

Supporting Information of

Selective Sulfuration at the Corner Sites of a Silver Nanocrystal and Its Use in Stabilization of the Shape

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Experimental section

1. Chemicals and materials

Silver nitrate (AgNO_3), L-ascorbic acid (AA), sodium citrate (Na_3CA), sodium hydrosulfide (NaHS), poly(vinyl pyrrolidone) (PVP, $\text{MW} \approx 29,000$ and $55,000$), sodium sulfide (Na_2S), and sulfur powders were all obtained from Sigma-Aldrich and used as received. Ethylene glycol (EG, lot no. G32B27) was obtained from J. T. Baker. Sodium borohydride (NaBH_4) was obtained from Fisher. The water used in all reactions was obtained by filtering through a set of Millipore cartridges (Epure, Dubuque, IA).

2. Preparation of polysulfide (Na_2S_x) aqueous solution

The Na_2S_x solution was prepared by reacting aqueous Na_2S with sulfur powders. In a typical process, 32 mg of sulfur powders were mixed with 11.7 mL of 50 mM Na_2S aqueous solution in a 20 mL vial. The suspension was agitated by vortexing and sonication for about 10 min. The vial was then capped and put in an oven held at 80°C for 12 h. The color of the solution turned to bright yellow once all the sulfur powders had completely dissolved.

3. Preparation of Ag nanocrystals

The triangular Ag nanoplates were prepared using a seed-mediated procedure described in our recent publication.^{1,2} Two steps were involved. In the first step, a suspension of seeds was prepared as follows: 11 mL of an aqueous solution containing 0.11 mM AgNO_3 and 2.05 mM Na_3CA was prepared. Under magnetic stirring, an aqueous solution of NaBH_4 (0.3 mL, 5 mM) was added all at once. Stirring was stopped after 10 min. This seed solution was then aged at room temperature for 5 h prior to future use. In the second step, triangular Ag nanoplates were prepared as follows: 100 mL of ultrapure water was mixed with 2.5 mL aqueous AgNO_3 (5 mM), 7.5 mL aqueous PVP ($\text{MW} \approx 29,000$, 0.7 mM in terms of the repeating unit), 7.5 mL aqueous Na_3CA (30 mM), and 0.2 mL of the seed solution, followed by slow dropping into 62.5 mL of aqueous AA (1 mM) under magnetic stirring. The color of the solution changed gradually and finally became stable at cyan. The products were cleaned by centrifugation and washing with water twice at 4°C to get rid of excess PVP and Na_3CA , and then re-dispersed

in water for future use.

Circular Ag nanoplates were prepared by aging the as-prepared triangular Ag nanoplates at an elevated temperature.³ In a typical synthesis, an aqueous suspension of the triangular Ag nanoplates was placed in a big glass jar (VWR, CAT. NO. 89000-234, 100 mL), capped, and then aged in a water bath at 80 °C for 9 h.

The Ag nanocubes were prepared using the polyol process.^{4,5} In a typical synthesis, 60 mL of EG was added into a round-bottomed flask (250 mL) and heated in an oil bath at 150 °C under magnetic stirring. After 1 h of preheating, a flow of argon was introduced using a glass pipette at a rate of 1,200 mL/min. After 10 min, 0.7 mL of a NaHS solution in EG (3 mM) was quickly added into the pre-heated EG solution, followed by injection of 15 mL of a PVP (MW≈55,000, 0.18 M calculated in terms of the repeating unit) solution in EG and 8 min later 5 mL of a AgNO₃ (0.28 M) solution in EG. The reaction solution turned to green ocher after 20 min of heating, indicating the formation of Ag nanocubes with an edge length of around 45 nm. The reaction solution was then quenched by placing the reaction flask in an ice-water bath. The sample was washed with acetone and then twice with deionized water to remove excess EG and PVP. After washing, the product was collected by centrifugation at 12,000 rpm for 8 min and then re-dispersed by brief sonication in deionized water (20 mL) for the sulfuration reaction with Na₂S_x²⁻.

Additional experimental data are provided in the captions for Figure 1B, as well as Figure S3 and Figure S4 in the Supplementary Information.

4. Sulfuration reaction

In a standard procedure for sulfuration, 0.2 mL of the Na₂S_x solution was added to 30 mL of the aqueous suspension of triangular Ag nanoplates (1.0 mM in terms of elemental silver) at room temperature under magnetic stirring. The reaction was quenched at a specific time point by centrifuging the solution at 12,000 rpm for 5 min. The product was then precipitated twice with 10 mL water by centrifugation and decantation. The final product was re-dispersed in water for further structural analysis and UV-vis measurements. For the reactions involving circular nanoplates or nanocubes of Ag, a similar procedure was used except the use of different suspensions of Ag nanocrystals.

5. Characterization

The sample for TEM was prepared by drying a drop of the aqueous suspension of nanoparticles on a carbon-coated copper grid under ambient conditions. The grid was then transferred to a gravity-fed flow cell and washed for 1 h with deionized water to remove the PVP coating as much as possible. Finally, the sample was dried and immediately used for TEM characterization. TEM images were captured using a Phillips 420 microscope operated at 120 kV. Energy-filtered TEM images for the chemical mapping of S (with an energy window of 15 eV and a collection angle smaller than 10 mrad) were carried out using a JEOL 3000F microscope operated at 300 kV. High-angle annular dark-field STEM images and the plasmonic (low energy-loss) spectra were acquired from an aberration corrected Hitachi HD2700C STEM. The UV-vis extinction spectra were recorded using a Varian Cary 50 spectrophotometer. The silver concentration was determined by inductively-coupled plasma mass spectrometry (ICP-MS).

6. Analyses of the optical properties of the Ag-Ag₂S nanoplates

Both extinction spectroscopy and electron energy-loss spectroscopy (EELS) were used to investigate the optical properties of the Ag-Ag₂S nanoplates. As shown in Figure S1, A, with the ratio of Ag₂S to Ag increasing, the in-plane dipole plasmon peak of the Ag nanoplates experienced a continuous depression and a red shift while the short-wavelength absorption derived from the Ag₂S region became more prominent. Figure S1, B, shows the EELS spectra taken from five distinct locations on a typical triangular Ag-Ag₂S nanoplate obtained after 1 min of reaction. Three peaks can be identified, respectively, for the in-plane dipole plasmon resonance at 1.8 eV, for the in-plane quadrupole at 2.7 eV, and for the out-of-plane quadrupole at 3.7 eV.⁶ In comparison with triangular Ag nanoplates reported by Nelayah *et al.*,⁷ our Ag-Ag₂S hybrid nanoplates exhibited a modified spatial pattern for the plasmonic modes: *i*) The in-plane dipole mode mostly came from the interface between Ag and Ag₂S (*i.e.*, positions b and c in the inset of Figure S1, B). This is very different from the Ag case, where the corners of the triangular nanoplates exclusively contribute to this mode. *ii*) The triangle center (position d) contributed greatly to both the in-plane and the out-of-plane

quadrupole modes, whereas it only contributed to the dipole mode in the Ag case. *iii*) Instead of only contributing to the in-plane dipole mode, the triangle edge (position e) became a major contributor to all the three modes after the corners of a triangular nanoplate had been transformed from Ag to Ag₂S.

References

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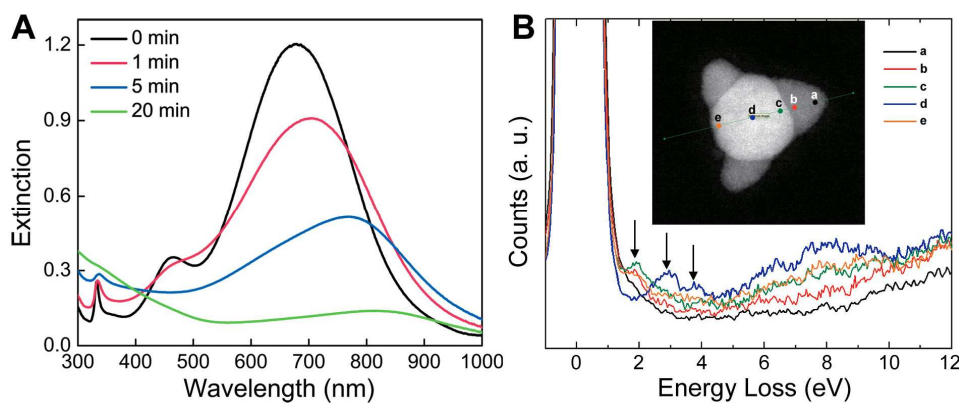


Figure S1. UV-vis and EELS measurements of the triangular Ag and Ag-Ag₂S nanoplates. (A) Extinction spectra recorded *in situ* from an aqueous suspension of the Ag nanoplates during sulfuration. The samples correspond to those shown in Figure 1, B-E. (B) EEL spectra (after the standard Richardson-Lucy deconvolution) taken from a triangular Ag-Ag₂S nanoplate obtained after sulfuration for 1 min. The spectra were acquired at five positions (a-e) along an axis of the triangular nanoplate as illustrated in the inset. The positions of the three main resonances detected along the line scan are marked by arrows.

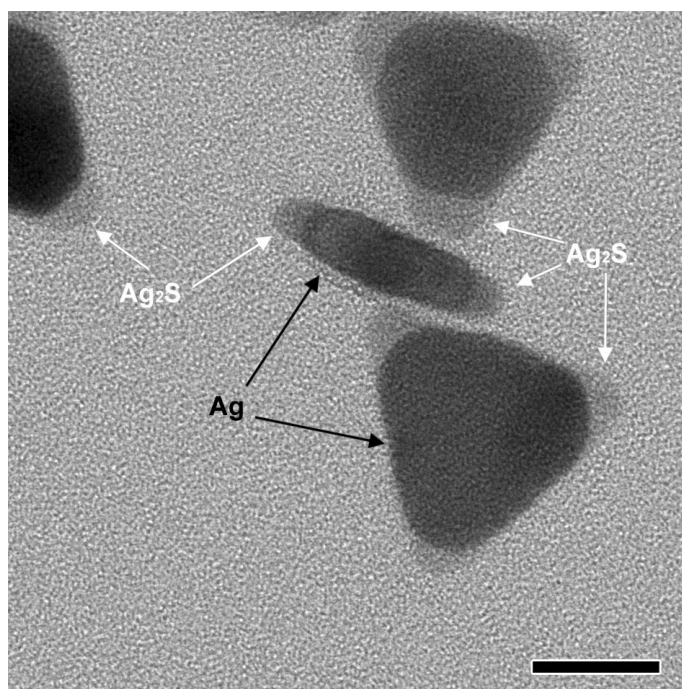


Figure S2. TEM image of the Ag-Ag₂S nanoplates obtained after sulfuration for 0.5 min. One of the plates happened to take an orientation perpendicular to the TEM grid. The white and black arrows indicate the Ag₂S and Ag portions, respectively. The scale bar is 20 nm.

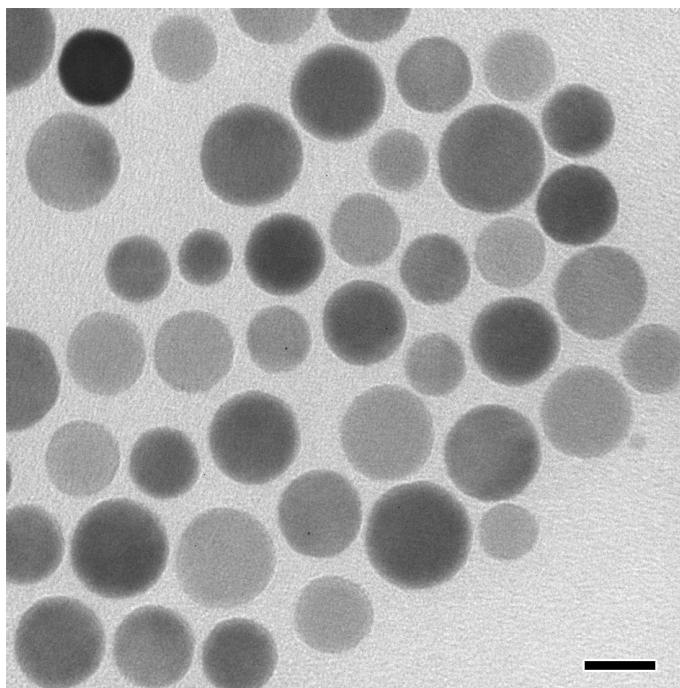


Figure S3. TEM image of the circular Ag nanoplates (or nanodisks) used for the sulfuration reaction. The scale bar is 20 nm.

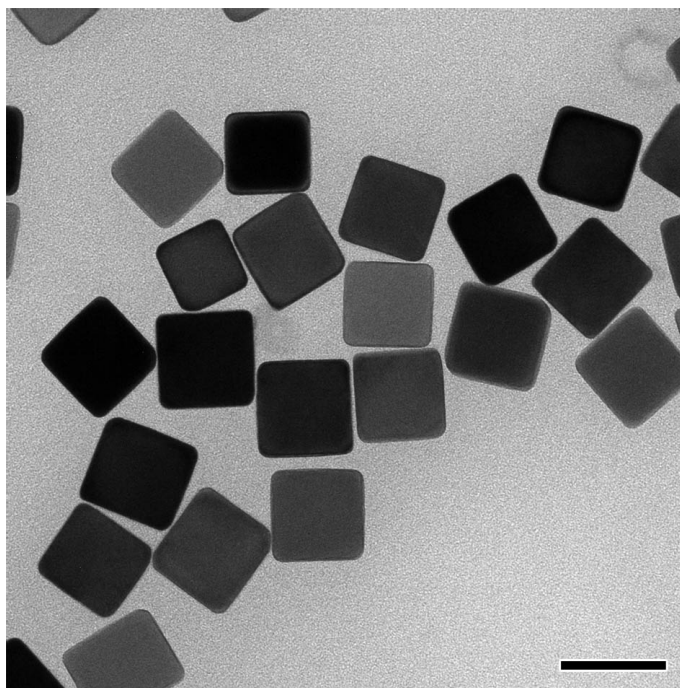


Figure S4. TEM image of the Ag nanocubes used for the sulfuration reaction. The scale bar is 50 nm.