Supporting Information for:

Manipulating the Optical Properties of Symmetrically Branched Au/Pd Nanocrystals through Interior Design

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Chemicals:

L-ascorbic acid (L-AA, C₆H₈O₆, 99%), palladium(II) chloride (PdCl₂, 99.98%), chloroauric acid (HAuCl₄•3H₂O, 99.9%), iron III chloride (FeCl₃•6H₂O, 98%), cetyltrimethylammonium bromide (CTAB, 98%, lot # SLBD0174 V), cetyltrimethylammonium chloride (CTAC, 0.78 M, lot # STBC 7888 V), and potassium bromide (KBr, 99%) were used as purchased from Sigma Aldrich. Concentrated hydrochloric acid (HCl, 12.1 M) was purchased from Mallinckrodt. Nanopure water (18.2 MΩ•cm) was used in all experiments. An aqueous 10 mM H₂PdCl₄ solution was prepared by stirring dissolved PdCl₂ (44.6 mg) in 25 mL of HCl (pH 1.69) for 1 h while heating at ~70 °C.

Synthesis of Pd Nanocube Seeds

The Pd nanocubes for use with seed-mediated co-reduction are prepared by a seeded method as well, and the procedure for Pd nanocubes was adapted from prior protocol.¹ In a 25 mL vial, 10.0 mL CTAB (12.5 mM) and 0.500 mL H₂PdCl₄ (10.0 mM) were heated at 95 °C for 5 minutes under moderate stirring. Next, 0.080 L-AA (100 mM) was rapidly added and the reaction was allowed to stir at 95 °C for 30 minutes. The orange-brown clear solution was transferred to a 30 °C oil bath to be used as seeds for the synthesis of Pd nanocubes.

In two separate 20 mL vials, 2.50 mL CTAC (200 mM), 2.5 mL NaBr (100 mM), and 0.125 mL H_2PdCl_4 (10.0 mM) were combined, followed by 0.040 mL of the Pd seeds and 0.050 mL L-AA. This solution was allowed to sit, without stirring, at 40 °C for 13 hours 30 minutes. Once the two

reactions were complete these two solutions were combined and the solution was washed and redispersed in 3 mL water.

Synthesis of core@shell Pd@Au/Pd Octopods

The procedure for Pd@Au/Pd octopods was adapted from prior protocol.² First, 2.00 mL CTAB (0.200 M) solution was added to a reaction vial. Next, 0.100 mL H₂PdCl₄ (10.0 mM) solution and 0.040 mL of HAuCl₄ (100 mM) solution were added followed by 1.50 mL L-AA (0.10 M) solution. Then 21.4 mL of water was added, followed by 3 mL of the Pd nanocube seed solution. These reaction vials were gently shaken then capped and allowed to sit undisturbed in a 25 °C oil bath for 24 hours. Afterward the dark blue colloidal solution was washed and redispersed in 3 mL water.

Synthesis of Au/Pd Octopods with Hollow Interiors

In a 25 mL vial, 10 mg NaBr, 60 mg CTAB, 0.25 mg FeCl₃· $6H_2O$, and 5.5 mL H₂O were added. Next, the Pd@Au/Pd octopods were added, followed by 0.10 mL concentrated HCl (12.1 M). This solution was heated at 90 °C for 24 hours under vigorous stirring. Afterward the gray-blue colloidal solution was washed and redispersed in 3 mL water.

Characterization:

Images of the nanoparticles were taken via a FEI Quanta 600F Environmental Scanning Electron Microscope operated at 30 kV and a spot size of 3. STEM and TEM images were taken on a JEOL JEM 3200FS Transmission Electron Microscope at 300 kV and a spot size of 1 with a Gatan 4k x 4k Ultrascan 4000. Energy dispersive X-ray spectra were obtained with an Oxford INCA dispersive X-ray system interfaced to the JEM 3200FS TEM, operating at 300 kV. Samples for TEM analysis were prepared by washing a carbon-coated copper grid with chloroform to remove Formvar then drop-casting a dispersed particle solution onto the grid. Samples for SEM analysis were prepared by drop-casting a dispersed particle solution onto a silicon wafer and then washing the wafer twice with methanol after initial solvent evaporation. SPR measurements were performed on a Varian CARY 5000 Bio UV-visible spectrophotometer using a quartz cuvette and a background scan of water. XPS was performed with a PHI VersaProbe II Scanning X-ray Microprobe system.



Figure S1. SEM/EDX spectrum of hollow Au/Pd octopods, which indicates that Fe is not detected in the structures. The C and Si peaks observed originate from the sample substrate.



Figure S2. XPS analysis of hollow Au/Pd octopods in the Fe $2p_{1/2}$ and $2p_{3/2}$ region, indicating that Fe is not present in the sample.



Figure S3. (A) A STEM image of one of the highly branched impurity structures after the etching procedure and (B-D) elemental mapping by STEM/EDX, where yellow indicates Au and red indicates Pd.



Figure S4. XPS analysis of core@shell Pd@Au/Pd octopods before etching (solid) and hollow Au/Pd octopods after etching (dashed) in the Au $4f_{7/2}$ and $4f_{5/2}$ region.



Figure S5. XPS analysis of core@shell Pd@Au/Pd octopods before etching (solid) and hollow Au/Pd octopods after etching (dashed) in the Pd $3d_{5/2}$ and $3d_{3/2}$ region. The shoulder near 337 eV is likely attributed to Au $4d_{5/2}$.



Figure S6. (A) A TEM image an etched particle, (B) its corresponding STEM image, and (C-E) elemental mapping by STEM/EDX where yellow indicates Au and red indicates Pd. Due to complete coverage of the Pd nanocube interior with overgrowth metal, the Pd seed cannot be removed by chemical etching.



Figure S7. (A) An SEM image of Pd@Au/Pd octopods before etching and (B) an SEM image of the same sample after etching for 48 hours.

References:

- 1. Y. Yu, Q. Zhang, X. Lu and J. Y. Lee, J. Phys. Chem. C, 2010, 114, 11119-11126.
- 2. C. J. DeSantis and S. E. Skrabalak, J. Am. Chem. Soc., 2013, 135, 10-13.