

Supporting Information

Seed-Mediated Co-Reduction in a Large Lattice Mismatch System: Synthesis of Pd-Cu Nanostructures

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Chemicals

L-ascorbic acid ($C_6H_8O_6$, 99%), palladium (II) chloride ($PdCl_2$, 99.98%), copper (II) chloride ($CuCl_2$ 99.99%), and cetyltrimethylammonium bromide (CTAB, $\geq 99\%$, lot # BCBP3807V), were used as purchased from Sigma Aldrich. Aqueous hydrochloric acid (1 M) was purchased from Macron. Nanopure water ($18.2\text{ M}\Omega\cdot\text{cm}$) was used in all experiments. An aqueous 10 mM H_2PdCl_4 solution was prepared by heating at $\sim 70\text{ }^\circ\text{C}$ and stirring dissolved $PdCl_2$ (40.0 mg) in 25 mL of HCl (pH 1.69-1.72) within 1 h.

Synthesis Details

The synthesis of Pd-Cu nanostructures by SMCR first required the synthesis of Pd nanocubes, which are prepared in a two-step process as outlined below. The Pd nanocubes are then used in the SMCR procedure.

Synthesis of Pd Cubes

Step 1: Synthesis of small cubic Pd seeds: 0.5 mL H_2PdCl_4 (10 mM) was added to 10 mL CTAB (12.5 mM) in a 20 mL vial and stirred in a $95\text{ }^\circ\text{C}$ oil bath for 5 minutes. Next, 0.08 mL L-aa (100 mM) was added. The solution was stirred for 30 minutes in a $95\text{ }^\circ\text{C}$ oil bath and stored at $40\text{ }^\circ\text{C}$ for up to 24 hours.

Step 2: Synthesis of larger cubic Pd seeds for use in SMCR: To synthesize larger Pd nanocubes ($\sim 20\text{ nm}$), 0.125 mL H_2PdCl_4 (10 mM) was added to 5 mL CTAB (50 mM)

in a 20 mL vial and placed in a 40 °C oil bath. Next, the smaller Pd seeds (Step 1, unwashed) were injected (0.2 mL) into the vial, followed by 0.025 mL L-aa (100 mM). The vials were capped, inverted once, and then left undisturbed for 14 hours in a 40 °C oil bath. The product was collected by centrifugation of the solution at 8000 rpm for 15 minutes; the supernatant was removed, and the final product was diluted and redispersed with 3 mL of water.

Seed-Mediated Co-Reduction

For branched Pd-Cu nanoparticle growth, 2 mL aqueous CTAB (0.2 M) solution was added to a 30 mL reaction vial. Next, 0.025 mL H_2PdCl_4 (10 mM) solution and 0.05 mL of aqueous CuCl_2 (10 mM) solution were added, followed by 1.5 mL aqueous L-aa (0.1 M) solution. Then 21.4 mL of water was added, followed by 1 mL of the solution containing the larger Pd nanocubes. These reaction vials were capped, inverted once, and allowed to sit undisturbed in a 25 °C oil bath overnight. The product was collected by centrifugation of the solution at 8000 rpm for 15 minutes; the supernatant was removed, and the final product was diluted and redispersed with 5 mL of water.

ICP-MS Analysis

The ICP-MS analysis was carried out using PerkinElmer SCIEX ELAN DRC-e ICP-MS at the University of Illinois Microanalysis Laboratory. Samples were prepared by quenching each NP reaction solution (26 mL) at each time point. The solutions were immediately quenched by injecting BSPP (2.6 mL, 0.5 mg/mL) and mixed vigorously to ensure uniform dispersion. The samples were then spun down at 10,500 RPM for 15 minutes and the supernatant was removed carefully. The solutions were sent to University of Illinois Microanalysis Laboratory as homogenous solutions (with known

volumes) where they were digested in concentrated nitric and hydrochloric acids. The results were given in units of ppm, which was then plotted as a function of time.

Characterization

Scanning electron microscopy (SEM) images of the NPs were taken with a FEI Quanta 600F field-emission SEM operated at 20 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. The composition of the NPs was determined with an Oxford INCA energy dispersive X-ray detector interfaced to the SEM operated at 20 kV. HRTEM and electron diffraction images and patterns were obtained on a JEOL JEM 3200FS TEM operated at 300 kV and using a spot size of 1 and a Gatan 4k × 4k Ultrascan 4000 CCD camera. EDS spectra were obtained with an Oxford INCA dispersive X-ray system interfaced to the JEOL JEM 3200FS TEM, operating in STEM mode at 300 kV. Samples for elemental mapping by STEM-EDS were prepared by dropcasting a dispersed particle solution onto a carbon-coated gold grid. Samples for SEM-EDS analyses were prepared by drop-casting a dispersed particle solution onto a silicon wafer and then washing the wafer several times with methanol after initial solvent evaporation. Samples for powder XRD were deposited onto a silicon sample holder and analyzed with Siemens/Bruker D-5000 using Cu K α radiation ($\lambda = 0.15418$ nm). X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI 5000 Versa Probe II scanning X-ray microprobe operated under ultrahigh-vacuum conditions and using a monochromatic Al K α X-ray source. Samples for XPS were prepared similarly to SEM-EDS sample preparation. The Fermi edge and Si were used for the calibration of the XPS binding energy scale.

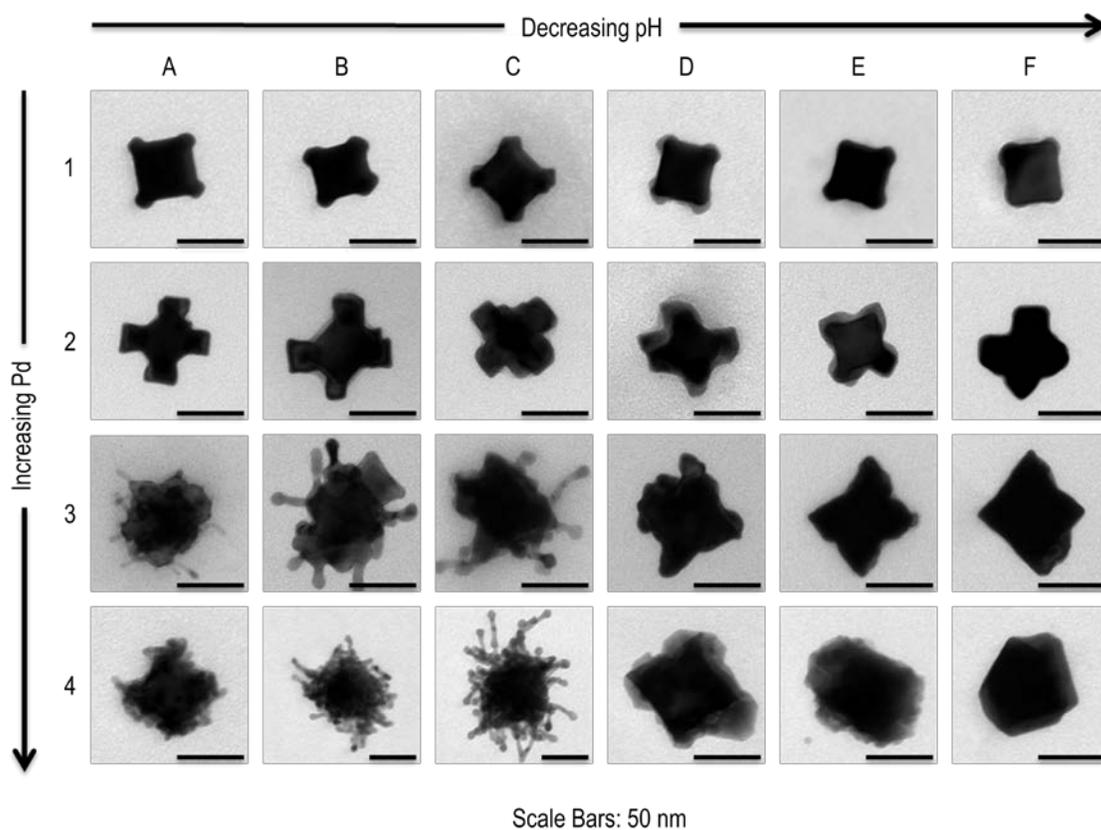


Figure S1. TEM images of Pd-Cu NPs synthesized by SMCR. The synthetic results represented by columns A - F involved the addition of an aqueous HCl solution prior to the Pd cube solution and co-reduction. The final HCl concentrations were for A - F: 0.0, 1.92, 3.85, 19.2, 26.9, and 38.5 mM, respectively. The synthetic results represented by rows 1 – 4 were acquired by holding the Cu precursor constant and varying the amount of Pd precursor. The final Pd precursor concentrations for rows 1 – 4 include: 1.92, 9.61, 19.2, and 28.8 μM , respectively. Scale bars: 50 nm.

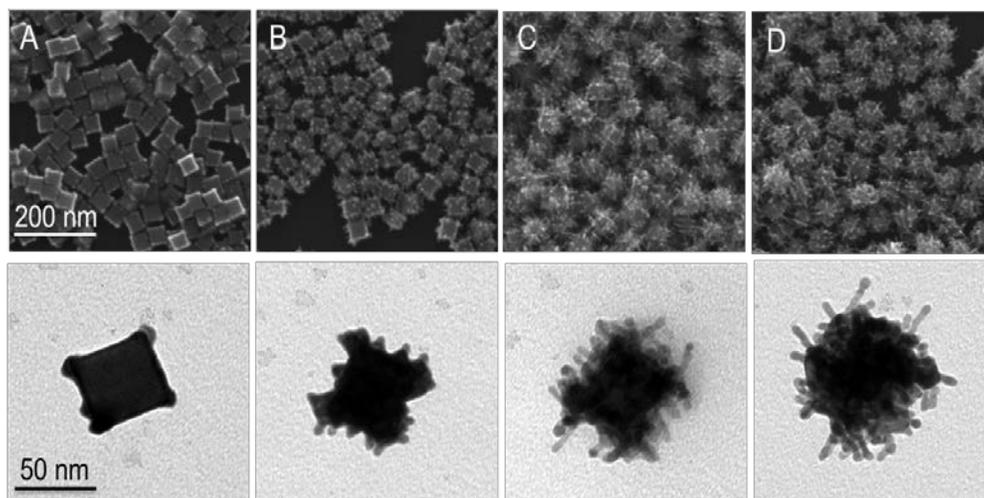


Figure S2. SEM and corresponding TEM images of Column A from Figure 1 where the total amount of moles of Cu and Pd were held constant. The resulting ratios of Pd:Cu were A) 1:10, B) 1:2, C) 1:1, and D) 3:2.

Table S1. pH values of reaction solution after completion from Figure 1.

	A	B	C	D	E	F
1	3.27	2.78	2.48	1.78	1.68	1.50
2	3.25	2.74	2.46	1.80	1.65	1.48
3	3.24	2.75	2.48	1.81	1.67	1.53
4	3.19	2.72	2.44	1.78	1.65	1.50

Table S2. Values of Cu atomic % from Figure 1 obtained using SEM-EDS by considering only the Cu and Pd signals.

	A	B	C	D	E	F
1	0 %	0 %	0 %	0 %	0 %	0 %
2	0.2 %	0.1 %	0.1 %	0.2 %	0 %	0 %
3	0.7 %	0.3 %	0.6 %	0.2 %	0.3 %	0 %
4	0.6 %	0.4 %	0.4 %	0.2 %	0.1 %	0.2 %

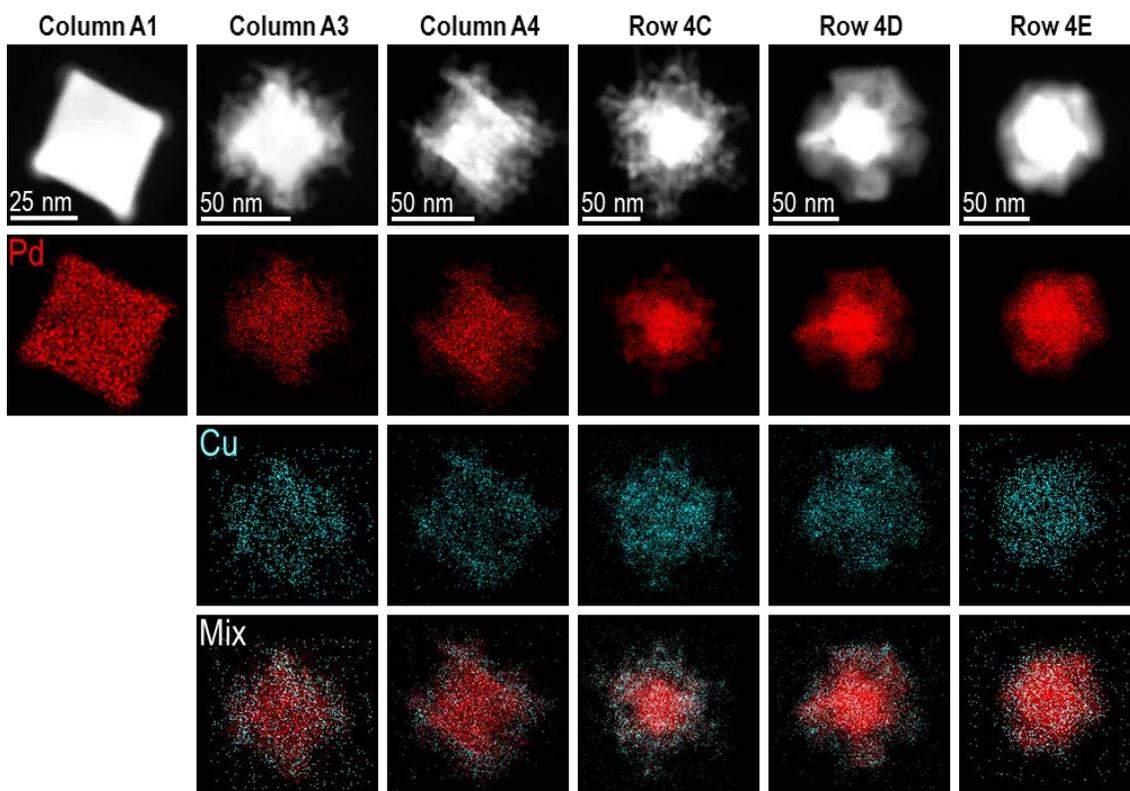


Figure S3. STEM and elemental mapping by STEM-EDS of nanostructures from Column A and Row 4 of Figure 1. Cu was not detected for Column A1.

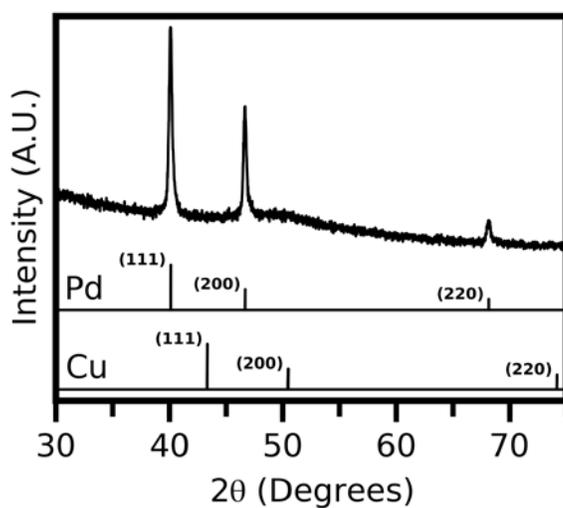


Figure S4. Powder XRD pattern of Sample 2A. Reference Pd (AMCSD- 0011155) and Cu (AMCSD- 0011145) are included. The broad rise in the background is from the Si sample holder.

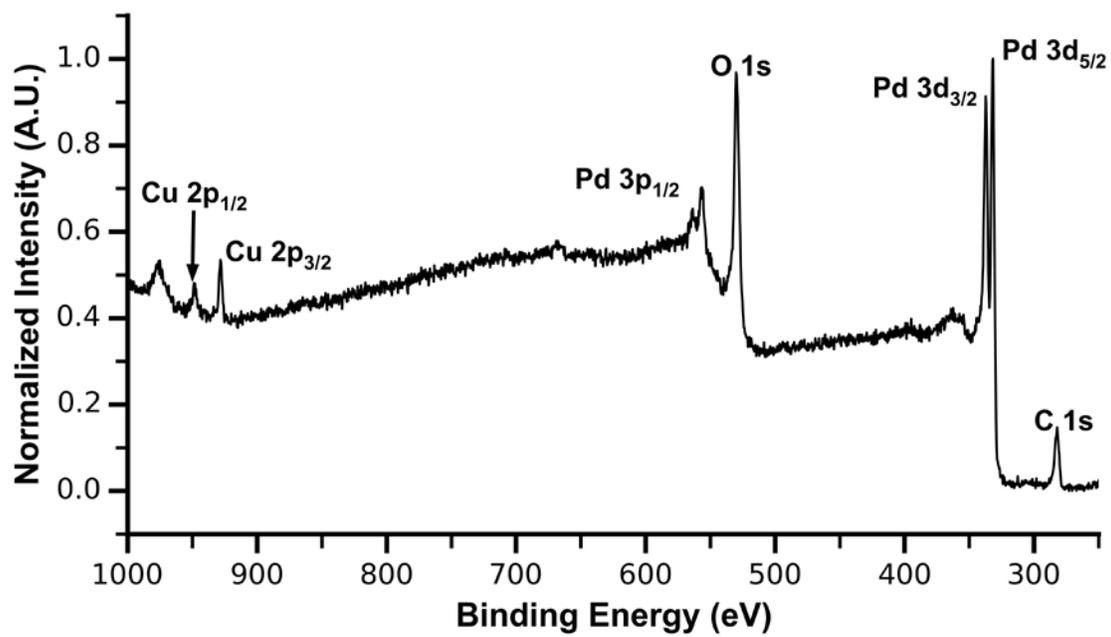


Figure S5. XPS survey scan of Sample 2A. The O 1s signal arises from SiO₂.

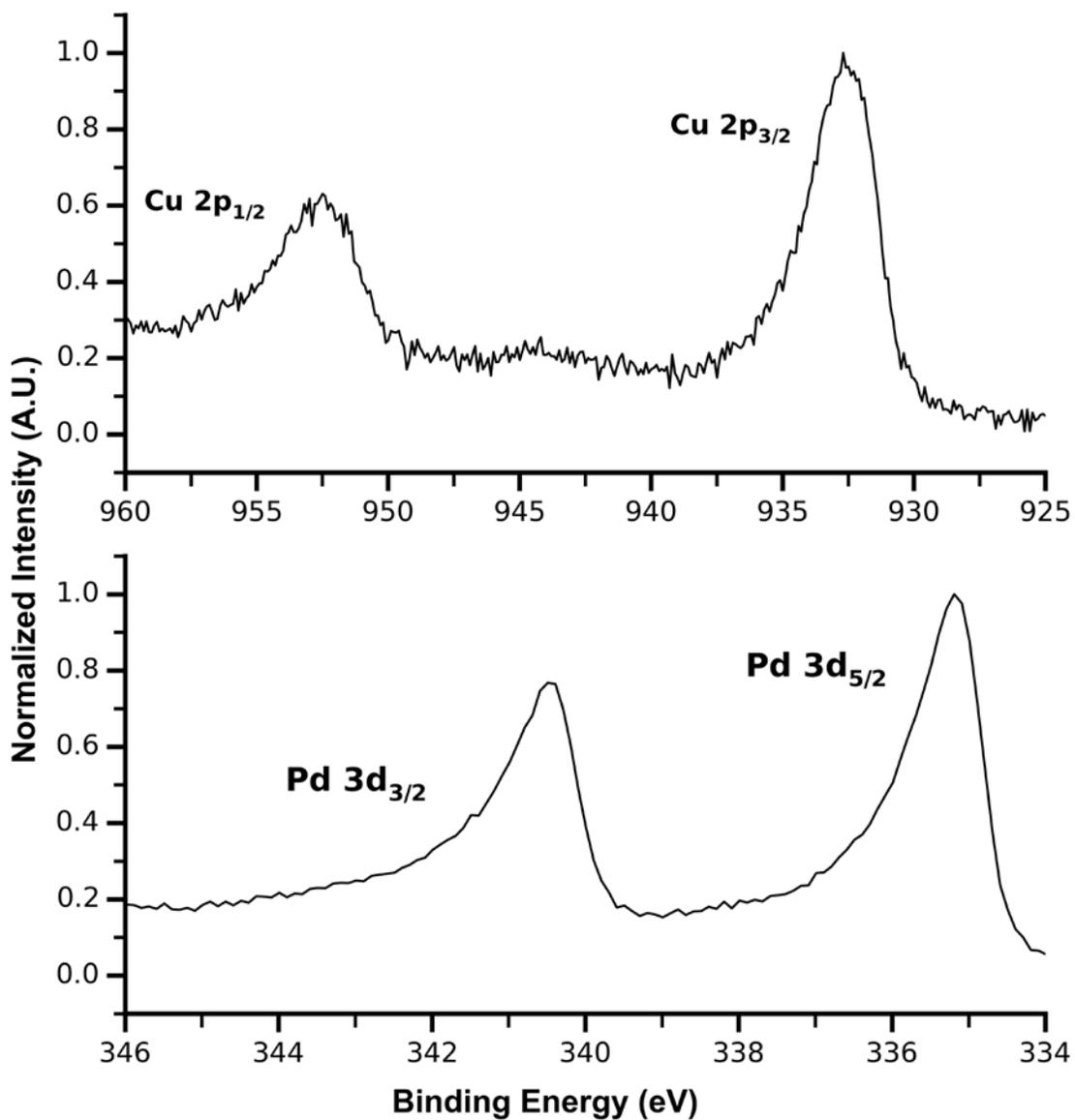


Figure S6. Pd and Cu XPS spectra for Sample 2A showing peaks for Pd 3d_{3/2} and Pd 3d_{5/2} states and Cu 2p_{1/2} and Cu 2p_{3/2} states. All binding energies were referenced to the Fermi edge.

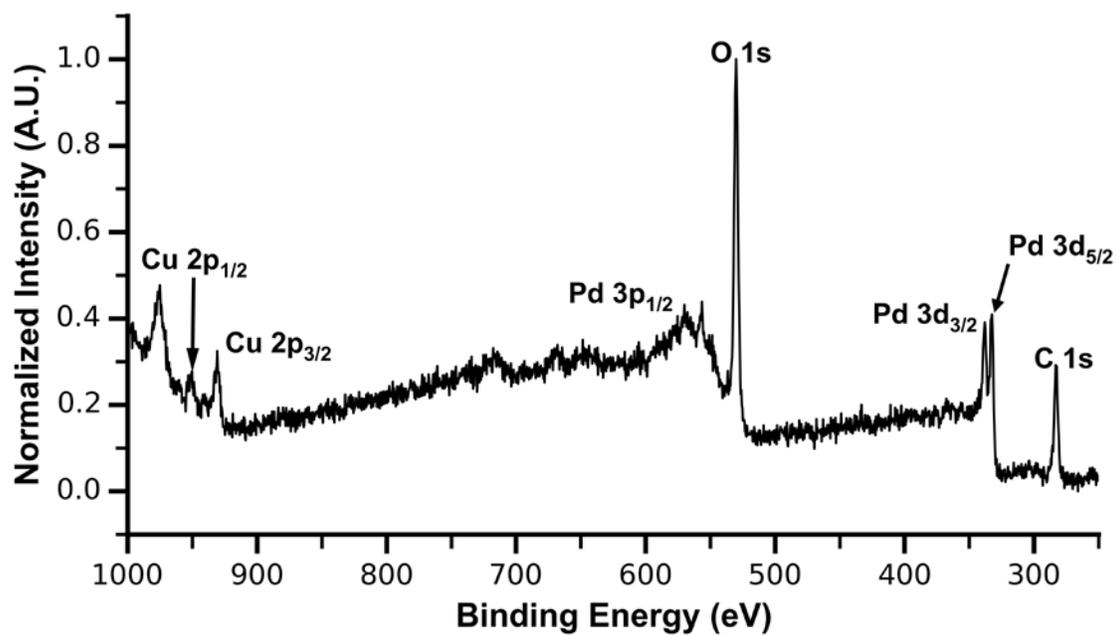


Figure S7. XPS survey scan of Sample 4B. The O1s signal arises from SiO₂.

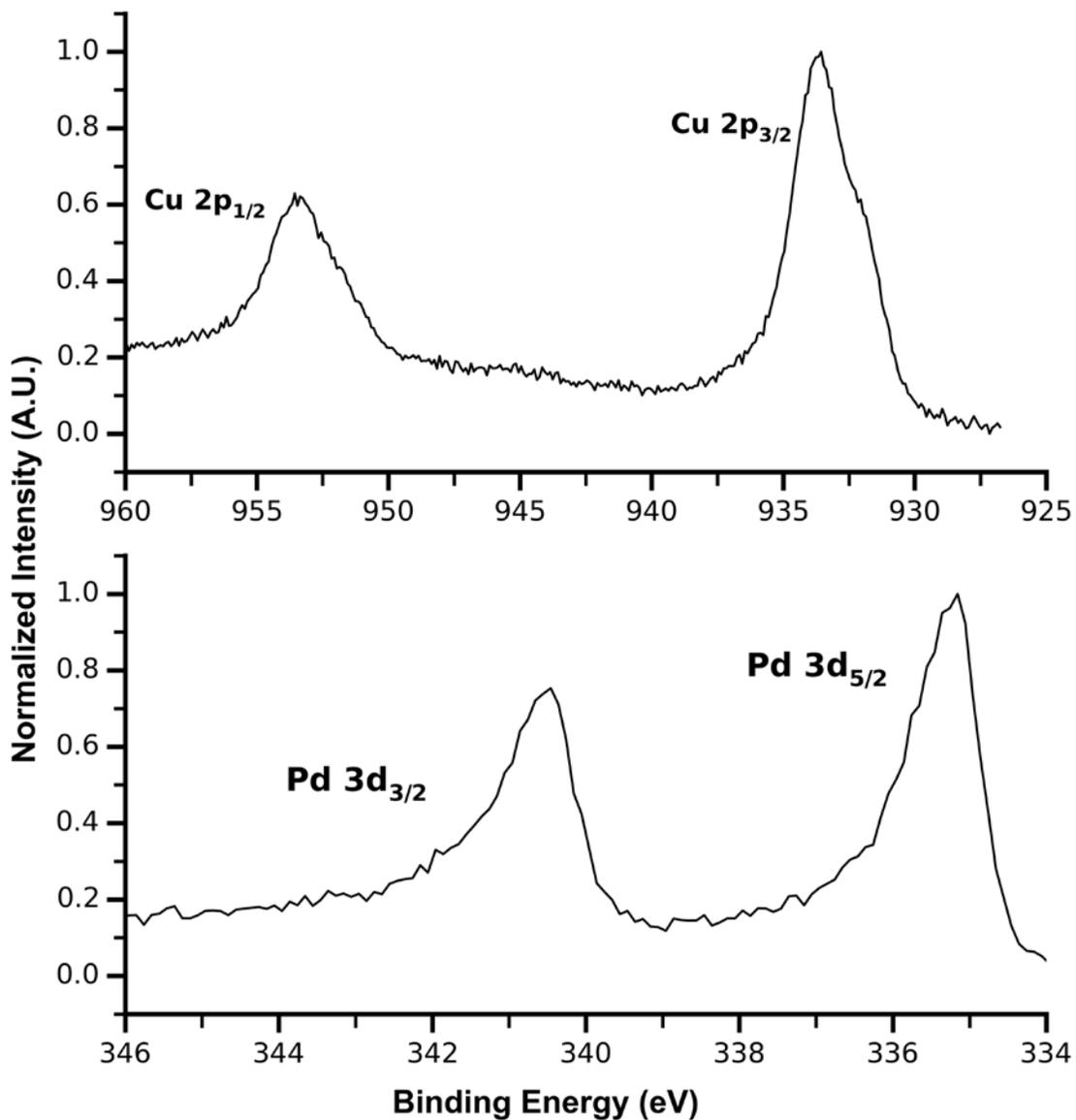


Figure S8. Pd and Cu XPS spectra for Sample 4B showing peaks for Pd 3d_{3/2} and Pd 3d_{5/2} states and Cu 2p_{1/2} and Cu 2p_{3/2} states. All binding energies were referenced to the Fermi edge.

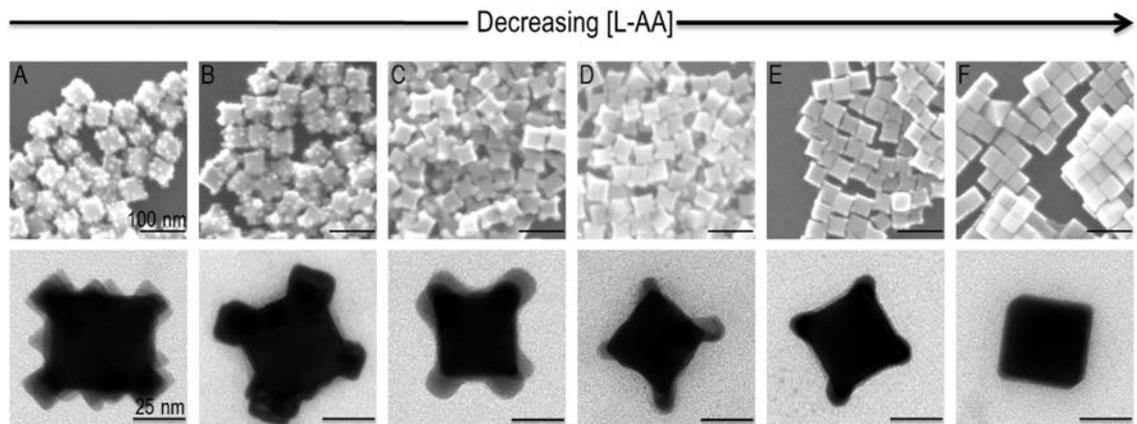


Figure S9. SEM and corresponding TEM images representing the results from varying the amount of L-AA. The final concentrations for A-F: 5.77, 1.44, 0.288, 0.192, 0.0962, and 0 mM.

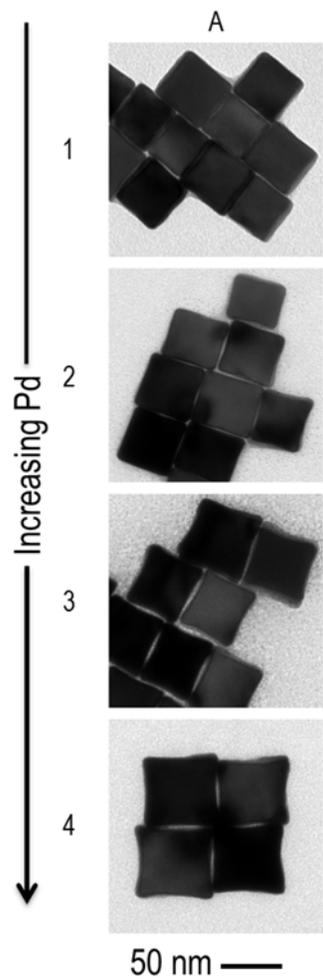


Figure S10. TEM images of Column A products achieved without Cu precursor. The final concentrations of Pd precursor used in the syntheses were: 1.92, 9.61, 19.2, and 28.8 μM .

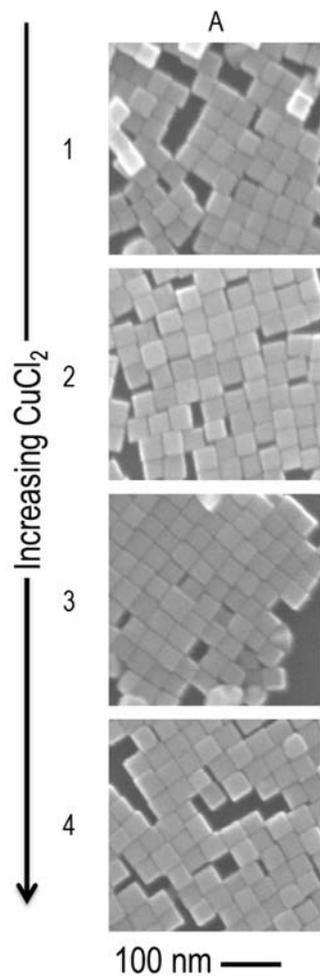


Figure S11. SEM images of Column A product achieved without use of the Pd precursor. The final concentrations of Cu precursor uses in the syntheses were: 1.92, 9.61, 19.2, and 28.8 μM .

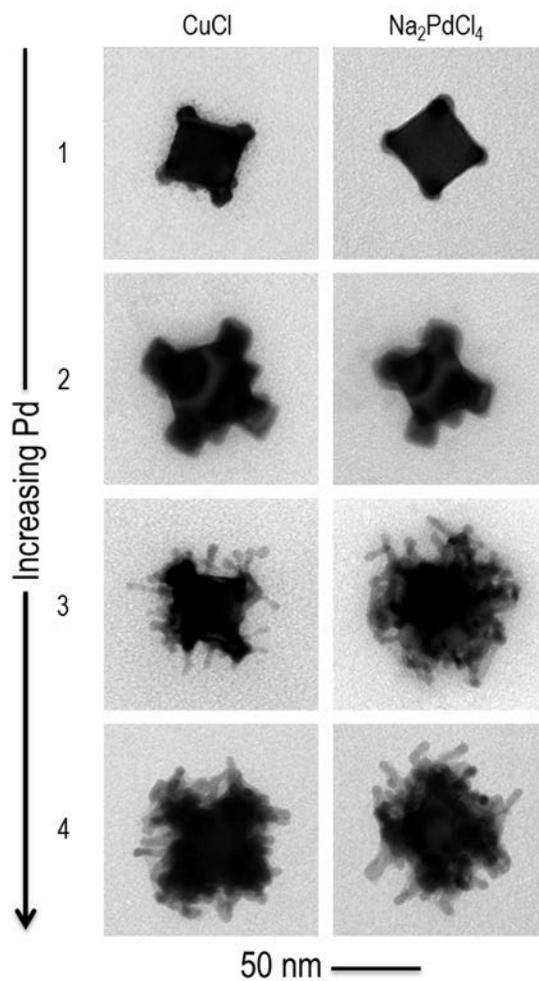


Figure S12. TEM images of the products from using CuCl and Na₂PdCl₄ as precursors. The synthetic conditions follow that of column A in Figure 1 otherwise.

Table S3. pH values of reaction solution with Na₂PdCl₄ precursor after completion from Figure S10.

	Na ₂ PdCl ₄
1	3.22
2	3.21
3	3.20
4	3.19

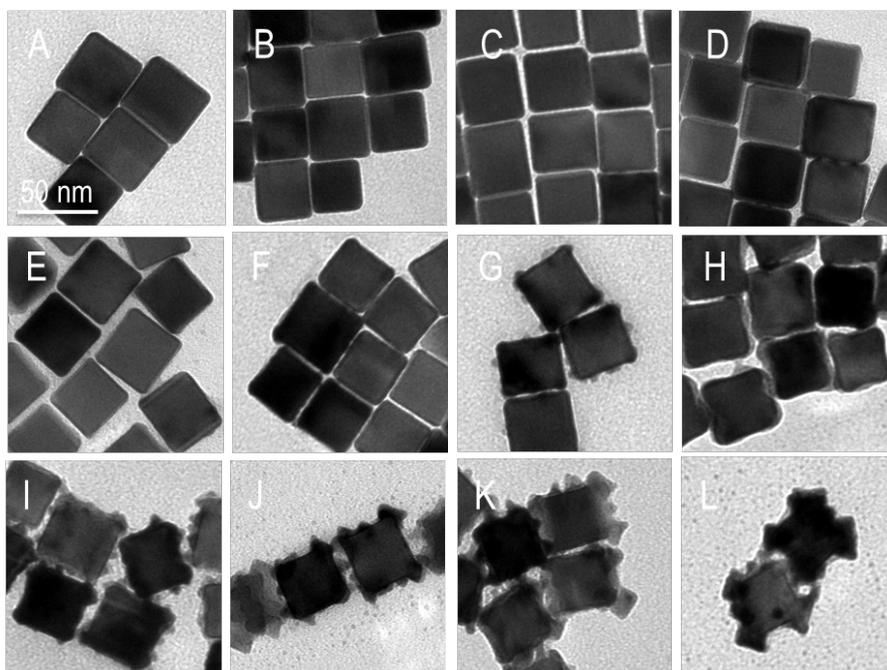


Figure S13. TEM images of aliquots of Sample 2A at different time points. Each sample was quenched at the following times: A) 2 min, B) 5 min, C) 15 min, D) 30 min, E) 45 min, F) 60 min, G) 2 hr, H) 3 hr, I) 4 hr, J) 6 hr, K) 8 hr, and L) 12 hrs. The small spots surrounding the NPs are residue from CTAB.

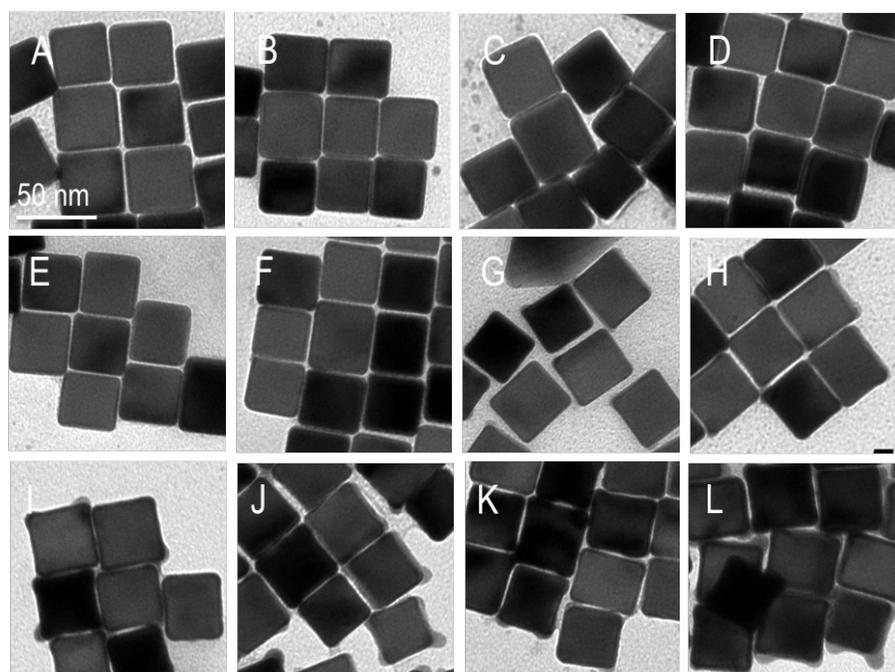


Figure S14. TEM images of aliquots of the nanostructure from S9D at different time points. Each sample was quenched at the following times: A) 2 min, B) 5 min, C) 15 min, D) 30 min, E) 45 min, F) 60 min, G) 2 hr, H) 3 hr, I) 4 hr, J) 6 hr, K) 8 hr, and L) 12 hrs. The small spots surrounding the NPs are residue from CTAB.

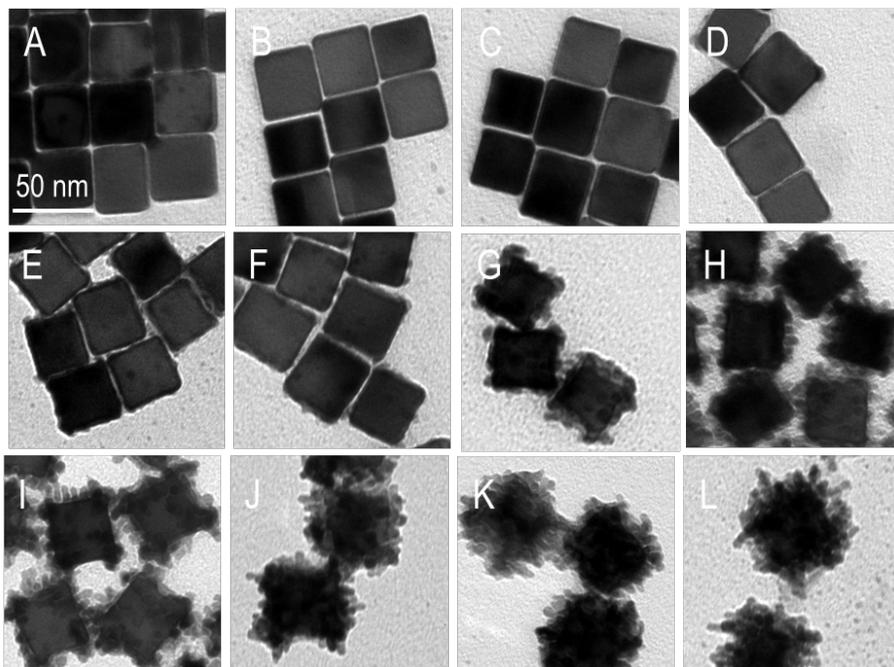


Figure S15. TEM images of aliquots of Sample 4A at different time points. Each sample was quenched at the following times: A) 2 min, B) 5 min, C) 15 min, D) 30 min, E) 45 min, F) 60 min, G) 2 hr, H) 3 hr, I) 4 hr, J) 6 hr, K) 8 hr, and L) 12 hrs. The small spots surrounding the NPs are residue from CTAB.

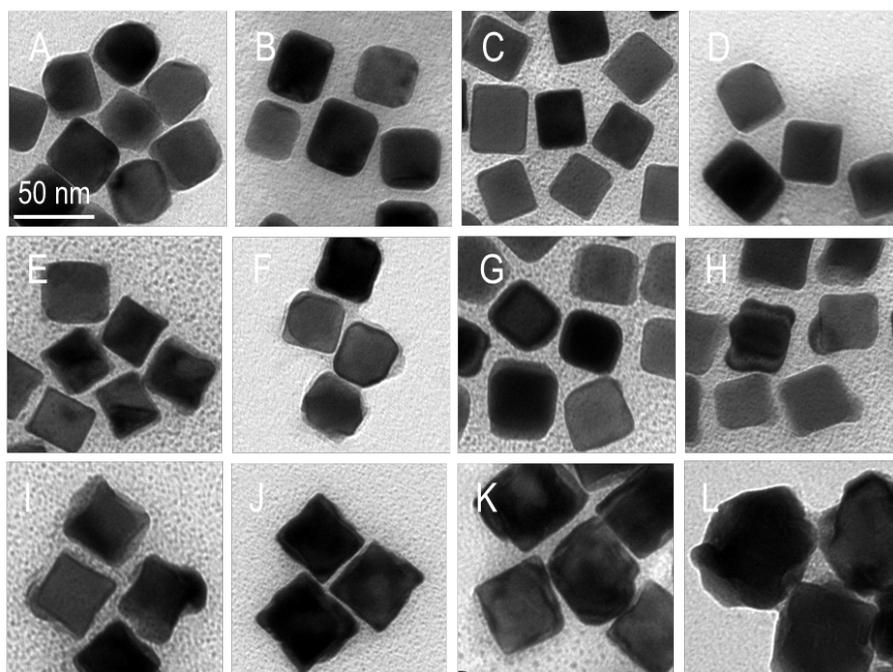


Figure S16. TEM images of aliquots of Sample 4F at different time points. Each sample was quenched at the following times: A) 2 min, B) 5 min, C) 15 min, D) 30 min, E) 45 min, F) 60 min, G) 2 hr, H) 3 hr, I) 4 hr, J) 6 hr, K) 8 hr, and L) 12 hrs. The small spots surrounding the NPs are residue from CTAB.

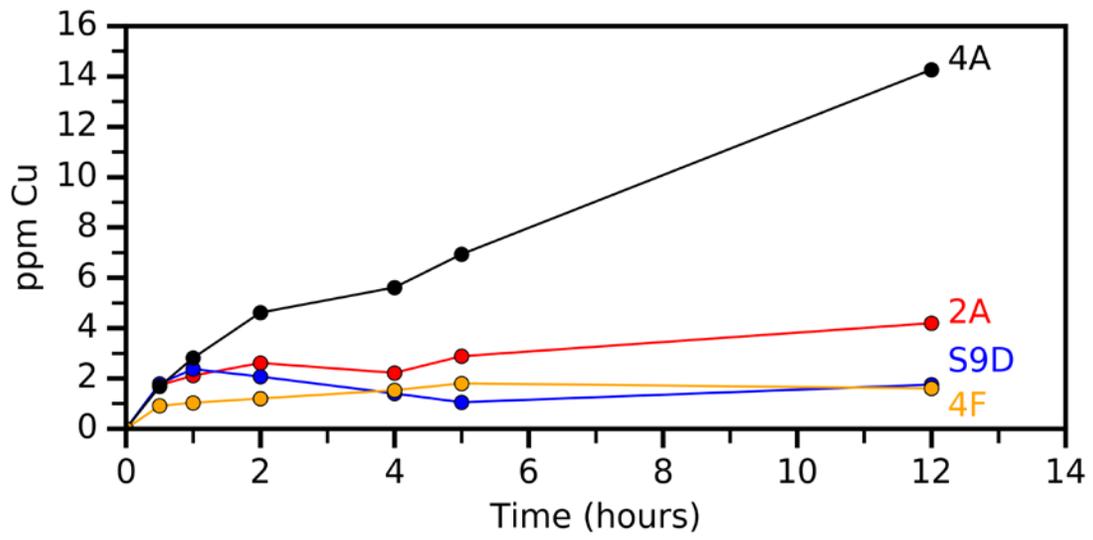


Figure S17. Plot of ppm of Cu precursor vs. Time in hours. The nanostructures were chosen from Figures 1 and S9.