Au Nanocrystal-Directed Growth of Au–Cu2O Core–Shell Heterostructures with Precise Morphological Control

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Synthesis of Au nanocrystals:

(a) Au octahedra

Octahedral Au nanocrystals were prepared as described in ref. 26. For the hydrothermal synthesis of octahedral gold nanocrystals, 9.7 mL of ultrahigh purity water, 0.055 g of cetyltrimethylammonium bromide (CTAB), 250 μL of 0.01 M hydrogen chloroaurate (HAuCl4), and 50 μL of 0.05 M trisodium citrate were added to a glass vial with a Teflon-lined polypropylene cap and a volume capacity of 22.5 mL. The oven temperature was set at 110 °C. The sample vial was loaded into the oven and heated for 24 h or more after it had reached this temperature.

(b) highly-faceted Au nanoparticles

To prepare these faceted particles, a seed-mediated strategy was adopted. Seed solution was prepared by heating 50 mL of an aqueous solution containing trisodium citrate (6.8 × 10−3 M) and HAuCl4 (2.5 × 10−4 M) to boil for 5 min. A growth solution was made containing HAuCl4 (2.5 × 10−4 M) and cetyltrimethylammonium chloride (CTAC, 0.05 M). After the seed solution was cooled to room temperature (~27 °C), 1 mL of the seed solution was transferred into 9 mL of the growth solution after adding 0.1 mL of 0.04 M ascorbic acid. After mixing for several sec, 1 mL of this particle solution was transferred to another 9 mL of the growth solution with the addition of 0.1 mL of 0.04 M ascorbic acid to obtain these highly-faceted Au nanoparticles.

(c) Au nanorods

Au nanorods were synthesized following the procedure described in ref. 25. First, a gold seed solution was prepared by adding 0.35 mL of ice-cold NaBH4 (0.01 M) to 10 mL of a solution containing HAuCl4 (2.5 × 10−4 M) and CTAB (0.1 M). A growth solution was prepared by fully dissolving CTAB (1 × 10−2 mol) in 100 mL of HAuCl4 (2.5 × 10−4 M) aqueous solution at 27 °C. Next, two 25-mL and one...
100-mL conical flasks were labeled A, B, and C. In flasks A and B, 0.025 mL of ascorbic acid (AA, 0.1 M) was added to 4.5 mL of growth solution. In flask C, 0.25 mL of AA (0.1 M) and 0.3 mL of nitric acid (0.1 M) were added to 45 mL of growth solution. Next, 0.4 mL of the gold seed solution was added to the solution in flask A, and the sample was stirred for 3 s. Then 0.4 mL of the solution in flask A was immediately added to flask B, and the sample was stirred for 5 s. Finally, 4 mL of the solution in flask B was transferred to flask C, and the sample was stirred for 5 s. Flask C was left undisturbed in a water bath set at 26–27 °C for 12 h for the reaction to go to completion. The top solution contained mostly spherical nanoparticles and was removed, leaving only high aspect ratio Au nanorods that settled to the bottom of the flask as a precipitate. Then 10 mL of deionized water was added to redisperse the precipitate.

(d) Au plates

Au plates were synthesized by adopting the heating approach described in ref. 24 with modifications. First, 15 mL of an aqueous solution containing trisodium citrate (9.5 × 10⁻⁴ M) was heated to 85 °C under reflux in a water bath. Then 10 mL of an aqueous solution containing HAuCl₄ (1.25 × 10⁻³ M) and CTAC (0.01 M) was made and poured to the heated trisodium citrate solution without stirring. The mixture was kept in this reflux condition at 85 °C for 15 min. Finally, the solution was cooled to room temperature without any disturbance for 12 h. Brownish green precipitate can then be collected.
Figure S1. Representative SEM images of the Au nanocrystals synthesized for the fabrication of Au–Cu$_2$O core–shell heterostructures. (a) Octahedra, (b) highly-faceted particles, (c) nanorods, and (d) plates.
Figure S2. Detailed TEM characterization of the Au–Cu$_2$O core–shell heterostructures.  (a) TEM image of a Au–Cu$_2$O core–shell cuboctahedron viewed down the $<$111$>$ zone.  (b) SAED pattern of the circled region of the cuboctahedron.  (c) HRTEM image of the square region of the cuboctahedron showing sets of lattice fringes corresponding to the (110) planes of Cu$_2$O.  (d–f) TEM image, SAED pattern (the circled region), and HRTEM image (the square region) of a Cu$_2$O pentagonal prism with a penta-twinned gold nanorod core.  Lattice fringes corresponding to the (200) planes of Cu$_2$O were observed near one end of this pentagonal prism.  (g–i) TEM image, SAED pattern (the circled region), and HRTEM image (the square region) of a Au–Cu$_2$O microplate viewed down the [1 $\bar{1}$ 1] zone axis.  Clear lattice fringes corresponding to the (110) planes of Cu$_2$O were observed.
Figure S3. EDS line scans of the various Au–Cu₂O core–shell heterostructures. In all the cases, it can be clearly seen that the Au nanocrystals are located in the centers of the heterostructures. Intensities of the Cu signals are roughly twice as strong as those of the O signals. EDS analysis of the elemental distribution is consistent with the TEM images shown.
Figure S4. HAADF images and EDS elemental mapping images of the various Au–Cu$_2$O core–shell heterostructures. Spatial distribution of the Cu, O, and Au signals corresponds to the HAADF images.

Figure S5. Highly faceted gold nanocrystals-directed growth of Au–Cu$_2$O core–shell heterostructures synthesized by adding (a) 0.45 and (b) 0.65 mL of 0.2 M NH$_2$OH·HCl. These unusual morphologies were derived from the interpenetrated growth of truncated octahedra and octahedra, respectively.
Figure S6. Au–Cu$_2$O concave plates prepared with the addition of (a) 0.45, (b), 0.65, and (c) 0.85 mL of 0.2 M NH$_2$OH·HCl. No significant variation in the product morphology was observed. This is likely due to the large sizes of the Au plate cores that significant morphological changes with the volume changes of NH$_2$OH·HCl used did not happen.
Figure S7. A schematic illustration of the plausible formation process of the Au–Cu$_2$O core–shell heterostructures by a hollow-shell-refilled (HSR) mechanism. The shells and the cores are connected by Cu$_2$O bridges.