Supporting Information for:

Iodide Ions Control Seed-Mediated Growth of Anisotropic Gold Nanoparticles

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Materials:

Hydrogen tetrachloroaurate trihydrate ($HAuCl_4•3H_2O$, 99.9%), sodium borohydride ($NaBH_4$, 99.995%), sodium hydroxide (NaOH, 99.998%), L-ascorbic acid (99%), trisodium citrate (99%), potassium iodide (99%), sodium iodide (99%), lithium iodide (99%) were obtained from Aldrich and used as received. Cetyltrimethlyammonium bromide (CTABr) was ordered from various manufacturers with various purities, see Table S1.

Preparation and Recrystallization of Cetyltrimethylammonium Bromide (CTABr):

For all experiments, 0.05M CTABr was prepared by dissolving 2.733g of CTABr in 150 mL of NANOpure$^{™}$ (18.1 MΩ) water. The solution was sealed with parafilm and heated until it appeared crystal clear. This sealed solution was then sonicated for ~30 s, to ensure that all CTABr was dissolved. The solution was cooled to room temperature before use in subsequent syntheses (~2 h).

To purify CTABr, 10 g samples of CTABr (SigmaUltra, Aldrich Chemical Company) were dissolved in a warm ethanol/water mixture (10:1) (~150mL) and allowed to recrystallize at 4^{o}C. The crystals were isolated by Buchner filtration, washed with ethyl ether, and dried in a vacuum oven at 55^{o}C for 6 h. The process was then repeated 2 additional times for each 10g sample, so that CTABr had been recrystallized three times before being used in the experiments.

Synthesis of Anisotropic Gold Nanoparticles:

In a typical experiment, all glassware was washed with aqua regia (3:1 ratio by volume of HCl and HNO_3), and rinsed copiously with NANOpure$^{™}$ (18.1 MΩ) water. *Hazard: aqua regia is highly toxic and corrosive and must be handled in fume hoods with proper personal protection equipment.* Gold nanoparticle seeds were prepared by reducing 1 mL of 10 mM $HAuCl_4$ with 1 mL of 100 mM $NaBH_4$ while stirring vigorously. The reduction was done in the presence of 1 mL of 10 mM sodium citrate and 36 mL of fresh, NANOpure$^{™}$ water. Upon addition of the $NaBH_4$, the solution turned a reddish-orange color and was allowed to continue stirring for one minute. The resulting mixture was aged for 2 - 6 hours in order to allow the hydrolysis of unreacted $NaBH_4$. The gold nanoparticle seeds exhibited a plasmon resonance peak at 500 nm, and had an average diameter of 5.2 ± 0.6 nm.

After the aging period, three growth solutions were prepared for the seed-mediated growth step. The first two solutions (**1** and **2**) contained 0.25 mL of 10 mM $HAuCl_4$, 0.05 mL of 100 mM NaOH, 0.05 mL of 100 mM ascorbic acid, and 9 mL of the prepared CTABr solution. The final growth solution (designated **3**), contained 2.5 mL of 10 mM $HAuCl_4$, 0.50 mL of 100 mM NaOH, 0.50 mL of 100 mM ascorbic acid, and 90 mL of the prepared CTABr solution. For syntheses involving the addition of iodide, controlled amounts of KI, NaI, or LiI were added to the original CTABr solutions such that growth solutions **1**, **2** and **3** were at the same iodide concentration. Final concentrations of 100, 75, 50, 25, 10, and 2.5 μM iodide were prepared by adding aliquots of a 0.1 M solution of either KI, NaI, or LiI to the previously prepared 150 mL CTABr solutions (prior to dissolving procedure by heating).

In all cases, particle formation was initiated by adding 1 mL of seed solution to growth solution **1**. The solution was gently shaken, and then 1 mL of growth solution **1** was immediately added to **2**, **2** was shaken, and all of the resulting growth solution was added to **3**. After the addition, the color of **3** changed from clear to deep magenta-purple over a period of 30 minutes for all preparations.

ICP-MS Analysis:

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; Thermo-Fisher) analysis was performed using an Argon gas generated plasma and a 5% NH_4OH matrix.[1] Experimental ICP values were compared to a standard curve generated using standards prepared from NaI by weight (1, 2, 5, 10, 25, 50, 100, and 200 ppb by weight) and dissolved in the NH_4OH matrix. A 1ppb Indium internal standard was used in all measurements.

XPS Analysis:

Particle solutions were washed by centrifugation at 8 krpm for 3 min, and nanoparticle pellets were resuspended in 1 mL of NANOpure™ water. This process was repeated three times, and the final pellet was resuspended in 200 μL of NANOpure™ water. Two 10 μL droplets of this mixture were applied to a silicon substrate (substrate was cleaned by sonication in ethanol, rinsed with acetone, and finally rinsed with water) and allowed to dry in a vacuum-sealed desiccator. The substrate was then rinsed again with water and dried under a stream of N_2.

After preparation, the sample was transferred to an analysis chamber equipped with an X-ray photoelectron spectrometer (XPS, Omicron). An aluminum Kα (1486.5 eV) anode with a power of 200 W (20 kV) was used. XPS spectra were gathered using a hemispherical energy analyzer operated at a pass energy of 70.0 eV for survey scans and 20.0 eV for elemental analysis. Binding energies were referenced to the Au_{4f} peak at 84.0 eV for pure Au.

UV-vis-NIR Spectrophotometry and TEM Analysis:

The seed mediated growth reaction of the nanoparticles was characterized by ultraviolet-visible-near infrared spectroscopy (UV-Vis-NIR) using a Cary 5000 spectrophotometer, baselined to the spectrum of NANOpure™ water. All nanostructures were characterized using a Hitachi-8100 transmission electron microscope (TEM) at 200kV.

Additional Notes:

Elucidating the Detection of Iodide by XPS: In our experiments, we observe the presence of iodide on the surface of gold nanoprisms by XPS which is very likely a result of the (111) crystal facet concentrating iodide ion out of the reaction solution. We confirmed by ICP-MS that the highest concentration of iodide in any CTABr analyzed was likely below the detection limit of XPS. However, to further evaluate the possibility that CTABr observed on the surface of the nanoprisms was a result of the high iodide in the CTABr itself we collected XPS spectra of pure powders from 3 different CTABr batches (#1, #2, and #3). As expected, we did not observed iodide in any sample (Figure S1).

Role of Other Halide Ions: We were not able to reproduce controlled nanoparticle growth using either Br or Cl sodium salts at the concentrations studied. For Br, these results are easily understandable because Br is already present in large quantities in the CTABr, and adding more does not change the effective chemistry of the reaction. In the case of chloride, it has a weaker binding affinity for the gold surface as compared to Br^- or I^- and is unable to effectively block growth in a particular crystal direction.[2]

1. Bu, X.; Wang, T.; Hall, G., *J. Anal. At. Spectrom.* **2003,** *18*, 1443–1451.
2. Magnussen, O. M., *Chem. Rev.* **2002,** *102*, 679-726.

Table S1. Iodide Concentrations of Reagents Used in Syntheses as Analyzed by ICP-MS

Chemical Reagent	Manufacturer, Purity, Batch Number	Iodide concentration in 0.01% aqueous CTAB solution (nM)
$HAuCl_4$	Aldrich, 99.99%	-
Ascorbic Acid	Aldrich, 99+%	-
NaOH	Aldrich, 97%	-
$NaBH_4$	Aldrich, 99.995%	-
Trisodium Citrate	Aldrich, 98%	-
CTABr #1	Sigma, 99%, #095K0187	-
CTABr #2	Aldrich, 95%, #06901CD	6.3
CTABr #3	Aldrich, 95%, #0590BH	-
CTABr #4	Aldrich, 95%, #06602KC	-
CTABr #5	GFS Chemical, 98%, #P452770	15.7
CTABr #6	Recrystallized CTABr #2	-

Figure S1

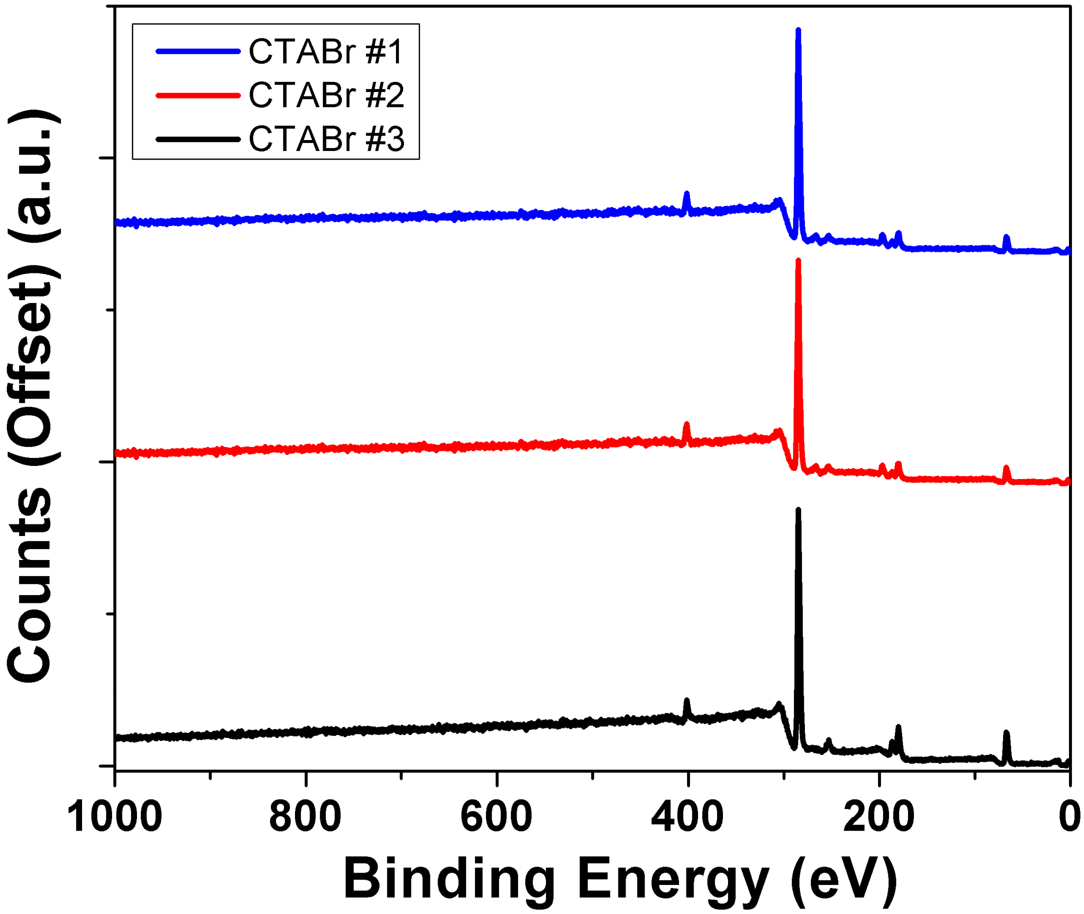

Figure S1. XPS Spectra of CTABr batches showing no presence of iodide.

Figure S2

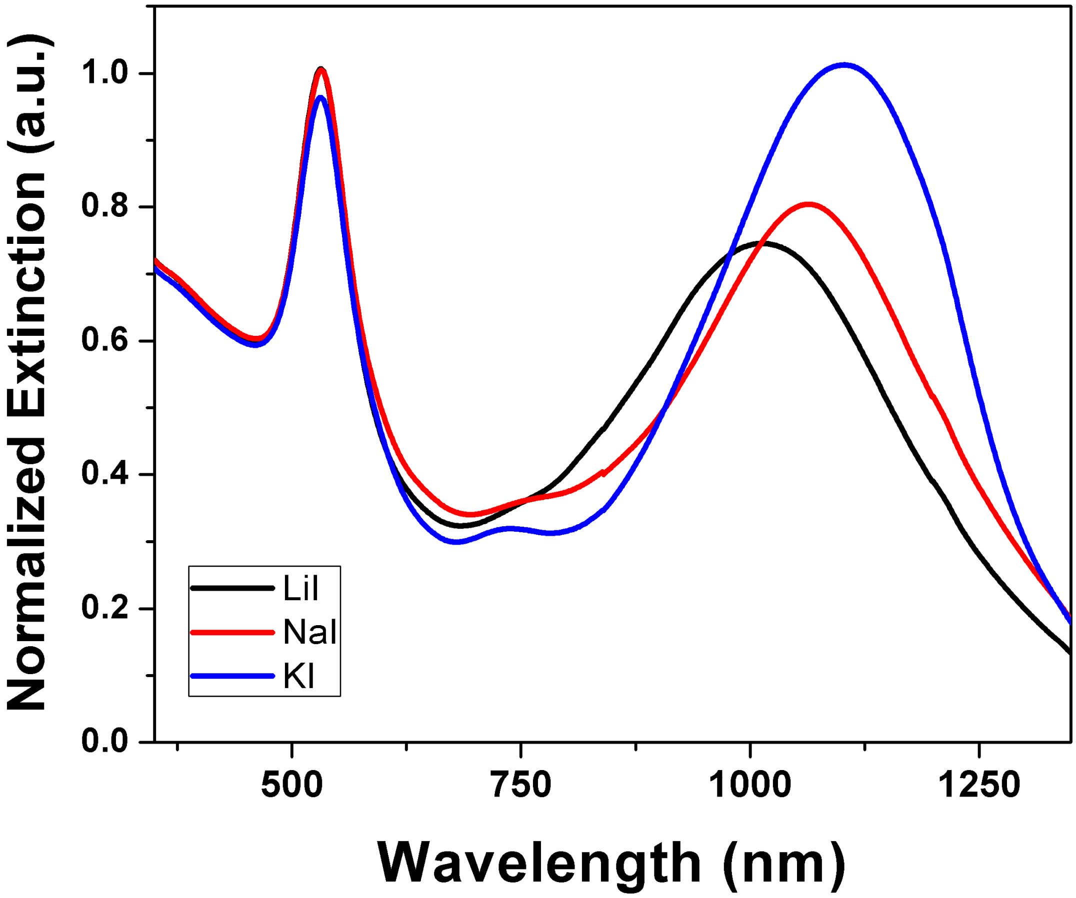

Figure S2. UV-vis-NIR spectra of nanoprism solutions made using 50 μM concentrations of LiI, NaI, and KI. Each batch shows the characteristic dipole and quadrupole plasmon resonances of Au nanoprisms.