

Supporting Information

Controlling Alloy to Core-Shell Structure Transformation of Au-Pd Icosahedral Nanoparticles

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Experimental

Materials

Chloroauric acid (HAuCl_4 , 99.9%), poly(vinyl pyrrolidone) (PVP, MW=5,5000), cetyltrimethylammonium bromide (CTAB, 99%) and cetyltrimethylammonium chloride (CTAC, 99%) were all obtained from Aladdin company. Palladium chloride (PdCl_2 , 99.9%) were purchased from J&K scientific company. High purity N_2 (99.999%) gas was purchased from Shengying company. The H_2PdCl_4 (10 mM) aqueous solution was prepared by completely dissolving PdCl_2 (17.7 mg) in HCl (0.02 M, 10 mL) with heating at 60 °C in a water bath and then cooled to room temperature. Other reagents were used without further purification, Milli-Q water ($>18.0 \text{ M}\Omega\cdot\text{cm}$) was used to prepare all aqueous solutions.

Preparation of alloy and core-shell Au-Pd IHNPs

In a typical synthesis of Au/Pd and Au@Pd IHNPs, 250.0 μL of HAuCl_4 (10 mM) and 250.0 μL of H_2PdCl_4 (10 mM) aqueous solution, 1 mmol CTAB and 100.0 mg PVP were introduced into 10.0 mL water in a 30.0 mL Teflon-lined stainless-steel autoclave and stirred for 10 min at room temperature. The autoclave was then charged with N_2 to 1.0 MPa and moved into an oil bath pan at 180 °C under magnetic stirring. After 70 min or 90 min, the autoclave was taken out and immersed into cold water to cool down. The final product was collected by centrifugation at 10000 rpm for 5 min, washed repeatedly with pure water and ultrasound to remove any residual CTAB or PVP. Au@Pd IHNPs with different shell thicknesses could be obtained by changing reaction time to 80 or 120 min. Pd nanoparticles could be obtained by only using H_2PdCl_4 as precursor and reacted for 120 min.

Characterizations

The products were characterized by TEM (JEOL-2100F), EDS (JEOL-2100), HRTEM (Titan G2 60-300), HRTEM (JEOL-2100), EDS (FEI Tecnai G2 F30). Samples for TEM examination were prepared by putting a droplet of the treated solution on a copper grid coated with a thin carbon film and then evaporated in air at room temperature. X-

ray photoelectron spectra (XPS) measurements for repeatedly washed sample were performed using a K-Alpha X-ray photoelectron spectrometer. XRD spectra were measured on an X-ray diffractometer (Bruker D8 ADVANCE). For ultraviolet-visible (UV-vis) spectroscopy measurements, the products were dispersed in water and the optical extinction spectra were recorded with a Hitachi U-3900H ultraviolet and visible spectrophotometer using a quartz cell with 10 mm path length.

Electrochemical Measurements

The electrochemical measurements for HER were conducted at room temperature in a standard three-electrode cell on a CHI 760E electrochemical workstation. Ag/AgCl electrode was used as the reference electrode. Each sample was dispersed in water (100 μL) containing Nafion (1 μL) and sonicated for 1 h to form a homogeneous ink. In all samples, the amount of Pd were kept constant. Then 10 μL of the dispersion was loaded onto a glassy carbon electrode with 3 mm diameter. Linear sweep voltammetry with scan rate of 5 mV/s were conducted in 1 M KOH. The obtained results were adjusted with 95% iR correction to minimize the influence of ohmic resistance. The potentials in this work were converted to a reversible hydrogen electrode (RHE) scale according to the Nernst equation ($E_{\text{RHE}}=E_{\text{Ag/AgCl}}+0.059\times\text{pH}+0.21$). The overpotential (η) of HER was calculated according to the following formula: $\eta(\text{V})=E_{\text{RHE}}$.

Fig. S1

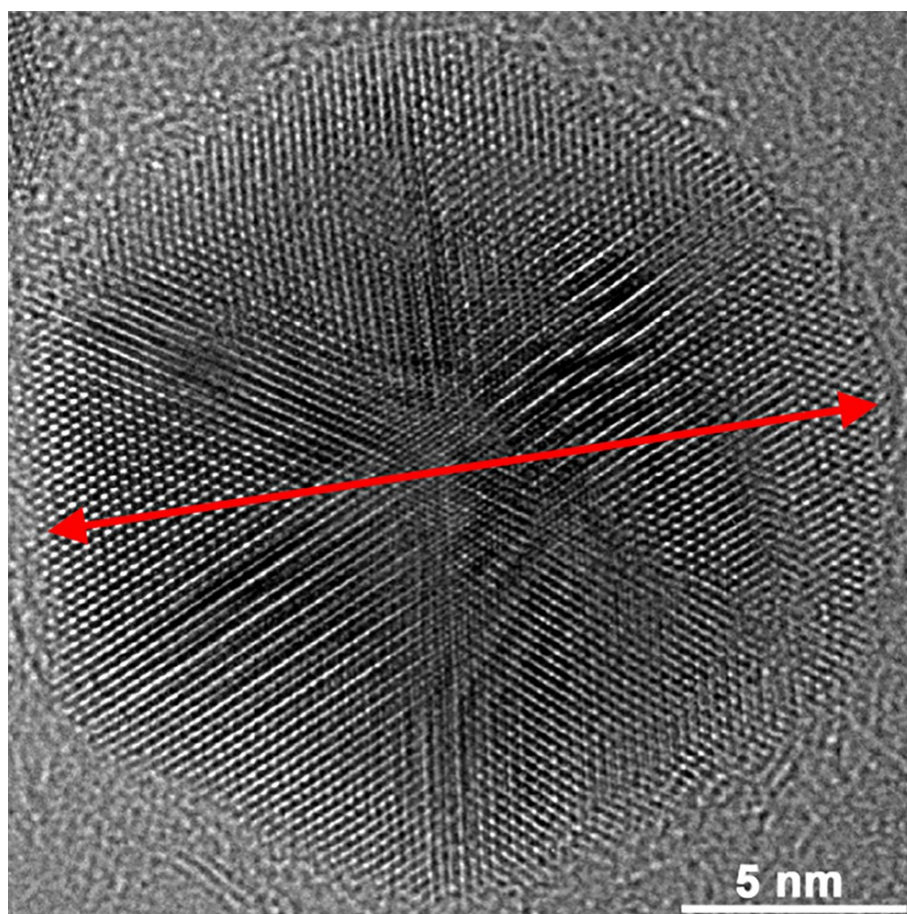


Fig. S1 The way we measured the size of nanoparticle.

Fig. S2

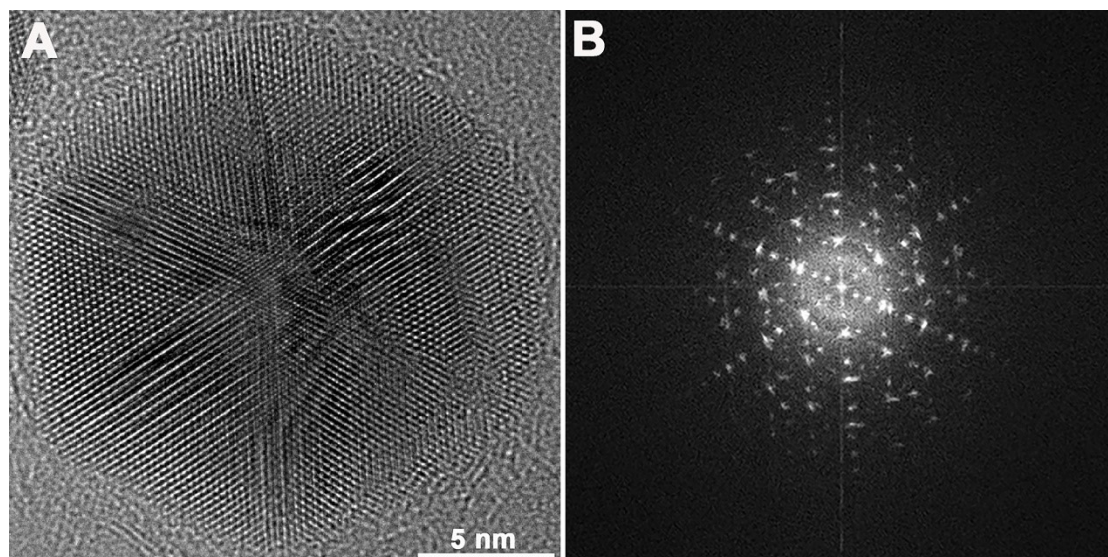


Fig. S2 HRTEM image and corresponding fast Fourier transformation (FFT) image of Au@Pd IHNPs.

Fig. S3

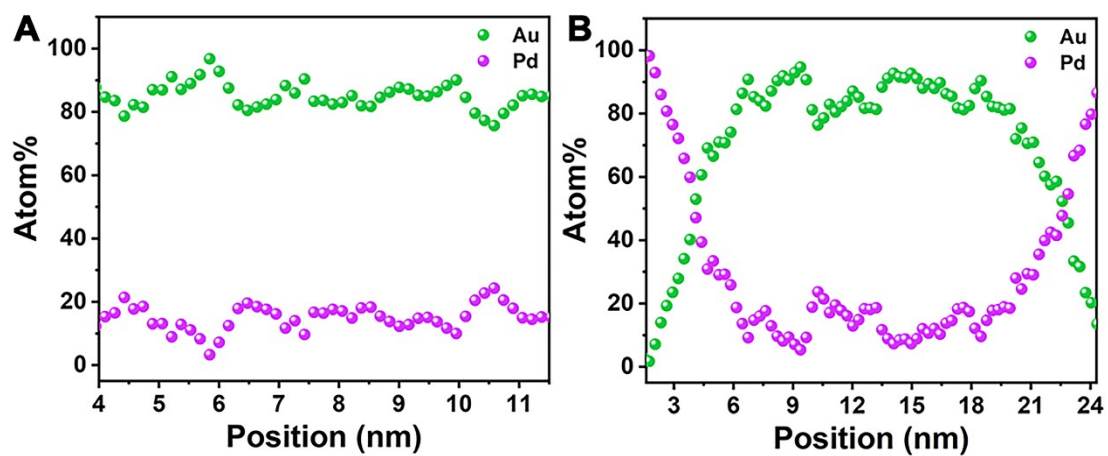


Fig. S3 EDS line scan profiles of (A) alloy Au/Pd IHNPs obtained at 70 min and (B) core-shell Au-Pd IHNPs obtained at 90 min.

Fig. S4

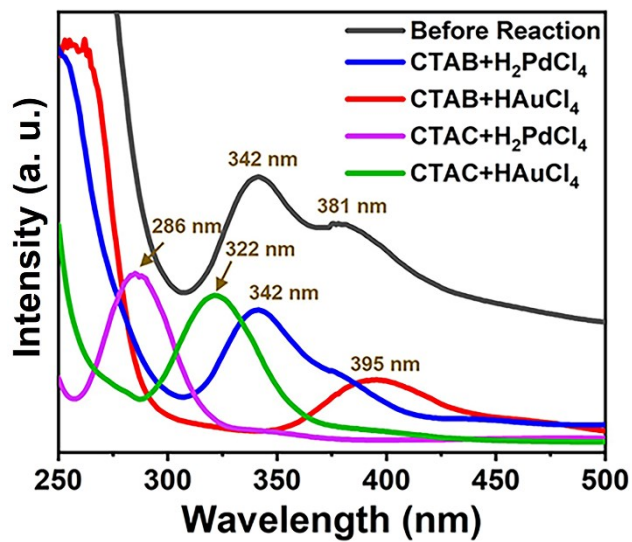


Fig. S4 UV-vis spectrum of reaction solutions before reaction (black line). The violet (CTAC+H₂PdCl₄), green (CTAC+HAuCl₄), blue (CTAB+H₂PdCl₄) and red (CTAB+HAuCl₄) lines are UV-vis spectra of the solution prepared by dissolving HAuCl₄ or H₂PdCl₄ in the corresponding CTAB or CTAC solutions, respectively.

Fig. S5

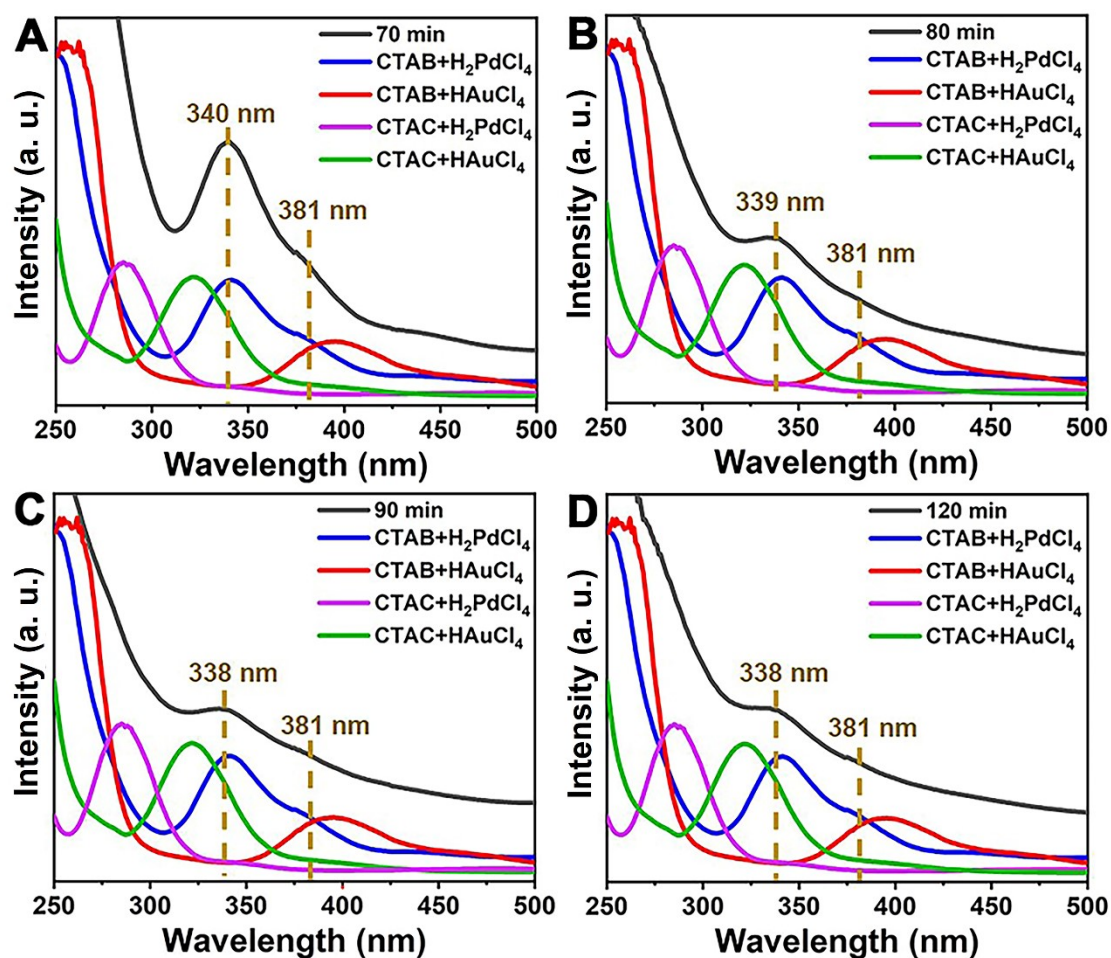


Fig. S5 UV-vis spectra of reaction solutions reacted for (A) 70, (B) 80, (C) 90 and (D) 120 min. The violet (CTAC+H₂PdCl₄), green (CTAC+HAuCl₄), blue (CTAB+H₂PdCl₄) and red (CTAB+HAuCl₄) lines are UV-vis spectra of the solution prepared by dissolving H₂AuCl₄ or H₂PdCl₄ in the corresponding CTAB or CTAC solutions, respectively.

Fig. S6

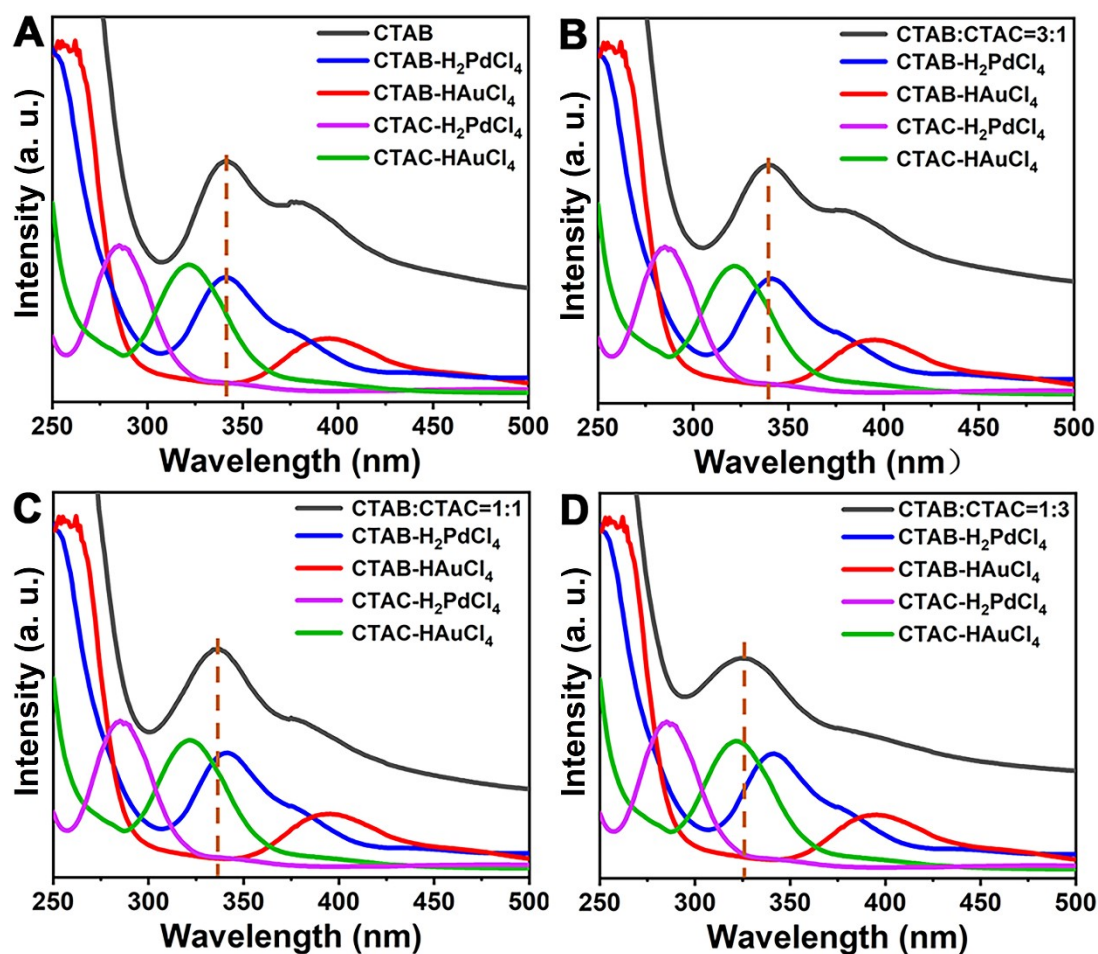


Fig. S6 UV-vis spectra of precursor solution with CTAB:CTAC molar ratios of (A) 4:0, (B) 3:1, (C) 1:1 and (D) 1:3, respectively. The violet (CTAC+H₂PdCl₄), green (CTAC+HAuCl₄), blue (CTAB+H₂PdCl₄) and red (CTAB+HAuCl₄) lines are UV-vis spectra of the solution prepared by dissolving HAuCl₄ and H₂PdCl₄ in the corresponding CTAB and CTAC solutions, respectively.