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

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ABSTRACT: This paper describes a new approach to site-selective sulfuration at the corner sites of Ag nanocrystals including triangular nanoplates and nanocubes. The reaction simply involved mixing an aqueous suspension of the Ag nanocrystals with an aqueous solution of polysulfide at room temperature. As a precursor to elemental S, polysulfide is highly soluble in water and can directly react with elemental Ag upon contact to generate Ag2S in the absence of oxygen. The reaction was easily initiated at the corner sites and then pushed toward the center. By controlling the reaction time and/or the amount of polysulfide added, the reaction could be confined to the corner sites only, generating Ag–Ag2S hybrid nanocrystals with greatly improved stability against aging at 80 and 100 °C in air than their counterparts made of pure Ag.

KEYWORDS: Site-selection, sulfuration, polysulfide, silver, nanocrystals, stability

Silver nanocrystals with well-defined and controllable shapes have received great interests in recent years due to their intriguing properties and potential applications in a number of areas including catalysis, photonics, electronics, and optical sensing/labeling/imaging.1–8 Thanks to the efforts from many research groups, Ag nanocrystals with a rich variety of different shapes have been synthesized with notable examples including cubes, plates, wires, rods, bars, right bipyramids, octahedrons, decahedrons, and asymmetrically truncated octahedrons.9–19 Most of these nanocrystals contain sharp features on the surface and are therefore unstable from the viewpoint of thermodynamics. They are expected to spontaneously evolve into new forms (e.g., spheres and circular disks) with lower surface energies over different time scales.8,20–22 As an immediate consequence of this shape transformation, the nanocrystal may lose its originally designed electronic, optical, and catalytic properties. For example, Ag nanoplates display a strong, in-plane dipole resonance mode in the near-infrared region, but its peak position is highly sensitive to the sharpness of the corners.8,22 As the corners become rounded, the peak position will experience significant blue shifts by as much as 300 nm.8,22 In a different case, Ag nanocubes enclosed by {100} facets have been demonstrated as a superb catalyst for epoxidation,4,23 but the selectivity of this catalytic reaction tends to drop drastically as the cubes become rounded at the corners to expose {111} facets.23 It is still a grand challenge to preserve the shape of a nanocrystal with sharp features on the surface.

Herein, we report a new strategy for preserving the shape of a Ag nanoplate or nanocube via selective sulfuration of the sharp corners. Previously, Song and co-workers reported the synthesis of Ag2S–Au–Ag2S nanorods through a reaction between Ag–Au–Ag nanorods and Na2S (or S2−) in the presence of oxygen.24 The reaction progressed so rapidly that the entire Ag segments of each nanorod were completely transformed into Ag2S within 1 min. Most recently, a similar approach was used by Ma and co-workers to achieve partial sulfuration of triangular Ag nanorods with truncated corners.25 However, it was still difficult to control the kinetics of sulfuration, and the morphology of the final product was found to deviate from the original shape possibly due to the involvement of oxidation of Ag to Ag3+, which then reacted with S2− to generate Ag2S. Here we demonstrate an effective strategy for maneuvering the sulfuration kinetics by using a polysulfide (Na2Sx) to react with Ag nanocrystals at room temperature. As a precursor to elemental S, Na2Sx is highly soluble in water and can directly react with elemental Ag upon contact to generate Ag2S even in the absence of oxygen. Significantly, we could easily and tightly control the kinetics and degree of sulfuration to obtain Ag–Ag2S hybrid nanocrystals with Ag2S only being formed at the corner sites.
In a typical synthesis, we mixed an aqueous suspension of triangular Ag nanoplates with a specific amount of aqueous polysulfide, \( \text{Na}_2\text{S}_x \), which was prepared in advance by reacting sulfur powders with an aqueous \( \text{Na}_2\text{S} \) solution at 80 °C for 12 h under ambient conditions.

**Figure 1.** Progression of the site-selected reaction between a triangular Ag nanoplate and \( \text{S}_x^{2-} \) ions. (A) Schematic illustration of the sulfuration reaction, by which elemental Ag reacts with \( \text{S}_x^{2-} \) in water to generate Ag\(_2\)S under the ambient conditions of a laboratory. (B) TEM image of the triangular Ag nanoplates with slight truncation at all corners. (C–E) TEM images of the products obtained after the sulfuration reaction had progressed for (C) 1, (D) 5, and (E) 20 min. The dark region in the center corresponds to Ag while the gray regions at corner sites correspond to Ag\(_2\)S. The scale bar is 50 nm in (B) and applies to all images.

**Figure 2.** Electron microscopy characterization of the Ag–Ag\(_2\)S hybrid nanoplate obtained by stopping the sulfuration reaction at \( t = 1 \) min. (A) High-angle annular dark-field STEM image of a typical Ag–Ag\(_2\)S nanoplate, clearly showing selective sulfuration at all corner sites of the Ag nanoplate. (B,C) High-resolution STEM images of the Ag–Ag\(_2\)S nanoplate taken from the two regions marked in (A). The insets of (B) show Fourier transform patterns of the images along the [102] zone axis of Ag\(_2\)S and the [111] zone axis of Ag. The dotted red lines in (B,C) mark the boundary dividing the adjacent Ag and Ag\(_2\)S regions. (D) Color-composite energy-filtered TEM image of another Ag–Ag\(_2\)S nanoplate in the same sample, where the orange color corresponds to the highest concentration for S. The inset gives the color scale indicating the electron counts of the image. The scale bars are 10 nm in (A,D), and 2 nm in (B,C).
conditions. The reaction can be described by the following equation:

$$2(x - 1)Ag + S^{2-} \rightarrow (x - 1)Ag_2S + S^{2-}$$

On the basis of the change in Gibbs free energy ($\Delta G^\circ = -74.6$ kJ/mol at 298 K), Ag$_2$S is expected to form spontaneously when elemental Ag and $S^{2-}$ ions encounter and react in the absence of oxygen. Figure 1A shows a schematic of the sulfuration process and all major intermediate products we have observed. Figure 1B–E, shows transmission electron microscopy (TEM) images of the original, triangular nanoplates of Ag and a series of intermediate products collected by quenching the reaction at different time points. Evidently, sulfuration reaction was selectively initiated at the corner sites of a triangular nanoplate, followed by progression toward the central region. As the reaction time was expanded, the Ag$_2$S regions at corners increased continuously in area while the Ag region in the center shrank concurrently. With the ratio of Ag$_2$S 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 Ag$_2$S region became more prominent (Supporting Information Figure S1A) probably due to the high dielectric constant of Ag$_2$S. In addition, the Ag–Ag$_2$S hybrid nanoplates exhibited a modified spatial pattern for the plasmonic modes in comparison with nanoplates made of pure Ag (for details, see Supporting Information and Figure S1B).

To reveal the sulfuration mechanism, we used a number of state-of-the-art imaging tools to characterize the structures and analyze the chemical compositions of the products obtained at different stages of a reaction. Figure 2A shows a high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) image of the product obtained at $t = 1$ min, where the bright and dark regions correspond to Ag and Ag$_2$S, respectively. Examination of the same sample by high-resolution STEM (Figure 2B,C) indicates that the sulfuration reaction resulted in a step-like interface between the neighboring Ag and Ag$_2$S regions. As marked by the dotted red lines, a majority of the interface was oriented parallel to the \{422\} planes of the face-centered cubic (fcc) lattice of Ag. The reciprocal lattices (the insets of Figure 2B) obtained from two-dimensional Fourier transform of the lattice-resolved images are in agreement with the [111] and [102] zone axes of fcc Ag and argentite Ag$_2$S,
respectively. It is worth noting that the well-known stacking faults along the zone axis of a Ag nanoplate were also passed on to the AgS regions. Specifically, the sets of spots with a spacing of 2.5 and 3.3 Å could be assigned to the 1/3{422} forbidden reflection of Ag and 1/3{402} forbidden reflection of AgS, respectively. The assignments of different regions to Ag and AgS are also consistent with the energy-filtered mapping for S (Figure 2D), where the intensity of color is directly proportional to the amount of Sx2−/C0.

It is worth pointing out that the triangular shape was essentially preserved even though the lattice of Ag atoms underwent massive transformation during sulfuration. As a result, the Sx2− species had to diffuse into the lattice of Ag atoms, most likely from both top and bottom surfaces of a nanoplate in order to continue the reaction. Thus, the reaction kinetics should be mainly determined by the diffusion rate of Sx2− into the crystal lattices of Ag. Typically, Sx2− has a much larger size (depends on the degree of polymerization) relative to the monomeric S or S2− species, and ultimately, Sx2− can only diffuse into the Ag lattice very slowly, leading to a great reduction for the reaction rate and thus a well-controlled sulfuration rate. This kinetic difference represents one of the major advantages for our method relative to previous studies involving Na2S. Our observations are also in good agreement with the previous studies of polysulfide, where it was found both experimentally and theoretically that any increase in degree of polymerization or size could lead to a significant reduction in diffusion coefficient for the polysulfide species across an interface between sulfur and sodium polysulfide.

Another obvious result is that the lateral dimensions of the Ag−AgS nanoplates were larger than those of the original Ag nanoplates. On the basis of the molar volumes of AgS and Ag (34.3 cm3/mol for AgS and 10.3 cm3/mol Ag), we anticipate that the volume of the AgS region must be 70% larger than that of the original Ag region. Since the thickness of the AgS region was essentially the same as the Ag region (Supporting Information Figure S2), there was only one possibility for the AgS region to expand its volume during the sulfuration reaction, that is, increasing its area laterally. This argument is supported by the observations in Figure 1C−E and Figure 2A. Once the AgS regions had started to appear at the corners of a triangular Ag nanoplate, they could grow in area until they met in the center of the plate as long as sufficient sulfur was supplied. The simultaneous reactions at different sites of a nanoplate indubitably increased the internal energy due to the strain at the interface caused by the lattice mismatch between Ag and AgS. However, it is likely that the shape of the nanoplate plays a more important role in determining the reaction rate and thus the sulfuration rate.

Figure 4. Comparison of the thermal stability of the triangular Ag and Ag−AgS nanoplates. (A,B) TEM images of the triangular Ag nanoplates before and after they had been aged at 80 °C for 9 h. The sharp corners of the Ag nanoplates were rounded to generate circular disks with reduced lateral dimensions. (C,D) TEM images of the triangular Ag−AgS nanoplates before and after they had been aged at 80 °C for 9 h. No distinct morphology change was observed before and after aging. The scale bar in (A) is 50 nm and applies to all images.
Structure shown in Figure 3A) was much slower than that of triangular Ag nanocubes (which only took 1 min to obtain the structure shown in Figure 1C). This large difference in sulfuration rate also indicates a relatively higher activity at the corner sites. The same trend was also observed in the sulfuration of Ag nanospheres and nanocubes.

In addition to the two-dimensional system like thin nanospheres and nanocubes, we have also successfully extended the new sulfuration method to a three-dimensional system by generating Ag−Ag2S hybrid nanocubes. As expected, the TEM image in Figure 3C and the S elemental mapping in Figure 3D indicate that the sulfuration reaction was also initiated from all the corner sites of a Ag nanocube and the reaction kinetics and the degree of sulfuration could be easily controlled. It is worth pointing out that, the Ag−Ag2S hybrid nanocubes could also tolerate large mismatch in lattice constants without forming dislocations or losing the original shape.

Interestingly, both triangular nanoplates and nanocubes of Ag exhibited enhanced thermal stability against aging after their corner sites had been selectively converted into Ag2S via sulfuration with Na2Sx. As shown in Figure 4A,B, the original triangular Ag nanoplates suffered a significant change to their morphology by rounding their sharp corners when they were dispersed in water and aged at 80 °C for 9 h. However, the Ag−Ag2S hybrid nanoplates were able to retain their triangular shape under the same aging conditions (Figure 4C,D). These changes were also reflected in their LSPR spectra recorded with a UV−vis spectrometer. The in-plane dipole peak was blue shifted more than 300 nm in the case of triangular Ag nanoplates, while the peak was changed very little for the Ag−Ag2S hybrid nanoplates (Figure 5A). Again, the same trend was also observed for Ag nanocubes without and with sulfuration at the corner sites (Figure 5B).

In conclusion, we have demonstrated an effective approach to site-selected modification of Ag nanocrystals by sulfuration with S2− at the corner sites. In comparison with previous studies involving S2− and oxygen, both the kinetics and degree of sulfuration could be better controlled by switching to S2−. With triangular nanoplates and nanocubes of Ag as two examples, we clearly showed that sharp corners played an important role in determining the initiation sites for sulfuration. Our studies also revealed that the Ag2S formed at the corners of Ag nanocrystals could effectively prevent the nanocrystals from changing their shapes during an aging process and thus improve their thermal stability, a feature vital to various applications in plasmonics and catalysis. Considering the high affinity of noble metals to sulfur, the concept demonstrated here is potentially extendable to many other systems.

**ASSOCIATED CONTENT**

1 Supporting Information. Additional information and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

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