Electronic Supplementary Information (ESI) for

The effect of surface capping on the diffusion of adatoms in the synthesis of Pd@Au core-shell nanocrystals

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Experimental Section

Chemicals and materials. Sodium tetrachloropalladate (II) (Na_2PdCl_4, 99.998%), gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, ≥99.9%), poly(vinyl pyrrolidone) (PVP, MW ≈ 55 000) and ascorbic acid (AA) were obtained from Sigma-Aldrich. Potassium bromide (KBr) was obtained from Fisher Scientific. Ethylene glycol (EG) was obtained from J.T. Baker. All chemicals were used as received without further purification. The water used in experiments was de-ionized with a resistivity of 18.2 MΩ·cm.

Preparation of Br^- capped 18-nm Pd cubic seeds. The Pd nanocubes were synthesized by adding a Na_2PdCl_4 solution into a mixture of AA, KBr, and KCl according to our previous report.[1] In a typical synthesis, an 8.0 mL aqueous solution containing 105 mg of PVP, 60 mg of AA, and 600 mg of KBr was hosted in a vial and preheated to 80 °C in an oil bath under magnetic stirring for 10 min. Subsequently, a 3.0 mL aqueous solution containing 57 mg of Na_2PdCl_4 was added with a pipette. After the vial had been capped, the reaction was allowed to continue at 80 °C for 3 h. The product was collected by centrifugation, washed three times with water, and then re-dispersed in 11 mL water.

Preparation of capping-free 18-nm Pd cubic seeds. The capping-free nanocubes were obtained by directly removing the surface-chemisorbed Br^- ions from the 18-nm Pd nanocubes by subjection to a mild reductive condition.[2] In a typical synthesis, 0.2 mL of an aqueous suspension of the 18-nm Pd nanocubes was introduced into 3 mL of EG containing 30 mg of PVP and 30 mg of CA. The mixture was hosted in a vial and then capped and aged at 100 °C for 18 h. The product was then collected after centrifuging and washing with water three times.

Preparation of core-shell Pd@Au nanocrystals. In a standard synthesis, 18-nm cubic Pd seeds (0.03 mL) were introduced into an 8.0 mL aqueous solution containing 60 mg of AA and 105 mg of PVP hosted in a 25 mL three-necked flask equipped with a reflux condenser. The obtained suspension was then aged at 60 °C for 10 min under magnetic stirring. Afterwards, 3.0 mL of an aqueous $HAuCl_4$ solution (0.4 μmol/mL) was injected into the suspension using a syringe pump. The reaction was allowed to continue for another 10 min post injection. The morphology of Pd@Au nanocrystals was controlled by varying the injection rate of $HAuCl_4$ solution. The product was collected after centrifuging and washing with water three times.

Instrumentations. Transmission electron microscope (TEM) images were taken using a Hitachi HT7700 TEM operated at 120 kV. High-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), and energy-dispersive X-ray (EDX) spectroscopy analyses were performed on an aberration corrected FEI Titan 80/300 kV TEM/STEM operated at 300 kV and an aberration-corrected JEOL 2200FS electron microscope equipped with a Bruker-AXS silicon drift detector detector. The X-ray photoelectron spectroscopy (XPS) data were recorded using a Thermo K-Alpha spectrometer with an Al Kα source (1468.6 eV) (Thermo Fisher Scientific, Waltham, MA). The samples for XPS analysis were prepared by drying drops of the suspensions on silicon substrates.

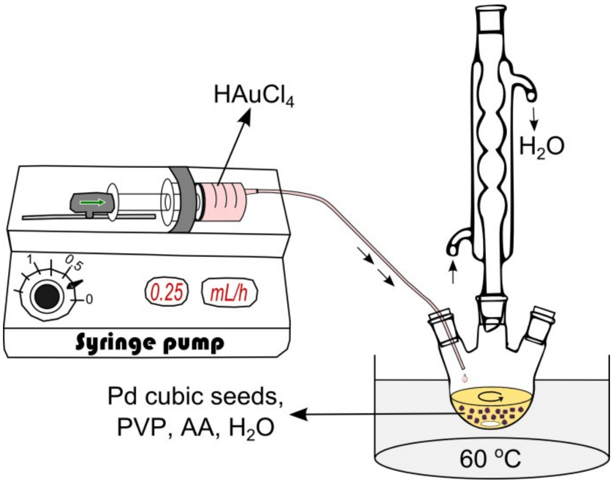

Figure S1. Schematic illustration of the experimental setup used for all seed-mediated syntheses where the rate of Au precursor addition was controlled by a syringe pump.

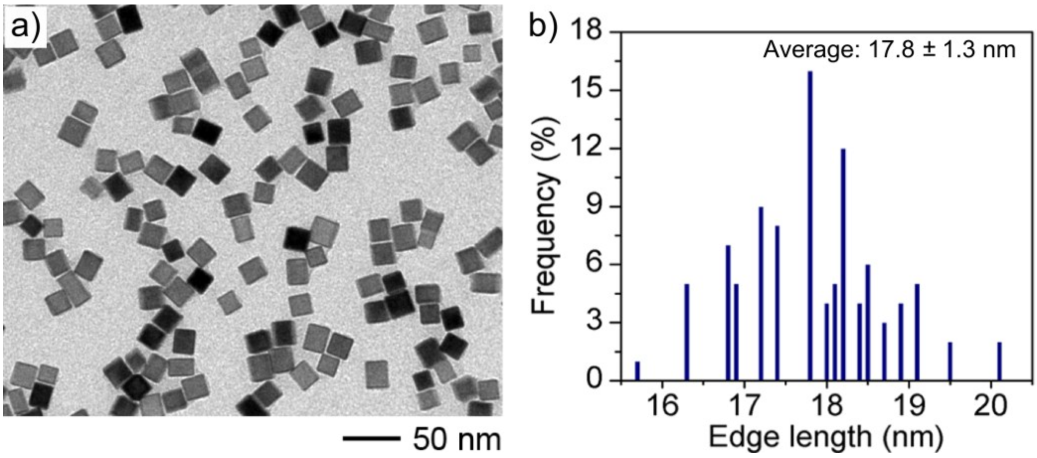

Figure S2. a) TEM image of the as-prepared Br$^-$ capped Pd cubic seeds and corresponding b) Histogram of the particle size distribution.

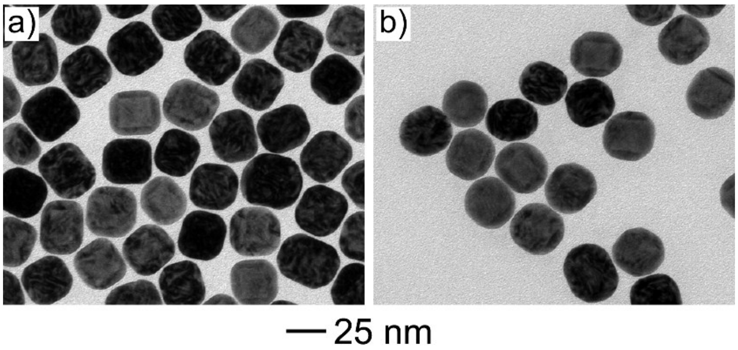

Figure S3. TEM images of Pd@Au core-shell nanocrystals obtained under different reaction conditions. (a) Structures produced using a similar protocol to the product shown in Fig. 2f except the reaction time was extended to 12 h. (b) The same Pd@Au nanocubes shown in Fig. 2f but after one month of aging at room temperature.

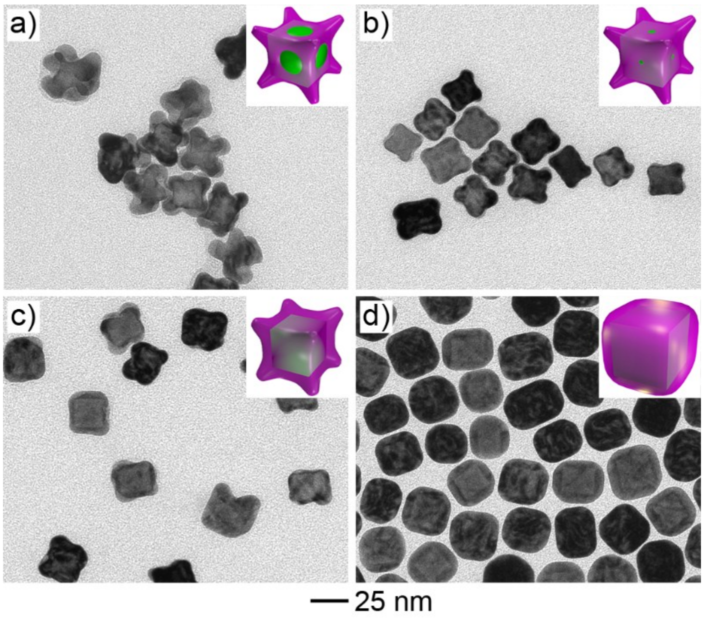

Figure S4. TEM images of Pd@Au nanocrystals obtained in a standard synthesis with Au precursor injected into the reaction solution at rates of a) 0.1 mL/h, b) 1 mL/h, c) 10 mL/h, and d) one-shot rapid injection.

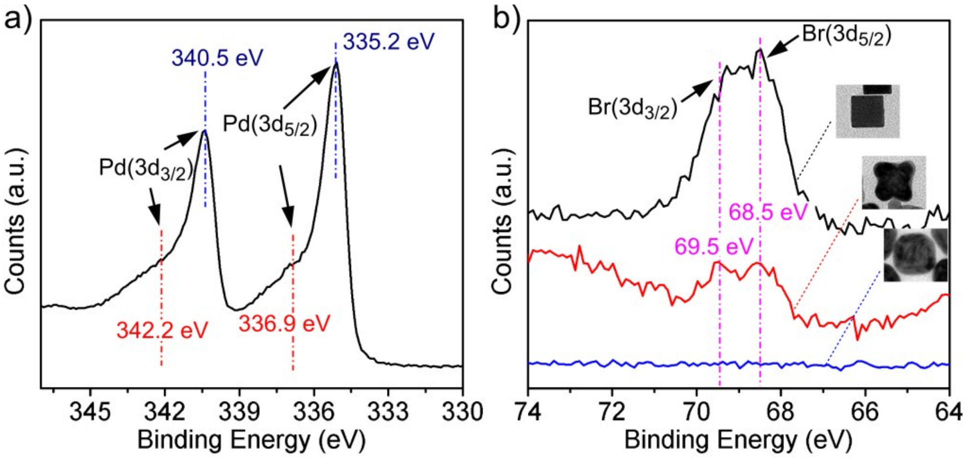

Figure S5. XPS spectra of Br⁻ capped Pd nanocubes and Pd@Au core-shell nanocrystals. a) XPS spectrum of Pd (3d) obtained from the Pd nanocubes, and b) XPS spectra Br (3d) obtained from the capped Pd nanocube seeds, Pd@Au core-shell concave nanocubes, and Pd@Au core-shell nanocubes with flat surfaces, respectively.

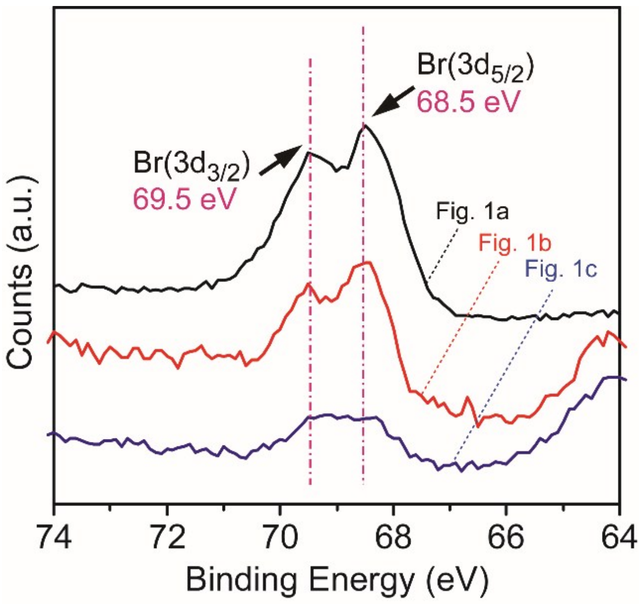

Figure S6. XPS spectra of structures derived from the slow-injection growth regime. Spectra were measured from structures seen in Figure 1a (black), 1b (red), and 1c (blue). Spectral signatures from Br^{-} were detected at all stages of growth.

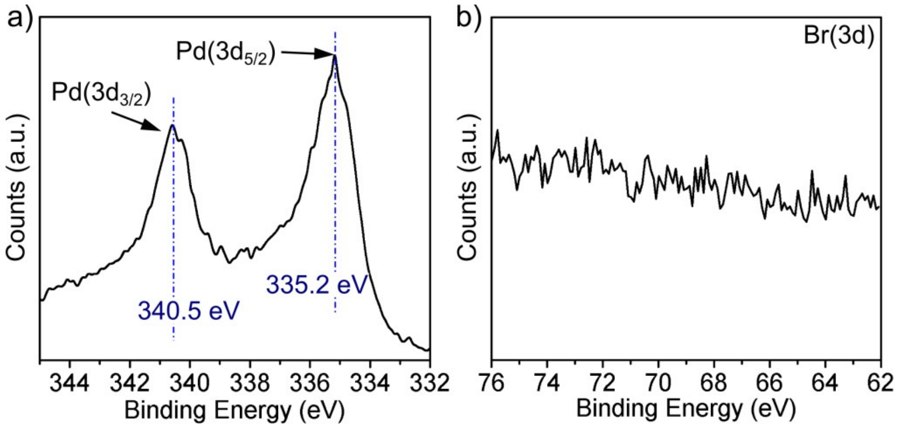

Figure S7. XPS spectra of a) Pd (3d) and b) Br (3d) that were collected from Pd nanocube seeds after removal of bromide ions. Spectral signatures from Pd^{2+} and Br^{-} were not detected.

Table S1. Dissociation constant (*K*) at 25 °C and 100 kPa for Au(III) halide complexes. All reactions are for dissociation to Au^{3+}, Cl^-, Br^-.[3]

Complex	$[AuCl_4]^-$	$[AuCl_3Br]^-$	$[AuBr_4]^-$	$[AuClBr_3]^-$	$[AuBr_4]^-$
K	$10^{-25.20}$	$10^{-27.43}$	$10^{-29.46}$	$10^{-31.03}$	$10^{-33.34}$

References

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