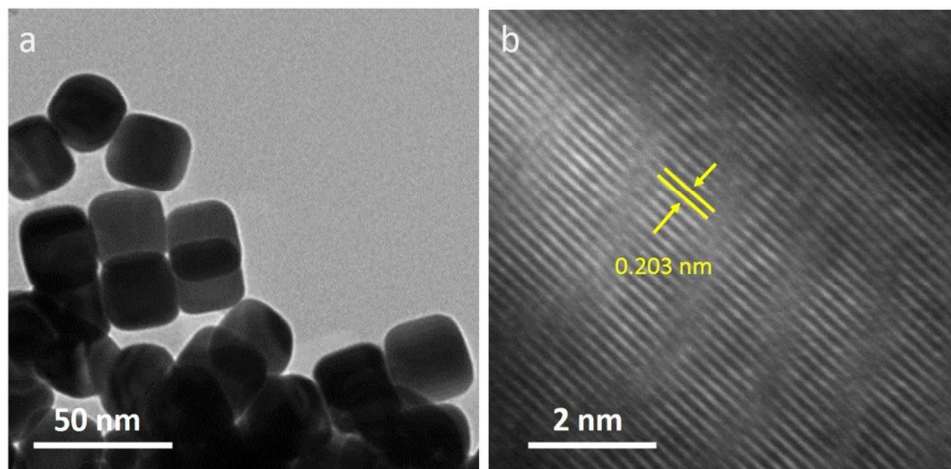


Figure S5. (a) TEM and (b) HRTEM images of Au nanocubes

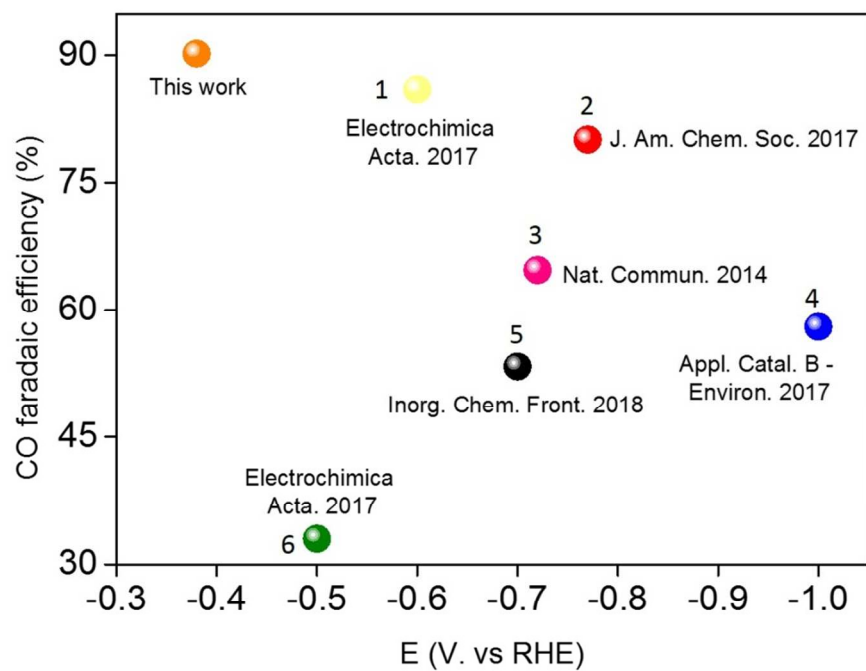


Figure S6. Performance comparison among all of AuCu alloy catalysts⁶⁻¹¹.

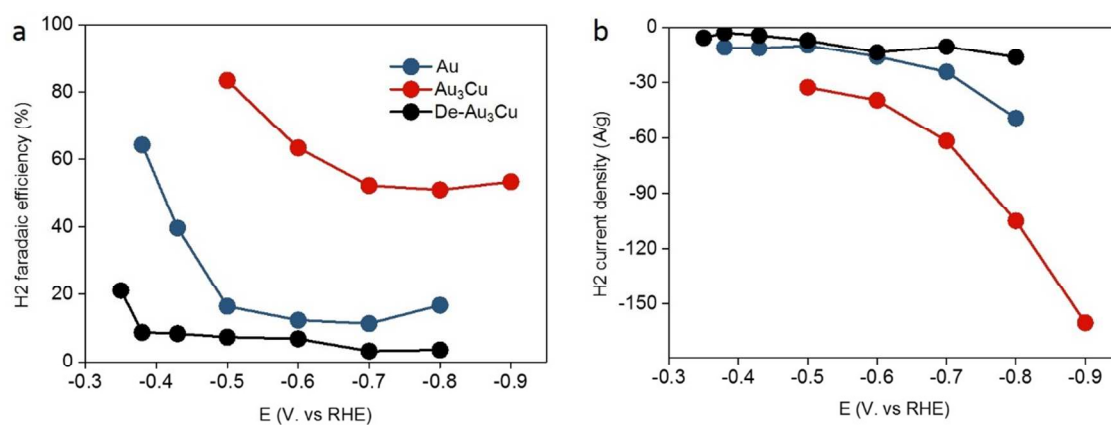


Figure S7. (a) H₂ faradaic efficiency and (b) H₂ mass current density for Au, Au₃Cu and dealloyed Au₃Cu.

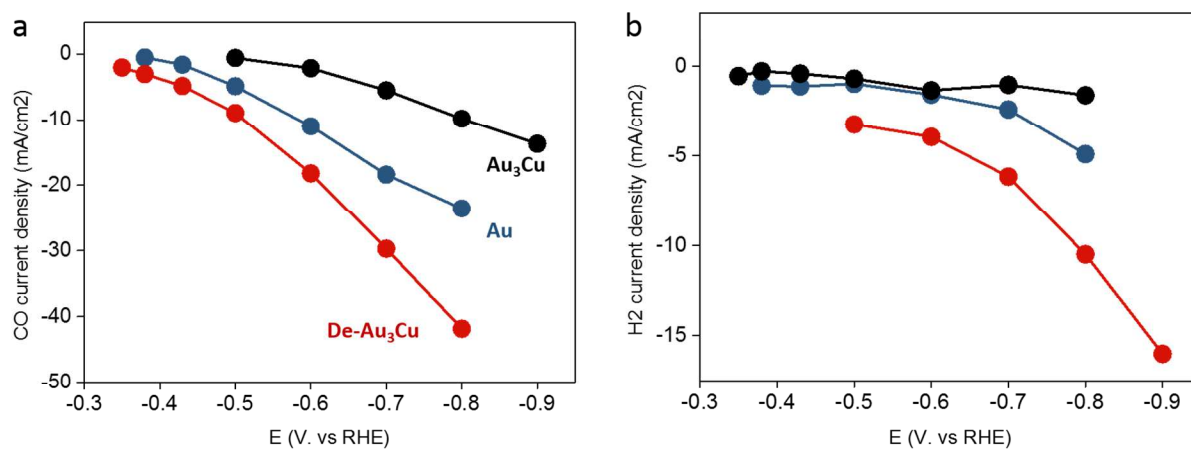


Figure S8. (a) CO and (b) H₂ geometric current densities of Au, Au₃Cu and dealloyed Au₃Cu

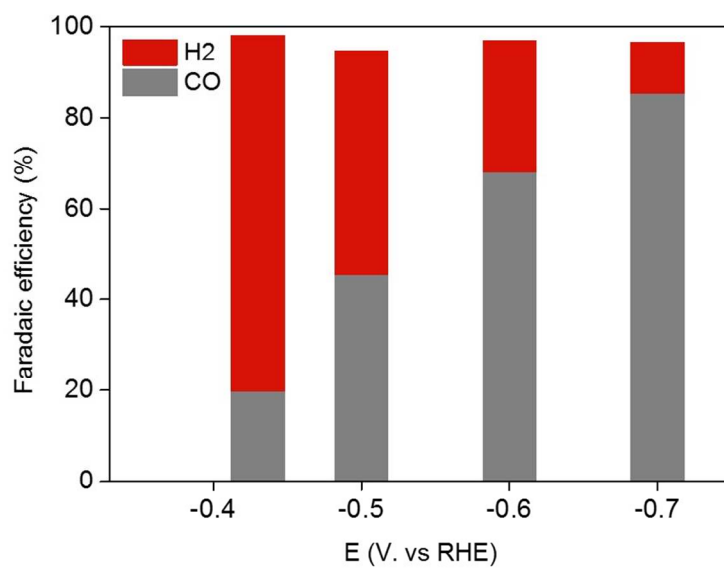


Figure S9. CO and H₂ faradaic efficiency of Au₃Cu (nitric acid for 30mins).

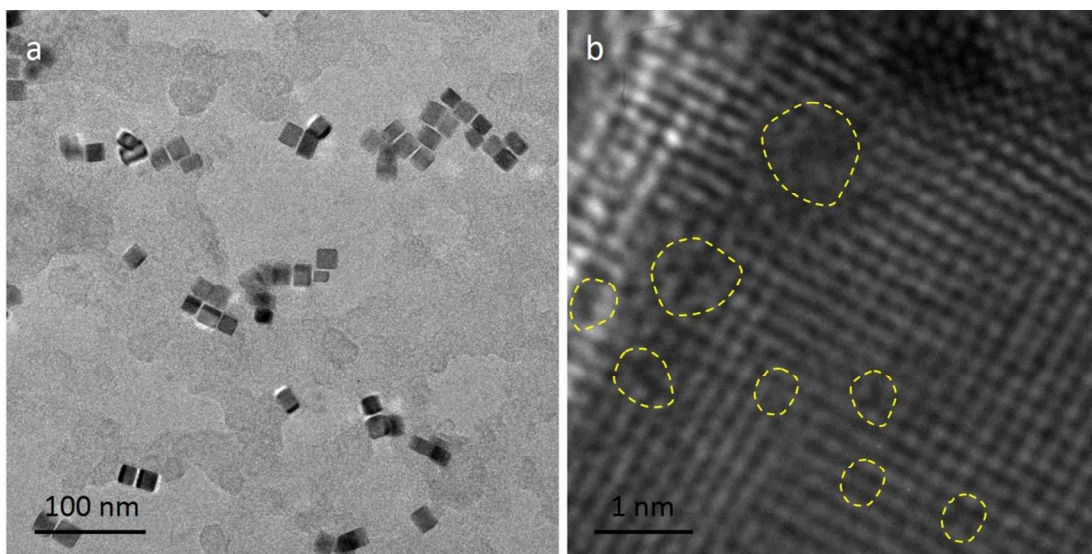


Figure S10. TEM images of dealloyed Au₃Cu after reaction: (a) Au₃Cu cubes on activated carbon, (b) HRTEM showing vacancies.

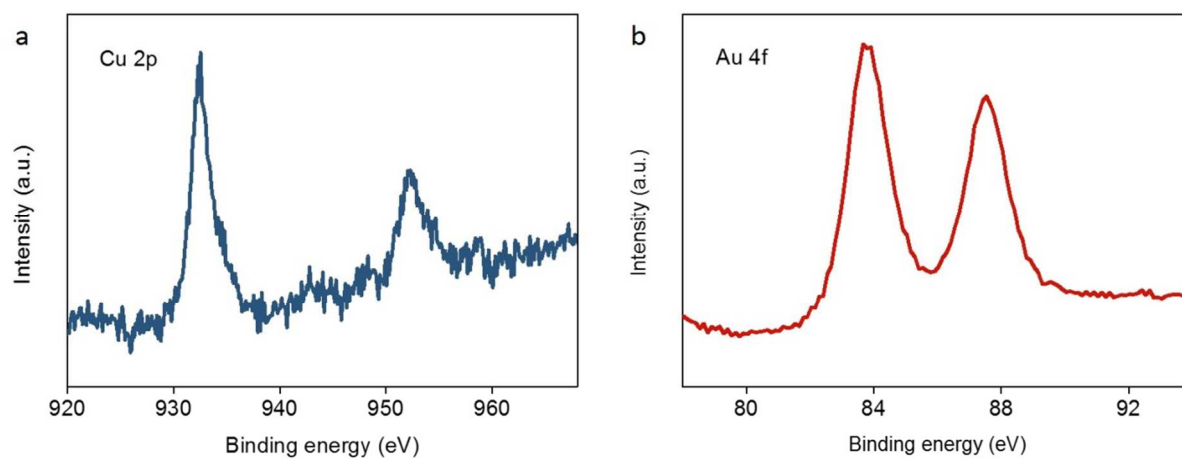


Figure S11. (a) Cu 2p and (b) Au 4f XPS spectra of dealloyed Au_3Cu after reaction.

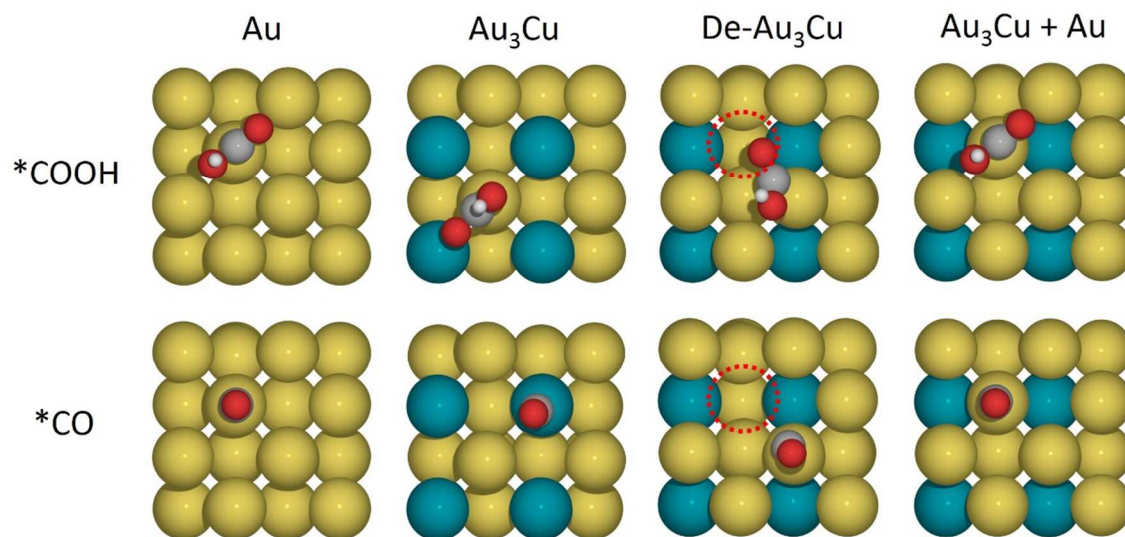


Figure S12. DFT models of *COOH and *CO adsorption on Au (100), Au₃Cu (100), De-Au₃Cu (100) and Au₃Cu + Au (100).

Table S1. Free energy of CO₂ absorption and its protonation to *COOH on various DFT models

DFT models	Free energy (eV)
Au ₃ Cu	0.79
De-Au ₃ Cu	0.55
Au	1.48
Au ₃ Cu+Au layer	1.59

References

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