Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

The Evolution of Size, Shape, and Surface Morphology of Gold Nanorods

Wenming Tong,[†] Hadas Katz-Boon,[‡] Michael J. Walsh,[‡] Matthew Weyland,[§] Joanne Etheridge,[§] Alison M. Funston[†]

[†]ARC Centre of Excellence in Exciton Science and School of Chemistry, Monash University, Clayton, Victoria, 3800, Australia

[§]Monash Centre for Electron Microscopy, Monash University, Clayton, Victoria, 3800, Australia

[‡]Department of Materials Science and Engineering, Monash University, Clayton, Victoria, 3800, Australia

Experimental

(1) Chemicals

Gold (III) chloride trihydrate ($AuHCl_4.3H_2O$) (≥99.9%), silver nitrate ($AgNO_3$) (≥99.0%), sodium borohydride ($NaBH_4$) (≥99.0%), and *L*-ascorbic acid (AA) (≥99.0%) were purchased from Sigma-Aldrich. Hexadecyltrimethylammonium bromide (CTAB) (98%) was purchased from Ajax Finechem. All chemicals were used without further purification. Ultrapure water (milli-Q) was used for the preparation of all solutions.

(2) Synthesis:

Gold nanorod synthesis was carried out using the method reported by Nikoobakht.[S1]

Gold seeds: An aqueous solution of $HAuCl_4$ (0.025 mL, 0.05 M) was added to an aqueous solution of CTAB (4.700 mL, 0.1 M). The solution was stirred for at least 5 minutes. Upon rapid addition of freshly prepared aqueous $NaBH_4$ (0.300 mL, 0.025 M) into the mixture under rigorous stirring, the initial yellow/orange solution became light brown. The resultant solution was stirred for 15 minutes. The final seed solution was kept at 30 ± 1°C for at least 45 min before further use.

Growth of gold nanorods from gold seeds: An aqueous solution of $HAuCl_4$ (0.100 mL, 0.05 M) was added into an aqueous solution of CTAB (10 mL, 0.1 M). The solution stirred for at least 5 minutes. Aqueous solutions of freshly prepared ascorbic acid (0.0552 mL, 0.1 M) and $AgNO_3$ (0.020, 0.040, 0.060, 0.080, or 0.100 mL, 0.01 M) were then added sequentially with thorough mixing following each addition. Finally, gold seeds (0.012 mL) were added with stirring. The colour of the solution gradually changed within 15 minutes. The final solution was held at 30 ± 1°C for up to 13 weeks.

(3) Instrumental

UV-visible extinction spectra were acquired using Cary 60 UV-Vis spectrophotometer or Cary 5000 UV-Vis-Near IR spectrophotometer.

Electron microscopy was carried out at the Monash Centre for Electron Microscopy on an FEI Tecnai G2 T20 TWIN TEM and a FEI Titan^3 80-300kV FEGTEM fitted with spherical

aberration-correctors on the probe and image forming lens systems. The gold nanorod solutions were centrifuged and redispersed in ultrapure water twice prior to deposition on a TEM grid. A droplet of the sample was allowed to sit on the TEM grid for 5 – 10 minutes before the TEM grid was soaked in high purity ethanol for ~20 min to remove excess CTAB. For quantitative STEM analysis and tomography reconstruction, thin (5nm) Si support membrane windows were used. There was then no further treatment of samples prior to electron microscopy analysis (in particular, the specimens were not plasma cleaned). The intensity was averaged within Voronoi cells around each peak to mitigate partially the effect of probe characteristics, such as defocus, aberration and source distribution[S1].

Quantitative STEM images were acquired using the aberration corrected FEI Titan^3 80-300 FEGTEM operating at 300kV. For the quantification of atoms per column, images were acquired using a 15mrad convergence angle and inner and outer HAADF detector angles of 46.3 and 200 mrad respectively. Response of the HAADF detector was characterized on the same day by scanning the incident beam over the detector in the absence of a specimen.

Electron tomograms were reconstructed using ADF-STEM tomography tilt series of a single nanorod acquired using the aberration corrected FEI Titan^3 80-300 FEGTEM, at magnifications of 1.81Mx (2048 pixels square, 24pm per pixel) and 1.3Mx (2048 pixels square, 33pm per pixel) for the 2 hour and 13 weeks samples, respectively. A series of 79 images were manually acquired at 300kV at tilt angles ranging from -78º to +80º in 2º steps. Processing of tomographic data was carried out using existing and new home coded software in IDL 8.1.[S2] The raw tilt series was processed to remove fast and slow scan distortions using the lattice spacings/angles in each image, this corrected both apparent shear and stretch caused by specimen drift/charging during scan frames and between scan frames. This is critical to achieve geometric correctness on such a small scale. Images were then aligned to sub-pixel accuracy using automated cross-correlation and manual adjustment. Final three dimensional reconstruction was carried out on background stripped data using the SIRT algorithm with 30 iterations. Amira 6.0.0 software was used to measure and visualize the shape from the reconstruction.

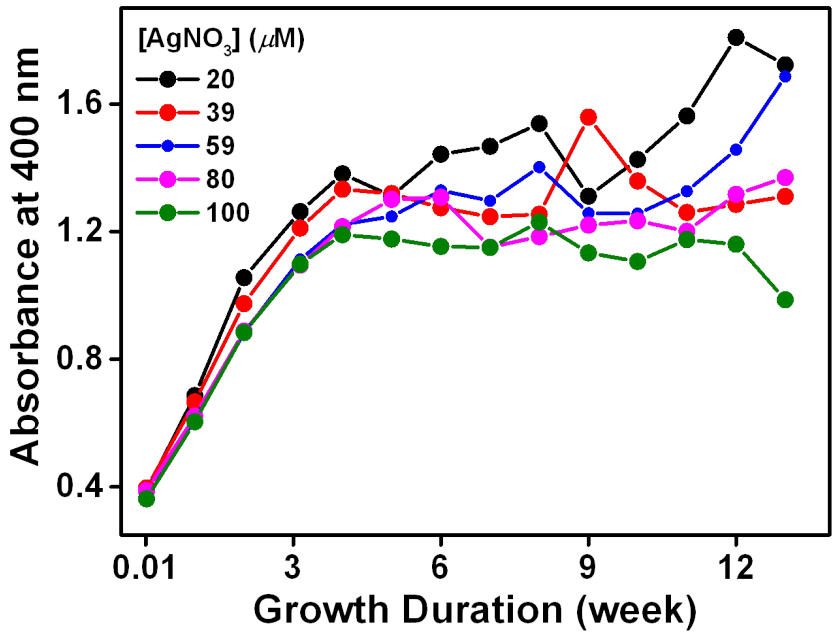

Figure S1. The absorbance of gold nanorod solutions at 400 nm as a function of growth duration.

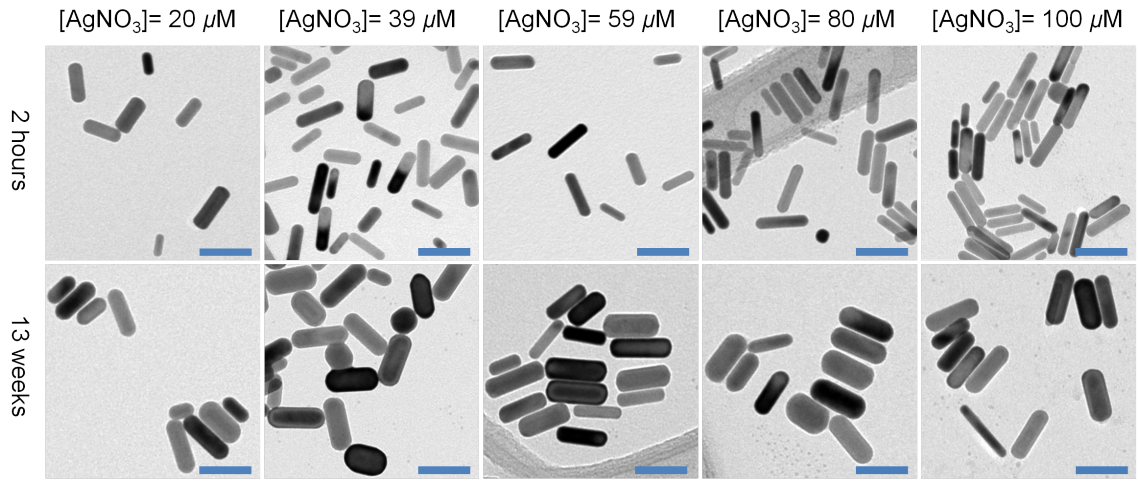

Figure S2. TEM images of gold nanorods grown for 2 hours and 13 weeks in the presence of different $AgNO_3$ concentrations. The scale bars represent 50 nm.

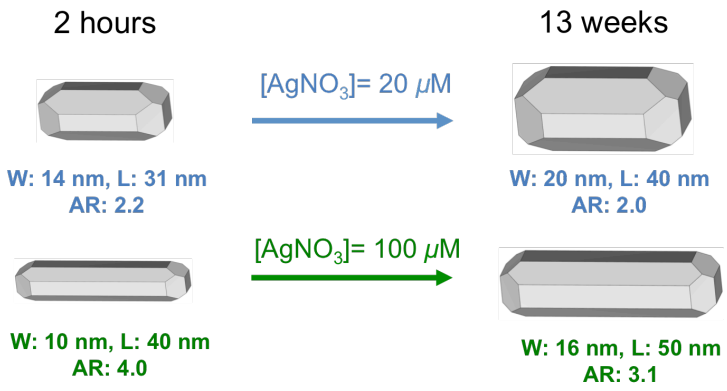

Figure S3. Schematic summary of gold nanorod dimensions at 2 hours and 13 weeks, drawn to scale. The average width (w), length (L), and aspect ratio (AR) are given for comparison. Faceting depicted is generic.

Table S1. Average sizes, aspect ratios, and particle volumes of gold nanorods grown for 2 hours and 13 weeks as measured via TEM. Standard deviation shown in parenthesis.

Ag (μM)	L_{2h} (nm)	L_{13w} (nm)	W_{2h} (nm)	W_{13w}(nm)	AR_{2h}	AR_{13w}	V_{2h} ($\times10^3$ nm^3)[a]	V_{13w} ($\times10^3$ nm^3)[a]	Particles Measured (2 h)	Particles Measured (13 weeks)
20	31(9)	40(11)	14(3)	20(6)	2.2(0.8)	2.0(0.8)	5(3)	12(7)	2015	1004
39	32(10)	45(9)	12(2)	19(4)	2.7(1.0)	2.4(0.7)	3(2)	12(5)	2204	1184
59	32(10)	47(9)	11(2)	18(4)	2.9(1.0)	2.6(0.8)	3(2)	11(6)	1825	2818
80	38(10)	49(10)	11(2)	18(4)	3.5(1.1)	2.7(0.8)	4(2)	12(6)	2883	1844
100	40(9)	50(8)	10(2)	16(4)	4.0(1.7)	3.1(0.9)	3(2)	10(5)	3506	3121

a) The average volume is calculated assuming hemispherical tips and is the mean of the volumes of individual nanorods.

Attached files:

Movie 1. Three dimensional morphologies of gold nanorods grown for 2 hours and 13 weeks.

Movie 2. Demonstration of cross sections along the length of gold nanorods grown for 2 hours and 13 weeks.

Bibliography

S1. B. Nikoobakht, M. A. El-Sayed, *Chem. Mater.* **2003**, *15*, 1957–1962.

S2. C. J. Rossouw, C. Dwyer, H. Katz-Boon, J. Etheridge, *Ultramicroscopy* **2014**, *136*, 216–223.