Supporting Information for

Use of Reduction Rate as a Quantitative Knob for Controlling the Twin Structure and Shape of Palladium Nanocrystals

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Experimental Methods

Polyol syntheses of Pd nanocrystals with different twin structures. The Pd nanocrystals with distinctive twin structures and shapes were prepared using the same procedure, except for the use of different polyols and temperatures to manipulate the reduction rate. Specifically, single-crystal, truncated octahedra and multiply twinned icosahedra of Pd, respectively, were obtained in ethylene glycol (EG, J. T. Baker) and diethylene glycol (DEG, Aldrich) at 140 °C. Stacking fault-lined nanoplates were prepared in DEG at 75 °C. In a standard procedure, 30 mg of poly(vinyl pyrrolidone) (PVP, $M_W \approx 55{,}000$, Aldrich) and 2 mL of EG (or DEG) were added into a glass vial, and heated to the desired temperature in an oil bath under magnetic stirring. Meanwhile, 15.5 mg of sodium tetrachloropalladate(II) (Na_2PdCl_4, 98%, Aldrich) was dissolved and preheated in 1 mL of EG (or DEG) at 60 °C. Afterwards, the solution containing Na_2PdCl_4 was quickly injected into the glass vial using a pipette. The reaction times for the synthesis of truncated octahedra (or icosahedra) and nanoplates were 3 h and 30 h, respectively. The vial was taken out of the oil bath after the synthesis and cooled down to room temperature. After centrifugation and washing with acetone and water three times, the product was collected and stored in water for further characterization.

Quantitative analysis of reaction kinetics for the synthesis of Pd nanocrystals. We measured the reaction rates between Pd precursor and different polyols by monitoring the absorbance of the reaction solution at different times through UV-vis spectroscopy. In detail, 2 mL of polyol were added into a glass vial and heated to a certain temperature in an oil bath under magnetic stirring. Na_2PdCl_4 (15.5 mg) was dissolved in 1.0 mL of polyol at 60 °C, and was quickly injected into the vial using a pipette. Meanwhile, the timer started running. An aliquot of 0.3 mL was sampled from the reaction solution at different times using a glass pipette and immediately injected into 2.7 mL of aqueous HCl solution (0.1 M, diluted from 37% HCl, Aldrich) at 0 °C. Then, the solution was centrifuged at 10,000 rpm for 10 min, and the supernatant was diluted into an appropriate concentration with the same aqueous HCl solution (0.1 M) for UV-vis measurement. The time-dependent concentrations of $PdCl_4^{2-}$ ions remaining in the solution could be calculated by comparing the obtained UV-vis spectrum with the standard curve of Na_2PdCl_4.

Based on the concentrations of $PdCl_4^{2-}$ ions remaining in the solution as a function of reaction time, the kinetic parameters including the rate constant, initial rate, and activation energy of the reduction of $PdCl_4^{2-}$ by a polyol, could be further acquired.

Characterizations. TEM images were taken using a Hitachi HT7700 microscope operated at 120 kV by drop casting the dispersions of nanocrystals on carbon-coated Cu grids and drying under ambient conditions. HAADF-STEM images were acquired with a JEOL 2200FS STEM/TEM microscope equipped with a CEOS GmbH probe corrector. UV-vis absorption spectra were recorded using a Perkin-Elmer Lambda 750 UV-vis-NIR spectrometer. The concentrations of $PdCl_4^{2-}$ remaining in the reaction solution and thus the conversions of $PdCl_4^{2-}$ into Pd atoms were calculated based on the absorbance at 279 nm from the UV-vis spectra.

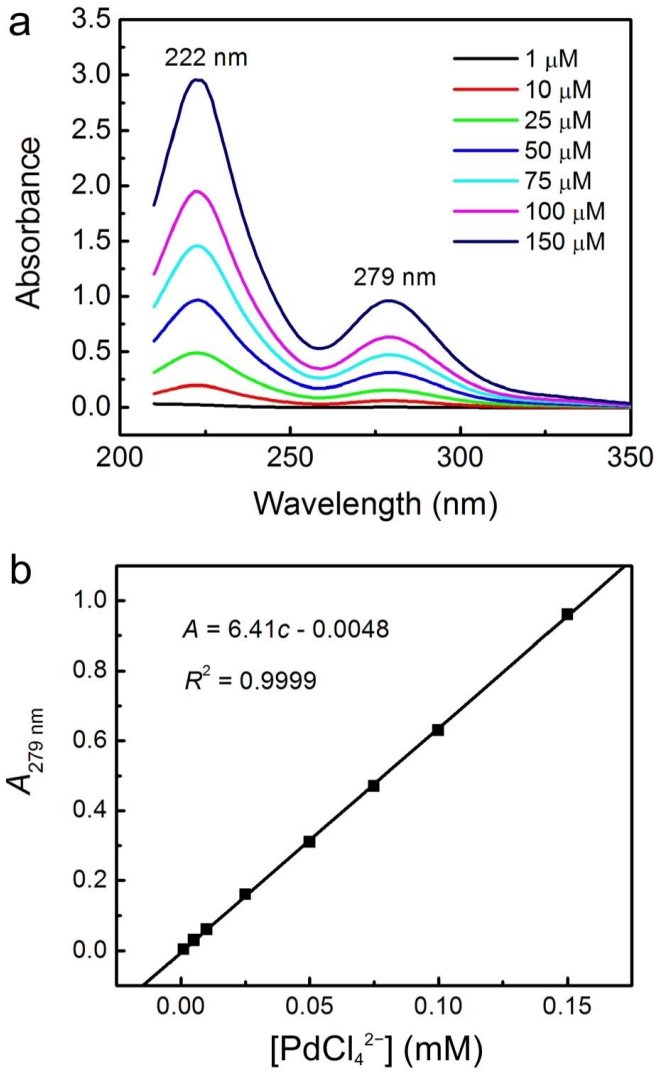

Figure S1. (a) UV-vis spectra of standard Na_2PdCl_4 solutions with different concentrations. (b) A plot showing the absorbance at 279 nm as a function of the concentration of $PdCl_4^{2-}$. This calibration curve can be used to calculate the concentration of $PdCl_4^{2-}$ remaining in the reaction solution from the UV-vis spectrum of the sample.

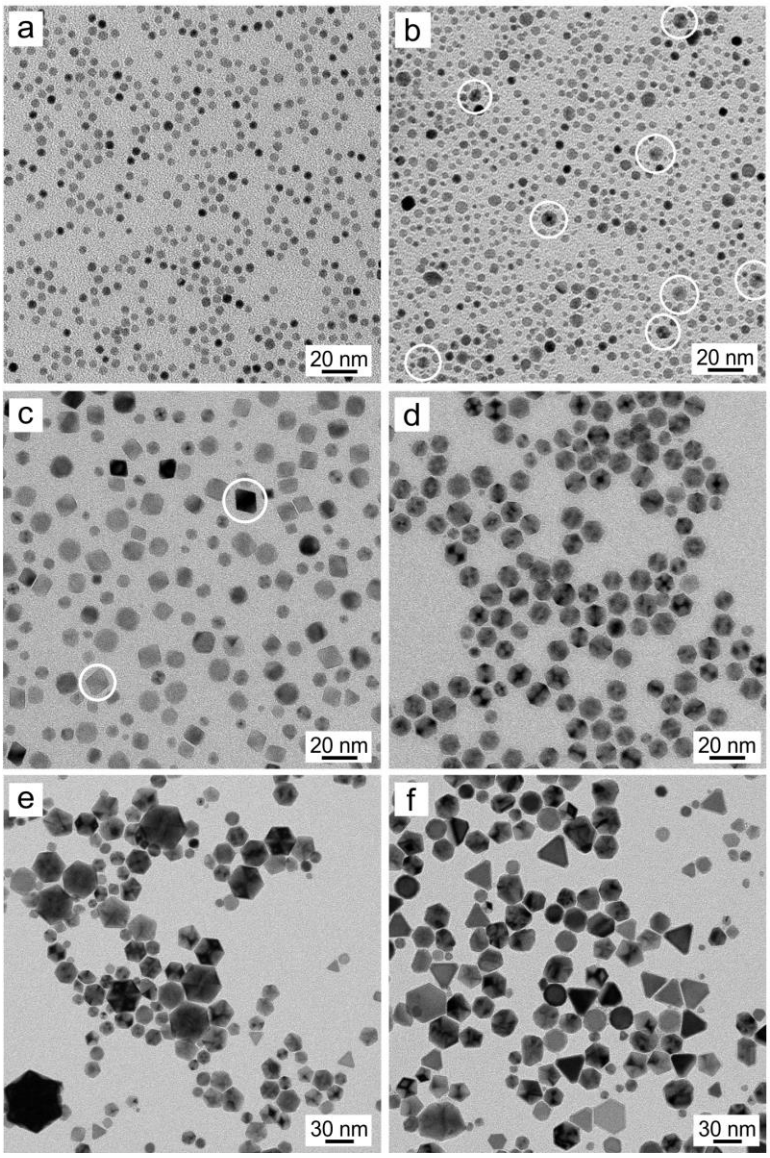

Figure S2. TEM images of Pd nanocrystals prepared using the standard procedure except for the variation in the type of polyol and reaction temperature at different initial reduction rates (r_0): (a) r_0=2.55×10^{-4} M·s^{-1} (in EG, at 160 °C, and k=1.45×10^{-2} s^{-1}); (b) r_0=1.54×10^{-4} M·s^{-1} (in EG, at 130 °C, and k=8.75×10^{-3} s^{-1}); (c) r_0=4.58×10^{-5} M·s^{-1} (in DEG, at 160 °C, and k=2.60×10^{-3} s^{-1}); (d) r_0=5.56×10^{-6} M·s^{-1} (in DEG, at 130 °C, and k=3.16×10^{-4} s^{-1}); (e) r_0=2.76×10^{-7} M·s^{-1} (in DEG, at 95 °C, and k=1.57×10^{-5} s^{-1}); and (f) r_0=1.08×10^{-7} M·s^{-1} (in DEG, at 85 °C, and k=6.11×10^{-6} s^{-1}). The white circles marked in (b) and (c) indicate multiply twinned and single-crystal Pd nanocrystals, respectively.

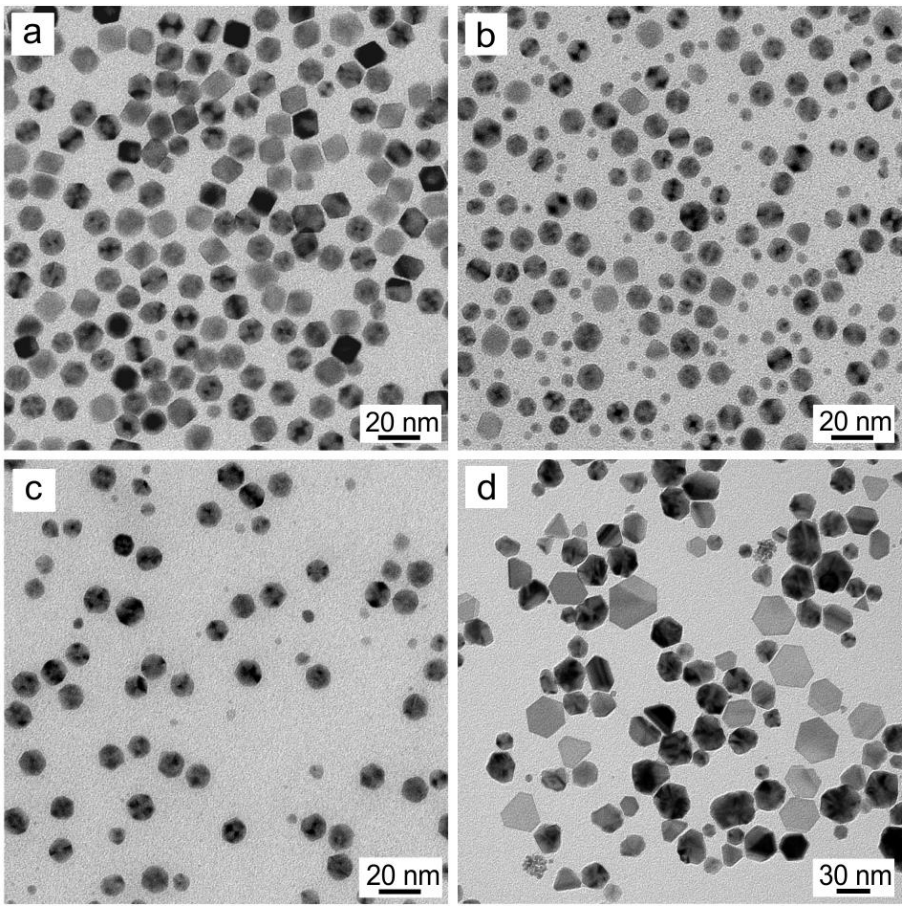

Figure S3. TEM images of Pd nanocrystals synthesized using the standard procedure in TEG except the variation in reaction temperature at different initial reduction rates (r_0): (a) r_0=2.46×10^{-5} M·s^{-1} at 160 °C; (b**)** r_0=1.02×10^{-5} M·s^{-1} at 150 °C; (c) r_0=5.54×10^{-6} M·s^{-1} at 140 °C; and (d) r_0=3.71×10^{-8} M·s^{-1} at 85 °C.

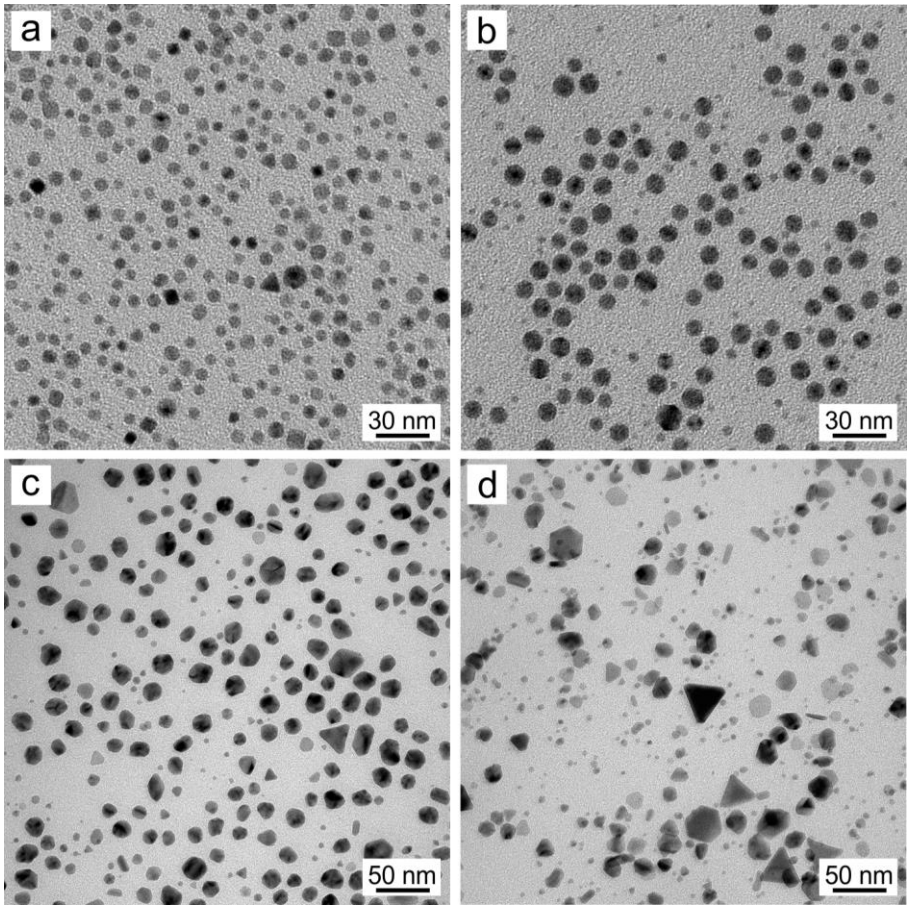

Figure S4. TEM images of Pd nanocrystals synthesized using the standard procedure except the variation in initial precursor concentration (c_0) at different initial reduction rates (r_0): (a) r_0=1.97×10^{-5} M·s^{-1} (in EG, at 140 °C, and c_0=1.76×10^{-3} M); (b) r_0=7.89×10^{-6} M·s^{-1} (in EG, at 140 °C, and c_0=7.04×10^{-4} M); (c) r_0=1.11×10^{-7} M·s^{-1} (in DEG, at 130 °C, and c_0=3.52×10^{-4} M); and (d) r_0=5.56×10^{-8} M·s^{-1} (in DEG, at 130 °C, and c_0=1.76×10^{-4} M).

Table S1. Summary of the experimental parameters for the reactions between $PdCl_4^{2-}$ and polyols at different conditions, and the corresponding rate constants (k) and initial rates (r_0)

Polyol	Temperature (°C)	Rate constant k (s^{-1})	Initial conc. of $PdCl_4^{2-}$ (M)	Initial rate r_0 ($M \cdot s^{-1}$)	Results (Figure)
EG	160	1.45×10^{-2}	1.76×10^{-2}	2.55×10^{-4}	S2a
	150	1.28×10^{-2}	1.76×10^{-2}	2.25×10^{-4}	
	140	1.12×10^{-2}	1.76×10^{-2}	1.97×10^{-4}	1a
	140	1.12×10^{-2}	1.76×10^{-3}	1.97×10^{-5}	S4a
	140	1.12×10^{-2}	7.04×10^{-4}	7.89×10^{-6}	S4b
	130	8.75×10^{-3}	1.76×10^{-2}	1.54×10^{-4}	S2b
DEG	160	2.60×10^{-3}	1.76×10^{-2}	4.58×10^{-5}	S2c
	150	1.24×10^{-3}	1.76×10^{-2}	2.18×10^{-5}	
	140	5.57×10^{-4}	1.76×10^{-2}	9.80×10^{-6}	1c
	130	3.16×10^{-4}	1.76×10^{-2}	5.56×10^{-6}	S2d
	130	3.16×10^{-4}	3.52×10^{-4}	1.11×10^{-7}	S4c
	130	3.16×10^{-4}	1.76×10^{-4}	5.56×10^{-8}	S4d
	95	1.57×10^{-5}*	1.76×10^{-2}	2.76×10^{-7}	S2e
	85	6.11×10^{-6}*	1.76×10^{-2}	1.08×10^{-7}	S2f
	75	2.26×10^{-6}*	1.76×10^{-2}	3.98×10^{-8}	1e
TEG	160	1.40×10^{-3}	1.76×10^{-2}	2.46×10^{-5}	S3a
	150	5.78×10^{-4}	1.76×10^{-2}	1.02×10^{-5}	S3b
	140	3.15×10^{-4}	1.76×10^{-2}	5.54×10^{-6}	S3c
	85	2.11×10^{-6}*	1.76×10^{-2}	3.71×10^{-8}	S3d

*These rate constants were derived from the Arrhenius equation.