

Supporting Information for

Au modified PtCu nanodendrites as a highly stable and active electrocatalyst

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Experimental Section

1. Materials. Hexadecylamine (HDA, 90%) and commercial Pt/C (20 wt% of Pt) were purchased from Sigma-Aldrich. Nafion (5%) was purchased from Alfa Aesar. Oleylamine (OLA) and copper 2,4-pentanedionate hydrate ($\text{Cu}(\text{acac})_2$) were purchased from Aladdin. Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), chloroauric acid tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), methanol (CH_3OH) and sulfuric acid (H_2SO_4) were purchased from Sinopharm Chemical Reagent Corporation. All chemicals were used as received.

2. Synthesis of PtCu_3 nanodendrites. PtCu_3 nanodendrites were synthesized by a colloidal reduction method. Briefly, HDA (17 mmol, 4.6 g) and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.05 mmol, 25.9 mg) were added to a 50 mL, three-neck, round-bottom flask. Nitrogen was used in advance to protect the reaction system. Then the temperature was raised under magnetic stirring with a heating rate of $20\text{ }^\circ\text{C min}^{-1}$. When the temperature was raised to $150\text{ }^\circ\text{C}$, $\text{Cu}(\text{acac})_2$ (39.3 mg, 0.15 mmol) in 1.0 mL of OLA (dissolved by mild heating in advance) was injected into the flask. The temperature was raised to $200\text{ }^\circ\text{C}$ and the reaction was allowed to proceed for 45 min at $200\text{ }^\circ\text{C}$. The collected samples were cooled to $100\text{ }^\circ\text{C}$ and toluene was added, followed by centrifugation for 2 min. After washed for three times, the obtained solid catalyst was re-dispersed in toluene.

3. Synthesis of Au modified PtCu_3 nanodendrites ($\text{PtCu}_3\text{-Au}$). Typically, 5 mL of ~ 0.05 mmol synthesized PtCu_3 nanodendrites in toluene was added to a small glass vial with the protection of N_2 . Then 0.50 mL of oleylamine was introduced into the vial while being magnetically stirred followed by the addition of freshly prepared gold precursor solution. The gold precursor was prepared by adding 0.05 mmol of HAuCl_4 to 1.0 mL of chloroform. The gold precursor was slowly injected into the vial in 10 min. The reaction was stopped after stirring for 30 minutes. The $\text{PtCu}_3\text{-Au}$ catalyst was then collected by centrifuging to remove the oleylamine ligand and unreacted gold precursor.

4. The preparation of carbon supported catalysts. A desired amount of PtCu₃ or PtCu₃-Au was dissolved in 40 mL of toluene. To this solution, a desired amount of carbon support (Vulcan XC-72) was added. The loading NPs on the carbon support was controlled at about 20% for mass fraction. After stirring for 6 h, the solid product was collected by centrifugation and washed twice with ethanol. The catalysts were dried in a vacuum box at 60 °C and then ground.

5. Physical Characterization. X-ray photoelectron spectrum (XPS) was measured on a Thermo Scientific ESCALAB 250Xi spectrometer using monochromatic Al K α X-ray source (1486.6 eV) with a 500 μ m spot and an anode power of 150 W. All XPS spectra were corrected using the C 1s line at 284.8 eV. The X-ray powder diffraction (XRD) patterns were recorded on an X-ray diffractometer (Rigaku Ultima IV) with Cu K α radiation ($\lambda = 1.54178$ Å) operated at the tube voltage of 40 kV and current of 40 mA. Transmission electron microscopy (TEM) images were recorded on a Hitachi HT-7700 electron microscope. Scanning electron microscope (SEM) images were obtained on a Hitachi SU-8010. High-resolution TEM (HRTEM) images were obtained on a JEOL JEM-2100F electron microscope. High-angle annular dark-field scanning TEM (HAADF-STEM) and Energy dispersive X-ray (EDX) mapping analyses were taken on the JEOL JEM-2100F microscope equipped with a probe-corrector and an EDX detector system. Ultraviolet-visible (UV-Vis) spectra were measured with a Cary 60 (Agilent Technologies) UV-Vis spectrometer. The actual metal loading on electrode in this work was determined by inductively coupled plasma mass spectrometry (ICP-MS), which was carried out in an Agilent 7700 using the diluted solution containing estimated amount of Pt-based catalyst dissolved by aqua regia.

6. Electrochemical Measurements. A three-electrode system was used to take the electrochemical measurement with a CHI750E electrochemical analyzer (CH Instrument, Shanghai) at room temperature (~25 °C). The cell consisted of a glassy carbon working electrode (3 mm diameter, 0.071 cm²), a carbon rod counter electrode and a saturated calomel electrode (SCE). The SCE was isolated by a double reference electrode to ensure the stability of SCE in acid medium. The potential vs. SCE was

transferred to that vs. RHE using the following equation: E (vs. RHE) = E (vs. SCE) + $0.059 \times \text{pH} + 0.2438$. To prepare catalyst-modified working electrodes, PdCu catalyst was dispersed in a mixture of water/2-propanol ($v/v = 4/1$) under sonication to form a 2 mg mL^{-1} catalyst ink (totally 1 mL). $\sim 3 \text{ }\mu\text{L}$ of this ink was dropped onto the surface of the GC electrode (the actual Pt loading on electrode was controlled at $15 \text{ }\mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$), and then dried under the ambient condition. The cyclic voltammetry (CV) experiments were conducted in N_2 -saturated $0.5 \text{ M H}_2\text{SO}_4$ solution with a scan rate of 50 mV s^{-1} . The methanol oxidation reaction (MOR) was conducted in N_2 -saturated $0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{OH}$ solution. The oxygen reduction reaction (ORR) was performed in O_2 -saturated 0.1 M HClO_4 solution. A rotating disk electrode (RDE) with 1600 rpm was used to conduct the ORR. The electrochemical active surface areas (ECSAs) were calculated by integrating the Coulombic charge for hydrogen desorption or CO stripping in the cyclic voltammetry (CV) recorded in N_2 -saturated $0.5 \text{ M H}_2\text{SO}_4$ aqueous solution.

For ECSAs obtained from hydrogen desorption:

$$\text{ECSA}_{\text{H}} = \frac{Q_{\text{H}}}{0.21[\text{Pt}]}$$

where Q_{H} (mC) is the charge due to the hydrogen desorption in the hydrogen region (0.05–0.45 V) of the CVs, 0.21 mC cm^{-2} is the electrical charge associated with monolayer adsorption of hydrogen on Pt, and [Pt] is the loading of Pt on the working electrode.

For ECSAs obtained from CO stripping:

$$\text{ECSA}_{\text{CO}} = \frac{Q_{\text{CO}}}{0.42[\text{Pt}]}$$

where Q_{CO} (mC) is the charge due to the CO desorption in the CO adsorbed region (0.7–1.0 V) of the CVs, 0.42 mC cm^{-2} is the electrical charge associated with

monolayer adsorption of CO on Pt, and [Pt] is the loading of Pt on the working electrode.

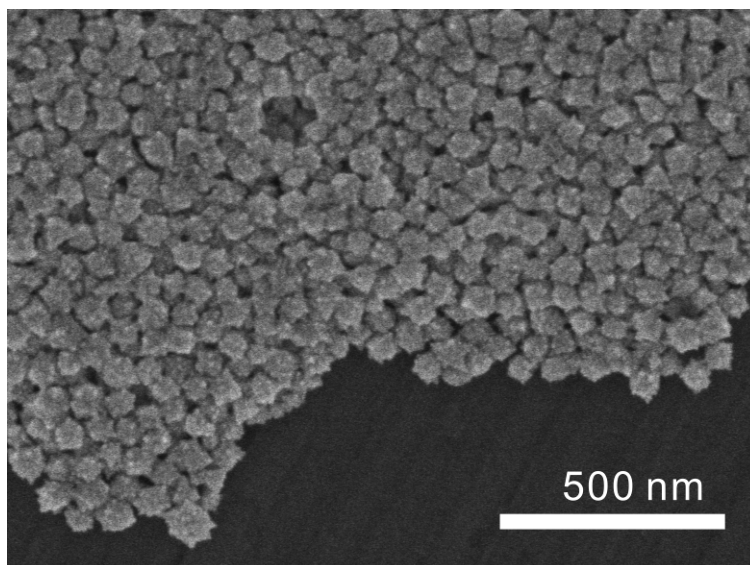


Figure S1. SEM image of PtCu₃ NDs.

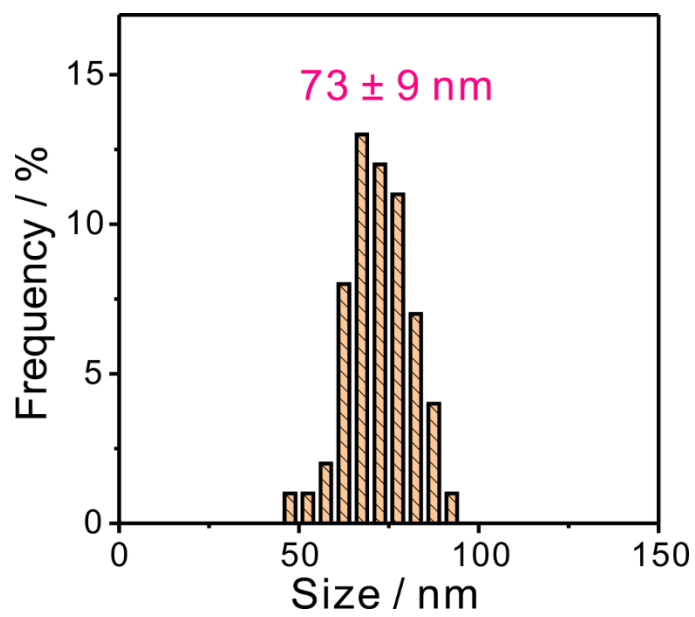


Figure S2. The size distribution of PtCu₃ NDs.

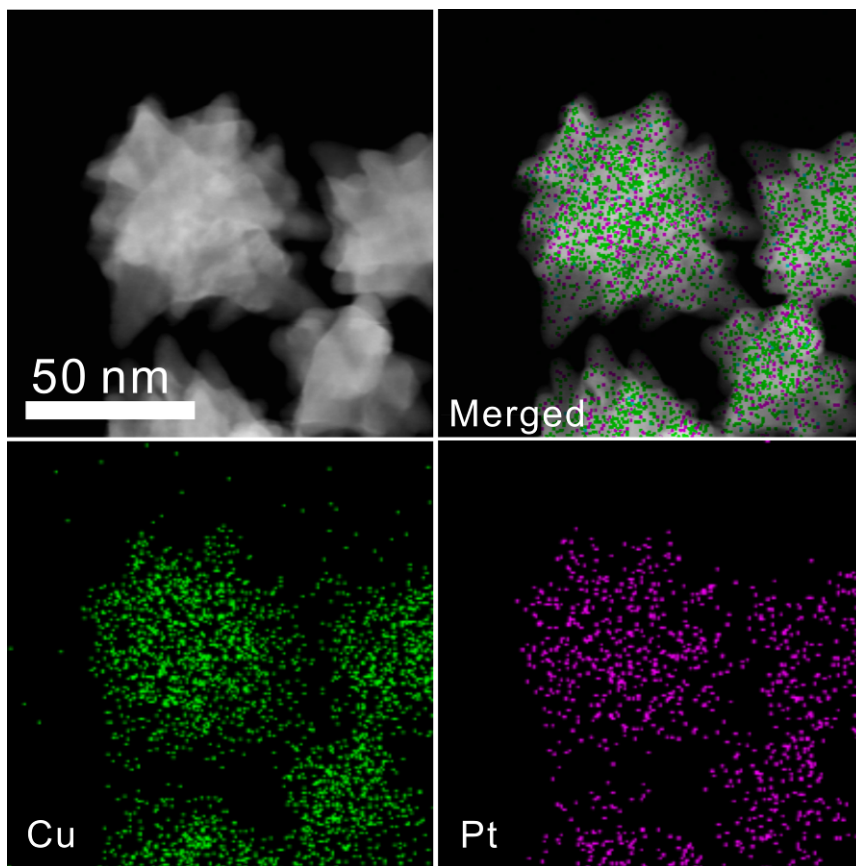
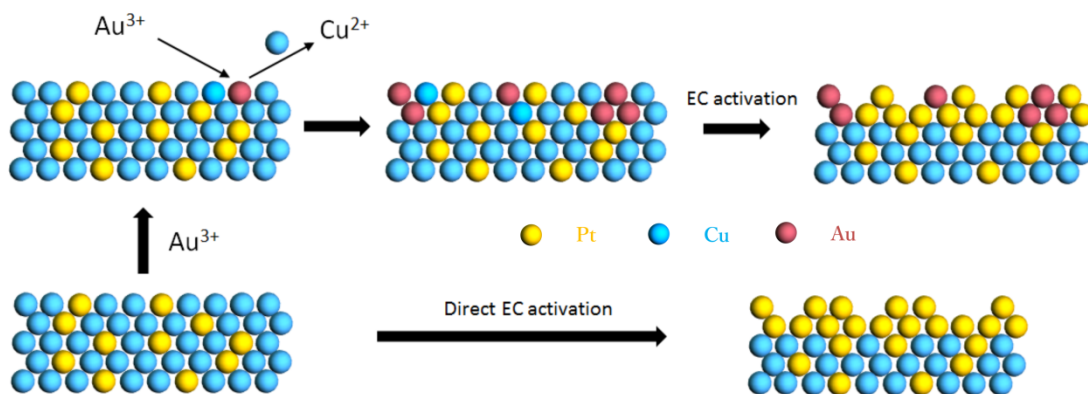


Figure S3. EDX mapping of PtCu₃ NDs.



Scheme S1. Scheme illustration of the preparation of PtCu₃-Au catalyst by surface galvanic replacement of Cu with Au³⁺.

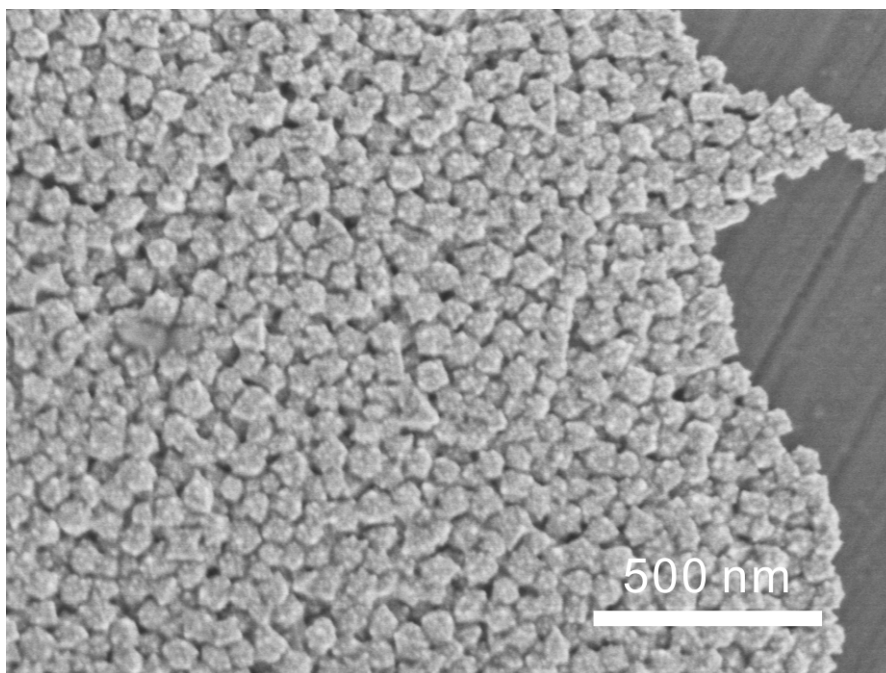


Figure S4. SEM image of Au modified PtCu₃ NDs.

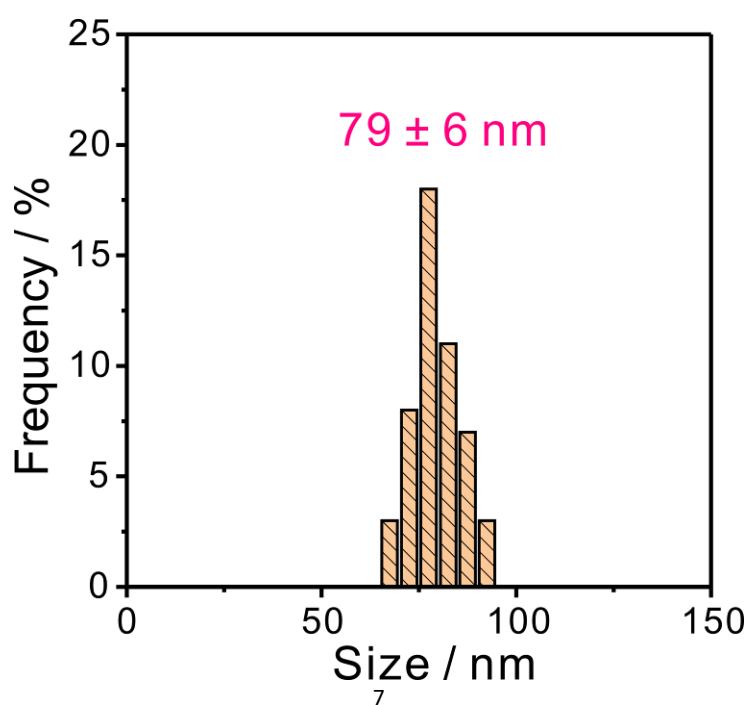


Figure S5. The size distribution of Au modified PtCu₃ NDs.

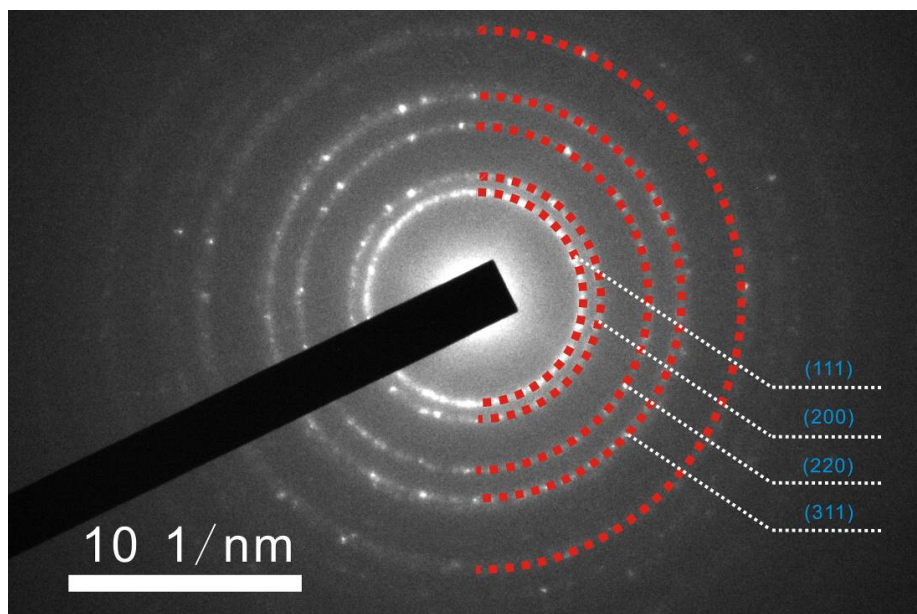


Figure S6. Selected area electron diffraction (SAED) of Au modified PtCu₃ NDs.

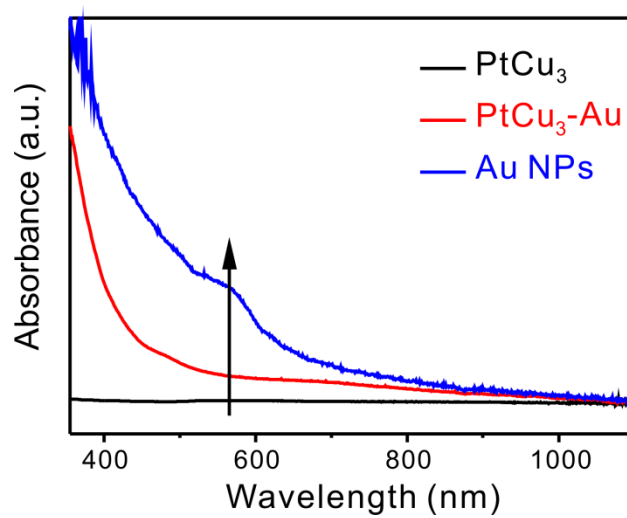


Figure S7. UV-Vis spectra of PtCu₃ NDs, PtCu₃-Au and Au nanoparticles.

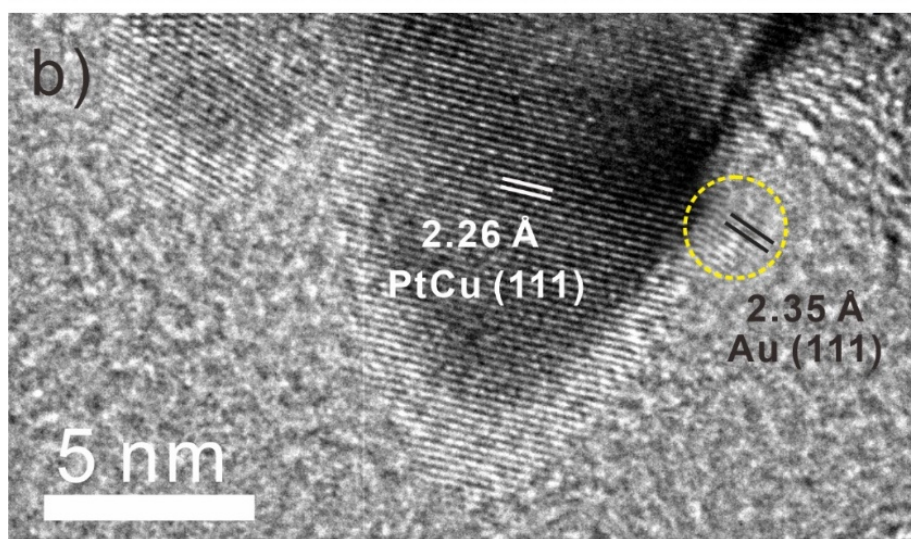
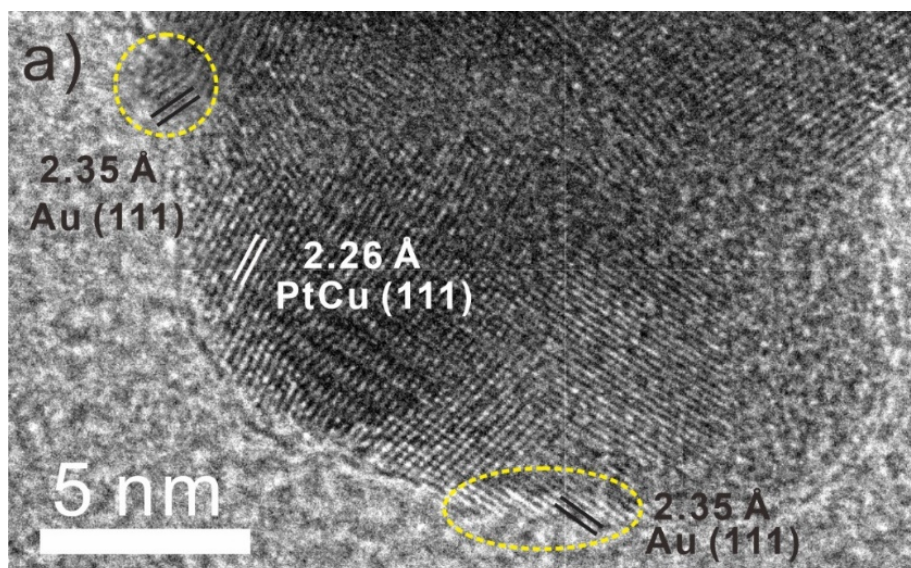


Figure S8. (a, b) HRTEM images of PtCu₃-Au.

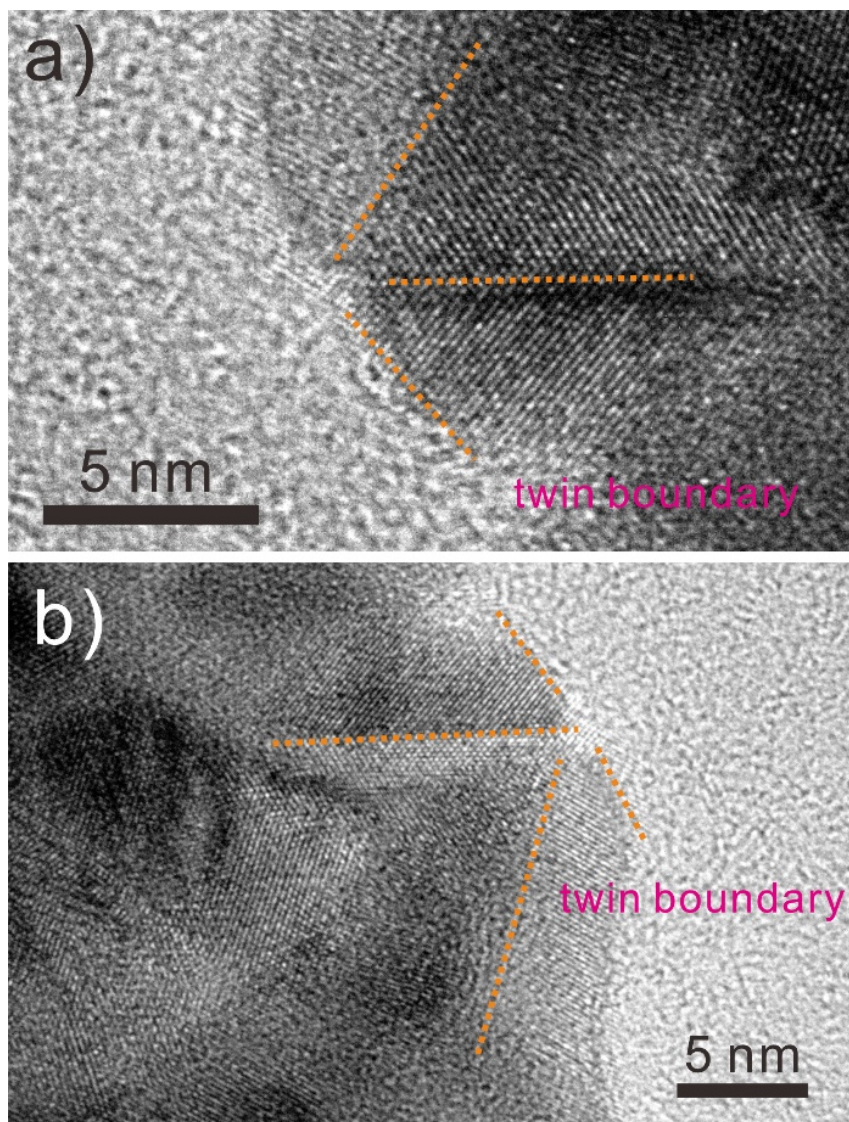


Figure S9. HRTEM images of PtCu₃ NDs (a) and PtCu₃-Au (b).

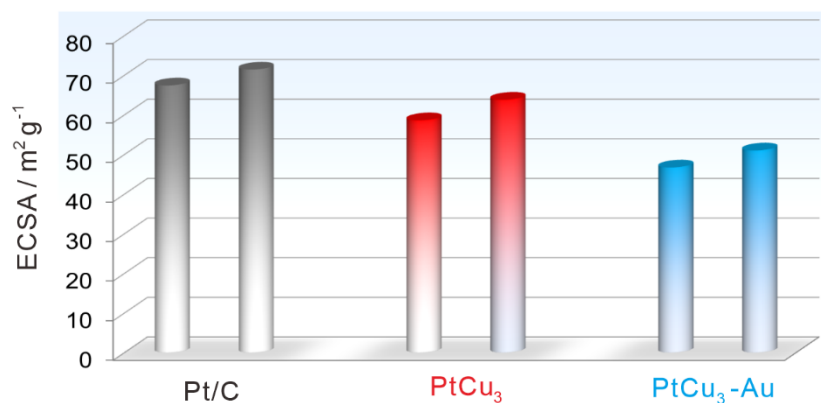


Figure S10. The comparison of ECSA of three catalysts measured by hydrogen desorption (left) and CO stripping (right).

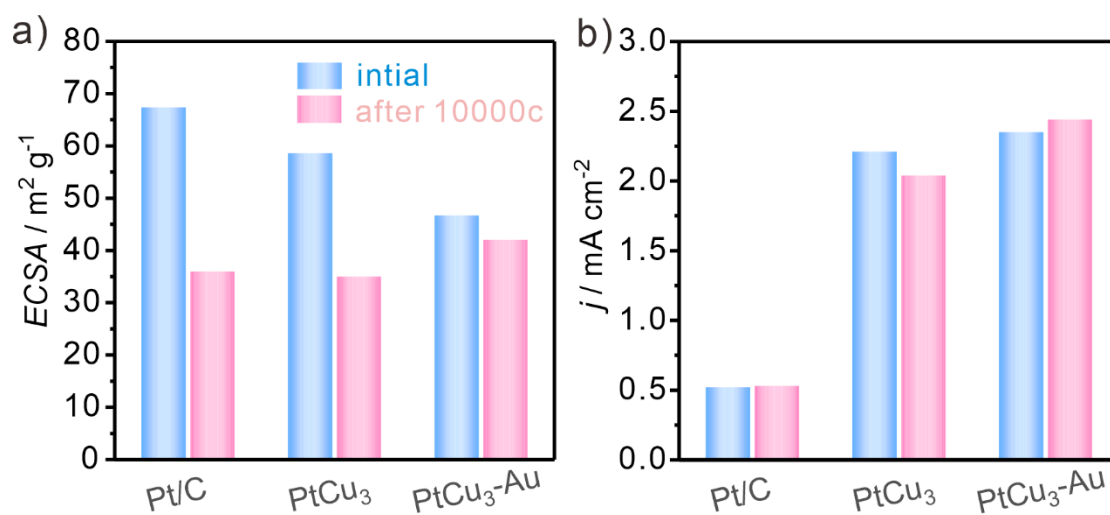


Figure S11. ECSA (a) and MOR specific activity (b) of different catalysts before and after 10000 cycles.

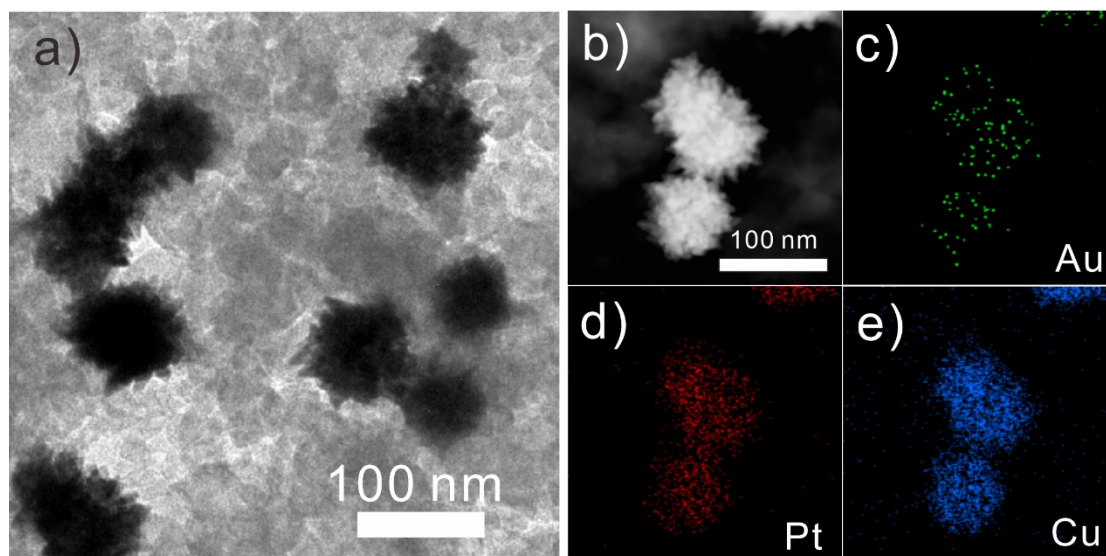


Figure S12. TEM image (a) and EDX mapping (b-e) of PtCu₃-Au catalyst after stability test.

Table S1. Comparison of element ratio of different catalysts before and after cycling measured by EDX.

Sample	Ratio	Initial	After cycling
PtCu ₃	Pt : Cu	1 : 2.54	1 : 1.13
PtCu ₃ -Au	Pt : Cu : Au	1 : 2.30 : 0.08	1 : 1.95 : 0.06