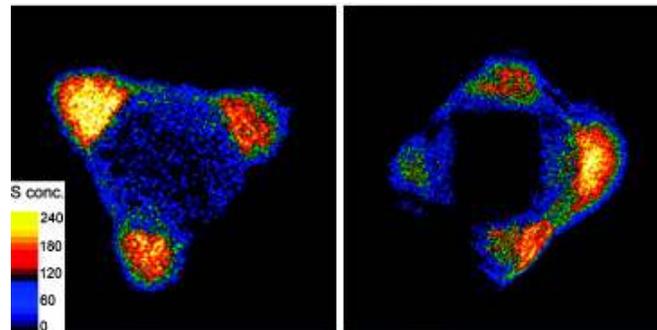


Selective Sulfuration at the Corner Sites of a Silver Nanocrystal and Its Use in Stabilization of the Shape



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Introduction

- Silver nanocrystals of different shapes has been synthesized and their potential application possibility in fields like catalysis, photonics, electronics and optical imaging has been demonstrated by many research groups.
- Most of these nanocrystals have sharp features on the surface which are thermodynamically unstable and spontaneously evolve into new shapes over time.
- As a consequence of change in shape, the nanocrystals has been found to loose the original property.
 - e.g. Ag nanocubes enclosed by $\{100\}$ facets has been found to be excellent catalyst for epoxidation but selectivity of this catalyst decreases with time as the corners become rounded to expose $\{111\}$ facets.
- It has been a challenging task so far to preserve the shape of the silver nanocrystals with sharp surface features.

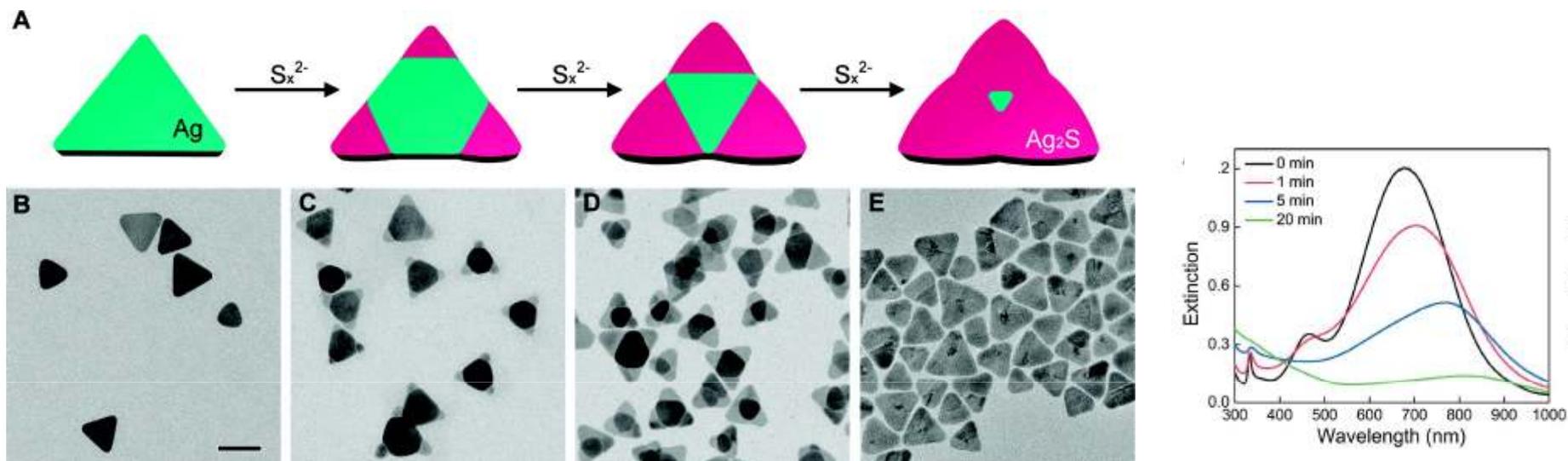
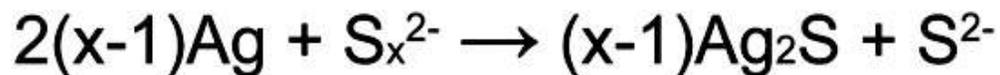
In this paper...

- A new strategy for preserving the shape of Ag nanoplate or or nanocube via selective sulfuration of the sharp corners has been demonstrated.

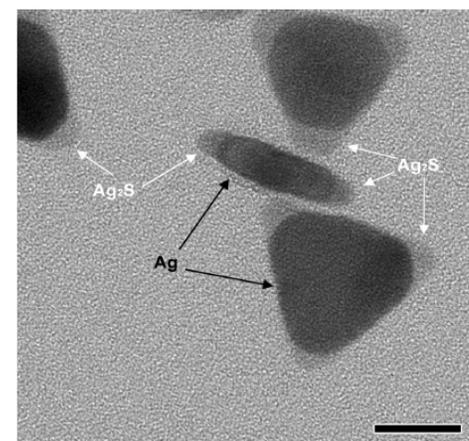
Experimental Section

- Na_2S_x was prepared by reacting aqueous solution of Na_2S with sulfur powder.
- Ag nanotriangle and nanocubes were synthesised by previesly reported seed mediated synthesis and polyol process respectively.
- Ag nanodiscs were obtained by aging the Ag nanotriangles.
- Sulfuration reaction was performed by adding Na_2S_x solution in aqueous suspension of Ag nanocrystals at room temperature under magnetic stirring.

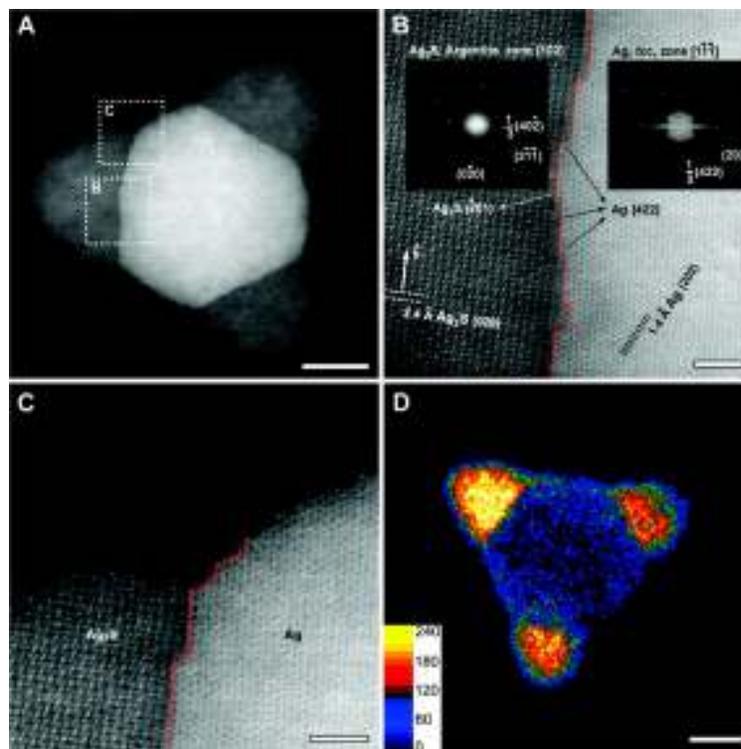
Result and discussion



Progression of the site-selected reaction between a triangular Ag nanoplate and S_x^{2-} ions. (A) Schematic illustration of the sulfuration reaction, by which elemental Ag reacts with S_x^{2-} in water to generate Ag_2S 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_2S . The scale bar is 50 nm in (B) and applies to all images.

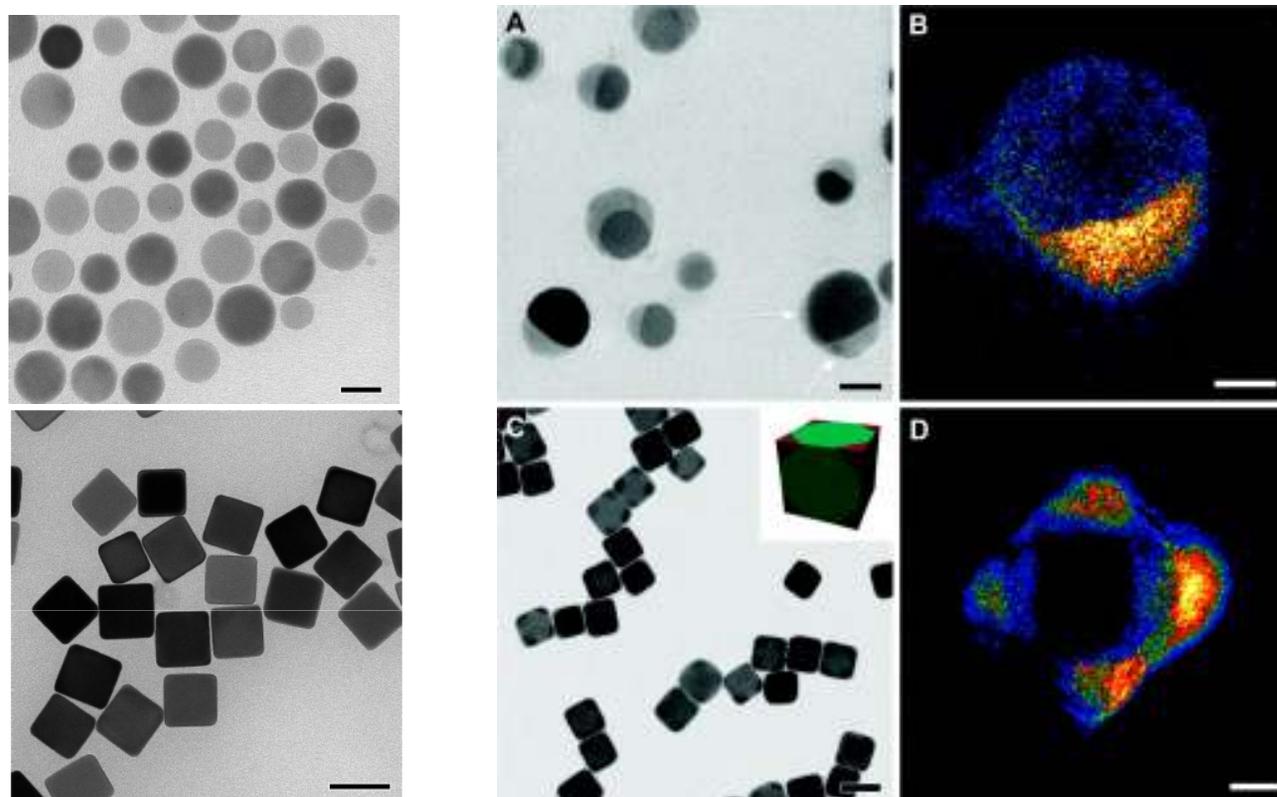


Result and discussion



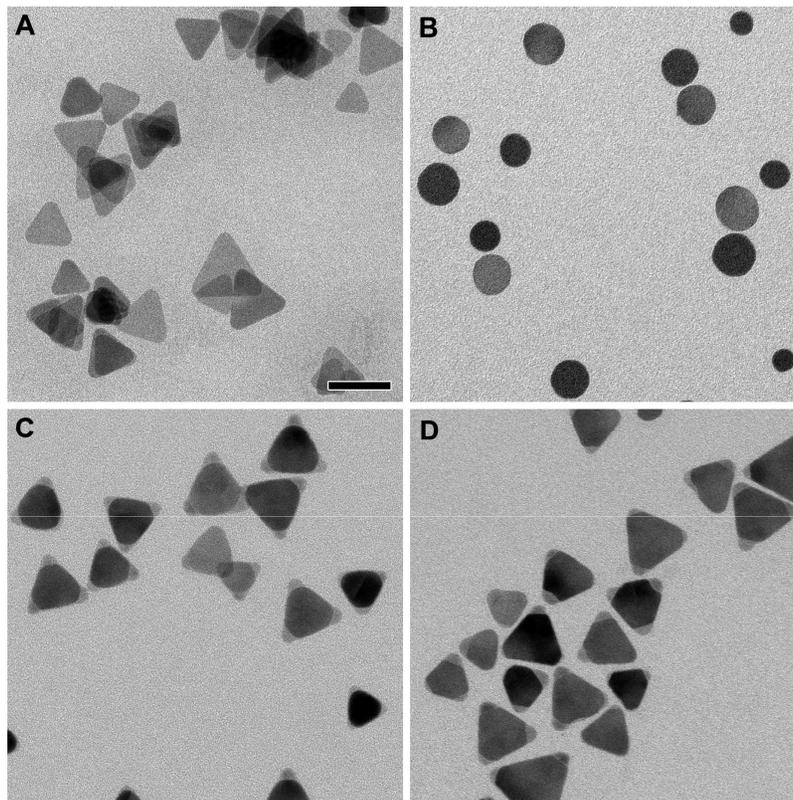
Electron microscopy characterization of the Ag–Ag₂S hybrid nanoplate obtained by stopping the sulfuration reaction at $t = 1$ min. (A) High-angle annular dark-field STEM image of a typical Ag–Ag₂S nanoplate, clearly showing selective sulfuration at all corner sites of the Ag nanoplate. (B,C) High-resolution STEM images of the Ag–Ag₂S 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 Ag₂S and the [111] zone axis of Ag. The dotted red lines in (B,C) mark the boundary dividing the adjacent Ag and Ag₂S regions. (D) Color-composite energy-filtered TEM image of another Ag–Ag₂S 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).

Result and discussion



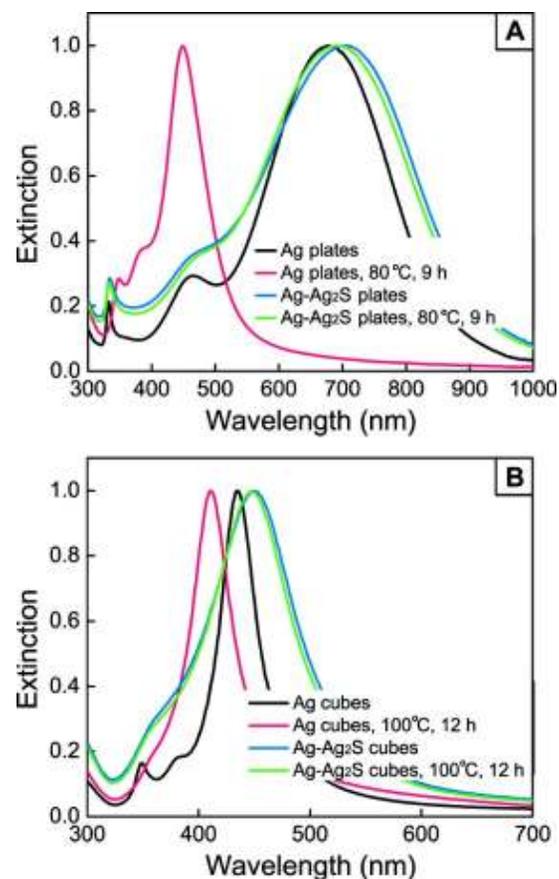
Sulfuration of Ag circular disks lacking sharp corners and Ag nanocubes with sharp corners. (A) TEM image of the product after sulfuration of the disks for 10 min, indicating that the reaction preferred to occur at one particular site of the disk. (B) Energy-filtered TEM image of a typical Ag–Ag₂S disk. (C) TEM image of the product after sulfuration of the Ag nanocubes for 20 min, showing that the reaction preferentially occurred at all corners of the nanocube. The inset shows an illustration of the Ag nanocube with Ag₂S formed at all corners. (D) Energy-filtered TEM image of a typical Ag–Ag₂S hybrid nanocube. The orange color in (B,D) corresponds to S with the same intensity scale as in Figure 2D. The scale bars are 20 nm in (A), 10 nm in (B,D), and 50 nm in (C).

Result and discussion



Comparison of the thermal stability of the triangular Ag and Ag–Ag₂S 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–Ag₂S 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.

Result and discussion



(A) Extinction spectra recorded from aqueous suspensions of the Ag nanoplates and Ag–Ag₂S nanoplates before and after the samples had been aged at 80 °C for 9 h. The samples correspond to those shown in Figure 4A–D. (B) Extinction spectra recorded from aqueous suspensions of the Ag nanocubes and Ag–Ag₂S nanocubes before and after the samples had been aged at 100 °C for 12 h.

Conclusion

- An effective approach to site-selected modification of Ag nanocrystals through sulfuration with S_x^{2-} at the corner sites
- In comparison with previous studies involving S^{2-} and oxygen, both the kinetics and degree of sulfuration could be better controlled by switching to S_x^{2-}
- Role of sharp corners in determining the initiation sites for sulfuration has been demonstrated taking Ag nanoplate and nanocube as examples
- The study has also revealed that Ag_2S 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.

Potential extensions

- Metal chalcogenide nanoparticles with various size and morphology can be made following this approach which is generally not possible starting from chalcogen nanoparticles as they generally form rod or wire shaped structure and size (and shape) dependency on properties like thermoelectric and optoelectric can be explored.
- Cation exchange in metal chalcogenide nanoparticles has been widely studied keeping the anionic framework constant, but anion exchange has been rarely studied.
- These metal-metal chalcogenide nanostructures can be used for new applications like data storage.

Thank You