Electronic Supplementary Material (ESI) for Nanoscale.

SUPPORTING INFORMATION

Large-Area Periodic Arrays of Gold Nanostars Derived from HEPES-, DMF-, and Ascorbic-Acid-Driven Syntheses

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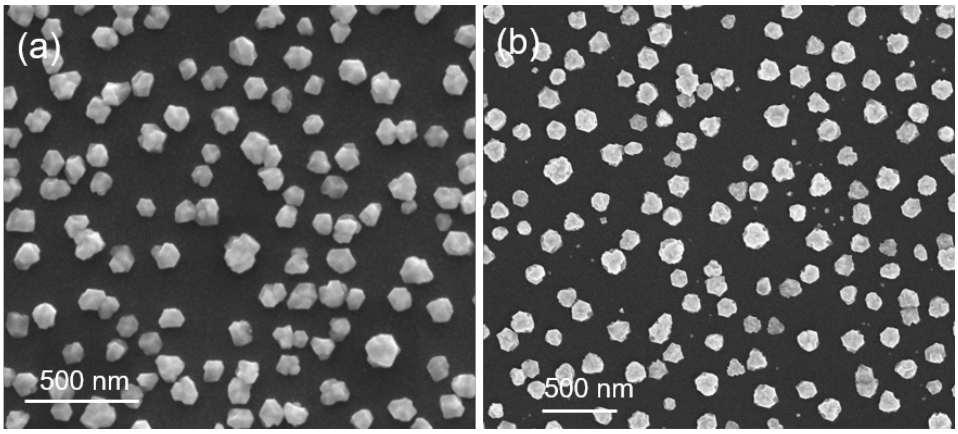

Fig.S1. SEM images showing the unsatisfactory results obtained for HEPES-driven syntheses where no $AgNO_3$ was added for HEPES/$HAuCl_4$ ratios of (a) 500:1 and (b) 1400:1. The structures are not arranged in periodic arrays because these syntheses, out of convenience, were carried out using Au seeds derived from solid-state dewetting.

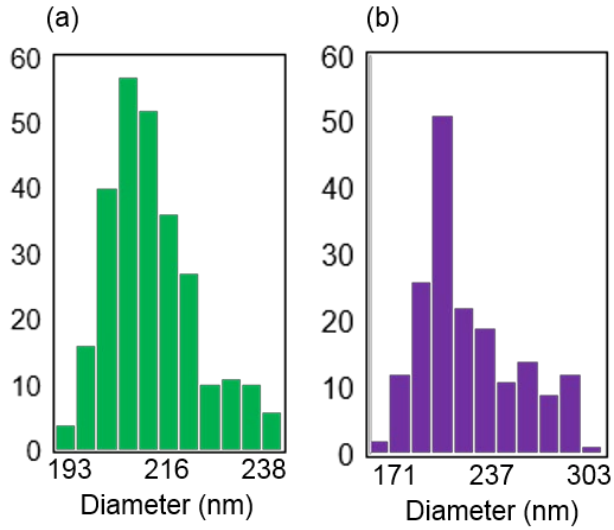

Fig. S2. Histograms showing the diameter distribution for the arrayed nanostructures shown in Fig. 2a,b that are derived from the HEPES-driven growth mode utilizing (a) 0 and (b) 80 μM of $AgNO_3$.

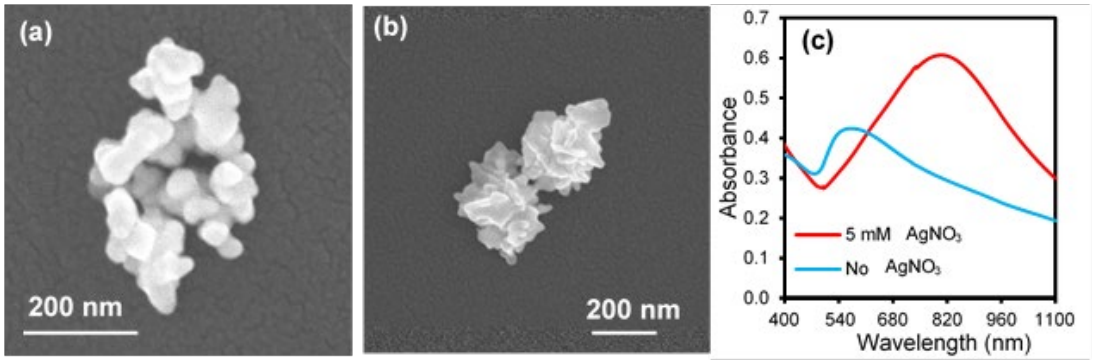

Fig. S3. SEM images of the spontaneously nucleated colloidal structures obtained when carrying out a substrate-based seed-mediated HEPES-driven synthesis in the (a) absence of Ag^+ ions and (b) when using a 200 μM concentration of Ag^+. (c) The corresponding absorbance spectra for these colloidal nanostructures.

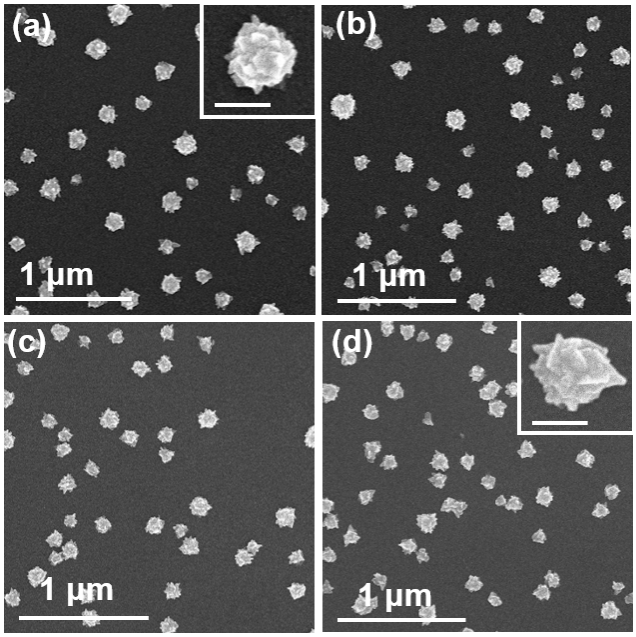

Fig. S4. SEM images of substrate-immobilized Au nanostars synthesized using a DMF-driven growth for NaOH concentrations of (a) 2.5 (b) 1.5, (c) 0.5, and (d) 0 mM. Note that the nanostar tips are much sharper for the NaOH-free syntheses. The structures are not arranged in periodic arrays because these syntheses, out of convenience, were carried out using Au seeds derived from solid-state dewetting. The scale bar for the insets is 150 nm.

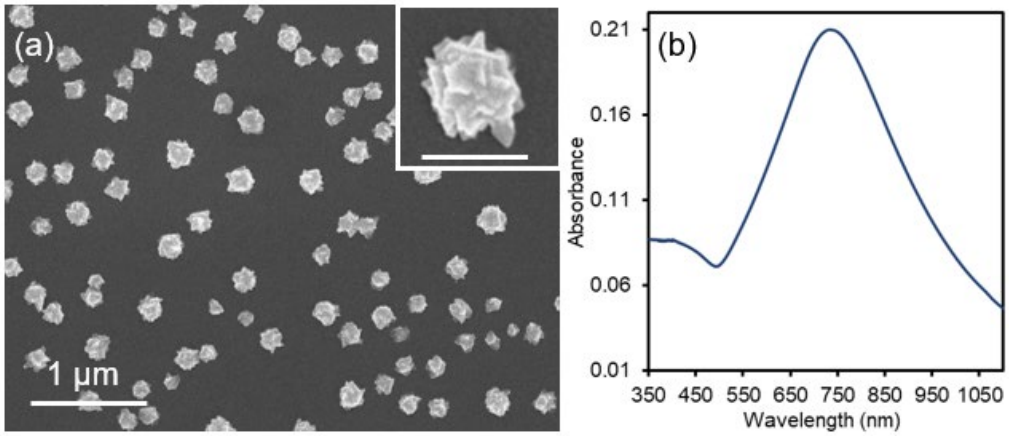

Fig. S5. (a) SEM image and (b) the corresponding absorbance spectrum for a DMF-driven nanostar growth that incorporates 1 mM HCl. The synthesis was carried out on seeds obtained using solid-state dewetting. Note that the nanostar limbs appear plate-like instead of the sharp tips that occur in the absence of HCl. The scale bar for the insets is 150 nm.

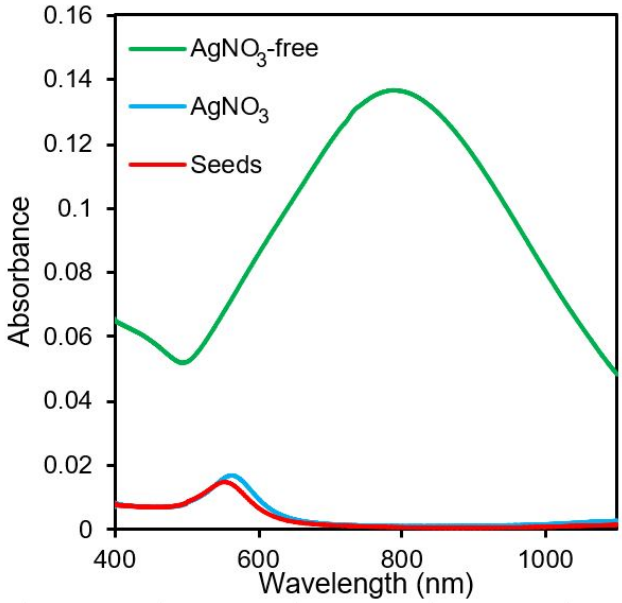

Fig. S6. Absorbance spectra for substrate-immobilized seeds (red) and for the structures that result from a DMF-driven nanostar synthesis containing $HAuCl_4$ (0.3 mM), PVP (4.5 mM) and $AgNO_3$ (80 µM) (blue) and for the same growth when no $AgNO_3$ is added (green). The much greater absorbance intensity for the $AgNO_3$-free synthesis provides a clear indication that Ag^+ ions severely limit the reduction of Au^{3+} onto the seeds.

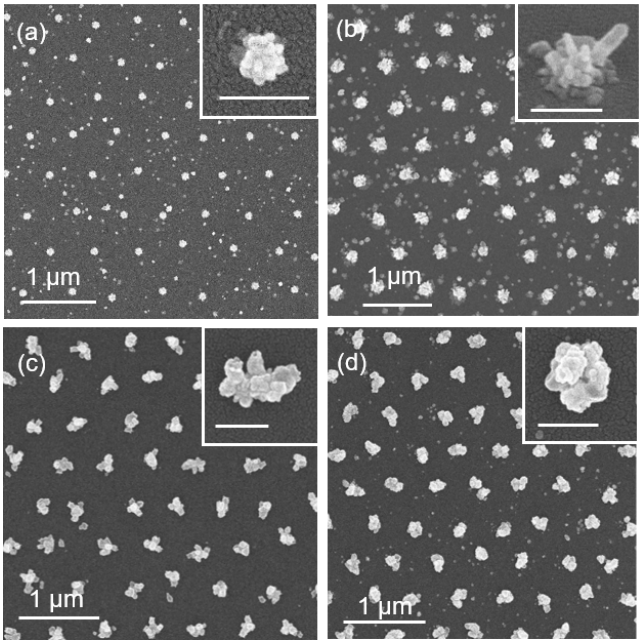

Fig. S7. SEM images of the structures synthesized when flowing the reactants $HAuCl_4$, $AgNO_3$, and AA over periodic arrays of Au seeds for $AgNO_3$ concentrations of (a) 0.5 mM, (b) 1 mM, (c) 1.5 mM, and (d) 2 mM. The inset scale bar is 200 nm.

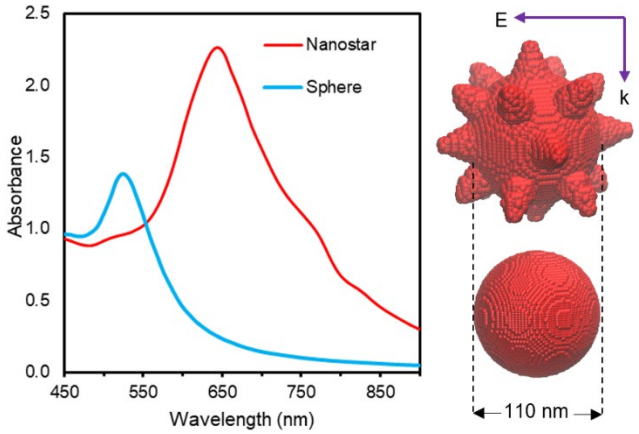

Fig. S8. DDA simulations of the absorbance spectrum of a free-standing Au nanostar characterized by eighteen tapered limbs (length = 27 nm) emanating from a spherical core compared to the spectrum expected for just the core. The schematics show the two nanostructures investigated.

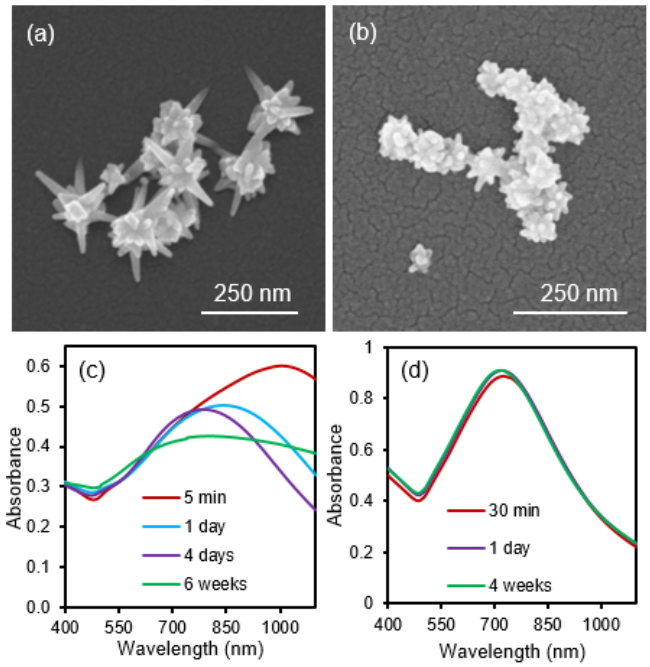

Fig. S9. SEM images for Au nanostars derived from the AA-driven growth mode after (a) being grown and drop-cast immediately and (b) after being stored for 1 day in an aqueous environment. Corresponding absorbance spectra for nanostars derived from (c) AA- and (d) HEPES-driven growth modes after being stored in aqueous environments for various time intervals. It should be noted that the HEPES-driven synthesis gives rise to stable nanostars due to the protection offered by the HEPES molecule as it acts as a capping agent.

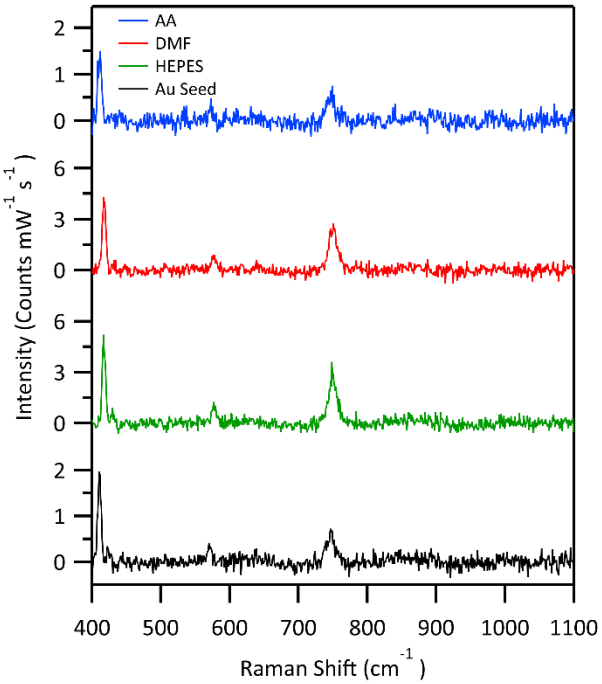

Fig. S10. SERS background spectra for large-area periodic arrays of Au seeds and DMF-, HEPES-, and AA- driven nanostar growth modes.

Calculations of the SERS Enhancement Factors (EF)

SERS enhancement factors (EF) for the HEPES-, DMF-, and AA-driven growth modes were calculated to be on the order of 10^6, 10^7, and 10^6, respectively. The table below summarizes the calculations made. For each nanostar type, the average number of limbs was estimated by examining SEM images. The limb shape was assumed to be conical. Limb radius was estimated as a portion of the substrate diameter with HEPES having the largest limbs and DMF having the smallest limbs. Once the total area of the limbs and core was calculated, the area of the circular interface of the core with the substrate as well as the total limb base area was subtracted from the total to yield the exposed surface area of the nanostar. Nanostar surface density was derived from the 600 nm spacing between lithographically determined array locations, which given the laser spot size, allowed for an approximation of total number of nanostars irradiated. It was also assumed that benzenethiol forms a self-assembled monolayer on the Au with a surface density 6.8 x 10^{14} molecules per cm^2.[1] It should be noted that the conservative assumptions and approximations have been made in calculating theses EF values.

	HEPES	DMF	Ascorbic Acid
Radius of hemisphere (nm)	120	83	89
Surface area of hemisphere (nm^2)	9.05 x 10^4	4.33 x 10^4	4.98 x 10^4
Cone radius (nm)	1.71 (radius / 70)	1.04 (radius / 80)	1.19 (radius / 75)
Cone height (nm)	3.43	2.08	2.37
Total Exposed cone surface area (nm^2)	309	265	247
Total cones	15	35	25
Total cone base surface area (nm^2)	138	118	111
Exposed hemisphere surface area (nm^2)	9.03 x 10^4	4.32 x 10^4	4.97 X 10^4
Total exposed surface area (nm^2)	9.06 x 10^4	4.34 x 10^4	4.99 X 10^4
Molecules per nanostar	6.16 x 10^5	2.95 x 10^5	3.39 X 10^5
Molecules per spectra	4.19 x 10^6	2.01 x 10^6	2.31 X 10^6
Mean enhancement factor (EF)	7.1 x 10^5	1.6 x 10^7	2.2 x 10^6
Confidence Interval for EF	$\pm$ 1.2 x 10^5	$\pm$ 8.6 x 10^6	$\pm$ 1.2 x 10^6
Laser spot diameter (um)	1.54		
Laser depth of field (um)	4.02		
Nanostar density (star per cm^2)	3.63		
Volume of thiophenol irradiated in Raman experiments (mL) (estimated as a cylinder)	7.53 x 10^{-12}		

[1] Whelan, C. M.; Smyth, M. R.; Barnes, C. J. HREELS, XPS, and Electrochemical Study of Benzenethiol Adsorption on Au(111). *Langmuir* **1999**, *15*, 116-126.