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## **Supporting Information**

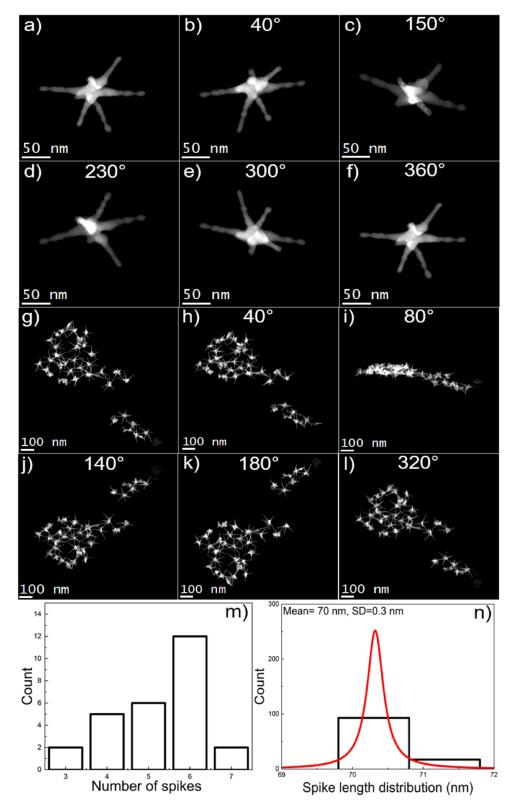
Understanding the Role of AgNO<sub>3</sub> Concentration and Seed Morphology to Achieve Tunable Shape Control in Gold Nanostars

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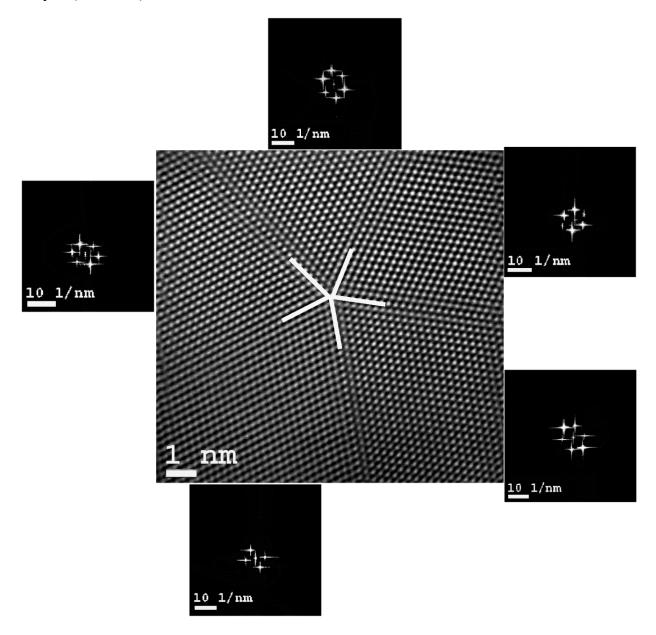
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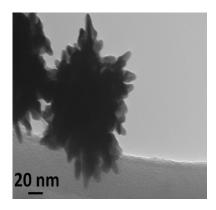


**Figure S1.** (a-f) Tomogram of a 6-branched gold nanostar at different tilt angles exhibiting a maximum of six spikes after examination at all orientations. (g-l) Tilt angle series of a set of nanostars. m) Statistical analysis of this sample reveals that around 44 % of these stars are 6-

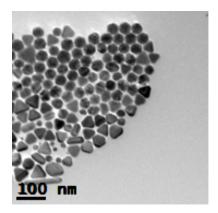
branched stars. n) Statistical analysis of the spike length for a sample designed to possess 70 nm spikes (0.15 M Triton X, 1.6 mM ascorbic acid, 30  $\mu$ M AgNO<sub>3</sub>, and 0.14 nM seeds). The measured standard deviation is ten times smaller than what measured using traditional 2D TEM statistical analysis (vide infra).



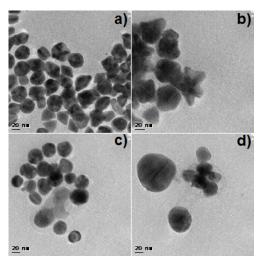
**Figure S2.** FFT images for the various planes observed in the STEM micrograph of the five-fold defect reported in Figure 2d exhibiting five different {111} facets.



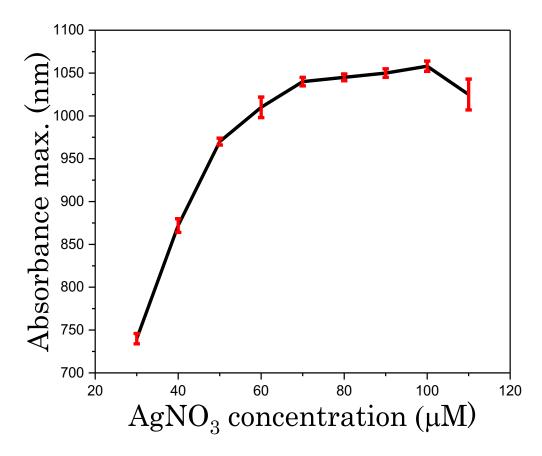
**Figure S3.** TEM micrograph of gold nanostars obtained in the absence of Triton X, where the concentration of the other variables was 1.6 mM (ascorbic acid),  $100 \,\mu\text{M}$  (AgNO<sub>3</sub>), and  $0.14 \,\text{nM}$  seeds.



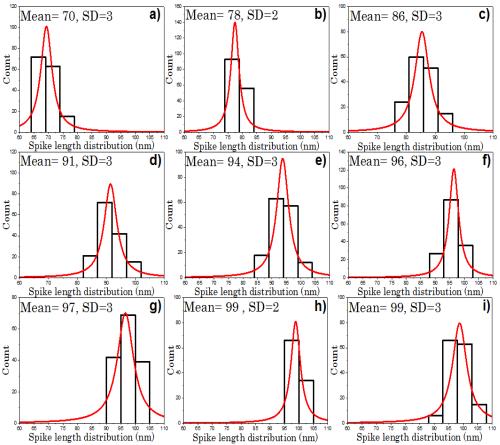
**Figure S4.** TEM micrograph of polyhedral gold nanoparticles formed in the absence of AgNO<sub>3</sub>. The concentrations of the other variables, Triton-X, ascorbic acid, and seeds, were 0.15 M, 1.6 mM, and 0.14 nM respectively.



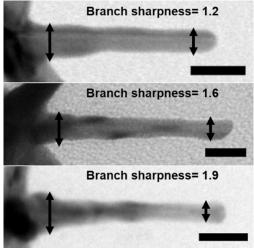
**Figure S5.** TEM micrographs of gold nanoparticles formed under different concentrations of AgNO<sub>3</sub> (25  $\mu$ M (a), 50  $\mu$ M (b), 100  $\mu$ M (c), and 150 (d)). The concentrations of the other variables Triton-X, ascorbic acid, and seeds were kept constant, at 0.15 M, 0.8 mM, and 0.14 nM respectively.



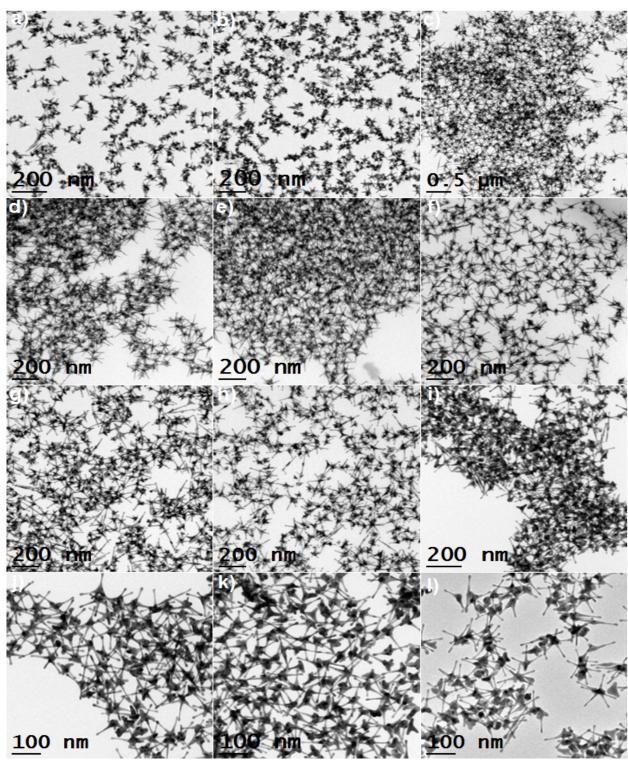
**Figure S6.** Evolution of the LSPR position with AgNO<sub>3</sub> concentration (30  $\mu$ M, 40  $\mu$ M, 50  $\mu$ M, 60  $\mu$ M, 70  $\mu$ M, 80  $\mu$ M, 90  $\mu$ M, 100  $\mu$ M, and 110  $\mu$ M) at constant concentration of Triton X (0.15 M), ascorbic acid (1.6 mM), and seeds (0.14 nM).



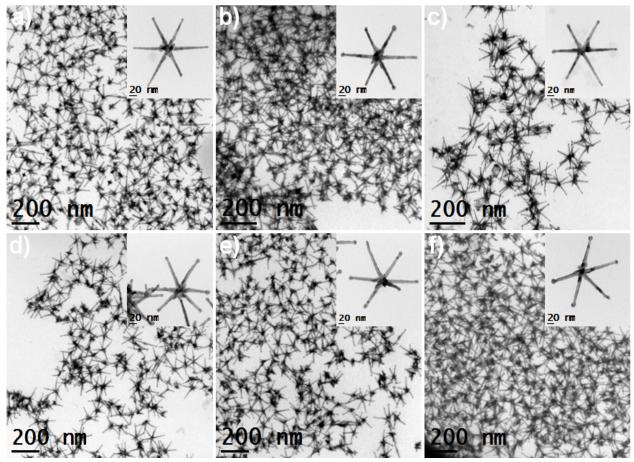
**Figure S7.** Statistical analysis of the spike length (the distance measured from the core to the tip) of 6-branched nanostars when the concentration of AgNO<sub>3</sub> was varied from 30  $\mu$ M to 110  $\mu$ M (30  $\mu$ M (a), 40  $\mu$ M (b), 50  $\mu$ M (c), 60  $\mu$ M (d), 70  $\mu$ M (e), 80  $\mu$ M (f), 90  $\mu$ M (g), 100  $\mu$ M (h), and 110 (i)) while the concentrations of Triton X (0.15 M), ascorbic acid (1.6 mM), and seeds (0.14 nM) were kept constant.



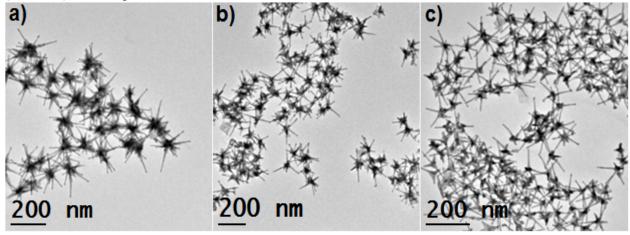
**Figure S8.** Detailed TEM micrographs of spikes having aspect ratios (the ratio of width at core and tip of a spike) of 1.2 (40  $\mu$ M AgNO<sub>3</sub>), 1.6 (60  $\mu$ M AgNO<sub>3</sub>), and 1.9 (100  $\mu$ M AgNO<sub>3</sub>). The concentration of Triton X (0.15 M), ascorbic acid (1.6 mM), and seeds (0.14 nM) were kept constant. Scale bars are 20 nm.



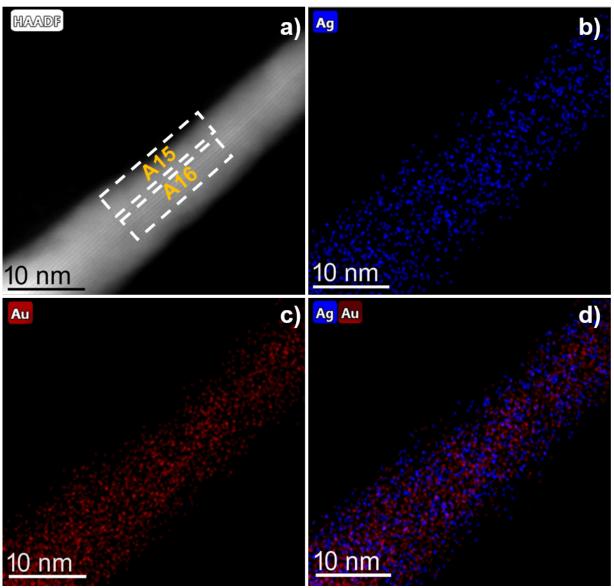
**Figure S9.** (a-l) TEM micrographs with many stars at different time interval-  $30 \sec (a)$ ,  $1 \min (b)$ ,  $1 \min 30 \sec (c)$ ,  $2 \min (d)$ ,  $5 \min (e)$ ,  $10 \min (f)$ ,  $30 \min (g)$ ,  $60 \min (h)$ ,  $120 \min (i)$ ,  $240 \min (j)$ ,  $480 \min (k)$ , and  $720 \min (l)$  when the concentrations of Triton X, ascorbic acid, AgNO<sub>3</sub>, and seeds were kept at 0.15 M, 1.6 mM,  $30 \mu\text{M}$ , and 0.14 nM respectively. These micrographs portray the consistently high monodispersity of these nanostar batches.



**Figure S10.** (a-f) TEM micrographs of 6-branched gold nanostars formed after 5 min reaction time under different AgNO<sub>3</sub> concentration-30  $\mu$ M (a), 40  $\mu$ M (b), 50  $\mu$ M (c), 60  $\mu$ M (d), 80  $\mu$ M (e), and 100  $\mu$ M (f) while the concentrations of Triton X (0.15 M), ascorbic acid (1.6 mM), and seeds (0.14 nM) were kept constant.



**Figure S11.** (a-c) TEM micrographs of gold nanostars obtained starting from different amounts of seeds (0.02 nM (a), 0.06 nM (b), and 0.1 nM (c)) added to the growth solution containing 1.5 M Triton X, 1.6 mM ascorbic acid, and 100  $\mu$ M of AgNO<sub>3</sub>.



**Figure S12.** HAADF-STEM image and elemental maps of the spike (a-d) for 110 μM AgNO<sub>3</sub> concentration after 12 hours.

Area	Element	Atomic Fraction (%)	Atomic Error (%)
A1	Ag	3.28	0.56
	Au	96.72	17.90
A2	Ag	8.84	1.47
	Au	91.16	16.44
A3	Ag	4.12	0.72
	Au	95.88	17.68
A4	Ag	2.46	0.40
	Au	97.54	18.12
A5	Ag	5.66	1.05
	Au	94.34	17.31
A6	Ag	4.94	0.99
	Au	95.06	17.55
A7	Ag	36.87	4.79
	Au	63.13	10.07
A8	Ag	23.61	3.39
	Au	76.39	12.82
A9	Ag	12.17	2.05
	Au	87.83	15.65
A10	Ag	8.34	1.29
	Au	91.66	16.52
A11	Ag	13.04	1.95
	Au	86.96	15.30
A12	Ag	17.62	2.55
	Au	82.38	14.15
A13	Ag	25.05	4.30
	Au	74.95	13.28
A14	Ag	18.70	3.51
	Au	81.30	14.62
A15	Ag	33.70	10.02
	Au	66.30	16.89
A16	Ag	13.78	2.56
	Au	86.22	15.56

Table S1. Area scan elemental profile of 6-branched stars at 30  $\mu M,\,100~\mu M,$  and 110  $\mu M$  AgNO<sub>3</sub>.