Supporting Information for

Quantitative Analysis of the Coverage Density of Br^- Ions on Pd{100} Facets and Its Role in Controlling the Shape of Pd Nanocrystals

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Experimental section

Chemicals and Materials. Ethylene glycol (EG) was purchased from J. T. Baker. Sodium tetrachloropalladate (Na_2PdCl_4), L-ascorbic acid (AA), citric acid (CA), formaldehyde (HCHO), poly(vinyl pyrrolidone) (PVP, $M_W \approx 55{,}000$), potassium chloride (KCl), and potassium bromide (KBr) were all purchased from Sigma-Aldrich. All chemicals were used as received without further purification. Deionized (DI) water with a resistivity of 18.2 MΩ·cm was used for preparing all aqueous solutions.

Synthesis of Pd Nanocubes with Various Sizes. The Pd nanocubes with three different edge lengths of 7.5, 10.5, and 18 nm were synthesized using a recently reported protocol with minor modifications.[1] In a typical synthesis, 8 mL aqueous solution containing PVP (105 mg), AA (60 mg), and different amounts of KBr and KCl were added into a 20 mL vial. The solution was pre-heated at 80 °C for 5 min before the addition of 3 mL Na_2PdCl_4 aqueous solution (64.6 mM). The addition of KBr and KCl in the following amounts gave the nanocubes with edge lengths of 7.5 nm (75 mg of KBr and 141 mg of KCl), 10.5 nm (300 mg of KBr), and 18 nm (600 mg of KBr), respectively. Each reaction was then allowed to proceed at 80 °C for 3 h. After the removal of excess PVP and KBr/KCl by centrifuging and washing four times with water, the final product was dissolved with concentrated HNO_3 for the ICP-MS analysis.

Synthesis of Pd Nanocrystals with Different Shapes. The Pd nanocrystals with different shapes, including truncated cube, cuboctahedron, truncated octahedron, and octahedron, were synthesized based on our previously established protocol.[2] Typically, 0.3 mL of an aqueous suspension of the 18-nm Pd nanocubes (1.8 mg/mL in concentration) and 8 mL of an aqueous solution containing PVP (105 mg) and HCHO (100 μL) were added into a 20 mL vial. After the mixture of reagents had been heated at 60 °C for 10 min, 3 mL of aqueous solution containing

different amounts of Na_2PdCl_4 was introduced. With the increase of the amount of Na_2PdCl_4, the shape of resultant Pd nanocrystals evolved from nanocubes to truncated cubes (5.8 mg), cuboctahedrons (8.7 mg), truncated octahedrons (17.4 mg), and octahedrons (29.0 mg). The reaction mixture was then allowed to proceed at 60 °C for 3 h. During the entire synthesis, the vial was capped except during the addition of reagents. The product was collected by centrifuging and washing with DI water four times before further characterization.

Synthesis of Pd Nanocrystals with the Introduction of a Specific Amount of Br^- Ions. In a standard synthesis, 4 mL aqueous solution containing PVP (53 mg), AA (30 mg), and different amounts of KBr (0 mg for the control synthesis, 0.87 mg for the truncated cubes, 1.75 mg for the perfect cubes, respectively) were added into a 20 mL vial. The solution was pre-heated at 40 °C for 5 min. Next, 1.5 mL of an aqueous solution containing Na_2PdCl_4 (28.5 mg) was added. The reaction mixture was allowed to proceed at 40 °C for 2 h. During the entire synthesis, the vial was capped except during the addition of reagents. After centrifuging and washing with DI water three times, the samples were characterized by transmission electron microscopy (TEM). Note that the minimum amount of Br^- for capping all the Pd{100} facets was calculated based on the coverage density and the critical value of KBr was found to be 1.74 mg for this protocol.

Removal of Chemisorbed Br^- Ions from the Surface of Pd Nanocubes. Removal of surface-chemisorbed Br^- ions was conducted for the 18-nm Pd nanocubes under a mild reductive condition. Typically, 0.2 mL of an aqueous suspension of the 18-nm Pd nanocubes was introduced into 3 mL DI water or EG containing PVP (30 mg) and CA (30 mg) hosted in a vial and then capped. The mixtures were then aged at different temperatures for 18 h. After centrifuging and washing with water three times, the product was collected for further analysis.

Characterization. The transmission electron microscope (TEM) images were taken using a

JOEL (JEM-1400) microscope operated at 120 kV. The samples for TEM analysis were prepared by drying a drop of the nanocrystals suspension onto carbon-coated copper grids. The X-ray photoelectron microscopy (XPS) data were collected using Thermo K-Alpha photoelectron spectrometer with an Al Kα source. The samples for inductively coupled plasma mass spectroscopy (ICP-MS) analysis were prepared by dissolving the nanocrystals with concentrated HNO_3 and further diluted with 1% HNO_3 solution to a level of 100 ppb.

Calculation of the Br^- Ion Coverage Density on the Pd{100} Facets and the Br^- to Surface Pd Atom Ratio. Based on the ratio of Br^- ions to all Pd atoms obtained from ICP-MS analysis, the Br^- ion coverage density was calculated according to the equation:

$$\frac{Br^-}{total\ Pd} = \frac{Pd\ cube\ surface\ area\ (nm^2) \times Br^-\ coverage\ density\ \left(\frac{ions}{nm^2}\right)}{number\ of\ Pd\ atoms\ per\ cube}$$

$$= \frac{6 \cdot l^2 \cdot \phi_{Br}}{4 \cdot \left(\frac{l^3}{a^3}\right)}$$

$$= \frac{3}{2} \cdot \frac{a^3 \cdot \phi_{Br}}{l}$$

Rearranging the equation gives

$$\phi_{Br} = \frac{2}{3} \cdot \frac{l}{a^3} \cdot \left(\frac{Br^-}{total\ Pd}\right)$$

Where *l* is the average edge length of Pd nanocubes (7.5 nm, 10.5 nm, or 18 nm); *a* is the lattice constant of Pd (0.389 nm); and ϕ_{Br} is the Br^- coverage density. It is worth pointing out that the sub-10-nm Pd nanocubes prepared using the present protocols generally have a rectangle cross section with an aspect ratio of 1.0-1.2. As a result, the average edge length of nanocubes was used to minimize the effect of variation in edge length for the calculation.

With the information of Br^- ion coverage density, the ratio between Br^- ions to surface Pd atoms was calculated by the following equation:

$$\frac{Br^-}{surface\ Pd} = \frac{Pd\ cube\ surface\ area\ (nm^2) \times Br^-\ coverage\ density\ \left(\frac{ions}{nm^2}\right)}{number\ of\ Pd\ atoms\ on\ the\ surface\ of\ cube}$$

$$= \frac{6 \cdot l^2 \cdot \phi_{Br}}{6 \cdot \left[2 \cdot \left(\frac{l^2}{a^2}\right)\right]}$$

$$= \frac{a^2 \cdot \phi_{Br}}{2}$$

Calculation of the Amount of Br^- Ions Needed for Generating Perfect Pd Nanocubes. Based on the Br^- ion coverage density information, the minimum ratio between Br^- ions to Pd precursor molecules for generating perfect Pd nanocubes was calculated according to the following equation:

$$\frac{Br^- \cdot \varphi_{Br}}{(total\ Pd) \cdot \varphi_{Pd}} = \frac{3}{2} \cdot \frac{a^3 \cdot \phi_{Br}}{l}$$

Where *l* is the particle size (6 nm) of Pd nanocrystals involved in the control synthesis (with no Br^-); φ_{Br} and φ_{Pd} are the yield of Pd (98.4%) and the ratio of Br^- ions adsorbed on the Pd surface (95.3%) under this experimental condition as determined by ICP-MS; amount of Pd precursor used in the synthesis was 0.0969 mmol (28.5 mg of Na_2PdCl_4); and ϕ_{Br} is the bromide coverage density determined in this work: ~10 ions/nm^2. By plugging these parameters into the equation, the critical value of Br^- ions was found to be 0.0146 mmol or 1.74 mg of KBr.

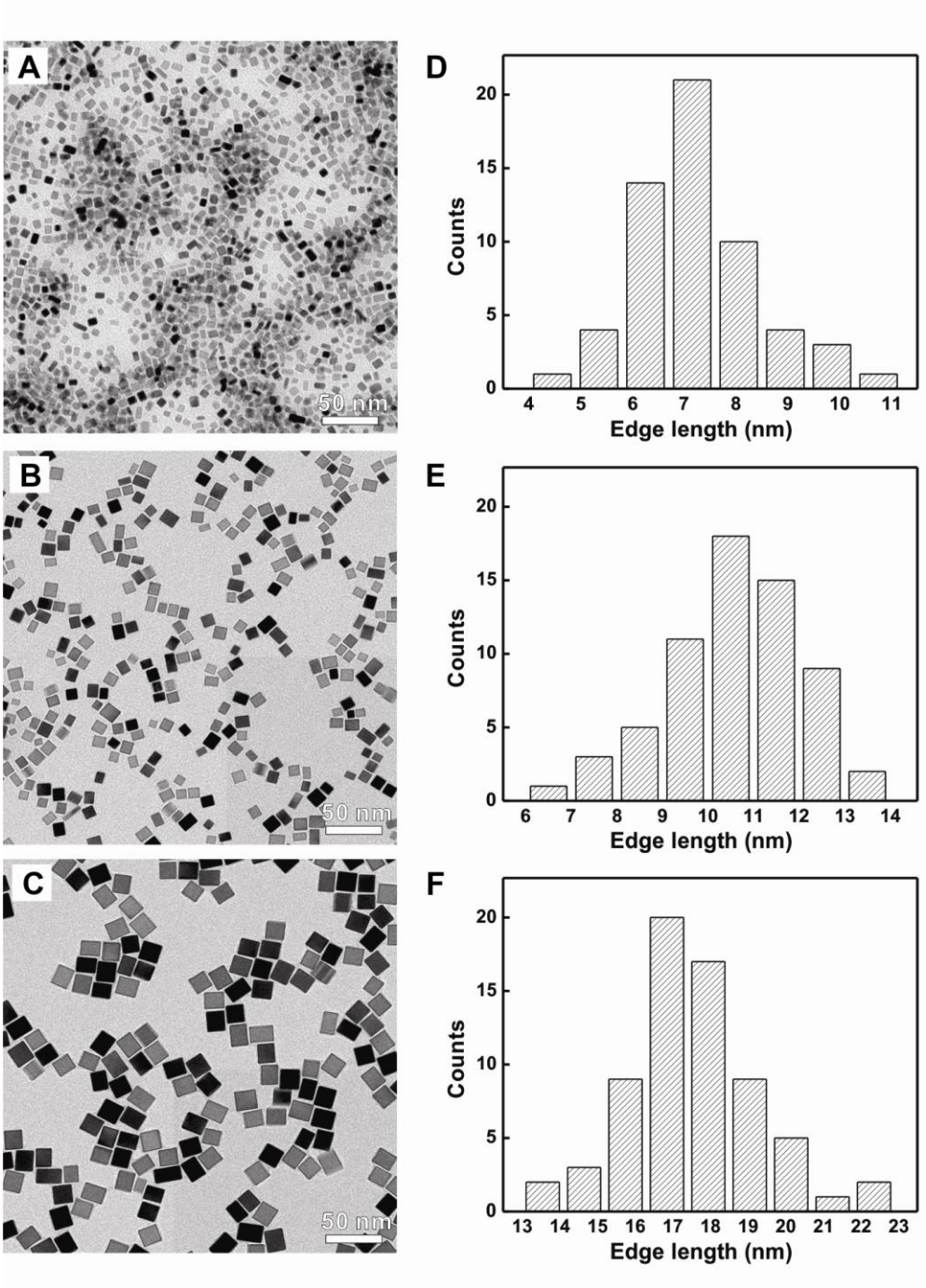

Figure S1. TEM images of Pd nanocubes with edge lengths of (A) 7.5 nm, (B) 10.5 nm, and (C) 18 nm, respectively; (D-F) The corresponding statistical analysis of size distribution for each sample.

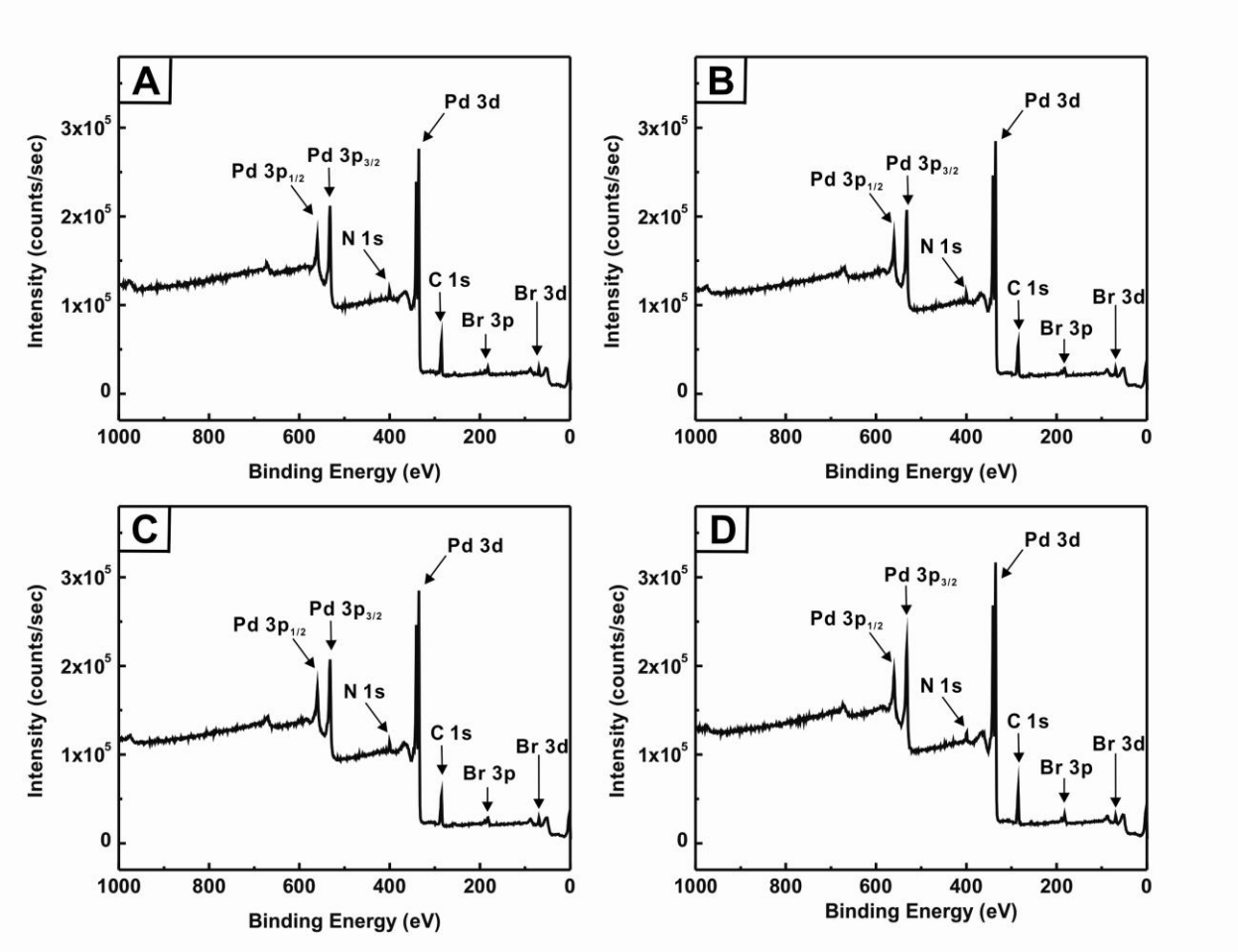

Figure S2. XPS survey spectra of Pd nanocubes (18 nm in edge length) that had been washed (A) 3, (B) 4, (C) 6, and (D) 8 times with DI water.

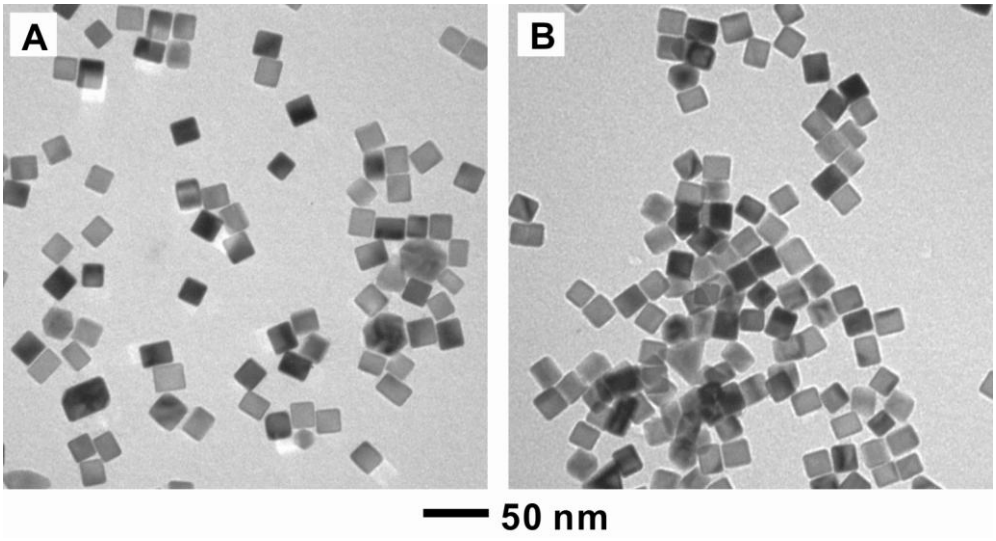

Figure S3. TEM images of Pd nanocubes (18 nm in edge length) that had been aged at (A) 80 ^{o}C and (B) 100 °C, respectively, for 18 hours.

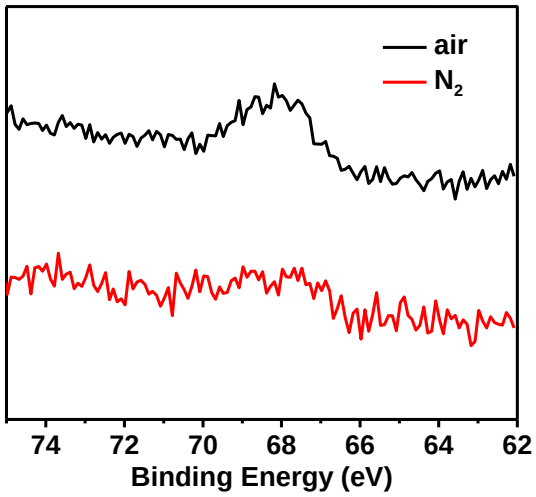

Figure S4. Br 3d XPS spectra taken from the Br^--free 18-nm Pd nanocubes after they had been subjected to aging in aqueous KBr solution (10 mM) under air or N_2 atmosphere for 3h.

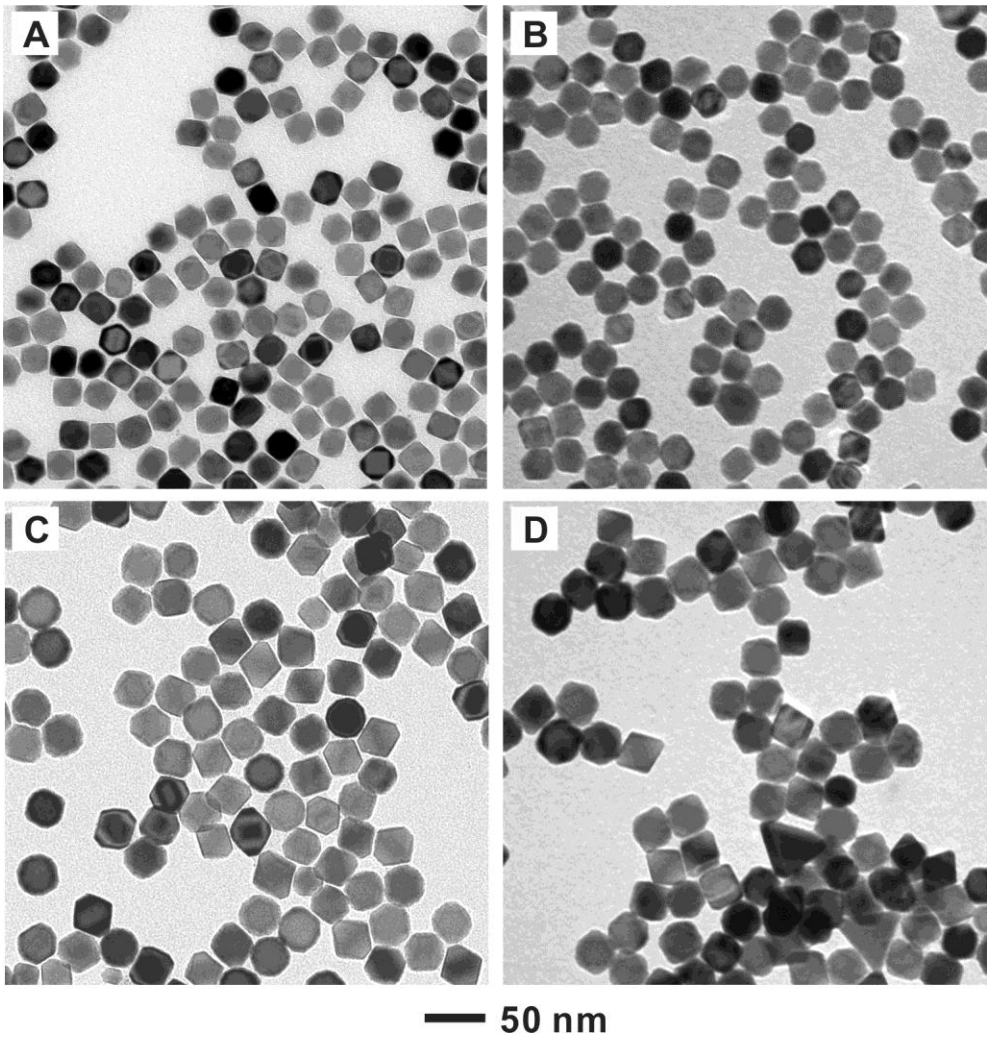

Figure S5. TEM images of Pd nanocrystals with different shapes: (A) truncated cubes, (B) cuboctahedrons, (C) truncated octahedrons, and (D) octahedrons.

References

(1) Jin, M.; Liu, H.; Zhang, H.; Xie, Z.; Liu, J.; Xia, Y. *Nano Res.* **2011**, *4*, 83.

(2) Jin, M.; Zhang, H.; Xie, Z.; Xia, Y. *Energy Environ. Sci.* **2012**, *5*, 6352.