Supplementary Information for

Exploring Size-Dependent Optical Property Alterations in Fine-Tuning Intermetallic PdCd Nanocube Sizes

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Experimental Section

Chemicals: Palladium(II) acetylacetonate ($Pd(acac)_2$, 99%, Sigma-Aldrich), cadmium acetate dihydrate ($Cd(OAc)_2{\cdot}2H_2O$, 99.999%, Alfa), DL-mandelic acid (99+%, Acros), oleylamine (OAm, 70%, Sigma-Aldrich), oleic acid (OA, 90%, Sigma-Aldrich), sodium acetate (CH_3COONa, 98.0%, Showa Chemical Co., Ltd.), Acetic acid (CH_3COOH, 99.8%, Honeywell Fluka), 4-nitrophenol (4-NP, 99%, Sigma-Aldrich), sodium borohydride ($NaBH_4$, 98.0%, Sigma-Aldrich).

Synthesis of PdCd nanocubes with sizes of 8, 9, 12, and 15 nm: $Pd(acac)_2$ (7.6 mg, 0.025 mmol), $Cd(OAc)_2{\cdot}2H_2O$ (16.7 mg, 0.063 mmol for 8 nm; 13.3 mg, 0.05 mmol for 9 nm; 9.9 mg, 0.038 mmol for 12 nm; 6.6 mg, 0.025 mmol for 15 nm), DL-mandelic acid (120.0 mg), OAm (4.0 mL), and OA (1.0 mL) were added to a three-necked flask and stirred for 45 min at 80 °C in a N_2 atmosphere. The resulting homogeneous mixture was heated without stirring from 80 to 160 °C and maintained at 160 °C for 1.5 h in a N_2 atmosphere. After cooling to room temperature with a water bath, the reaction mixture was purified using a mixture of n-hexane and ethanol through centrifugation at 12,000 rpm for 10 min twice, then redispersed in n-hexane (2.0 mL).

Catalysis for the 4-nitrophenol reduction reaction: The PdCd nanocubes were first washed by removing the n-hexane under reduced pressure, followed by adding acetic acid (1.0 mL) and stirring for 14 h at room temperature to remove the surfactant. After the washing, the PdCd nanocubes were

rinsed with ethanol through centrifugation at 12,000 rpm for 10 min twice, then redispersed in ethanol (1.0 mL). Subsequently, the PdCd nanocubes with a total surface area of 15 cm^2 (0.022 mg for 8 nm; 0.024 mg for 9 nm; 0.032 mg for 12 nm; 0.037 mg for 15 nm) were added to a deionized water solution containing a mixture of 4-NP (0.2 mM, 1.0 mL) and $NaBH_4$ (7.5 mM, 1.0 mL) in a quartz cell for catalysis. The catalytic reactions were conducted both in a dark environment and upon illumination, by monitoring the degradation of the peak at 406 nm every three minutes. Illumination was provided using a Xe lamp with a wavelength range from 400 to 700 nm (Asahi Spectra Co. Ltd., MAX-350). The light intensity reaching the cell was measured to be 550 mW cm^{-2} using a power meter.

Calculation of the surface area of 15 cm^2 for the PdCd nanocubes (taking 8 nm as an example): The edge length of the PdCd nanocubes is 8±0.8 nm. The volume of a single PdCd nanocubes at 8 nm is 5.12×10^{-19} cm^3. The density of PdCd is 10.92 g/cm^3. Given that 0.022 mg of 8 nm PdCd nanocubes was used in the 4-nitrophenol reduction reaction, the number of PdCd nanocubes is calculated as (2.2×10^{-5} g) / (10.92 g/cm^3 × 5.12×10^{-19} cm^3) = 3.9×10^{12}. The surface area of a single PdCd nanocube is 3.84×10^{-12} cm^2. Therefore, the total surface area of the PdCd nanocubes used is (3.9×10^{12}) × (3.84×10^{-12} cm^2) = 15 cm^2.

Characterization: Transmission electron microscopy (TEM) characterization was conducted using JEM-1400 electron microscopes (JEOL) operating at 100 kV. Powder X-ray diffraction (XRD) patterns were recorded on Bruker D2 Phaser system with Cu Kα radiation. UV-vis spectra were obtained using a Shimadzu UV-2600 spectrophotometer.

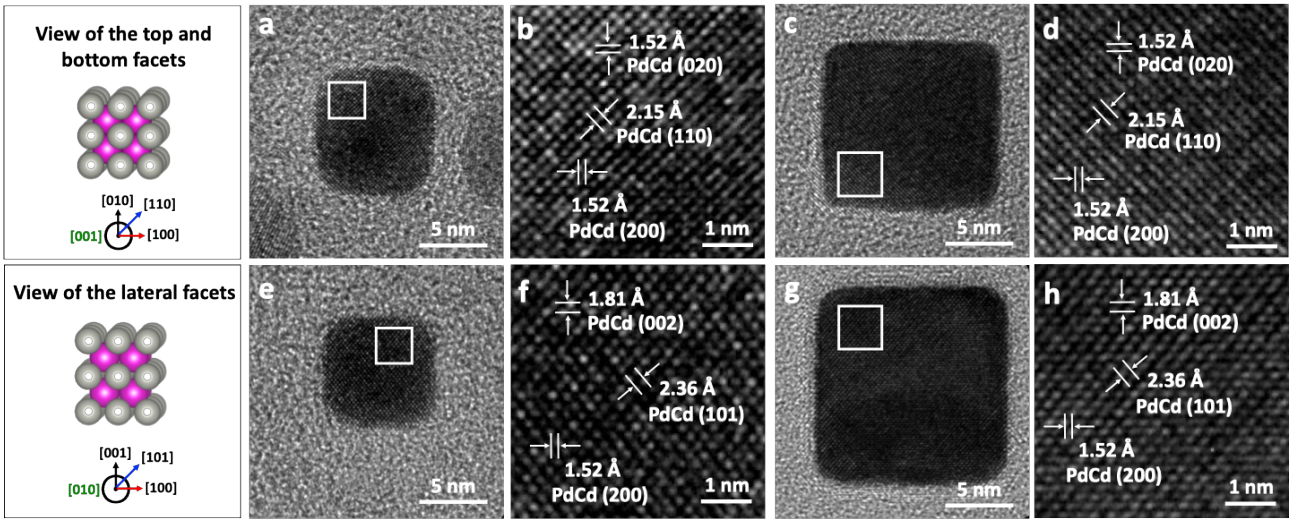

Figure S1. (a) HR-TEM image, (b) magnified HR-TEM image of the region within the white box in (a), showing the top view of a single intermetallic PdCd nanocube with the smallest size (~8 nm). (c) HR-TEM image, (d) magnified HR-TEM image of the region within the white box in (c), showing the top view of a single intermetallic PdCd nanocube with the largest size (~15 nm). (e) HR-TEM image, (f) magnified HR-TEM image of the region within the white box in (e), showing the side view of a single intermetallic PdCd nanocube with the smallest size (~8 nm). (g) HR-TEM image, (h) magnified HR-TEM image of the region within the white box in (g), showing the side view of a single intermetallic PdCd nanocube with the largest size (~15 nm).

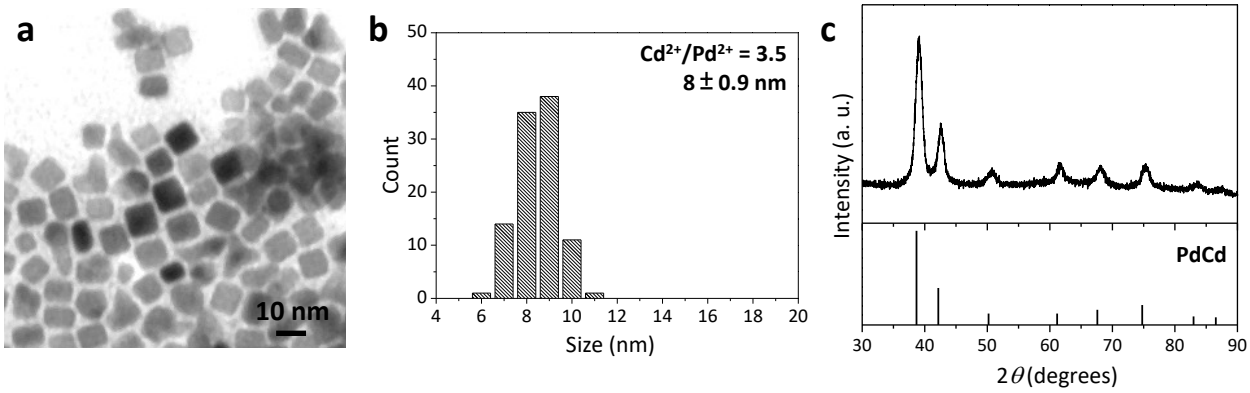

Figure S2. (a) TEM images, (b) the average size, and (c) XRD patterns of intermetallic PdCd nanocubes synthesized with an increased molar ratio of Cd^{2+}/Pd^{2+} to 3.5.

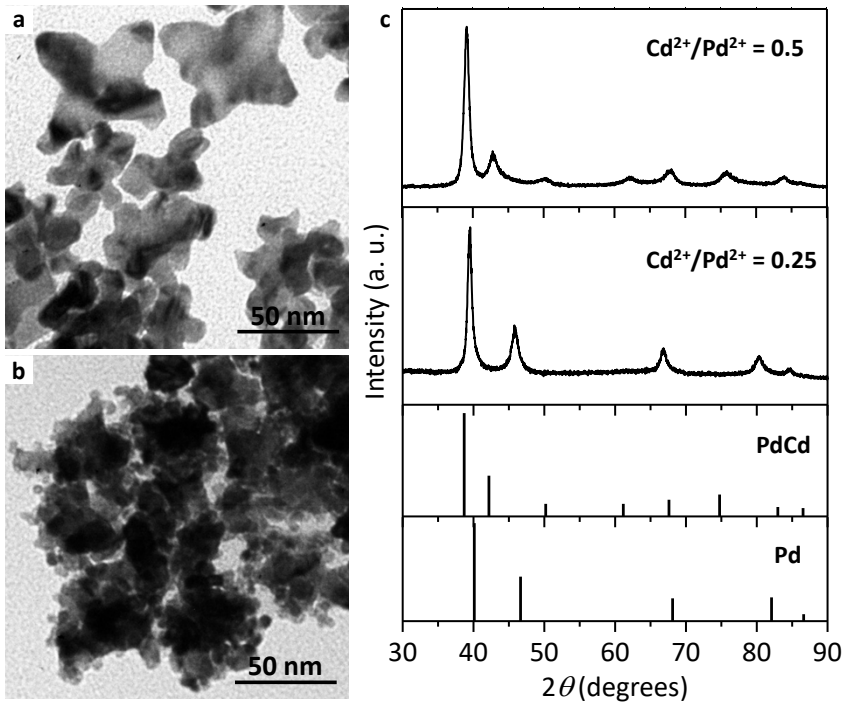

Figure S3. (a, b) TEM images and (c) XRD patterns of intermetallic PdCd nanocubes synthesized with decreased molar ratios of Cd^{2+}/Pd^{2+} to (a) 0.5 and (b) 0.25.

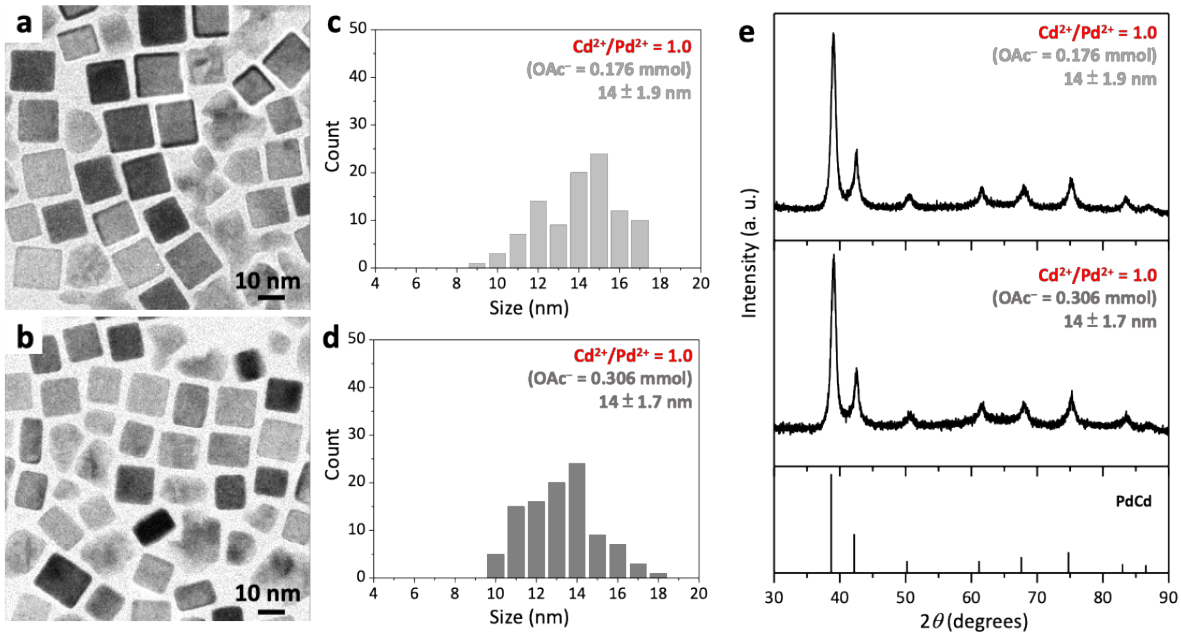

Figure S4. (a, b) TEM images, (c, d) average sizes, and (e) XRD patterns of PdCd nanocubes with acetate amounts: (a, c) 0.176 mmol (0.126 mmol additional sodium acetate + 0.050 mmol from Cd precursor) and (b, d) 0.306 mmol (0.256 mmol additional sodium acetate + 0.050 mmol from Cd

precursor). These conditions were applied for synthesizing the largest PdCd nanocubes (molar ratio Cd^{2+}/Pd^{2+} of 1.0, including 0.050 mmol of acetate).

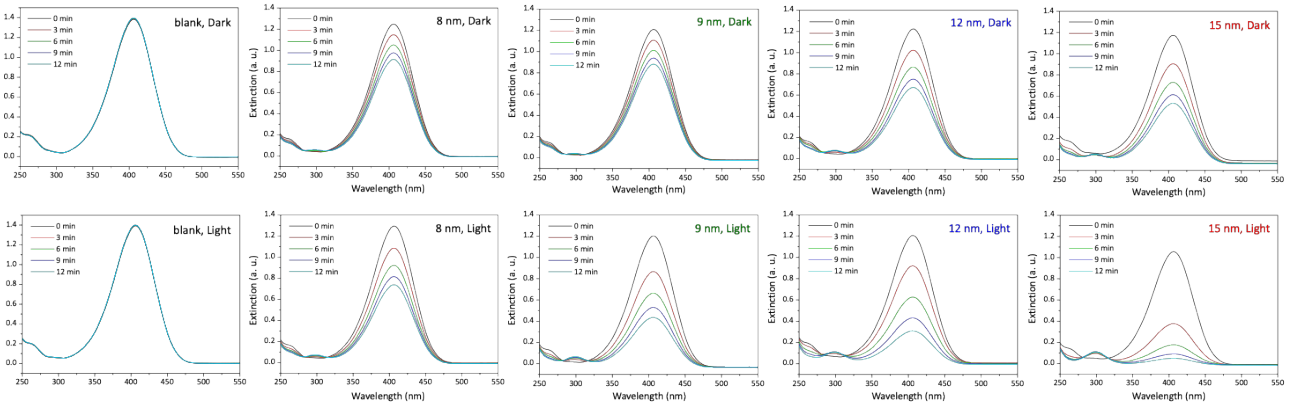

Figure S5. UV-vis spectra of 4-nitrophenol reduction reactions catalyzed by intermetallic PdCd nanocubes with sizes of 8, 9, 12, and 15 nm, as well as a control reaction with no catalyst, recorded under both dark and illuminated conditions.

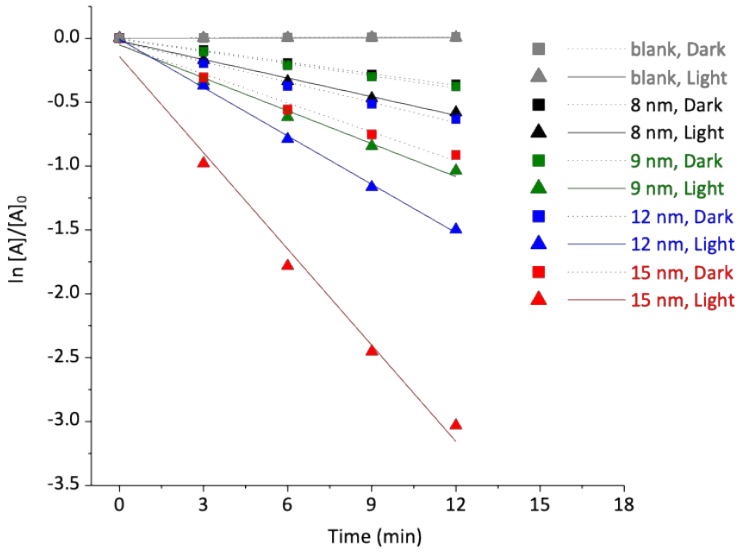

Figure S6. The plot of $\ln(A/A_0)$ against time for the 4-nitrophenol reduction reactions catalyzed by intermetallic PdCd nanocubes with sizes of 8, 9, 12, and 15 nm, as well as a control reaction with no catalyst. The dashed lines indicate the reactions conducted in the dark, while the solid lines represent those conducted under illumination.