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**Figure S1.** Comparison of STEM tomogram and model as employed for dimensional matching.
Figure S2. Additional TEM micrographs, collected at increasing magnification, of representative NSs used in this work. Scale bars are 100 nm (a), 20 nm (b), 5 nm (c), and 2 nm (d). Atomic packing in both core and tips can be observed.

Figure S3. Representation of the nanostar model as defined by the analytical equation for its volume:

\[ V = \frac{4}{3} \pi a^3 + \sum_{i=1}^{n} \left( \frac{h_i}{3} \pi (R_i^2 + R_i r_i + r_i^2) + \frac{2}{3} \pi r_i^3 - \frac{\pi}{6} \left( a - \sqrt{a^2 - R_i^2} \right) \left[ 3R_i^2 + (a - \sqrt{a^2 - R_i^2})^2 \right] \right) \]
**Figure S4:** UV-Vis-NIR spectra of an aqueous suspension of gold nanostars, as prepared (green line), at the time that the STEM measurements took place (red line) and at the time that the dark field spectroscopy measurements took place (magenta).

**Figure S5.** Additional dark field spectra collected from the areas highlighted in the insets, depicting a broadening and a slight redshift in the case of a denser nanostar configuration (right). The average number of spikes is 18 ± 4.
Figure S6. Number of spikes calculated from the 117 nanostars observed in the TEM micrograph of Figure S2 a. Raw data on the right and categorized frequency data on the left along with a Gaussian fit seen as a red line.