

Supporting Information

Fabrication of Cubic Nanocages and Nanoframes by Dealloying Au/Ag Alloy Nanoboxes with an Aqueous Etchant Based on $\text{Fe}(\text{NO}_3)_3$ or NH_4OH

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Synthesis of Ag nanocubes

50-nm nanocubes. 6 mL of ethylene glycol (EG, J.T. Baker, 9300-03) was preheated to 155 °C for 1 hour under magnetic stirring. EG solutions containing Na_2S (3 mM, Aldrich, 208043), poly(vinyl pyrrolidone) (PVP, 0.18 M, MW~55,000, Aldrich, 856568, the concentration was calculated in terms of the repeating units) and AgNO_3 (0.28 M, Aldrich, 209139) were prepared. 80 μL of the Na_2S solution was injected into the hot ethylene glycol, followed by 1.5 mL of the PVP solution and 0.5 mL of the AgNO_3 solution. The reaction underwent color changes from yellow to reddish brown to opaque brown within 10 min. The sample was washed with acetone and then twice with deionized water. After washing, the product was collected by centrifugation at 132,000 rpm for 5 min and then re-dispersed by brief sonication in 4 mL of deionized water.

80-nm nanocubes. 5 mL of EG was placed in a 20-mL vial, capped, and heated with magnetic

stirring in an oil bath at 150 °C for 1 h. 0.75 mL of 12 mM HCl in EG was then quickly added to the vial, and the vial was recapped. After 10 min, 1.5 mL each of 94 mM AgNO₃ and 147 mM PVP (MW~55,000), both dissolved in EG, were simultaneously added through a two-channel syringe pump (KDS-200, Stoelting, Wood Dale, IL) at a rate of 22.5 mL per hour to the stirring solution. The vial was then capped and continued with heating at 150 °C. Upon injection of the AgNO₃ solution, the reaction mixture went through a series of color changes that included milky white, light yellow, transparent, red, and ocher. The final product was obtained by centrifugation and washed with acetone once and ethanol twice to remove excess EG and PVP and finally re-dispersed in 4 mL of deionized water.

Galvanic replacement reaction to form nanoboxes

A fixed amount (100 µL) of silver nanocubes was dispersed in 5 mL water containing 2 mg/mL PVP in a 50-mL flask under magnetic stirring and then heated to boil for 10 min. A specific amount (as indicated in the text) of 0.2 mM HAuCl₄ aqueous solution was added to the flask through a syringe pump at a rate of 0.5 mL/min under magnetic stirring. The solution was boiled for another 10 min until the color of the system became stable. Once cooled down to room temperature, the sample was centrifuged and washed with saturated NaCl solution to remove AgCl and with deionized water several times to remove excess PVP and NaCl. The sample was then re-dispersed and stored in 0.2 mL deionized water.

Truncation of 80-nm Ag nanocubes

1 mL of an aqueous suspension of the as-synthesized ~80 nm Ag nanocubes was transferred into 1.0 mL ethanol and then to 4.5 mL of EG containing ~0.1 mM PVP by centrifugation and re-dispersion. The suspension was heated to 145 °C in a glass vial under magnetic stirring. After 2 min, 12 mM HCl was added to a total concentration of 1 mM, and the mixture was heated for an additional 5 min. Once cooled down to room temperature, the product was centrifuged and washed with acetone and ethanol several times to remove EG and excess PVP, and finally re-dispersed in 1 mL deionized water.

Etching of Au/Ag alloy nanoboxes

Etching with $Fe(NO_3)_3$. 100 μ L of the nanoboxes obtained from galvanic replacement reaction was diluted to 1.5 mL with deionized water. Under stirring, the nanobox suspension was mixed with a certain volume of 50 mM $Fe(NO_3)_3$ (Fisher Scientific) aqueous solution as indicated in the text. After the reaction had proceeded at room temperature for 10 min, the product was collected by centrifugation at 8000 rpm and washed three times with DI-water. The sample was then re-dispersed in 1 mL deionized water.

Etching with NH_4OH solution. 100 μ L of the nanoboxes obtained from galvanic replacement reaction was added to 2 mL of 28% NH_4OH (Fisher Scientific) aqueous solution. After the reaction had proceeded at room temperature for 12 hours, the resultant nanostructures were collected by centrifugation and then washed with deionized water. The final product was re-dispersed in 1 mL deionized water.

Characterization

For SEM or TEM sample preparation, a drop of the aqueous suspension of nanostructures was placed on a piece of silicon wafer or carbon-coated copper grid (Ted Pella, Redding, CA), respectively, and allowed to dry in the fume hood. The sample was then washed for 15 min with deionized water to remove excess PVP. SEM images and EDX data were taken using a field-emission microscope (Sirion XL, FEI) operated at an accelerating voltage of 15 kV. TEM was performed with a Phillips CM100 microscope operated at 100 kV. The TEM images were obtained with a Gatan digital camera. The UV-Vis-NIR absorbance spectra were taken at room temperature with a Cary 500 (Varian Inc.) spectrophotometer using a quartz cuvette with an optical path of 1 cm.

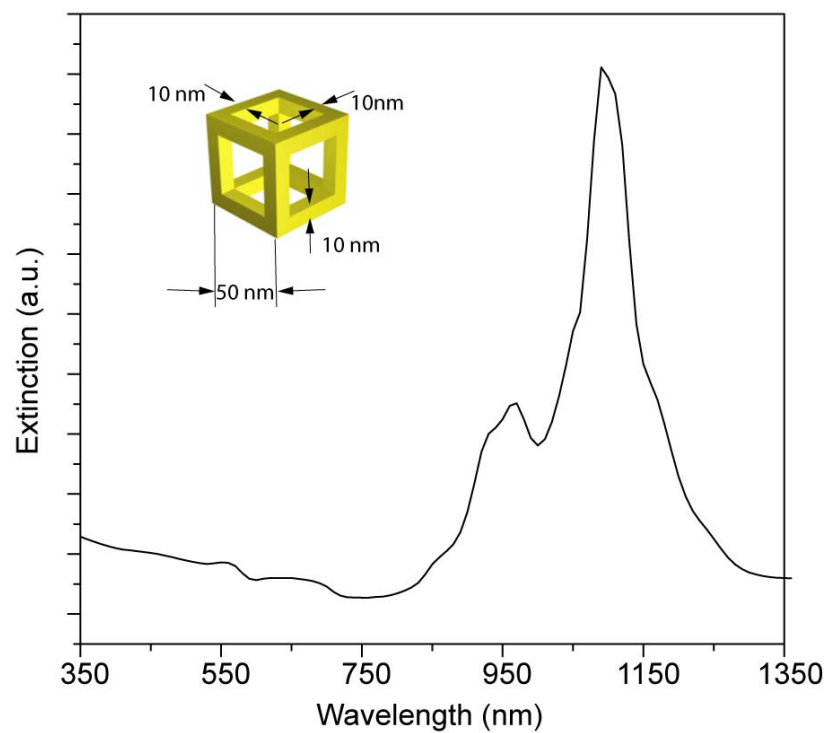


Figure S1. The extinction spectrum calculated using the DDA method for a cubic nanoframe of gold with the dimensions indicated in the drawing. The major extinction peak is located around 1100 nm.

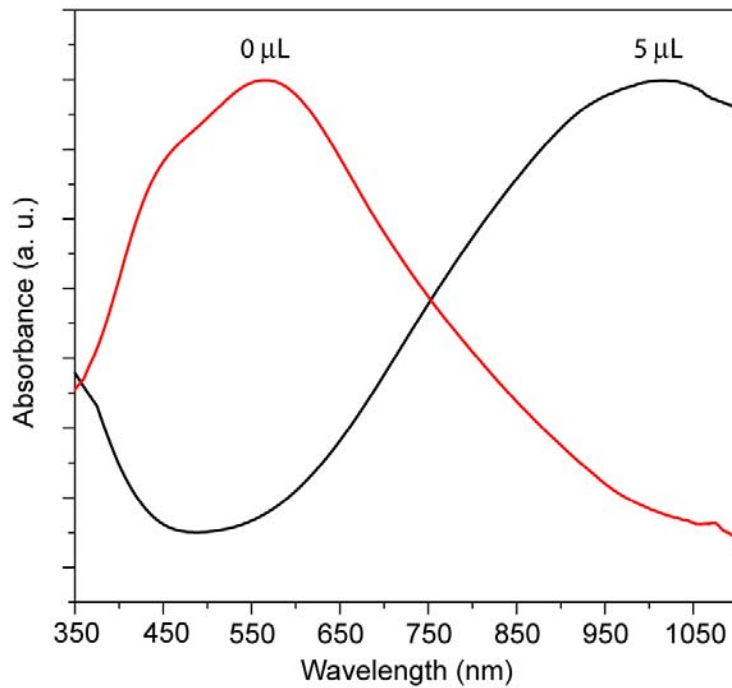


Figure S2. Absorbance spectra taken from 80-nm nanocages before (A) and after (B) they had reacted with 5 μL of 50 mM aqueous $\text{Fe}(\text{NO}_3)_3$ solution. The nanocages were prepared using the galvanic replacement reaction between 0.8 mL of 0.2 mM aqueous HAuCl_4 solution and 80-nm Ag nanocubes with truncated corners.

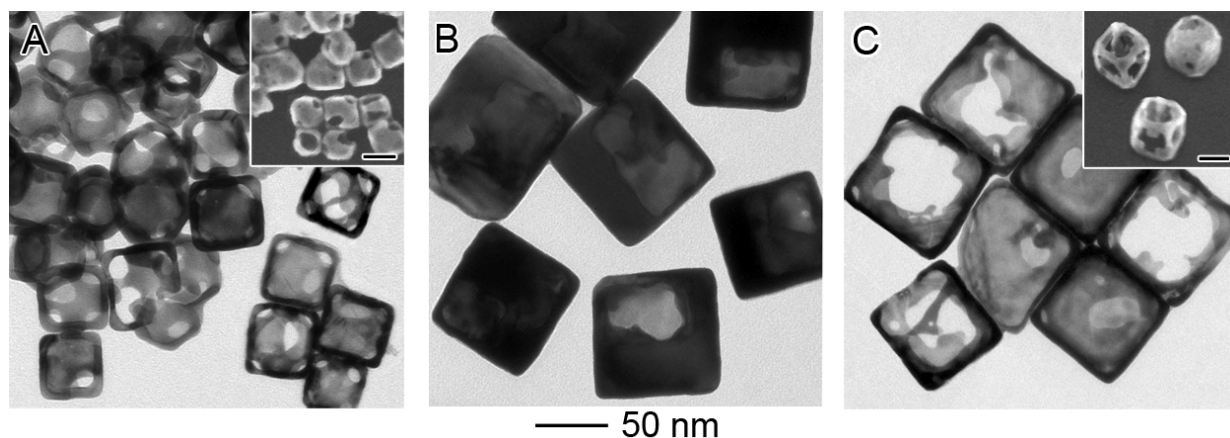


Figure S3. Etching of Au/Ag alloy nanoboxes with 2 mL of 28% aqueous NH_4OH solution. (A) Nanocages and cubic nanoframes obtained by etching nanoboxes prepared from the galvanic replacement reaction between 50-nm Ag nanocubes and 4 mL of 0.2 mM HAuCl_4 solution. The inset gives an SEM image of the same product. (B) TEM image of nanoboxes prepared by the galvanic replacement reaction between 80-nm Ag nanocubes and 8 mL of 0.2 mM HAuCl_4 . (C) Cubic nanoframes obtained by etching the Au/Ag nanoboxes shown in (B) with NH_4OH solution. The inset shows an SEM of the same product at a tilting angle of 45 degrees. The scale bars in both insets are 50 nm.