

Supplementary Information

Shape-Controlled Synthesis of Au@Pd Core-Shell Nanoparticles and Their Corresponding Electrochemical Properties

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Experimental Part

All chemicals and solvents were used as received from commercial sources. Ultrafiltration system (Milli-Q, Millipore) was used to obtain deionized water with a resistivity above 18 M Ω ·cm. Optical extinction spectra (400–1000 nm) were measured with Cary-50 spectrophotometer (Varian) using a cell path length of 1 cm. Powder X-ray diffraction (XRD) measurements of Au and Au@Pd core-shell NPs were performed with a Bruker D8-Focus diffractometer using Cu K α radiation (30 V, 30 mA, $\lambda = 1.54056 \text{ \AA}$) in a θ – θ mode from 25 to 95 degrees (2θ). TEM images were obtained with either Tecnai G² Spirit TWIN, a 20-120 kV/LaB₆ Transmission Electron Microscope, or FEI Titan 80-300 kV (ST and CT) using field emission gun operating at 300 kV. TEM samples were prepared by dropcasting dilute solutions onto carbon-coated Cu grids, and drying them in air for 1 hour before the measurement. Gold NPs were dispersed in chloroform and Au@Pd core-shell NPs were dispersed in aqueous medium. They were sonicated for 10 seconds before casted on the grids.

Synthesis of gold NPs For the synthesis of 32.8 nm Au NPs, mixture of AuCl₃ hydrate (30 mg), 10 mL octyl ether, 1.2 mL oleylamine, and 1,2-hexadecanediol (40 mg, 0.155 mmol) were stirred under nitrogen at 130 °C for 30 minutes. Temperature was increased to 190 °C and stirred for 1 hour. Temperature was further increased to 280 °C, and stirred for 2 hours. Mixture was cooled down and the products were obtained by adding hexane (10 mL) and EtOH (10 mL), followed by centrifugation at 4000 rpm for 5 minutes. For the synthesis of 11.3 nm Au NPs, octadecylamine (136 mg) and oleylamine (0.9 mL) were added to the reaction mixture of AuCl₃ hydrate (30 mg), 10 mL octyl ether, and 1,2-hexadecanediol (40 mg, 0.155 mmol) with other conditions the same as the synthesis of 32.8 nm Au NPs. For the transfer of gold NPs into aqueous medium, we

adopted modified literature method.¹ Precipitated Au NPs from hexane/EtOH were dried in air, and 3 mg of dried Au NPs was mixed with chloroform (2 mL) and sonicated for 20 seconds. CTAB (6 mL, 0.1 M) was added and the mixture was stirred (260 rpm) at room temperature for 3 days.

Synthesis of Au@Pd core-shell NPs Aqueous suspension of Au NPs in 1 mL of 0.1 M CTAB was dissolved in 5 mL of deionized water in 25 mL round-bottomed-flask. The mixture was stirred vigorously (980 rpm) for 3 minutes, followed by the addition of 1 mL of ascorbic acid (0.30 M). The mixture was further stirred for 5 minutes before the addition of 2.8 mg of PdCl₂ in 500 μL of deionized water. Stirring continued for 1 hour. After the reaction, product was obtained by centrifugation at 4000 rpm for 5 minutes. Supernatant was further centrifuged at 10000 rpm for 7 minutes in order to obtain Pd nanocubes. For the synthesis of branched Au@Pd core-shell NPs, Au NPs with an average diameter of 32.8 nm were transferred to the aqueous medium in a mixture of 0.2 M CTAB (6 mL) and chloroform (2 mL). When phase transfer completed, 1 mL of Au seeds were mixed with 5 mL of deionized water in 25 mL round-bottomed-flask. After 3 minutes of stirring, 1 mL of ascorbic acid (0.30 M) was added and the mixture was stirred for 5 minutes, which was followed by the addition of 2.8 mg of PdCl₂ in 500 μL of deionized water. After 1 hour of reaction, branched Au@Pd core-shell NPs were obtained by centrifugation at 4000 rpm for 5 minutes.

Electrochemical measurement Cyclic voltammograms were measured with Gamry Reference 600 Potentiostat/Galvanostat/ZRA. Three-electrode setup was used with working electrode employing glassy carbon electrode (GCE) with active surface area of 0.0707 cm². Counter electrode is Pt thin wire, and a reference electrode is Ag/AgCl. All the potentials were recorded with respect to the reference electrode. After removal of excess CTAB by centrifugation three times, 2 mg of Au@Pd core-shell NPs were dispersed in a mixture of deionized water (0.8 mL) and isopropanol (0.2 mL), then 100 μL of each sample was loaded onto the GCE. GCE was dried in air, and it was further modified by dropping 3.0 μL of 0.1% Nafion on its surface. After drying in air, all three electrodes were transferred to the electrochemical cell which contains 40 mL of 0.5 M H₂SO₄. Before the measurement, electrochemical cell was purged with N₂ gas for 10 minutes. At least 25 cycles of cyclic voltammetry were performed before recyclable voltammograms were obtained and recorded. Throughout the cyclic voltammetry experiment, the scan rate is 80 mV/s with a potential range between -0.5 V and 0.9 V, and the sensibility of the electrodes was set at 100 mA.

Reference

1. H. Fan, E. W. Leve, C. Scullin, J. Gabaldon, D. Tallant, S. Bunge, T. Boyle, M. C. Wilson and C. J. Brinker, *Nano Lett.*, 2005, **5**, 645-648.

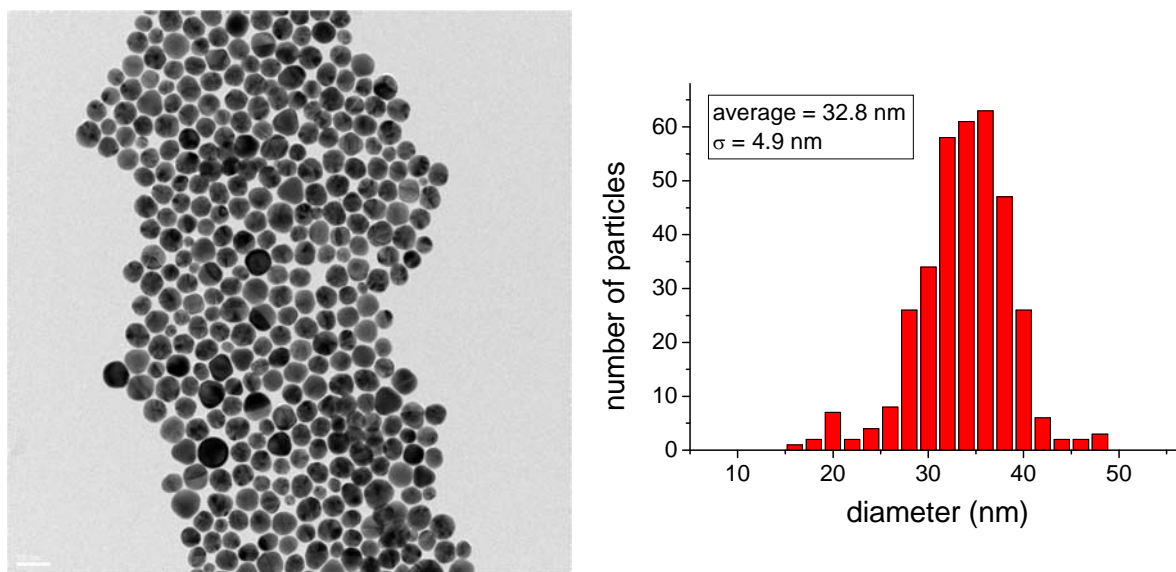


Fig. S1. (left) TEM image and (right) size analysis of 32.8 (\pm 4.9) nm Au NPs.

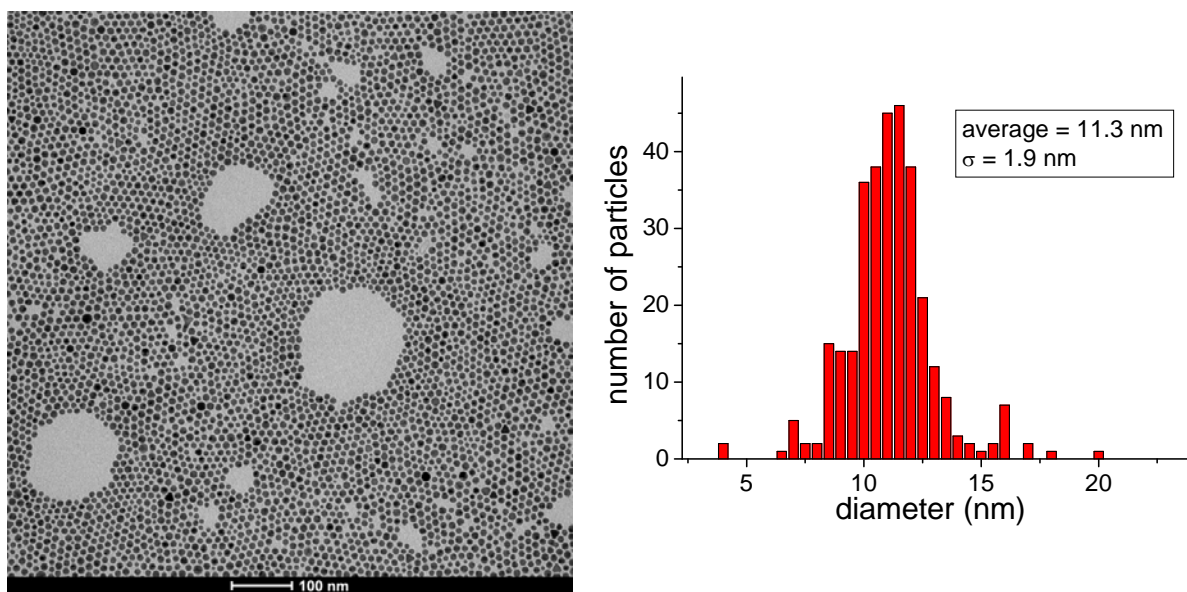


Fig. S2. (left) TEM image and (right) size analysis of 11.3 (\pm 1.9) nm Au NPs.

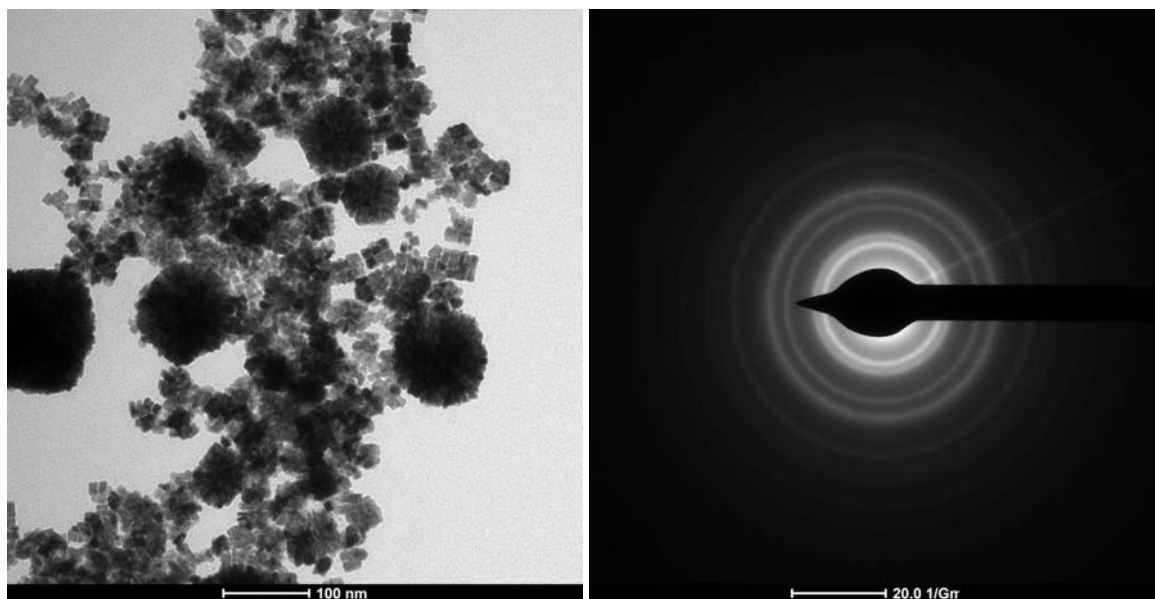


Fig. S3. (left) TEM image of Pd NPs synthesized in the absence of Au NP seeds, with other conditions the same as the synthesis of spherical Au@Pd NPs. (right) SAED pattern of Pd NPs shown in left image.

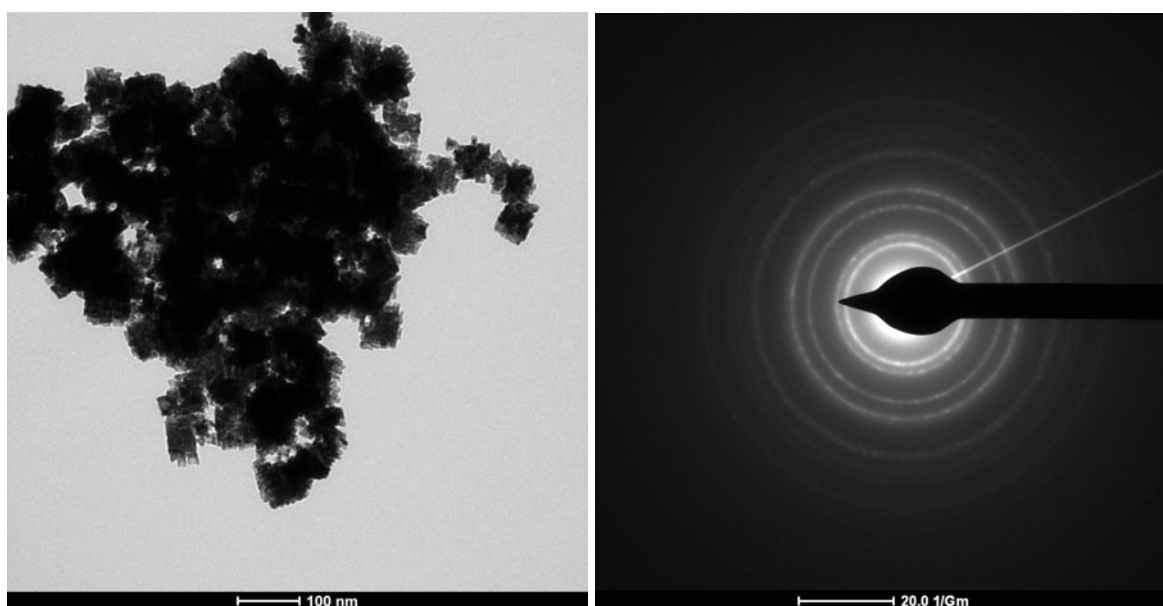


Fig. S4. (left) TEM image of Pd NPs synthesized in the absence of Au NP seeds. Before addition of Pd source, 2 mL of chloroform and 6 mL of CTAB were stirred for 3 days to make a microemulsion environment, which is similar to the surface of Au NPs during the transfer to aqueous medium. (right) SAED pattern of Pd NPs shown in left image.

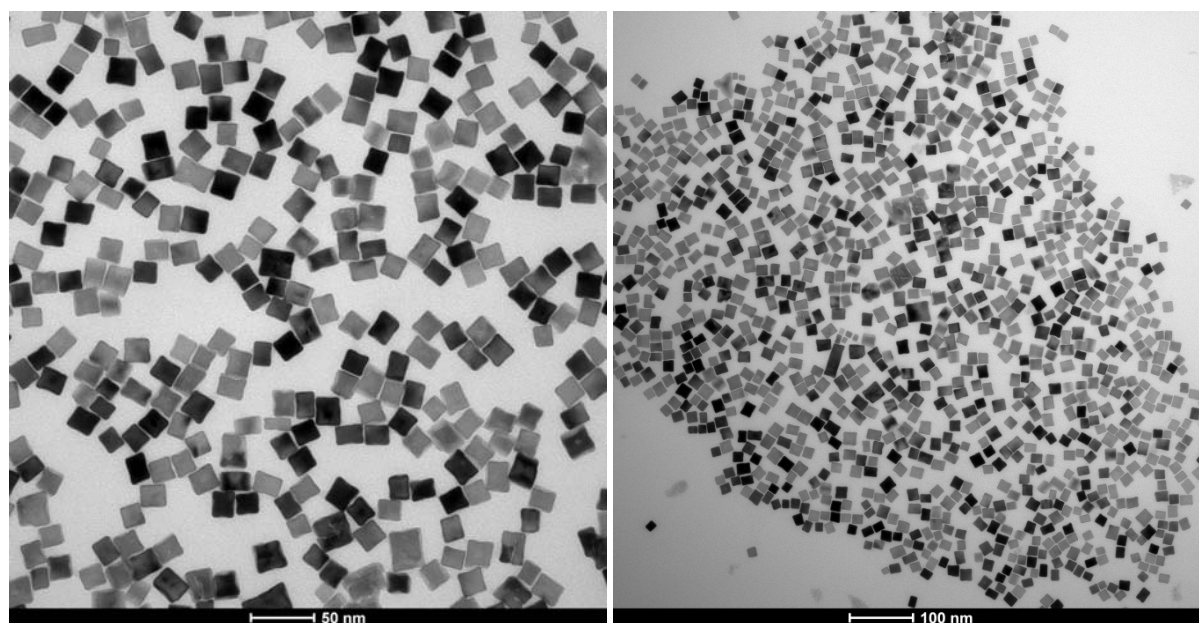


Fig. S5. TEM images of Pd nanocubes obtained as a side product during the synthesis of spherical Au@Pd core-shell NPs.

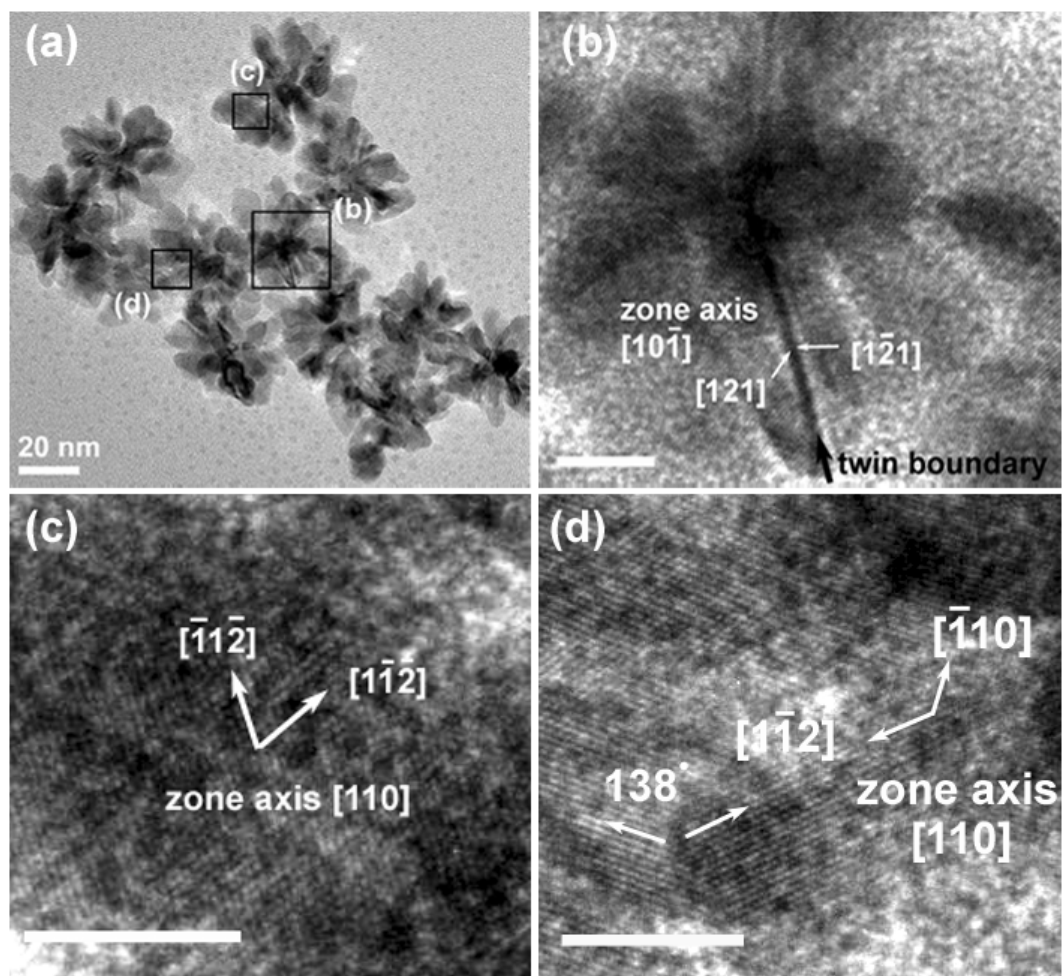


Fig. S6. (a) TEM image of Au@Pd core-shell NPs grown from 11.3 nm Au NPs. HRTEM images of (b) core region showing Pd growth along twin boundary, (c) a single tip region with dominant $\langle 110 \rangle$ zone axis, and (d) ripened region between two tips. Fig. 2b, 2c, and 2d are the enlarged regions indicated in Fig. 2a. Scale bars in 2b, 2c, 2d are 5 nm.

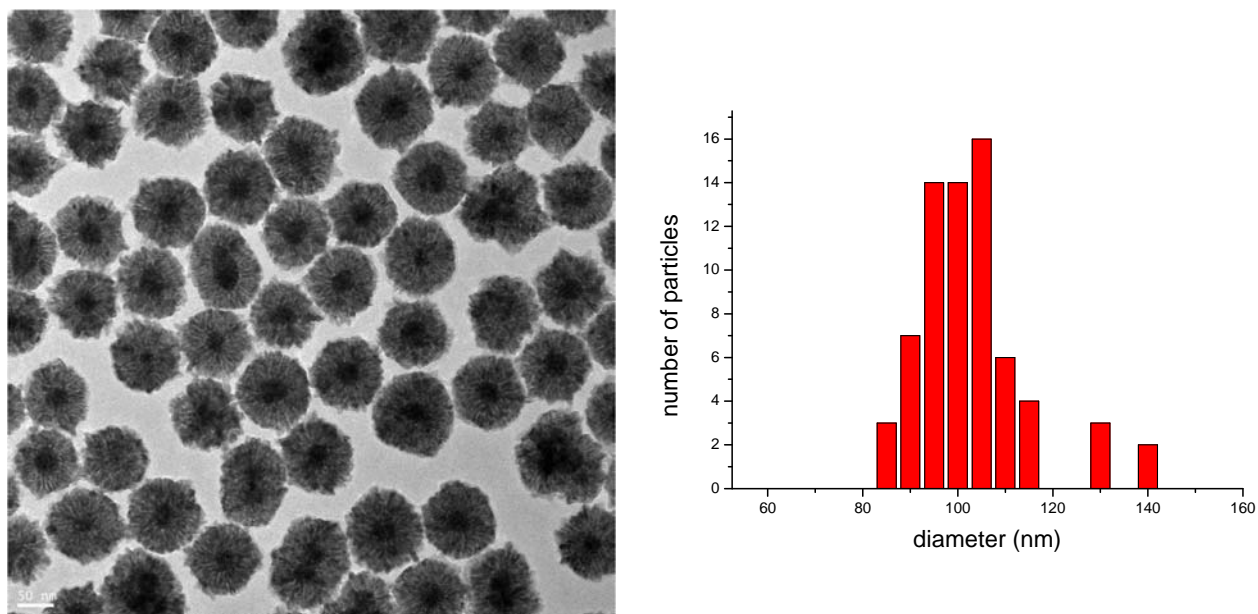


Fig. S7. (left) TEM image of spherical Au@Pd core-shell NPs and (right) size analysis of 100 (\pm 11.7) nm.