Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information

Photothermal Effects from Au–Cu_2O Core–Shell Nanocubes, Octahedra, and Nanobars with Broad Near-Infrared Absorption Tunability

Hsiang-Ju Wang, Kung-Hsun Yang, Shih-Chen Hsu, and Michael H. Huang*
Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan

Synthesis of Octahedral Gold Nanocrystals

The octahedral Au nanocrystals were obtained following a hydrothermal method developed in our laboratory.[21] For the synthesis of 41 and 57 nm Au octahedra, 0.55 g of CTAB was dissolved in 97.0 and 95.5 mL of deionized water, followed by the introduction of 2.5 and 4.0 mL of 0.01 M $HAuCl_4$ solution, respectively. Finally, 0.5 mL of 0.1 M trisodium citrate solution was added. The total volume in the glass bottle is 100 mL. The glass bottle was then sealed by a Teflon bolt with an O-ring, and the bolt was wrapped with a polyimide tape to prevent leakage of steam. After sealing tightly, the bottle was put into an oven set at 110 °C for 12 and 16 h to yield 41- and 57-nm Au octahedra, respectively. After nanocrystal synthesis, the solution was centrifuged at 6000 rpm for 10 min. After removing the top solution containing CTAB, the particles were dispersed in 1 mL of deionized water. The concentration of Au octahedra (number of particles/mL) was determined by ICP mass spectroscopy using a known amount of Au particle solution. Assuming a perfect octahedral shape, the concentration of 41-nm Au cores is 1.17×10^{13}/mL, and 9×10^{12}/mL for 57-nm Au cores.

Synthesis of Au Nanorods

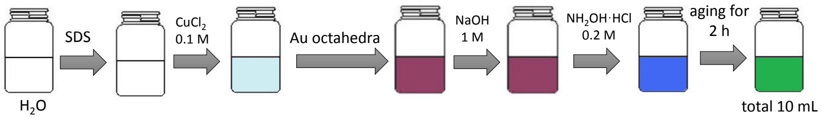
Au nanorods were prepared by first dissolving 0.36 g of CTAB surfactant in 9.3 mL of deionized water, and then 0.25 mL of 0.01 M $HAuCl_4$ solution and 0.45 mL of 0.02 M ice-cold $NaBH_4$ solution were added with stirring in a 20-mL glass bottle. The solution was aged for 1 h at 30 ºC to decompose excess $NaBH_4$. The solution turned brown immediately, indicating the formation of Au seed nanoparticles.

The growth solution was prepared by dissolving 1.8 g of CTAB in 50 mL of deionized water in a flask, and then 2.5 mL of 0.01 M $HAuCl_4$ solution was added. To make Au nanorods with slightly different aspect ratios, 300, 450, 500, or 650 μL of 0.01 M $AgNO_3$ solution was introduced. Next, 1 mL of 1.0 M HCl solution and 0.4 mL of 0.1 M ascorbic acid were added. The solution turned colorless after adding ascorbic acid, indicating the reduction of Au^{3+} to Au^+ species. Finally, 0.15 mL of the Au seed solution was added. The solution was stirred for 2 h at 30 ºC, and centrifuged at 9000 rpm for 10 min. After removal of the top solution containing surfactant, 35 mL of deionized water was added and the solution was centrifuged again. After removing the solution, the nanorods were dispersed in 5 mL of deionized water.

Synthesis of Au–Cu_2O Core–Shell Truncated Nanobars

To make Au–Cu_2O truncated nanobars with different sizes, 0.05 mL of 0.1 M $CuCl_2$ solution was first added to 9.275, 9.225, 9.175, and 9.125 mL of deionized water in each bottle, and then 0.05, 0.1, 0.15, and 0.2 mL of the Au nanorod solution were respectively introduced. Next, 0.087 g of SDS powder was added with vigorous stirring until complete dissolution, followed by the addition of 0.5 mL of 0.2 M $NH_2OH{\cdot}HCl$ solution. After stirring for 10 sec, 0.25 mL of 1.0 M NaOH was injected and the bottle was stirred for 20 sec. The solution was aged for 2 h at 30 ºC for shell growth. The total solution volume in each bottle is 10 mL. Copper ion and SDS concentrations are 5.0×10^{-4} and 3.0×10^{-2} M, respectively. To collect the truncated nanobars, the same centrifugation and washing steps were used.

Table S1 Amounts of reagents used in the growth of Au–Cu_2O core–shell nanocubes and octahedra from 41- and 57-nm octahedral Au cores.



sample	water	SDS	$CuCl_2$ (0.1 M)	Au octahedra (41 nm)	NaOH (1.0 M)	$NH_2OH{\cdot}HCl$ (0.2 M)
Oh-41-89	7.9 mL	0.087 g	0.1 mL	0.09 mL	0.25 mL	0.85 mL
Oh-41-157	25.5 mL	0.261 g	0.3 mL		0.75 mL	2.55 mL
Cube-41-73	8.65 mL	0.087 g	0.1 mL		0.25 mL	0.15 mL
Cube-41-108	27.6 mL	0.261 g	0.3 mL		0.75 mL	0.45 mL

sample	water	SDS	$CuCl_2$ (0.1 M)	Au octahedra (57 nm)	NaOH (1.0 M)	$NH_2OH{\cdot}HCl$ (0.2 M)
Oh-57-105	8.836 mL	0.087 g	0.041 mL	0.023 mL	0.25 mL	0.85 mL
Oh-57-162	8.663 mL		0.214 mL			
Cube-57-87	9.557 mL		0.06 mL			0.15 mL
Cube-57-118	9.433 mL		0.184 mL			

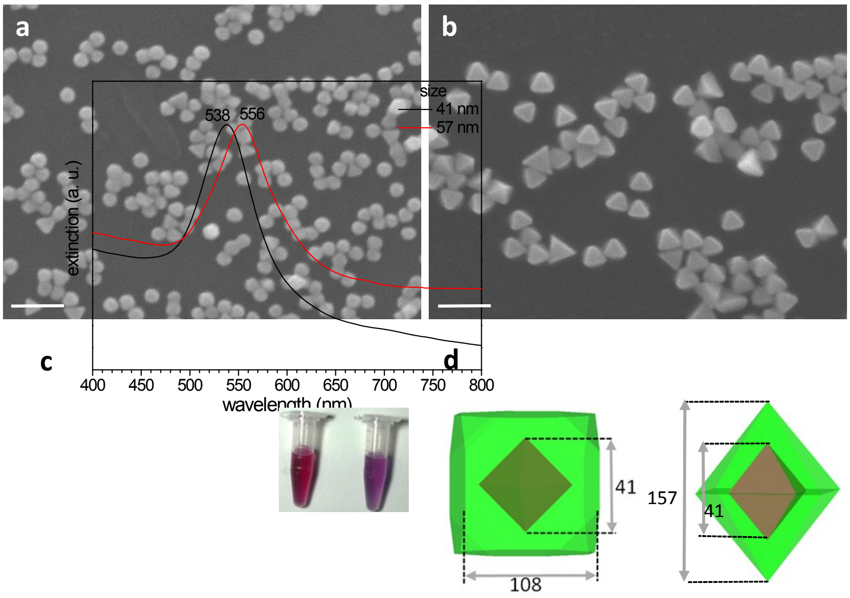


Fig. S1 SEM images of octahedral Au nanocrystals with sizes of (a) 41 and (b) 57 nm. (c) UV–vis spectra of the octahedral Au nanocrystals and a photograph of the solutions. The right sample contains 57-nm octahedra, while the left sample contains 41-nm octahedra. (d) Illustrations of Au–Cu_2O cube and octahedron with their measured dimensions.

Table S2 Average sizes and size distributions of the synthesized Au–Cu_2O core–shell cubes and octahedra.

Core size: 41 nm

shape	size (nm)	coefficient of variation (%)
octahedra	157 ± 19	12
	89 ± 9	10
cubes	108 ± 9	8
	73 ± 6	9

Core size: 57 nm

shape	size (nm)	coefficient of variation (%)
octahedra	162 ± 19	12
	105 ± 14	13
cubes	118 ± 16	14
	87 ± 9	10

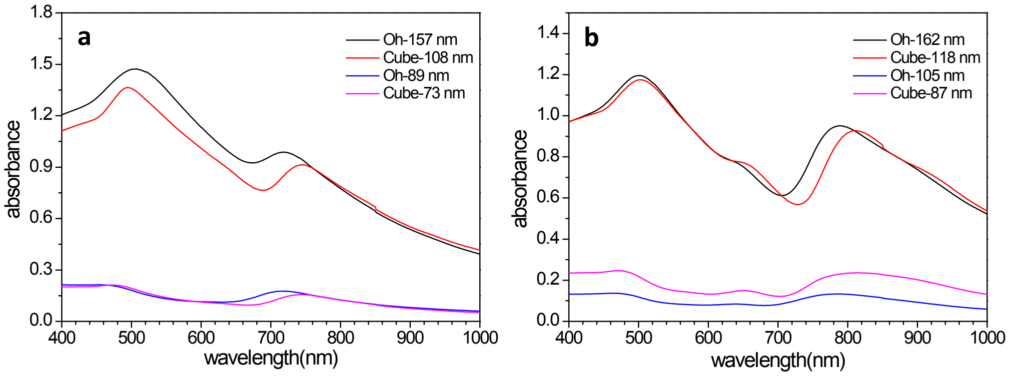


Fig. S2 UV–vis spectra of the various Au–Cu_2O nanocrystal samples using (a) 41-nm and (b) 57-nm Au cores. The actual absorbance values recorded are shown. Larger particle give much higher extinction values.

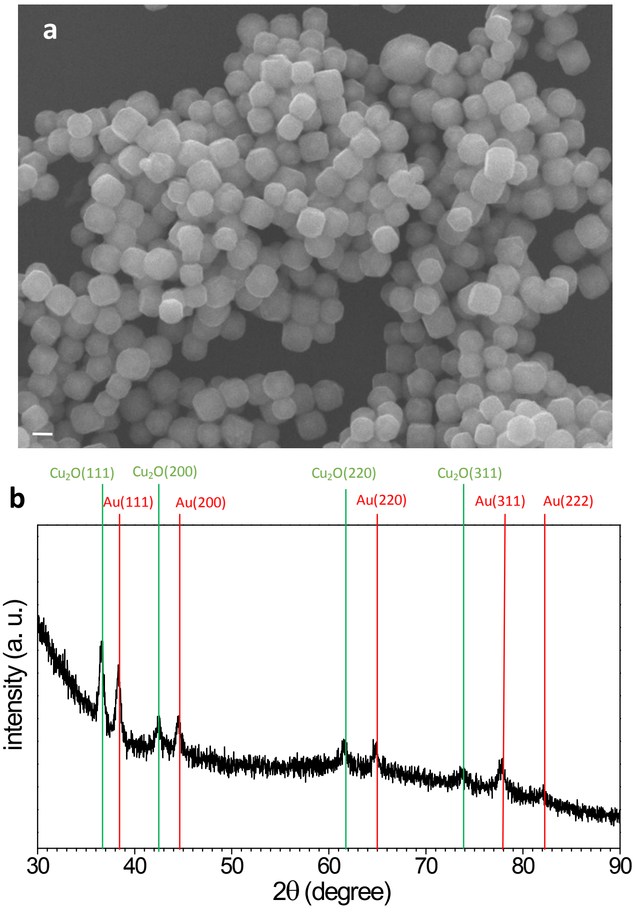


Fig. S3 (a) SEM image and (b) XRD pattern of 118-nm Au–Cu_2O nanocubes after 6 cycles of photothermal treatment. Scale bar is equal to 100 nm.

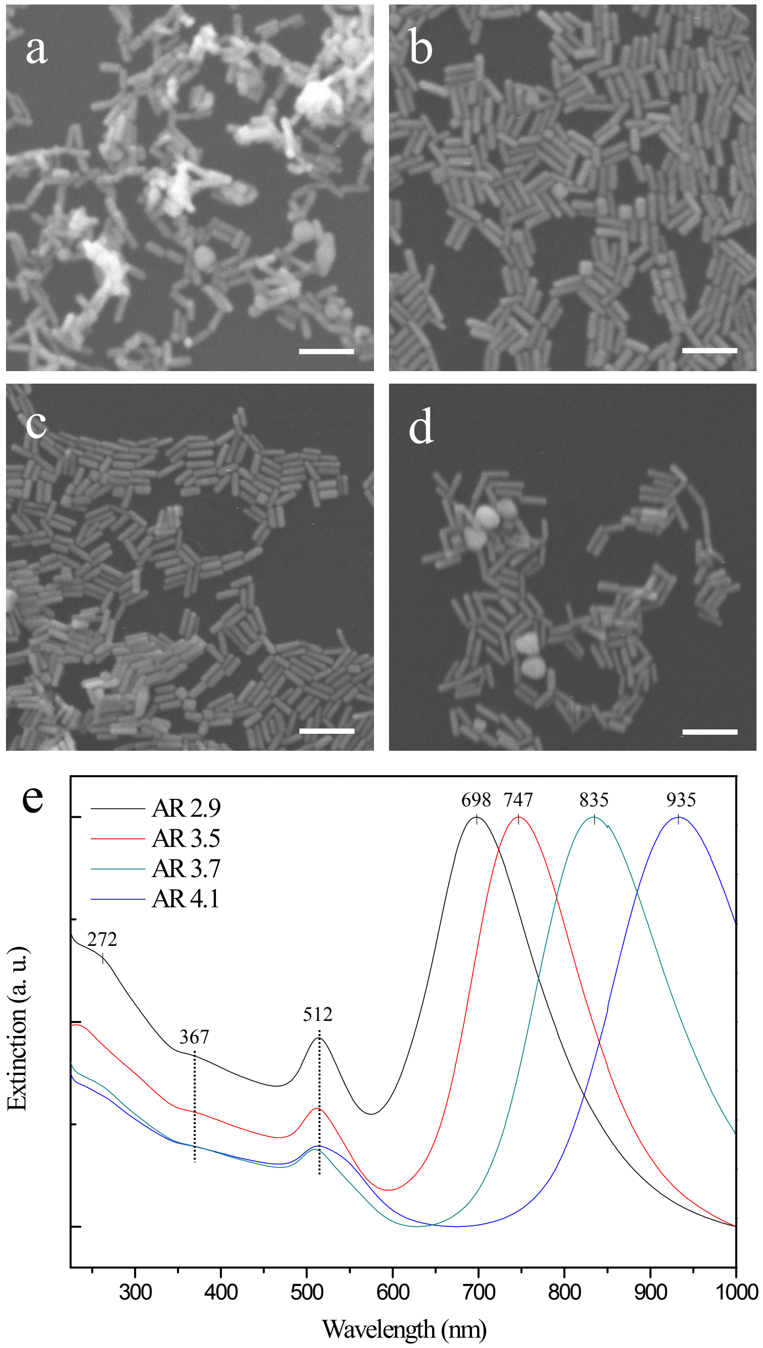


Fig. S4 (a–d) SEM images of Au nanorods with average aspect ratios of (a) 2.9, (b) 3.5, (c) 3.7, and (d) 4.1. Scale bars are 100 nm. (e) UV–vis spectra of these Au nanorods.

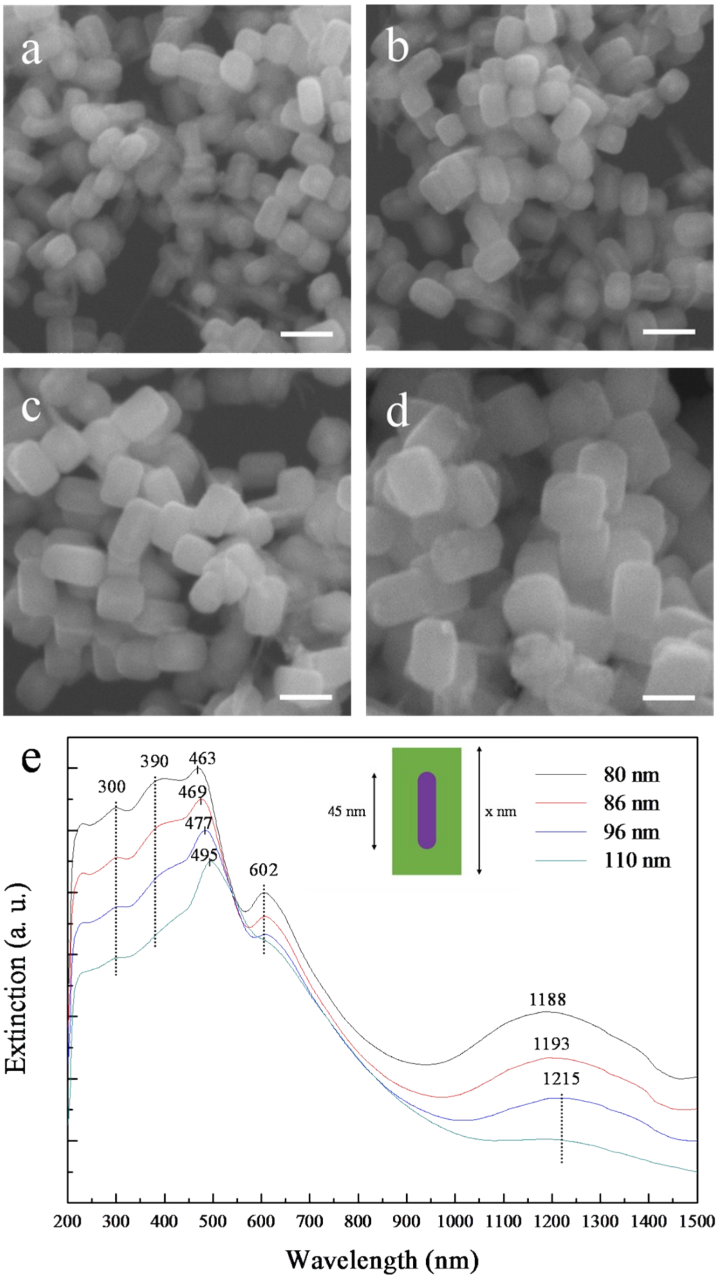


Fig. S5 (a–d) SEM images of Au–Cu_2O rectangular nanobars with dimensions of (a) 80 nm × 51 nm, (b) 86 nm × 56 nm, (c) 96 nm × 65 nm, and (d) 110 nm × 83 nm synthesized from Au nanorods with an average aspect ratio of 3.5. Scale bar are 100 nm. (e) UV–vis–NIR spectra of the Au–Cu_2O nanobars. A drawing of the particle is provided showing the core length.

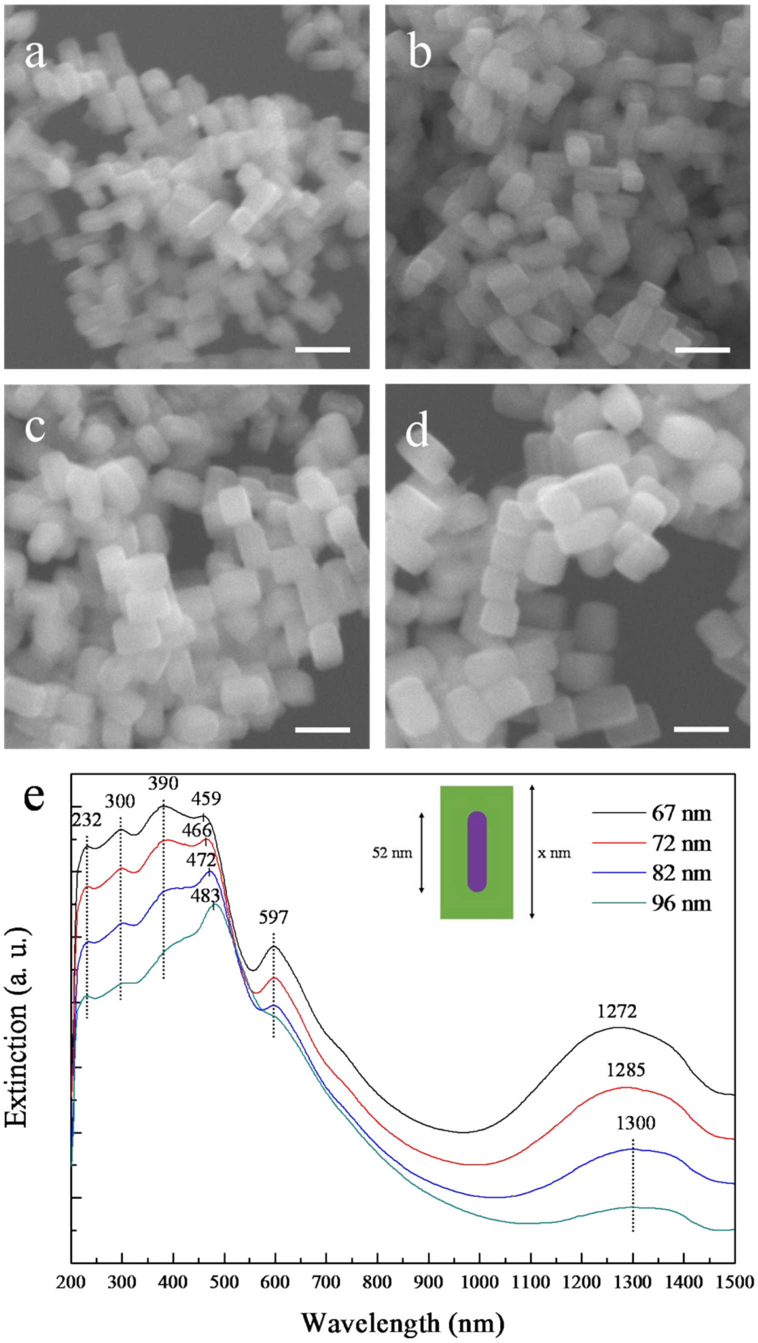


Fig. S6. (a–d) SEM images of Au–Cu_2O rectangular nanobars with dimensions of (a) 67 nm × 38 nm, (b) 72 nm × 41 nm, (c) 82 nm × 52 nm, and (d) 96 nm × 63 nm synthesized from Au nanorods with an average aspect ratio of 3.7. Scale bar are 100 nm. (e) UV–vis–NIR spectra of the Au–Cu_2O nanobars.

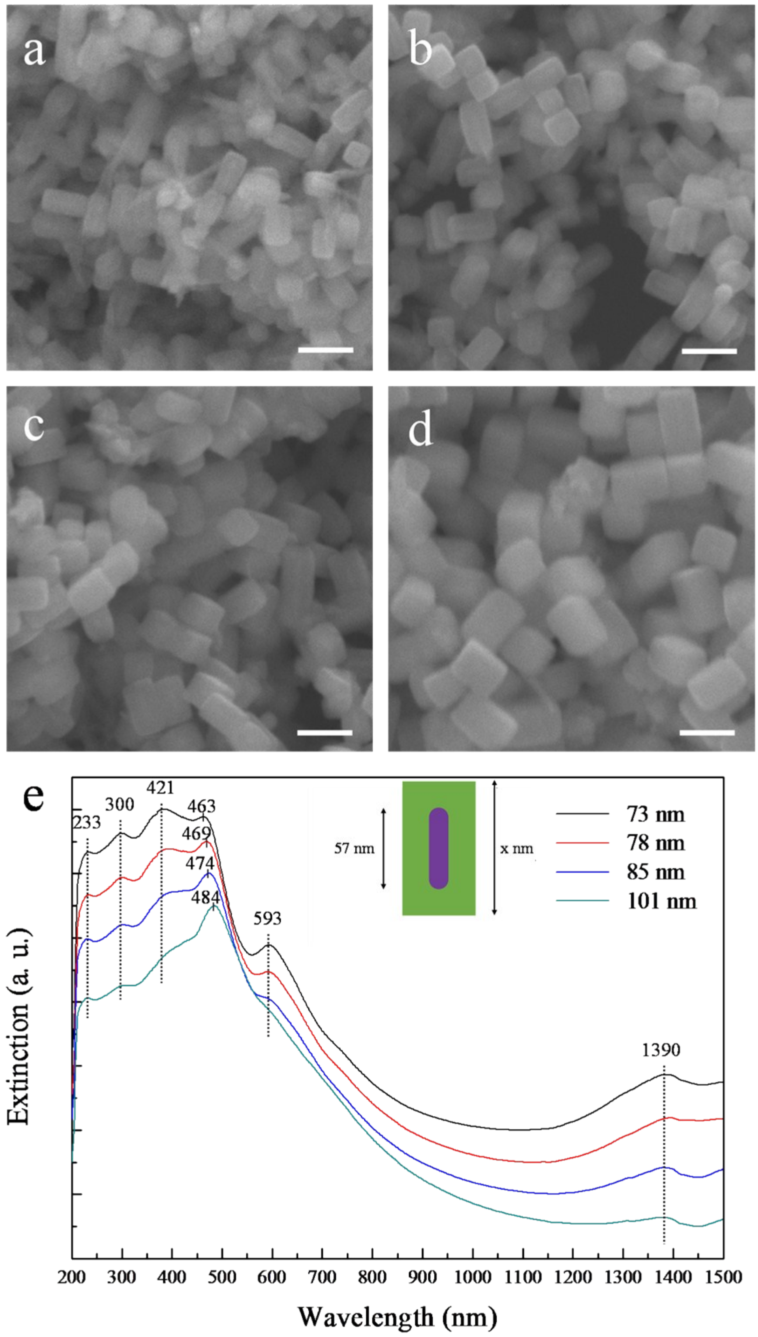


Fig. S7 (a–d) SEM images of Au–Cu_2O rectangular nanobars with dimensions of (a) 73 nm × 44 nm, (b) 78 nm × 47 nm, (c) 85 nm × 53 nm, and (d) 101 nm × 67 nm synthesized from Au nanorods with an average aspect ratio of 4.1. Scale bar are 100 nm. (e) UV–vis–NIR spectra of the Au–Cu_2O nanobars.

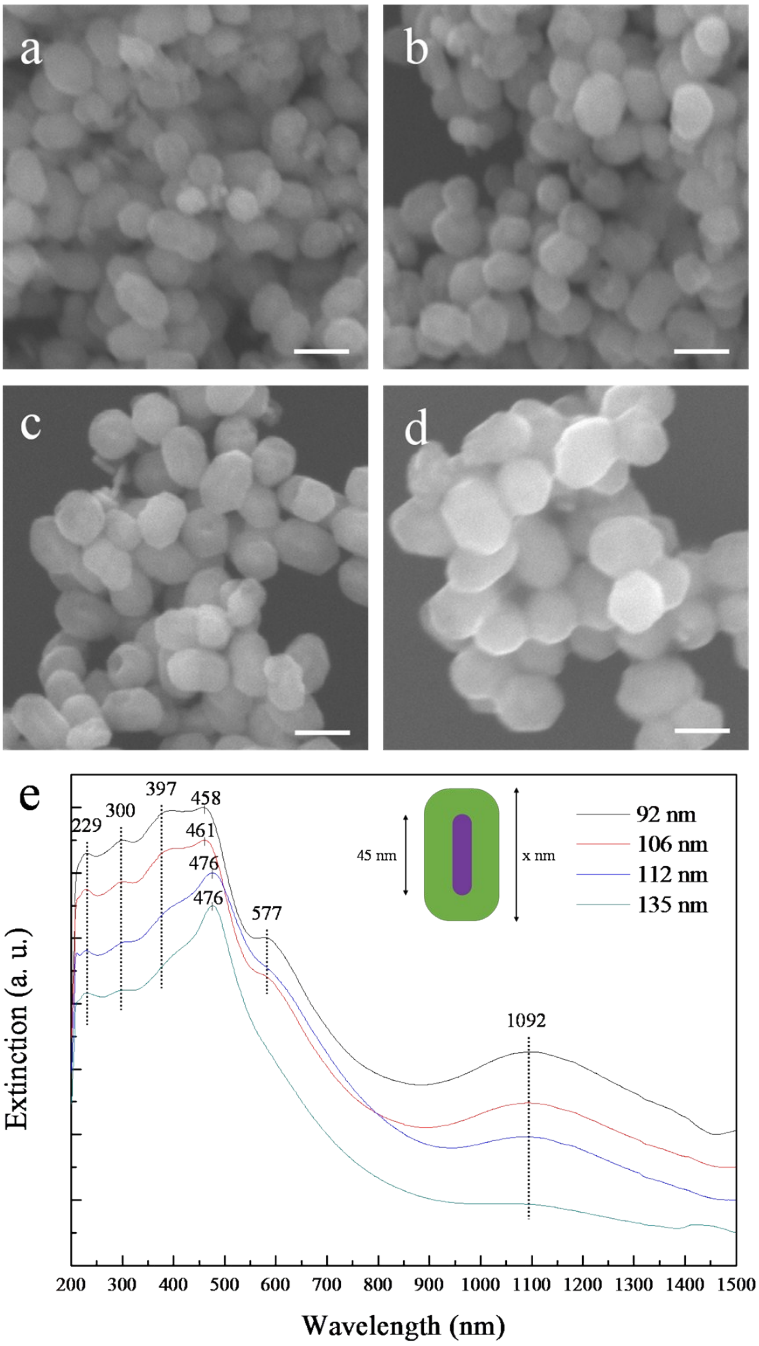


Fig. S8 (a–d) SEM images of Au–Cu$_2$O truncated nanobars with average lengths of (a) 92, (b) 106, (c) 112, and (d) 135 nm grown from Au nanorods with an aspect ratio of 3.5. Scale bar are 100 nm. (e) UV–vis–NIR spectra of the Au–Cu$_2$O truncated nanobars.

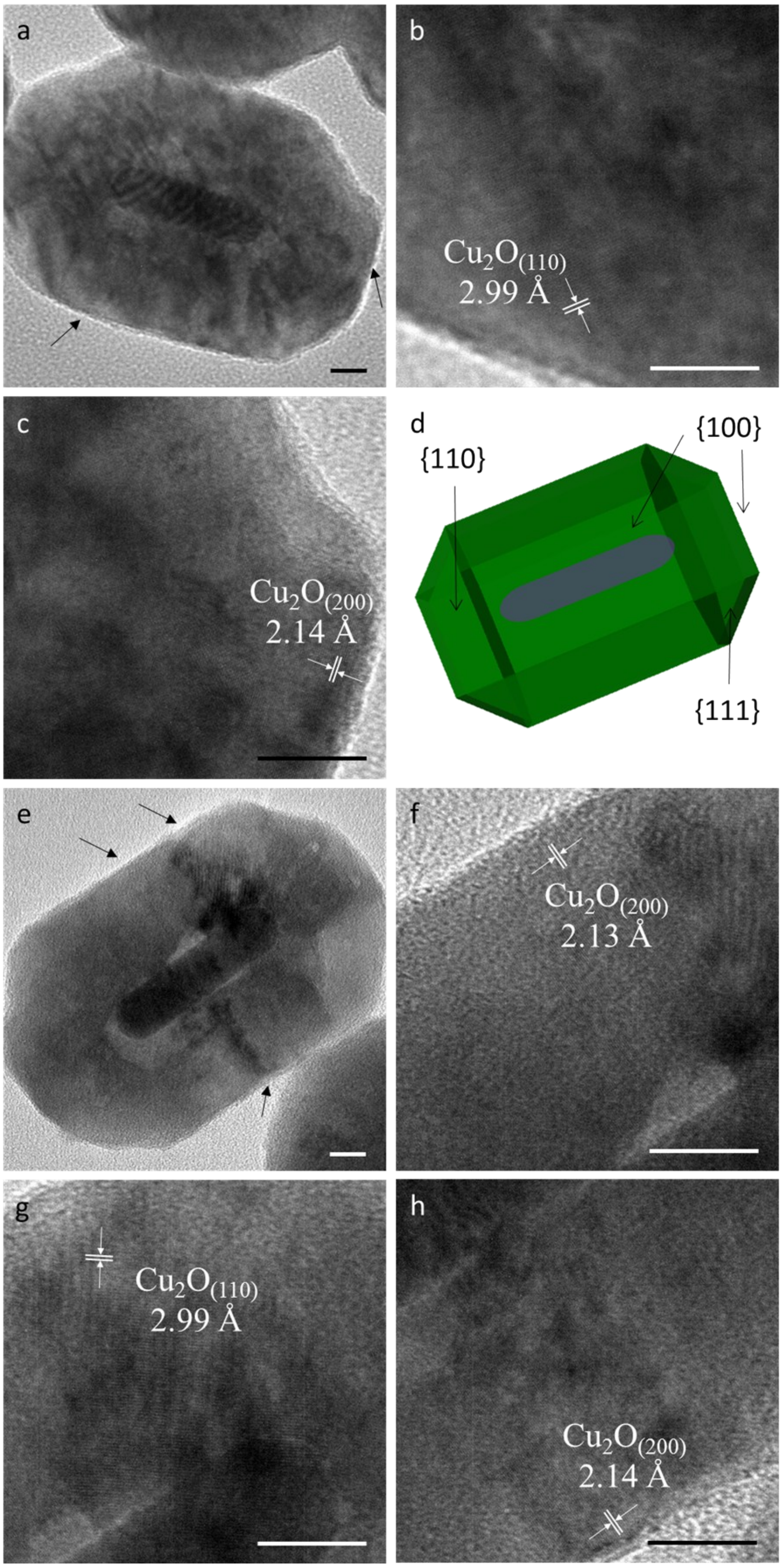


Fig. S9 (a) TEM image of a Au–Cu_2O truncated nanobar. (b, c) HR-TEM images of the pointed regions in panel a. (d) Illustration of the particle with its facets marked. (e) TEM image of another Au–Cu_2O truncated nanobar. (f–h) HR-TEM images of the pointed regions in panel e. Scale bars are equal to 10 nm.

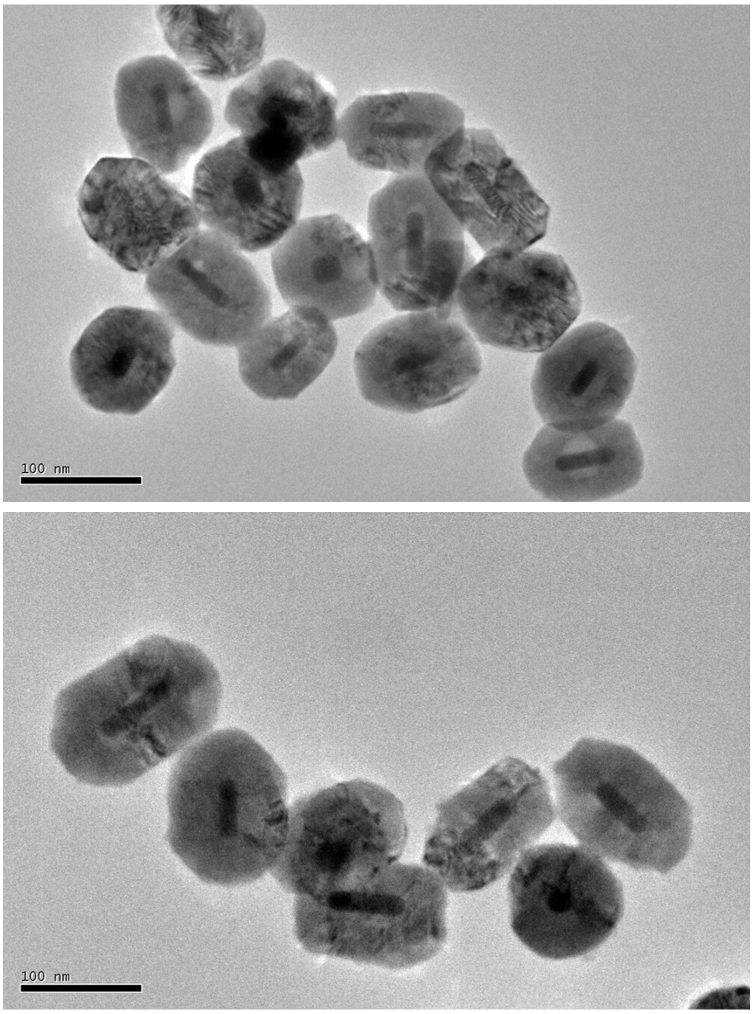


Fig. S10 Additional TEM images of the Au–Cu_2O truncated nanobars.

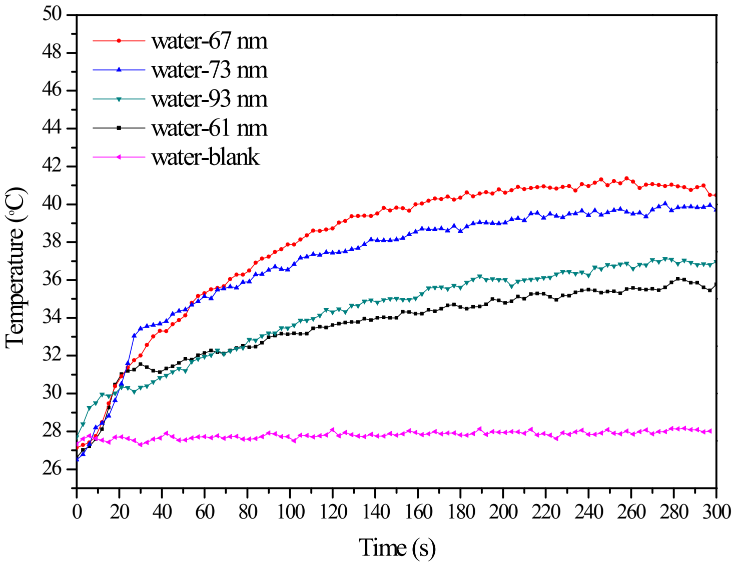


Fig. S11 Temperature profiles of Au–Cu_2O nanobars irradiated by a 1064-nm CW laser at a power of 282 mW. The nanobars were dispersed in water. Nanobar lengths are indicated.