Supporting Information

An Integrated Electrochemistry Approach to the Design and Synthesis of Polyhedral Noble Metal Nanoparticles

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Experimental Methods

Materials

Cetyltrimethylammonium chloride solution (CTAC, 25 wt% in H_2O), hexadecyltrimethylammonium bromide (CTAB, BioXtra ≥99%), L-ascorbic acid (ACS reagent, ≥99%), sodium tetrachloropalladate(II) (Na_2PdCl_4, ≥99.99% trace metal basis), and sodium borohydride ($NaBH_4$, granular, 99.99%) were purchased from Sigma-Aldrich. Palladium(II) chloride ($PdCl_2$, 99.9%), hydroquinone (99%), trisodium citrate dihydrate (99.0%), hydroxylamine hydrochloride (99%), sodium bromide (99.99%), and sodium iodide (99.9%) were purchased from Alfa Aesar. Cetyltrimethylammonium hydrogen sulfate ($CTAHSO_4$, >98.0%) and CTAC (95%) were purchased from Tokyo Chemical Industries (TCI). Hydrochloric acid (HCl, 1 M solution) was purchased from Fluka. Nitric acid concentrate (HNO_3, 1 M solution) was purchased from Fisher Chemical. 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 50 mL round bottom flask. The solution was capped and stirred for 3 hours until the solid fully dissolved and the solution became a clear dark orange color. All chemicals were used without further purification and all

solutions were prepared with deionized (DI) water (18.2 MΩ resistivity, Labconco Water Pro PS). CTAC from Sigma-Aldrich was used unless otherwise specified.

Synthesis of Pd seeds

Into a 20 mL scintillation vial, 10 mL of 12.5 mM CTAB and 0.25 mL of 10 mM Na_2PdCl_4 were added and stirred to a constant vortex. To this stirring solution, 0.60 mL of 10 mM $NaBH_4$ was rapidly injected to facilitate rapid reduction, which resulted in a color change of the solution from light brown to a dark brown. The solution was stirred at maximum stir rate (vortex) for one minute and was then allowed to stand for two hours covered but uncapped to allow for degradation of the remaining $NaBH_4$.

Preparation of glassy carbon electrodes and dropcasting of Pd seeds

Glassy carbon (GC) electrodes (5 mm OD x 4 mm thick disk insert, Pine Research) were prepared by polishing with 0.05 μm alumina polishing powder (Gamry Masterprep Solution), 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 ml solution of Pd seeds was serially diluted in DI water. 1 μL of 10-1000x diluted seeds was then dropcast onto the center of a dry GC electrode and allowed to completely dry over one hour in a fume hood.

Standard electrochemical cell setup

A five-port electrochemical cell (Gamry Instruments Dr. Bob's Cell) was set up with the prepared GC working electrode with dropcast Pd seeds, a platinum wire counter electrode (Gamry Instruments), a saturated silver/silver chloride reference electrode (Gamry Instruments), and a stir bar. The counter and reference electrodes were isolated from the reaction solution by bridge tubes

with glass frits. The cell was then clamped above a stir plate with a 40 ºC water bath and the electrode leads were connected to the potentiostat (Gamry Instruments 1010B or 1000T).

Electrochemical synthesis of corrugated Pd nanoparticles

To a prepared cell, 10 mL of 12.5 mM CTAC, 0.1 mL of 12.5 mM CTAB, and 0.5 mL of 10 mM Na_2PdCl_4 were added and allowed to stir at 200 rpm until the open circuit potential of the cell stabilized (< 3-5 mV change per five minutes). A direct current profile was then applied to the cell at -2.55 μA/cm^2 for 30 seconds, followed by –25.5 μA/cm^2 for 30 minutes.

Electrochemical synthesis of Pd icosahedra

To a prepared cell, 10 mL of 100 mM $CTAHSO_4$ and 0.5 mL of 10 mM H_2PdCl_4 were added and allowed to stir at 200 rpm until the open circuit potential of the cell stabilized (< 3-5 mV change per five minutes). A direct current profile was then applied to the cell at -2.55 μA/cm^2 for 30 minutes.

Electrochemical synthesis of homogeneously nucleated Pd cubes

A solution was prepared by adding 10 ml of 15 mM CTAC (TCI), 0.525 mL of 10 mM H_2PdCl_4, and 75 μL of 1 mM NaBr to a 20 mL scintillation vial, which was placed in a 35 ºC water bath and allowed to come to temperature for 30 minutes. The solution was then transferred to a prepared electrochemical cell with a clean GC electrode (no dropcast seeds) in a 35 ºC water bath. The solution was not stirred (no stir bar) and a galvanodynamic ramp current profile was immediately applied to the cell starting at -25.5 μA/cm^2 and ending at 0 μA over 30 minutes.

Electrochemical synthesis of homogeneously nucleated Pd octahedra

A solution was prepared by adding 10 ml of 15 mM CTAC (TCI), 1.050 mL of 10 mM H_2PdCl_4, and 7.5 μL of 1 mM NaI to a 20 mL scintillation vial, which was placed in a 35 ºC water bath and allowed to come to temperature for 30 minutes The solution was then transferred to a

prepared electrochemical cell with a clean GC electrode (no dropcast seeds) in a 35 ºC water bath. The solution was not stirred (no stir bar) and a galvanodynamic ramp current profile was immediately applied to the cell starting at -20.4 μA/cm^2 and ending at -2.55 μA/cm^2 over 30 minutes.

Standard workup of GC electrode for characterization

The cell was removed from the water bath and the GC working electrode was removed from the cell and washed lightly with DI water. The GC tip was then removed from the Teflon holder and allowed to dry before being directly characterized by scanning electron microscopy (Hitachi SU5000 FE-SEM). Average particle size (ImageJ) and particle shape distribution were determined using >100 particles.

Colloidal synthesis of corrugated Pd particles

Corrugated Pd particles were synthesized according to a previously reported method.[1] A growth solution was prepared by adding 10 ml of 12.5 mM CTAC, 0.5 mL of 10 mM Na_2PdCl_4, and 30 μL of 1 M HNO_3 to a 20 mL scintillation vial. 0.1 mL of 100 mM L-ascorbic acid was then added and the solution swirled before injecting 0.1 mL of 1000x diluted (in 12.5 CTAB) Pd seeds. The solution was swirled again following seed addition. The vial was left at room temperature in a drawer for at least two hours to ensure reaction completion. Growth solution conditions were varied as described in the main text.

Colloidal synthesis of Pd icosahedra

A growth solution was prepared by adding 10 ml of 12.5 mM $CTAHSO_4$ and 0.5 mL of 10 mM H_2PdCl_4 to a 20 mL scintillation vial, which was placed in a 40 ºC water bath and allowed to come to temperature for at least ten minutes. To this warm solution, 0.1 mL of 10 mM hydroquinone was added, the solution swirled, then 0.1 mL of 1000x diluted (in 12.5 mM

$CTAHSO_4$) Pd seeds were injected and the solution was swirled again. The vial was then put back into the 40 °C water bath for at least two hours to ensure reaction completion.

Colloidal synthesis of homogeneously nucleated Pd cubes and octahedra

Pd cubes and octahedra were synthesized via modification of a previously reported method.[2] A solution was prepared by adding 10 ml of 15 mM CTAC (TCI), 1.050 mL of 10 mM H_2PdCl_4, and 75 μL of 1 mM NaBr (cubes) or 7.5 μL of 1 mM NaI (octahedra) to a 20 mL scintillation vial, which was placed in a 35 °C water bath and allowed to come to temperature for 30 minutes. To this warm solution, 1 mL of 100 mM ascorbic acid was added, the solution swirled, and the vial was then put back into the 35 °C water bath for at least 30 minutes until reaction completion.

Characterization of Pd nanoparticles from colloidal syntheses

To prepare samples of colloidal syntheses for characterization, the vial was vortexed and 1 mL of the solution was transferred to a microcentrifuge tube. The solution was then centrifuged at 6000 rpm for four minutes to spin down a pellet. The supernatant was removed and the microcentrifuge tube refilled to 1 mL with DI water, vortexed, then centrifuged again at 6000 rpm for four minutes. The supernatant was removed again, a minimal amount of DI water (20-50 μL) was added, and the tube was sonicated to disperse the particles. 1 μL of this solution was then dropcast onto a prepared silica wafer and allowed to dry before characterization by scanning electron microscopy (Hitachi SU5000 FE-SEM). Average particle size (ImageJ) and shape was determined using >100 particles.

Measurement of potential profiles for common reducing agents

To a prepared cell with a clean GC electrode (no dropcast seeds), 10 mL of 100 mM $CTAHSO_4$ and 0.5 mL of 10 mM H_2PdCl_4 were added and allowed to stir at 400 rpm until the open

circuit potential of the cell stabilized (< 3-5 mV change per five minutes). An open circuit measurement was then initiated by the potentiostat to record the subsequent profile. 0.1 mL of 100 mM L-ascorbic acid (or hydroquinone, trisodium citrate or hydroxylamine hydrochloride; or 0.025 mL sodium borohydride) was added and then 0.1 mL of 1000x diluted (in 12.5 mM $CTAHSO_4$) Pd seeds were injected and the solution was allowed to stir for ten seconds before stirring was stopped. The reaction was measured for 30 minutes or until the potential became stagnant.

Measurement of potential profiles for homogeneously nucleated Pd cubes and octahedra

A solution was prepared by adding 10 ml of 15 mM CTAC (TCI), 1.050 mL of 10 mM H_2PdCl_4, and 75 μL of 1 mM NaBr (cubes) or 7.5 μL of 1 mM NaI (octahedra) to a 20 mL scintillation vial, which was placed in a 35 ºC water bath and allowed to come to temperature for 30 minutes. The solution was then transferred to a prepared electrochemical cell with a clean GC electrode (no dropcast seeds) in a 35 ºC water bath. An open circuit measurement was then initiated by the potentiostat to record the subsequent profile, stirring was initiated at 400 rpm, and 1 mL of 100 mM L-ascorbic acid was added with stirring for ten seconds before stirring was stopped. The reaction was measured for 30 minutes or until the potential became stagnant.

Table S1. Size and Shape Distributions of the Corrugated Pd Particles Shown in Figure 3.[a]

	Size (nm)	20-Fold Twin (%)	Pentatwinned (%)	Planar Twinned (%)	Single Crystal (%)
A	121 ± 25	13	6	8	73
B	150 ± 27	36	11	17	37
C	245 ± 59	34	8	28	30
D	268 ± 71	33	7	31	29
E	73 ± 20	c	c	c	63
F	258 ± 55	15	11	35	39
G	283 ± 53	19	13	28	39
H	165 ± 46	12	14	74	0

[a] 20-fold twins are icosahedra, pentatwinned particles are pentatwinned rods, planar twinned particles are bipyramids, and single crystalline particles are cubes. Particle size distributions are excluding single crystalline cubes.
[b] C and G represent the ideal synthesis conditions shown in Figure 2A and B, respectively.
[c] Different twin structures were not distinguishable for the products of this condition. The total twin population is 37%.

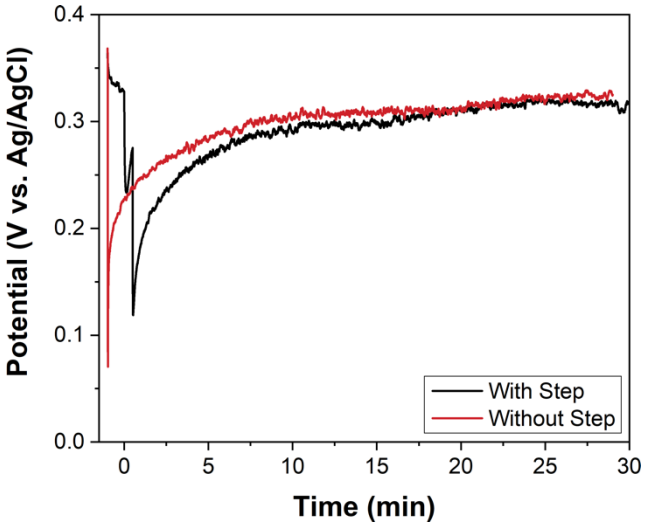

Figure S1. Measurement of the potential profile of the electrochemical synthesis of corrugated Pd particles with and without an initial step of -2.55 μA/cm^2 for 30 seconds.

Table S2. Size and Shape Distributions of the Corrugated Pd Particles Shown in Figure 4.[a]

	Size (nm)	20-Fold Twin (5%)	Pentatwinned (%)	Planar Twinned (%)	Single Crystal (%)
A	225 ± 31	4	1	10	84
B	283 ± 53	19	13	28	39

[a] 20-fold twins are icosahedra, pentatwinned particles are pentatwinned rods, planar twinned particles are bipyramids, and single crystalline particles are cubes. Particle size distributions are excluding single crystalline cubes.

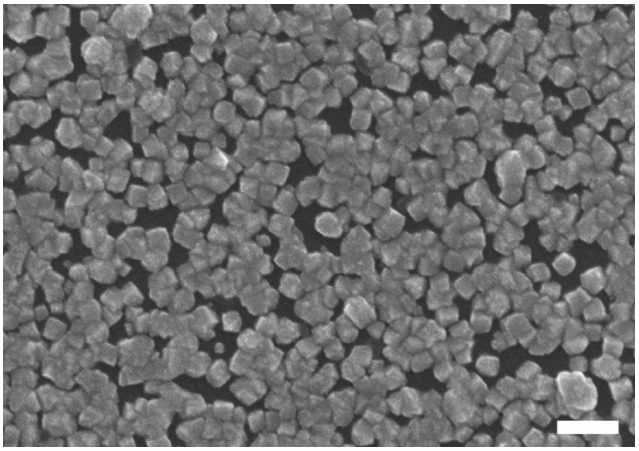

Figure S2. Corrugated Pd particles grown via electrochemical synthesis with an applied current of -153 μA/cm^2 that begin to plate the surface of the electrode. Scale bar: 200 nm.

Table S3. Size and Shape Distributions of the Corrugated Pd Particles Shown in Figure 5.[a]

	Size (nm)	20-Fold Twin (5%)	Pentatwinned (%)	Planar Twinned (%)	Single Crystal (%)
A	245 ± 59	34	8	28	30
B	234 ± 46	33	15	39	12
C	215 ± 46	32	8	36	25
D	153 ± 58	26	9	28	37
E	283 ± 53	19	13	28	39
F	209 ± 30	4	5	8	83
G	252 ± 41	7	3	13	77
H	157 ± 35	5	3	4	88

[a] 20-fold twins are icosahedra, pentatwinned particles are pentatwinned rods, planar twinned particles are bipyramids, and single crystalline particles are cubes. Particle size distributions are excluding single crystalline cubes.

Table S4. Size Distributions of the Pd Particles shown in Figure 6.

	Size (nm)
A	130 ± 16
B	344 ± 67

Table S5. Size and Shape Distributions of the Corrugated Pd Particles Shown in Figure 7.[a]

	Size (nm)	20-Fold Twin (5%)	Pentatwinned (%)	Planar Twinned (%)	Single Crystal (%)
A	245 ± 59	34	8	28	30
B	220 ± 66	29	10	22	39
C	261 ± 37	30	13	36	22
D	233 ± 40	56	13	19	12
E	283 ± 53	19	13	28	39
F	149 ± 31	33	29	30	8
G	187 ± 23	10	5	12	73
H	133 ± 23	4	5	7	84

[a] 20-fold twins are icosahedra, pentatwinned particles are pentatwinned rods, planar twinned particles are bipyramids, and single crystalline particles are cubes. Particle size distributions are excluding single crystalline cubes.

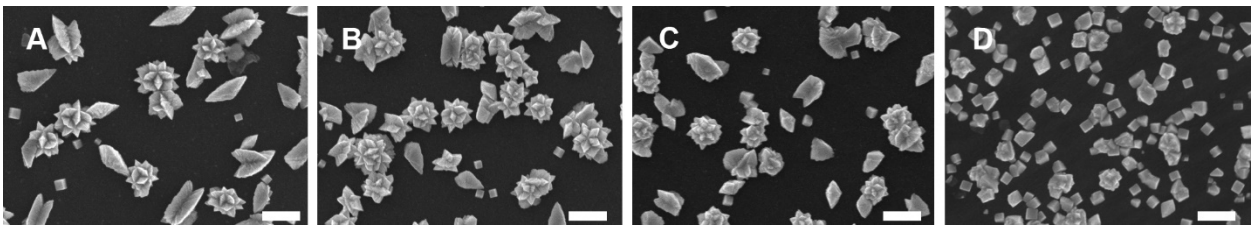

Figure S3. Pd nanoparticles synthesized electrochemically at a constant CTAB concentration of 0.125 mM and (A) 12.5, (B) 25, (C) 50, or (D) 100 mM CTA^+ (total CTA^+ from CTAB and CTAC). Scale bars: 300 nm.

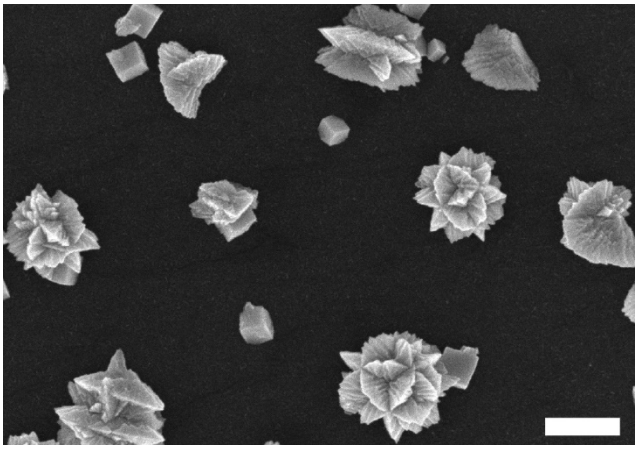

Figure S4. Corrugated Pd particles synthesized electrochemically with a 200:1 Cl:Br ratio in the growth solution. Scale bar: 300 nm.

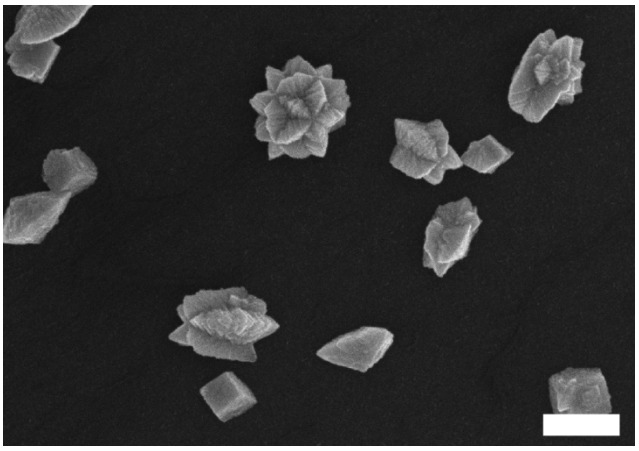

Figure S5. Corrugated Pd particles synthesized electrochemically in the presence of 3 mM CTAC with a 100:1 Cl:Br ratio. Scale bar: 300 nm.

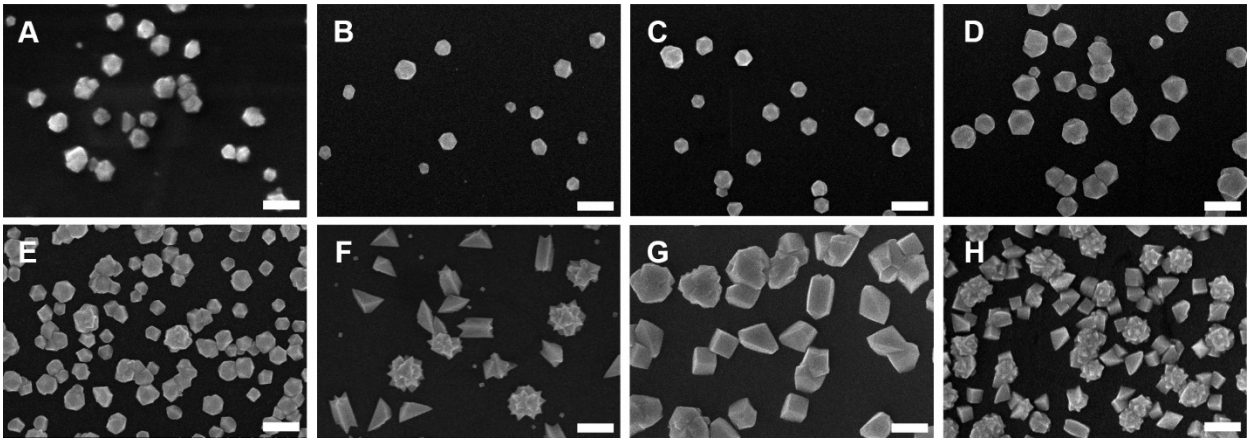

Figure S6. Pd nanoparticles synthesized electrochemically in 12.5 mM $CTAHSO_4$ with applied current profiles at (A) -1.02 μA/cm^2, (B) -1.5 μA/cm^2, (C) -2.04 μA/cm^2, (D) -5.09 μA/cm^2 (E) -15.28 μA/cm^2, (F) -25.47 μA/cm^2, (G) -38.21 μA/cm^2, or (H) -50.94 μA/cm^2 for 30 minutes. Scale bars: 300 nm.

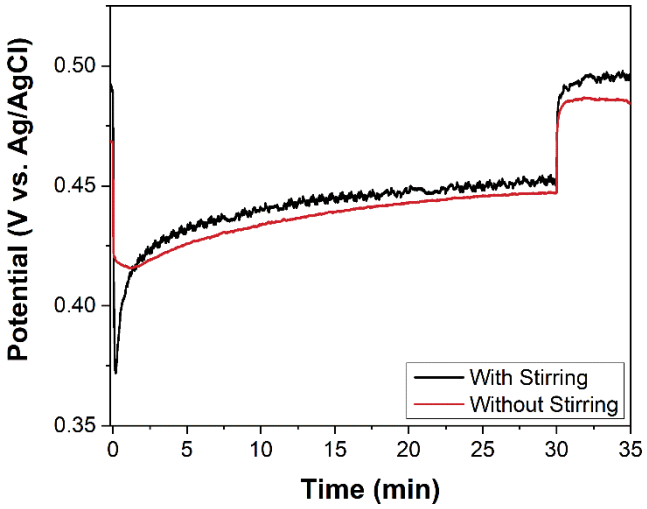

Figure S7. Measured potential profiles of electrochemically-synthesized Pd icosahedra particles with and without stirring (400 rpm stir rate).

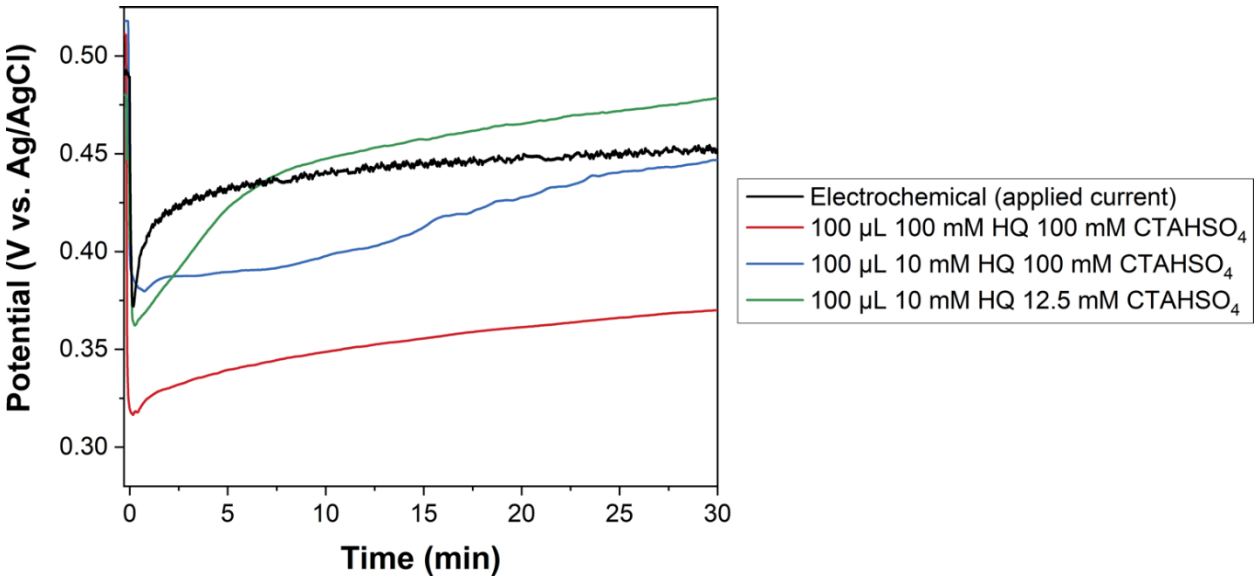

Figure S8. Measured potential profiles of colloidal Pd nanoparticle syntheses carried out with different concentrations of hydroquinone (HQ) and $CTAHSO_4$ overlaid with the profile of the electrochemically-synthesized Pd icosahedra particles for comparison.

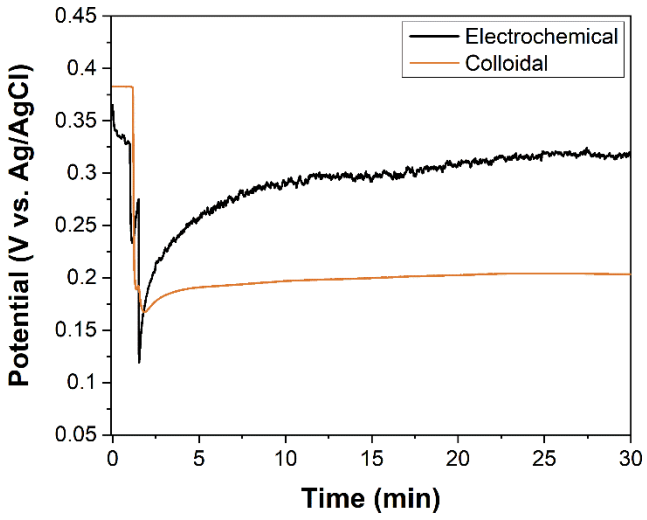

Figure S9. Comparison of the measured potential profiles for the electrochemical and colloidal syntheses of corrugated Pd particles.

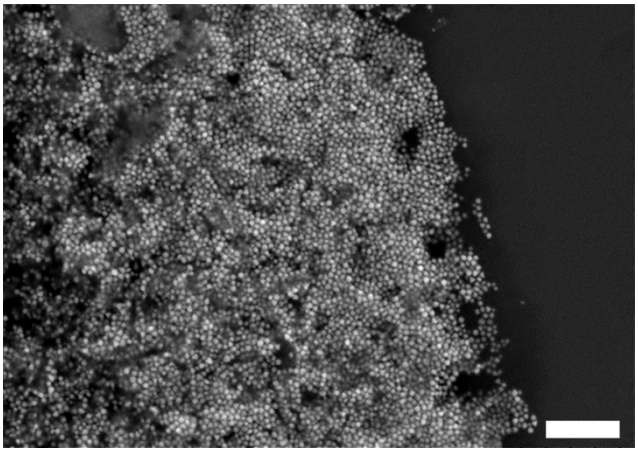

Figure S10. Pd particles synthesized via a colloidal approach in 100 mM $CTAHSO_4$ with 100 µL of 10 mM hydroquinone. Scale bar: 300 nm.

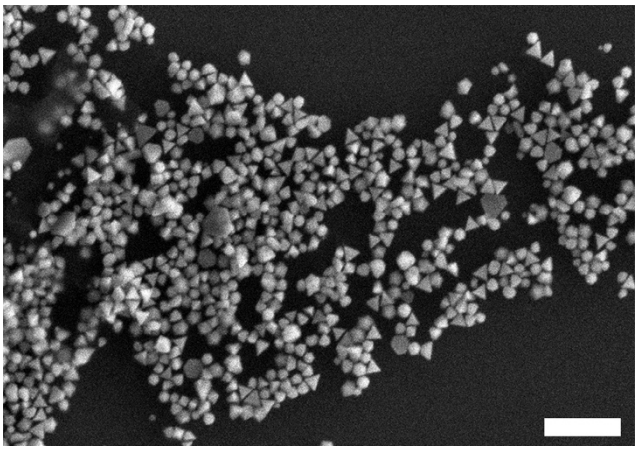

Figure S11. Pd particles synthesized via a colloidal approach in 12.5 mM $CTAHSO_4$ with 50 µL of 10 mM hydroquinone. Scale bar: 300 nm.

Table S6. Size and Shape Distributions of the Homogeneously Nucleated Cubes and Octahedra Shown in Figure 16.

	Size (nm)	Single Crystal (%) (Cubes/Octahedra)	Other (%)
A	99 ± 32	71	29
B	64 ± 14	80	20
C	108 ± 19	80	20
D	84 ± 14	73	27

References

1. King, M. E.; Personick, M. L. Defects by Design: Synthesis of Palladium Nanoparticles with Extended Twin Defects and Corrugated Surfaces. *Nanoscale* **2017,** *9*, 17914-17921.
2. Liu, S.-Y.; Shen, Y.-T.; Chiu, C.-Y.; Rej, S.; Lin, P.-H.; Tsao, Y.-C.; Huang, M. H. Direct Synthesis of Palladium Nanocrystals in Aqueous Solution with Systematic Shape Evolution. *Langmuir* **2015,** *31*, 6538-6545.