SUPPORTING INFORMATION

for

In Situ X-Ray Diffraction Study of the Formation, Growth and Phase Transition of Colloidal Cu_{2-x}S Nanocrystals

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Supporting figures for the experiment done at 260 °C



Figure S1. Contour plot of the raw data for the nanocrystals synthesis at 260 °C.

Supporting figures for the experiment done at 280 °C



Figure S2. Contour plot of the raw data for the nanocrystals synthesis at 280 °C

Supporting figures for the experiment done at 300 °C



Figure S3. Contour plot of the raw data for the nanocrystals synthesis at 300 °C



Figure S4. Refined weight fractions, normalized scale factor and crystallite size for the nanocrystals synthesized at $300 \,^{\circ}C$

Supporting figures for the experiment done at 320°C



Figure S5. Contour plot of the raw data for the nanocrystals synthesis at 320°C



Figure S6. Refined weight fractions, normalized scale factor and crystallite size for the nanocrystals synthesized at 320°C

Supporting figures for the experiment done at 340°C



Figure S7. Contour plot of the raw data for the nanocrystals synthesis at 340°C

Nanocrystals synthesized *ex situ* in open flask

Nanocrystals were synthesized following the procedure by Zhuang *et al.*¹ Subsequently, the synthesized nanocrystals were investigated with TEM, thermogravametric/differential thermal analysis (TG/DTA) and with X-ray diffraction at beam line I711 MAX II² (MAX-lab, Lund, Sweden) and at the RIKEN beamline BL44 (SPring-8, Japan). At MAX-lab, X-ray powder diffraction (PXRD) patterns were collected while the sample was heated from room-temperature to 500°C (heating rate: 5°C/min). At Spring-8 high resolution PXRD patterns were collected from - 173°C to 727°C in appropiate steps. TG/DTA data was acquired on a NETZSCH STA 449C apparatus (heating rate: 4 °C/min, Ar atmosphere).

There are two phase transitions in the *ex situ* nanocrystals, from γ -chalcocite to β -chalcocite at approximately 100°C and from β -chalcocite to high digenite at 400°C.³ This is consistent with the bulk phase diagram for the Cu-S system. From both TG data and multi-temperature PXRD from MAX-lab it is clear that the ligands is decomposing between 230°C and 330°C, with a second step from 330°C to 430°C. The armophous peak at 2.2 Å⁻¹ in the PXRD decreases and at temperatures above 400°C there are not armphous background in the PXRD patterns.



Figure S8. a) TEM picture of the synthesized colloidal nanocrystals with both a large image and a zoom-in, b) SPring-8 PXRD patterns with a phase transition at 427 °C. c) Heating-ramp measurement from MAX-lab, where it is clear that the ligands decompose around 330 °C and with phase transition to digenite at 400 °C. d) The TG/DTA data show that the ligands are completely decomposed at around 430 °C.

Nanocrystals synthesized ex situ in autoclaves

Powder X-ray diffraction of the samples synthesized at 260°C and 340°C in autoclaves was measured on a Rigaku SmartLab diffractometer with Cu-radiation (K α_1) and parallel beam optics equipped with Soller5° receiving slits. The 260°C sample was measured at room-temperature after being heated to 200°C. The 340°C sample was measured at 180 °C in order to be above the low digenite phase transition temperature.

It can be seen that at 260 °C both high digenite (indicated with # in figure S10a) and β -chalcocite (indicated with * in figure S10a) are present. At 340 °C only the high digenite is present and the fit obtained by Rietveld refinement is shown in figure S10b. The uncorrected calculated nanocrystal size is 29(1) nm, which is too small since the instrument broadening has not been considered in this

refinement. Hence, the nanocrystals are much larger than the nanocrystals obtained in the *in situ* experiments.



Figure S9. a) PXRD pattern for the nanocrystals synthesized in autoclave at 260 °C, measured at room-temperature. # indicates high digenite, * indicates β -chalcocite and Δ indicates an unidentified phase. b) Rietveld refinement of the PXRD pattern obtained for the nanocrystals synthesized at 340 °C. The PXRD pattern is measured at 180 °C. Scherrer's formula is used to calculate the nanocrystal size. The R-values are: $R_f = 1.45\%$, $R_{Bragg} = 2.77\%$

Sequential Rietveld refinement

The sequential Rietveld refinements were done in the *FullProf Suite* program package.⁴ The refinements were performed in reverse order with refinement of the unit cell parameters, scale factor(s), and background. The background was modeled using linear interpolation. Thermal parameters in the form of *B*-values were fixed to 1. The positions of the atoms were fixed to the coordinates from the ICSD (Inorganic crystal structure database) *i.e.* high-temperature chalcocite and high digenite were based on the ICSD database code 43323 and 57213, respectively. The atomic sites in high-temperature chalcocite were assumed to be fully occupied, and for high digenite it was assumed that the stoichiometry was $Cu_{1.8}S$. This may induce a small error in the refinement since the stoichiometry might be different, but a refinement of the occupancies was not possible. The zero point is fixed. The peak profiles were described by the Thompson-Cox-Hastings pseudo-Voigt function.⁵ The effect of instrumental peak broadening was eliminated by performing a LeBail refinement of data on a strain-free micrometer-sized LaB₆ standard sample. Anisotropic size broadening from the sample was modelled as:

$$FWHM(\Theta_{\rm h}, \Phi_{\rm h}) = \frac{0.94 \cdot \lambda}{\cos(\theta)} \sum_{lmp} A_{lmp} Y_{lmp}(\Theta_{\rm h}, \Phi_{\rm h}) = \frac{0.94 \cdot \lambda}{\langle D(\Theta_{h}, \Phi_{h}) \rangle \cos(\theta)}$$

where FWHM(Θ_h , Φ_h) is the size contribution to the full-width at half maximum of reflection **h**, and $Y_{lmp}(\Theta_h, \Phi_h)$ are the real spherical harmonics with the normalization used by Järvinen.⁶ The refined coefficients, A_{lmp} , were used to calculate the volume-weighted crystallite size, $\langle D(\Theta_h, \Phi_h) \rangle$ for a given crystallographic direction. Two different models were tested, 1) two spherical harmonics for each phase (Y_{00} , Y_{20} and K_{00} , K_{41}), 2) one spherical harmonic for each phase (Y_{00} and K_{00}). The last model gives spherical nanocrystals. The volume-weighted crystallite size for high-chalcocite ($P6_3/mmc$) could be calculated as:

$$\langle \mathsf{D}(\Theta_h, \Phi_h) \rangle = \frac{1}{\mathsf{A}_{00}\mathsf{Y}_{00}(\Theta_h, \Phi_h) + \mathsf{A}_{20}\mathsf{Y}_{20}(\Theta_h, \Phi_h)}$$

$$Y_{00}(\Theta_h, \Phi_h) = 1$$
$$Y_{20}(\Theta_h, \Phi_h) = \frac{1}{2}(3\cos^2\Theta - 1)$$

For the digenite phase (*Fm-3m*):

$$\langle \mathsf{D}(\Theta_h, \Phi_h) \rangle = \frac{1}{\mathsf{A}_{00}\mathsf{K}_{00}(\Theta_h, \Phi_h) + \mathsf{A}_{41}\mathsf{K}_{41}(\Theta_h, \Phi_h)}$$

$$\begin{split} \mathrm{K}_{00}(\Theta_h, \Phi_h) &= 1\\ \mathrm{K}_{41}(\Theta_h, \Phi_h) &= \frac{5}{2}(\sin^4\Theta\cos^4\Phi + \sin^4\Theta\sin^4\Phi + \cos^4\Theta) - \frac{3}{2} \end{split}$$

The arguments to the functions are the polar angles of reflection **h** with respect to the spherical coordinate system. Θ is the inclination angle (defined to go from the *z*-axis to the vector towards the xy-plane), while Φ is the azimuthal angle (from the *xz*-plane to the vector towards the *y*-axis). A comparison between models with one and two spherical harmonics are made in figure S12. The morphology extracted from the model with two spherical harmonics can be seen in figure S13 and S14. It can be seen that the high-temperature chalcocite nanocrystals are slightly elongated in the *c*-direction, whereas the morphology for the digenite phase is a truncated cube.



Figure S10. Comparison between a model with two and one spherical harmonics. Nanoparticles synthesised at 280 $^{\circ}\mathrm{C}$



Figure S11. Particle morphology after 340 seconds as extracted from Rietveld refinement for the high-temperature chalcocite phase, when two spherical harmonics are used in the model



Figure S12. Crystallite morphology after 720 seconds as extracted from Rietveld refinement for the digenite phase, when two spherical harmonics are used in the model

The model with one spherical harmonic was chosen as the model for all data since it displays the same trend as the model with two spherical harmonics. Furthermore, the morphology observed by TEM is in agreement with the one spherical harmonic model.

Example of a fit to the data (spherical model)

1M, 280 °C, 1528 seconds (last frame)		
Wavelength	1.0000(8) Å	
2θ range	5-33.5	
Number of points	472	
Number of parameters (not including background points)	3	
Number of refined background points	25	
R _F	0.5%	
Scale factor	0.0065(1)	
A	5.6128(2) Å	
A ₀₀	95(2) μm ⁻¹	



Figure S13. Example of Rietveld refinement of data. Last frame used in the experiment done at 280° C. Digenite is formed and the stoichiometry is fixed to Cu_{1.8}S

SEM-EDX data

The washed $Cu_{2-x}S$ samples from the *in situ* experiment where subject to SEM-EDX analysis. Five different positions have been measured for each sample. It can be seen in figure S11 that there is no clear trend in the copper content as a function of synthesis temperature. Owing to the way the nanocrystals are synthesized, with a hot spot in the middle and unreacted precursor at both sides, the washed samples do contain a mixture of nanocrystals and precursor. Hence, the shown copper content should be considered as averaging over the content of the whole reaction mixture in the capillary.



Figure S14. Copper content of washed Cu_{2-x}S samples as a function of synthesis temperature.

Additional TEM picture



Figure S15. TEM images revealing three different steps in the synthesis of nanocrystals at 320° C. The needle-like nanoclusters $Cu_n(SR)_m$, an intermediate particle size, and the final sized nanocrystal.

The nanoclusters display a needle-like morphology as they are anisotropic (very long *c*-axis compared to the *a*- and *b*-axes).

1H-NMR spectra



Peaks from ethyl acetate (4.12 ppm, q & 2.05 ppm, s), water (1.56 ppm, s) and a long hydrocarbon chain are observable in both the precursor and supernatant.⁷

Reaction kinetics

The growth of high digenite crystallites from β -chalcocite have also been modeled with a reactionorder model as described in detail by Lock *et al.*⁸

Zero-order reaction kinetics

$$\langle V_{1NP} \rangle = -k_1(t - t_0)$$

First order reaction kinetics

$$\langle V_{1NP} \rangle = \frac{1 - exp(-k_1(t - t_0))}{k_2}$$

Second order reaction kinetics

$$\langle V_{1NP} \rangle = k_1 \left(1 - \frac{1}{k_2(t - t_0) + 1} \right)$$

Figure S17-S19 show that the transition to high digenite displays an initial fast growth followed by subsequently slower growth for the nanocrystals synthesized at 280-320 °C, respectively. In the reaction-order model for the nanocrystals synthesized at 280 °C the two parts have been fitted separately, whereas at 300 °C and 320 °C the first- and second-order reaction models have been fitted over the whole time span. The zero-order kinetic model has only been fitted in the initial fast growing stage, as there is a linear dependency between average volume and time. At 300 °C and 320 °C both first- and second-order reaction kinetics provide the best model coincide with the period where both β -chalcocite and high digenite are present (see figure 2 in manuscript) and it is hence associated with a solid state phase transformation. Here, the growth rate is diffusion limited as it depends solely on the rate at which the rearrangement of sulfur and copper atoms within the phase transforming nanocrystals can take place; hence it is independent of the

concentration of copper thiolate nanoclusters in the reaction environment. After the average nanocrystal volume has reached approximately 2/3 of the final volume there is a large deviation from linearity and the kinetics changes to higher order, indicating that the copper precursor in the vicinity of the hot spot is depleted and the copper has been incorporated into the high digenite structure. Table S1 shows that there is a small difference between the first- and second-order fits. The first-order models produce asymptotic values that are smaller than the final average nanocrystal volume, whereas the second-order models result in values that are slightly larger. This indicates that the growth after the initial rearrangement diffusion limited growth, which corresponds to 2/3 of the total average nanocrystal volume, follows a second-order mechanism.



Figure S16. Left: Kinetics for the nanocrystals synthesized at 280 °C. It can be seen that the reaction might starts out as a zeroth order reaction, which increases to second order reaction. Right: The volume of the nanocrystals and scale factor plotted as a function of time in the same plot in order to show that Ostwald ripening is not happening during the reaction.



Figure S17. Left: Kinetics for the nanocrystals synthesised at 300 °C. It can be seen that the reaction might starts out as a zeroth order reaction, which increases to second order reaction. Right: The volume of the nanocrystals and scale factor plotted as a function of time in the same plot in order to show that Ostwald ripening is not happening during the reaction.



Figure S18. Left: Kinetics for transition from β -chalcocite to high digenite in the nanocrystals synthesized at 320 °C. For clarity only every third data point is shown in the main figures. Right: The volume of the nanocrystals and scale factor plotted as a function of time for nanocrystals. Ostwald ripening is not happening during the reaction.

Table S1. Asymptotic values for first- and second order kinetics and value for the last frame

Model/Temperature	280 °C	300 °C	320 °C
1. order	599 nm^3	574 nm^3	588 nm^3
2. order	619 nm^3	631 nm^3	629 nm^3
Last frame volume	606 nm^3	609 nm^3	615 nm^3

Illustration emphasizing the temperature profile



Figure S19. Representation of reaction setup with the sapphire capillary and the temperature profile over the length of the capillary emphasized. Details by Becker *et al.*⁹

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