

Solution Synthesis of Anisotropic Gold Microcrystals

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Supporting Information (SI)

EXPERIMENTAL

Material and Characterization: Unless otherwise stated all the chemicals were purchased from commercial suppliers and used without further purification. Cetyltrimethylammonium bromide (CTAB) was purchased from Acros Organics Inc. Hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), ascorbic acid, sodium borohydride, and sodium citrate were purchased from Sigma-Aldrich. De-ionized (DI) water was used for all the experiments. SEM images were collected by using FEI Quanta 400 ESEM FEG SEM equipment. TEM images were obtained on a JEOL 1200EX transmission electron microscope operating at 100 kV accelerating voltage, and JEOL 2010 TEM microscope using carbon-coated copper grid (Electron Microscopy Sciences). Optical extinction spectra were obtained with a Cary 5000 UV/Vis/NIR spectrophotometer using H_2O solutions of CTAB stabilized nanostructures. SEM samples were prepared by air drying a

drop of microstructures solution in a piece of silicon wafer. After drying, white crystal of CTAB were seen on silicon surface which were ringed with DI water very carefully.

AuMR's Size calculation: ImageJ software from NIH was used for AuMRs size calculation. The images used for size calculation were randomly selected from different locations of SEM samples for representative SEM images selection. From each image used, 10 nanostructures were randomly selected and their size (l x w) was carefully measured by using photoshop ruler tool. Next, the representative SEM images were imported to ImageJ for size calculation. The size of nanostructures from ImageJ output was verified and compared with that of photoshop manual measurement. The ImageJ size calculation algorithms were adjusted until its output size matched with that of manual measurement. All the partial nanostructures from the edge of image were excluded from size calculation. Photoshop ruler tool was used to calculate the size when ImageJ software was not able to isolate individual nanostructures for size calculation when the AuMRs were closely packed. The data output from ImageJ and manual measurement method was analyzed by using statistical software JMP from SAS.

Synthesis and isolation of gold nanorods (AuNRs): AuNRs were synthesized by using seed mediated method¹ and their purification and isolation was done by selective dissolution and gravitational sedimentation technique as described on our earlier report.² In a typical experiment, of sodium citrate (1.47 mg) and of H₂AuCl₄·3H₂O (1.97 mg) were dissolved in 20 mL water. To this solution of 0.1 M ice-cold NaBH₄ (0.6 mL) solution was added upon vigorous stirring (1200 rpm). The solution turned brownish-red, indicating the formation of 3-4 nm gold particles. These seed particles were used within 10 min after the preparation.

In a 2 L flask, of CTAB (64.06 g) was dissolved in water (880 mL) upon gentle heating (~35 °C). In a separate flask, of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (173.4 mg) was dissolved in water (880 mL) and mixed with CTAB solution. Three flasks with the capacity of 100, 250, and 2000 mL were labeled as A, B, and C, respectively. The prepared solution in the amount of 45, 140, 1575 mL was placed into flasks A, B, and C, respectively, and kept at 27 °C. Next, 0.1 M ascorbic acid solution in water was prepared by dissolving of ascorbic acid (176 mg) in 10 mL of water. After that, 0.25, 0.77, and 8.75 mL of ascorbic acid solution was added into flasks A, B, and C, respectively. All three flasks were hand shaken and the solutions became colorless. Then, 4 mL of seed solution was added to flask A and gently mixed. Immediately after that 12.4 mL of the resulting mixture was transferred from flask A to flask B within 3 seconds and gently mixed. This was immediately followed by transferring all of the content of flask B into flask C within 3 seconds before quick mixing by shaking the flask. The flask C was then left undisturbed and the color of the resulting solution slowly changed to purple after 2-3 min and then to dark-red after 30 min. Flask C was then kept undisturbed for additional 14 h at 27 °C. AuNRs along with significant amount of faceted 2D platelets precipitate from the solution and form a thin barely noticeable film at the bottom of the flask. The resulting supernatant, which contained mostly spherical nanoparticles, was carefully removed and the walls of the flask as well as the film on the bottom were carefully rinsed with a small portion of DI water to remove the residual amount of the supernatant. The film of nanorods and platelets was re-dispersed into 10 mL of 0.1 M CTAB solution upon brief sonication (30 sec). Separately, an oxidizing Au(III)/CTAB complex for the partial dissolution of platelets was prepared by dissolving 364 mg of CTAB (364 mg) and 1.97 mg of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in 10 mL of DI water. Next, 1 mL of this solution was added to suspension of nanorods and platelets in CTAB aqueous solution upon stirring and left

undisturbed for 14 h. Nanorods along with a small amount of large disks precipitated and formed a thin film on the bottom of the flask. The greenish-blue supernatant containing small nanodisks was carefully collected and the film of the precipitate was again re-dispersed in 10 mL of 0.1 M CTAB solution followed by addition of another 1 mL of the Au(III)/CTAB solution. This process of partial dissolution was repeated several times (typically 3-4) until the examination of the precipitate confirmed complete removal of platelets. The pure AuNRs were dispersed in 20 mL of 0.1M CTAB solution and used as seed particles.

Synthesis of gold microrods (AuMRs): AuMRs were synthesized by the fast deposition of Au(I) ions on pure AuNRs. The growth solution was prepared by dissolving $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and 3.64 g of CTAB in 100 mL of DI water. Appropriate amount of 0.1 M ascorbic acid was used for the initial reduction. The amount of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ dissolved, ascorbic acid and the dimension of AuMRs obtained is given in a table 1.

In a typical synthesis of AuMRs, 500 μL of AuNRs seed solution was used as seed. The

Table 1. Amount of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and Ascorbic Acid used to synthesized various sizes AuMRs

$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (mg)	Ascorbic Acid (mL)	Length (nm)	Width (nm)
4.925	0.27 mL	500-600	100-110
9.85	0.55 mL	700-900	150-170
19.7	1.1 mL	900-1100	200-230
39.4	1.65 mL	1200-1400	290-320

flask was hand stirred every 1-2 h for 10-12 h and left undisturbed for another 12 h As the AuNRs grew and become AuMRs, they tend to precipitate fast and settle at the bottom of flask.

The colorless supernatant which mainly contains small amount of unconsumed Au(I) was discarded. The precipitate was re-dispersed into 15 mL of 0.1 M CTAB in H_2O solution and left

undisturbed for another 12 h. Next, the colorless supernatant was discarded and the microrods were re-dispersed into 0.1 M CTAB in H₂O solution. This process was repeated three times until all the residual Au(I) was removed. A drop of AuMRs solution was cast on silicon wafer for SEM characterization.

Tip selective dissolution of AuMRs: The tip selective dissolution technique³ was applied to synthesize low aspect ratio AuMRs. In a typical experiment, the oxidizing agent was prepared by dissolving CTAB (0.1M) and H₂AuCl₄·3H₂O (5×10⁻⁴ M) in H₂O. In general, 5 mL of oxidizing agent was added to the AuMRs solution and the reaction was let go for at least 2 h. The reaction flask was hand shaken 10-15 mins to prevent AuMRs precipitation. The dissolution process by the addition of oxidizing agent was repeated until the desired length of AuMRs was achieved.

Tip selective growth of AuMRs: High aspect ratio AuMRs were prepared by tip selective growth of AuMRs.³ The growth solution was prepared by dissolving CTAB (0.1M) and 9.85 mg of H₂AuCl₄·3H₂O in 100 mL DI water. To this solution 1 mL of concentrate HCl was added and mixed gently. After ~2 min of 0.1 M ascorbic acid (0.55 mL) solution was added. The flask was hand shaken until the solution became colorless (typically 3-5 min). At this point 0.1 mL solution of AuMRs solution was introduced and the flask was hand shaken for 30 sec. The flask was hand shaken every ~1 h. for 12 h and left undisturbed for 12 h at 25 °C. The amount of Au(I) and equimolar amount of ascorbic acid was adjusted per desired length of high aspect ratio AuMRs. For the removal of excess of Au(I) and HCl, the AuMRs was let undergo gravitational precipitation for ~10- 12 h and the supernatant was discarded followed by re-dispersion of AuMRs into fresh aqueous CTAB (0.1M) solution. This process was repeated at least three times to confirm removal of all the excess of Au(I) and HCl.

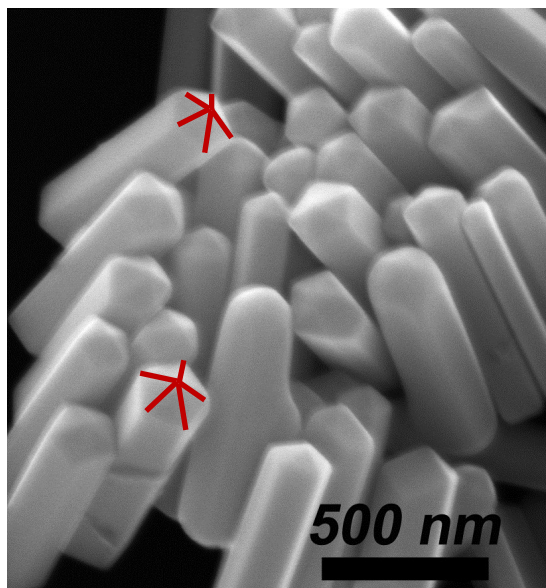


Figure SI 1. SEM images vertically standing AuMRs which shows the very clear pentahedrally twinned crystal geometry on the tips and startlingly smooth side facets.

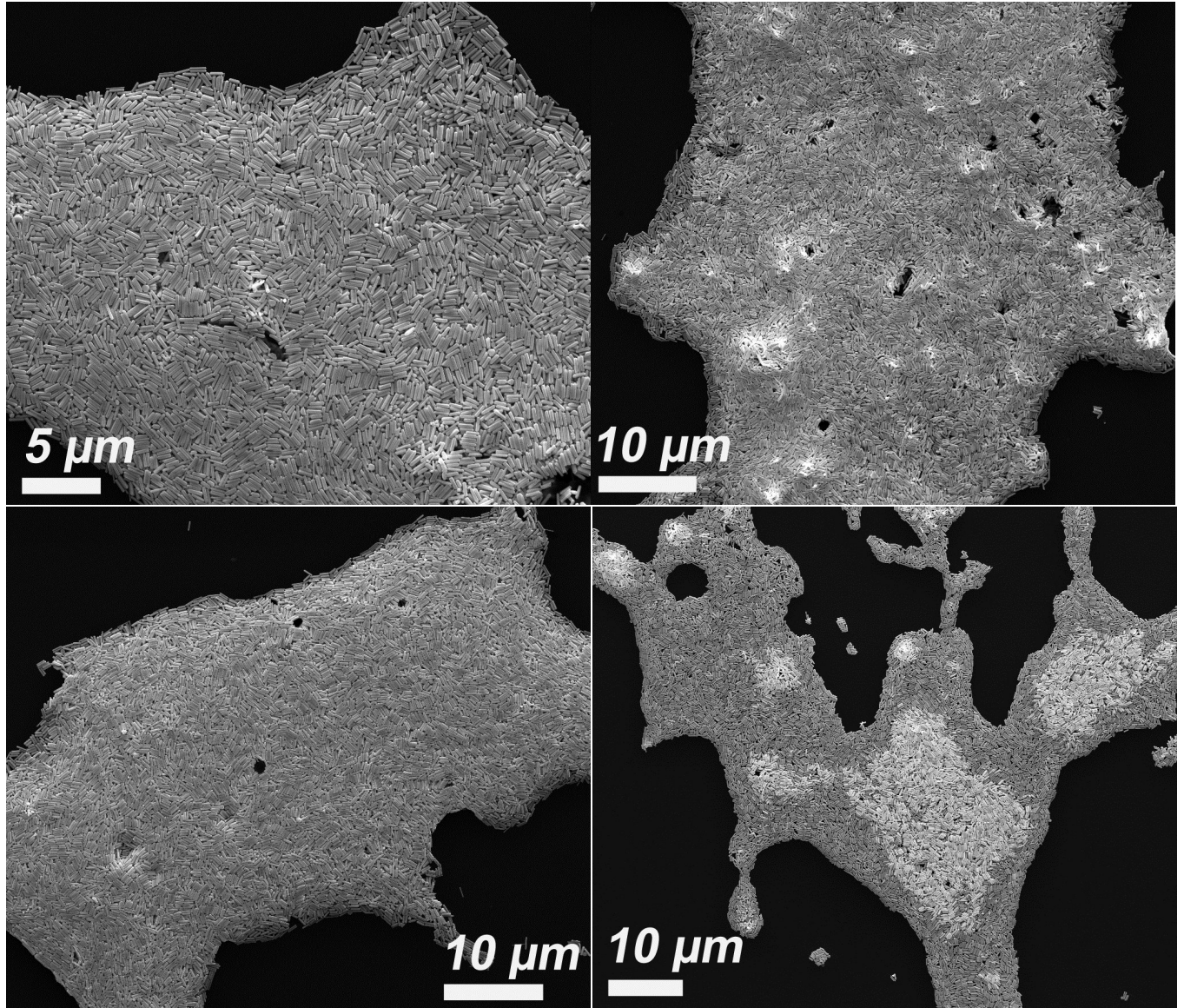


Figure SI 2. SEM images of AuMRs at low magnification showing the overall yield and purity of the synthetic procedure

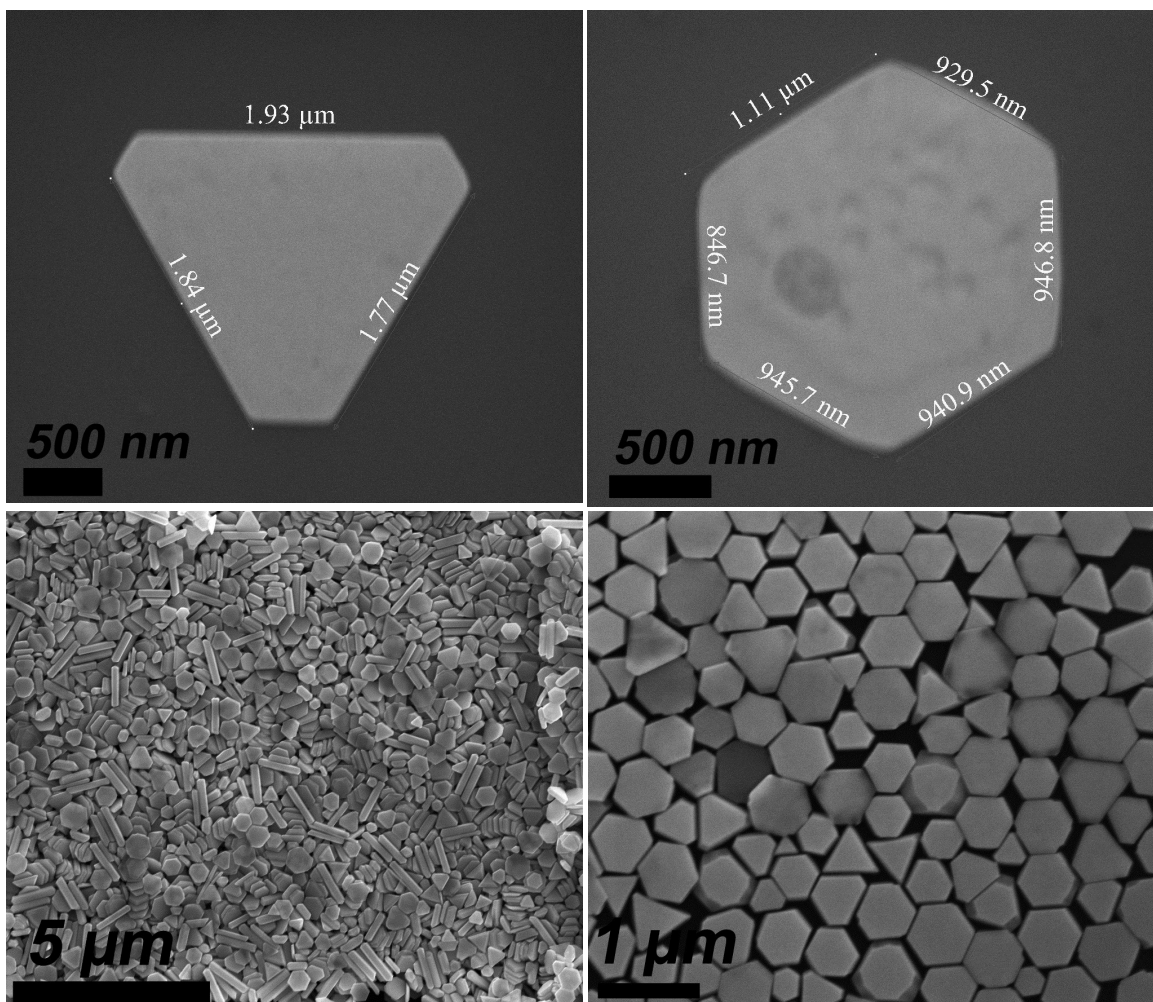


Figure SI 3. SEM images of 2D faceted edge platelets after growth. The platelets very well maintained their faceted edges and shapes due to uniform deposition of Au(0).

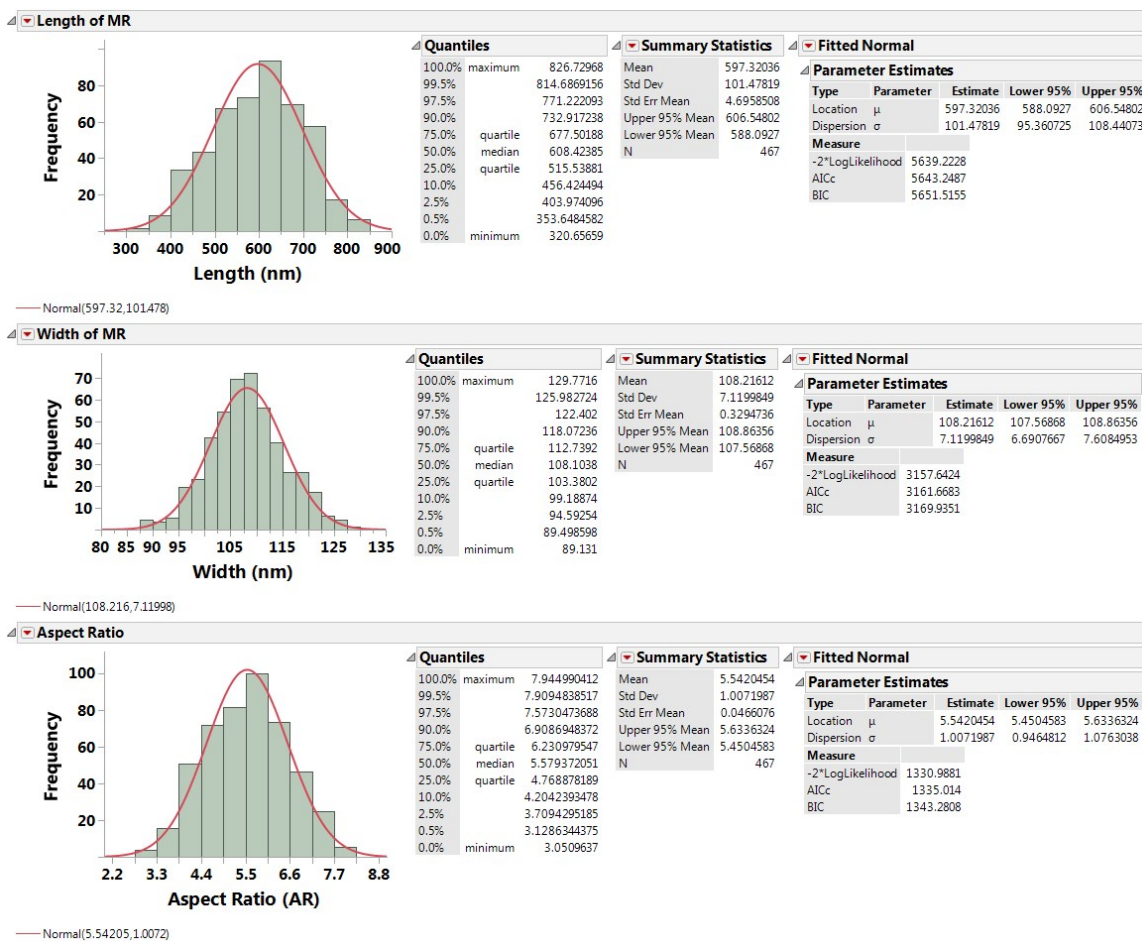


Figure SI 4. Statistical data analysis for the dimensions and aspect ratio of AuMRs synthesized by using 12.5 μmol of Au(I) in growth solutions. Representative SEM images shown in main text Fig 6 and SI 9 were used for the size calculations.

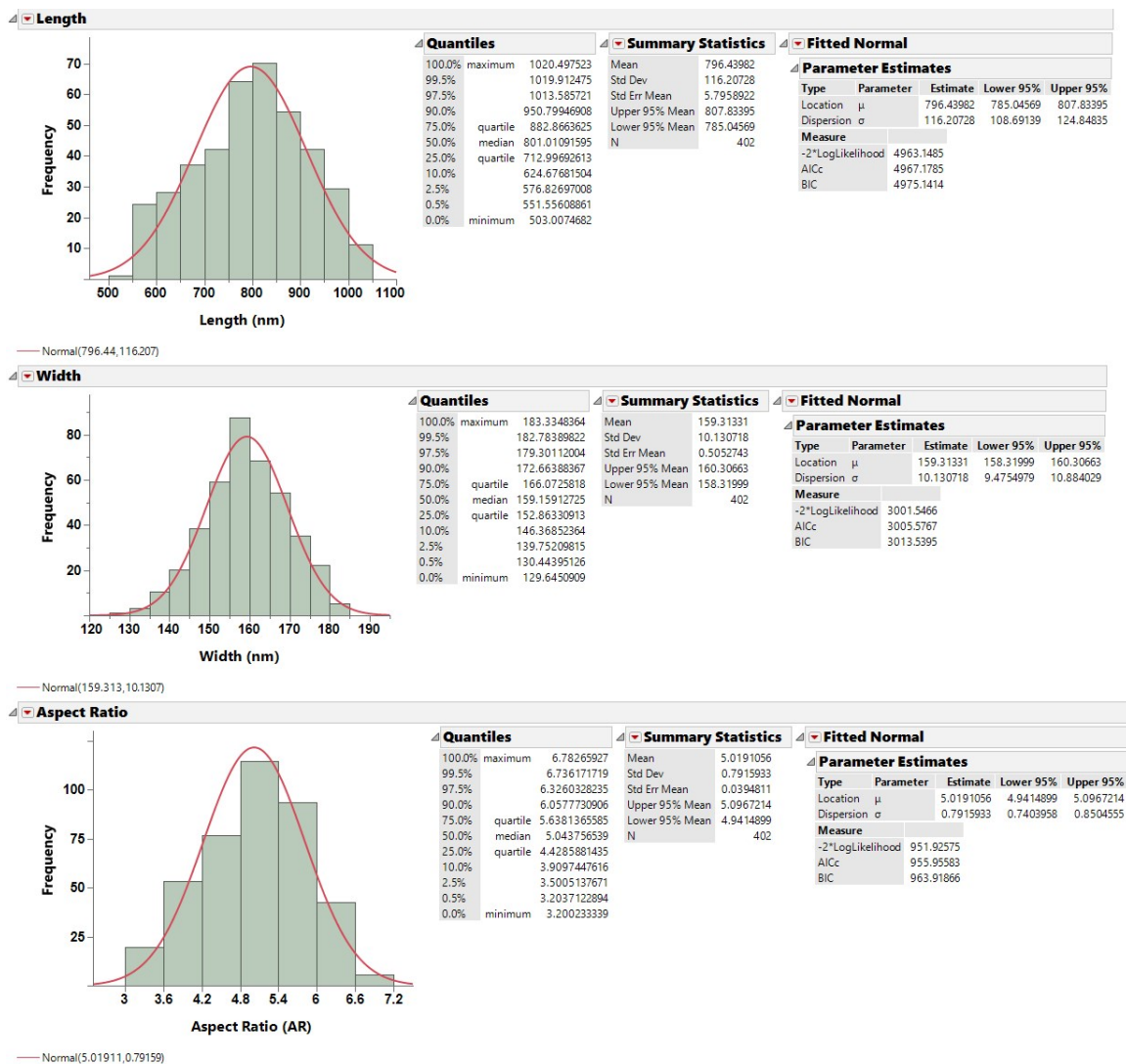


Figure SI 5. Statistical data analysis for the dimensions and aspect ratio of AuMRs synthesized by using 25.01 μmol of Au(I) in growth solutions. SEM images shown in main text Fig 6 and SI 9 were used for the size calculations.

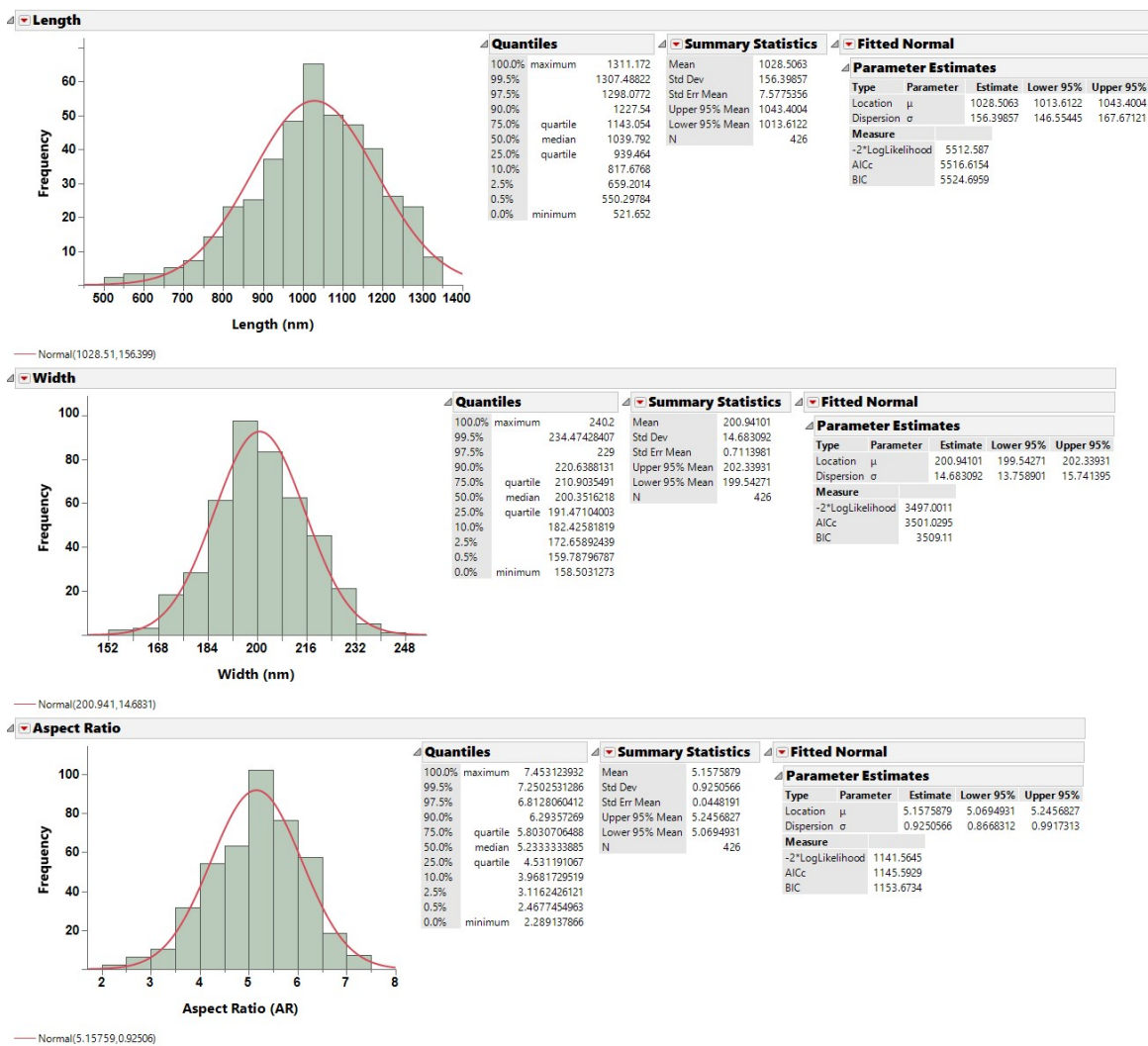


Figure SI 6. Statistical data analysis for the dimensions and aspect ratio of AuMRs synthesized by using 50.02 μmol of Au(I) in growth solutions. SEM images shown in main text Fig 6 and SI 9 were used for the size calculations.

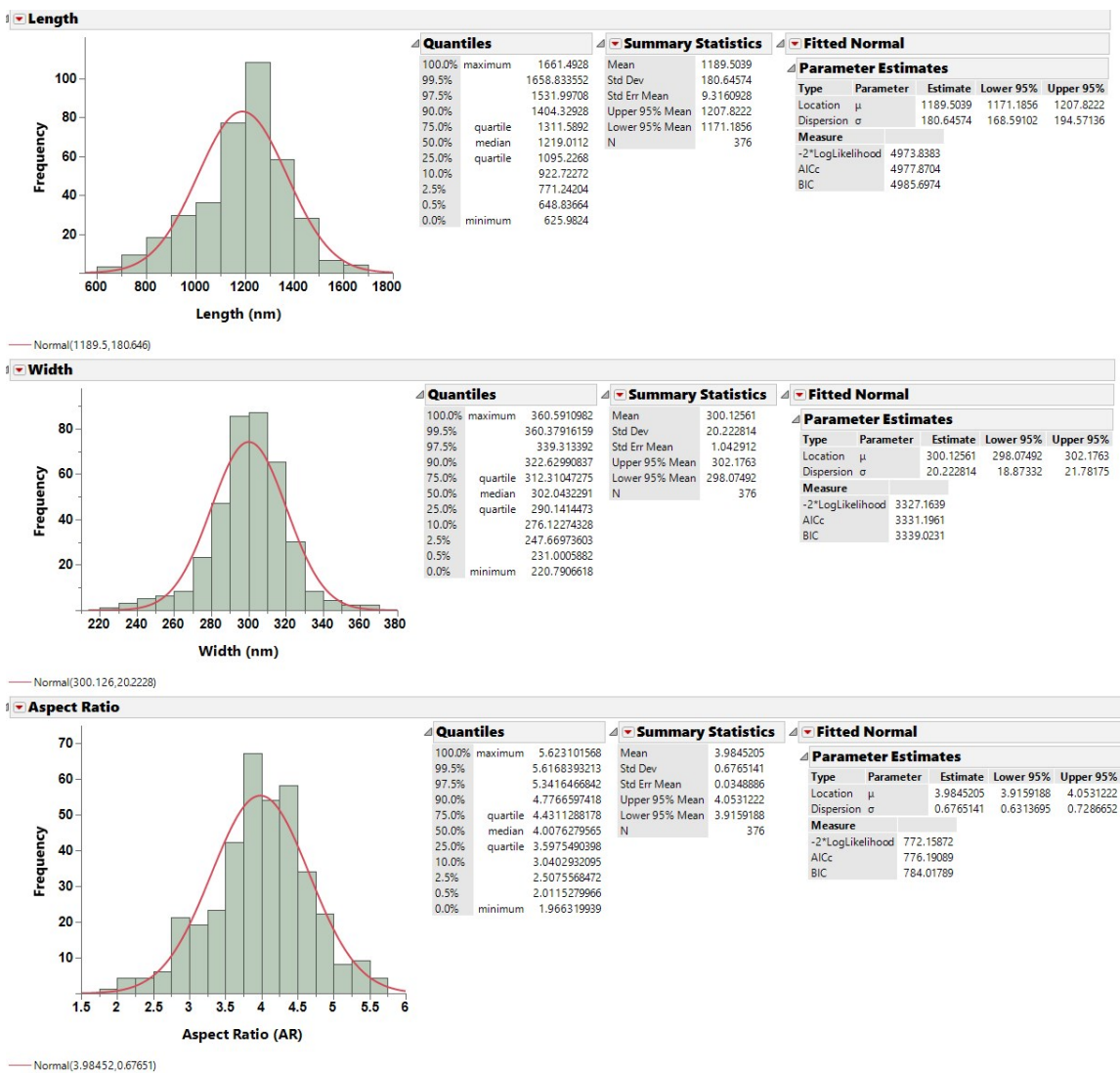


Figure SI 7. Statistical data analysis for the dimensions and aspect ratio of AuMRs synthesized by using 100.04 μmol of Au(I) in growth solutions. SEM images shown in main text Fig 6 and SI 9 were used for the size calculations.

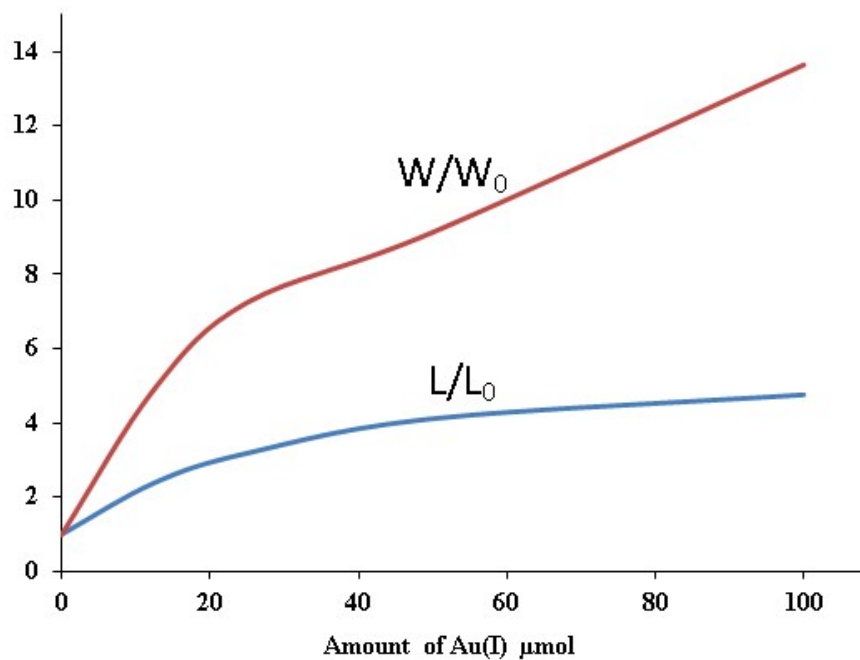


Figure SI 8. Graph showing increase in width and length of AuMRs with the amount of Au(I) in growth solution. Width of AuMRs/width of AuNRs (Red) and length of AuMRs/length of AuNRs (blue). W = width of AuMRs and W_0 = width of AuNRs seed and L = length of AuMRs and L_0 = length of AuNR seed.

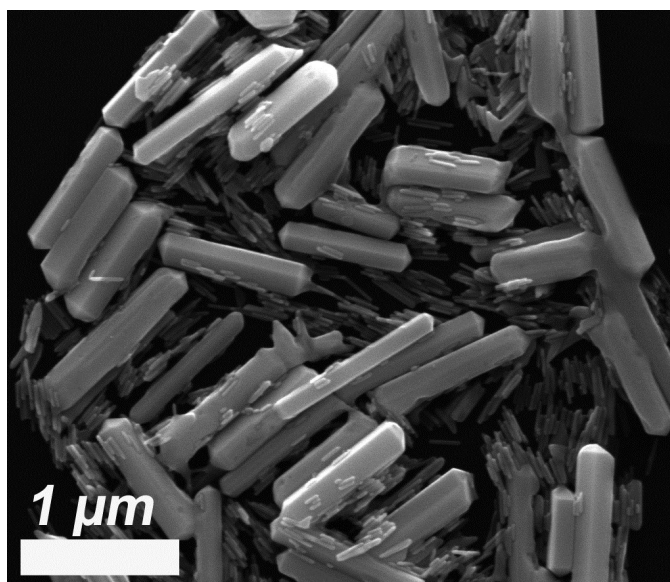


Figure SI 9. SEM image of mixture of AuNRs seed and AuMRs which very evidently shows the significant increase in length and width of AuNRs without any morphological distortion.

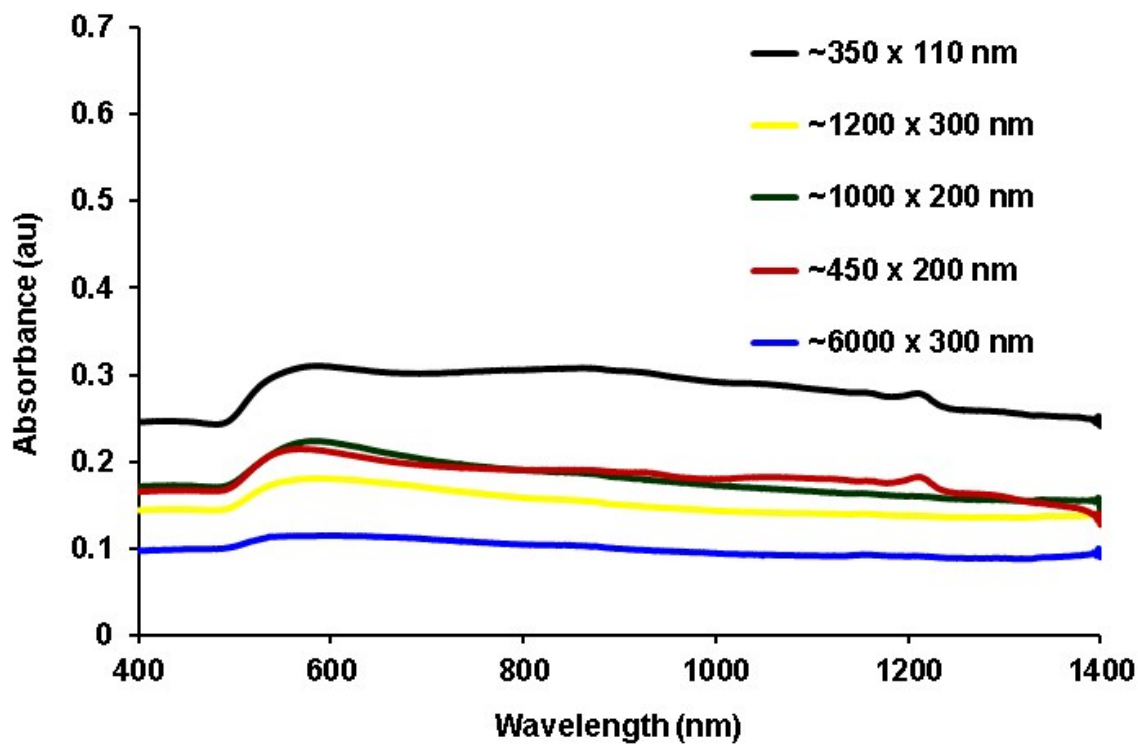


Figure SI 10. UV-Vis-NIR spectra of AuMRs of various dimensions shown in inset.

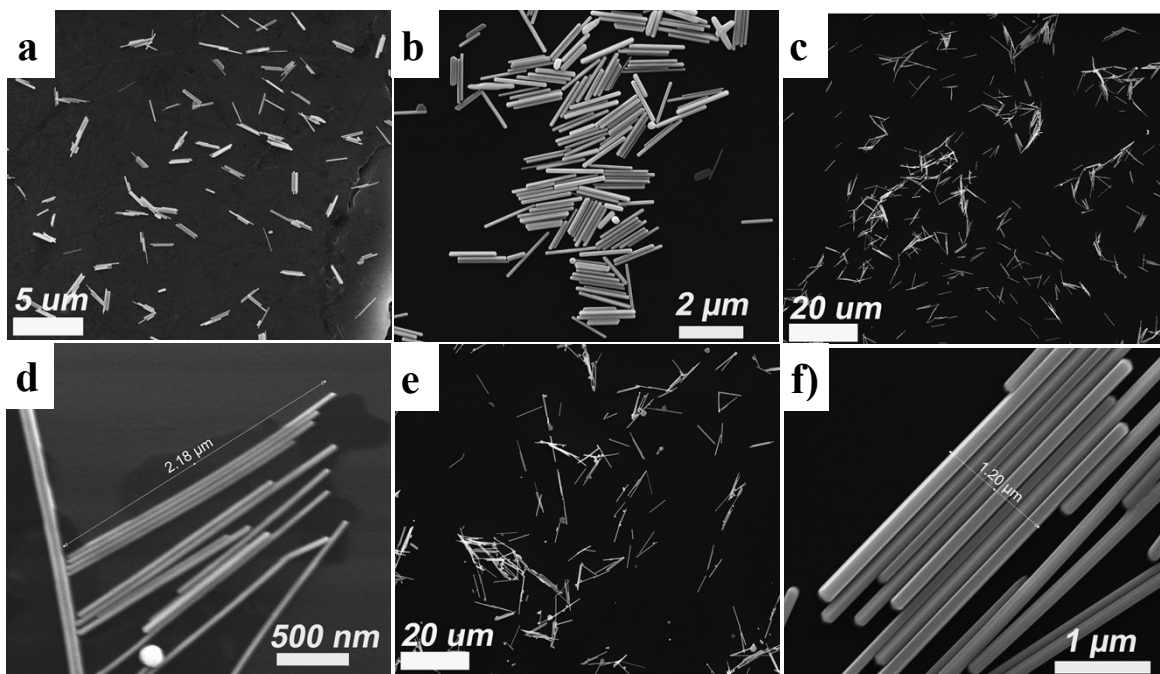


Figure SI 11. High and low magnification SEM image of AuMWs (1.5 μm (a & b), 3 μm (c & d), 5.5 μm (e & f)) synthesized by growing AuMRs of 600 nm x 110 nm.

References:

1. N. R. Jana, L. Gearheart and C. J. Murphy, *J. Phy. Chem. B*, 2001, **105**, 4065-4067.
2. B. P. Khanal and E. R. Zubarev, *J. Am. Chem. Soc.*, 2008, **130**, 12634-12635.
3. B. P. Khanal and E. R. Zubarev, *ACS nano*, 2019, **13**, 2370-2378.