

An Investigation of the Effects of Polyhedral Gold Nanocrystal Morphology and Facets on the Formation of Au–Cu₂O Core–Shell Heterostructures

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Synthesis of Trisoctahedral, Rhombic Dodecahedral, and Edge- and

Corner-Truncated Octahedral Au Nanocrystals. The synthetic procedure for making trisoctahedral and rhombic dodecahedral Au nanocrystals follows our reported method.¹⁹

Synthesis of Gold Seeds. A volume of 10 mL aqueous solution containing 2.5×10^{-4} M HAuCl₄ and 0.10 M CTAC was prepared. Concurrently, 10 mL of 0.02 M ice-cold NaBH₄ solution was made. To the HAuCl₄ solution was added 0.45 mL of the NaBH₄ solution with stirring. The resulting solution turned brown immediately, indicating the formation of gold particles. The seed solution was aged for 1 h at 30 °C to decompose excess borohydride.

Synthesis of Trisoctahedral and Rhombic Dodecahedral Gold Nanocrystals.

Two vials were labeled A and B. A growth solution was prepared in each of the two vials. First, 0.32 g of CTAC surfactant was added. The concentration of CTAC in the final solution is equal to 0.10 M. Depending on the morphology of gold nanocrystals to be synthesized (trisoctahedra or rhombic dodecahedra), slightly different volumes of deionized water (9.605 or 9.565 mL) were respectively added to each vial. The vials were then kept in a water bath set at 30 °C. To both vials were added 250 µL of 0.01 M HAuCl₄ solution and 10 µL of 0.01 M NaBr. Finally 110 or 150 µL of 0.04 M ascorbic acid was respectively introduced for making trisoctahedra or rhombic dodecahedra. Total solution volume in each vial is 10 mL. The solution color turned colorless after the addition of ascorbic acid, indicating the reduction of Au³⁺ to Au⁺ species. Next, 25 µL of the gold seed solution was added to the solution in vial A with shaking until the solution color turned light pink. Then 25 µL of the solution in vial A was transferred to vial B with thorough mixing. The solution in vial B was left undisturbed for 15 min for particle growth, and centrifuged at 3000 rpm for 10 min (Hermle Z323 centrifuge).

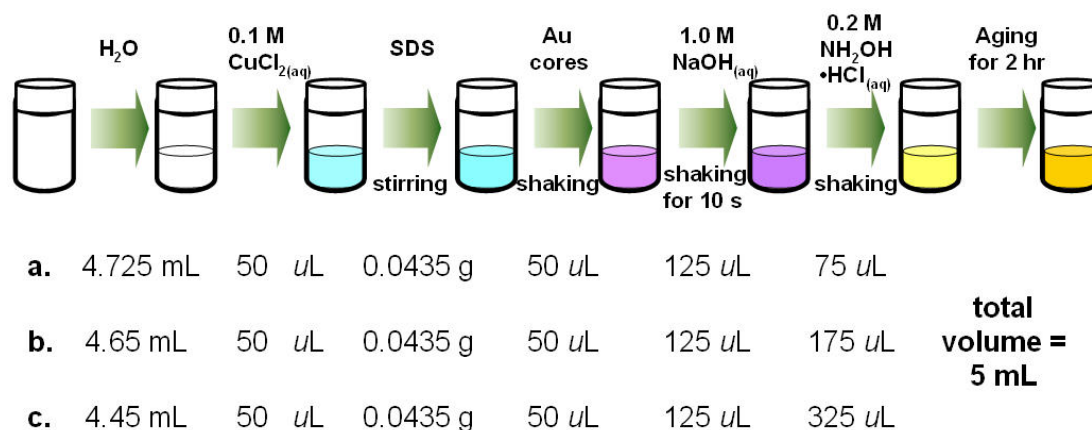
Synthesis of Edge- and Corner-Truncated Octahedral Gold Nanocrystals. Two vials were labeled A and B. A growth solution was prepared in each of the two vials. First, 0.32 g of CTAC surfactant was added. The concentration of CTAC in the final solution is equal to 0.10 M. To each vial, 9.495 mL of deionized water was added.

The vials were then kept in a water bath set at 30 °C. Then 250 μL of 0.01 M HAuCl_4 solution and 10 μL of 1×10^{-4} M KI were added. Finally 220 μL of 0.04 M ascorbic acid was introduced. Total solution volume in each vial is 10 mL. Next, 25 μL of the seed solution was added to the solution in vial A with shaking until the solution color turned light pink. Then 25 μL of the solution in vial A was transferred to vial B with thorough mixing. The solution in vial B was left undisturbed for 15 min for particle growth, and centrifuged at 3000 rpm for 10 min. Details of the structural and spectral analysis have been submitted elsewhere.

Synthesis of Icosahedral Gold Nanocrystals. The synthetic procedure follows our reported method for making penta-branched Au nanocrystals but without the addition of AgNO_3 .²⁰ The procedure has been slightly modified to yield more icosahedra.

Synthesis of Gold Seeds. A volume of 10 mL aqueous solution containing 2.5×10^{-4} M HAuCl_4 and 2.5×10^{-4} M trisodium citrate was prepared. Concurrently, 10 mL of 0.1 M ice-cold NaBH_4 solution was made. To the HAuCl_4 solution was added 0.6 mL of the NaBH_4 solution with stirring. The resulting solution turned orange-red immediately, indicating the formation of gold particles. The seed solution was aged for 1 h at 30 °C to decompose excess borohydride.

Synthesis of Icosahedral Gold Nanocrystals. Three vials were labeled A, B and C. A growth solution was prepared in each of the three vials. First, 0.364 g of cetyltrimethylammonium bromide (CTAB) surfactant was added. The concentration of CTAB in the final solution is equal to 0.10 M. Next, 9.2 mL of deionized water was added. The vial was then kept in a water bath set at 30 °C. To each vial were added 250 μL of 0.01 M HAuCl_4 solution and 50 μL of 0.1 M ascorbic acid. Total solution volume in each vial is 10 mL. Next, 500 μL of the seed solution was added to the solution in vial A with shaking until the solution color turned light pink. Then 500 μL of the solution in vial A was transferred to vial B with thorough mixing. After shaking vial B until the solution color turned light pink, 500 μL of the solution in vial B was added to vial C and shaken for 10 s. The solution in vial C was left undisturbed for 12 hr for particle growth. The solution was centrifuged at 4000 rpm for 10 min.



Scheme S1. Schematic illustration of the procedure used to grow Au–Cu₂O core–shell heterostructures with various shapes.

Morphology	Average Particle Size	Standard Deviation
face-raised cubes	304 ± 24 nm	8 %
cuboctahedra	345 ± 18 nm	5 %
octahedra	373 ± 24 nm	7 %

Table S1. Average particle sizes and standard deviations of the Au–Cu₂O core–shell nanocrystals synthesized using rhombic dodecahedral Au nanocrystal cores.

Morphology	Average Particle Size	Standard Deviation
face-raised cubes	283 ± 21 nm	7 %
cuboctahedra	331 ± 28 nm	8 %
truncated octahedra	363 ± 25 nm	7 %

Table S2. Average particle sizes and standard deviations of the Au–Cu₂O core–shell nanocrystals synthesized using edge- and corner-truncated octahedral Au nanocrystal cores.

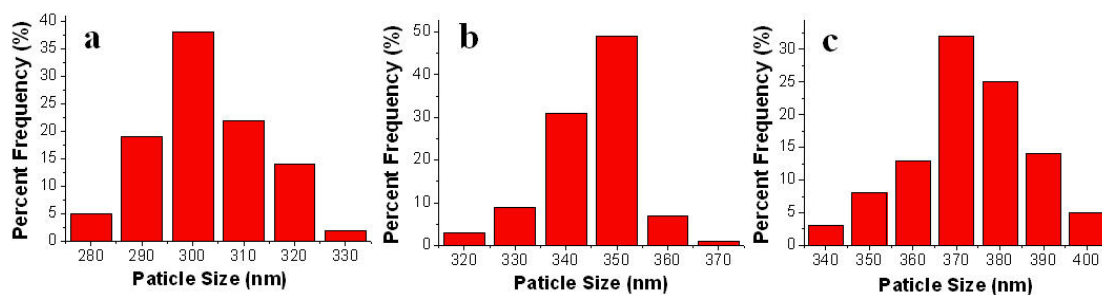


Figure S1. Size distribution histograms of the synthesized Au-Cu₂O core-shell nanocrystals using rhombic dodecahedral Au nanocrystal cores. (a) face-raised cubes. (b) cuboctahedra. (c) octahedra.

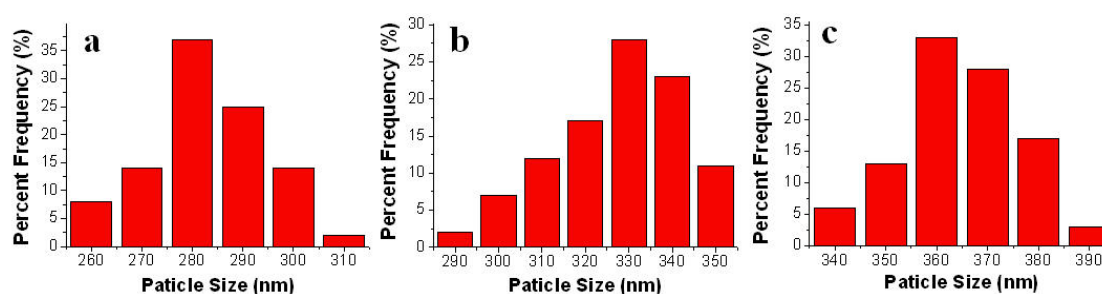


Figure S2. Size distribution histograms of the synthesized Au-Cu₂O core-shell nanocrystals using edge- and corner-truncated octahedral Au nanocrystal cores. (a) face-raised cubes. (b) cuboctahedra. (c) truncated octahedra.

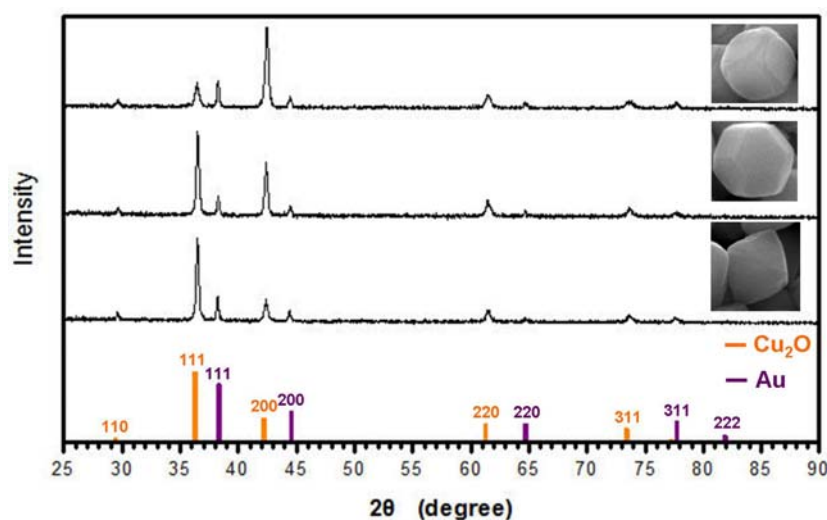


Figure S3. X-ray diffraction patterns of Au-Cu₂O core-shell face-raised cubes, cuboctahedra, and octahedra using rhombic dodecahedral Au nanocrystal cores. Standard diffraction patterns of Cu₂O and Au are also given. The intensity scale for all the samples are the same.

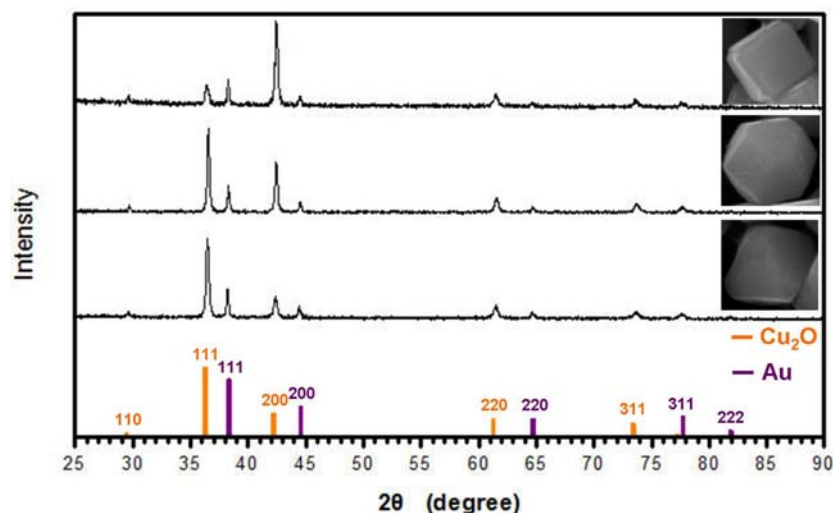


Figure S4. X-ray diffraction patterns of Au–Cu₂O core–shell face-raised cubes, cuboctahedra, and truncated octahedra using edge- and corner-truncated octahedral Au nanocrystal cores. Standard diffraction patterns of Cu₂O and Au are also given. The intensity scale for all the samples are the same.

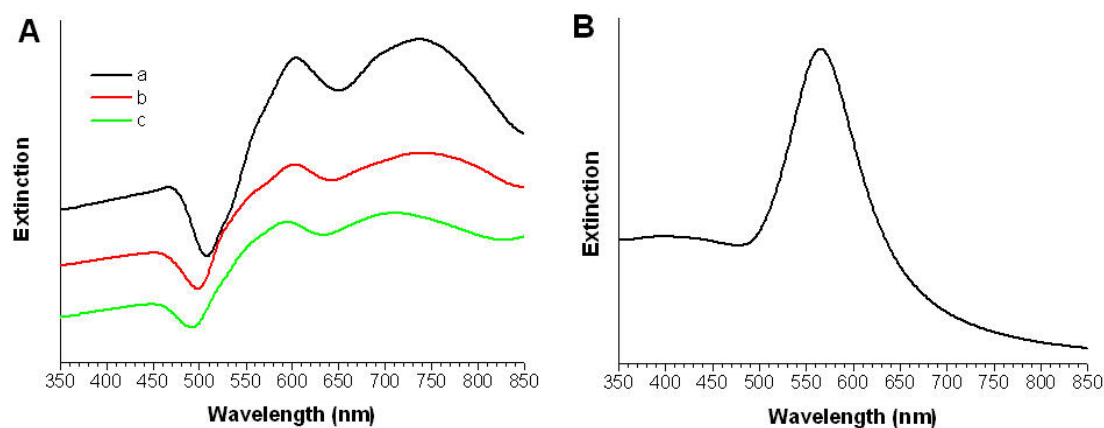


Figure S5. (A) UV–vis absorption spectra of the various Au–Cu₂O core–shell nanocrystals synthesized using rhombic dodecahedral Au nanocrystal cores: (a) face-raised cubes, (b) cuboctahedra, and (c) octahedra. (B) UV–vis absorption spectrum of the rhombic dodecahedral gold nanocrystals.

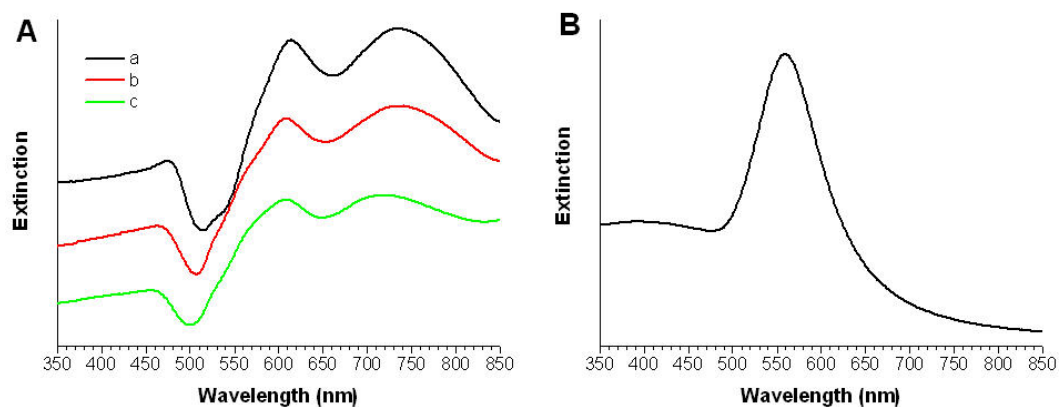


Figure S6. (A) UV-vis absorption spectra of the various Au-Cu₂O core-shell nanocrystals synthesized using edge- and corner-truncated octahedral Au nanocrystal cores: (a) face-raised cubes, (b) cuboctahedra, and (c) truncated octahedra. (B) UV-vis absorption spectrum of the edge- and corner-truncated octahedral gold nanocrystals.

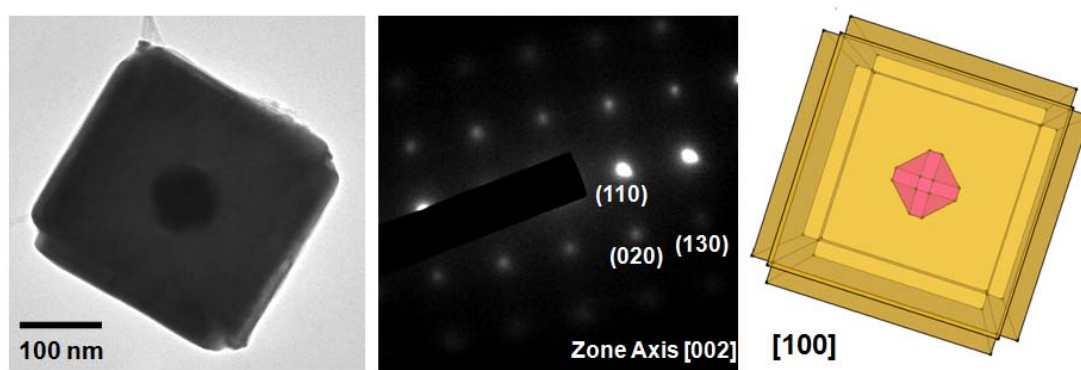


Figure S7. TEM and its corresponding SAED pattern of a face-raised Au-Cu₂O core-shell cube viewed along the [100] direction. The gold core is an edge- and corner-truncated octahedron.

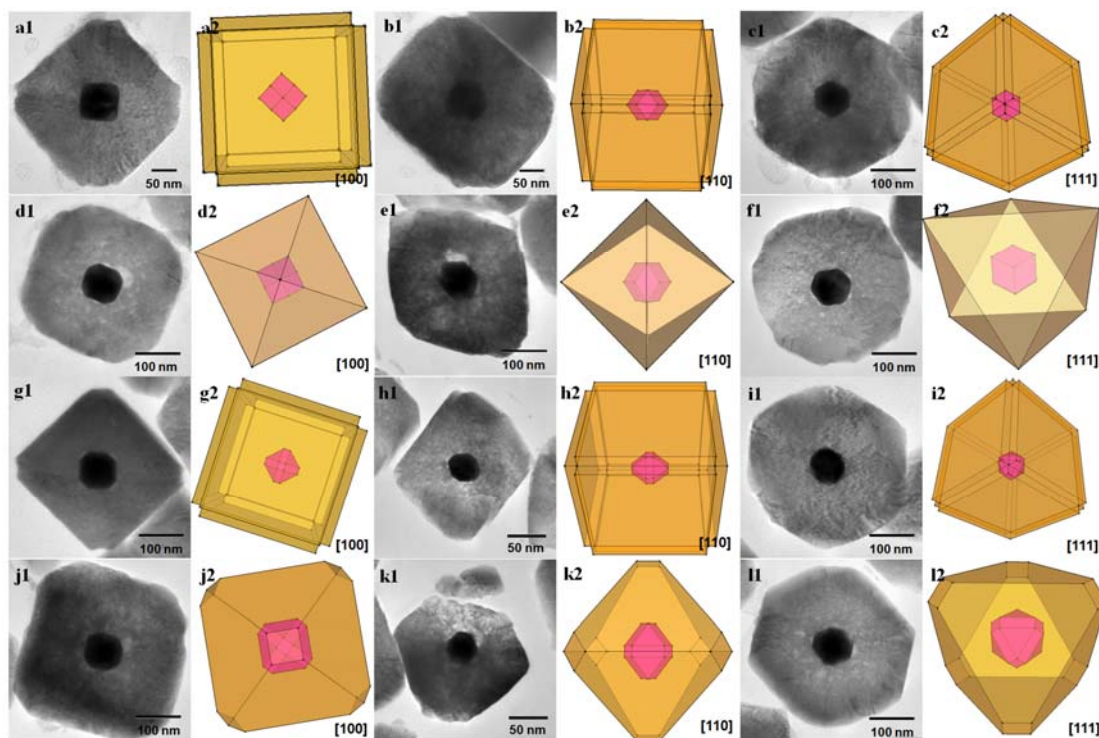


Figure S8. Cross-sectional TEM images of (a–c) Au–Cu₂O core–shell face-raised cubes with rhombic dodecahedral cores, (d–f) Au–Cu₂O core–shell octahedra with rhombic dodecahedral cores, (g–i) Au–Cu₂O core–shell face-raised cubes with edge- and corner-truncated octahedral cores, and (j–l) Au–Cu₂O core–shell truncated octahedra with edge- and corner-truncated octahedral cores viewed along the [100], [110], and [111] directions. The corresponding drawings are also given.

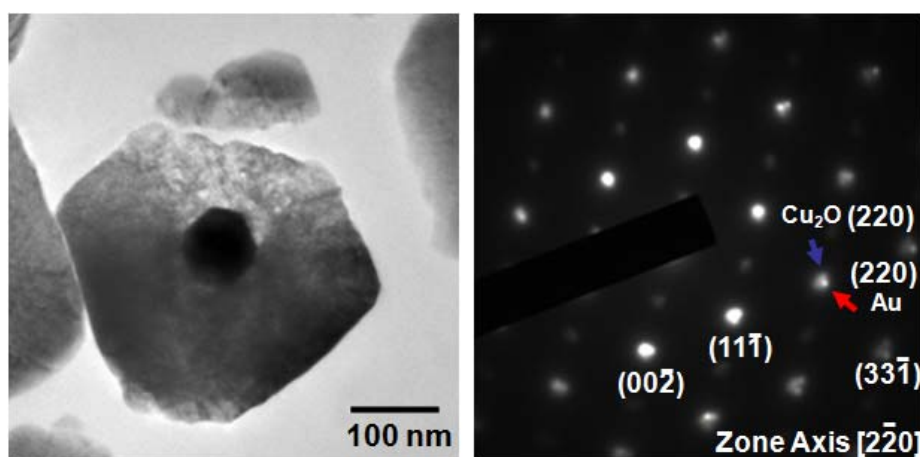


Figure S9. Cross-sectional TEM image of a truncated octahedron with an edge- and corner-truncated octahedral gold core and its corresponding SAED pattern. The diffraction spots of Au match the corresponding spots of Cu₂O, indicating their exact orientation relationship.

Morphology	Average Particle Size	Standard Deviation
cubes	343 ± 22 nm	6 %
cuboctahedra	374 ± 26 nm	7 %
face-raised octahedra	378 ± 24 nm	6 %

Table S3. Average particle sizes and standard deviations of the Au–Cu₂O core–shell nanocrystals synthesized using trisoctahedral Au nanocrystal cores.

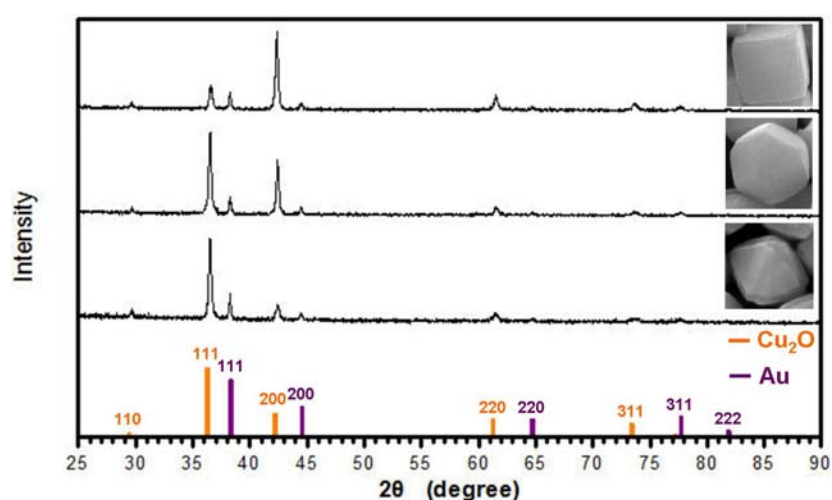


Figure S10. X-ray diffraction patterns of Au–Cu₂O core–shell cubes, cuboctahedra, and face-raised octahedra using trisoctahedral Au nanocrystal cores. Standard diffraction patterns of Cu₂O and Au are also given. The intensity scale for all the samples are the same.

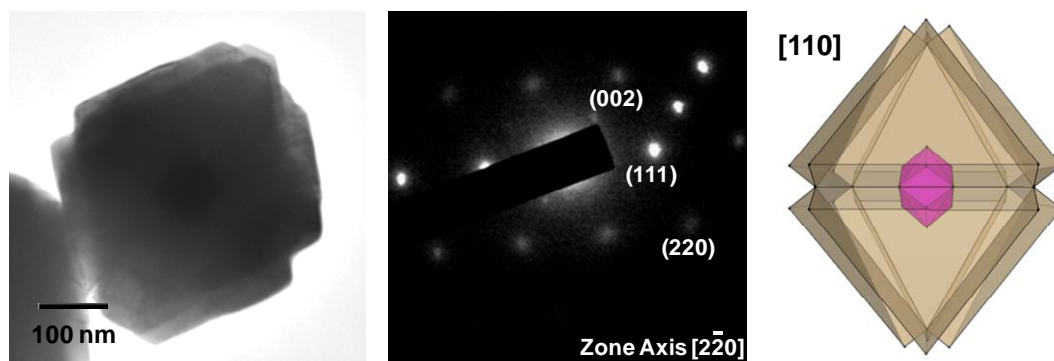


Figure S11. TEM and its corresponding SAED pattern of a face-raised Au–Cu₂O core–shell octahedron viewed along the [110] direction. The gold core is a trisoctahedron.

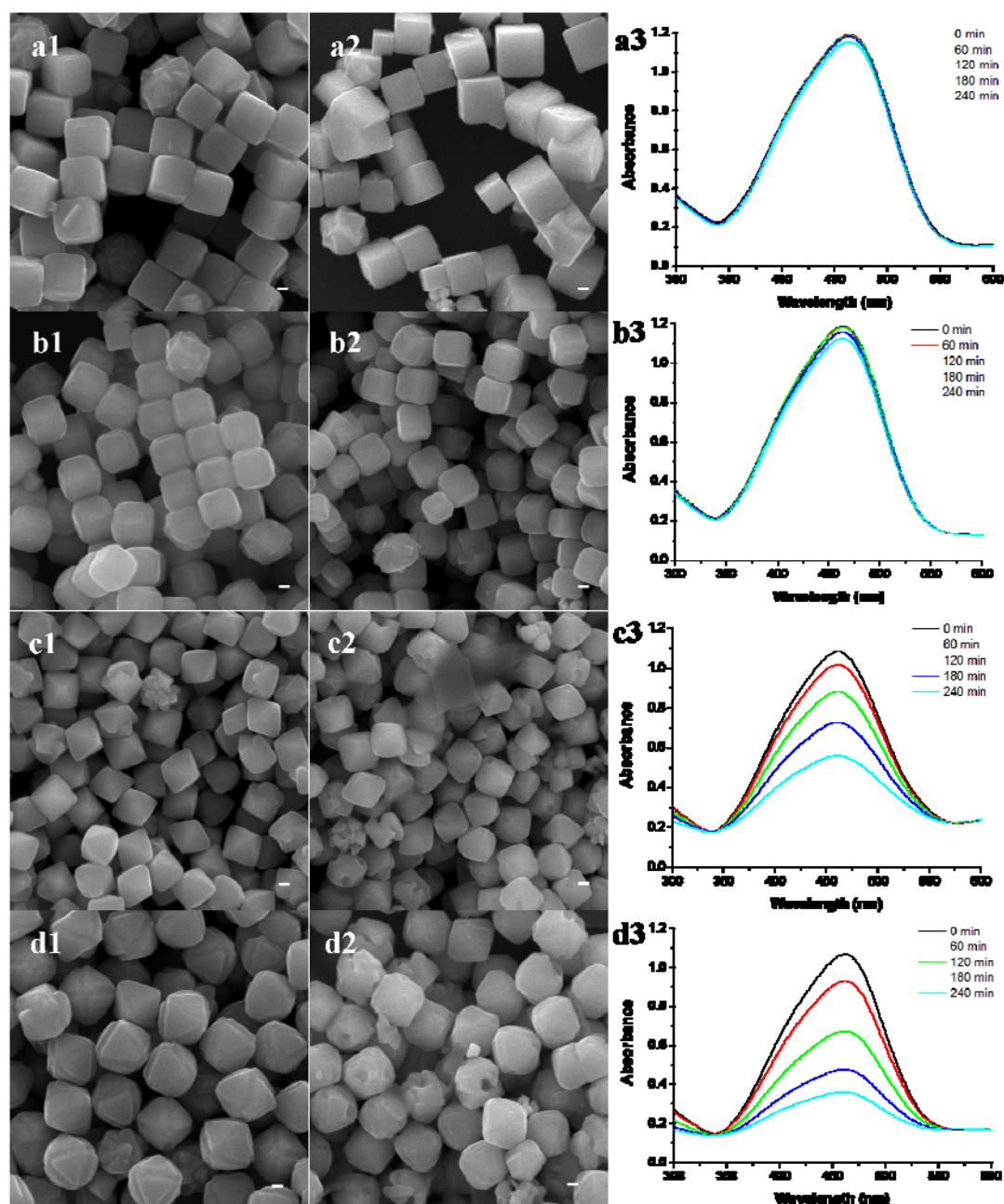


Figure S12. SEM images of the Au-Cu₂O core-shell cubes, face-raised cubes, octahedra, and face-raised octahedra before (a1–d1) and after (a2–d2) photocatalysis for 4 h. All scale bars are equal to 100 nm. (a3–d3) The corresponding UV-vis absorption spectra of methyl orange as a function of irradiation time.