

Electronic Supplementary Information for

**Probing local charge transfer processes of Pt-Au heterodimers in
plasmon-enhanced electrochemistry by CO stripping techniques**

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EXPERIMENTAL SECTION

1. Reagents and Chemicals.

Chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) was obtained from Shanghai Shiwu Chemical Reagent Science and Technology Co., Ltd., polyvinylpyrrolidone (PVP, $M_w = 55000$), N, N-Dimethylformamide (DMF) and chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) were obtained from Sigma-Aldrich. Glycine was obtained from Sinopharm Chemical Reagent Co., Ltd. Methanol (CH_3OH) and potassium hydroxide (KOH) were obtained from Xilong Scientific Co., Ltd. Carbon monoxide (CO) was obtained from Dalian Special Gases CO., Ltd. Ultra-pure water ($18.2 \text{ M}\Omega \text{ cm}$) was used throughout the experiments.

2. Synthesis of Pt concave cube seeds for Pt-Au dimers.

The synthesis of Pt concave cubes was adapted from literature reports. Briefly, 666 mg of PVP and 125 mg of glycine were dissolved in 10 mL of ultra-pure water. Then 3.33 mL of H_2PtCl_6 (20 mM) was added to the uniform solution and the mixture was stirred to obtain a yellow solution. The resulting solution was heated in an autoclave at 180°C for 8 h. Then, the solution was centrifuged (11000 rpm, 15 min) and was washed twice, and then dispersed in DMF for Pt-Au dimers synthesis.

3. Synthesis of Pt-Au dimers.

400 mg PVP was dissolved in 5 ml of DMF. Then 13.3 μL of HAuCl_4 (0.25 M) and 0.73 ml of seeds were added to the uniform solution. The mixture was then stirred in an oil bath at 80°C for 4.5 h, and the resulting solution was washed three times with water and ethanol.

4. Instrumentation.

Transmission electron microscopy (TEM) images and high-resolution TEM (HRTEM) images, scanning transmission electron microscopy (STEM) images and energy dispersive X-ray spectroscopy (EDX) images were acquired using a JEOL JEM-2100F TEM operating at 200 kV. X-ray diffraction (XRD) patterns were obtained on a Bruker D8 ADVANCE and $\text{Cu K}\alpha$ radiation. Scanning electron microscopy (SEM) images were taken using a JEOL JSM-6700F microscope operating at 20 kV. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher ESCALAB 250Xi spectrometer using a monochromatic $\text{Al K}\alpha$ X-ray source (1486.6 eV). C 1s at

284.5 eV was used as the charge reference to determine core-level binding energies. The element ratio of the Pt-Au dimer was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Thermo Scientific iCAP7400 instrument (Thermo Fisher Scientific, USA). UV-visible (UV-Vis) spectrometry was measured by UV-1800 (Shimadzu, Japan).

5. Electrochemical measurements.

All the electrochemical measurements were conducted in a three-electrode system with the CHI760E electrochemical workstation (CH Instruments, Instrument Corporation, China). Glassy carbon electrodes (GCE, 3.0 mm diameter) were used as the working electrode. calomel electrode (SCE, saturated KCl) and Pt nets were used as the reference and counter electrodes, respectively. The 0.5 mL test ink dispersed in water contains ~0.69 mg of as-synthesized Pt-Au dimer with a mass ratio between Au and Pt is 1.98:1. The mixture was then sonicated vigorously for 30 min to form a homogeneous suspension. Subsequently, 4 μ L of the above suspension was dropped on the GCE and used for electrochemical measurements after solvent evaporation. All the potentials in the pictures were reported on a reversible hydrogen electrode (RHE) scale by the Nernst equation ($E_{\text{RHE}} = E_{\text{SCE}} + 0.0591 \cdot \text{pH} + 0.241$). All of these catalysts were activated through the cyclic voltammetry (CV) technique at the 1 M KOH between -1.0 and 0.4 V vs. SCE at a scan rate of 100 mV s⁻¹. The optical filter cut-on 515 nm was chosen to control the light wavelength.

The CO-stripping experiments were conducted in a single cell with 1.0 M potassium hydroxide (KOH) electrolyte under ambient conditions. The activated electrodes were first adsorbed with CO in the CO-saturated electrolyte with CO bubbling at a potential of 0.1 V vs. RHE for sufficient adsorption. Then the CO-stripping experiments were conducted after removing CO from the electrolyte by high-purity nitrogen through the CV technique at a scan rate of 50 mV s⁻¹ between -0.4 and 1.2 V vs. RHE.

Before the methanol oxidation reactions (MOR) began, a CV scanning from 1.0 and 0.4 V vs. SCE at a scan rate of 50 mV s⁻¹ was conducted to obtain catalysts' hydrogen adsorption regions for electrochemical active surface area (ECSA) calculation through hydrogen underpotential deposition (HUPD). Then the MOR were conducted in a

single cell with the electrolyte containing 1.0 M KOH and 1.0 M methanol under ambient conditions. The activated electrodes were scanned through the CV technique at a scan rate of 50 mV s⁻¹ between -0.3 and 1.5 V vs. RHE. The datums were recorded after curves stabilization. The chrono-potentiometry curves were assessed at a current of 1 mA in 1.0 M KOH and 1.0 M methanol.

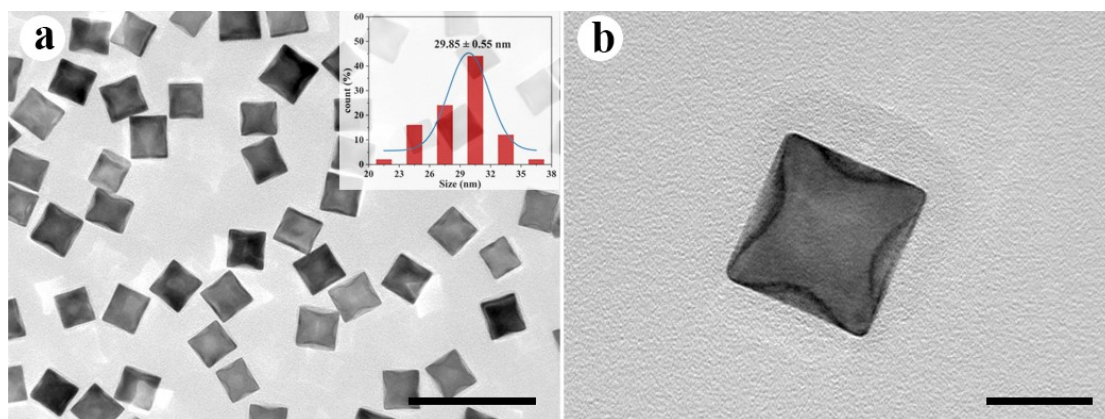


Fig. S1 (a) Large-scale TEM image of Pt concave nanocubes and their size distribution statistics (inset, ~ 29.85 nm). (b) TEM image of an individual Pt concave nanocube. Scale bars: (a) 100 nm (b) 20 nm

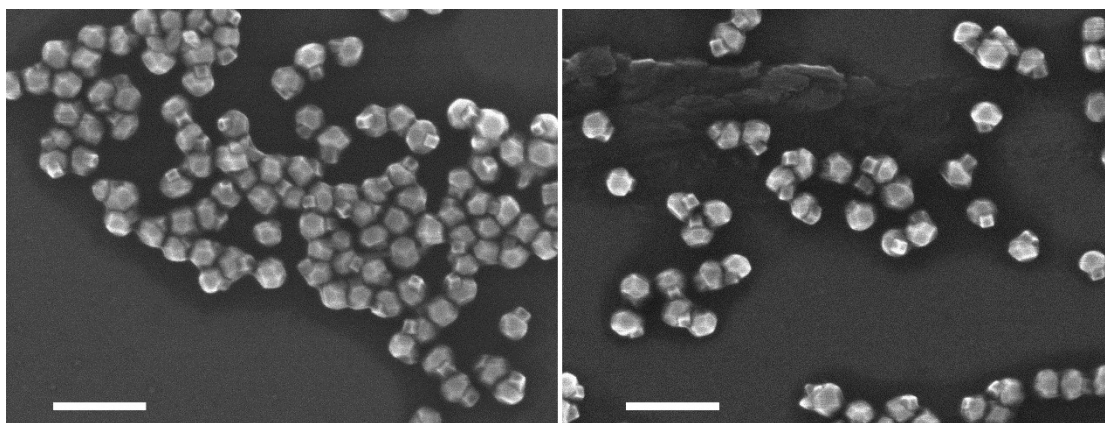


Fig. S2 SEM images of Pt-Au heterodimers. Scale bars: 100 nm

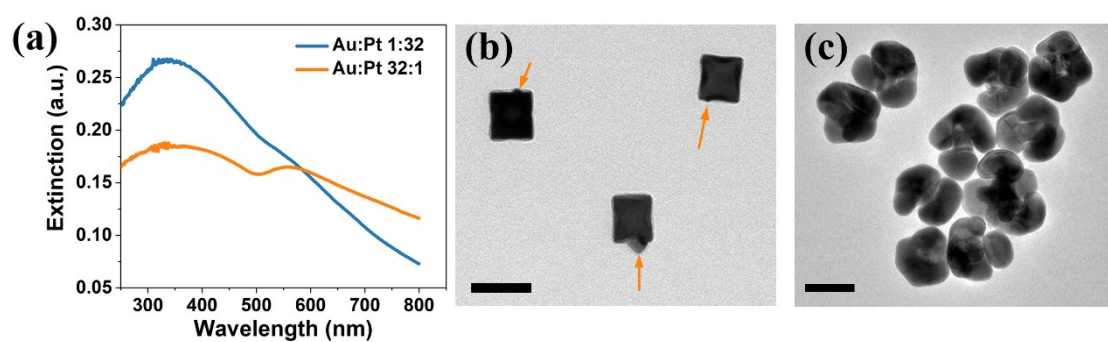


Fig. S3 (a) UV-vis extinction spectra of Pt-Au heterostructures with a low content (blue line) and a high content (orange line) of Au, and (b, c) their corresponding TEM images. The orange arrows in (b) point to the Au component. Scale bars: 50 nm.

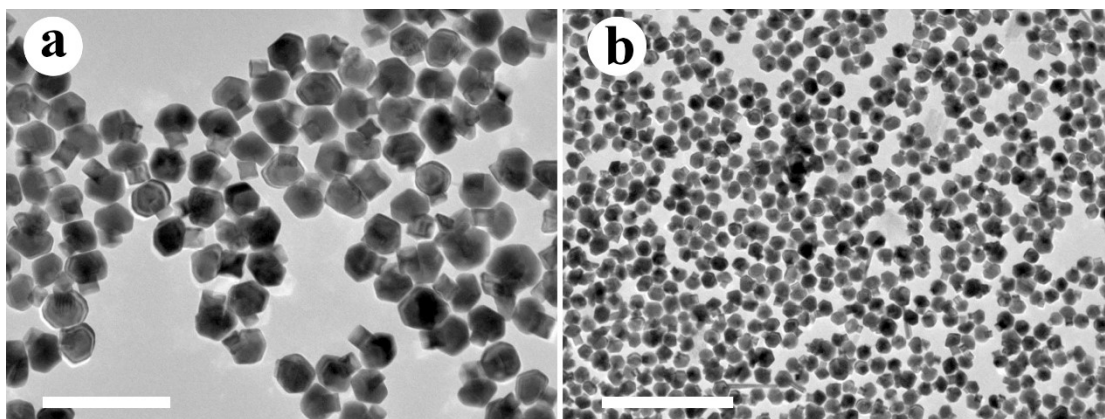


Fig. S3 Large-scale TEM images of Pt-Au heterodimers. Scale bars: (a) 200 nm (b) 500 nm.

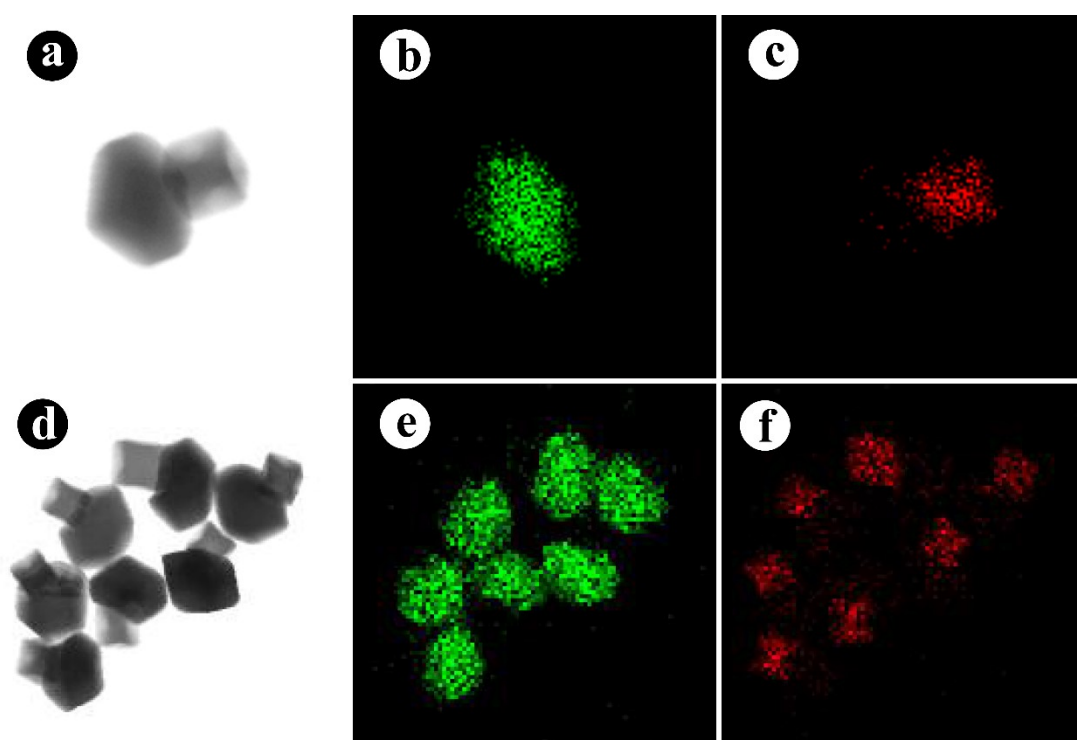


Fig. S4 Additional STEM and corresponding EDS-mapping images of Pt-Au heterodimers.

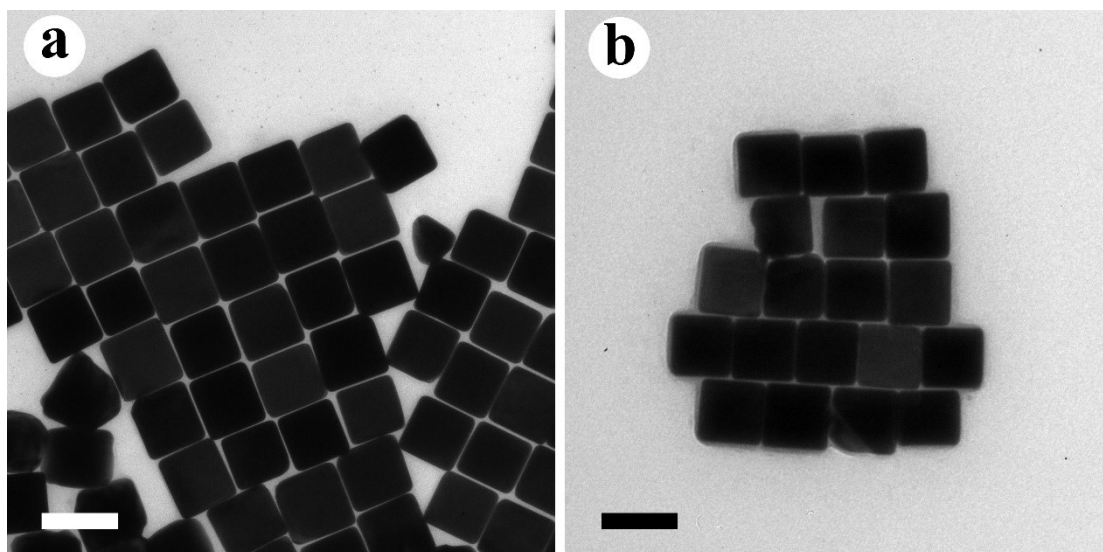


Fig. S5 TEM Images of Au nanocubes. Scale bars: 100 nm

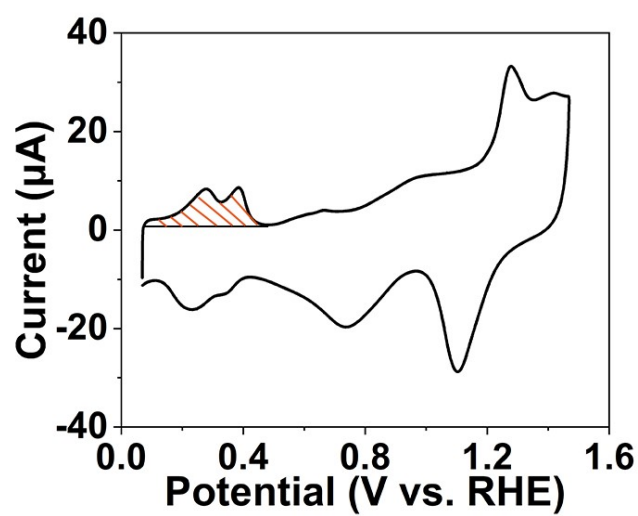


Fig. S6 CV scanning of Pt-Au heterodimers in 1.0 M KOH electrolyte from 1.0 and 0.4 V vs. SCE at a scan rate of 50 mV s^{-1} to obtain catalysts' hydrogen adsorption regions (shadow area) for ECSA calculation through HUPD.

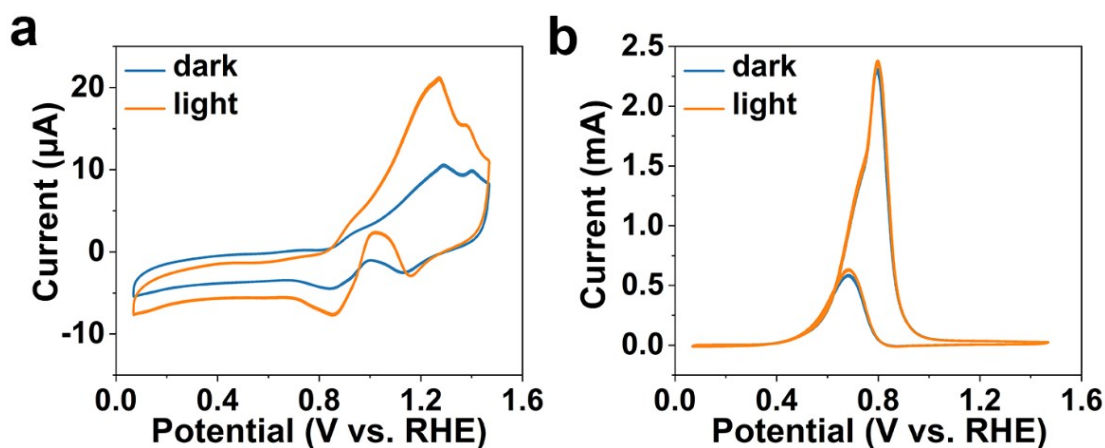


Fig. S7 Electrocatalyst MOR curves of (a) Pt concave nanocubes and (b) Au nanocubes.

Table. S1 ICP-MS results of Pt-Au heterodimer.

Au component	Pt component	Mass ratio (Au:Pt)	Molar ratio (Au:Pt)
91.83 ppm	46.39 ppm	1.98	1.96

Table. S2 Comparison of the Pt-Au heterodimers with reported plasmonic electrocatalysts.

Catalyst	Activity Enhancement	Refs.
Pt-Au heterodimer	53 %	This work
Au@Pt octahedral	11 %	<i>Nano Lett.</i> , 2023, 23 , 1774-1780
Pt-Au nanodisk	230 %	<i>Nanoscale</i> , 2019, 11 , 11888-18874
PtAu Nanoframe	500 %	<i>Small</i> , 2023, 19 , 2206377
Au Nanohole/PtRu	30 %	<i>ACS Appl. Mater. Inter.</i> , 2020, 12 , 50426-50432
Au@AgPt urchin	23.5 %	<i>J. Mater. Chem. A</i> , 2020, 8 , 6638-6646
PtAu dendrites	80 %	<i>ChemElectroChem</i> , 2018, 5 , 1191-1196
Au@Pd@Pt NPs	240 %	<i>Electrochim. Acta</i> , 2016, 209 , 591-598

