

Supporting Information for

Troubleshooting the Influence of Trace Chemical Impurities on Nanoparticle Growth Kinetics via Electrochemical Measurements

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Experimental Methods

Materials

Cetyltrimethylammonium bromide (CTAB, BioXtra $\geq 99\%$ and BioUltra $\geq 99.0\%$), L-ascorbic acid (AA, ACS reagent $\geq 99\%$), cetyl bromide (97%), trimethylamine (anhydrous, $\geq 99\%$), acetonitrile (ACS reagent grade $\geq 99.5\%$) and sodium tetrachloropalladate(II) (Na_2PdCl_4 , $\geq 99.99\%$ trace metal basis) were purchased from Sigma-Aldrich/MilliporeSigma. Additional cetyltrimethylammonium bromide (CTAB) was purchased from Tokyo Chemical Industries (TCI, 98.0%) and Thermo Scientific/Thermo Fisher Scientific ($\geq 99\%$). Hydrochloric acid (HCl, 1M solution) was purchased from both Fluka and Fisher Chemical/Thermo Fisher Scientific. Nitric acid solution (HNO_3 , 1M solution), concentrated hydrochloric acid (HCl, ACS grade), concentrated nitric acid (HNO_3 , ACS grade), sulfuric acid solution (H_2SO_4 , 1N solution), acetone (ACS grade), ethanol (96% v/v), methanol (ACS grade), isopropanol (ACS grade), and sodium

iodide (99.9%) were purchased from Fisher Chemical/Thermo Fisher Scientific. Palladium(II) chloride (PdCl_2 99.9%), sodium chloride (99.99%), and sodium bromide (99.99%) were purchased from Alfa Aesar. Calcium sulfate dihydrate was purchased from J.T. Baker Chemical Co. Sodium sulfate (anhydrous, 98.0%) and sodium carbonate (anhydrous, 99.5%) were purchased from Mallinckrodt Chemicals. Iron(III) chloride ($\geq 99\%$) was purchased from Acros Organics. Concentrated sulfuric acid (95-98%, ACS grade) was purchased from VWR. Deuterium oxide (99.9%) was purchased from Cambridge Isotope Laboratories. Alumina powder (0.05 μm and 0.3 μm MicroPolish) was purchased from Buehler. All chemicals were used without further purification (with the exception of oven drying of CTAB as described below) and all solutions were prepared with deionized (DI) water (18.2 $\text{M}\Omega$ resistivity, Labconco Water Pro PS and MilliQ IQ 7000).

Sodium tetrachloropalladate(II) (Na_2PdCl_4 , 50 mM solution) was prepared by combining 0.294 g Na_2PdCl_4 and 20 mL of DI water. The solution was capped and stirred for 3 hours until fully dissolved. The reported syntheses are highly sensitive to the concentration of Pd^{2+} in the growth solution; for that reason, all the nanoparticle synthesis reactions were conducted by diluting a more stable 50 mM stock solution of Na_2PdCl_4 to 10 mM. This 10 mM solution was then used the same day. When a new stock solution (50 mM) was created, a tight gradient (0.200-0.300 mL of 10 mM Na_2PdCl_4 in a BioUltra A CTAB-based standard growth solution, described below) was conducted to establish a consistent, high-quality THH product due to apparent solubility issues between prepared Pd stock solutions.

Tetrachloropalladic acid (H_2PdCl_4 , 100 mM solution) was prepared by combining 0.354 g PdCl_2 and 20 mL of 0.2 M HCl in a 30 mL glass scintillation vial. The solution was capped and stirred for 3 hours until the solid fully dissolved and the solution became a clear dark orange. This

solution did not suffer from the solubility issues that the sodium salt did, so calibration was not required.

Concentrated H₂SO₄ was diluted to 100 mM by adding acid dropwise to DI water over ice (**caution: strong acid**).

Synthesis of Pd Nanocube Seeds

22 nm nanocube seeds were synthesized according to a previously reported method.¹ 10 mL of 12.5 mM BioXtra CTAB, 0.5 mL of 10 mM H₂PdCl₄, and a stir bar were added into a tall 30 mL scintillation vial. The vial was then placed in 95 °C silicone oil bath with stirring and allowed to equilibrate for five minutes. 80 µL of 100 mM ascorbic acid was then injected while stirring at 600 rpm. The solution was stirred in the oil bath for 20 minutes, then transferred to a 30 °C water bath. The seeds were allowed to sit for at least an hour to finish reacting and maintained their quality for up to 24 hours after synthesis. 10-fold diluted solutions of seeds in 12.5 mM BioUltra A or BioUltra B CTAB only maintained quality for about 15 minutes at room temperature before beginning to aggregate.

Standard Synthesis of Pd THH Nanoparticles in BioUltra A CTAB

The Pd nanoparticles produced in this work all followed the same standard method and the amounts of specific components were then systematically varied or further chemicals added as described in the main text. In the ideal BioUltra A reaction which produces the THH particles, a growth solution was prepared by adding 10 mL of 50 mM CTAB (BioUltra A), 0.2 mL of 10 mM Na₂PdCl₄ (subject to equilibration as described in previous section), and 50-100 µL of 0.1 M HNO₃ to a 20 mL scintillation vial. The vial was placed in a 40 °C water bath and allowed to come to temperature for at least 10 minutes. To this warm solution, 0.1 mL of fresh 100 mM ascorbic acid was added, the solution was swirled, 50 µL of 10x diluted nanocube seeds (seeds diluted in 12.5

mM BioUltra A or BioUltra B CTAB) were injected, and the solution was swirled again. The vial was then put back into the 40 °C water bath for at least 12 hours (typically overnight).

Drying Procedure for CTAB (BioUltra B and BioXtra)

Commercial CTAB powder was placed into a tall 30 mL glass scintillation vial. The vial was placed uncapped in an oven (VWR) at 80 °C for at least 24 hours. CTAB was dried in 1 g to 12 g batches. Batches larger than 2g were stirred with a Pasteur pipette after 24 hours and returned to the oven for at least 12 more hours to ensure appropriate drying of powder at the bottom of the vial. Vials of dried CTAB were then stored capped on the benchtop without further purification.

Synthesis of Pd THH Nanoparticles in Dried BioUltra B CTAB

This reaction was prepared identically to the ideal BioUltra A reaction, with the exception of the addition of NaI (70 µL of 0.1 mM solution, prepared fresh daily) and acetone (190-200 µL) into the growth solution before placement in the 40 °C water bath to equilibrate.

Synthesis of Pd THH Nanoparticles in Dried BioXtra CTAB

This reaction was prepared identically to the ideal BioUltra A reaction, with the exception of the addition of NaI (60 µL of 0.1 mM solution, prepared fresh daily) and acetone (230 µL) into the growth solution before placement in the 40 °C water bath to equilibrate.

Synthesis of Pd THH Nanoparticles in Dried Thermo Scientific CTAB

This reaction was prepared identically to the ideal BioUltra A reaction, with the exception of the addition of NaI (50 µL of 0.1 mM solution, prepared fresh daily) and acetone (220 µL) into the growth solution before placement in the 40 °C water bath to equilibrate.

Synthesis of Pd THH Nanoparticles in Dried TCI CTAB

This reaction was prepared identically to the ideal BioUltra A reaction, with the exception of the addition of NaI (50 μ L of 0.1 mM solution, prepared fresh daily) and acetone (90 μ L) into the growth solution before placement in the 40 °C water bath to equilibrate.

Synthesis of Smaller Pd TC Nanoparticles in BioXtra CTAB

This reaction was prepared identically to the THH-forming reaction in dried BioUltra B CTAB (including NaI and acetone additives), with the exception of the seed addition step. The seed colloid solution was not diluted, and was instead injected directly into the growth solution. 100 μ L of nanocube seeds were used for production of \sim 70 nm particles, and 200 μ L of nanocube seeds were used for production of \sim 45 nm particles. Larger volumes of seed colloid were not successful in producing particles smaller than \sim 45 nm.

Electrodeposition of Shaped Pd Nanoparticles and Chronopotentiometry Measurements

Glassy carbon electrodes (GCEs; 5 mm OD x 4 mm thick disk insert, Pine Research) were prepared by polishing on MasterTex Buehler polishing pad with a slurry of 0.3 μ M alumina polishing powder (Gamry Masterprep Solution and MicroPolish Alumina, Buehler), rinsed with DI water, polished again with 0.05 μ m alumina polishing powder on a different polishing pad and rinsed again, sonicated in DI water, and rinsed before being inserted into a Teflon electrode tip holder (Pine Research). Once assembled, the electrode in the Teflon tip holder was rinsed and dried again. A 1 μ l solution of undiluted Pd seeds was dropcast onto the center of the dry GCE and allowed to completely dry for 30 minutes in a fume hood.

The general procedure for all electrochemical syntheses involved use of a five-port glass electrochemical cell (Gamry Instruments Dr. Bob's Cell) with a GCE as the working electrode, a Pt wire as the counter electrode (Gamry Instruments), a saturated Ag/AgCl or Hg/Hg₂SO₄

reference electrode (both from Koslow Scientific Co.), and a miniature (3 x 10 mm) stir bar. Hg/Hg₂SO₄ reference electrodes were used in all cases except for the measurement of electrodeposition syntheses without NaI and solvent addition, where an Ag/AgCl reference electrode was used, and the development of the electrodeposition synthesis, where no reference electrode was used (final syntheses were measured as described previously). The reference electrode was isolated from the reaction solution by a bridge tube with glass frit containing 100 mM sulfuric acid to stop leakage of chloride and to prevent damage to the reference electrode. Standard colloidal conditions were measured with both reference electrodes, and the measured potentials were found to be in good agreement (accounting for the conversion between reference electrode types), with a variance between all Ag/AgCl reference electrodes tested of ± 0.003 V and between all Hg/Hg₂SO₄ reference electrodes tested of ± 0.008 V across a 200 second measurement of the same standard growth solution with the same bridge tube.

The electrochemical cell was clamped above a stir plate with a 40°C water bath, and electrode leads were connected to the potentiostat (Gamry Instruments 1010T or 1010B for synthesis and 1010B or 1010E for measurement). To a prepared cell, a growth solution containing 10 mL of 50 mM CTAB, 0.2 mL of 2.5 to 25 mM H₂PdCl₄ (2.5 mM for CC, 4-10 mM for THH, 12.5-25 mM for RD), and 50 μ L of 0.1 M HNO₃ (plus acetone and/or NaI as applicable) was added and stirred at 200 RPM for ten minutes. Stirring was used only during temperature equilibration and then turned off upon beginning a measurement. Electrochemical synthesis and simultaneous measurement were programmed using the chronopotentiometry script in the Gamry Instruments interface. A direct current of 0 μ A/cm² was applied to the cell for 10 seconds, followed by -2.04 μ A/cm² for 3 hours (10800 seconds). Chronopotentiometry data was analyzed using Gamry Echem Analyst software and MATLAB. Measured solution potentials were normalized to a standard

hydrogen electrode (SHE) scale to streamline comparison between measurements by adding 0.197 V to all Ag/AgCl electrode measurements and 0.640 V to all Hg/Hg₂SO₄ electrode measurements.

Stir bars, bridge tube frits, glassware, and Teflon electrode tip holders were cleaned with aqua regia (1:3 ratio of concentrated nitric acid: concentrated hydrochloric acid; **caution: strong acid**) between uses.

Electrochemical Measurement of Colloidal Particle Synthesis

GCEs were prepared by polishing, rinsing, and sonicating as described above before being inserted into a Teflon electrode tip holder. The GCE was placed in a five-port glass electrochemical cell as the working electrode, with a Pt wire as the counter electrode, a saturated Hg/Hg₂SO₄ reference electrode, and a miniature (3 x 10 mm) stir bar. The reference electrode was isolated from the reaction solution by a bridge tube with glass frit containing 100 mM sulfuric acid. The cell was clamped above a stir plate with a 40°C water bath and electrode leads were connected to the potentiostat (Gamry Instruments 1010B or 1010E). A growth solution containing 10 mL of 50 mM CTAB, 0.2 mL of 10 mM Na₂PdCl₄, and 50 µL of 0.1 M HNO₃ (plus acetone and/or NaI as applicable) was added to the electrochemical cell and stirred at 200 RPM for ten minutes. After 10 minutes, an open-circuit potential measurement was started using the Gamry Instruments software interface. The electrochemical cell was uncapped, and 50 µL of ten-fold diluted seeds (in 12.5 mM BioUltra B CTAB) were injected, followed by 100 µL of 0.1M AA. Stirring was continued for 10 seconds after injection of seeds and reducing agent, then stopped (to prevent noise from the magnetic stir plate). Colloidal reactions were measured for 11000 seconds (for an 10800 second/3 hour observation) to allow for “dead time” at the beginning of the reaction before injecting seeds and reducing agent. Open-circuit potential data was analyzed using Gamry Echem Analyst

software and MATLAB. Any time before 60 seconds prior to the introduction of both seeds and reducing agent was omitted from plotting of open-circuit potential traces of colloidal reactions.

Care and Storage of Reference Electrodes

Reference electrodes were stored at room temperature, away from direct sunlight. Ag/AgCl electrodes were kept in saturated potassium chloride storage solution (KCl, solution in water with potassium hydrogen phthalate, Fisher Chemical/Thermo Fisher Scientific Accumet Electrode Storage Solution), and Hg/Hg₂SO₄ reference electrodes were kept in saturated potassium sulfate storage solution (K₂SO₄, in water, Koslow Scientific Co.) at all times when not in use. Saturated Hg/Hg₂SO₄ reference electrodes were prone to the formation of salt crystals near the porous frit, preventing appropriate ion exchange. These crystals were periodically eliminated by placing a drop of hot DI water in the K₂SO₄ storage solution container and putting the reference electrode (in the storage solution) in a 30°C water bath for 30-60 minutes. Reference electrodes were kept in storage solution undisturbed for at least 48 hours after use in a 3-hour measurement.

Characterization of Palladium Nanoparticles by Electron Microscopy

To prepare colloidal samples for characterization via scanning electron microscopy (SEM), the completed reaction vial was vortexed, sonicated briefly (around 30 seconds), and vortexed again. From this dark, cloudy solution, 1 mL was removed and transferred to a microcentrifuge tube. The solution was then centrifuged (VWR Micro Star 21) at 6000 rpm for four minutes to spin down a pellet. The supernatant was removed with a Pasteur pipette, and the microcentrifuge tube refilled to 1 mL with DI water, vortexed, sonicated, vortexed, and then centrifuged again at 6000 rpm for four minutes. The supernatant was removed again, and a minimal amount of DI water (200-500 μ L) was added, and the tube was sonicated and vortexed to disperse the particles. 1 μ L of this solution was then dropcast onto a prepared silicon wafer (washed repeatedly with acetone or

metanol, then dried) and allowed to dry for at least 45 minutes before characterization by SEM (Hitachi SU5000 FE-SEM and FEI Quanta 650 FE-SEM). Average particle size (ImageJ) and shape were determined using >100 particles, and size was measured diagonally across each particle.

Electrodeposited particles on GCEs were washed 3-4 times with 40°C DI water and placed in a custom metal sample holder to dry for at least 30 minutes before characterization by SEM.

Higher-magnification characterization of select colloidal samples was conducted via scanning transmission electron microscopy (STEM). Samples were prepared as described above and were then dropcast on a formvar/carbon film 400 mesh copper PELCO® TEM grid (Ted Pella, Inc.), held with freshly cleaned electron microscopy tweezers. Each sample was allowed to dry for at least one hour in a desiccator before characterization. STEM imaging was conducted on a Themis Z Transmission Electron Microscope (Thermo Fisher Scientific) using bright field (BF) and high-angle annular dark-field (HAADF) imaging modes. Brightness and contrast of electron microscopy images were normalized when necessary using the Curves adjustment tool in Adobe Photoshop.

Synthesis of CTAB

The synthesis of cetyltrimethylammonium bromide was adapted from a previously reported procedure.² Cetyl bromide (1.5 mL, 4.9 mM) and 25 mL acetonitrile were added to a 50 mL round-bottom flask. The flask was sealed and degassed with N₂ for fifteen minutes. Chilled trimethylamine (0.86 mL, 9.9 mM) was added via syringe. The reaction was stirred at room temperature for 48 hours. The resulting foamy white substance was transferred to a 250-mL round-bottom flask, mixed with 100 mL additional acetonitrile, and degassed with air while stirring for 40 minutes to remove trimethylamine. The solvent was removed under vacuum, affording a flaky

white substance. The crude product was recrystallized via a procedure adapted from a method developed by Skrabalak and coworkers.³ The crude product was suspended in 70 mL acetone while heating until barely simmering, and 1.75 mL methanol was added to barely dissolve the solid. The flask was cooled at room temperature for 40 minutes, then chilled in a refrigerator for 24 hours. The solid was removed by vacuum filtration and rinsed with 50 mL diethyl ether. This recrystallization procedure was repeated twice more for the resulting solid, using only 20 mL of acetone each subsequent time. The resulting small white crystals were dried in an oven for 20 minutes and under vacuum for 40 minutes, affording the product (59-70% yield across two batches).

Characterization of CTAB by NMR

NMR spectra were recorded on a Varian Mercury spectrometer (400 MHz, 1 H; synthesized CTAB only) and a Bruker Avance III 600 spectrometer (600 MHz, 1 H; all commercial CTAB samples). The spectrum of BioUltra A CTAB was taken in a 9:1 mixture of DI water (18.2 M Ω resistivity) and D₂O. All other samples were dissolved in D₂O, and all were vortexed prior to spectra being taken. All spectra were obtained at room temperature and were 50 mM CTAB. All NMR tubes were cleaned thoroughly with DI water and methanol, and oven-dried at 100 °C overnight before use. NMR data was processed using vnmr (Varian spectra), TopSpin (Bruker spectra), and MestreNova/Mnova software.

Elemental Analysis of Potential Contaminants in CTAB

Inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography (IC) of CTAB samples were carried out by Robertson Microlit Laboratories (Ledgewood, NJ). ICP-MS analysis was conducted using a semi-quantitative scan of multiple elements.

NMR Data for Characterization of CTAB:

All spectra were referenced with respect to the water exchange peak at 4.79 ppm during data processing.

Synthesized CTAB:

^1H NMR (400 MHz, D_2O) δ 3.44 (s, 0.3H), 3.41 (t, $J = 8.6$ Hz, 2H), 3.19 (s, 9H), 2.22 (s, 0.2H), 1.79 (m, 2H), 1.45 (s, 2H), 1.37 (s, 24H), 0.89 (t, $J = 6.4$ Hz, 3H).

BioUltra A CTAB:

^1H NMR (600 MHz, 90% H_2O + 10% D_2O) δ 3.48 (t, $J = 8.5$ Hz, 2H), 3.25 (s, 9H), 1.84 (m, 2H), 1.44 (m, 2H), 1.36 (m, 24H), 0.94 (t, $J = 6.8$ Hz, 3H).

As-received BioUltra B CTAB:

^1H NMR (600 MHz, D_2O) δ 3.46 (t, $J = 8.6$ Hz, 2H), 3.21 (s, 9H), 2.23 (s, 0.02H), 1.80 (t, $J = 8.6$ Hz, 2H), 1.41 (d, $J = 5.3$ Hz, 2H), 1.34 – 1.29 (m, 24H), 0.93 (t, $J = 6.8$ Hz, 3H).

As-received BioXtra CTAB:

^1H NMR (600 MHz, D_2O) δ 3.47 (t, $J = 8.6$ Hz, 2H), 3.22 (s, 9H), 2.23 (s, 0.2H), 1.82 (t, $J = 8.5$ Hz, 2H), 1.43 (d, $J = 5.3$ Hz, 2H), 1.34 (s, 24H), 0.92 (t, $J = 6.7$ Hz, 3H).

Dried BioUltra B CTAB:

^1H NMR (600 MHz, D_2O) δ 3.47 (t, $J = 8.6$ Hz, 2H), 3.22 (s, 9H), 1.82 (t, $J = 8.6$ Hz, 2H), 1.43 (d, $J = 5.3$ Hz, 2H), 1.36 – 1.30 (m, 24H), 0.92 (t, $J = 6.8$ Hz, 3H).

Dried BioXtra CTAB:

^1H NMR (600 MHz, D_2O) δ 3.47 (t, $J = 8.6$ Hz, 2H), 3.23 (s, 9H), 1.82 (q, $J = 7.5$ Hz, 2H), 1.43 (d, $J = 5.7$ Hz, 2H), 1.36 – 1.30 (m, 24H), 0.92 (t, $J = 6.7$ Hz, 3H).

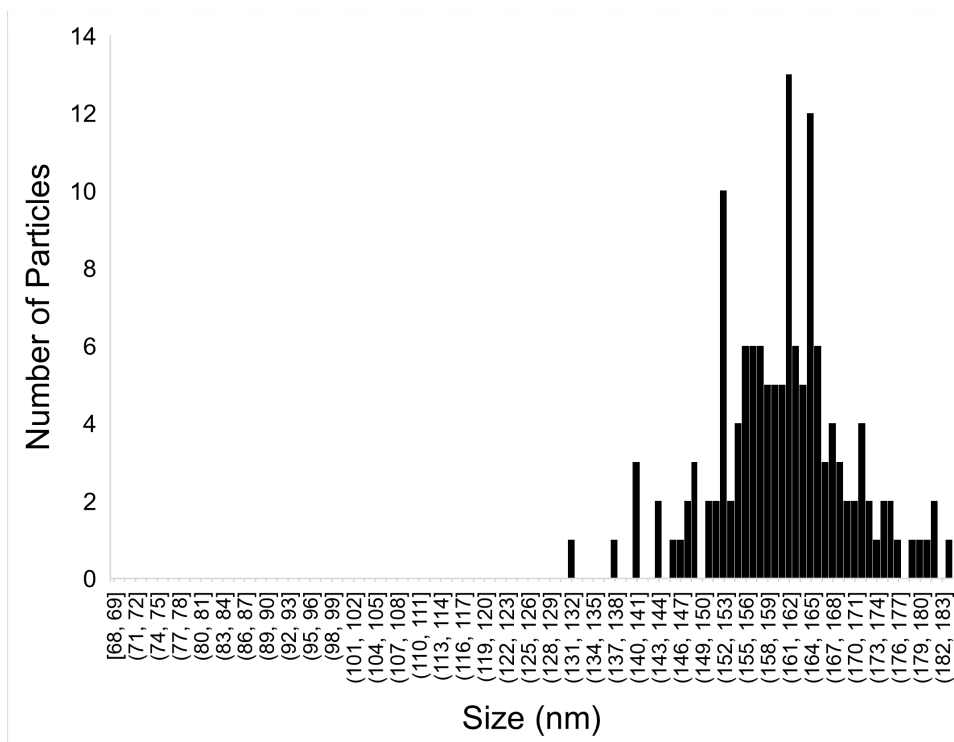


Figure S1. Histogram of nanoparticle size distribution for THH produced via the standard synthesis route in BioUltra A CTAB. Average particle size for 140 particles measured diagonally was 161 ± 9 nm.

Table S1. Elemental Analysis of BioUltra A, BioXtra, and BioUltra B CTAB.

Element	BioUltra A (ppm)	BioXtra (ppm)	Difference from BioUltra A (ppm)	BioUltra B (ppm)	Difference from BioUltra A (ppm)
Na ^a	19	241	222	25	6
K ^a	31	84	53	14	- 17
Ca ^a	727	1011	284	<1 ppb	- 727
Fe ^a	190	305	115	26	- 164
S ^c	<50	<500	<450	<50	--
Cl ^b	70	128	58	--	--
Br ^a	Sat ^d	Sat ^d	--	Sat ^d	--
I ^a	87	21	- 68	33	- 54

^a Data from ICP-MS.

^b Data from IC.

^c Data from specifications included with the products from Sigma-Aldrich.

^d Bromide is saturated for ICP-MS, but IC shows differences by total mass percent: BioUltra A is 20.79%, and BioXtra is 20.99%. IC was not performed for BioUltra B.

Table S2. Calculation of Contaminant Levels for Addition to 10 mL of 50 mM CTAB.

Element	Volume of 10 mM Solution (μL)	Volume of 0.1 mM Solution (μL)
Na	175.9	–
K	24.7	–
Ca	129.1	–
Fe	37.46	–
S	Up to 255 ^a	–
Cl	29	–
Br	450 ^b	–
I	–	Up to 287

^a Most likely present as sulfate (SO₄²⁻).

^b Calculated from differences in mass percent; this number may seem large but represents a small difference relative to total Br⁻ concentrations in 50 mM CTAB solution.

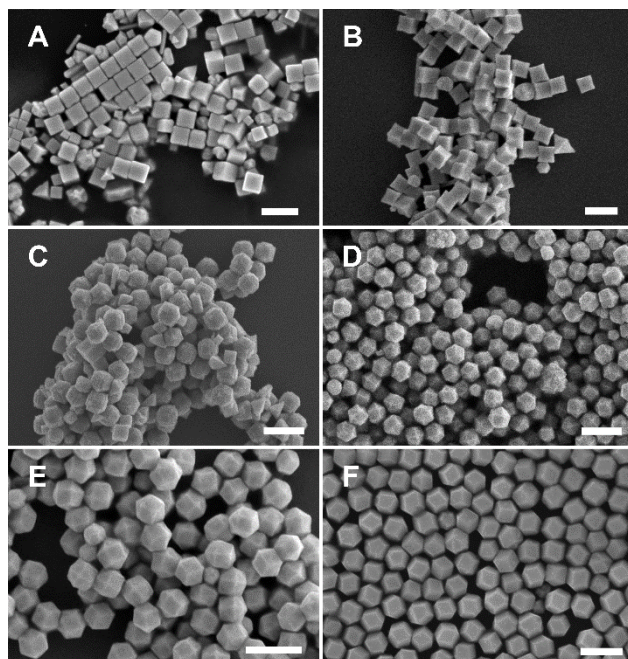


Figure S2. SEM images of Pd nanoparticle shape as a function of iodide concentration in BioUltra B CTAB. (A) 0.24, (B) 0.48, (C) 0.97, (D) 1.45, (E) 1.94, and (F) 2.90 μM added NaI in a standard growth solution that would produce THH in BioUltra A. Scale bars: 300 nm.

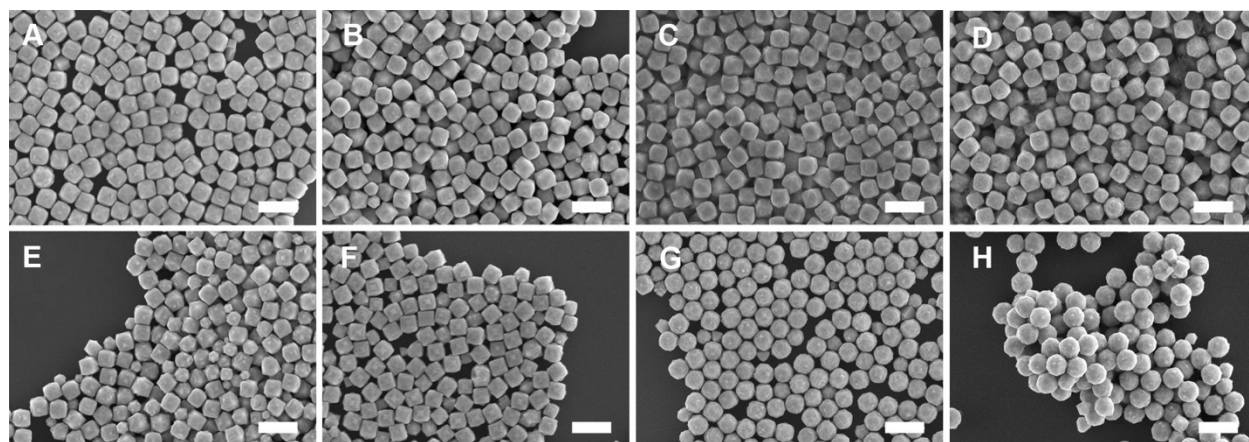


Figure S3. SEM images of Pd nanoparticle shape change with contaminants added in amounts near those calculated in Table S2. Reactions under standard THH conditions in BioUltra A CTAB with (A) 200 or (B) 450 μL of 10 mM NaBr; (C) 200 μL of 10 mM NaCl; (D) 50 μL of 10 mM FeCl_3 ; (E) 100 or (F) 300 μL of 10 mM Na_2CO_3 ; (G) 100 or (H) 300 μL of 10 mM Na_2SO_4 added. These volumes correspond to overall concentrations of (A) 0.165 mM NaBr, (B) 0.372 mM NaBr, (C) 0.165 mM NaCl, (D) 41.3 μM FeCl_3 , (E) 82.6 μM Na_2CO_3 , (F) 0.248 mM Na_2CO_3 , (G) 82.6 μM Na_2SO_4 and (H) 0.248 mM Na_2SO_4 in the growth solution. Scale bars: 300 nm.

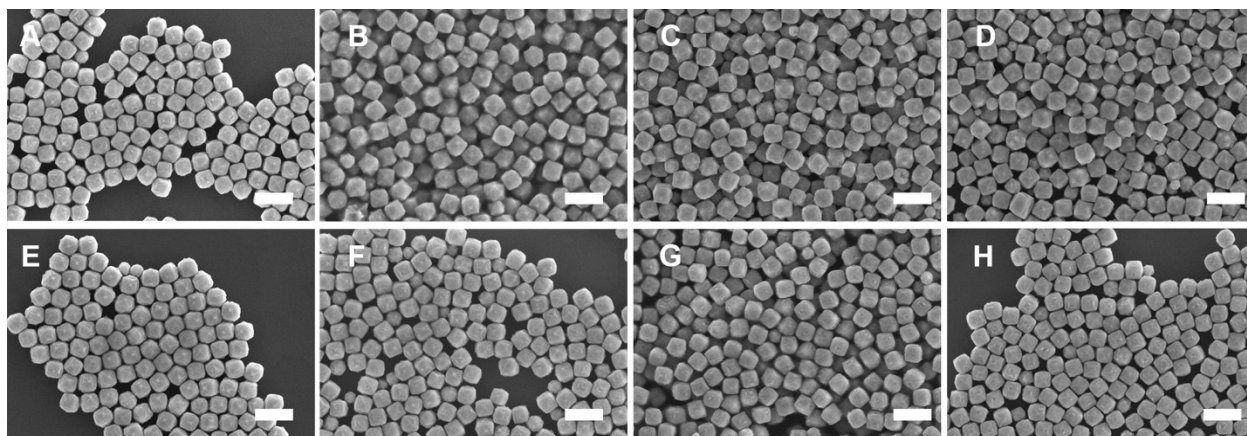


Figure S4. SEM images of Pd nanoparticle shape change with contaminants added in amounts near those calculated in Table S2. Reactions under standard THH conditions in BioUltra A CTAB with (A) 150 μL of 10 mM CaCl_2 ; (B) 100, (C) 150, or (D) 200 μL of 10 mM CaCO_3 ; (E) 150 or (F) 300 μL of 10 mM CaSO_4 ; (G) 50 or (H) 450 μL of 10 mM KBr . These volumes correspond to overall concentrations of (A) 0.124 mM CaCl_2 , (B) 82.6 μM CaCO_3 , (C) 0.124 mM CaCO_3 , (D) 0.165 mM CaCO_3 , (E) 0.124 mM CaSO_4 , (F) 0.248 mM CaSO_4 , (G) 41.3 μM KBr and (H) 0.372 mM KBr in the growth solution. Scale bars: 300 nm.

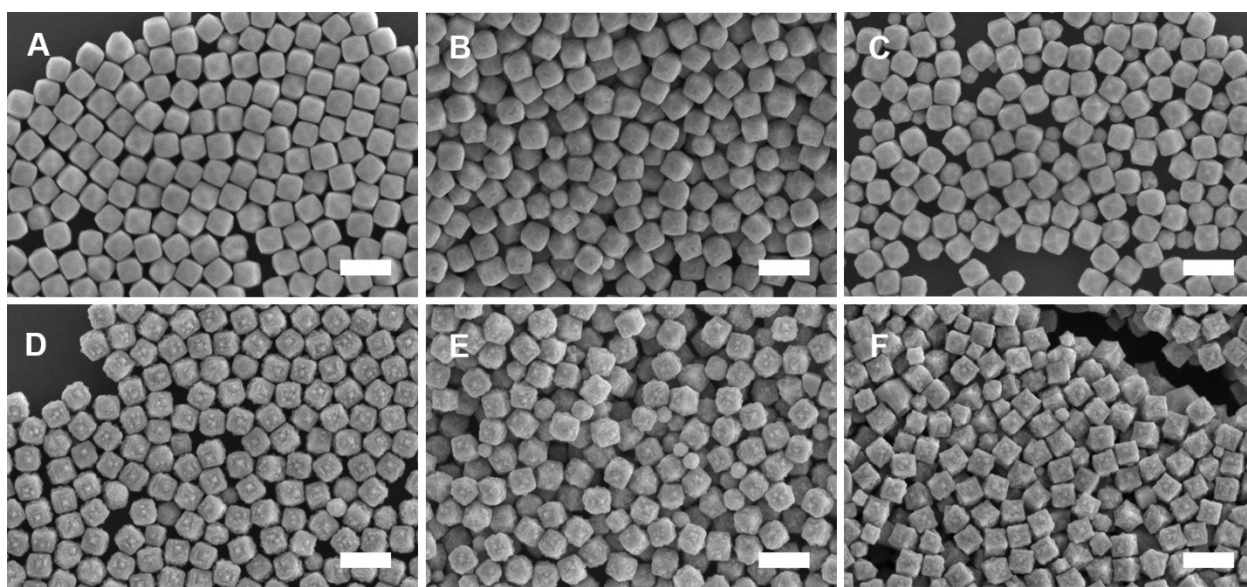


Figure S5. SEM images of Pd nanoparticle shape as a function of ascorbic acid concentration. (A) 25, (B) 50, (C) 100, (D) 150, (E) 200, and (F) 300 μL of 100 mM ascorbic acid in BioUltra A CTAB. These volumes correspond to overall concentrations of (A) 0.24, (B) 0.48, (C) 0.96, (D) 1.43, (E) 1.90, and (F) 2.82 mM AA. Scale bars: 300 nm.

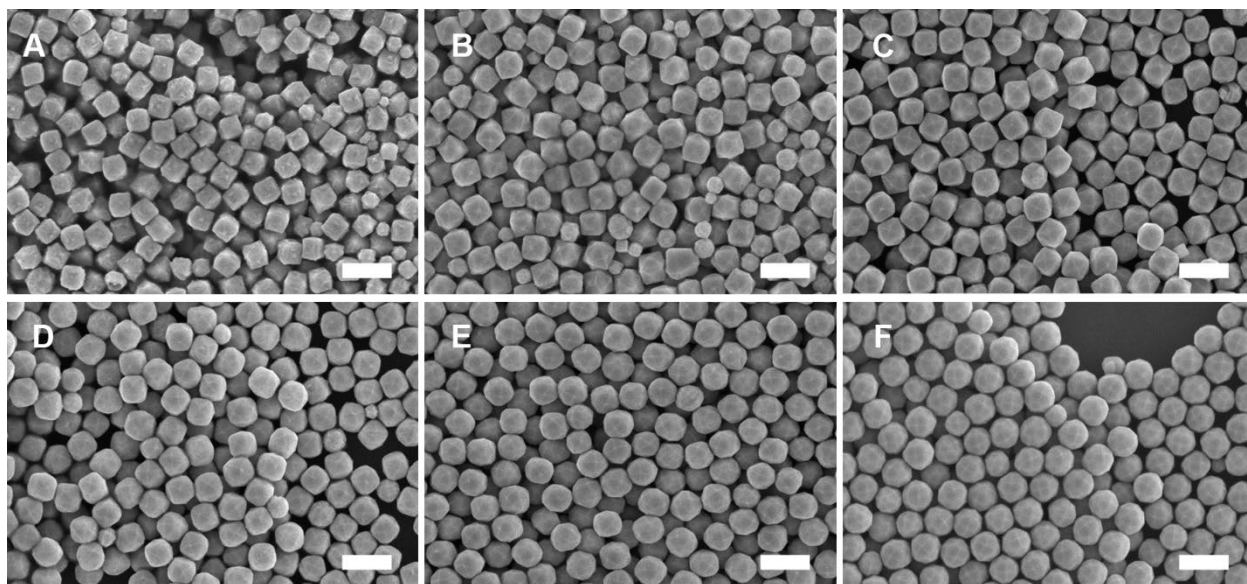


Figure S6. SEM images of Pd nanoparticle shape as a function of nitric acid concentration. (A) 25, (B) 50, (C) 100, (D) 150, (E) 200, and (F) 300 μL of 100 mM HNO_3 added to BioUltra A CTAB. These volumes correspond to overall concentrations of (A) 0.24, (B) 0.48, (C) 0.96, (D) 1.43, (E) 1.90, and (F) 2.82 mM HNO_3 . Scale bars: 300 nm.

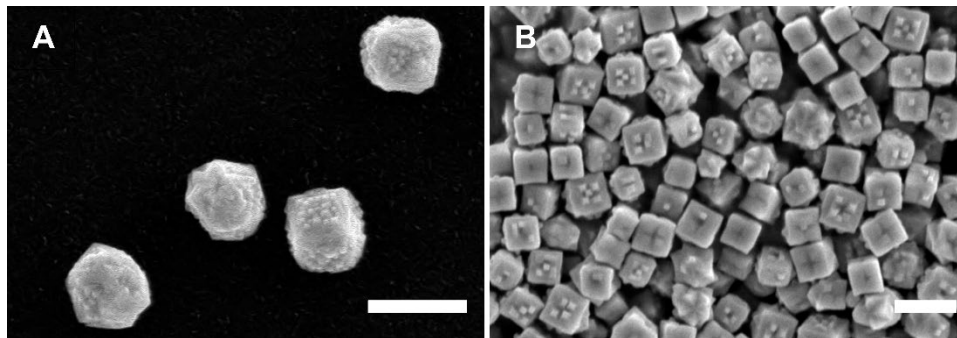


Figure S7. SEM images of the concave-to-convex transition in (A) electrodeposited particles synthesized in BioUltra A CTAB with 0.073 mM of Pd precursor and (B) colloidal particles made in BioUltra B CTAB with 0.12 mM Pd precursor and 0.24 μM NaI. Scale bars: 300 nm.

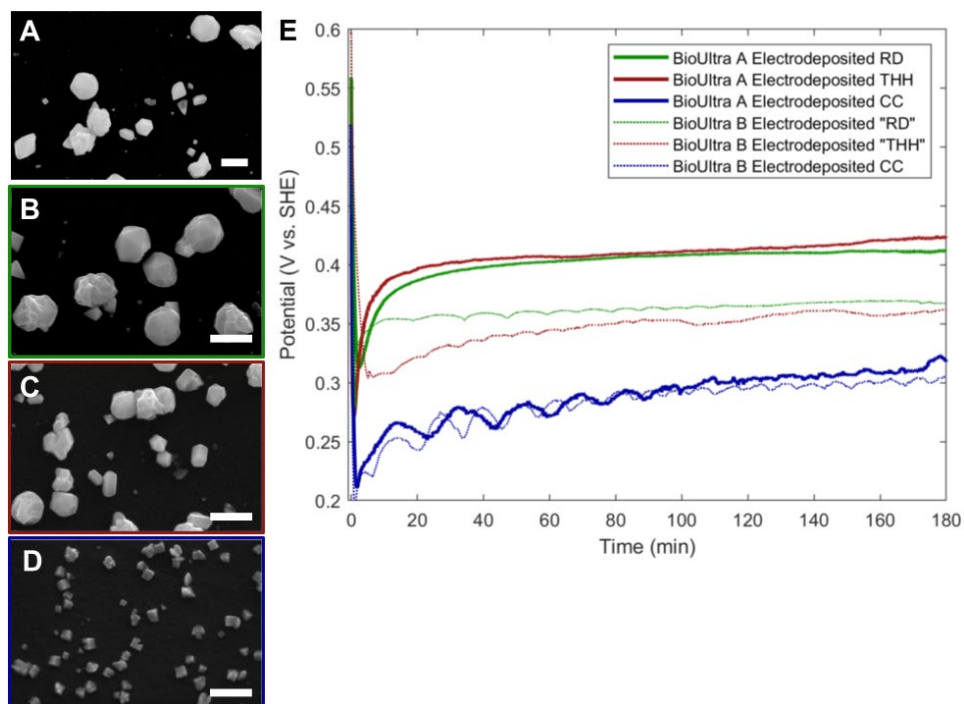


Figure S8. Electrodeposited Pd particles in BioUltra B CTAB. All other conditions are identical to the electrochemical synthesis of Pd particles in BioUltra A CTAB. SEM images of particles synthesized with (A) 0.061 mM Pd²⁺, (B) 0.12 mM Pd²⁺, (C) 0.30 mM Pd²⁺, (D) 0.48 mM Pd²⁺, and (E) chronopotentiometry measurements of electrodeposition syntheses (A)-(C), compared to chronopotentiometry measurements of identical syntheses in BioUltra A. Note: Electrodeposition at THH- and RD-forming conditions from BioUltra A does not result in successful formation of those shapes in BioUltra B. Scale bars: 300 nm.

Table S3. pH measurements of 50 mM CTAB solutions in DI water.

CTAB Formulation	pH	Temp (°C)
As-received BioUltra A	8.40	25.0
As-received BioUltra B	8.43	27.5
As-received BioXtra	6.33	25.0
Dried BioUltra B	8.02	26.3
Dried BioXtra	7.63	27.3

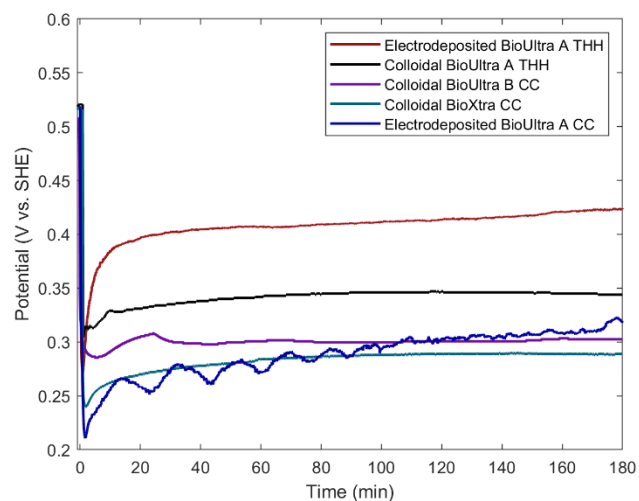
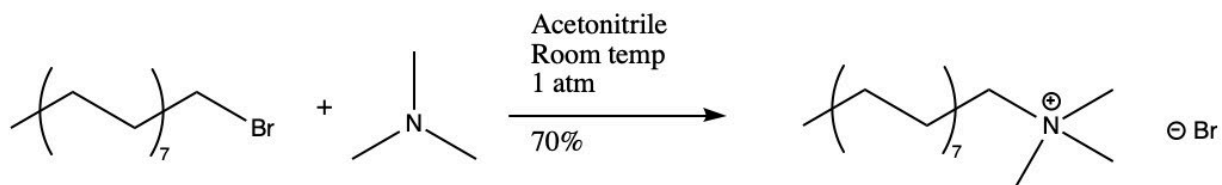


Figure S9. Comparison between chronopotentiometry measurements of electrodeposited CC and THH and open-circuit potential measurements of colloidal syntheses using standard THH conditions in different CTAB formulations.

Scheme S1. Synthesis of CTAB from cetyl bromide and trimethylamine.



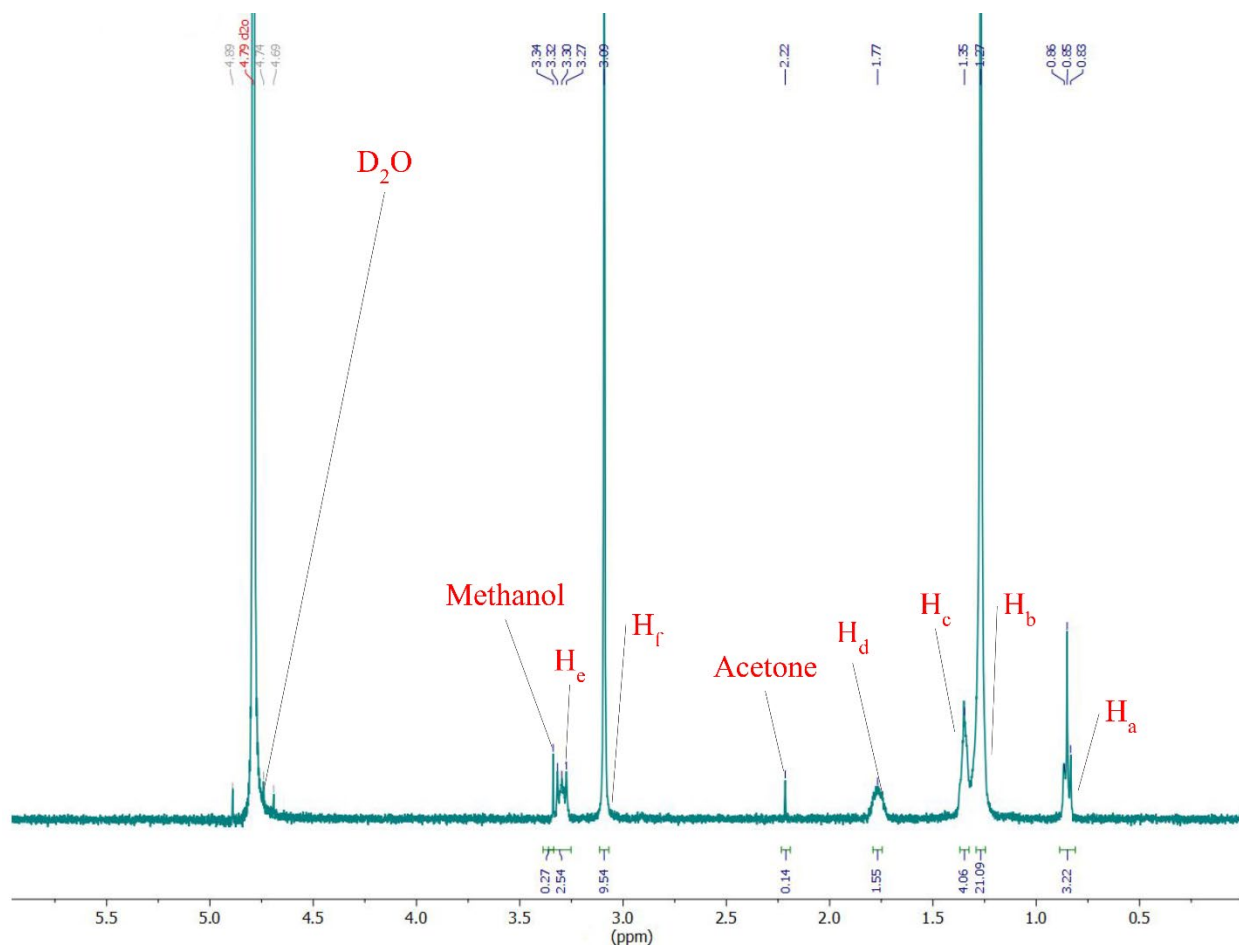
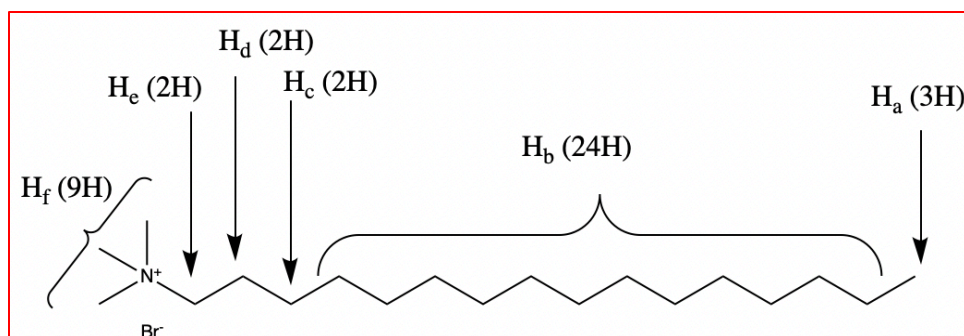


Figure S10. Labeling scheme for CTAB NMR spectra and 1H NMR spectrum of synthesized CTAB showing solvent impurities.

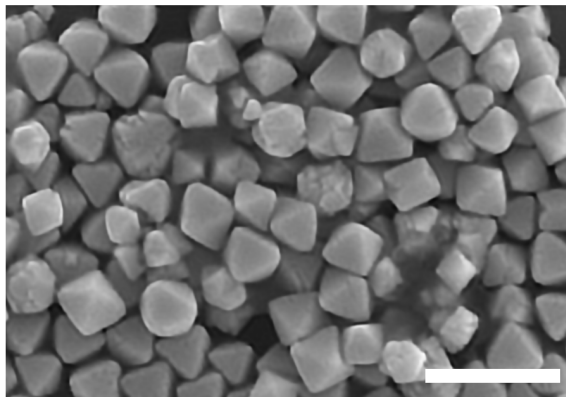


Figure S11. SEM images of Pd octahedra produced in a growth solution made with synthesized CTAB and containing 0.33 mM Pd²⁺ (all other conditions standard). Scale bar: 300 nm.

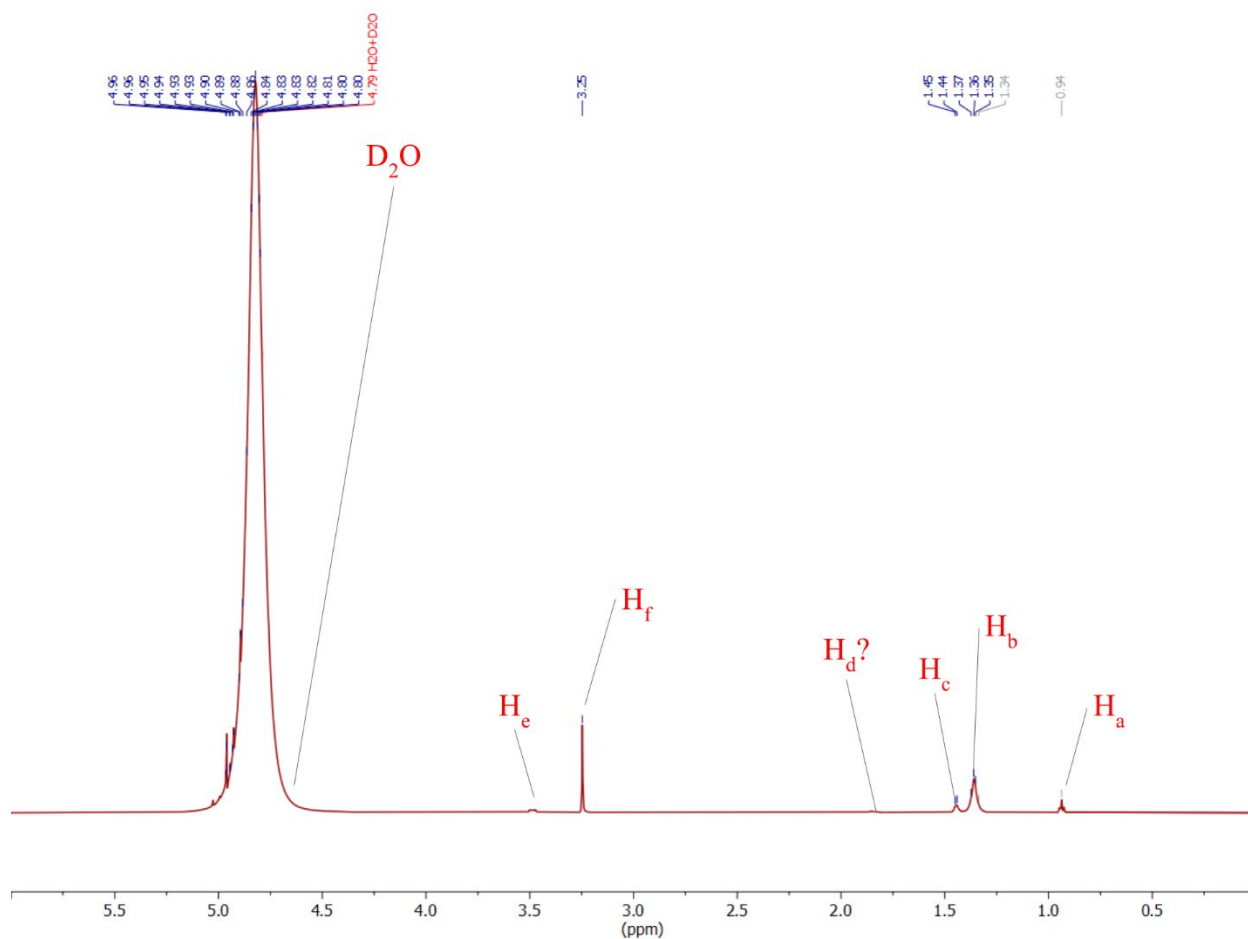


Figure S12. ¹H NMR spectrum of BioUltra A CTAB (in 90% DI water and 10% D₂O). See Fig. S10 for labeling scheme.

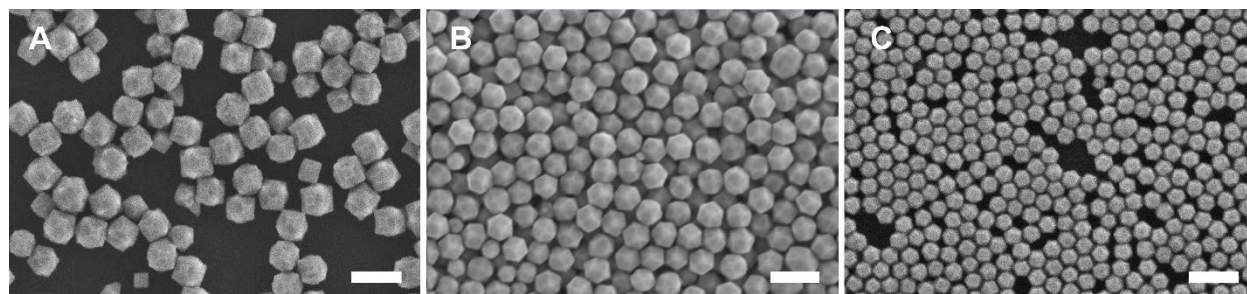


Figure S13. SEM images of Pd THH particles in as-received BioUltra B CTAB with 50 μL added acetone (68 mM in the growth solution) and varying $[\text{I}^-]$. (A) 0.29 μM NaI, (B) 0.68 μM NaI, (C) 0.87 μM NaI. All other growth solution conditions standard. Scale bars: 300 nm.

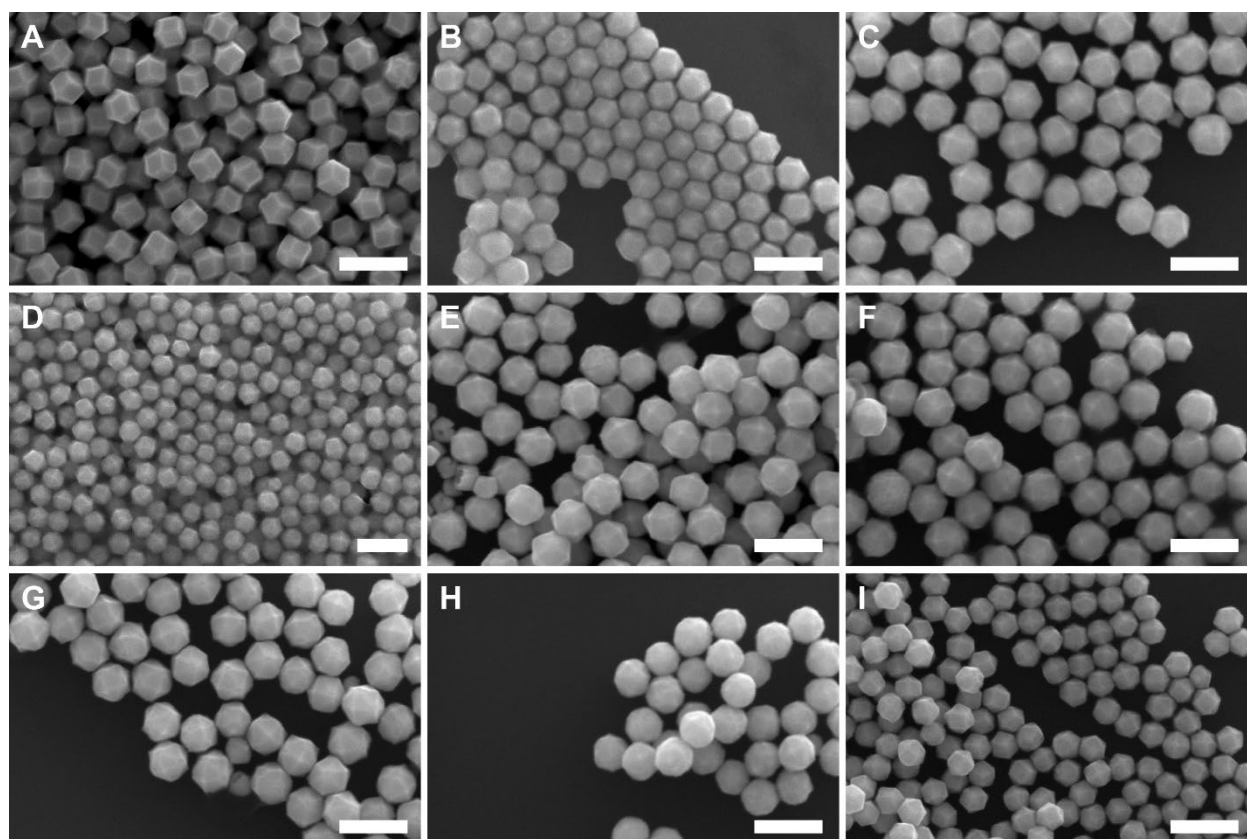


Figure S14. SEM images of Pd particle morphology in dried BioUltra B CTAB as a function of acetone concentration. All growth solutions contained 0.68 μM NaI and 1.21 mM HNO_3 , all other growth conditions standard. (A) 0 μL (0 M), (B) 120 μL (0.16 M), (C) 160 μL (0.22 M), (D) 170 μL (0.23 M), (E) 190 μL (0.26 M), (F) 270 μL (0.36 M), (G) 290 μL (0.39 M), (H) 300 μL (0.40 M), and (I) 360 μL (0.49 M) added acetone. Values in parentheses indicate concentration in the growth solution. Scale bars: 300 nm.

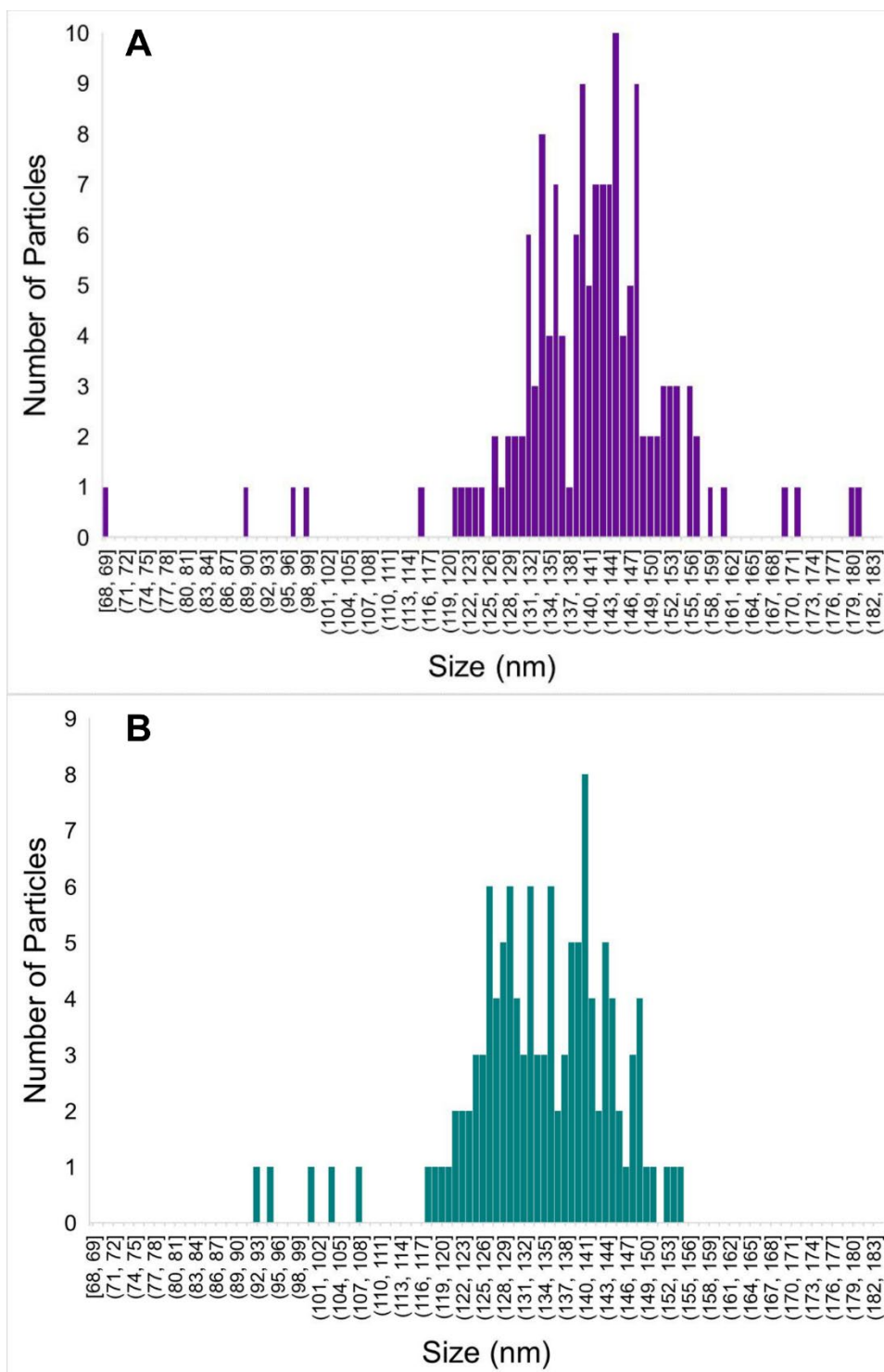


Figure S15. Histograms of nanoparticle size distribution for THH produced in (A) dried BioUltra B CTAB and (B) dried BioXtra CTAB, both with added iodide and acetone. Average particle size was (A) 141 ± 12 nm (145 particles measured) and (B) 134 ± 11 nm (119 particles measured). Particles were measured diagonally.

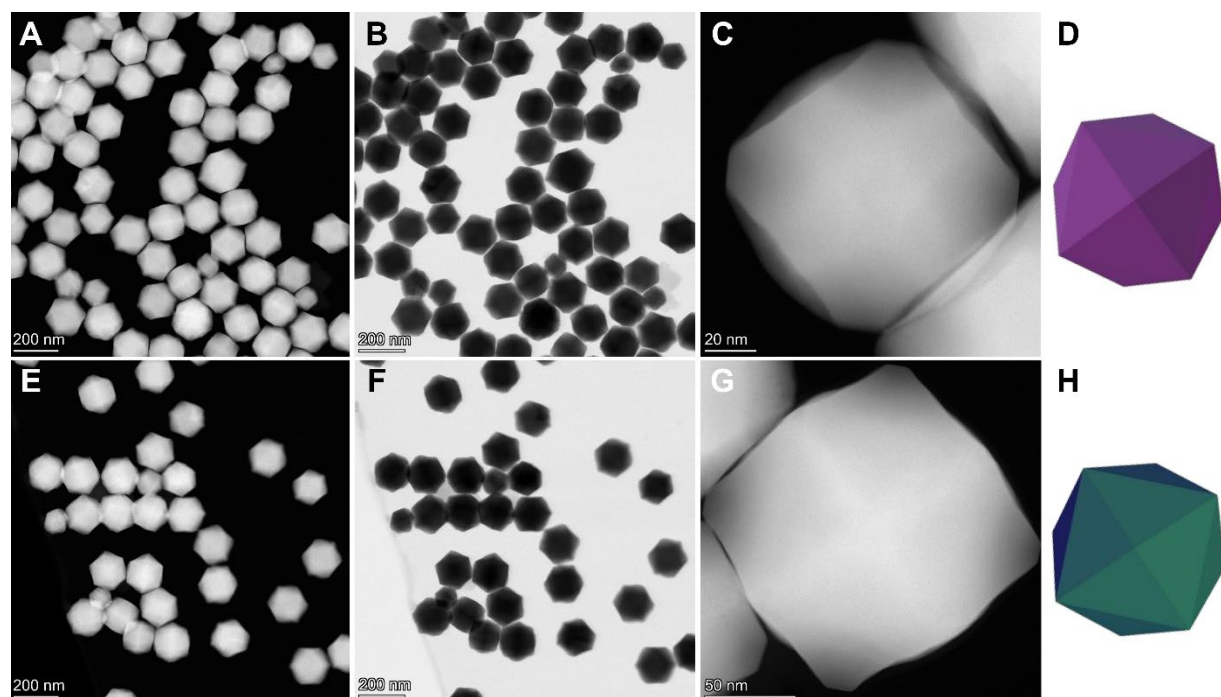


Figure S16. STEM images and 3D models of THH made in dried, modified BioUltra B and dried, modified BioXtra CTAB. (A) Dark field image of BioUltra B THH; (B) bright field image of BioUltra B THH; (C) high-magnification dark field image of a single small, truncated BioUltra B THH particle; (D) 3D model of a THH tilted at the same angle as the particle in (C); (E) Dark field image of BioXtra THH; (F) bright field image of BioXtra THH; (G) high-magnification dark field image of a single, slightly truncated BioXtra THH particle; (H) 3D model of a THH tilted at the same angle as the particle in (G). Scale Bars: (A, B, E, F) 200 nm; (C) 20 nm; (G) 50 nm.

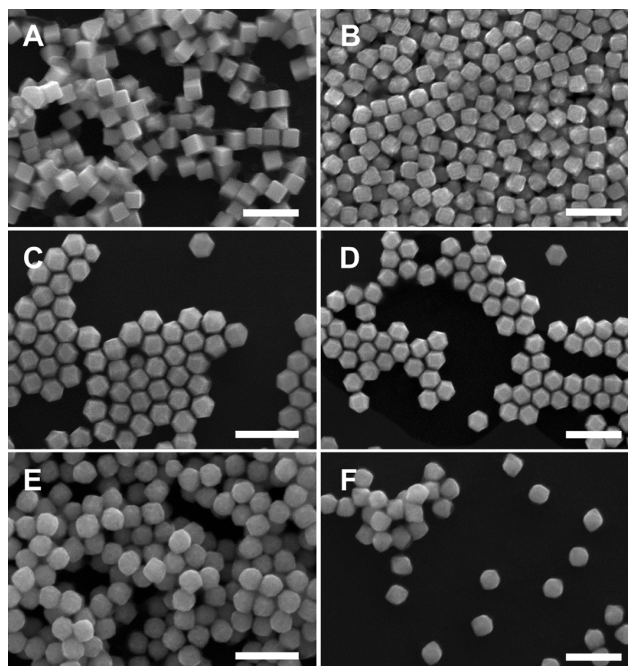


Figure S17. SEM images of Pd nanoparticle shape as a function of iodide concentration in dried BioUltra B CTAB with 190 μL acetone (0.26 M in the growth solution). (A) 0.24, (B) 0.48, (C) 0.97, (D) 1.45, (E) 1.94, and (F) 2.90 μM added NaI. Scale bars: 300 nm.

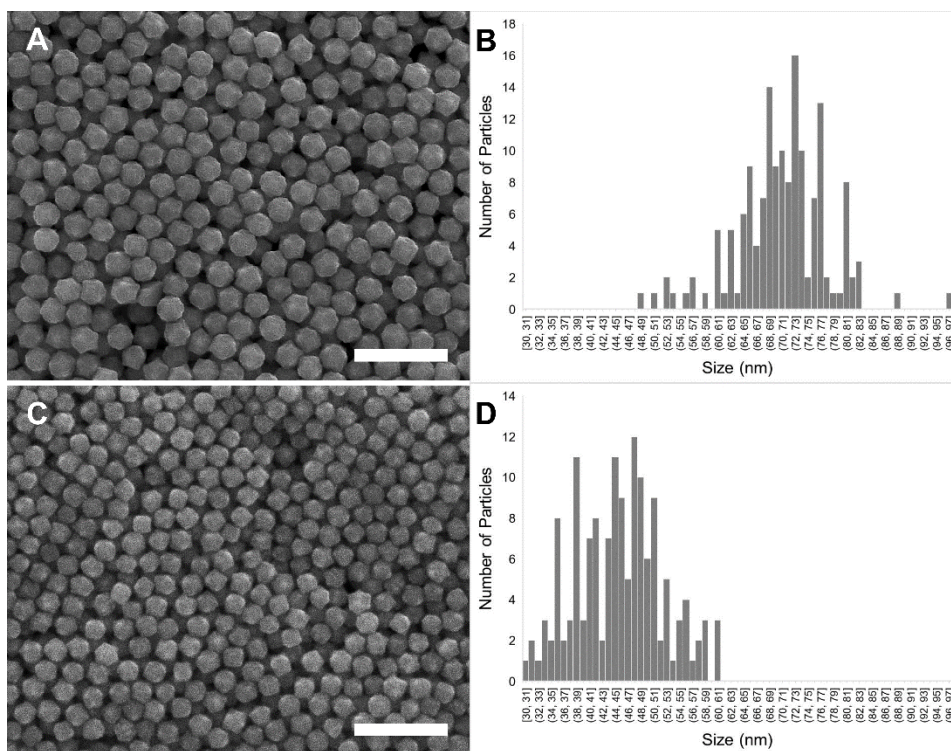


Figure S18. (A-B) SEM images and (C-D) size distribution histograms of smaller TC nanoparticles synthesized with a higher seed colloid concentration. (A) SEM image of particles synthesized with 100 μL of undiluted nanocube seeds (20x standard concentration) and (B) SEM image of particles synthesized with 200 μL of undiluted nanocube seeds (40x standard concentration). (C) Size distribution histogram of 154 particles synthesized with 100 μL undiluted seeds (70 ± 7 nm) and (D) size distribution histogram of 146 particles synthesized with 200 μL undiluted seeds (45 ± 7 nm). Samples were produced in dried BioUltra B CTAB using THH forming conditions, including 190 μL (0.26 M) added acetone and 0.68 μM added NaI. Particles were measured diagonally. Scale bars: 300 nm.

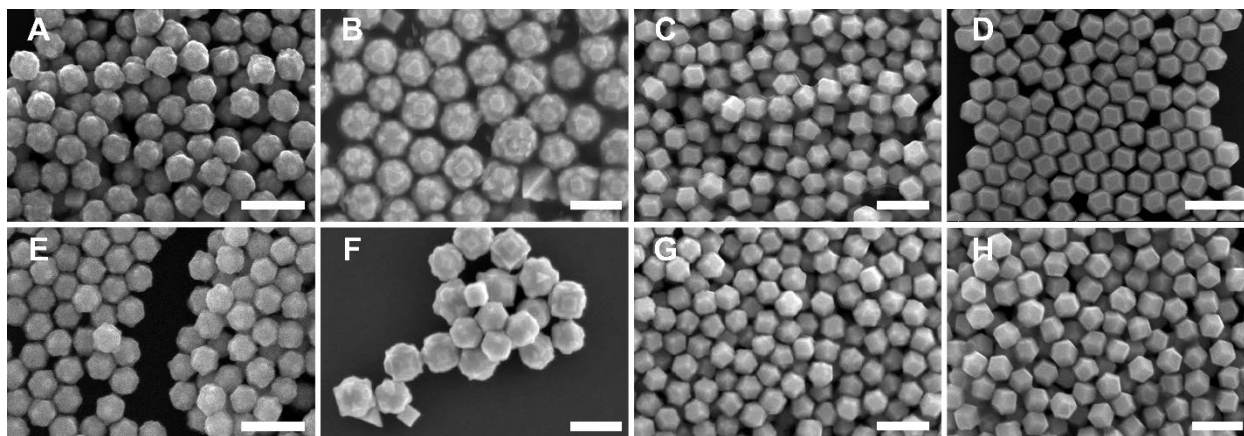


Figure S19. SEM images of Pd particle morphology in dried BioXtra CTAB as a function of acetone and iodide addition. (A) 0.63 μM NaI and 175 μL acetone (0.24 M), (B) 0.73 μM NaI and 175 μL acetone (0.24 M), (C) 0.82 μM NaI and 175 μL acetone (0.24 M), (D) 0.92 μM NaI and 175 μL acetone (0.24 M), (E) 0.63 μM NaI and 200 μL acetone (0.27 M), (F) 0.73 μM NaI and 200 μL acetone (0.27 M), (G) 0.82 μM NaI and 200 μL acetone (0.27 M), and (H) 0.92 μM NaI and 200 μL acetone (0.27 M) added to the growth solution. All other growth conditions standard. Values in parentheses indicate concentration in the growth solution. Scale bars: 300 nm.

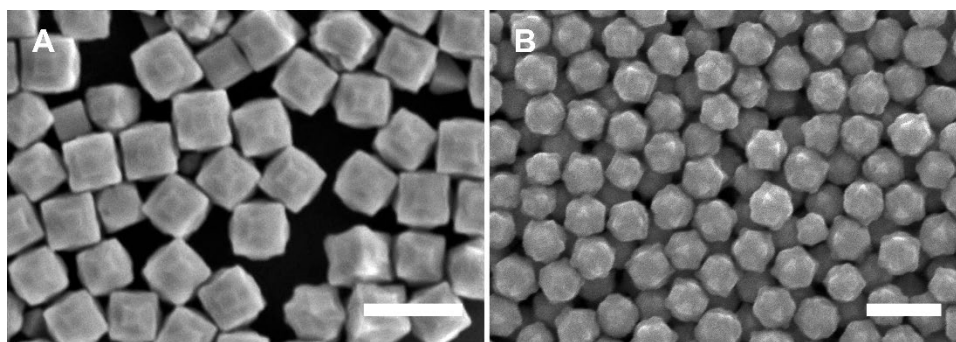


Figure S20. SEM images of Pd particle morphology in BioXtra CTAB growth solutions with excess acetone. (A) As-received BioXtra CTAB with 0.58 μM NaI and no acetone, (B) dried BioXtra CTAB with 0.58 μM NaI and 340 μL acetone (0.46 M in the growth solution). All other growth conditions standard. Scale bars: 300 nm.

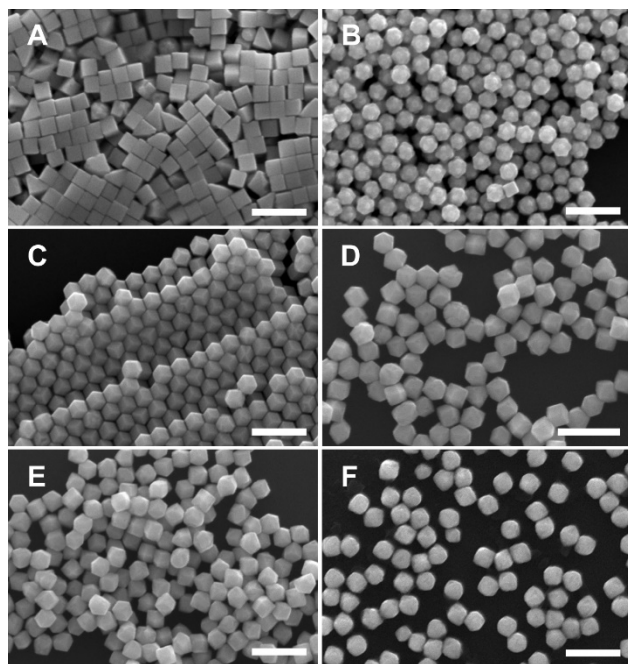


Figure S21. SEM images of Pd nanoparticle shape as a function of iodide concentration in dried BioXtra CTAB with 230 μ L acetone (0.31 M in the growth solution). (A) 0.24, (B) 0.48, (C) 0.97, (D) 1.45, (E) 1.94, and (F) 2.90 μ M added NaI. Scale bars: 300 nm.

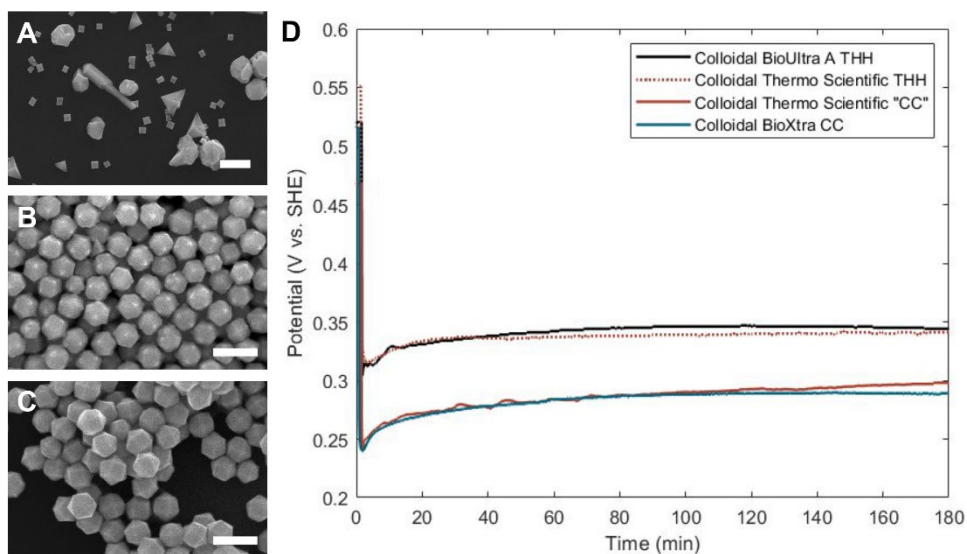


Figure S22. Colloidal Pd particles synthesized in Thermo Scientific CTAB. SEM images of particles synthesized with (A) as-received Thermo Scientific CTAB under standard conditions; (B) dried Thermo Scientific CTAB with 0.58 μM added NaI and 230 μL added acetone (0.31 M in the growth solution), all other conditions standard; (C) dried Thermo Scientific CTAB with 0.48 μM added NaI and 220 μL added acetone (0.30 M in the growth solution), all other conditions standard; and (D) open-circuit potential measurements of colloidal syntheses (A) and (C), compared to open-circuit potential measurements of standard conditions in BioUltra A (THH-forming) and as-received BioXtra (CC-forming). Note that while the BioUltra A trace was the benchmark of interest, the BioXtra measurement was included due to its similarity to the time-dependent potential of synthesis (A). Scale bars: 300 nm.

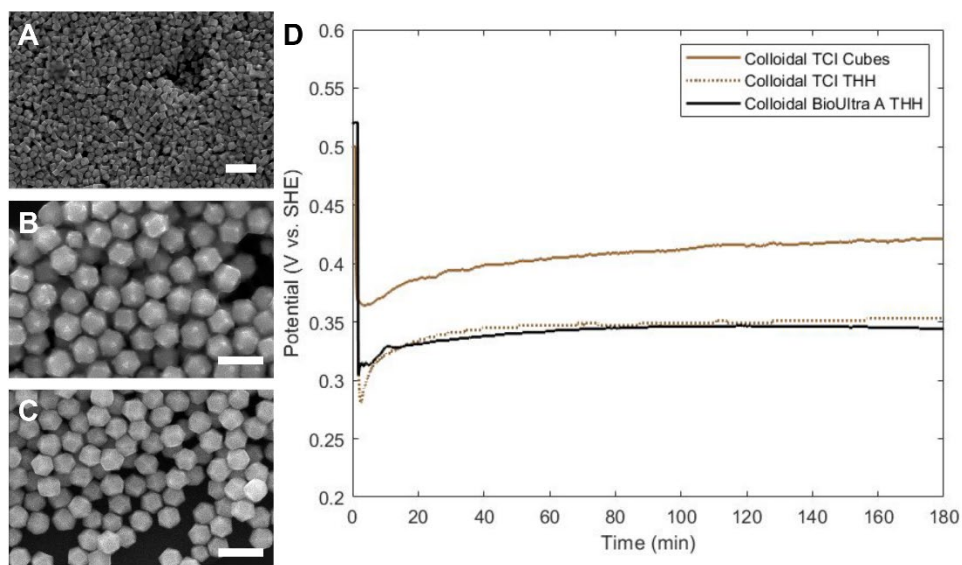


Figure S23. Colloidal Pd particles synthesized in TCI CTAB. SEM images of particles synthesized with (A) as-received TCI CTAB under standard conditions; (B) dried TCI CTAB with 0.58 μM added NaI and 100 μL added acetone (0.14 M in the growth solution), all other conditions standard; (C) dried TCI CTAB with 0.48 μM added NaI and 90 μL (0.12 M in the growth solution, all other conditions standard; and (D) open-circuit potential measurements of colloidal syntheses (A) and (C), compared to the open-circuit potential trace for standard THH-forming conditions in BioUltra A. Scale bars: 300 nm.

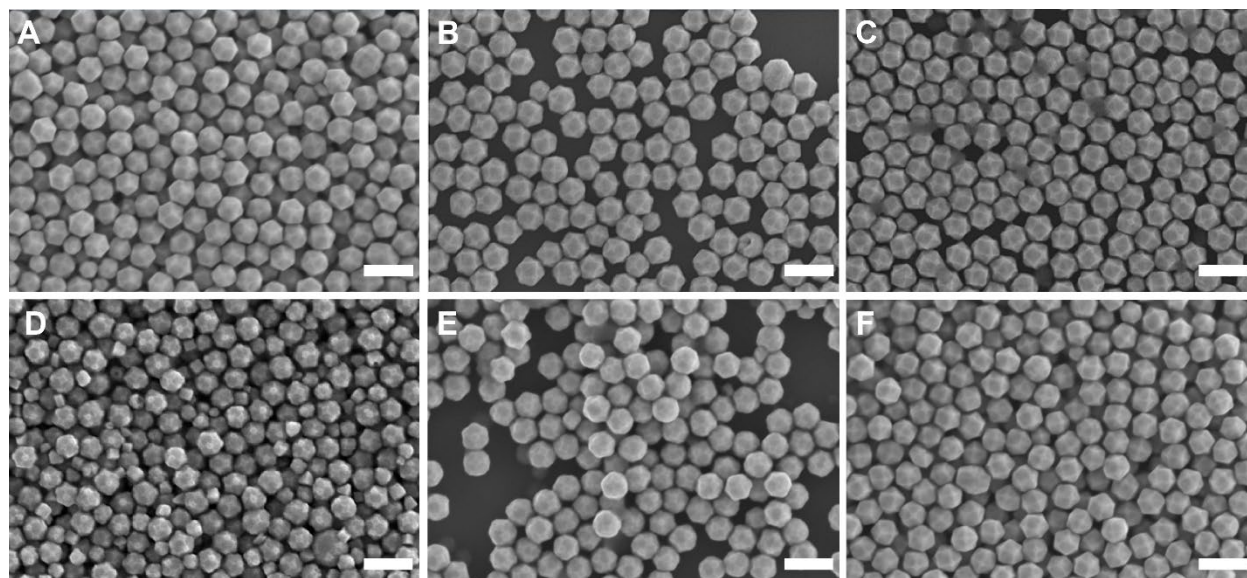


Figure S24. SEM images of Pd THH particles in as-received BioUltra B CTAB with added solvent. (A) 50 μL acetone (68 mM) and 0.68 μM NaI, (B) 50 μL ethanol (85 mM) and 0.68 μM NaI, (C) 50 μL methanol (0.12 M) and 0.68 μM NaI, (D) 200 μL acetone (0.27 M) and 0.48 μM NaI, (E) 200 μL ethanol (0.34 M) and 0.48 μM NaI, (F) 200 μL methanol (0.49 M) and 0.48 μM NaI. All other growth solution conditions standard. Scale bars: 300 nm.

References

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2. K. Dai, N. Kuniharu, U. Shinji, T. Kazuaki, and M. Kazuo. *Bull. Chem. Soc. Jap.* 2011, **84**, 312-319.
3. K. Koczkur and S. Skrabalak, personal communication.