**Supporting Information for:**

# Anisotropic Etching of Silver Nanoparticles for Plasmonic Structures Capable of Single Particle SERS

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Table S1: Half reactions relevant to redox etching of silver.

| Reaction | E° Volts |
|---|---|
| $Ag(s) \rightleftharpoons Ag^+ + e^-$ | -0.799 |
| $H_2O_2 + 2H^+ 2e^- \rightleftharpoons 2H_2O$ | 1.763 |
| $NH_3OH^+ + 2H^+ + 2e^- \rightleftharpoons NH_4^+ + H_2O$ | 1.33 |
| $NO_3^- + 3H^+ + 2e^- \rightleftharpoons HNO_2 + H_2O$ | 0.940 |
| $S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ | 2.01 |

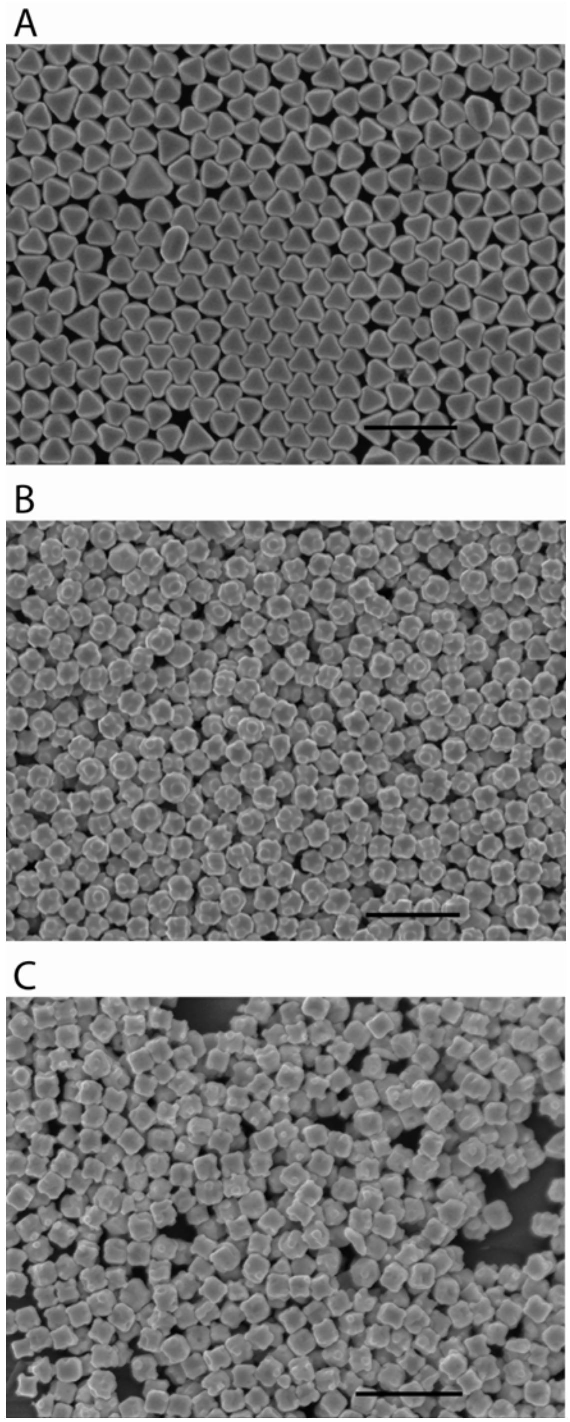


**Figure S1**: From top to bottom the etching progression of Octahedra when exposed to an etchant solution containing a ratio of 1:5:0.08 composed of $H_2O_2$: $NH_4OH$:$CrO_3$. (A) Starting octahedra silver nanoparticles. (B) Truncated structures resulting from exposure of silver octahedra to low etchant concentrations. (C) Cubic particles which are formed after exposure of octahedra to higher concentrations of the etchant. All scale bars represent 1 μm.

A close examination of these cubes reveal that their body diagonal, which corresponds to the thickness in the [111] direction of the original octahedral structure, is unchanged during the reaction. Conversely, the thickness of the original octahedra in the [100] direction is significantly decreased. This clearly indicates a reversal of the reaction kinetics seen during the original overgrowth process, where {100}-bound cubes grow to become {111}-bound octahedral. Briefly, the growth process proceeds more rapidly in the [100] direction while the {111}-capped corners of the cubes are bound, finally resulting in the {111}-bound octahedra. The observation that the $NH_4OH/H_2O_2/CrO_3$ etching mixture is selective for etching in the [100] direction encouraged further research into the modification of this etchant system for the development of new nanostructures.

**Figure S2:** Electron diffraction of a single octapod structure sitting on the three-fold symmetric axis as shown in the SEM inset (scale bar represents 100 nm). This Condensed Beam Electron Diffraction (CBED) pattern shows distinct HOLZ lines and HOLZ disks which reflect the six-fold symmetry of the fcc silver lattice. These single particle diffraction patterns are possible because of our larger (>100 nm) nanoparticle size.

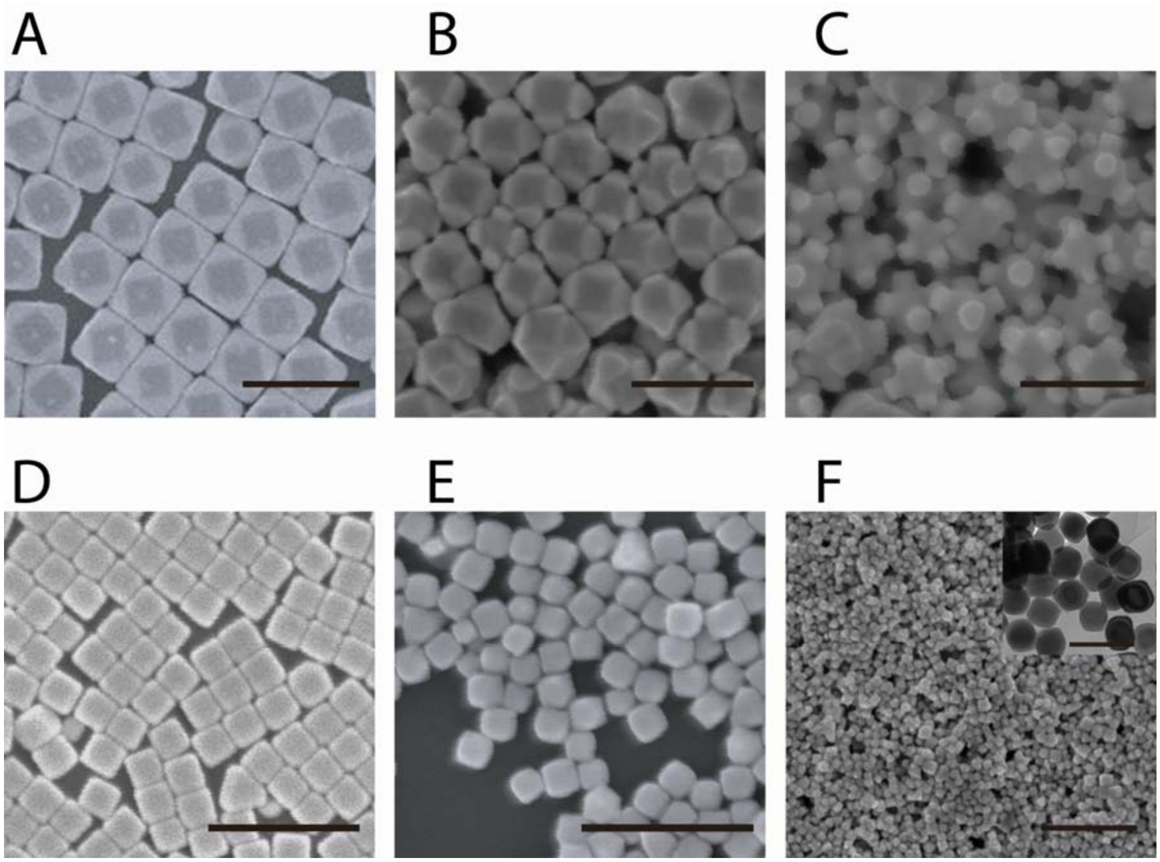


**Figure S3:** SEM images following the etching progress for silver cube-octahedra and cubes. (A-C) Cube-octahedra shaped starting material (A) then exposed to a low concentration of etching solution (B) and finally a higher concentration of etching solution to give octapod structures (C). (D-F) Cube shaped starting material (D) then exposed to a low concentration of etching solution (E) and finally a higher concentration of etching solution (F) Inset shows a TEM image of the cubic particles after being exposed to the higher concentration of etchant. The cubes retain there general shape while rounding at the edges and corners. All Scale bars shown represent 1 µm, except the TEM inset where the scale bar represents 100 nm.