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Size-Controlled Synthesis of Gold Bipyramids using an Aqueous Mixture of CTAC and Salicylate Anions as Soft Templates

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Experimental

Reagents

Cetyltrimethylammonium chloride solution (CTAC, $CH_3(CH_2)_{15}N(CH_3)_3Cl$, 25 wt% in H_2O, Sigma-Aldrich), cetyltrimethylammonium bromide (CTAB, $CH_3(CH_2)_{15}N(CH_3)_3Br$, 99+%, Acros organic), hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.9%, Sigma–Aldrich), silver nitrate ($AgNO_3$, 99+%, Sigma-Aldrich), L-ascorbic acid ($C_6H_8O_6$, 99+%, Sigma-Aldrich), ethyl alcohol (CH_3CH_2OH, 99.9+%, Burdick & Jackson), hydrochloric acid (HCl), and nitric acid (HNO_3) were used as received. All stock solutions were freshly prepared before each reaction. Prior to use, all glassware were washed with aqua regia (3:1 volume ratio of HCl and HNO_3; *Caution: Aqua regia is highly toxic and corrosive and must be handled in a fume hood with proper personal protection equipment*) and rinsed thoroughly using nanopure water.

Synthesis of Au bipyramids

Au bipyramids were synthesized through the reduction of Au^{3+} ions (from $HAuCl_4$) onto Au seed nanoparticles (prepared as per guidelines reported).[1] Two growth solutions were prepared. For the preparation of the first growth solution (**A**), 2 mL of aqueous CTAC (50 mM) was thoroughly mixed with 0.2 mL of sodium salicylate (NaSal), 10 μL of $AgNO_3$ (50 μM or of variable concentration), 20 μL of ascorbic acid (aq.) (100 mM), and 80 μL of $HAuCl_4$ (aq.) (10 mM) by shaking for 30 s. Similarly, the second growth solution (**B**) was formed by mixing 20 mL of aqueous CTAC (50 mM) with 2 mL of NaSal, 100 μL of $AgNO_3$ (50 μM or of variable concentration), 200 μL of ascorbic acid (aq.) (100 mM), and 800 μL of $HAuCl_4$ (aq.) (10 mM), by shaking for 30 s. The concentrations of NaSal in both **A** and **B** were varied as 0, 5, 10, 50, and 100 mM; the corresponding CTAC:NaSal molar ratio were 0, 100:1, 50:1, 10:1, and 5:1, respectively. The formation of Au bipyramids was initiated by adding 100 μL of Au seed nanoparticles solution to **A**. 100 μL of **A** was then added to **B**, and the mixture was shaken vigorously for more than 1 min, and subsequently aged for 12 h. The mixture was then purified *via* centrifugation (7 min; 2500 rpm), redispersed three times in nanopure water, and characterized.

Characterization

The resulting nanoparticles were imaged using a Hitachi S-4800 scanning electron microscope (SEM) and a LEO-912AB OMEGA, Carl Zeiss, Germany transmission electron microscope (TEM). High-resolution transmission electron microscopy (HRTEM), energy dispersive X-ray (EDX) analysis, and selected-area electron diffraction (SAED) patterns were measured using JEOL JEM-2100F microscope. Ultraviolet-visible-near infrared (UV-Vis-NIR) spectra were recorded using UV-3200 Shimadzu spectrophotometer and UV-1800 Shimadzu spectrophotometer. Samples for TEM analysis were prepared by centrifuging the nanoparticle mixture twice for 5 min at 13,500 rpm. Next, the particles were resuspended in 100 μL of nanopure water and immobilized from 10 μL portions of the solution on Formvar-coated Cu grids.

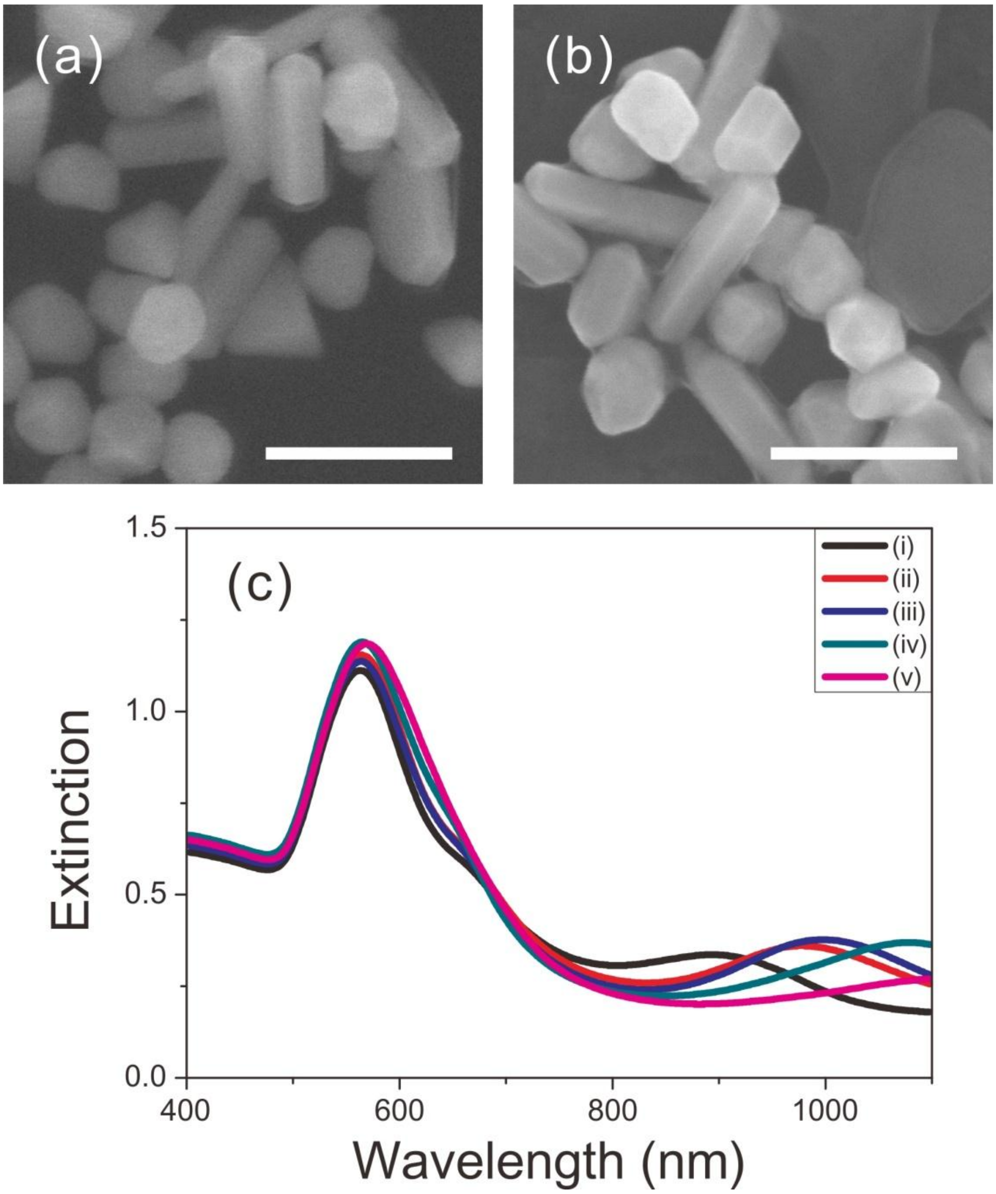

Figure S1. SEM images of Au nanocrystals that were synthesized using (a) no NaSal and (b) CTAB and NaSal in a ratio of 5:1 (Scale bars: 200 nm); (c) Changes in the UV-vis-NIR spectrum of Au nanocrystals on varying the CTAC-to-NaSal molar ratio; (i) no NaSal, (ii) 100:1, (iii) 50:1, (iv) 10:1, (v) 5:1.

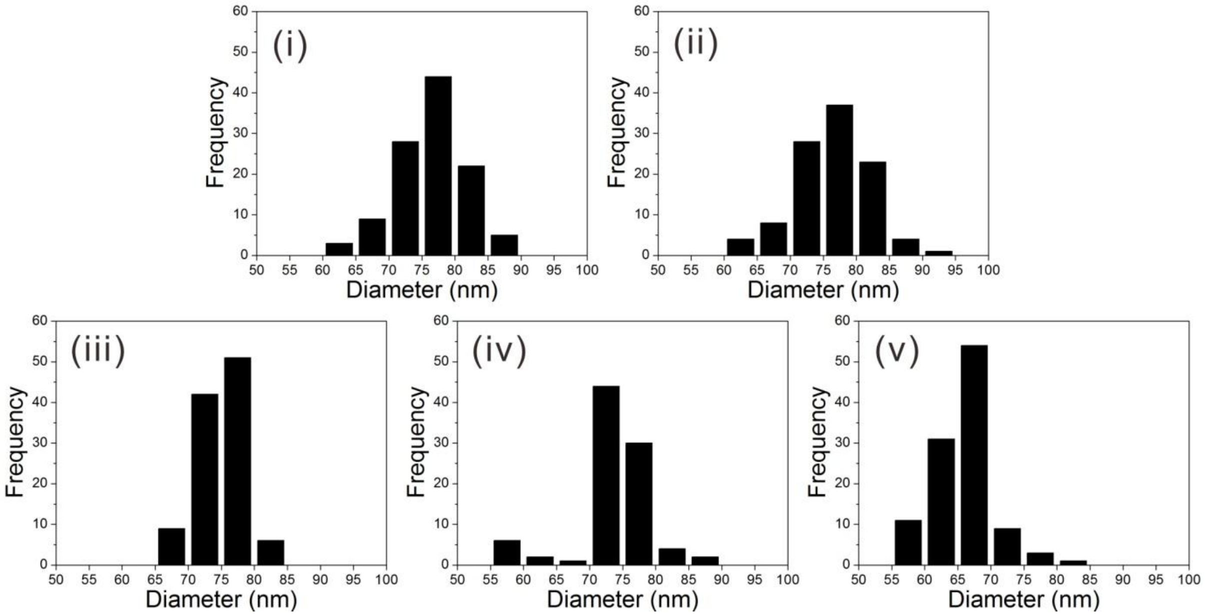

Figure S2. Distributions showing the change in the central widths of Au bipyramids owing to variations in the CTAC-to-NaSal molar ratio of (i) 0 (no NaSal used), (ii) 100:1, (iii) 50:1, (iv) 10:1, (v) 5:1.

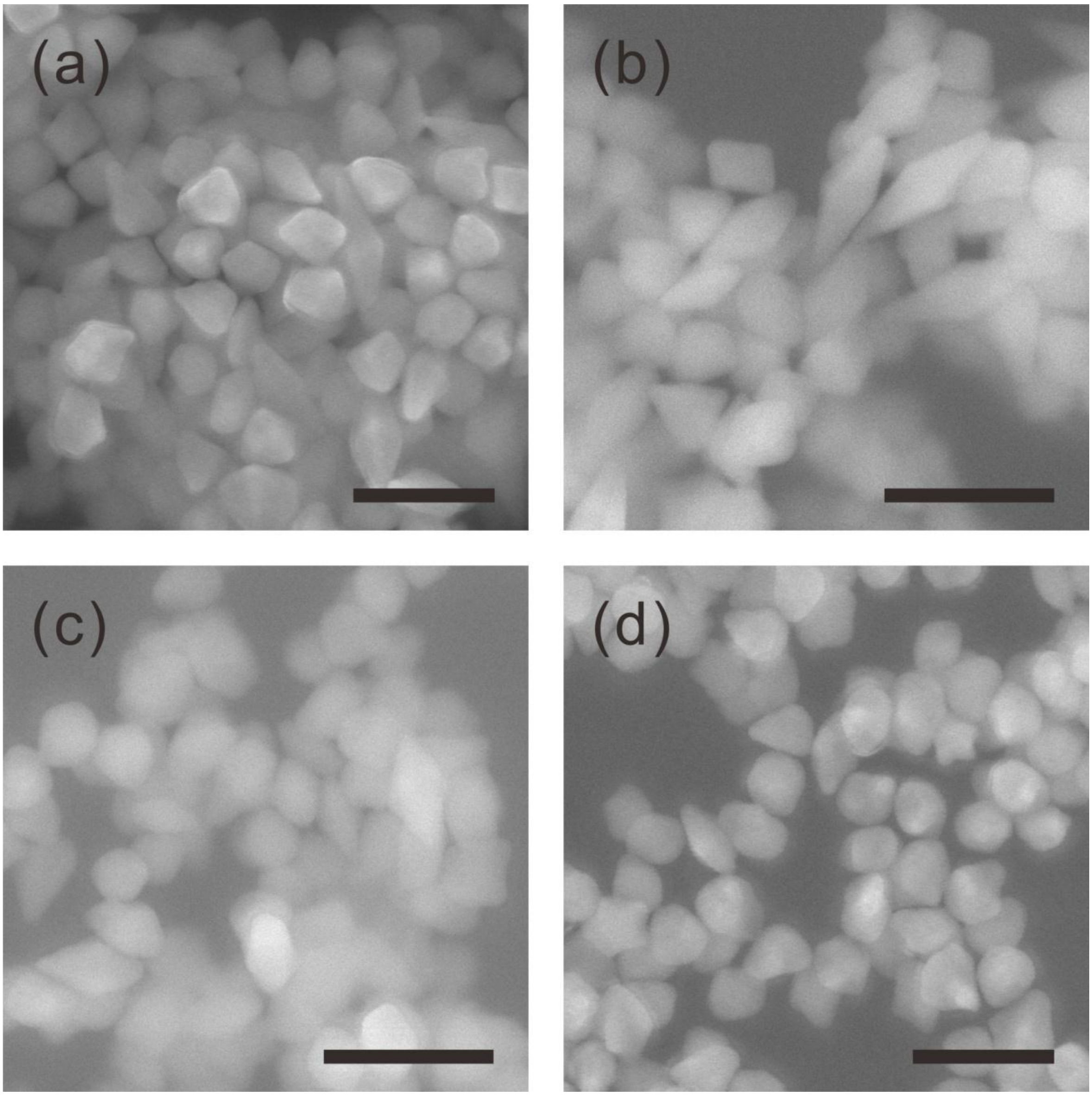

Figure S3. SEM images of Au nanocrystals that were synthesized by varying the concentration of $AgNO_3$ (aq); (a) no $AgNO_3$ used; (b) 0.001, (c) 500, and (d) 1000 μM of $AgNO_3$ used (Scale bars: 200 nm);

References for Supporting Information

(1) (a) Millstone, J. E.; Park, S.; Shuford, K. L.; Qin, L.; Schatz, G. C.; Mirkin, C. A. *J. Am. Chem. Soc.* **2005**, *127*, 5312–5313. (b) Millstone, J. E.; Wei, W.; Jones, M. R.; Yoo, H.; Mirkin, C. A. *Nano Lett.* **2008**, *8*, 2526–2529.