Supporting Information for:

Diffusion and Seed Shape: Intertwined Parameters in the Synthesis of Branched Metal Nanostructures

Rebecca G. Weiner,[1] Christopher J. DeSantis,[1] Mariana B.T. Cardoso,[2] and Sara E. Skrabalak[1,*]

AUTHOR ADDRESSES: [1]Department of Chemistry, Indiana University, Bloomington, Indiana 47405, United States; [2]Universidade de São Paulo, Instituto de Química, Departamento de Química Fundamental Av Prof Lineu Prestes 748 São Paulo, São Paulo, BR 05508000

Synthetic Details

Chemicals: L-ascorbic acid ($C_6H_8O_6$, L-AA, 99%), palladium (II) chloride ($PdCl_2$, 99.98%), chloroauric acid ($HAuCl_4•3H_2O$, 99.9%), cetyltrimetylammonium bromide (CTAB, 98%, LOT # BCBK3869V), cetyltrimetylammonium chloride (CTAC, 0.78 M), sodium borohydride ($NaBH_4$, 98.5%), trisodium citrate ($Na_3C_6H_5O_7•2H_2O$, ≥99%), silver nitrate ($AgNO_3$, 99.9999%), Bis(*p*-sulfonatophenyl)phenylphosphine dihydrate dipotassium salt (BSPP, 97%), potassium iodide (KI, 99%), sodium tetrachloropalladate (Na_2PdCl_4, 98%), and hydroquinone ($C_6H_6O_2$, ≥99%) were purchased from Sigma Aldrich. Copper sulfate ($CuSO_4$, 98%) was purchased from Alpha Aesar. Sodium bromide (NaBr, 99.50%) was purchased from J.T. Baker. 5-bromosalacylic acid ($C_7H_5BrO_3$, 5-BrSA, 99.0%) was purchased from TCI America. Concentrated hydrochloric acid (HCl, 12.1M) was purchased from Mallinckrodt. Citric acid (99.5-100%) was purchased from VWR. Nanopure water (18.2 MΩ•cm) was used in all experiments. An aqueous 10 mM H_2PdCl_4 solution was prepared by stirring dissolved $PdCl_2$ (44.6 mg) in 25 mL of HCl (pH 1.69) for 1 hour while heating at ~70 °C.

Synthesis of Au Cubes: The synthesis of Au nanocubes is adapted from a previous literature protocol.[1] Gold seeds were initially prepared. To synthesize seeds, 0.25 mL $HAuCl_4•3H_2O$ (10 mM) and 7.5 mL CTAB (0.1 M) were mixed together. Next, 0.6 mL freshly prepared $NaBH_4$ (0.01 M) was added and the solution was mixed by inversion and aged one hour in an oil bath set to 25°C. After one hour, seeds were diluted 10:1. Into a separate vial, 0.2 mL $HAuCl_4•3H_2O$ (10 mM), 8 mL nanopure water and 1.6 mL CTAB (0.1 M) were added and mixed by inversion. Next, 0.95 mL L-AA (0.1 M) was added. Last, 5 µL seed was added. The reaction vial was capped and allowed to sit undisturbed in a 25°C oil bath overnight. Particles were collected by centrifugation for 30 minutes at 3900 RPM and diluted with water to a total volume of 3 mL.

Synthesis of Au Octahedra: The synthesis of Au octahedra is adapted from a previous literature protocol.[2] To prepare octahedra, 1.5 mL CTAB (0.1 M) was diluted by 8.2 mL nanopure water. Next, 250 µL $HAuCl_4•3H_2O$ (0.01 M) and 50 µL trisodium citrate were added to the vial. The reaction vial was capped and allowed to sit undisturbed in a 110°C oil bath for 6 hours. Particles were collected by centrifugation for 30 minutes at 3900 RPM and diluted with water to a total volume of 3 mL.

Synthesis of Au Rhombic Dodecahedra: The synthesis of Au rhombic dodecahedra is adapted from a previous literature protocol.[3] To prepare initial seeds, 5 mL $HAuCl_4•3H_2O$ (0.5 mM) solution was added to 1.28 mL CTAC (0.78 M) and 3.72 mL water and stirred in a vial. Next, 0.45 mL freshly prepared $NaBH_4$ (0.02 M) was added to the vial. The seeds were allowed to age one hour in a 30 °C oil bath. In two separate vials (A and B), 1.28 mL CTAC (0.78 M), 8.45 mL water, 0.250 mL $HAuCl_4•3H_2O$ (0.01 M), and 0.01 mL NaBr (0.01 M), 0.150 mL L-AA (0.04 M) were mixed. Next, 65 µL seed was added to vial A. 65 µL of solution from vial A was added to vial B. This reaction vial was shaken for 5 seconds, capped and allowed to sit undisturbed in a 25 °C oil bath for 15 minutes. Particles were collected by centrifugation for 30 minutes at 3900 RPM and diluted with water to a total volume of 3 mL.

Synthesis of Short Au Rods: The synthesis of short Au rods is adapted from a previous literature protocol.[4] To prepare Au seeds, a solution of 5 mL $HAuCl_4•3H_2O$ (0.5 mM) and 5 mL CTAB (0.2 M) was stirred in a vial. Next, 0.6 mL freshly prepared $NaBH_4$ (0.01 M) and 0.4 mL water were added to this vial. The vial was capped and stirred for two minutes in a 25°C oil bath. After two minutes, stirring stopped and the seeds were allowed to age for exactly 30 minutes.

To prepare growth solution, a solution of CTAB and 5-BrSA was prepared by adding 7.2 g of CTAB, 0.88 g 5-BrSA and 200 mL water in a volumetric flask. This solution was heated at approximately 70°C and stirred until the CTAB and 5-BrSA had completely dissolved. Next, 12.5 mL of the CTAB/5-BrSA solution were added to a vial in a 30°C oil bath. 0.6 mL $AgNO_3$ was added to the vial. Fifteen minutes later, 12.5 mL $HAuCl_4•3H_2O$ (1mM) was added to the vial and stirred slowly for 15 minutes. Next, 0.1 mL L-AA (0.064 M) was added to the vial and stirred rapidly. Last, 20 µL seed was added to the vial. This reaction vial was capped and allowed to sit undisturbed in a 30 °C oil bath overnight. Particles were collected by centrifugation for 30 minutes at 3900 RPM and diluted with water to a total volume of 3 mL.

Synthesis of Long Au Rods: The synthesis of Au long nanorods is adapted from a previous literature protocol.[5] To prepare Au seeds, a solution of 5 mL $HAuCl_4 \bullet 3H_2O$ (1 mM) and 5 mL CTAB (0.2 M) was stirred in a vial. Next, 0.460 mL freshly prepared $NaBH_4$ (0.01 M in 0.01 M NaOH) and 0.4 mL water were added to this vial and stirred.

To prepare growth solution, a solution of 5 mL $HAuCl_4 \bullet 3H_2O$ (1 mM), 5 mL CTAB (0.2 M) and 0.07 mL $AgNO_3$ (0.1 M) was prepared. Next, 0.5 mL hydroquinone (0.1 M) was added to the solution, followed by 160 μL seed. This reaction vial was capped and allowed to sit undisturbed in a 25 °C oil bath overnight. Particles were collected by centrifugation for 30 minutes at 3900 RPM and diluted with water to a total volume of 3 mL.

Synthesis of Au Decahedra: The synthesis of Au decahedra is adapted from a previous literature protocol.[6] To prepare Au seeds, a solution of 6.25 mL $HAuCl_4 \bullet 3H_2O$ (1 mM) and 18.75 mL CTAB (0.1 M) was stirred in a vial. Next, 0.15 mL freshly prepared ice-cold $NaBH_4$ (0.1 M) was added. The vial was capped and stirred for two minutes in a 25°C oil bath. After two minutes, stirring stopped and the seeds were allowed to age for at least 4 hours.

For the growth solution, 20 mL CTAB (0.02 M) was mixed with 5 mL $HAuCl_4 \bullet 3H_2O$ (2 mM) and 0.4 mL $CuSO_4$ (0.01 M). Next, 3 mL L-AA was promptly added, followed by 5 μL seed solution. This reaction vial was capped and allowed to sit undisturbed in a 25 °C oil bath overnight. Particles were collected by centrifugation for 30 minutes at 3900 RPM and diluted with water to a total volume of 3 mL.

Synthesis of Concave Au Cubes: The synthesis of Au concave cubes is adapted from a previous literature protocol.[7] To prepare Au seeds, a solution of 0.25 mL $HAuCl_4 \bullet 3H_2O$ (10 mM) and 10 mL CTAC (0.1 M) was stirred in a vial. Next, 0.6 mL freshly prepared ice-cold $NaBH_4$ (0.01 M) was added. The vial was capped and stirred for one minute in a 25°C oil bath. After one minute, stirring was stopped and the seeds were allowed to age for exactly two hours.

To prepare concave cubes, a solution of 10 mL CTAC (0.1 M), 0.5 mL $HAuCl_4 \bullet 3H_2O$ (0.01 M), 0.1 mL $AgNO_3$ (0.01 M), and 0.2 mL HCl (1 M) was prepared. To this solution, 0.1 mL L-AA (0.1 M) was added, followed by 5 μL seed. This reaction vial was capped and allowed to sit undisturbed in a 25 °C oil bath for 2 hours. Particles were collected by centrifugation for 30 minutes at 3900 RPM and diluted with water to a total volume of 3 mL.

Synthesis of Pd Octahedra: Pd octahedra were synthesized by a previously published literature method.[8] A solution of 1.024 mL CTAC (0.78 M), 1 mL citric acid (60 mg/mL), 1 mL L-AA (60 mg/mL) and 4.976 mL water was prepared and heated to 100°C with stirring. Next, 3 mL Na_2PdCl_4 (20 mg/mL) was added to the solution. This reaction vial was capped and allowed to sit undisturbed in a 100 °C oil bath for 3 hours. Particles were collected by centrifugation for 30 minutes at 3900 RPM, 3 times and finally, diluted with water to a total volume of 3 mL.

Synthesis of Pd Rhombic Dodecahedra: Pd rhombic dodecahedra were prepared by adapting a seed-mediated synthesis protocol.[9] For the synthesis of the Pd seeds, 1.00 mL of H_2PdCl_4 (10.0 mM) was added to 20.0 mL CTAB (12.5 mM) and heated to 95 °C under 800 RPM stirring for 5 min. Next, 160 μL L-AA (100 mM) was rapidly injected into the solution *via* pipette, and the solution was kept stirring at 95 °C for 20 min. This seed solution was left stirring at 30 °C for 2.5 hours. To prepare the rhombic dodecahedra cores, 2.5 mL CTAC (200 mM), 2.5 mL NaBr (100 mM), 15 μL KI (1 mM), 0.125 mL H_2PdCl_4 (10 mM), 0.050 mL L-AA (100 mM), and 0.040 mL of the Pd seed solution were combined. This solution was allowed to heat, unstirred, at 60 °C for 2 hours. The brown-black solution was centrifuged at 3000 RPM for 30 min, the supernatant was removed, and the particles were redispersed in 3 mL water.

Seed-Mediated Co-Reduction: Seed mediated co-reduction is adapted from previous literature protocols.[10-11] For branched nanocrystal growth typically, 2 mL CTAB (0.2 M) solution was added to a reaction vial. Next, 0.1 mL H_2PdCl_4 (10 mM) solution and 0.1 mL of $HAuCl_4 \bullet 3H_2O$ (0.1 M) solution were added followed by 1.5 mL L-AA (0.1 M) solution. Then 21.4 mL of water was added, followed by shape-controlled Au seed solution. These reaction vials were gently shaken then capped and allowed to sit undisturbed in a 25 °C oil bath for 24 hours. Reaction conditions were optimized for each seed shape due to variation in size and surface structure. The optimized conditions are summarized in Table S1.

Table S1. Optimized SMCR Conditions

Seed (Composition)	CTAB (0.2M)	$HauCl_4 \bullet 3H_2O$ (0.1M)	H_2PdCl_4 (0.01 M)	L-AA (0.1M)	Seed Volume
Cubes (Au)	2 mL	0.1 mL	0.1 mL	1.5 mL	1 mL
Octahedra (Au)	2 mL	0.1 mL	0.1 mL	1.5 mL	1 mL
Rhombic Dodecahedra (Au)	2mL	0.1 mL	0.1 mL	1.5 mL	1.5 mL
Short Rods (Au)	2 mL	0.1 mL	0.1 mL	1.5 mL	0.3 mL
Long Rods (Au)	2 mL	0.1 mL	0.1 mL	1.5 mL	0.3 mL
Decahedra (Au)	2 mL	0.1 mL	0.1 mL	1.5 mL	0.3 mL
Concave Cubes (Au)	2 mL	0.1 mL	0.1 mL	1.5 mL	3 mL
Rhombic Dodecahedra (Pd)	2 mL	0.1 mL	0.1 mL	1.5 mL	3 mL

Note: all solutions are diluted to 25 mL with water prior to seed addition. Seed volume was optimize for each system to achieve the most defined branching patterns; this optimization procedure is required on account of the different surface areas associated with each seed shape.

Co-Reduction on Pd Octahedra at 30, 40 and 50°C: Seed mediated co-reduction is adapted from previous literature protocol. For branched nanocrystal growth typically, 2 mL CTAC (0.2 M) and 2 mL NaBr (50 mM) was added to a reaction vial. Next, 0.1 mL H_2PdCl_4 (10 mM) solution and 0.1 mL of $HAuCl_4 \bullet 3H_2O$ (0.1 M) solution were added followed by 1.5 mL L-AA (0.1 M) solution. Then 19.3 mL of water was added, followed by 0.15 mL Pd octahedra seeds. These reaction vials were gently shaken then capped and allowed to sit undisturbed in a 30-50 °C oil bath overnight.

Co-Reduction with Small Quantities of Au and Pd onto Pd Rhombic Dodecahedra: Seed mediated co-reduction is adapted from previous literature protocol. For branched nanocrystal growth typically, 2 mL CTAB (0.2 M) was added to a reaction vial. Next, 0.2 mL H_2PdCl_4 (0.1 mM) solution and 0.2 mL of $HAuCl_4 \bullet 3H_2O$ (10 mM) solution were added followed by 1.5 mL L-AA (0.1 M) solution. Then 21.1 mL of water was added, followed by 3 mL Pd rhombic dodecahedra seeds. These reaction vials were gently shaken then capped and allowed to sit undisturbed in a 25 °C oil bath overnight.

Time studies: The typical seed-mediated co-reduction protocol was conducted. At each time point (0-3 minutes after seed injection for Au seeds, 10 seconds for Pd seeds), a 1.5 mL aliquot was removed and added to 0.02 mL BSPP (0.1 M).

BSPP Control Study: Au octahedra seeds (1 mL) were added to 25 mL water. Three minutes after seed injection, a 1.5 mL aliquot was removed and added to 0.02 mL BSPP (0.1 M).

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 TEM was conducted with a JEOL JEM 1010 TEM operating at 80 kV. Images were acquired with a ROM CCD camera. STEM and high-resolution TEM (HR-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. EDX spectra were obtained with an Oxford INCA dispersive X-ray system interfaced to the JEM 3200FS TEM, operating at 300 kV. Selected area electron diffraction (SAED) was performed on the JEM 3200FS TEM. 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. Grids were rinsed with methanol. SEM samples were prepared by drop-casting a dispersed particle solution onto a silicon wafer and then washing the wafer with methanol after initial solvent evaporation.

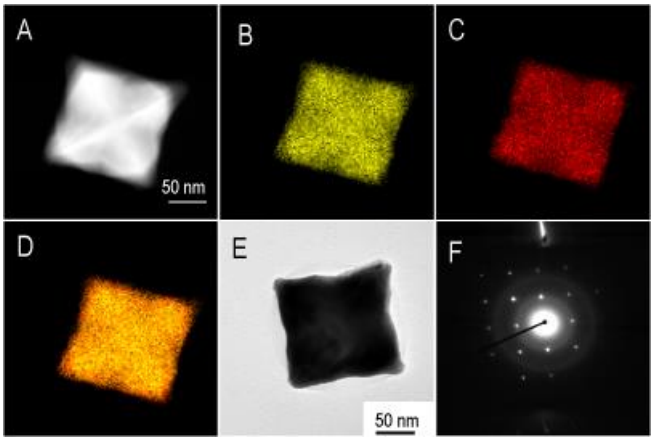

Figure S1. (A) STEM of an individual octopod built from a Au nanocube. (B-D) STEM-EDX elemental mapping of the octopod where Au is represented by yellow and Pd is red; (D) is an overlay of Au and Pd signals, shown separately in (B) and (C). (E,F) TEM and corresponding electron diffraction.

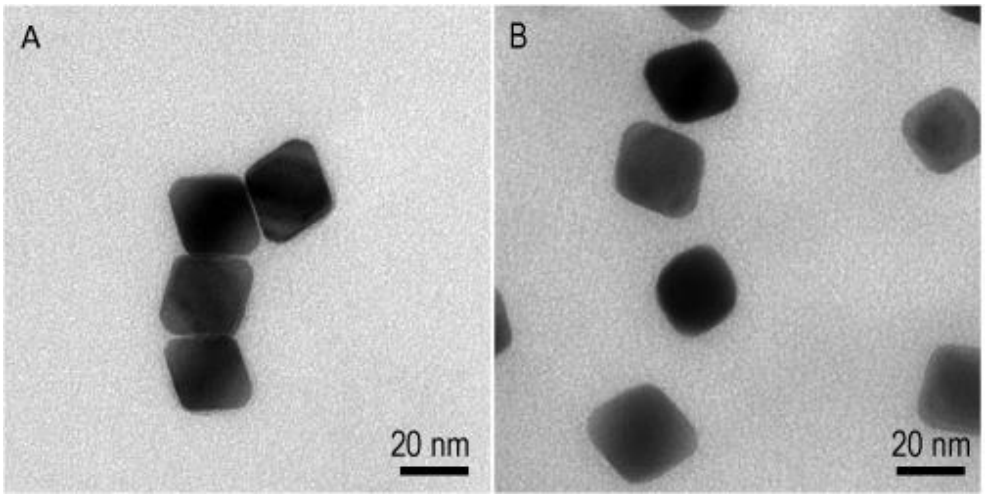

Figure S2. (A) TEM of Au octahedra before treatment with BSPP. (B) TEM of NCs after treatment with BSPP. The morphology of the particles does not change.

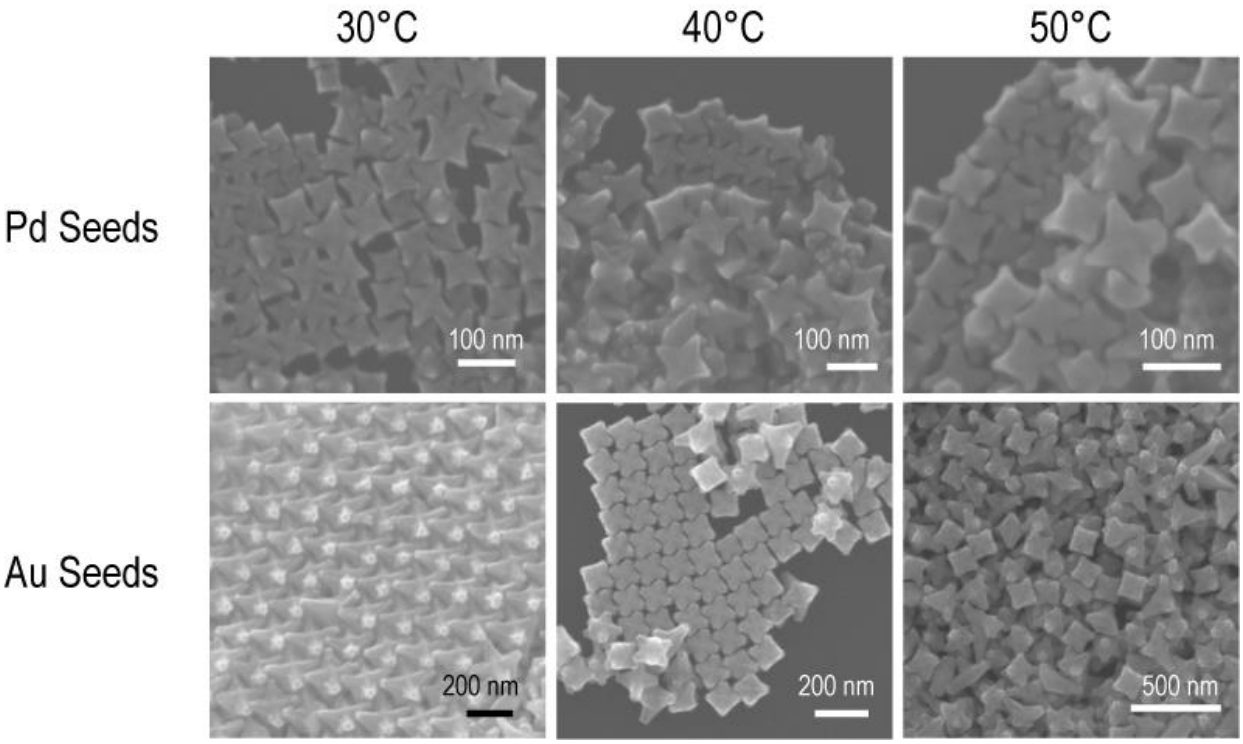

Figure S3.SEM of NCs synthesized by the SMCR method at various temperatures (30-50°C) from Pd (row 1) or Au (row 2) octahedral seeds.

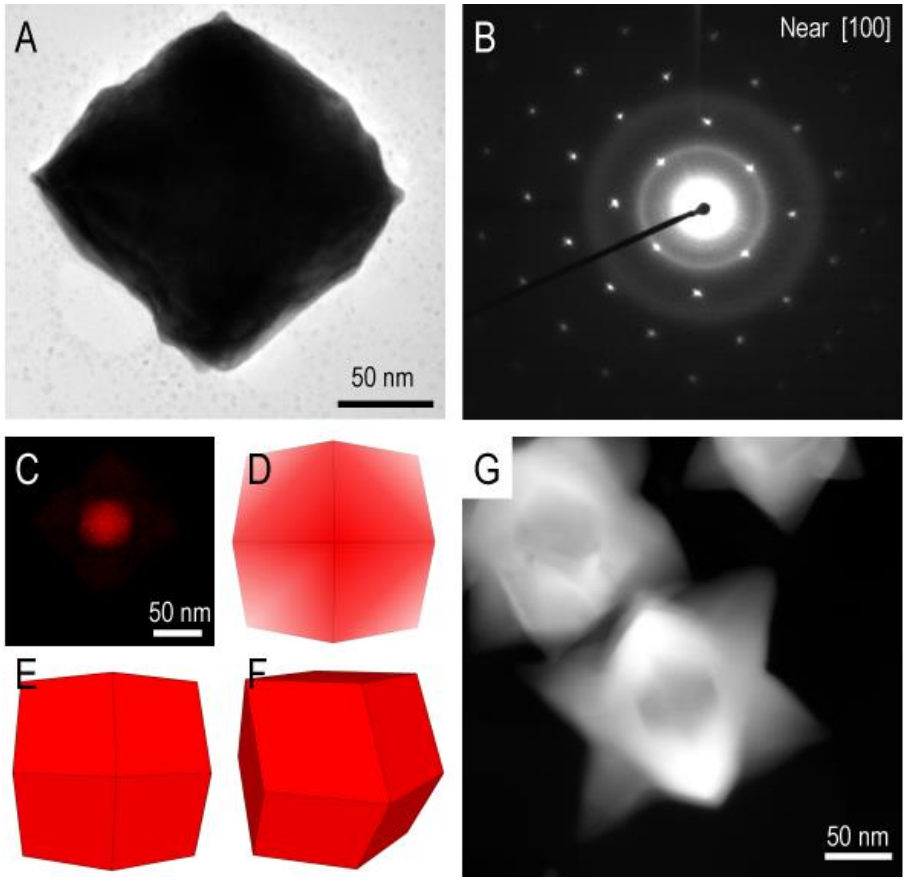

Figure S4. (A) TEM image of a Au/Pd octopod prepared from Pd rhombic dodecahedral seed and (B) its corresponding electron diffraction pattern. (C) Pd-only STEM-EDX map of the same particle. (D-F) Structural models of the rhombic dodecahedral seed where (D) indicates areas of the most Pd content with the brightest intensity. (G) STEM image of Au/Pd octopods prepared from Pd rhombic dodecahedral seeds.

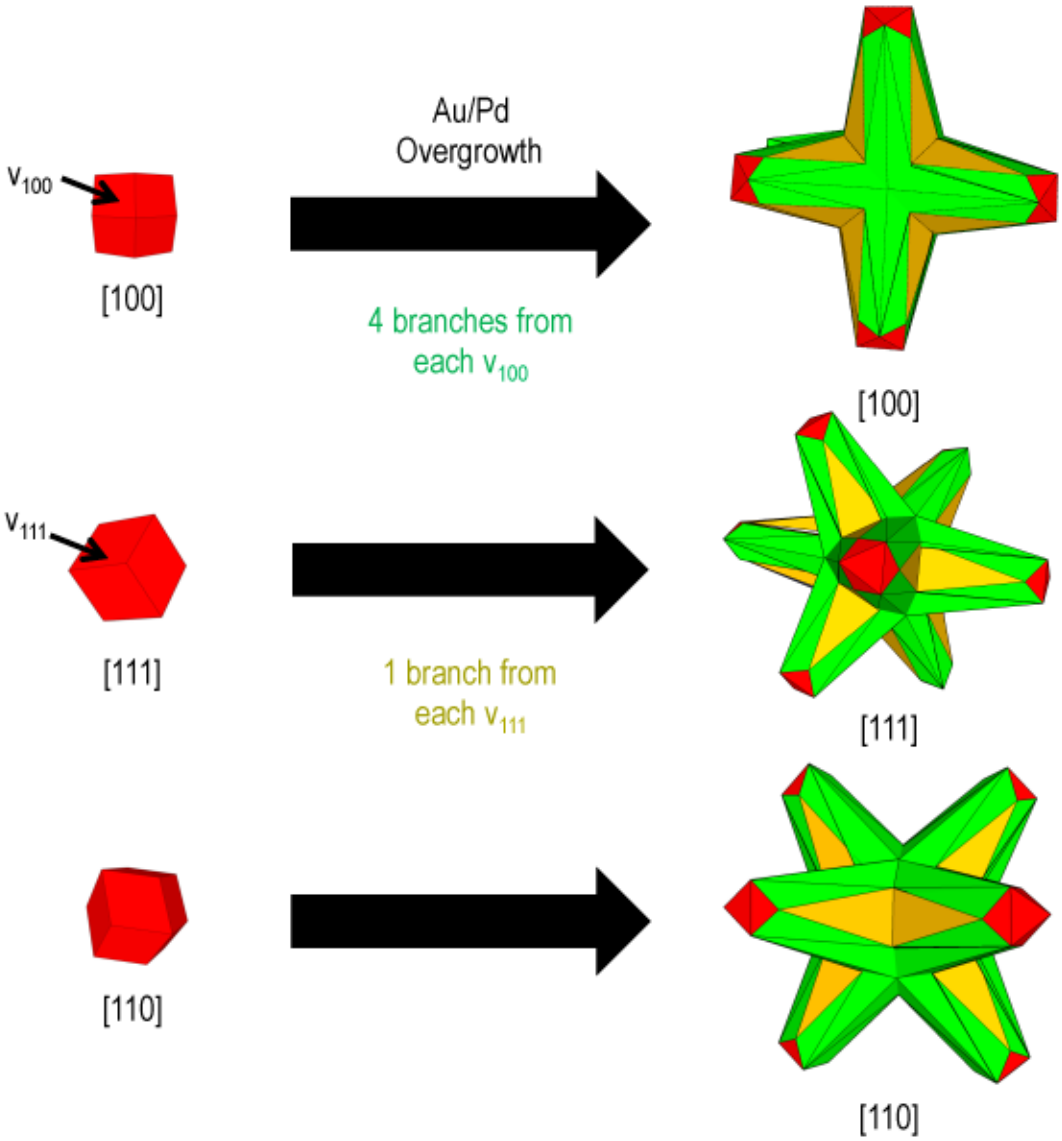

Figure S5. An illustration of the various overgrowth domains that account for Au/Pd octopod formation from rhombic dodecahedral Pd seeds. The green regions indicate where Au/Pd growth primarily originates from V_{100}, gold regions indicate where Au/Pd growth primarily originates from V_{111}, and red is where Pd-rich areas are located.

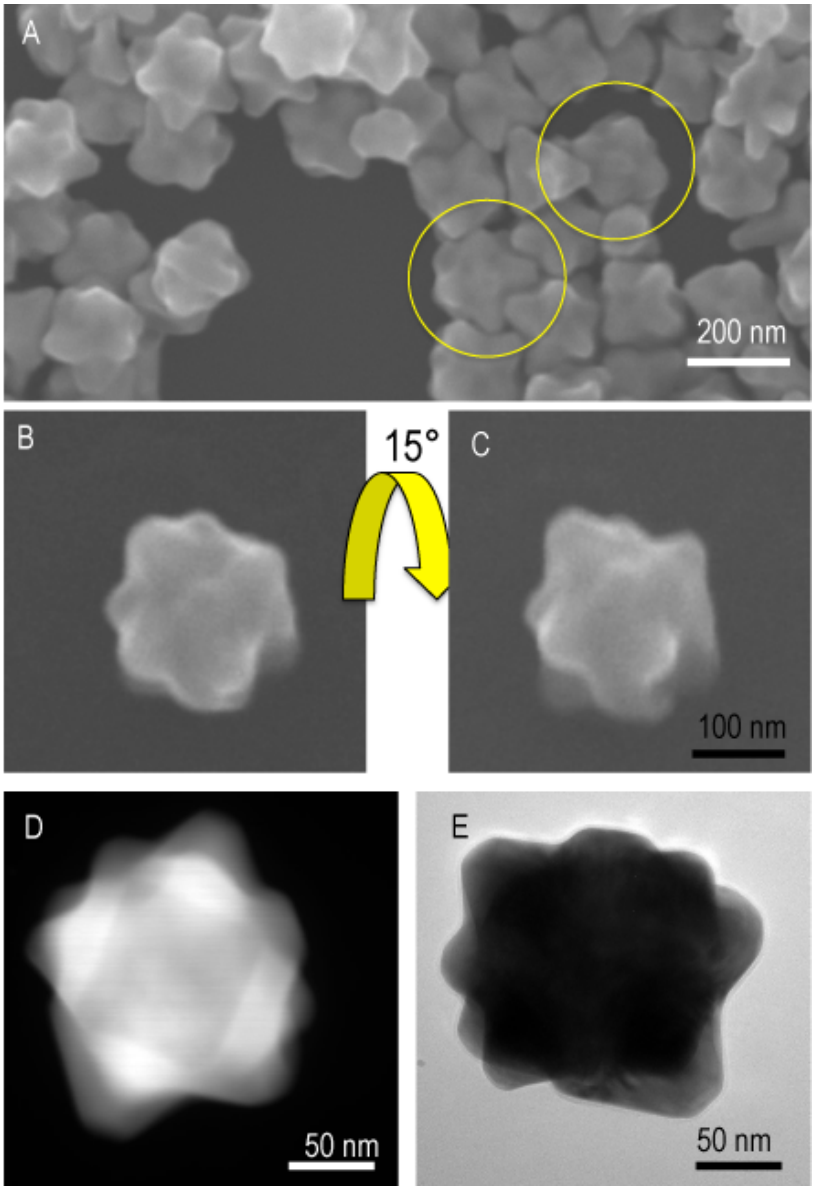

Figure S6. (A) SEM image of NCs prepared *via* SMCR with rhombic dodecahedral Pd seeds and a decreased amount of metal precursors. (B, C) SEM tilt study of an individual NC with greater than eight branches. (D) TEM and (E) STEM of an individual NC where the rhombic dodecahedral Pd seed is evident in the STEM image, corresponding to the top orientation in Figure S4.

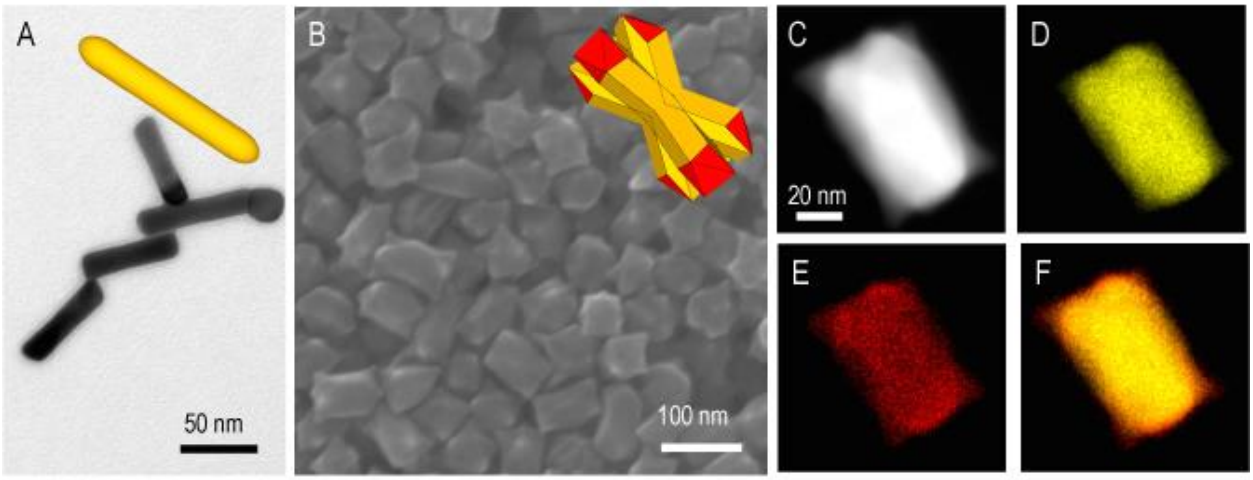

Figure S7. (A) TEM of long Au nanorods. (B) SEM of Au/Pd octorods from the seeds shown in A. (C) STEM on an individual octorod. (D-F) STEM-EDX elemental mapping of the octorod where Au is represented by yellow and Pd is red; (F) is an overlay of Au and Pd signals, shown separately in (D) and (E).

As Au nanorods are synthesized in the presence of a very small amount of Ag^+, which remains adsorbed to their surfaces, a control experiment of SMCR on Au concave cubes was performed to evaluate if the Ag^+ could contribute to the final morphologies. Specifically, concave Au cubes, which are similarly prepared with Ag^+, were used as seeds with SMCR (to the best of our knowledge, synthetic routes to Au nanocubes or octahedra in the presence of Ag^+ have not been reported). The current hypothesis is that single-crystalline Au seeds generate Au/Pd octopods upon co-reduction, thus if Ag^+ has no effect on final morphology, then octopods should be the product. Au and Pd precursors were co-reduced to deposit metal on to single-crystalline Au concave cubes,[7] the result was octopods (Figure S8). Therefore, it is likely that small concentrations of Ag^+ on the surface of the Au cores do not have an effect on the final morphology of the branched product. This finding expands the number of shape-controlled Au nanostructures available for use as seeds and should enable the symmetry classes of branched nanostructures accessible by SMCR to be expanded.

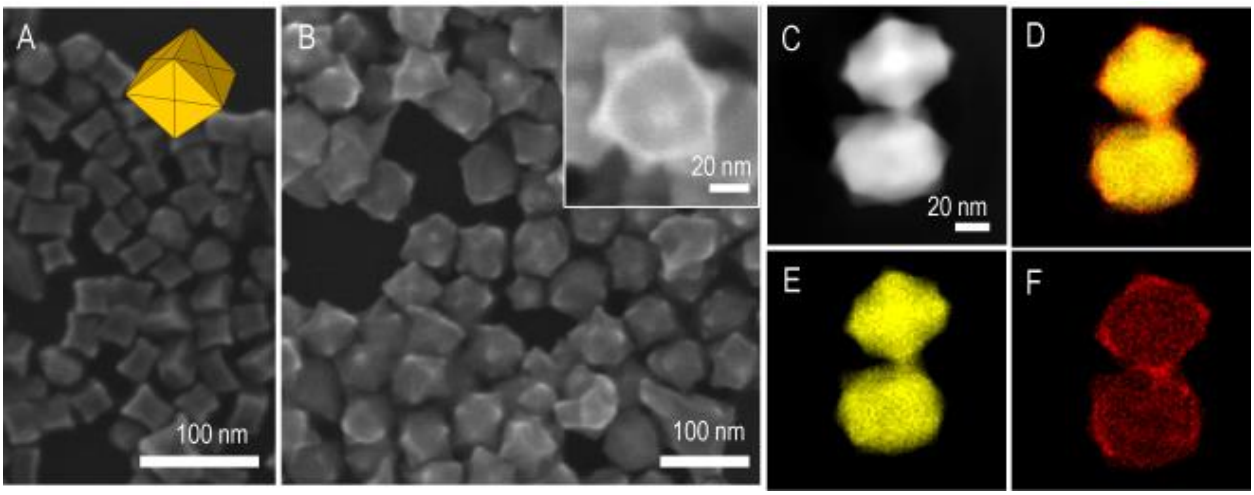

Figure S8. (A) SEM of concave Au cubes. (B) SEM of Au/Pd octopods built from seeds shown in A. (C) STEM of two NCs from the sample in B. (D-F) Corresponding STEM-EDX elemental mapping where Au is represented by yellow and Pd is red; (D) is an overlay of Au and Pd signals, shown separately in (E) and (F).

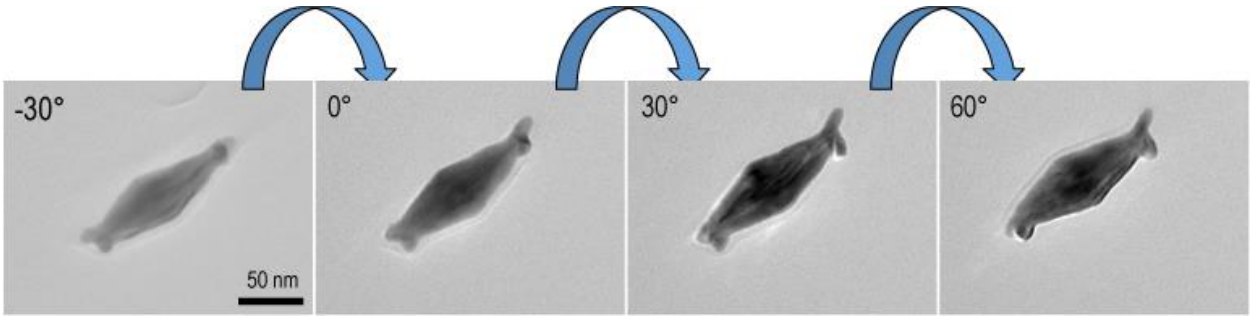

Figure S9. TEM images from a tilt study of a Au/Pd NC built from pentagonally twinned Au bipyramid core.

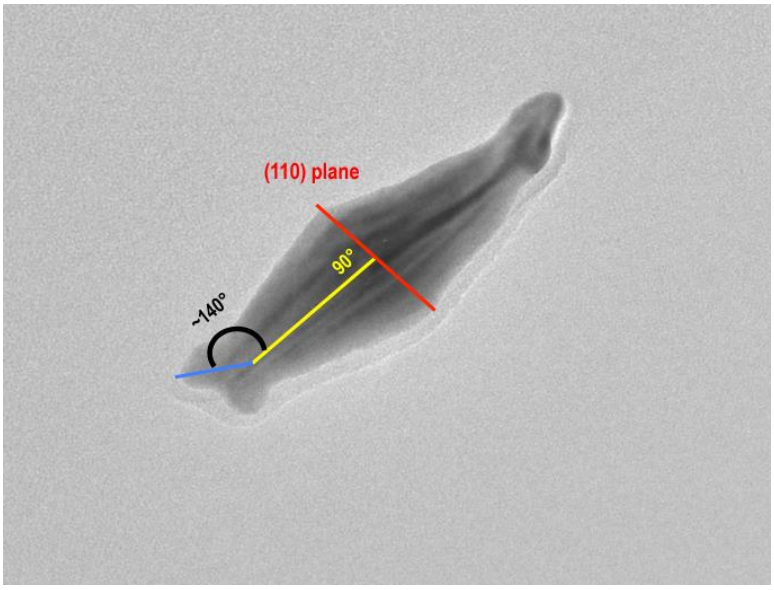

Figure S10. TEM image with schematic of the back of the envelope calculation to determine branched growth direction.

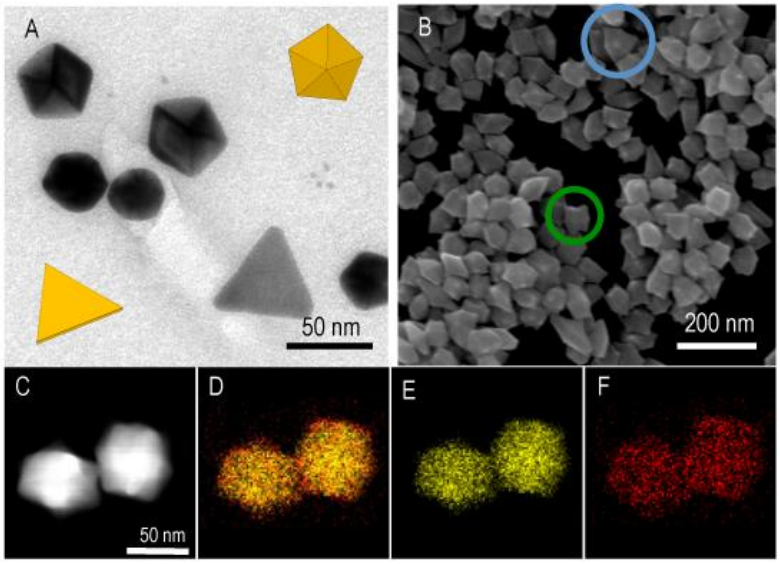

Figure S11. (A) TEM of Au decahedral and triangular plate seeds. (B) SEM of Au/Pd NCs where a particle built from a decahedral seed is circled in green and a particle built from a nanoplate seed is circled in blue. (C) STEM of two NCs from this sample. (D-F) Corresponding STEM-EDX elemental mapping of NCs where Au is represented by yellow and Pd is red; (D) is an overlay of Au and Pd signals, shown separately in (E) and (F).

References

1. Dovgolevsky, E.; Haick, H. Direct Observation of the Transition Point Between Quasi-Spherical and Cubic Nanoparticles in a Two-Step Seed-Mediated Growth Method. *Small* **2008,** *4*, 2059-2066.

2. Chang, C.-C.; Wu, H.-L.; Kuo, C.-H.; Huang, M. H. Hydrothermal Synthesis of Monodispersed Octahedral Gold Nanocrystals with Five Different Size Ranges and Their Self-Assembled Structures. *Chem. Mater.* **2008,** *20*, 7570-7574.

3. Wu, H.-L.; Kuo, C.-H.; Huang, M. H. Seed-Mediated Synthesis of Gold Nanocrystals with Systematic Shape Evolution from Cubic to Trisoctahedral and Rhombic Dodecahedral Structures. *Langmuir* **2010,** *26*, 12307-12313.

4. Ye, X.; Jin, L.; Caglayan, H.; Chen, J.; Xing, G.; Zheng, C.; Doan-Nguyen, V.; Kang, Y.; Engheta, N.; Kagan, C. R. *et al*. Improved Size-Tunable Synthesis of Monodisperse Gold Nanorods through the Use of Aromatic Additives. *ACS Nano* **2012,** *6*, 2804-2817.

5. Vigderman, L.; Zubarev, E. R. High-Yield Synthesis of Gold Nanorods with Longitudinal SPR Peak Greater than 1200 nm Using Hydroquinone as a Reducing Agent. *Chem. Mater.* **2013,** *25*, 1450-1457.

6. Sun, J.; Guan, M.; Shang, T.; Gao, C.; Xu, Z.; Zhu, J. Selective Synthesis of Gold Cuboid and Decahedral Nanoparticles Regulated and Controlled by Cu^{2+} Ions. *Cryst. Growth Des.* **2008,** *8*, 906-910.

7. Langille, M. R.; Personick, M. L.; Zhang, J.; Mirkin, C. A. Defining Rules for the Shape Evolution of Gold Nanoparticles. *J. Am. Chem. Soc.* **2012,** *134*, 14542-14554.

8. Hong, J. W.; Kim, D.; Lee, Y. W.; Kim, M.; Kang, S. W.; Han, S. W. Atomic-Distribution-Dependent Electrocatalytic Activity of Au–Pd Bimetallic Nanocrystals. *Angew. Chem.* **2011,** *123*, 9038-9042.

9. Niu, W.; Zhang, L.; Xu, G. Shape-Controlled Synthesis of Single-Crystalline Palladium Nanocrystals. *ACS Nano* **2010,** *4*, 1987-1996.

10. DeSantis, C. J.; Skrabalak, S. E. Core Values: Elucidating the Role of Seed Structure in the Synthesis of Symmetrically Branched Nanocrystals. *J. Am. Chem. Soc.* **2012,** *135*, 10-13.

11. DeSantis, C. J.; Peverly, A. A.; Peters, D. G.; Skrabalak, S. E. Octopods *versus* Concave Nanocrystals: Control of Morphology by Manipulating the Kinetics of Seeded Growth *via* Co-Reduction. *Nano Lett.* **2011,** *11*, 2164-2168.