

Surfactant-Directed Fabrication of Supercrystals from the Assembly of Polyhedral Au–Pd Core–Shell Nanocrystals and Their Electrical and Optical Properties

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EXPERIMENTAL SECTION

Chemicals. Hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.9%, Aldrich), PdCl_2 powder (UniRegion Bio-Tech), silver nitrate (AgNO_3 , 99.8%, Showa), cetyltrimethylammonium chloride (CTAC, 95%, TCI), cetyltrimethylammonium bromide (CTAB, 98%, Alfa Aesar), trisodium citrate dihydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, 99%, MACRON), ascorbic acid (AA, 99.7%, Sigma-Aldrich), lead acetate ($\text{Pb}(\text{CH}_3\text{COO})_2$, Alfa Aesar), thioacetamide (TAA, Sigma-Aldrich), nitric acid (HNO_3 , Fluka) were used as received. Ultrapure distilled and deionizes water (18.3 M Ω) was used for all solution preparations.

Growth of Au–Pd Core–Shell Truncated Cubes to Octahedra. To grow Au–Pd core–shell truncated cubes, cuboctahedra, truncated octahedra, and octahedra, 8.80, 8.58, 9.07, and 8.90 mL of deionized water and 0.33, 0.33, 0.055, and 0.33 g of CTAB were added to glass vials, followed by the introduction of 200, 500, 500, and 500 μL of 35-nm gold octahedra, respectively. Next, 0.5, 0.7, 0.3, and 0.3 mL of 10 mM H_2PdCl_4 solution was added to the vials. Then 500, 220, 130, and 300 μL of 0.1 M ascorbic acid was added and the solutions were kept in a water bath set at 50 °C for the growth of Pd shells for 2 h. The reaction was stopped by centrifugation at 6000 rpm for 10 min. The reaction conditions have been previously described.¹⁷

Formation of Supercrystals by Droplet Evaporation Technique. The volume of final nanocrystal colloidal solution was 10 mL with a CTAC or CTAB concentration of 0.1 M. Then 10 mL of water was added to reduce the surfactant concentration to 5×10^{-2} M and the solution was centrifuged. The solution with 30–40 nm nanocrystals was centrifuged at 9000 rpm for 10 min, while 40–65 nm nanocrystals were centrifuged at 6500 rpm for 10 min. Next, the top solution in the centrifuge tube was carefully removed to leave behind just approximately 50 μL of

the concentrated particle solution, and then 50 μL of the concentrated particle solution was withdrawn and transferred to a small Eppendorf tube.

We used various polyhedral nanocrystals to form supercrystals in a saturated moist atmosphere by using a simple drop-casting method at different temperatures (60, 90, and 110 $^{\circ}\text{C}$). First, 1 μL of the colloidal solution was added to a clean silicon wafer ($\sim 2.5\text{ mm} \times 2.5\text{ mm}$). The substrate was placed over an inverted vial cap, which was placed on top of a 5-mL vial filled with 4 mL of water to prevent the vial from tilting.² The 5-mL vial was placed inside a 50-mL vial with 15 mL of water added to provide a moist environment. The vial was placed in an oven set at 60, 90, or 110 $^{\circ}\text{C}$ to slowly evaporate the droplet. The drying time is 3 h. Supercrystals formed on the wafer.

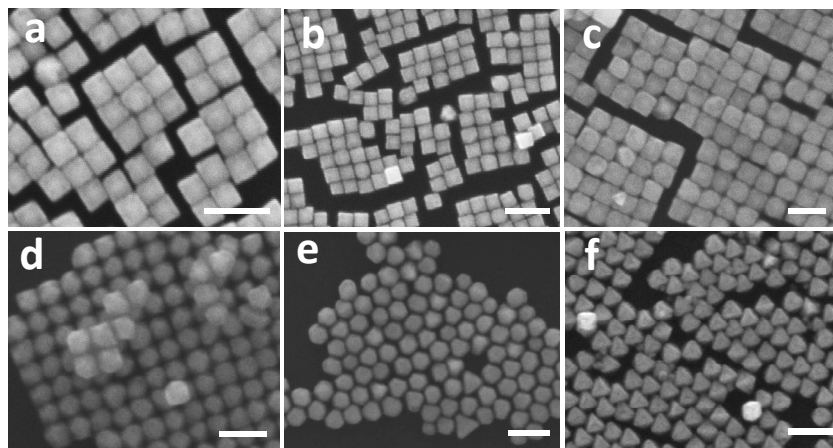


Figure S1. SEM images of the synthesized Au-Pd core-shell (a) cubes using CTAC surfactant, (b) cubes using CTAB surfactant, (c) truncated cubes, (d) cuboctahedra, (e) truncated octahedra, and (f) octahedra using 35-nm octahedral gold cores. Some images are identical to those shown in ref. 17. Scale bar is equal to 100 nm.

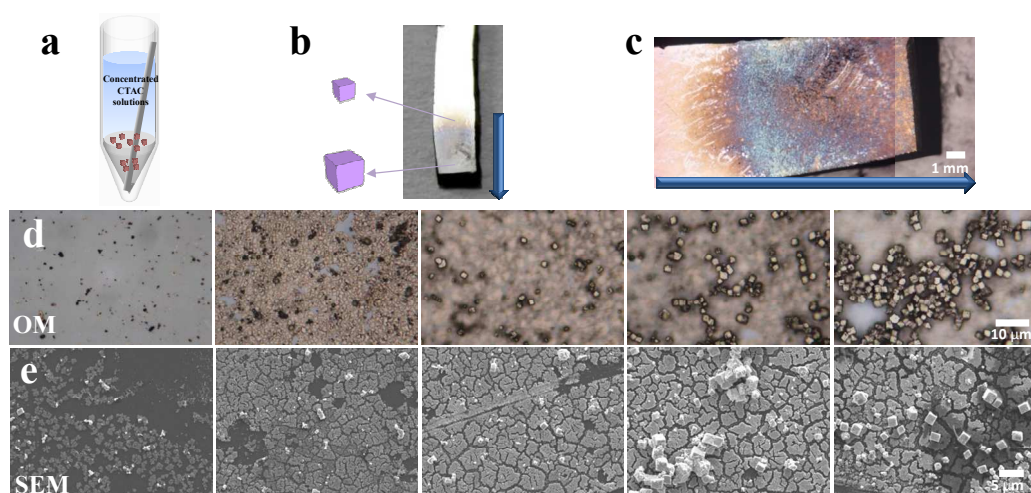


Figure S2. Examination of cubic supercrystals deposited on a silicon substrate using the surfactant diffusion method. (a) The scheme illustrates the setup for growing supercrystals through surfactant diffusion with a Si wafer inserted. (b, c) Optical micrographs of the substrate. The various colors of the reflected light indicate different amounts of nanocrystal deposition and supercrystal aggregation. Because of the large substrate size, the entire substrate is presented by combining two images. This gives a sharp line observed on the substrate and background. (d) Optical micrographs of 3D supercrystals and 2D layers on the silicon substrate. Left to right panels correspond to the arrows in panels b and c with increasingly larger supercrystals. (e) SEM images of 3D supercrystals and 2D layers on the silicon substrate.

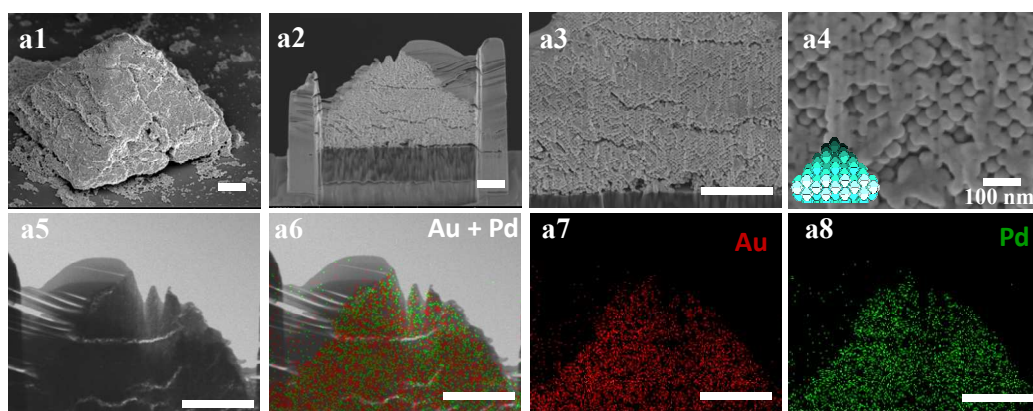


Figure S3. (a1) SEM, (a2–a4) cross-sectional SEM, and (a5) STEM images of a pyramidal supercrystal assembled by Au–Pd octahedra. The Pt columns are used to support the supercrystal before FIB milling. Some interior nanocrystals appear to fuse as a result of FIB slicing. (a6–a8) EDS elemental mapping images. All scale bars are equal to 1 μm .

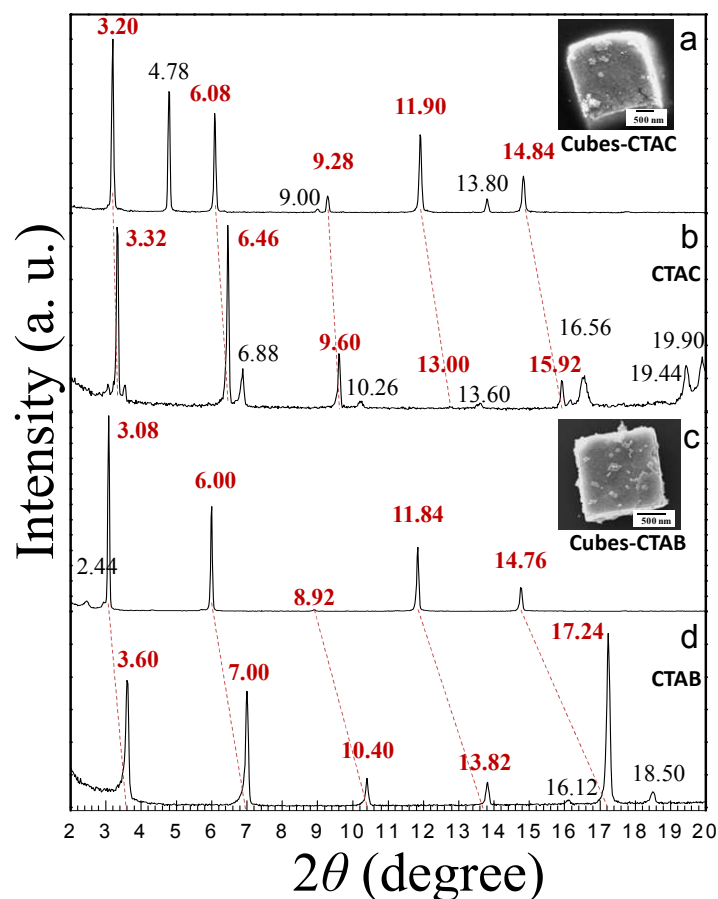


Figure S4. Low-angle XRD patterns of (a) cubic Au–Pd supercrystals assembled in the presence of CTAC, (b) dried CTAC, (c) cubic Au–Pd supercrystals assembled in the presence of CTAB, and (d) dried CTAB. The first-order peak should be present below 2° 2θ . Peak connections between supercrystals and surfactants are marked.

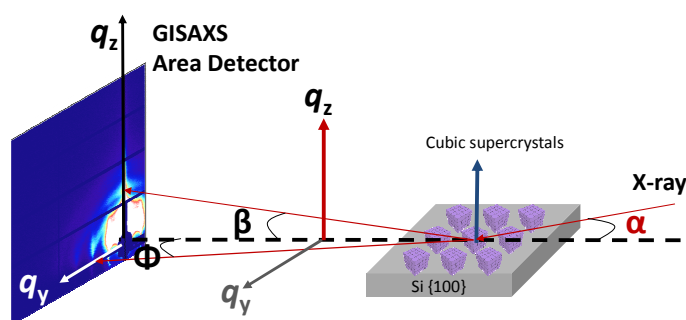


Figure S5. Schematic of the setup for synchronized grazing-incidence small-angle X-ray scattering (GISAXS) with the X-ray beam incident angle α and the scattering angles β and Φ in the out-of-plane (q_z) and in-plane (q_y) directions to capture detailed structure information of cubic supercrystals.

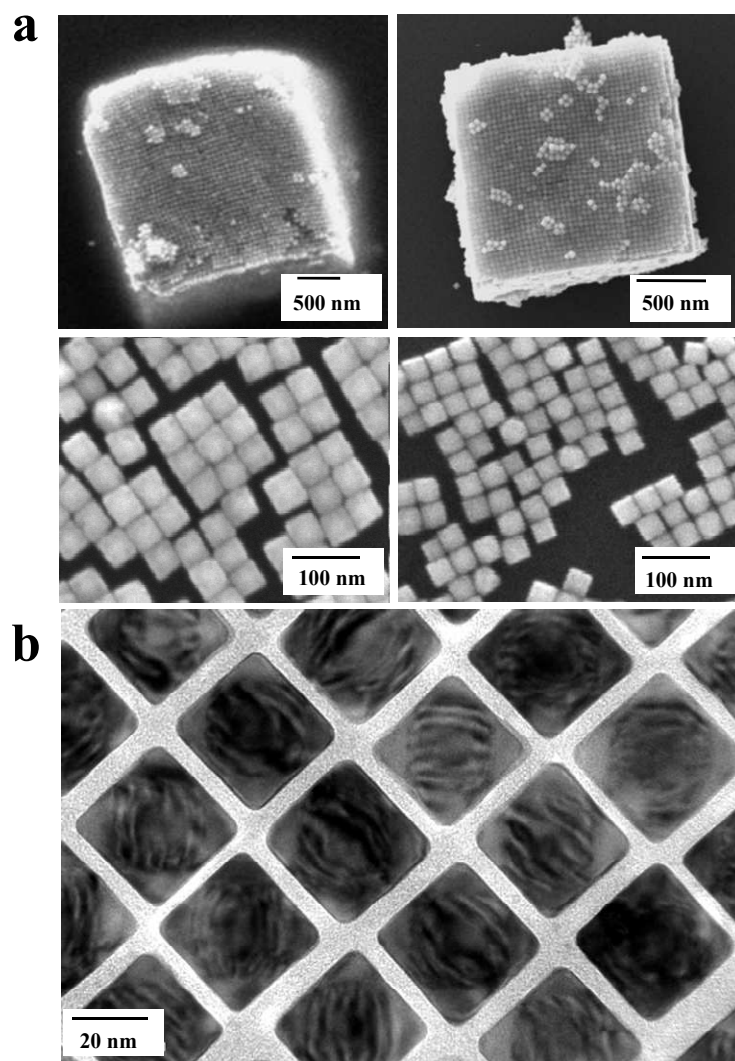


Figure S6. (a) SEM images of a cubic Au–Pd supercrystal assembled by 40-nm cubes in the presence of CTAC (left) and a Au–Pd supercrystal assembled by 30-nm cubes in the presence of CTAB (right). SEM images of the dispersed Au–Pd nanocubes are also shown. (b) TEM image of well-assembled 30-nm Au–Pd core–shell nanocubes separated by the CTAB bilayer of roughly 6.5 nm in most cases.

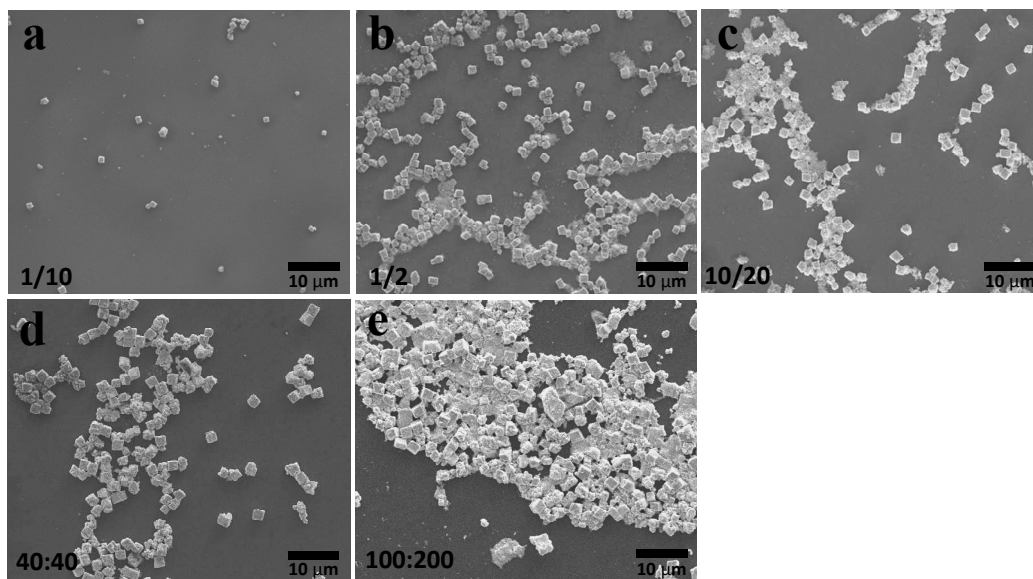


Figure S7. Large-scale SEM images of the synthesized cubic supercrystals with size control by (a–c) adjusting the nanocrystal concentration in the solution through dilution, and by (d, e) varying the volumes of nanocrystal and surfactant solutions added.

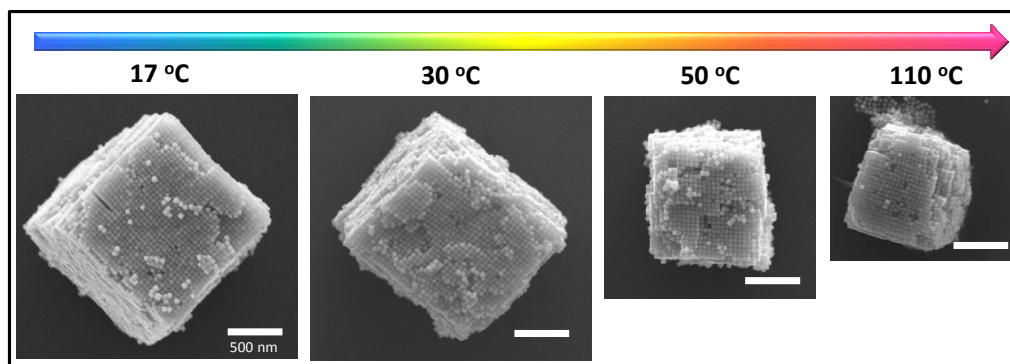


Figure S8. SEM images showing how solution temperature can be used to tune the size of supercrystals. Here 40-nm Au–Pd nanocubes were used to produce supercrystals by the surfactant diffusion method. All scale bars represent 500 nm.

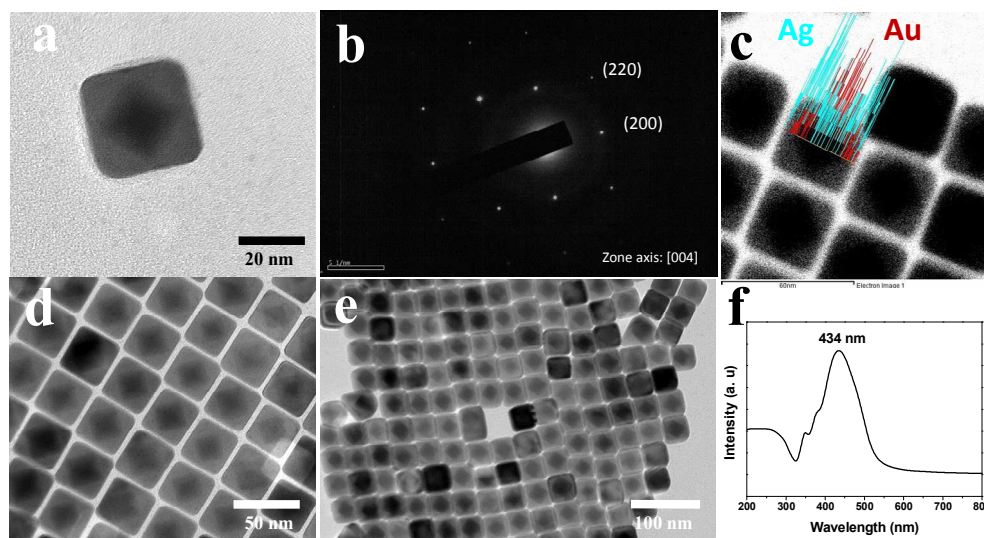


Figure S9. (a, b) TEM image and its corresponding SAED pattern of a single Au–Ag core–shell nanocube with an octahedral gold core. (c) STEM EDS line scan of a Au–Ag core–shell nanocube confirming the presence of a Au core. (d, e) TEM images of Au–Ag core–shell nanocubes viewed at different magnifications. (f) UV–vis spectrum of the Au–Ag core–shell nanocubes dispersed in deionized water.

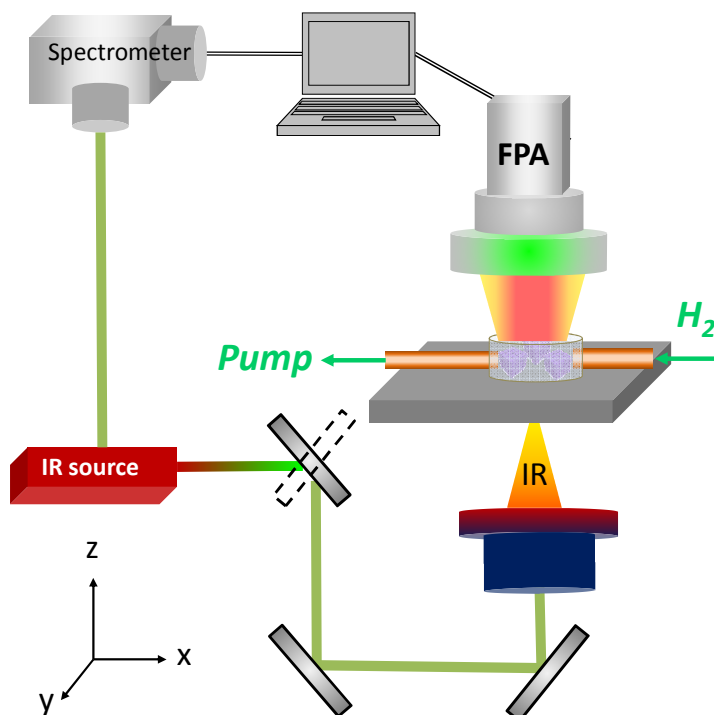


Figure S10. Experimental setup for taking IR transmittance spectra. The supercrystals are illuminated by an infrared light along the z direction. Hydrogen gas can pass through the sample chamber.