

Supporting Information

Kinetically Controlled Synthesis of Bimetallic Nanostructures by Flowrate Manipulation in a Continuous Flow Droplet Reactor

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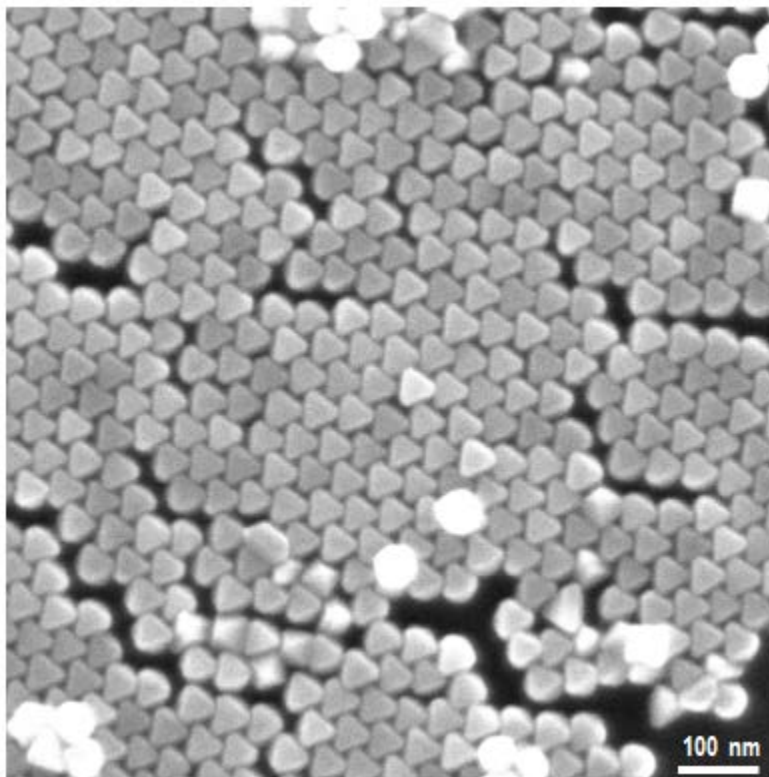


Figure S1. SEM image of Au octahedral seeds used in the seed-mediated co-reduction syntheses.

Increasing $[H_2PdCl_4]$ and $[HAuCl_4]$

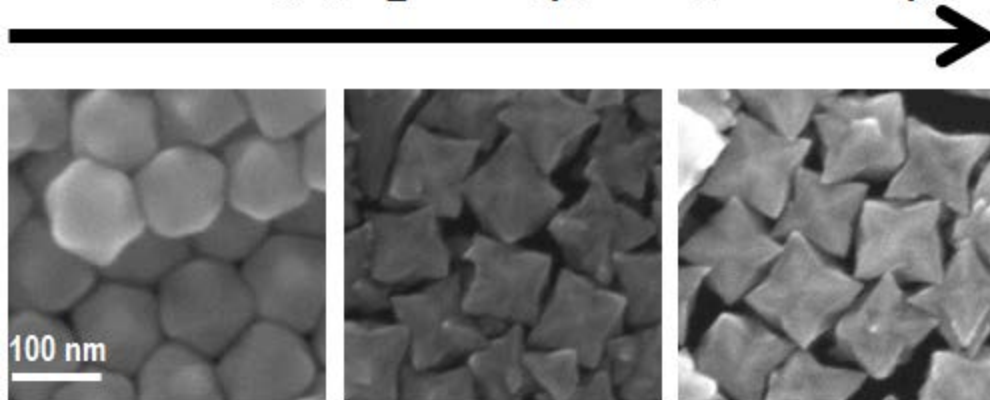


Figure S2. Concentration study of SMCR octopod syntheses via a microreactor keeping all syringe flowrates constant while changing both initial metal precursors concentrations in their syringes. Syringe pump 1 (Au precursor, CTAC, NaBr) and 2 (Pd precursor, CTAC, NaBr) pumped at 0.3 mL/hr, syringe pump 3 (HCl) pumped at 0 mL/hr, syringe pump 4 (Au octahedral seeds) pumped at 0.1 mL/hr, syringe pump 5 (L-aa) pumped at 0.6 mL/hr, and syringe pump 6 (silicone oil) pumped at 1.6 mL/hr. From left to right, the SEM images show the effects of changing the starting concentrations of $HAuCl_4$ (0.96-1.92mM) and H_2PdCl_4 (0.19-0.38mM), while increasing the CTAC (38.46-76.92mM) and NaBr (11.10-22.19mM) concentration in Syringe pump 1 and 2 for increased stabilization at higher metal precursor concentrations. Longer and sharper tips were observed as the starting concentrations of both metal precursors were increased.

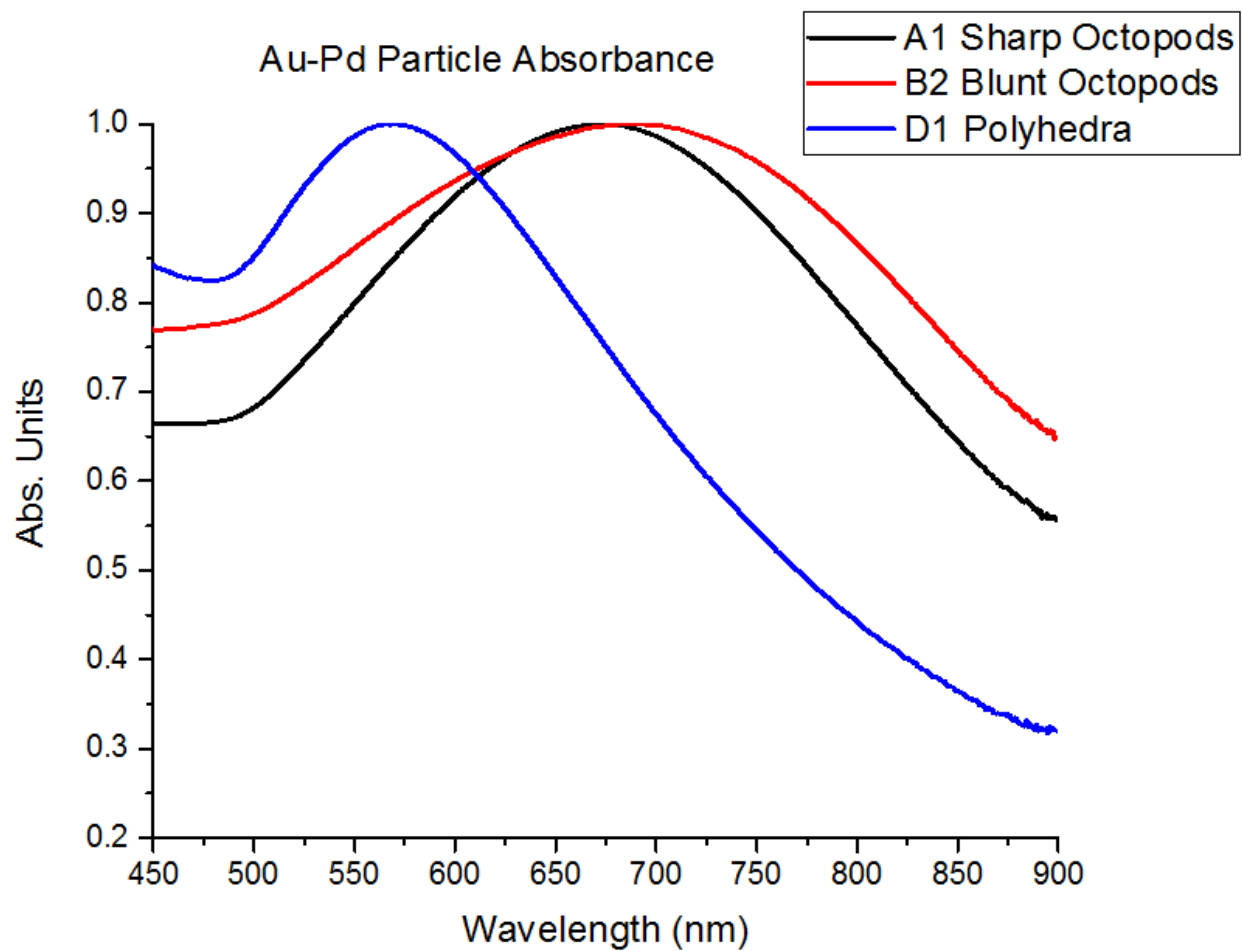


Figure S3. UV-Vis absorbance measurements for particles shown in Figure 3.

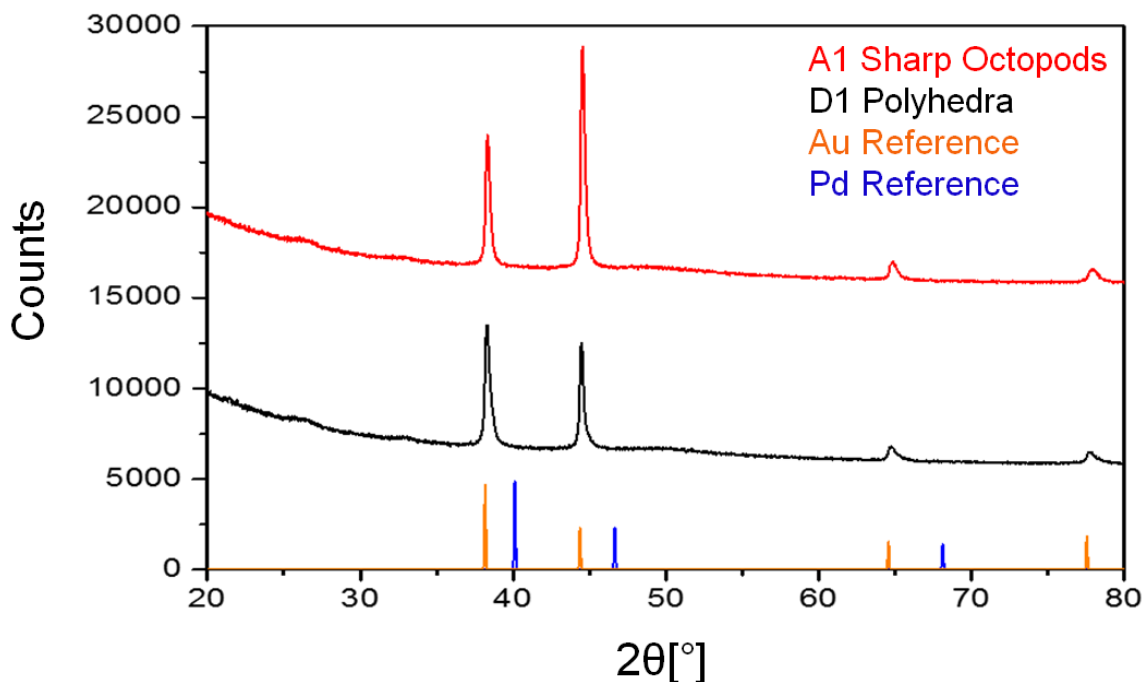
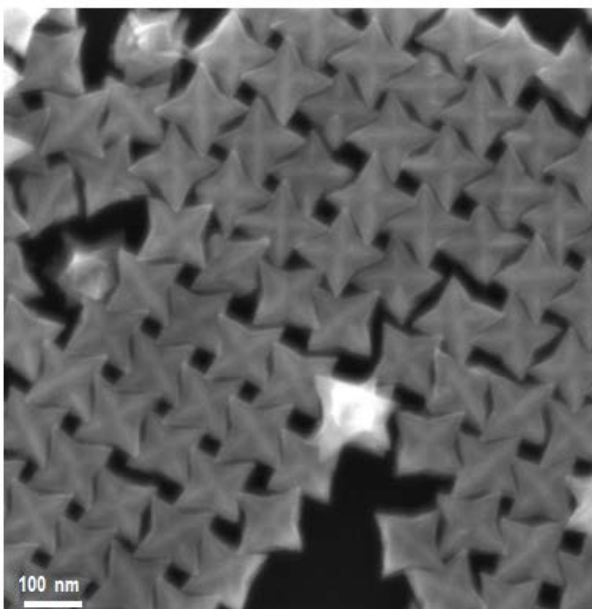
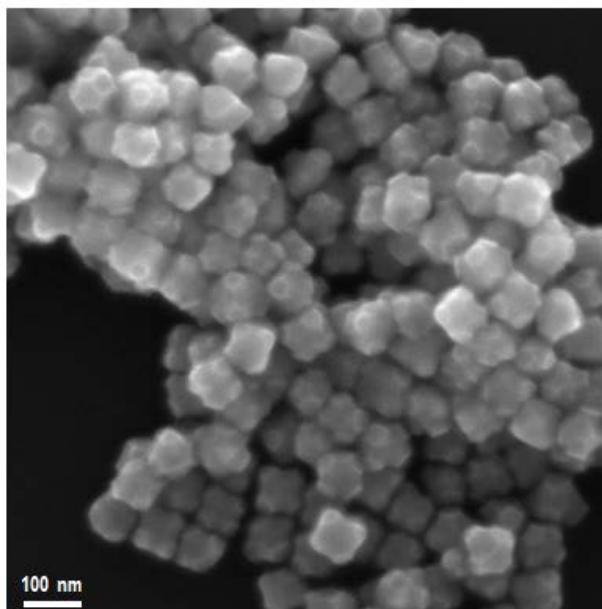


Figure S4. Powder X-ray diffraction patterns of the A1 sharp octopods and D1 polyhedra shown in Figure 2. The orange lines correspond to reference Au - ICSD 44362 and the blue lines correspond to reference Pd - ICSD 52251. The slight asymmetry of the diffraction peaks to higher 2-theta is consistent with a Au-rich Pd phase. The small features below 30 degrees are from residual CTAB which is capping the particles.

A1 Batch



D1 Batch



A1 Tip to Tip Length

Microreactor= 134.69 ± 10.59 nm

Batch= 156.24 ± 6.29 nm

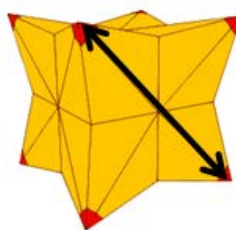


Figure S5. SEM images of the product from batch reactions with equal equivalents of the A1 and D1 reactions after 1.5 hours residence time. Tip to tip lengths were measured for the microreactor and batch species and recorded above.

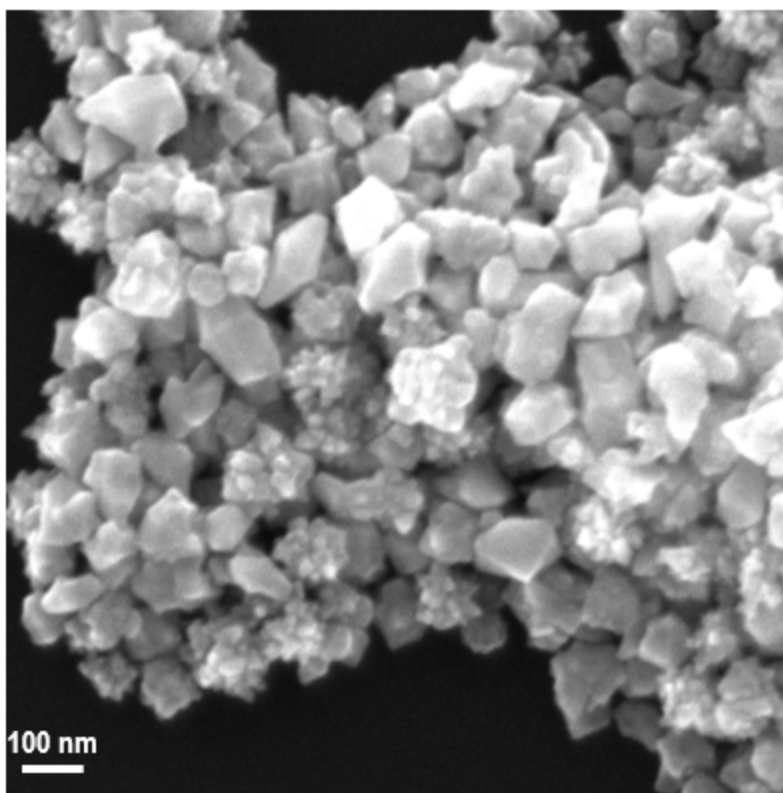


Figure S6. SEM image of the product obtained from the synthesis that yields the A1 product shown in Figure 2; however, here, no octahedral Au seeds were used in the synthesis.

Figure 2 Particles	HCl Flowrate (mL/hr)	[HCl]	Au Seeds Flowrate (mL/hr)	[Au] Octahedra	Metal Precursor Flowrate (mL/hr)	[HAuCl ₄]	[H ₂ PdCl ₄]	[CTAC]	[NaBr]	[L-aa]
A1	0	0 mM	0.1	15.4 μM	0.30	0.44 mM	87.7 μM	35.5 mM	10.2 mM	46.2 mM
B1	0.20	38.5 mM	0.1	15.4 μM	0.20	0.30 mM	58.4 μM	23.7 mM	6.83 mM	46.2 mM
C1	0.30	57.7 mM	0.1	15.4 μM	0.15	0.22 mM	43.8 μM	17.7 mM	5.12 mM	46.2 mM
D1	0.40	76.9 mM	0.1	15.4 μM	0.10	0.15 mM	29.2 μM	11.8 mM	3.42 mM	46.2 mM
E1	0.58	111.5 mM	0.1	15.4 μM	0.01	14.7 μM	2.9 μM	1.18 mM	0.34 mM	46.2 mM

Figure 2 Particles	HCl Flowrate (mL/hr)	[HCl]	Au Seeds Flowrate (mL/hr)	[Au] Octahedra	Metal Precursor Flowrate (mL/hr)	[HAuCl ₄]	[H ₂ PdCl ₄]	[CTAC]	[NaBr]	[L-aa]
A2	0	0 mM	0.05	7.70 μM	0.325	0.48 mM	95.0 μM	38.5 mM	11.1 mM	46.2 mM
B2	0.20	38.5 mM	0.05	7.70 μM	0.225	0.33 mM	65.8 μM	26.6 mM	7.68 mM	46.2 mM
C2	0.30	57.7 mM	0.05	7.70 μM	0.175	0.26 mM	51.2 μM	20.7 mM	5.98 mM	46.2 mM
D2	0.40	76.9 mM	0.05	7.70 μM	0.125	0.18 mM	36.5 μM	14.8 mM	4.20 mM	46.2 mM
E2	0.58	111.5 mM	0.05	7.70 μM	0.035	51.6 μM	10.2 μM	4.14 mM	1.20 mM	46.2 mM

Table S1. Detailed flowrate and concentration chart of each droplet reaction shown in Figure 2.

Experimental Section.

Chemicals. Gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99.9\%$ trace metal basis, Lot# MKCC8511), hexadecyltrimethylammonium bromide (CTAB, BioUltra, $\geq 99.0\%$, Lot# BCBS1424V), L-ascorbic acid (L-aa, $\text{C}_6\text{H}_8\text{O}_6$, 99.0%, Lot# BCBS0460V), sodium citrate ($\text{HOC}(\text{COONa})(\text{CH}_2\text{COONa})_2 \cdot 2\text{H}_2\text{O}$, Batch# 020M0026), cetyltrimethylammonium chloride solution (CTAC, 25 wt.% in H_2O , Lot# STBG7166), palladium(II) chloride (PdCl_2 , 99.9%, Lot# MKBV5028V), and methanol (CH_3OH , anhydrous, 99.8%) were purchased from Sigma Aldrich and used as received. Sodium bromide (NaBr , 99.99%, Lot# W08A041) was purchased from Alfa Aesar and used as received. Chloroform (CHCl_3 , ACS) was purchased from Macron and used as received. Hydrochloric acid (HCl , 1.0 N, Lot# 174569) and silicone oil (Lot# 166612) were purchased from Fisher Chemical and used as received. Milli-Q nanopure water ($18.2 \text{ M}\Omega \cdot \text{cm}$) was used in all experiments.

Synthesis of Au Octahedra. The synthesis of Au octahedra was adopted from a literature protocol.¹

Preparation of H_2PdCl_4 . The synthesis of H_2PdCl_4 was adopted from a literature protocol.¹

Design of Microreactor for Core@Shell Syntheses. The design of the microreactor was adapted from various microreactors reported in the literature (Figure 1).^{1,2} Six syringes were placed on six different syringe pumps (KD Scientific Inc.) and connected to polytetrafluoroethylene (PTFE) tubing (I.D. = 1.58 mm) through silica capillaries (I.D. = 0.250 mm) and held in place by epoxy. These capillaries were placed such that the end of the capillaries met at the same point in the injector site. After the injector site, the PTFE tubing was pinched three times separated by ~ 1 cm to help induce mixing within the droplet as the reaction had to squeeze through the pinching zone.² Around five feet of tubing was placed into an oil bath so that

an overall reaction time of 1.5 hours could be met by the overall flowrate of the individual reaction droplets. After exiting the tubing, the droplets were then collected in a centrifuge vial and washed with nanopure water.

Synthesis of Au@Pd Particles. The SMCR syntheses of Au-Pd kinetic products was adapted from a batch reaction literature protocol.³ The syringe on syringe pump 1 contained a solution of 1.92 mM HAuCl₄, 22.2 mM NaBr, and 76.9 mM cetyltrimethylammonium chloride (CTAC). The syringe on syringe pump 2 contained a solution of 0.38 mM H₂PdCl₄, 22.2 mM NaBr, and 76.9 mM CTAC. Syringes on syringe pumps 3, 4, and 5 contained solutions of 250 mM HCl, Au octahedral seeds, and 100 mM L-ascorbic acid (L-aa), respectively. Immiscible silicone oil was held in the syringe on syringe pump 6 and created the separation of aqueous reaction droplets. The flow rates of syringe pumps 1 (Au precursor, CTAC, NaBr), 2 (CTAC, Pd precursor, NaBr), and 3 (HCl solution) were held equal or varied depending on the experiment. Syringe Pump 4 was held constant at either 0.1 or 0.05 mL/hr and syringe pump 5 was held constant at 0.6 mL/hr. The total additive flowrate of the aqueous media was 1.3 mL/hr for each reaction. Kinetic and thermodynamic products were synthesized by varying the relative flowrates of Syringe pumps 1 (Au metal precursor, CTAC, and NaBr solution), 2 (Pd metal precursor, CTAC, and NaBr solution), 3 (250 mM HCl), and 4 (Au octahedra seed solution) while keeping the additive total flowrate of these four syringe pumps at 0.7 mL/hr. Syringe pump 6 was held constant at 1.6 mL/hr. Exact concentrations of reagent material within the droplets were calculated using the ratio: $[Droplet] = [Reagent] \frac{Aq. Reagent Flowrate}{Total Aq. Reagent Flowrate}$. Concentrations and flowrates of reagents in the reaction droplet are summarized in SI Table 1. By ensuring a 1.3 : 1.6 flowrate ratio of aqueous media to silicone oil, uniform droplets and similar residence times were observed for each reaction. Each synthesis was run at 25°C with a residence time of 1.5 hours.

Characterization. Samples for scanning electron microscopy (SEM) were prepared by drop-casting a 3 μ L droplet of particle solution onto a cleaned Si wafer. After the solvent evaporated, the Si wafers were washed with methanol several times to remove excess surfactant. Images were obtained with a FEI Quanta FEG 600 field-emission environmental SEM.

For high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), and scanning transmission electron microscopy (STEM), a dispersed particle solution was drop-casted on a 300 mesh Cu grid (Ted-Pella, Formvar removed by dipping grid in chloroform). After 5 minutes, the grid was dipped in methanol, air dried for 30 minutes and then soaked in acetone overnight. Sample analysis by HRTEM and STEM were conducted on a JEOL JEM 3200FS TEM, equipped with a Gatan 4k x 4k UltraScan 4000 CCD camera, operating at 300 kV with a spot size of 1. Energy dispersive X-ray spectroscopy (EDS) spectra were obtained with a liquid nitrogen cooled Oxford INCA dispersive X-ray system interfaced to the JEOL JEM 3200FS TEM. Elemental mapping was conducted in STEM-EDS mode. ICP-MS analysis of the Au seed solutions was carried out using a PerkinElmer SCIEX ELAN DRC-e ICP-MS by staff at the University of Illinois Microanalysis Laboratory using standard dilution and digestion procedures.

References.

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