Supporting Information

Aggregation-based abrupt crystallization from amorphous Ag$_2$S to Ag$_2$S nanocrystal

Ruding Zhang$^{a,c}$, Xiaogang Xue$^{a,c}$, Zanyong Zhuang$^{a,c}$, Jinsheng Zheng$^{a,c}$ and Zhang Lin$^{*,a,b,c}$

$^a$Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

$^b$School of Environment and Energy, South China University of Technology, Guangzhou 510006, China

$^c$Fujian Provincial Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

* To whom correspondence should be addressed.
E-mail: zlin@fjirsm.ac.cn

List of Contents

1. Experimental Section.

2. Uv-Vis absorption spectra of Ag$_2$S samples (125 °C, 0 h, 2 h, 5 h and 150 °C, 0 h, 1 h) and Size distribution histogram of primary sample, 6 h, 50 h and 120 h sample.

3. More TEM or HRTEM images of Ag$_2$S samples (125 °C, 0 h, 2 h, 5 h).

4. DLS analysis of Ag$_2$S samples (125 °C 0 h, 2 h, 5 h, 6 h, 9h, 50h and 120h).

5. XRD patterns, TEM images, ED patterns and the relative amount of adsorbed 3-MPA vs. crystallization time of Ag$_2$S samples at representative time points at 150 °C during hydrothermal crystallization.

6. More HRTEM images of Ag$_2$S samples (125 °C, 6 h, and 150 °C, 1.33 h).

7. Quantitative FTIR analysis to track the variation of relative amount of ligands vs. time at 150 °C.
1. Experimental Section.

**Materials.** 3-mercaptopropionic acid (3-MPA, 99%) was purchased from Alfa Aesar. Silver nitrate (AgNO₃) and sodium sulfide nonahydrate (Na₂S·9H₂O) were of analytical grade and purchased from Sigma Aldrich. All chemicals were used as received without further purification.

**Preparation of Primary MPA-capped Ag₂S.** 3-MPA-capped Ag₂S used in this study was prepared using a previously reported method with minor modifications.¹ In a typical procedure, 0.425 g AgNO₃ was first dissolved in 150 ml deionized water followed by an injection of 12.5 mmol 3-MPA under continuous and vigorous stirring. Then the pH value of the solution was adjusted to 7.5 with a NaOH solution. After stirring for several minutes, 50 ml of 12.5 mM Na₂S solution was added dropwise at room temperature under N₂ protection and constant stirring. The reaction proceeded until Na₂S solution was drained. The obtained MPA-capped Ag₂S was washed with ethanol, redispersed into deionized water, and stored in the dark as a stock solution.

**Hydrothermal Crystallization of Primary MPA-capped Ag₂S.** A 12 mL aliquot of 3-MPA-capped Ag₂S solution was loaded into a Teflon-lined stainless steel autoclave with 23 mL capacity. Several autoclaves were prepared. The autoclaves were then sealed and put into a large oven. The oven temperature was precisely controlled at 125°C or 150°C as required, to insure that all autoclaves in the oven were thermally equilibrated and of the same conditions. For the time series experiments, autoclave containers were taken out at the appropriate time intervals and immediately quenched to room temperature with cold water. The collected samples were then characterized as follows.

**Characterization.**

**X-ray Diffraction (XRD).** The sample structures and average sizes were identified by a PANalytical X’Pert PRO diffractometer with Cu Kα radiation (40 kV, 40 mA) in a continuous scanning mode. The scanning range of 2θ was from 15° to 85° in steps of 0.02° with a collection time of 30 seconds per step. The average crystallite size of the large nanocrystal was calculated from the peak broadening using the Scherrer equation $d = \frac{0.89\lambda}{B\cos\theta}$.

**High-resolution transmission electron microscopy (HRTEM).** HRTEM was used to confirm the particle size, shape, element composition and microstructures information of the sample by a TECNAI F20 at 200kV equipped with energy-dispersive X-ray (EDX) spectrometry. Electron diffraction (ED) pattern was taken simultaneously. Samples for HRTEM measurement were prepared by dripping a drop of solution containing Ag₂S onto 200-mesh ultrathin-carbon-coated copper grids.

**Fourier Transform Infrared Spectroscopy (FTIR) spectra.** Quantitative FTIR analyses were performed to follow the change of the capping state of MPA-capped Ag₂S samples taken at different hydrothermal treatment time points. The spectra were collected on a Perkin-Elmer Spectrum One spectrometer using the KBr method and KSCN as an internal standard. Detailed description can be found in Fig. S8.

**Ultra violet-Visible (Uv-Vis) spectra.** The Uv-Vis absorbance data were recorded on a Perkin-Elmer Lambda-35 double monochromator Uv-Vis-NIR spectrophotometer at room temperature (298 K) with the wavelength ranging from 300 nm to 1100 nm. The average particle size was calculated from the measured absorption edge by using the Brus equation.

**Dynamic Light Scattering (DLS).** A Malvern Zetasizer Nano-ZS90 (red badge) ZEN 3690 was used to characterize the hydrodynamic particle size as well as aggregate size of the samples.
2. The Uv-Vis absorption spectra of Ag₂S samples (125 °C, 0 h, 2 h, 5 h and 150 °C, 0 h, 1 h).

![Uv-Vis absorption spectra of Ag₂S samples](image)

Figure S1. Uv-Vis absorption spectra of Ag₂S samples at 125 °C (a) and 150 °C (b). The average particle size calculated from the measured absorption edge was about ~3.2 nm, which agrees well with the TEM observations and DLS analysis.

The average particle size was calculated from the measured absorption edge using the Brus equation:

\[
E_R^* = E_g + \frac{\hbar^2}{8R^2} \left( \frac{1}{m_e m_0} + \frac{1}{m_e m_h} \right) - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 R}
\]

where \(E_R^*\) is the band gap of the nanoparticle (\(E_R^* = \frac{\hbar c}{\lambda}\)), \(E_g\) is the band gap of the corresponding bulk material, \(R\) is the radius of the particle, \(m_0\) is the mass of a free electron, \(m_e\) and \(m_h\) are the effective electron and hole masses, respectively, \(\varepsilon\) is the relative dielectric constant, \(\varepsilon_0\) is the absolute dielectric constant, \(\hbar\) is Planck constant, and \(e\) is the charge of an electron.

![Size distribution histogram](image)

Figure S2. A-D are size distribution histogram of primary sample, 6 h, 50 h and 120 h sample obtained from the TEM statistics respectively (statistical number is over 100).

To calibrate the size calculation by the two methods, in our preliminary work we have use the TEM images (particles were relatively dispersed) to analyze the sizes and size distribution of particles at different time points. As the pictures shown above, the particle size of primary sample is in the range of ~2-5 nm according to TEM statistics, and the average size is ~3.2 nm by Brus equation; particle size of 6 h, 50 h and 120 h samples mainly are in the range of ~11-15 nm a, ~12-15 nm and ~13-16 nm, respectively. In addition, the average size are ~12.3 nm, ~13.8 nm and ~15.4 nm respectively by the Scherrer equation. Based on the above analysis, the size calculation via absorption spectra data for 0-5 h samples and via the Scherrer equation for 6-120 h samples fit
3. More TEM or HRTEM images of Ag₂S samples (125 °C, 0 h, 2 h, 5 h).

Figure S3. Typical TEM or HRTEM images of Ag₂S samples coarsened for 0, 2, and 5 h. Samples in this stage had no crystallinity and there was little change in particle size in the range of ~2-5 nm.
4. DLS analysis of Ag$_2$S samples (125 °C 0 h, 2 h, 5 h, 6 h, 9h, 50h and 120h).

Figure S4. DLS images of Ag$_2$S samples 0 h, 2 h, 5h, 6 h, 9h, 50h and 120h at 125 °C.
Table S1. Hydrodynamic diameter measured by DLS and reported as the number average, peak value read from Figure S3.

<table>
<thead>
<tr>
<th>time</th>
<th>peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 h</td>
<td>~4 nm</td>
</tr>
<tr>
<td>2 h</td>
<td>~40 nm</td>
</tr>
<tr>
<td>5 h</td>
<td>~10 nm</td>
</tr>
<tr>
<td>6 h</td>
<td>~20 nm</td>
</tr>
<tr>
<td>9 h</td>
<td>~20 nm</td>
</tr>
<tr>
<td>50 h</td>
<td>~20 nm</td>
</tr>
<tr>
<td>120 h</td>
<td>~20 nm</td>
</tr>
</tbody>
</table>

The data obtained by DLS were the hydrodynamic diameters of Ag₂S samples.

As shown in Figure S3 and Table S1, the peak at ~4 nm (in good agreement with Uv-Vis analysis and TEM observations) indicates the existence of small particles at 0 h. In the stage of 0-5h, the hydrodynamic diameter first increases from ~4 nm to ~40 nm and then decreases to ~10 nm (close to those of crystalline nanocrystals) as a function of time (Figure S3 and Table S1), while the particle size of samples at 2 h and 5 h were below ~5 nm on the basis of Uv-Vis analysis and TEM observation. It indicates an aggregation (in line with rapid removal and departure process of 3-MPA) occurred during 0-5 h, wherein the aggregation state of particles changed from looseness to compactness. The DLS results confirm that the changes before 5 h were to prepare for the following fusion and crystallization. The hydrodynamic diameter of 6-120 h samples were ~20 nm, which well agreed with that of XRD calculation and TEM observation.
5. XRD patterns, TEM images, ED patterns and the relative amount of adsorbed 3-MPA vs. crystallization time of Ag$_2$S samples at representative time points at 150 °C during hydrothermal crystallization.

Figure S5. (a) Time dependent XRD spectra and (b) Particle size analysis of primary MPA-capped Ag$_2$S samples hydrothermally treated at 150 °C.

Figure S6. Typical TEM images of low magnification (a-e) and high magnification (f-j), showing the primary sample treated hydrothermally in water at 150 °C for 0, 1, 1.33, 1.67, and 14 h, respectively. Scale bar in (a-e) represents 100 nm. Insets in (a-e) show electron diffraction (ED) patterns of corresponding sample. Scale bar represents 1 nm$^{-1}$.

Figure S7. Time dependent absorption curve of 3-MPA on the surface of Ag$_2$S samples crystallized at 150 °C.

Ag$_2$S coarsening experiment was also performed at a higher temperature (150 °C). Similar rules in the evolution of XRD patterns and particle size were obtained as shown in Fig. S4a and 4b. The onset of the abrupt crystallization moved to ~1.33 h, earlier than that of the samples coarsened at 125 °C. The abrupt crystallization phenomenon which is consistent with those when samples are coarsened at 125 °C, was confirmed by TEM images and corresponding ED patterns in Fig. S5. This supports the standpoint that amorphous small particles and aggregates are the precursors of nanocrystals. The time dependent 3-MPA absorption curve (Fig. S6) is similar to that of samples coarsened at 125 °C, which suggests possibly the same crystal evolution mechanism. In addition, the change of PH in 125 °C doesn't affect the abrupt crystallization phenomenon, it merely prolongs the transition time of abrupt crystallization (data not show and not the main content).
6. More HRTEM images of Ag$_2$S samples (125 °C, 6 h, and 150 °C, 1.33 h).

Figure S8. Typical HRTEM images of Ag$_2$S samples collected after 6 h at 125 °C and 1.33 h at 150 °C. Based on systematic TEM analysis, the lattice of as-formed nanocrystal was a single-crystal type, and there didn’t exist the particles with the outer sphere of the Ag$_2$S amorphous particles undergoing the phase transition while the inner part is still amorphous. Noted that many defects existed inside the newly formed complete nanocrystals.
7. Quantitative FTIR analysis to track the variation of relative amount of ligands vs. time in 150 °C.

Figure S9. (a) FT-IR spectra of 3-MPA coated Ag₂S primary samples. No S-H vibration peak (~2500 cm⁻¹) of 3-MPA can be observed, demonstrating that 3-MPA is bound to the surface of Ag₂S nanoparticles via the thiolate functional group. (b) FTIR spectra of samples hydrothermally treated in water at 150 °C for different periods of crystallization time.³

Quantitative Fourier Transform Infrared Spectroscopy (FTIR) analysis was conducted to study the state and amount of surface-adsorbed 3-MPA. All measurements were carried out at room temperature using potassium thiocyanate (KSCN, peak center near 2100 cm⁻¹) as the internal standard and potassium bromide (KBr, without characteristic vibration peak during 400-4000 cm⁻¹) as background. For the FTIR characterization of every sample, the ratio of Ag₂S sample/KSCN/KBr mixture was kept constant at a ratio of 3:5:100, then followed by grinding and drying. A pellet was then pressed from the above mixture powder to make assure for every pressed pellet the ratio of Ag₂S/KSCN was kept constant, and which has also been confirmed by ICP measurement. Hence, the ratio between the intensity of C=O (1626 cm⁻¹ – 1415 cm⁻¹) characteristic vibrational peak and the intensity of KSCN (near 2100 cm⁻¹) characteristic vibrational peak was quantified. The 3-MPA amount of primary sample was defined as 100%.

References: