Supporting Information

Octopods vs. Concave Nanocrystals: Control of Morphology by Manipulating the Kinetics of Seeded Growth via Co-reduction

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1. Experimental Details

Chemicals. Ascorbic acid ($C_6H_8O_6$, 99%), palladium(II) chloride ($PdCl_2$, 99.98%), chloroauric acid ($HAuCl_4 \cdot 3H_2O$, 99.9%), cetyltrimethylammonium bromide (CTAB, 98%), sodium tetrachloropalladate (Na_2PdCl_4, 98%), and sodium borohydride ($NaBH_4$) were used as purchased from Sigma Aldrich. Formic acid (90% in water) was purchased from J. T. Baker. Nanopure water was used in all experiments. A 10 mM H_2PdCl_4 solution was prepared by heating at ~40 °C and stirring dissolved $PdCl_2$ (44.5 mg) in 25 mL of HCl (0.1 M) for one hour.

Gold Nanoparticle Seeds. To make the initial Au seeds, 4 mL of H_2O and then 1 mL of $HAuCl_4$ (2.5 mM) solution were added to 5 mL of CTAB (150 mM) solution in a 30 mL reaction vial. 0.6 mL of ice-cold $NaBH_4$ (10 mM) solution was added immediately with stirring, forming a clear brown solution. This solution was capped and allowed to stir at room temperature for 3 hours. A 0.3 mL aliquot was then diluted with 29.7 mL of H_2O. This seed solution can then be used for the synthesis of Au cores. The seeds may be used immediately to prepare Au cores for Au@Pd nanocrystal formation (either convex or concave). Alternatively, the seeds may be aged at room temperature and used after 3 days to prepare Au cores for Au/Pd octopod or concave nanocrystal formation.

Gold Nanoparticle Cores. To synthesize the Au cores, 0.1 mL of $HAuCl_4$ (10 mM) solution was added to 2 mL of CTAB (0.2 M) solution followed immediately by 1.5 mL of ascorbic acid (0.1 M) solution. This solution was immediately diluted to 25 mL with H_2O followed promptly by adding 0.3 mL of the seed solution. This reaction vial was capped and allowed to sit undisturbed in a 25 °C oil bath for 8 hours.

Gold/Palladium Nanocrystal Formation. For the formation of nanostars (Figure S4B), octopods (Figure 1A), and concave nanocrystals (Figure 1D), the 10 mM H_2PdCl_4 solution was diluted to 0.05 mM, 0.5 mM, and 5.0 mM, respectively, with water. To the entire Au core solution (prepared from aged seeds), 2 mL of the diluted H_2PdCl_4 solution and 0.1 mL of the $HAuCl_4$ (100 mM) solution are simultaneously added via separate pipettes, followed promptly by the addition of 0.5 mL of ascorbic acid (0.1 M) solution. The reaction vial was capped and allowed to sit undisturbed in a 25 °C oil bath for 30 minutes. For the formation of convex Au@Pd nanocrystals (Figure 3A), 2 mL of the 0.5 mM H_2PdCl_4 solution and 0.1 mL of the $HAuCl_4$ (100 mM) solution were simultaneously added via separate pipettes to the freshly prepared Au core solution, followed by the addition of 0.5 mL of ascorbic acid (0.1 M) solution.

Characterization. Images of the nanoparticles were taken via a JEOL JEM 1010 Transmission Electron Microscope (TEM) with a ROM CCD camera and on a FEI Quanta 600F Environmental Scanning Electron Microscope (SEM) operated at 30 kV and a spot size of 3. Composition of nanoparticles was determined with an Oxford INCA Energy Dispersive X-Ray operated at 30 kV. High-resolution 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 drop-casting a dispersed particle solution onto a carbon-coated copper grid and then washing the grid twice with H_2O. Samples for SEM and EDX 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. The optical properties of various samples were measured with a Varian CARY 5000 Bio UV-Visible Spectrophotometer, using a quartz cuvette and a background scan of water.

Electrochemical Catalysis. Electrochemical measurements were performed on an Obbligato & Objectives, Inc. Faraday MP system scanning from –0.2 to 1.0 to –0.2 V at a rate of 50 mV s^{-1}. A three-electrode cell was used with Ag/AgCl as the reference electrode and a platinum wire as the counter electrode. Samples of the Au/Pd octopods or concave nanocrystals were shaken until evenly dispersed in water and then 10.0 µL of this mixture was added dropwise to a glassy carbon electrode (area = 0.077 cm^2) and allowed to dry under ambient conditions. For all experiments, the electrolyte solution, 0.1 M H_2SO_4 in nanopure water was sparged with argon for 10 min before an experiment.

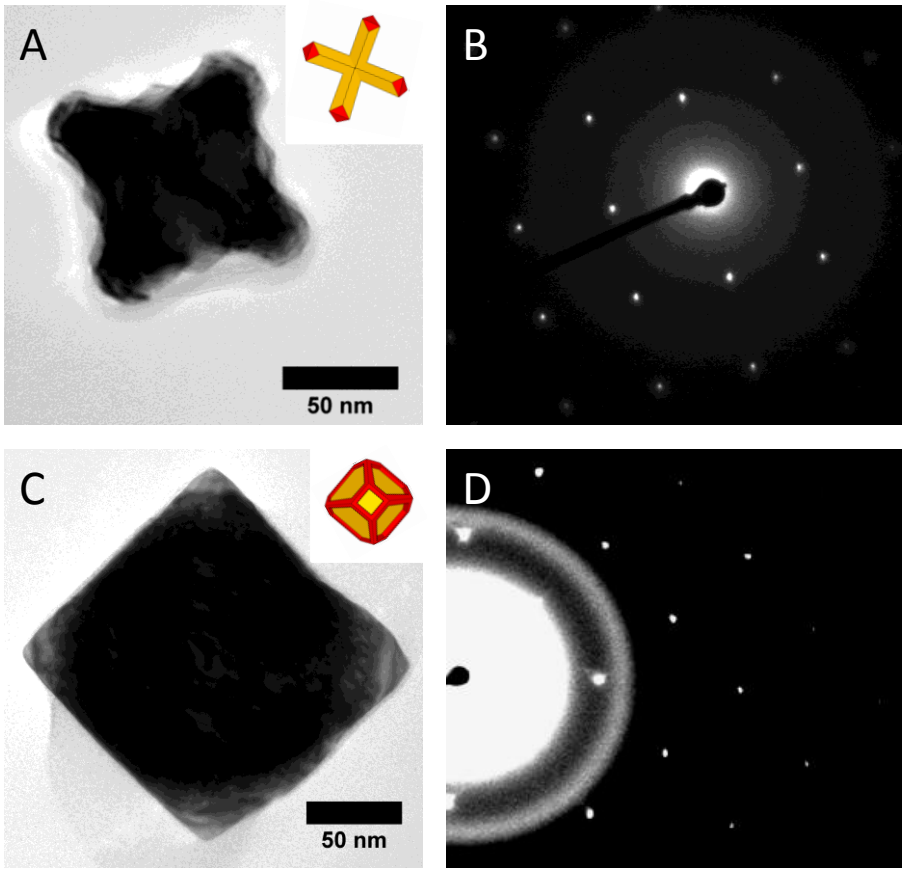

Figure S1. (A) TEM and (B) electron diffraction from an individual Au/Pd octopod oriented with four branches toward the substrate. (C) TEM and (D) electron diffraction from a concave Au@Pd cuboctahedron oriented with a (100)-terminating facet perpendicular to the electron beam.

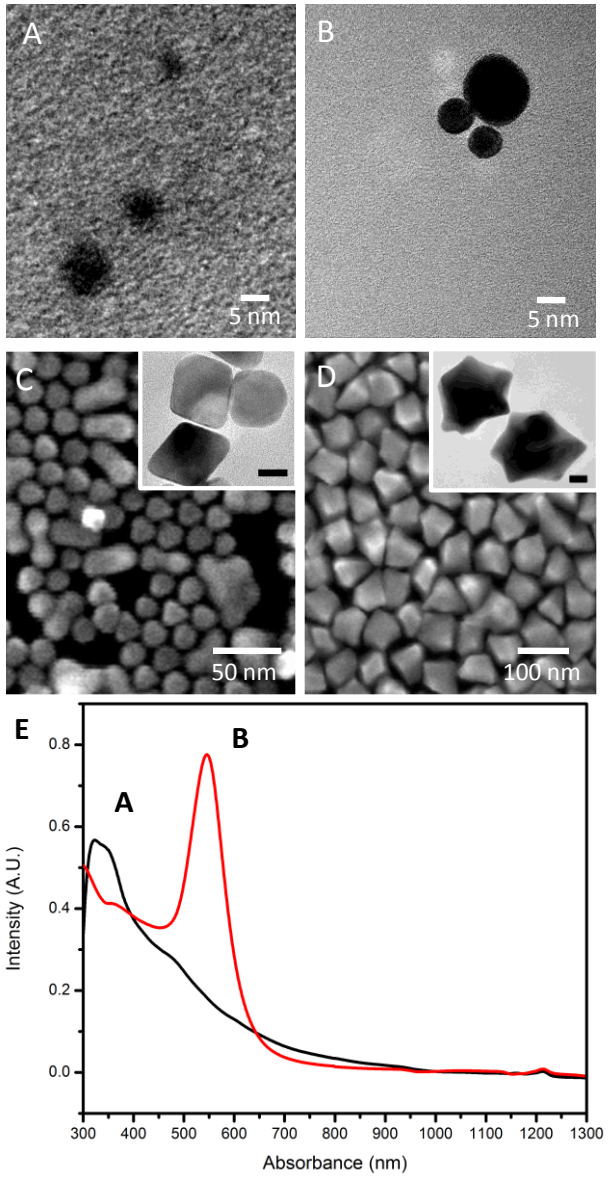

Figure S2. TEM images of Au seeds (A) freshly prepared and (B) after they are aged. SEM images, insets TEM images (scale bars 10 nm), of (C) Au cores prepared from freshly prepared Au seeds and (D) after the seeds were aged. In (E), the absorbance spectra for the freshly prepared and aged seeds, denoted A and B. The red-shift associated with the aged seeds is consistent with their larger size.

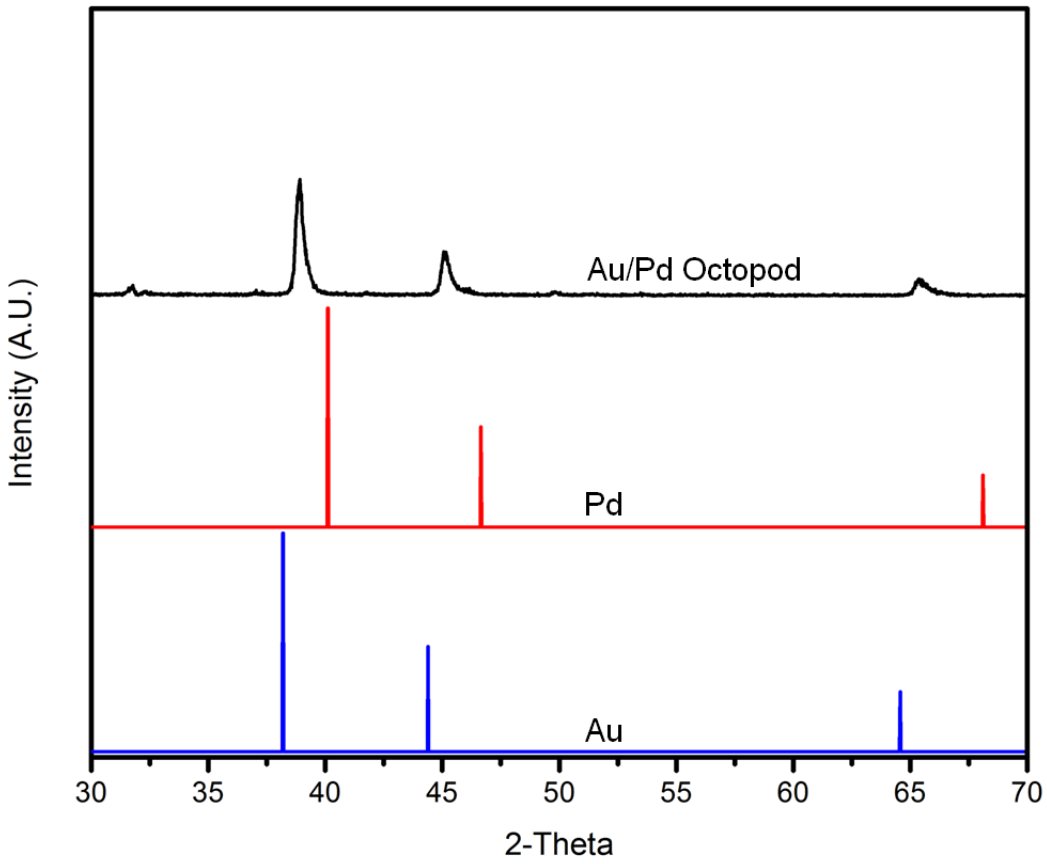

Figure S3. X-ray powder diffraction of Au/Pd octopods compared to Pd and Au standard cards. Peak positions are similar to those of Au as the Pd content is too low to give rise to distinct diffraction peaks. The shoulder peaks observed, however, can be attributed to Pd.

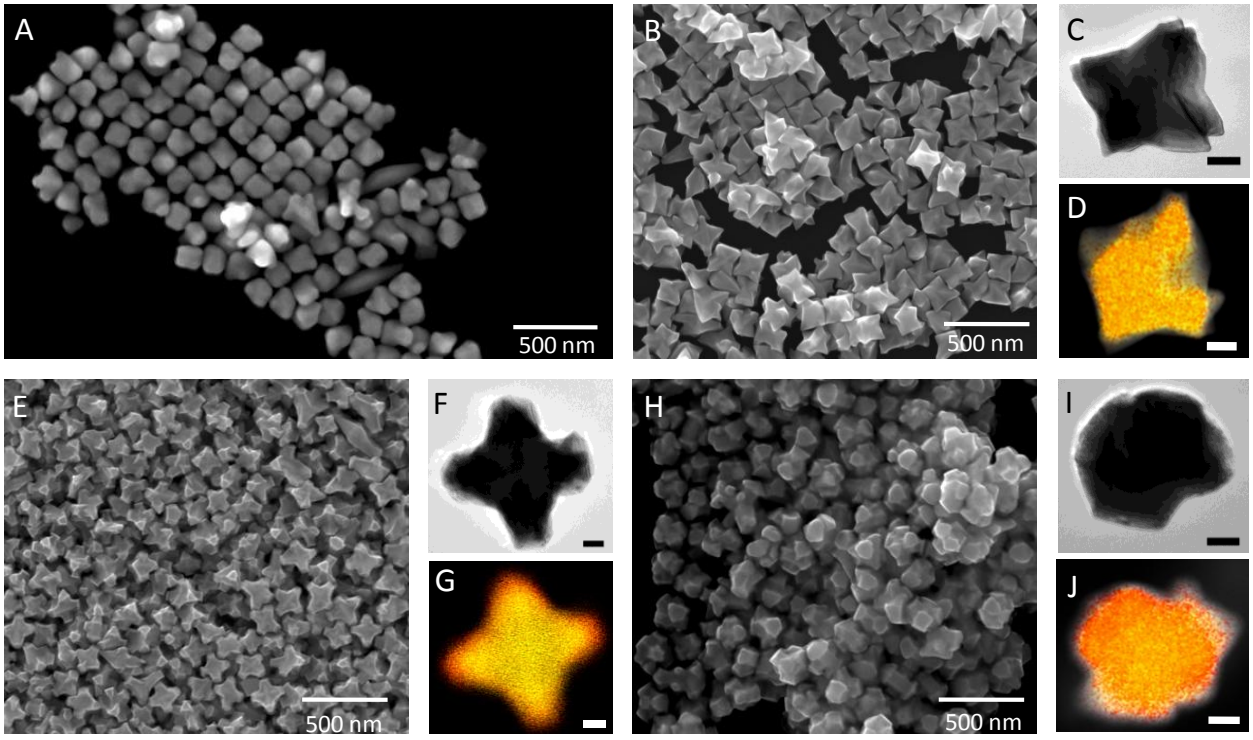

Figure S4. SEM (A, B, E, and H), TEM (C, F, and I) and STEM-EDX elemental mapping (D, G, and J) of Au/Pd nanoparticles, where yellow corresponds to Au and red corresponds to Pd. The Au:Pd mole ratio of precursors were: (A) 1-to-0, (B-D) 1-to-0.01, (E-G) 1-to-0.2, and (H-J) 1-to-0.5. Scale bars 25 nm (C, D, F, G, I, and J).

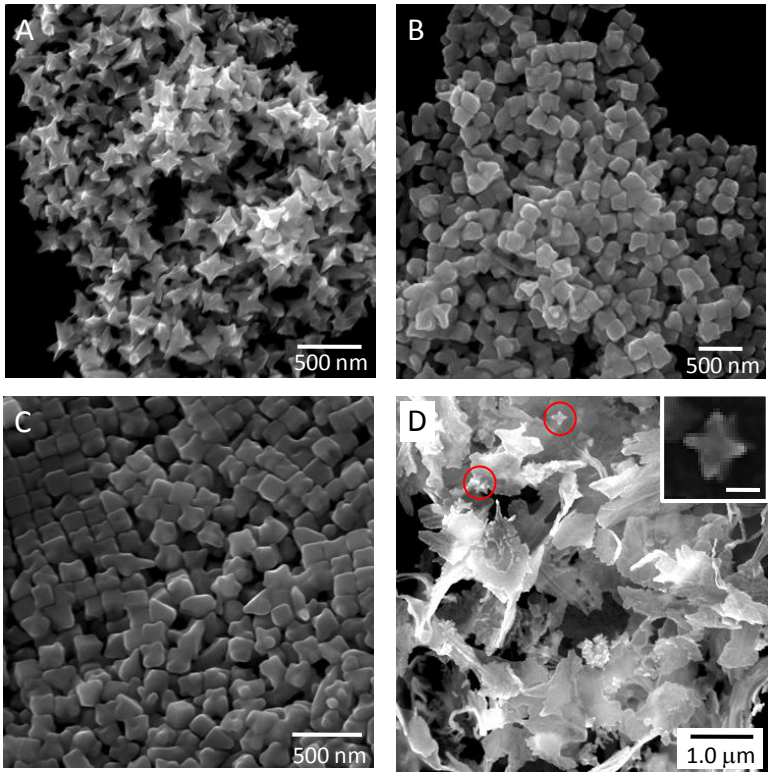

Figure S5. SEM images of the product obtained in control experiments, wherein H_2PdCl_4 was replaced with (A) Na_2PdCl_4 (1.0-to-0.1 Au:Pd ratio), (B) NaCl, (C) HCl, and (D) Na_2PdCl_4 (1.0-to-1.0 Au:Pd ratio). In (A) 2 mL of a 0.5 mM Na_2PdCl_4 solution was added to the synthesis to match the Pd(II) concentration used in the Au/Pd octopod synthesis. In (B) 2 mL of a 2.0 mM NaCl solution was added to match the Cl^- concentration used in the Au/Pd octopod synthesis. In (C) 2 mL of a 5.0 mM HCl solution was added to match that from the H_2PdCl_4 precursor added to the Au/Pd octopod synthesis. In (D) 2 mL of a 5 mM Na_2PdCl_4 solution was added to match the Pd(II) concentration used in the concave Au@Pd nanocrystal synthesis. Branched particles were observed occasionally, with several examples circled. The inset provides a high magnification image of one of these branched nanocrystals (inset scale bar = 100 nm).

Seed Age*	Au Core Structure	Au:Pd Ratio	pH/Growth Rate	Synthetic Outcome
Fresh (< 24 hrs)	Octahedral	1:0.1	High/Fast	Convex core@shell Au@Pd Nanocrystals (Figure 3A-C)
Fresh (< 24 hrs)	Octahedral	1:1	Low/Slow	Concave core@shell Au@Pd nanocrystals (Figure 3D-H)
Aged (3^+ days)	Branched	1:0.1	High/Fast	Au/Pd Octopods (Figure 1A-C)
Aged (3^+ days)	Branched	1:1	Low/Slow	Concave core@shell Au@Pd nanocrystals (Figure 1D-H)

Table S1. Summary of the structures achieved under different experimental parameters. *Seed age corresponds to how long the prepared seeds were allowed to sit before being used to prepare Au cores.