

Structurally Modulated AuPd Alloy Nanorods for Plasmon-Promoted Methanol Electrooxidation

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S1. Additional Experimental Details

S1.1 Synthesis of Au Nanorods (NRs)

Au NRs were synthesized using a seed-mediated growth protocol following a previously published work with minor modifications [1]. The Au seeds were prepared by reducing HAuCl₄ with NaBH₄ in the presence of CTAB. Briefly, 5.0 mL of 0.5 mM HAuCl₄ was added to 5.0 mL of 200 mM CTAB solution. Then, 1.0 mL of ice-cold, freshly prepared 6.0 mM NaBH₄ was quickly injected into the mixture under magnetic stirring (1200 rpm). The seed solution was stirred for 2 min and then left undisturbed for 30 min before use. To prepare the Au NRs growth solution, 9.0 g of CTAB and 1.234 g of NaOL were dissolved in 250 mL of water at 60 °C. The solution was cooled to 30 °C, and then 12 mL of 4.0 mM AgNO₃ was added. The mixture was kept undisturbed at 30 °C for 15 min, followed by the addition of 250 mL of 1 mM HAuCl₄. The solution became colorless after being stirred at 700 rpm for 90 min, and then 2.2 mL of HCl (37 wt % in water, 12.1 M) was introduced into the mixture. After another 15 min with magnetic stirring at 700 rpm, 1.25 mL of 64 mM AA was added. Finally, 0.4 mL of seed solution was injected into the growth solution, and the mixture solution was vigorously stirred for another 30 s and then left undisturbed at 30 °C for 12 h. The resulting Au NRs were collected by centrifugation at 8000 rpm for 10 min, followed by removal of the supernatant and finally re-dispersed in 30 mL of 100 mM CTAB.

S1.2 Synthesis of Au@Au_xPd_y and Au@Au_xPd_yAg_n Core-Shell NRs

Au@Au_xPd_y core-shell NRs with different structures were prepared through the overgrowth of the Au NRs in the presence of HAuCl₄, PdCl₂, CTAB, and AA, following a previously published work with minor modifications [1]. In a typical procedure, H₂O (3.30 mL), HAuCl₄ (0.20 mL, 10 mM), CTAB (0.90 mL, 0.10 M), and AA (0.50 mL, 0.10 M) were sequentially added to a 20 mL glass bottle. Then, a total of 0.20 mL of different proportioned HAuCl₄ (10 mM) and PdCl₂ (10 mM) solution was added. After gently mixing the solution for 30 s, 100 μL of prepared Au NRs (in 100 mM CTAB) was injected into the growth solution. The reactants were gently mixed for another 30 s and then left undisturbed at 30 °C for 1 h. The obtained Au@Au_xPd_y Core-Shell NRs were washed with water twice through centrifugation/redispersion cycles, and finally redispersed in 200 μL of 20 mM CTAB. The synthesis method of adding Ag to the shell is generally the same, only the corresponding proportion of AgNO₃ is added to the growth solution.

S2. Additional Figures

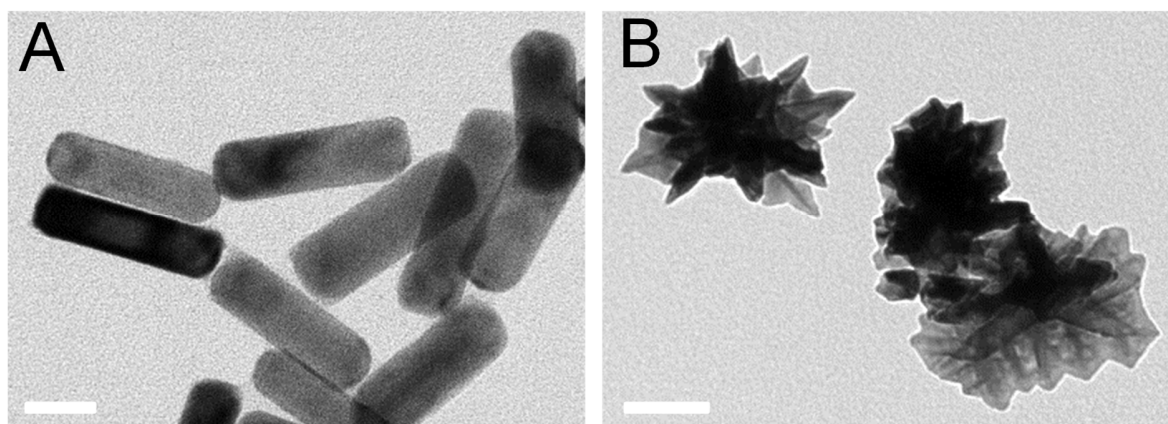


Figure S1. TEM images of (A) Au NRs and (B) Pd NSs. The scale bars of the images are 20 nm (A) and 100 nm (B), respectively.

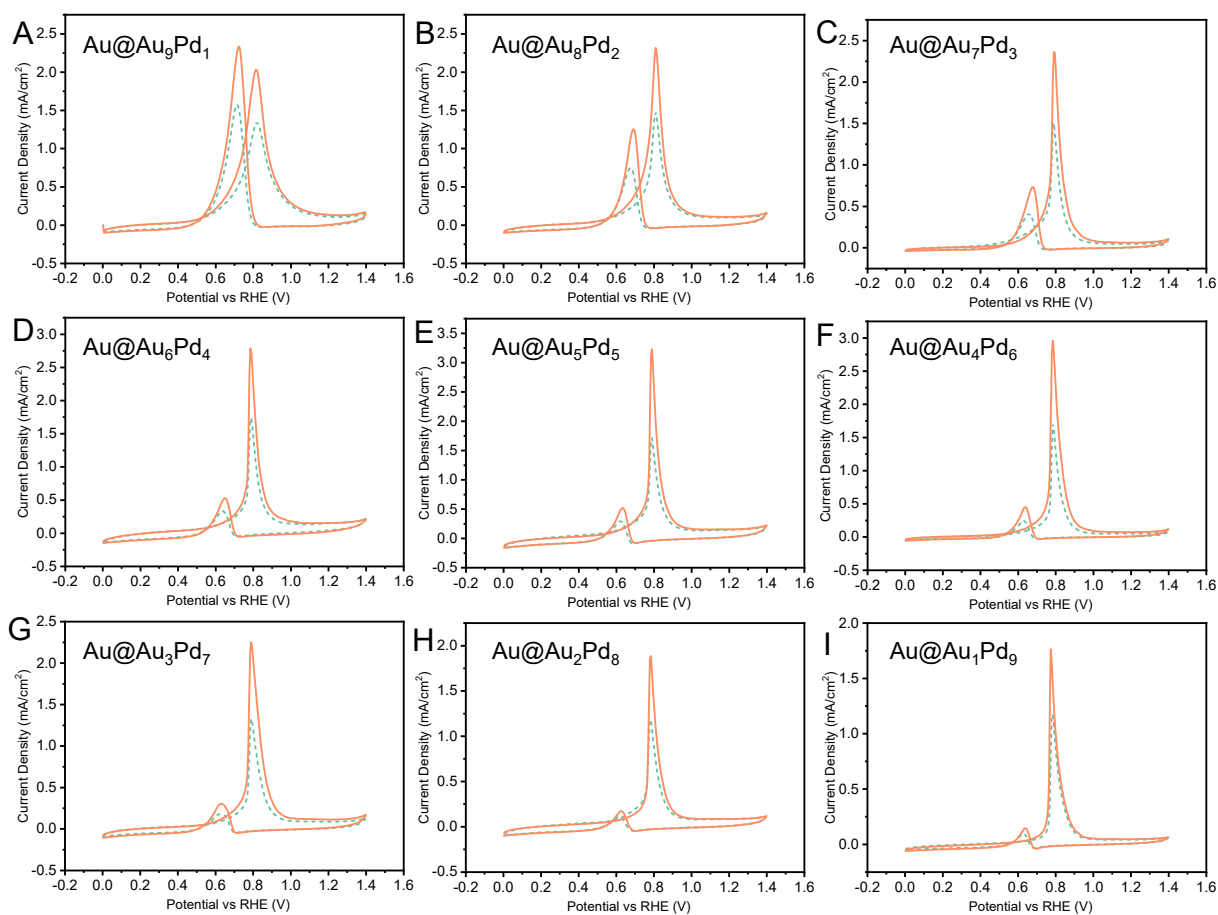


Figure S2. MOR curves of catalysts with different Au/Pd ratios obtained in 1 M KOH + 0.5 M methanol at a scan rate of 50 mV s^{-1} under darkness (dashed lines) and white-light illumination (solid lines).

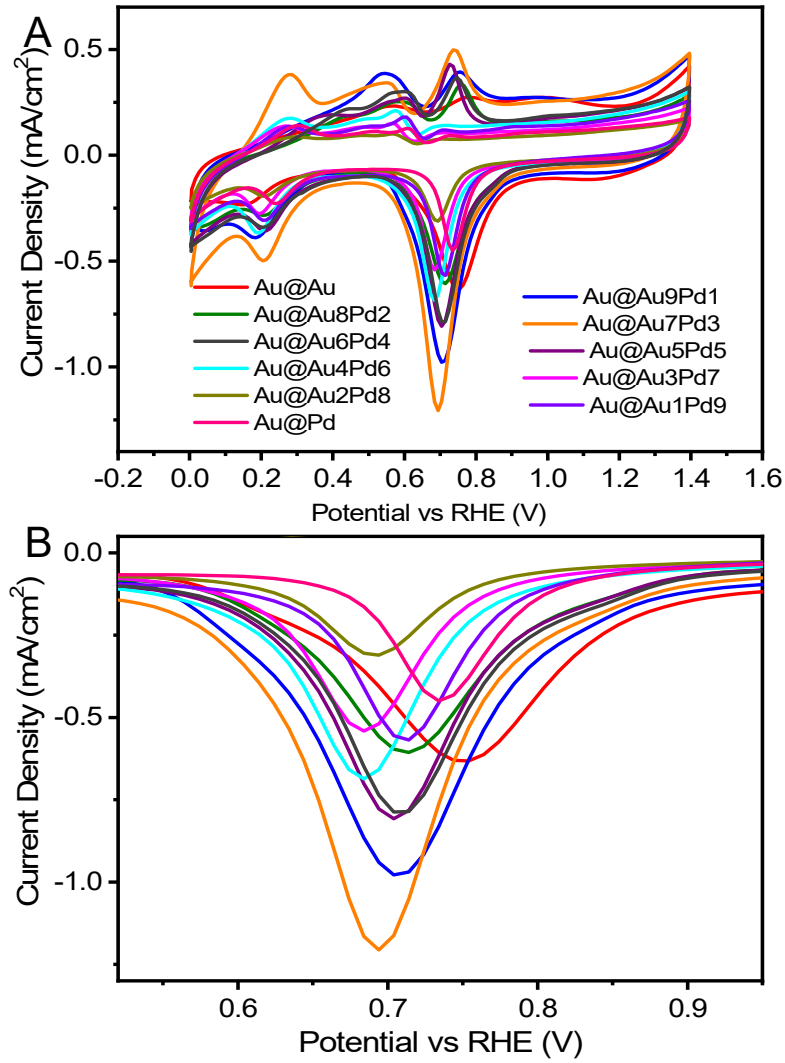


Figure S3. CV curves of catalysts with different Au/Pd ratios obtained in 1 M KOH with saturated Ar at a scan rate of 50 mV s⁻¹. **(A)** Complete curve. **(B)** Locally enlarged images of PdO reduction peaks. The specific activity (SA) was obtained by the equation:

$$SA = \frac{J}{A_{real}}$$

And the A_{real} can be calculated by the equation:

$$A_{real} = \frac{Q_{real}}{Q_{Pd}}$$

Q_{real} can be measured through integrating the PdO reduction peak in the CV curve, and Q_{Pd} refers to the specific amount of electricity corresponding to the full coverage of the Pd surface by one monolayer of oxygen. Generally, $Q_{Pd} = 420 \mu\text{C cm}^{-2}_{Pd}$.

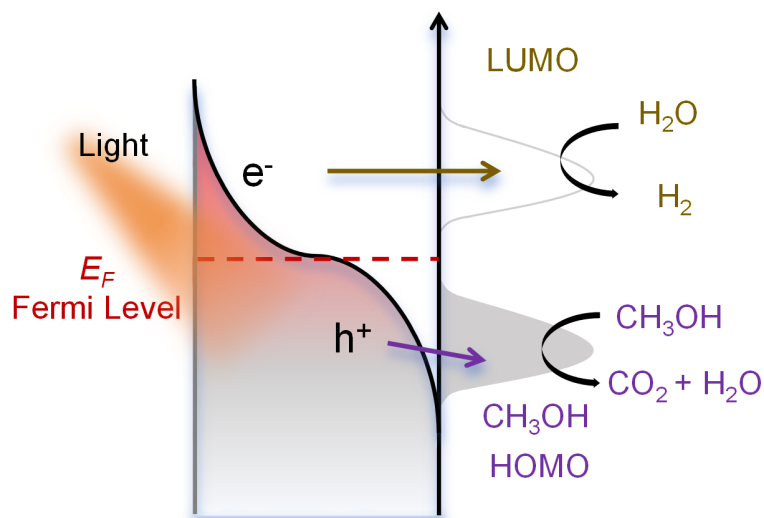


Figure S4. Schematic illustration of the plasmon-induced generation of hot carriers and their involvement in driving the MOR and HER. The hot holes were mainly used for the oxidation of methanol, while the hot electrons could be transferred to reduce H_2O to form H_2 .

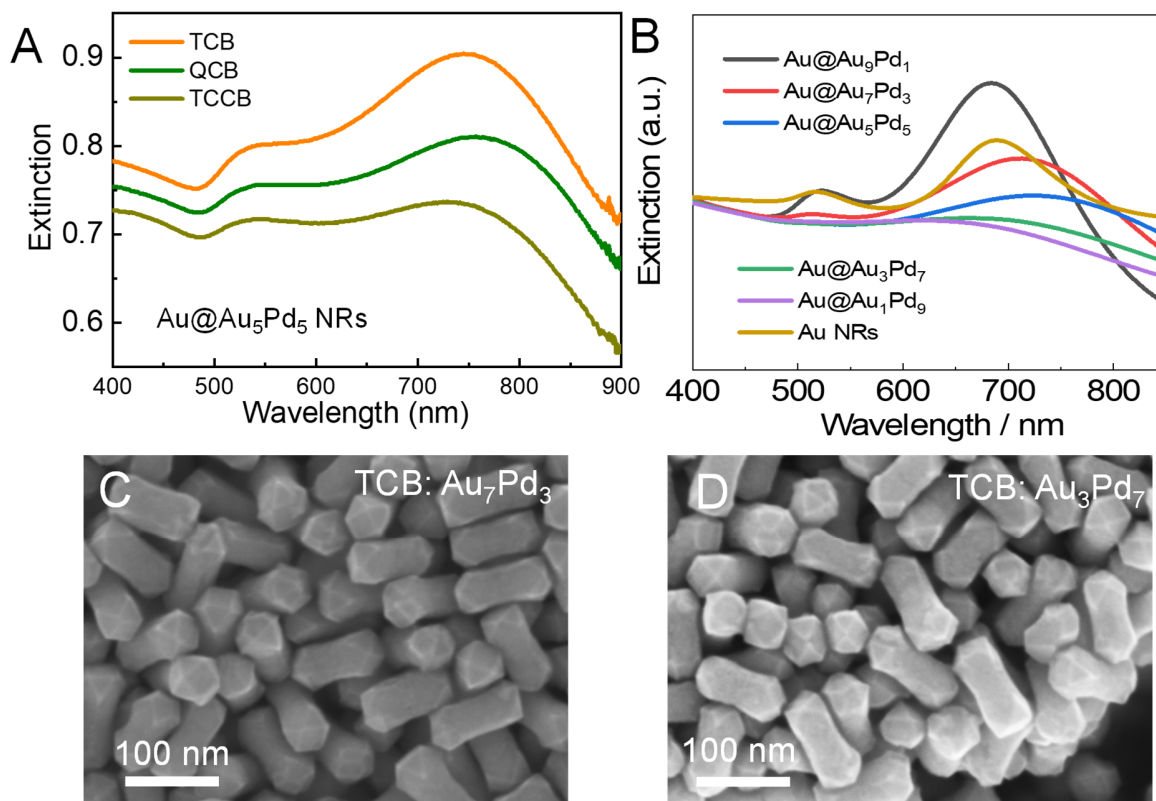


Figure S5. (A) Extinction spectra of Au@Au₅Pd₅ NRs with TCB, QCB, and TCCB structures, respectively. The concentration of AA to obtain TCB, QCB, and TCCB structures is 0.4 mM, 2 mM, and 10 mM, respectively. (B) Extinction spectra of Au@Au_xPd_y NRs with TCB structure and varying Au:Pd ratios as marked. (C,D) SEM images (C) Au@Au₃Pd₇ NRs with TCB structure and (D) Au@Au₇Pd₃ NRs with TCB structure, respectively.

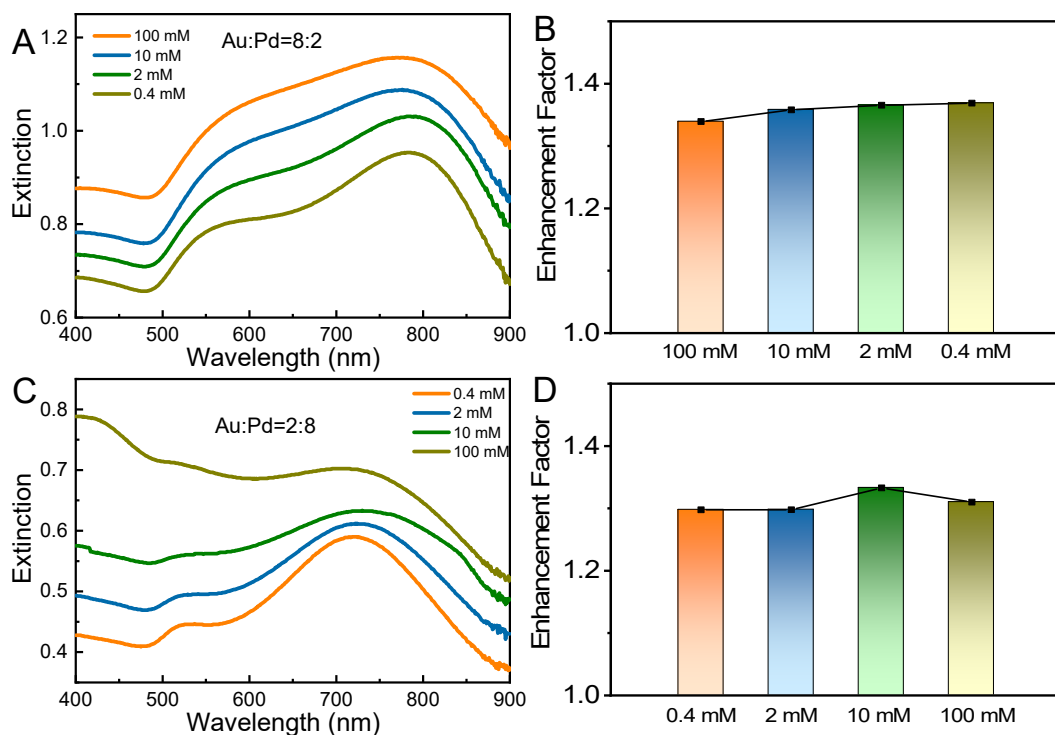


Figure S6. Extinction spectra and enhancement factor (EF) of (A,B) Au@Au₈Pd₂ and (C,D) Au@Au₂Pd₈ NRs, respectively. The AuPd alloy samples were synthesized in the presence of 40 mM CTAB and 0.4 mM, 2 mM, 10 mM, and 100 mM of AA at a corresponding [H₂PdCl₄]/[HAuCl₄] molar ratio.

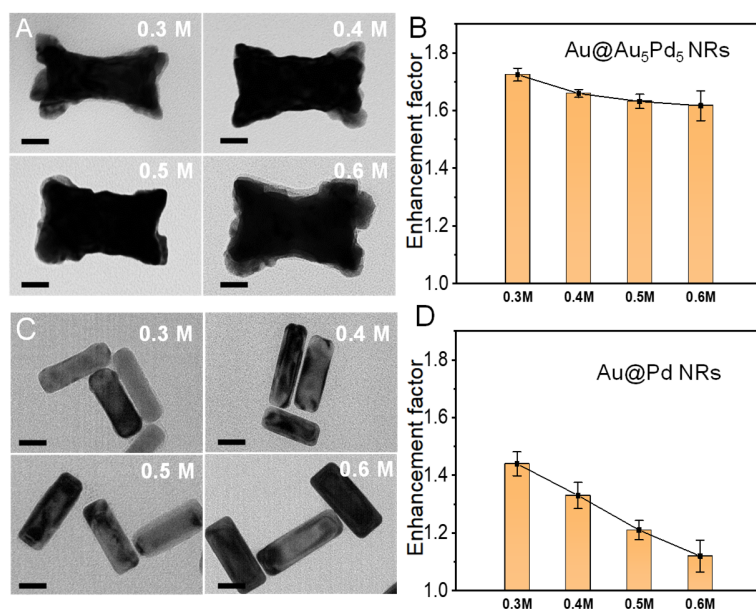


Figure S7. (A) TEM images of Au@Au₅Pd₅ NRs with total [H₂PdCl₄] + [HAuCl₄] at 0.3 M, 0.4 M, 0.5 M, and 0.6 M. (B) EF of corresponding Au@Au₅Pd₅ NRs. (C) TEM images of Au@Pd NRs with [H₂PdCl₄] at 0.3 M, 0.4 M, 0.5 M, and 0.6 M. (D) EF of corresponding Au@Pd NRs. Scale bars: 20 nm.

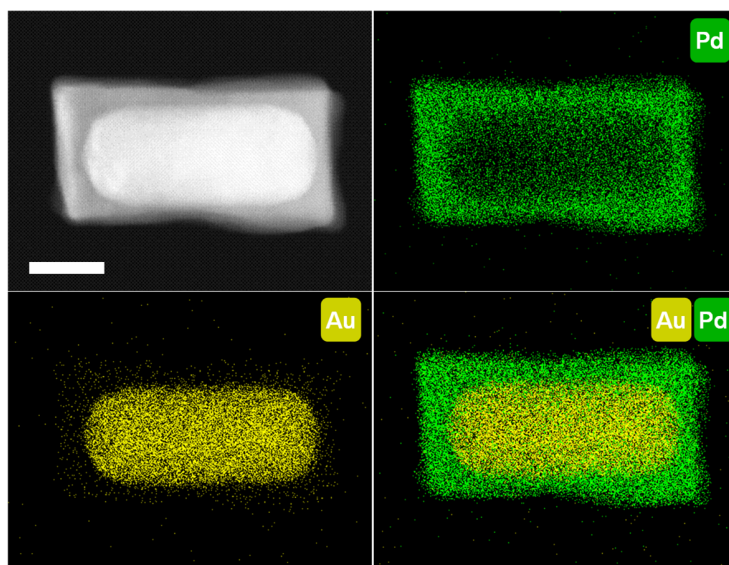


Figure S8. Corresponding EDX mapping images of Pd and Au elements of Au@Pd NRs, which further confirmed the core-shell structure. The above images share the same scale bar (20 nm).

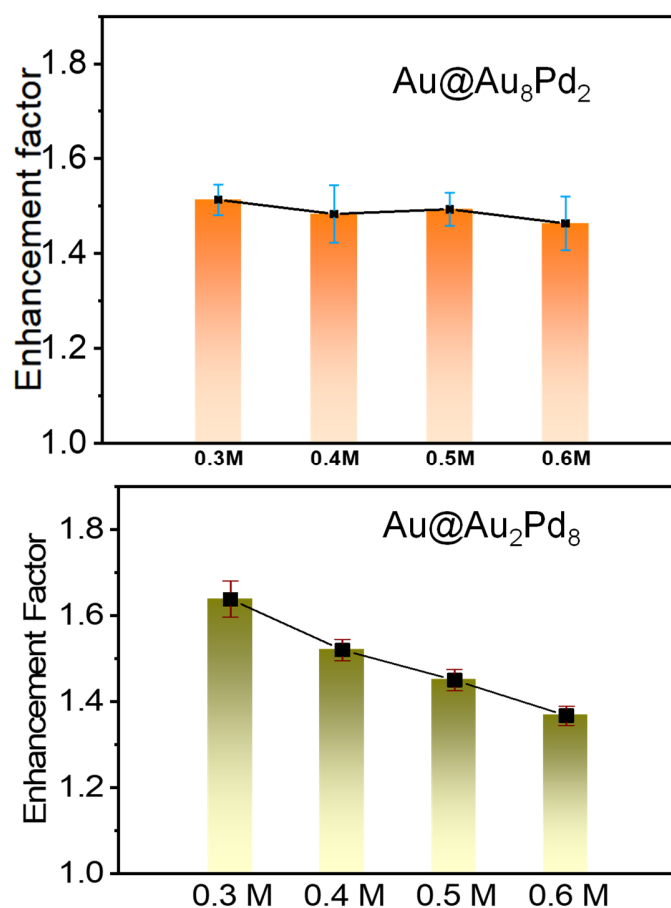


Figure S9. EF of Au@Au₈Pd₂ NRs (top panel) and Au@Au₂Pd₈ NRs (bottom panel) with different shell thickness through changing the total amount of [H₂PdCl₄] + [HAuCl₄] at 0.3 M, 0.4 M, 0.5 M, and 0.6 M during the synthesis.

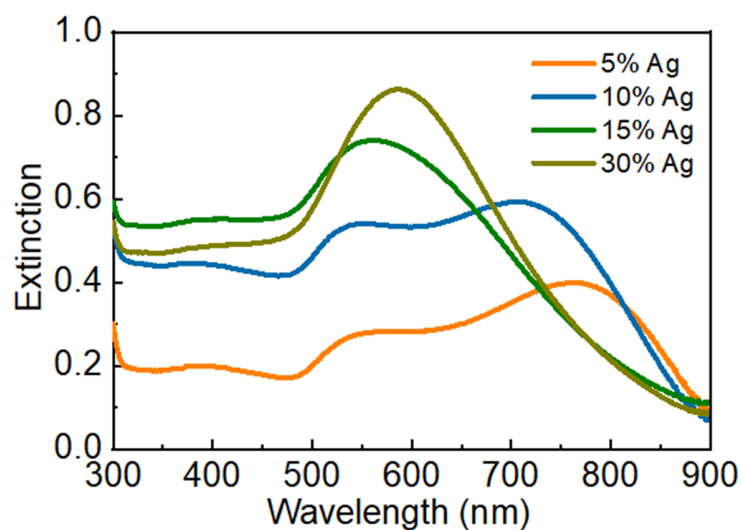


Figure S10. Extinction spectra of Au@AuPdAg NRs with different amounts of Ag that are added during the synthesis.

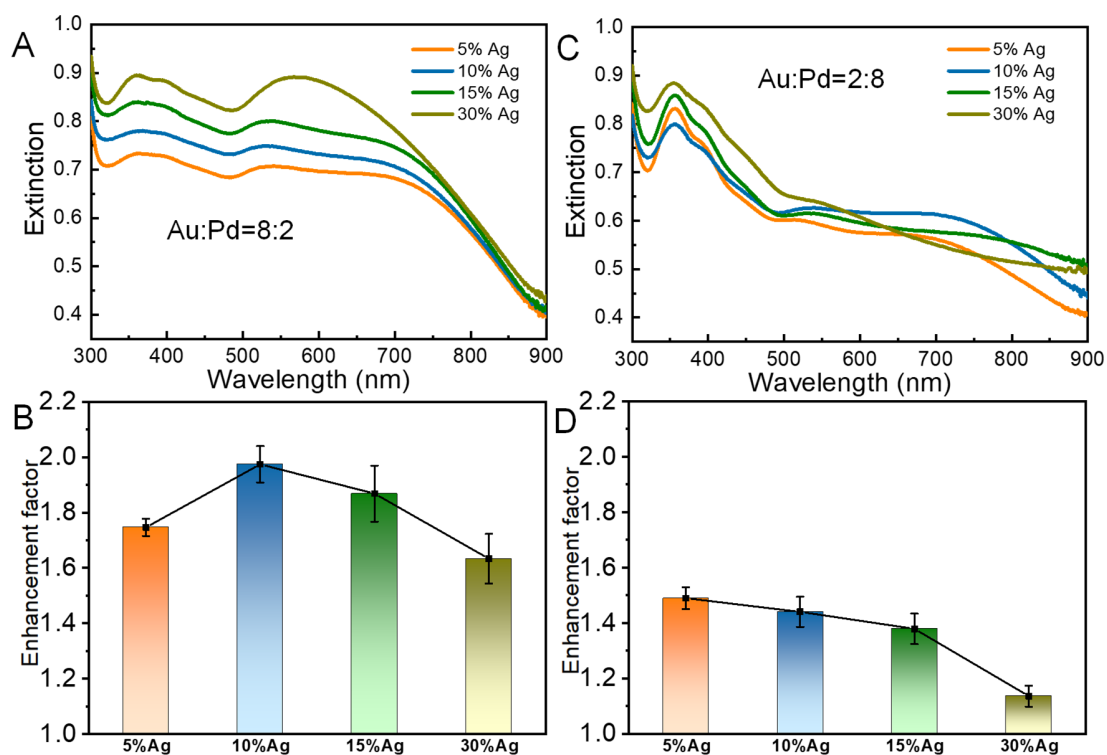


Figure S11. Extinction spectra and EF of (A,B) Au@Au₈Pd₂Ag_n and (C,D) Au@Au₂Pd₈Ag_n NRs, respectively. The AuPdAg alloy samples were synthesized in the presence of 20 mM CTAB and 10 mM AA at a corresponding [H₂PdCl₄]/[HAuCl₄]/[AgNO₃] molar ratio.

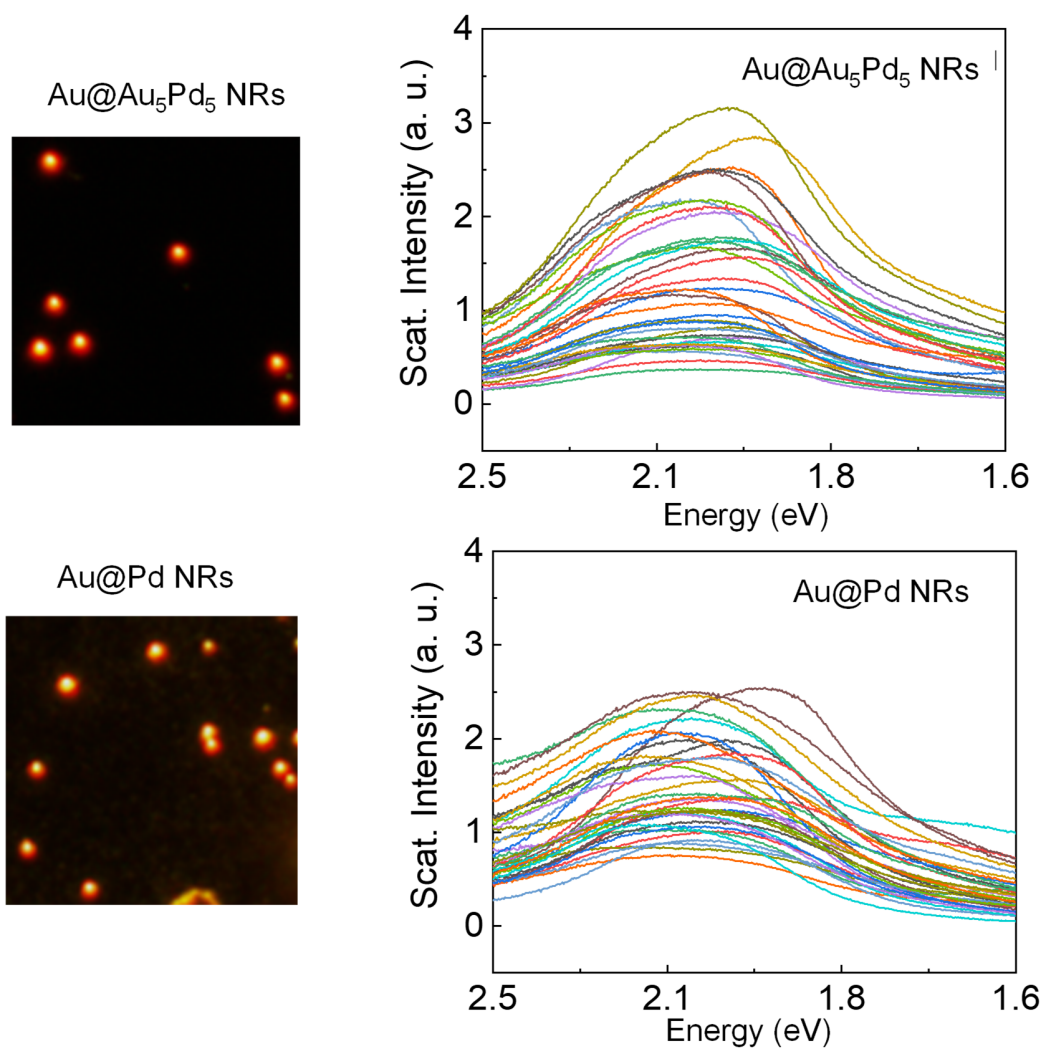


Figure S12. Photographic images and single-particle scattering spectra of the Au@Au₅Pd₅ and Au@Pd NRs under dark-field microscopy.

S3. Additional Tables

Table S1. Vibrational assignment of the most intense band observed in experimental normal. Raman of TP adsorbed on Au@Au_xPd_y NRs [2].

SERS / cm ⁻¹	Assignment
944, 1004	In-plane bending vibration of the benzene ring
1025	C-S stretching vibration
1578	Phenyl-C stretching

Table S2. Vibrational assignments of the absorption bands observed in in-situ Raman spectroscopy of the electrochemical MOR over the Au@Au_xPd_y NRs [3,4].

SERS / cm ⁻¹	Assignment
471	Pd-C stretching of adsorbed CO
527	Pd-O stretching of adsorbed CO
1022	C-O stretching of methanol
1490	Stretching vibrations of COO ⁻ and CO ₃ ²⁻
2150	C-O stretching of adsorbed CO

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