

Supporting Materials

Table S1: Dimensions of nanorods obtained by overgrowth at constant $\text{Au}^{3+}/\text{Au}^0 = 12.5$.

Seed volume	CTAB (mM)	Length (nm)	Width (nm)	Aspect ratio	Side length (nm)	Volume ($10^3 \cdot \text{nm}^3$)	LSPR (nm)	Simulated LSPR (nm)
30 μL	0.5	202 $\pm$ 11	60 $\pm$ 3	3.4 $\pm$ 0.3	166 $\pm$ 12	404 $\pm$ 13	936	974
	1	203 $\pm$ 11	66 $\pm$ 3	3.0 $\pm$ 0.2	165 $\pm$ 11	487 $\pm$ 15	901	948
	2	171 $\pm$ 11	70 $\pm$ 5	2.5 $\pm$ 0.2	129 $\pm$ 11	434 $\pm$ 30	846	835
	5	154 $\pm$ 12	71 $\pm$ 4	2.2 $\pm$ 0.2	112 $\pm$ 13	387 $\pm$ 25	751	771
	10	154 $\pm$ 7	82 $\pm$ 6	1.8 $\pm$ 0.2	102 $\pm$ 11	481 $\pm$ 53	680	705

Table S2: Dimensions of nanorods obtained using different amounts of CTAB.

CTAB	$\text{Au}^{3+}/\text{Au}^0$ (volume seeds, μL)	Length (nm)	Width (nm)	Aspect ratio	Side length (nm)	Volume (nm^3)	LSPR (nm)	Simulated LSPR (nm)
0.5 mM	6.25(60)	172 $\pm$ 14	53 $\pm$ 3	3.3 $\pm$ 0.3	139 $\pm$ 14	265 $\pm$ 14	855	906
	18.75(20)	240 $\pm$ 17	72 $\pm$ 3	3.4 $\pm$ 0.3	196 $\pm$ 17	688 $\pm$ 27	998	1068
	25(15)	266 $\pm$ 17	76 $\pm$ 4	3.5 $\pm$ 0.3	219 $\pm$ 18	855 $\pm$ 36		1142
1 mM	6.25(60)	153 $\pm$ 11	55 $\pm$ 3	2.8 $\pm$ 0.3	118 $\pm$ 12	244 $\pm$ 14	788	924
	18.75(20)	211 $\pm$ 14	70 $\pm$ 4	3.9 $\pm$ 0.3	168 $\pm$ 14	559 $\pm$ 24	930	964
	25(15)	231 $\pm$ 15	80 $\pm$ 5	2.8 $\pm$ 0.3	184 $\pm$ 15	801 $\pm$ 44	988	1005
2 mM	6.25(60)	147 $\pm$ 10	59 $\pm$ 2	2.5 $\pm$ 0.2	112 $\pm$ 10	267 $\pm$ 8	768	782
	18.75(20)	158 $\pm$ 19	72 $\pm$ 5	2.2 $\pm$ 0.3	116 $\pm$ 19	593 $\pm$ 38	843	870
	25(15)	165 $\pm$ 12	76 $\pm$ 4	2.2 $\pm$ 0.2	119 $\pm$ 12	8101 $\pm$ 44	886	927
5 mM	6.25(60)	126 $\pm$ 8	60 $\pm$ 3	2.1 $\pm$ 0.2	87 $\pm$ 9	220 $\pm$ 15	696	710
	18.75(20)	163 $\pm$ 12	83 $\pm$ 4	2.0 $\pm$ 0.2	109 $\pm$ 13	530 $\pm$ 40	750	769
	25(15)	178 $\pm$ 11	90 $\pm$ 5	2.0 $\pm$ 0.2	122 $\pm$ 12	689 $\pm$ 45	783	802
10 mM	6.25(60)	132 $\pm$ 7	64 $\pm$ 5	2.1 $\pm$ 0.2	91 $\pm$ 11	252 $\pm$ 27	701	715
	18.75(20)	166 $\pm$ 11	87 $\pm$ 7	1.9 $\pm$ 0.2	111 $\pm$ 15	588 $\pm$ 70	705	738
	25(15)	184 $\pm$ 14	93 $\pm$ 8	2.0 $\pm$ 0.3	127 $\pm$ 19	749 $\pm$ 88	807	819

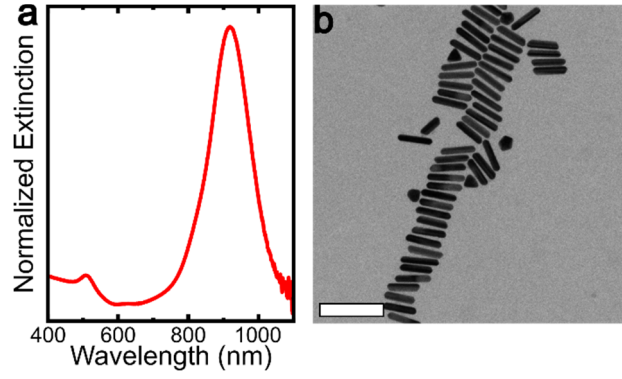


Figure S1. (a) UV-Vis-NIR spectrum of the seeds used for overgrowth. (b) TEM image of the 113×26 nm seeds used for overgrowth, The scale bar is 200 nm.

Details on the estimation of PT-AuNR volume

Detail of the expression of the volume from the measured length, as shown in **Figure S2**.

Area of a pentagon:

$$A = \frac{5R^2}{4} \sqrt{\frac{5 + \sqrt{5}}{2}} \approx R^2 \times 2.3776$$

R is the distance from a vertex to the center, which can be expressed as:

$$R = \frac{2D}{2\sin(36^\circ) \times (1 + \sqrt{5})}$$

Giving a final expression for the area:

$$A = \left(\frac{2D}{2\sin(36^\circ) \times (1 + \sqrt{5})} \right)^2 \times 2.3776 \approx D^2 \times 0.6571$$

The volume of the “central” pentagonal prism would be:

$$V_{PP} = D^2 \cdot l \cdot 0.6571$$

Considering the general estimation for the volume of a pyramid:

$$V_P = \frac{1}{3} \times B \times H$$

Where B and H are the base and height of the pyramid. Therefore:

$$V_P = D^2 \times 0.6571 \times \frac{L-l}{2} \times \frac{1}{3}$$

Considering then the total volume of the two pyramidal tips plus the pentagonal prism:

$$V_T = 2 \times 0.219 \cdot D^2 \cdot \left(\frac{L-l}{2} \right) + 0.6571 \cdot l \cdot D^2 = 0.219 \cdot D^2 \cdot (L-l) + 0.6571 \cdot l \cdot D^2$$

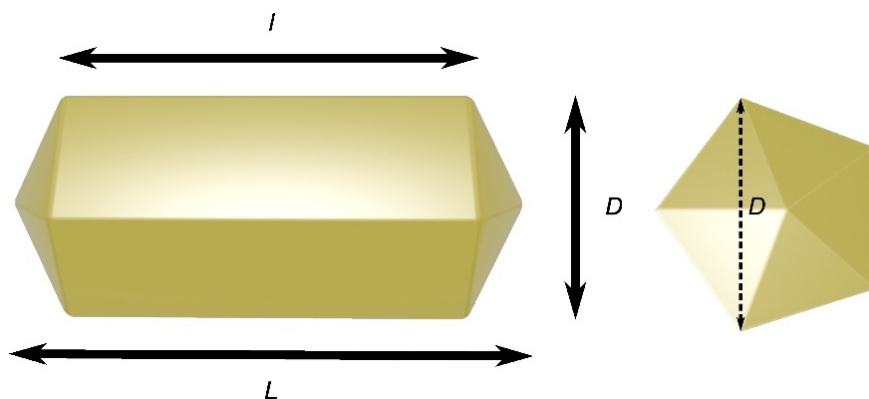


Figure S2. Schematic representation of a pentatwinned rod and its pentagonal tip, showing the data measured on TEM 2D projections and used for volume estimation. See detail calculations in the **Experimental Section**.

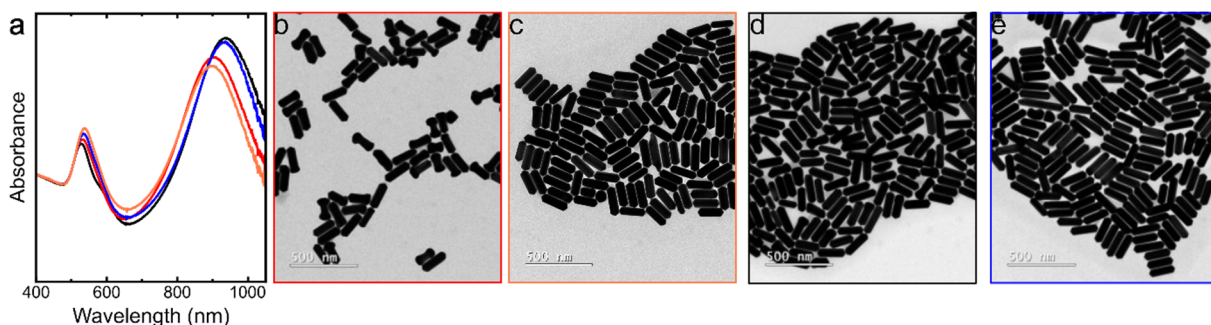


Figure S3. (a) UV-Vis-NIR spectra of nanorods prepared using 1 mM CTAB, both without (red) and with H₂AuCl₄ pre-reduction (orange), and using 0.5 mM CTAB without (black) and with H₂AuCl₄ pre-reduction (blue). (b,c) Representative TEM micrograph of the particles obtained using 0.5 mM CTAB without (a) and with H₂AuCl₄ pre-reduction (b). (d,e) Representative TEM images of the particles obtained using 1.0 mM CTAB without (d) and with H₂AuCl₄ pre-reduction (e).

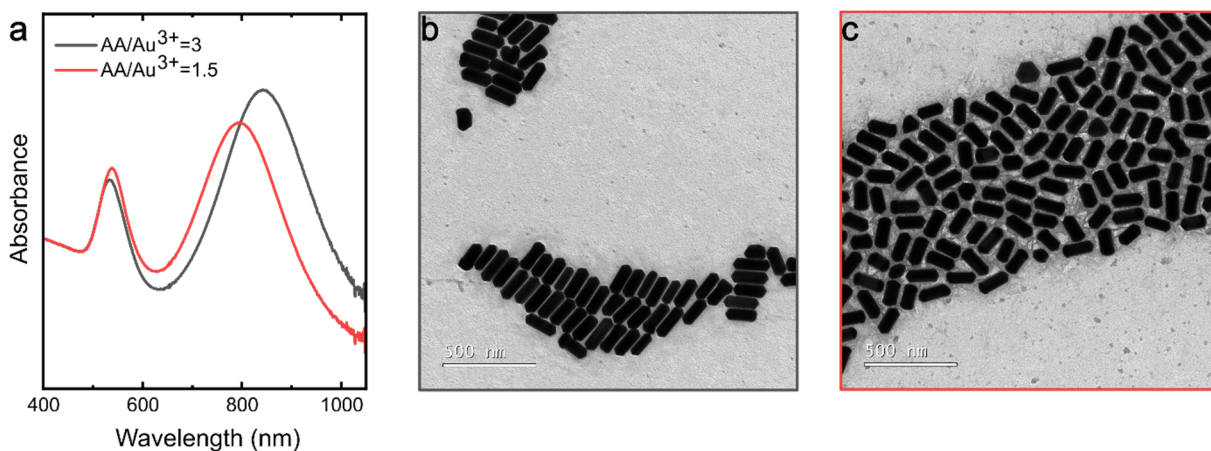


Figure S4. (a) UV-vis-NIR spectra of PT-AuNRs overgrown in the presence of 2 mM CTAB with Au³⁺/Au⁰ = 12.5 and AA/Au³⁺ = 1.5 (red) and AA/Au³⁺ = 3.0 (black). (b,c) TEM images of PT-AuNRs obtained using AA/Au³⁺ = 1.5 (b) and AA/Au³⁺ = 3.0 (c).

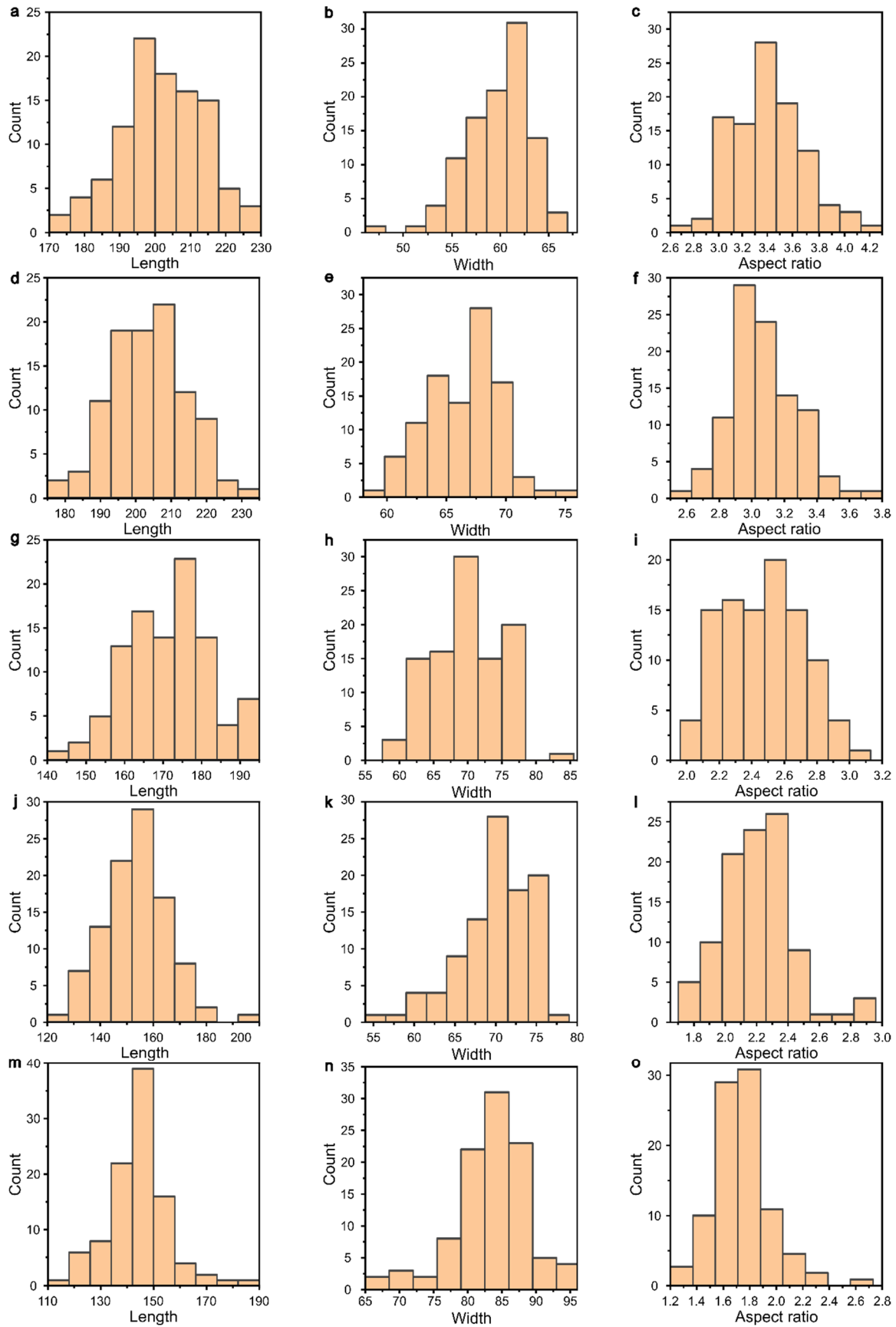


Figure S5. Histograms of the dimensions of samples obtained at different CTAB concentrations: 0.5 mM (a-c), 1 mM (d-f), 2 mM (g-i), 5 mM (j-l), and 10 mM (m-o), including length (a, d, g, j, m), width (b, e, h, k, n), and aspect ratio (c, f, i, l, o).

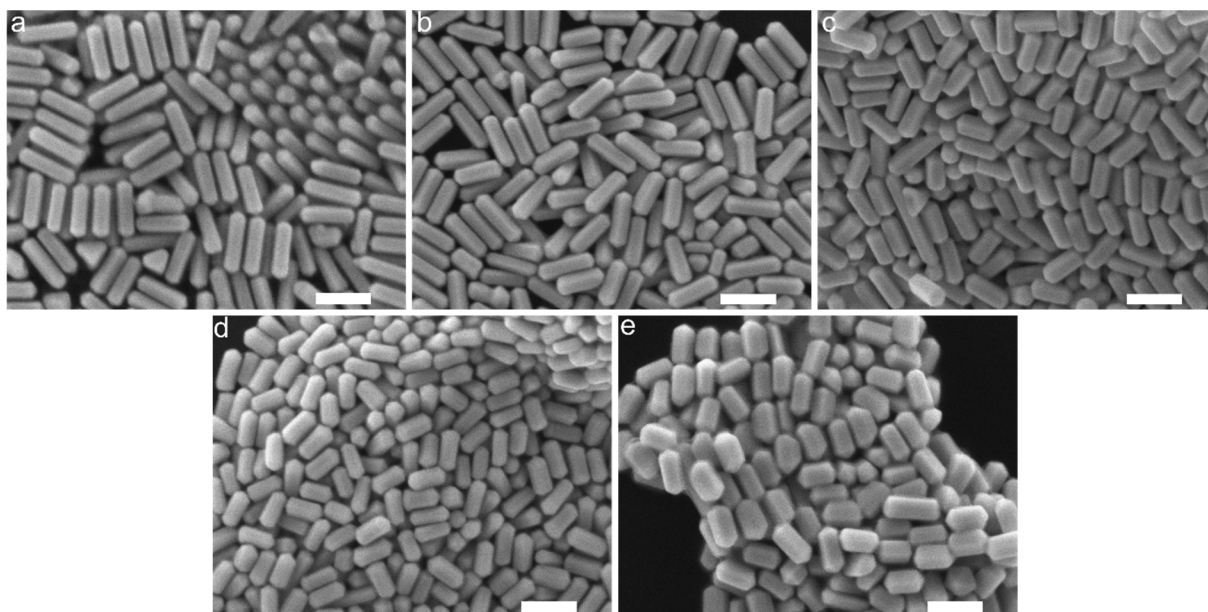


Figure S6. Lower magnification SEM images of nanorods obtained using $\text{Au}^{3+}/\text{Au}^0 = 12.5$ and different CTAB concentrations of: 0.5 mM (a), 1 mM (b), 2 mM (c), 5 mM (d), and 10 mM (e).

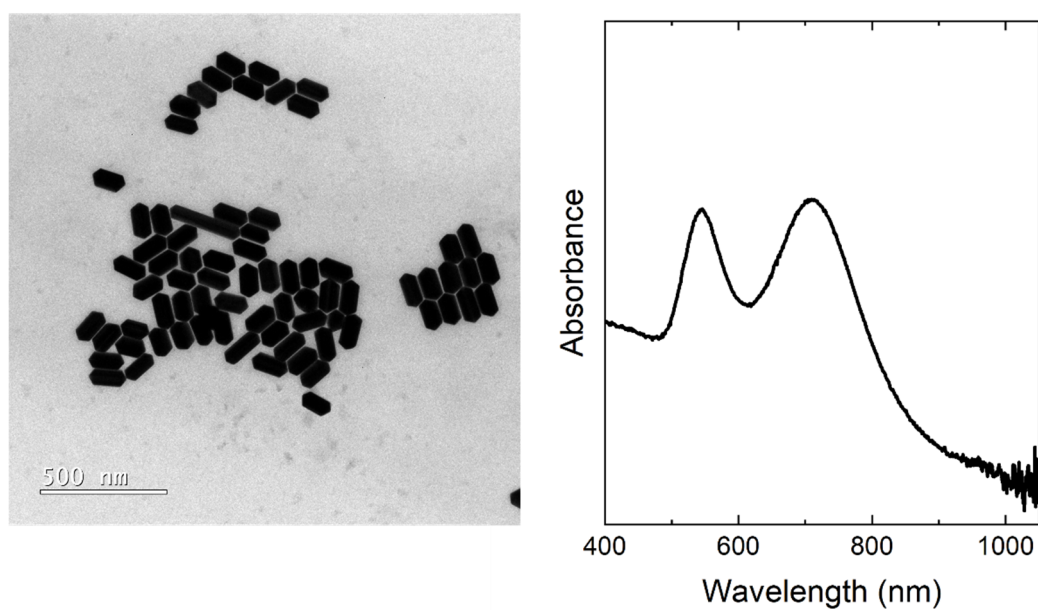


Figure S7. Results of an upscaled synthesis in a total volume of 100 mL, using $\text{Au}^{3+}/\text{Au}^0 = 12.5$ and 5 mM CTAB. Left: Representative TEM micrograph of the obtained particles. Right: Corresponding UV-Vis-NIR spectrum. The dimensions of the obtained particles are 140 ± 7 nm by 71 ± 4 nm.

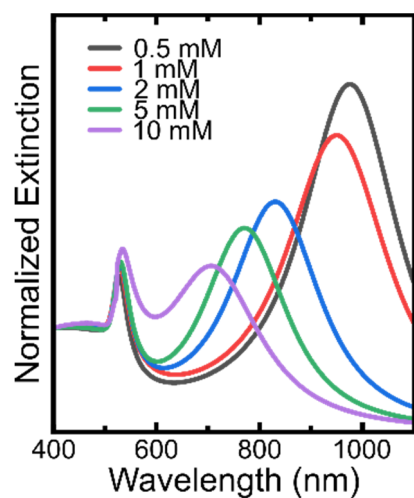


Figure S8. Simulated UV-vis-NIR spectra, normalized at 400 nm, for a model of cylindrical rods using the average dimensions reported in **Table S1** for PT-AuNRs grown with different CTAB concentrations, as indicated in the labels.

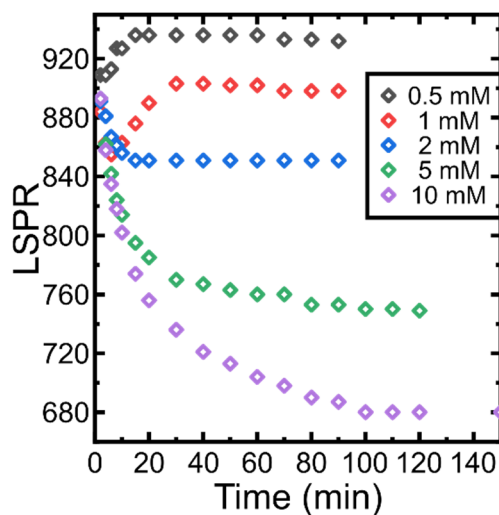


Figure S9. Evolution of the LSPR maximum wavelength during the overgrowth of 113nm-PT-AuNRs using $\text{Au}^{3+}/\text{Au}^0 = 12.5$ and varying CTAB concentration.

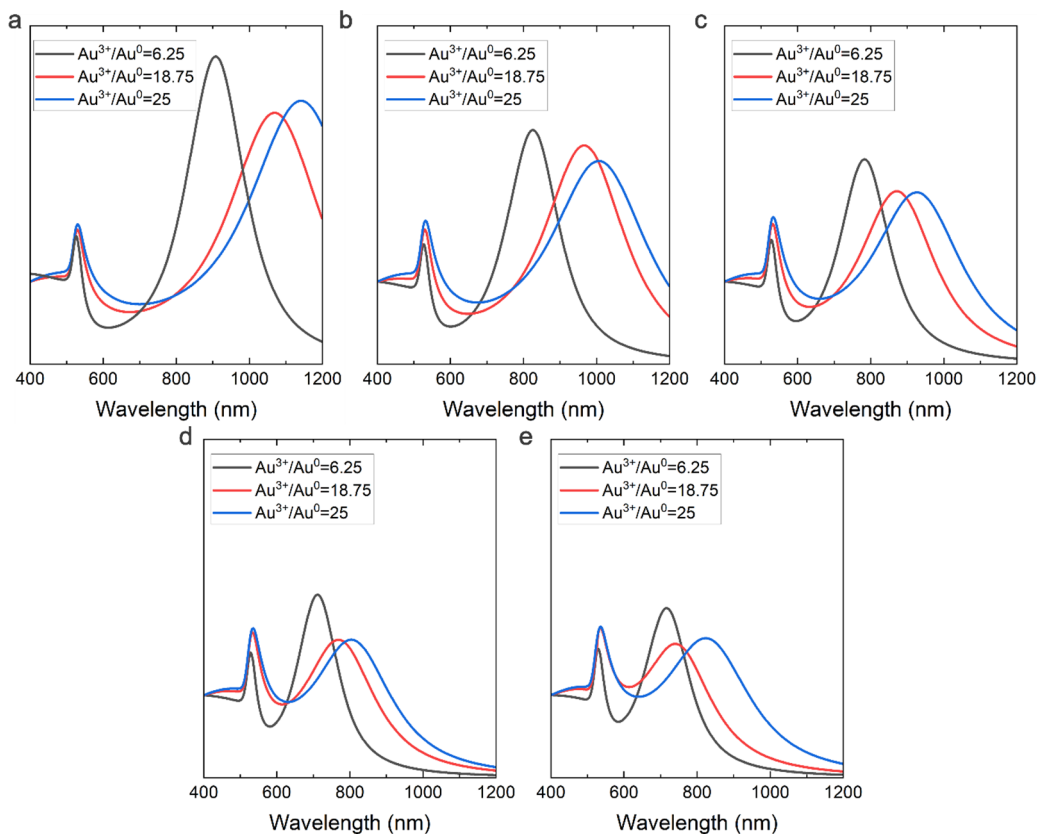


Figure S10. (a) Simulated UV-vis-NIR spectra of nanorods overgrown with 0.5 mM CTAB, and $\text{Au}^{3+}/\text{Au}^0$ ratios of: 6.25 (black), 18.75 (red), and 25 (blue). (b) Simulated UV-vis-NIR spectra of nanorods overgrown with 1 mM CTAB, and $\text{Au}^{3+}/\text{Au}^0$ ratios of: 6.25 (black), 18.75 (red), and 25 (blue). (c) Simulated UV-vis-NIR spectra of nanorods overgrown with 2 mM CTAB, and $\text{Au}^{3+}/\text{Au}^0$ ratios of: 6.25 (black), 18.75 (red), and 25 (blue). (d) Simulated UV-vis-NIR spectra of nanorods overgrown with 5 mM CTAB, and $\text{Au}^{3+}/\text{Au}^0$ ratios of: 6.25 (black), 18.75 (red), and 25 (blue). (e) Simulated UV-vis-NIR spectra of nanorods overgrown with 10 mM CTAB, and $\text{Au}^{3+}/\text{Au}^0$ ratios of: 6.25 (black), 18.75 (red), and 25 (blue).

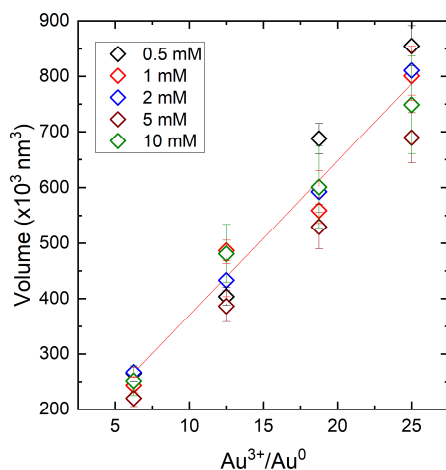


Figure S11: Estimated volume of nanorods prepared with different $\text{Au}^{3+}/\text{Au}^0$ ratios. The red line is a linear fit through the data.