

Supplementary Information

**Morphological changes in Ag nanocrystals triggered by
citrate photoreduction and governed by oxidative etching**

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Experimental Procedure:

The Ag nanocubes were synthesized by following the protocol published in ref. 4 (Q. Zhang, W. Li, L.-P. Wen, J. Chen and Y. Xia, *Chem. Eur. J.*, 2010, **16**, 10234). The sample was obtained after a 90-min reaction, which was followed by the washing with acetone once and deionized (DI) water once. The concentration of Ag nanocubes was measured by inductively coupled plasma mass spectrometry (ICP-MS) after the dissolution with a mixture of HCl and HNO₃ (3:1).

In a typical synthesis, an aqueous solution was firstly prepared by dissolving 0.115 g of citric acid (Sigma Aldrich, 251275-100G) in 4 mL of deionized water. Subsequently 200 µL of as-synthesized Ag nanocubes (at the concentration of 4.3 g/L) was added into the solution. The reaction was kept for different period of time, and a set of samples were taken over the course of each synthesis with a glass pipet. The samples were washed via centrifugation and redispersion in DI water a minimum of 3 times to remove excessive citric acid, before being redispersed in water for imaging. The particles were typically collected by spinning at 11,000 rpm for 10 min. Between washing cycles, the samples were kept in DI water for 30 min to dissolve the physically bound citric acid completely. The as-obtained samples were then characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), UV-vis, surface-enhanced Raman spectroscopy (SERS), and zeta-potential measurements. The supernatants after the first centrifugation were collected, evaporated, and dissolved in D₂O for NMR spectroscopy.

Instrumentation:

A drop of the aqueous suspension of nanoparticles was placed on a piece of carbon-coated copper grid (Ted Pella, Redding, CA, for TEM) or silicon wafer (for SEM), and dried under ambient conditions. TEM images were taken on a FEI G2 Spirit Twin TEM operated at 120 kV. SEM images were captured on a FEI Nova 2300 Field Emission SEM operated at 30 kV and spot size of 3. The zeta potential of nanoparticles was measured with a Malvern NanoZS dynamic light scattering (DLS) system. UV-vis spectra were obtained using a Varian Cary 50 UV-visible spectrometer. NMR spectra were collected at 25°C on a Varian Mercury-300 instrument. The concentration of nanoparticles was determined by a Perkin Elmer Elan DRC II ICP-MS. The SERS spectra were recorded from the nanoparticles on a piece of silicon wafer using a Renishaw inVia confocal Raman spectrometer coupled to a Leica microscope with a 50×

objective in a backscattering configuration. The 514 nm wavelength was generated from an argon laser and used with a holographic notch filter based on a grating of 1200 lines per millimeter. The backscattered Raman signals were collected on a thermoelectrically cooled (-60 °C) CCD detector. SERS data was collected with $\lambda_{\text{ex}} = 514 \text{ nm}$, $P_{\text{laser}} = 3.1 \text{ mW}$, and $t = 30 \text{ s}$.

Table S1. Comparison by volume for the nanocrystals in Fig. 1a and Fig. 1e. The volume shrinkage after the morphological changes indicates that oxidative etching is predominant in the process.

Unit	Ag Nanocubes in Fig. 1a	Ag Nanospheres in Fig. 1e
Diameter (nm)	58.5	61.6
Volume (nm ³)	200,201.625	122,388.541

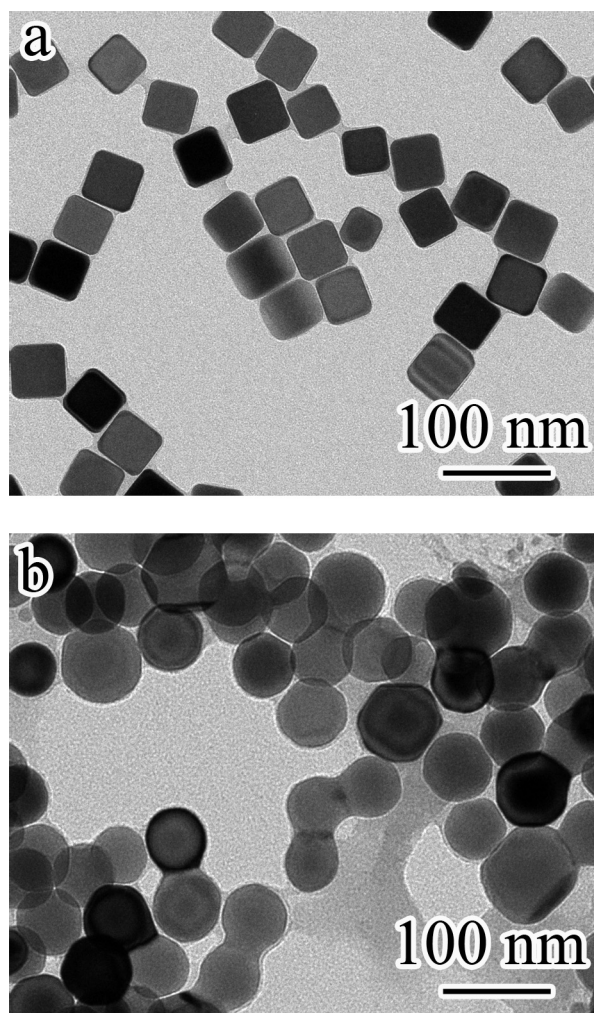


Fig. S1. TEM images showing the morphological evolution for 40-nm Ag nanocubes: (a) starting Ag nanocubes; and (b) Ag nanospheres formed after 120 min.

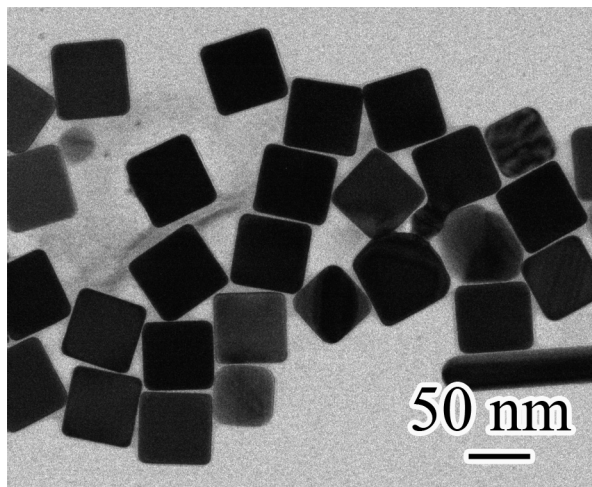


Fig. S2. TEM images of a sample prepared under the same conditions as in Figure 1 after 24 hours, except the complete exclusion of light from the reaction system. In the absence of light, the photoreduction function of citric acid could not occur, and as a result, the nanocubes largely preserved the original shape.

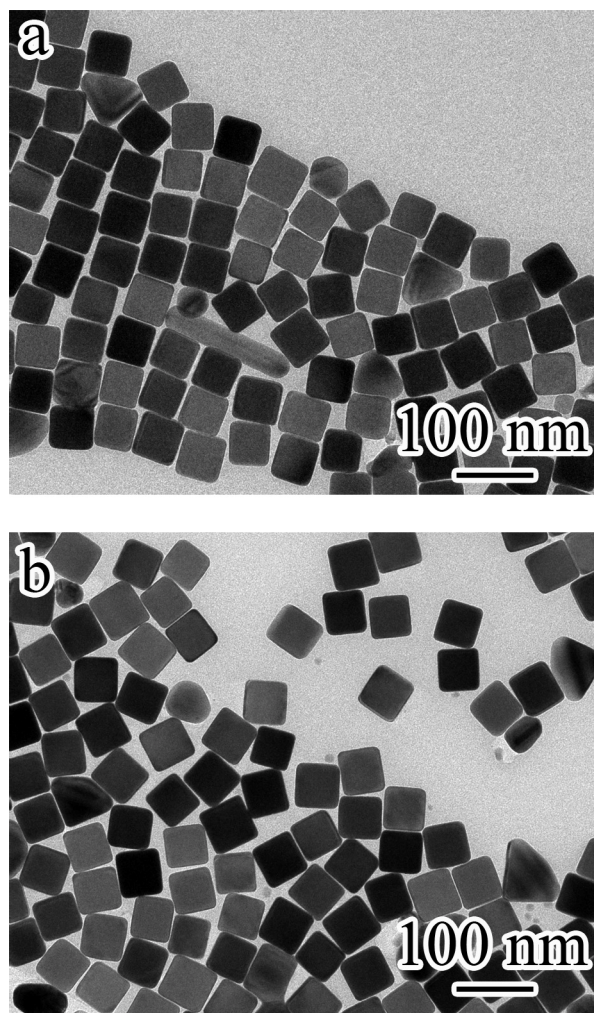


Fig. S3. TEM images of a sample prepared under the same conditions as in Figure 1 after 24 hours, except the use of acetoacetate instead of citric acid: (a) with light; and (b) without light. It confirms that the photoreduction of citric acid is the key to triggering the shape evolution.

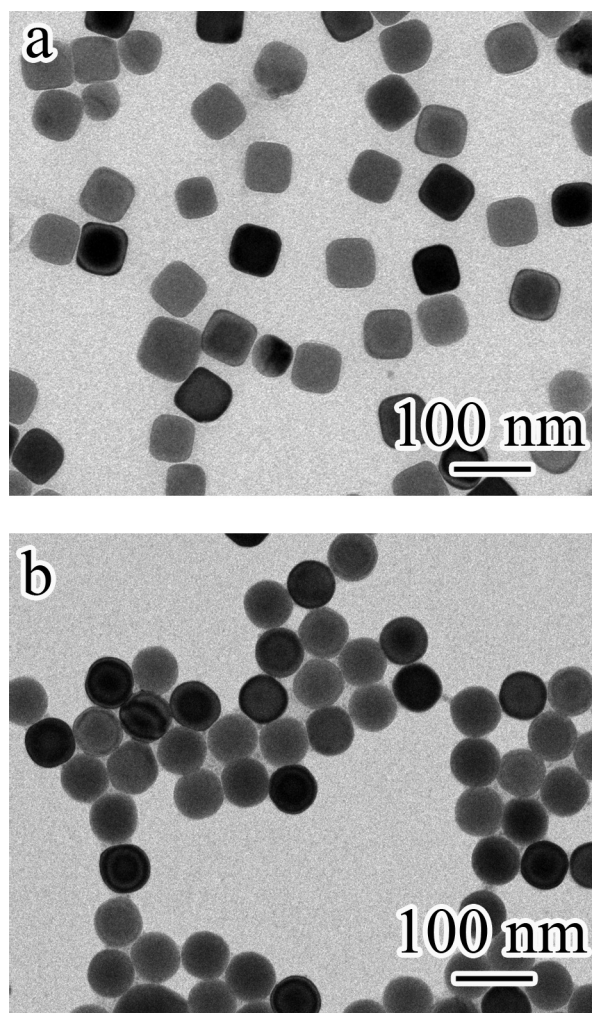


Fig. S4. TEM images of a sample prepared under the same conditions as in Figure 1, except the use of sodium citrate instead of citric acid: (a) 2 hours; and (b) 8 hours. It indicates that the acidity of citric acid is critical to the morphological changes in nanocrystals.

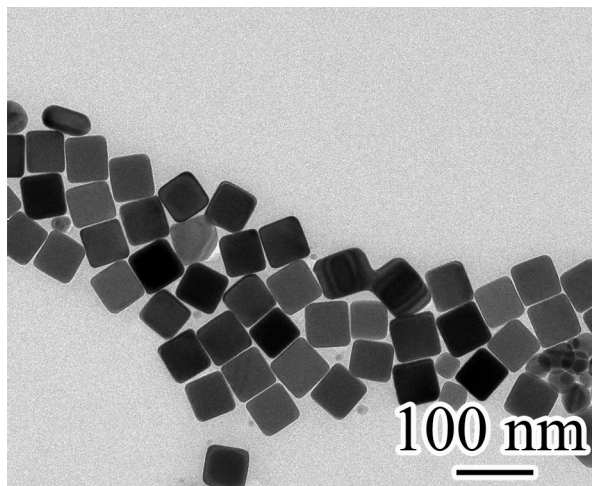


Fig. S5. TEM image of a sample prepared under the same conditions as in Figure 1 after 24 hours, except the exclusion of oxygen from the system by bubbling argon. The negligible morphological change observed in this experiment clearly demonstrates the critical role of oxidative etching in governing the morphological transformation.

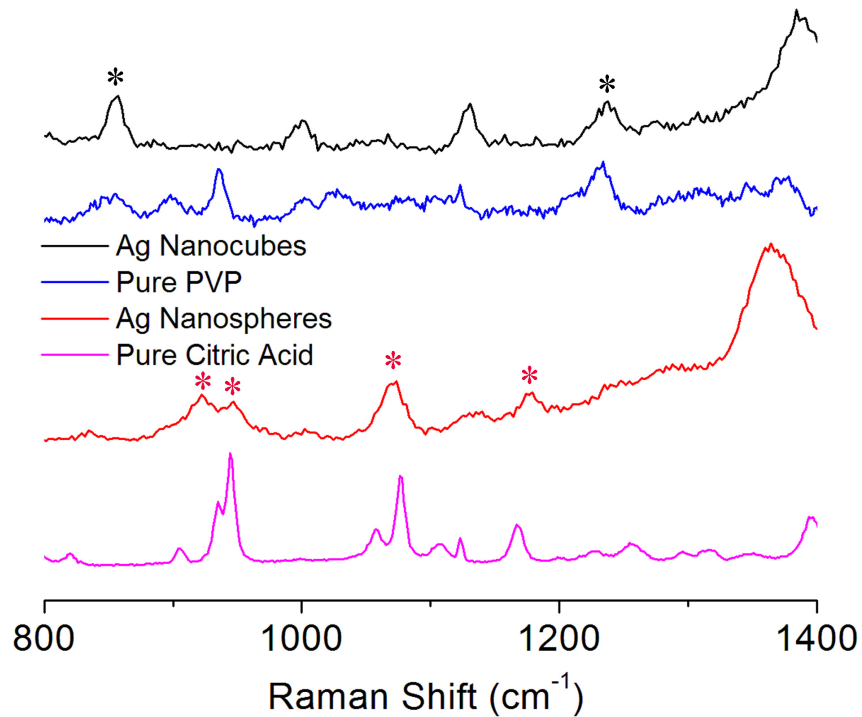


Fig. S6. SERS spectra of Ag nanocubes and nanospheres, with pure PVP and citric acid as references. The spectra show that PVP (the peaks marked with black stars) was replaced by citric acid (the peaks marked with red stars). This ligand exchange was also confirmed by zeta-potential measurements: -0.1 mV (nanocubes) *versus* -52.7 mV (nanospheres). The negative charge of nanospheres is attributed to the citrate anions on surface.

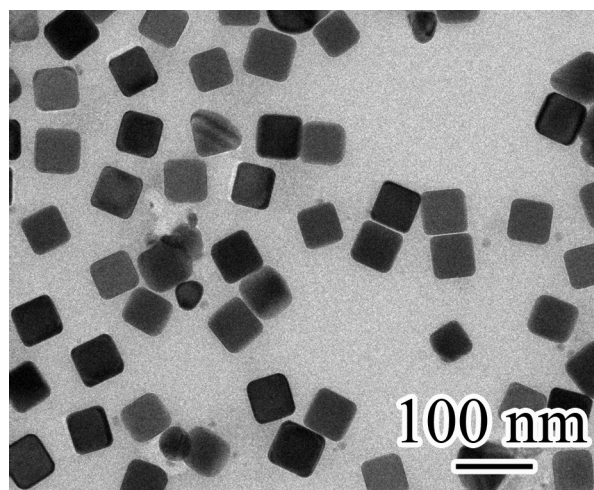
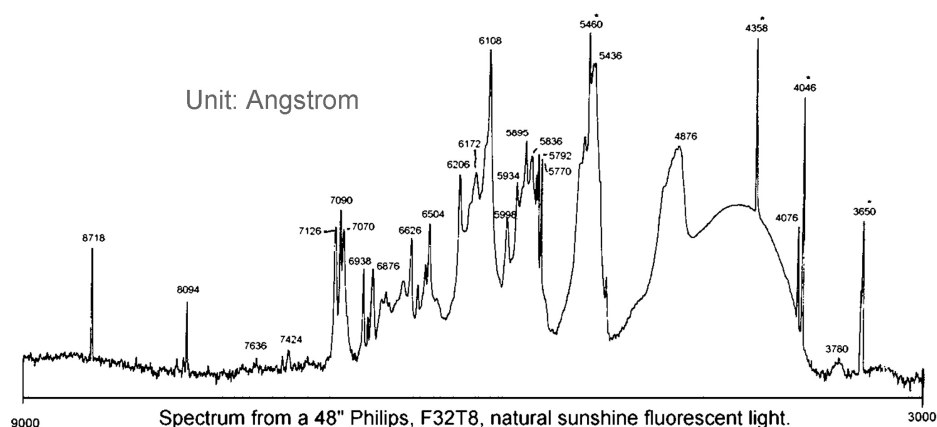
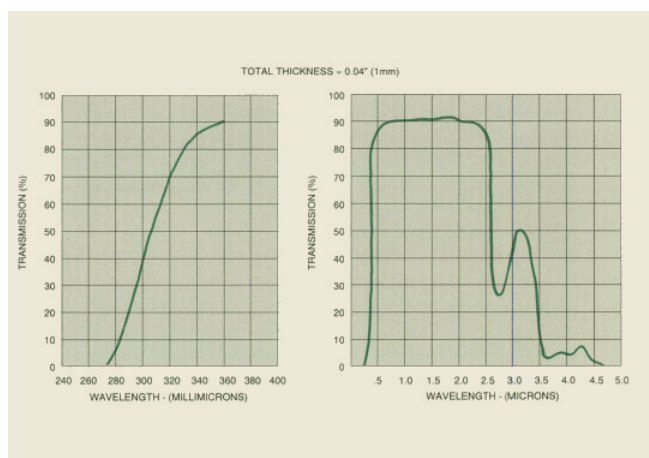


Fig. S7. TEM images of a sample prepared under the same conditions as in Figure 1 after 24 hours, except the use of ascorbic acid instead of citric acid. It indicates that the binding of citric acid to Ag {111} surface is critical to the morphological changes in nanocrystals.

(a)



(b)



(c)

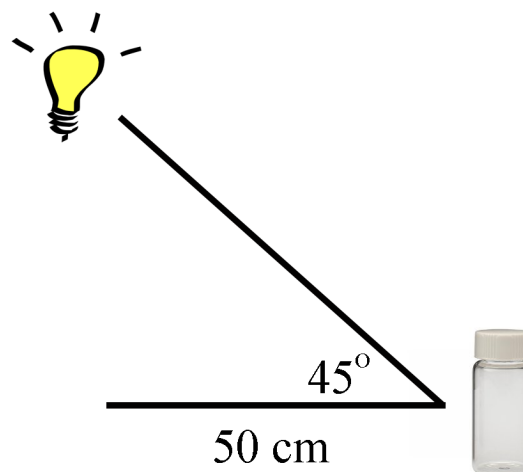


Fig. S8. (a) Spectrum of light emitted from the fluorescent tubes (adapted from Wikipedia, http://en.wikipedia.org/wiki/File:Spectra-Philips_32T8_natural_sunshine_fluorescent_light.png). In the experiments, two 48-inch fluorescent light tubes (Philips, 32 watts) with T-8 ballast (118V, 60Hz, AC 160 watts) were used for illumination. (b) Transmission curve of borosilicate glass (adapted from "Transmission Curves - Soda Lime, Borosilicate, UV Glasses & Sapphire", Sinclair Manufacturing Company, retrieved 2009-12-11, <http://www.sinclairmfg.com/nonflash/datasheets/optical3.html>). The reaction solution was contained in a 20-mL vial (Research Products International Corp., 121002, liquid scintillation vial, low background borosilicate glass, with a urea cap and polyseak cone liner). (c) Orientation of the glass vial relative to the light source.