Supporting Information for:

Synthesis of Hollow and Trimetallic Nanostructures by Seed-Mediated Co-Reduction

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Experimental

Chemicals: L-ascorbic acid (C₆H₈O₆, L-aa, 99%), palladium (II) chloride (PdCl₂, 99.98%), chloroauric acid (HAuCl₄•3H₂O, 99.9%), cetyltrimetylammonium chloride (CTAC, 0.78 M), poly(vinyl pyrrolidone) (PVP, MW=55,000), sodium hydrosulfide hydrate (NaHS, \geq 60%), ethylene glycol (EG, anhydrous, 99.8%), bis(p-sulfonatophenyl)phenylphosphine dihydrate dipotassium salt (BSPP, 97%), and silver trifluoroacetate (CF₃COOAg, \geq 99.99%) were purchased from Sigma Aldrich. Concentrated hydrochloric acid (HCl, 12.1M) 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 hour while heating at ~70 °C.

Synthesis of Ag Nanocubes: The synthesis of Ag nanocubes is adapted from previous literature protocol.[1] Into a round bottom flask, 5 mL EG was stirred at 150° C for two minutes. Next, 0.06 mL NaHS (2 mM, prepared in glovebox) was added. After two minutes, 0.5 mL HCl (3 mM) and 1.25 mL PVP (20 mg/mL) were added and stirred for an additional two minutes. Last, 0.4 mL CF₃COOAg (282 mM) was added and stirred for 30 minutes. The reaction was quenched in an ice bath and particles were collected by centrifugation for 30 minutes at 3900 RPM three times (acetone followed by two water washes) and diluted with water to a total volume of 3 mL.

Seed-Mediated Co-Reduction: Seed mediated co-reduction is adapted from previous literature protocol.[2] For branched nanocrystal growth, 2 mL CTAC (0.2 M) solution was added to a reaction vial. Next, 0.2 mL H₂PdCl₄ (10 mM) solution and 0.2 mL of HAuCl₄•3H₂O (10 mM) solution were added followed by 1.5 mL L-aa (0.1 M) solution. Then 21.4 mL of water was added, followed by 1 mL Ag seed solution. These reaction vials were gently shaken then capped and allowed to sit undisturbed in a 25 °C oil bath for 6-24 hours.

Time studies: The typical seed-mediated co-reduction protocol was conducted. At each time point a 1.5 mL aliquot was removed and added to 0.02 mL BSPP (0.1 M). EDX was taken in triplicate and therefore percentages in Table 1 do not necessarily add up to 100%.

NaOH studies: For branched nanocrystal growth, 2 mL CTAC (0.2 M) solution was added to a reaction vial. Next, 0.2 mL H_2PdCl_4 (10 mM) solution and 0.2 mL of $HAuCl_4 \cdot 3H_2O$ (10 mM) solution were added followed by 1.5-6 mL 0.2 M NaOH (see Figure S3) and 1.5 mL L-aa (0.1

M) solution. Then water was added to a total volume of 25 mL, followed by 1 mL Ag seed solution. These reaction vials were gently shaken then capped and allowed to sit undisturbed in a 25 $^{\circ}$ C oil bath for 6 hours.

Characterization: Images of the nanoparticles were taken via a FEI Quanta 600F Environmental Scanning Electron Microscope (SEM) operated at 30 kV and a spot size of 3. Routine transmission electron microscopy (TEM) was conducted with a JEOL JEM 1010 TEM operating at 80 kV. Images were acquired with a ROM CCD camera. Scanning transmission electron microscopy (STEM) and high-resolution TEM images were taken on a JEOL JEM 3200FS TEM at 300 kV and a spot size of 1 with a Gatan 4k x 4k Ultrascan 4000 camera. Energy dispersive X-ray spectra were obtained with an Oxford INCA dispersive X-ray system interfaced to the JEM 3200FS TEM, at 300 kV. Samples for TEM analysis were prepared by washing a carbon-coated Cu grid with chloroform to remove Formvar then drop-casting a dispersed particle solution onto a silicon wafer and then washing the wafer with methanol after initial solvent evaporation. LSPR measurements were measured with a Varian CARY 5000 Bio UV–visible spectrophotometer, using a quartz cuvette and a background scan of water. ICP-MS was performed with a Perkin Elmer Sciex ELAN DRCe ICP-MS at the Microanalysis Laboratory at the University of Illinois at Urbana-Champaign.

Finite difference time domain (FDTD) calculations were performed with Lumerical software. The particles were modeled after those synthetically accessed. The first model is a Ag cube with a 38 nm side length and a 5 nm corner radius of curvature with a 2 nm shell of 1:5 atomic % Au:Pd also with a 5 nm corner radius of curvature. The second model is a hollow cube with side length 50 nm comprised of 28:39:32 atomic % Au:Pd:Ag and a 5 nm corner radius of curvature.; the interior is a cube with side length 30 nm comprised of a dielectric with RI = 1.3333 (water). A plane wave with a wavelength range of 200 nm to 1200 nm propagating along the z-direction was used as the incident source using the total field scattered field analysis method. The real and complex dielectric constants of Pd was modeled using values from Palik;[3] the dielectric function of Au and Ag were obtained from Johnson and Christy[4]. The external dielectric (water) was set to a RI value of 1.3333. The Yee cell size was (1 nm)³.



Figure S1. TEM of typical results after SMCR in the absence of L-aa. Inset is a seldom observed thin hollow Ag-Au-Pd NP.



Figure S2. TEM images from a time study after addition of Ag nanocube seeds. At times (A) 1 minute, (B) 5 minutes, (C) 30 minutes, and (D) 1 hour.



Figure S3. (A) TEM image of three Ag@Au-Pd NPs synthesized in the presence of 1.5 mL NaOH. (B) Higher magnification TEM of the area boxed in (A), where the lattice fringes reveal the single-crystalline nature of the Ag@Au-Pd NPs.



Figure S4. TEM of resulting Ag-Au-Pd NPs after the addition of (A) 1.5 mL, (B) 3 mL, (C) 4.5 mL, and (D) 6 mL 0.2 M NaOH.



Figure S5. A. TEM of an individual Ag@Au-Pd NP synthesized in the presence of 4.5 mL NaOH. B. STEM of an individual Ag@Au-Pd NP with hollow features. C-F. EDX/Elemental mapping of the NP shown in (B) where Pd is represented by red, Au by yellow and Ag by green. An overlay of the signals is shown in (G).



Figure S6. UV-Visible spectra of Ag-Au-Pd hollow NPs (top) and Ag@Au-Pd NPs (bottom). FDTD simulations are represented by red dotted lines and experimental results are in black. In the Ag-Au-Pd experimental trace, a plateau is observed due to the changeover of the detector at that wavelength.

References:

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