Monitoring Nanocrystal Self-Assembly in Real Time Using In Situ Small-Angle X-ray Scattering

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Self-assembled nanocrystal superlattices have attracted large scientific attention due to their potential technological applications. However, the nucleation and growth mechanisms of superlattice assemblies remain largely unresolved due to experimental difficulties to monitor intermediate states. Here, the self-assembly of colloidal PbS nanocrystals is studied in real time by a combination of controlled solvent evaporation from the bulk solution and in situ small-angle X-ray scattering (SAXS) in transmission geometry. For the first time for the investigated system a hexagonal closed-packed (hcp) superlattice formed in a solvent vapor saturated atmosphere is observed during slow solvent evaporation from a colloidal suspension. The highly ordered hcp superlattice is followed by a transition into the final body-centered cubic (bcc) superlattice upon complete drying. Additionally, X-ray cross-correlation analysis (XCCA) of Bragg reflections is applied to access information on precursor structures in the assembly process, which is not evident from conventional SAXS analysis. The detailed

evolution of the crystal structure with time provides key results for understanding the assembly mechanism and the role of ligand–solvent interactions, which is important both for fundamental research and for fabrication of superlattices with desired properties.

1. Introduction

Nanocrystals (NCs) are known to be able to form periodically ordered structures by self-assembly from colloidal solutions upon solvent evaporation or destabilization.^[1,2] These highly ordered superlattices do not only possess the size- and shape-dependent properties of individual NCs but also yield novel properties resulting from collective interactions, such as electronic or plasmonic coupling of NC arrays, inter-NC energy transfer and charge carrier migration.^[3–5] However, due to the complex interplay of physical and chemical processes that govern the self-assembly it is difficult to predict and control the superstructure organization.^[2,6] Thus, nanoparticle assemblies involve a variety of interactions and driving forces between inorganic hard core, organic soft surface-coating ligands, and surrounding solvent molecules.^[2,7–9] As a consequence, a thorough understanding of a solvent-mediated assembly process is required to produce NC solids with programmable properties.

Here, we have chosen lead sulfide (PbS) nanocrystals as a model system for the investigation of the in situ self-assembly due to the possibility to produce monodisperse particles in a colloidal solution with a precisely controlled size. Additionally, the unique electronic properties of semiconductor PbS NCs with tunable band gap make them attractive for many potential technological applications, including solar cells, light-emitting diodes, transistors, photodetectors, etc.^[10–13] The structure and degree of order in NC superlattices depend on several factors, such as NC size and shape, ligand length, grafting density, ligand–solvent interactions, NC concentration, solvent evaporation rate (in case of evaporative assembly), and cell geometry or substrate where the assembly takes place. Thus, recent studies on lead chalcogenide NC assemblies revealed the formation of face-centered cubic (fcc) or body-

centered cubic (bcc) superstructures as well as lattice distorted face-centered tetragonal (fct) and body-centered tetragonal (bct) superlattices.^[14–18] However, their assembling mechanism remains largely unresolved mainly due to the challenge in measuring intermediate transitions between the initial colloidal state and the final superlattice state, especially in real time.

Recently, in situ scattering methods have emerged as a powerful characterization tool to study the nucleation and growth of nanoparticle superlattices.^[19–22] Small-angle X-ray scattering (SAXS) allows for monitoring the self-assembly dynamics with subsecond temporal resolution over large sample volumes under controlled conditions (e.g., controlled solvent vapor environment and temperature) and provides real-time information on long range order in the assembled structures. Often, the grazing-incidence small-angle X-ray scattering (GISAXS) technique is applied for in situ measurements, where a drop of nanocrystal suspension is placed on a substrate and evaporated in a controlled manner.^[16,20,23,24] However, at small incident angles of the X-ray beam GISAXS is able to probe only up to several monolayers and is thus limited to the surface regime. For bulk measurements transmission SAXS is required, even though its implementation can be more challenging experimentally. In this work, we investigate real-time PbS NC assembly using in situ SAXS in transmission geometry through the control of solvent evaporation in a bulk colloidal solution at a slow evaporation rate. Thus, time-resolved evolution of the assembly process from a colloidal suspension into highly ordered superstructures can be observed at different points of a specially designed three-dimensional sample cell, where the superlattice crystallization occurs along the cell windows upon movement of the evaporation front. Using this approach, we were able to monitor the detailed self-organization process by recording intermediate superlattice states, including the formation of critical nuclei and precursor clusters in the very beginning of the self-assembly as well as superlattice transformations at later stages of assembly caused by a removal of trapped solvent molecules upon complete drying. The

results presented here show that the superlattice in the swollen state, i.e., under saturated solvent vapor environment, exhibits a different crystal structure (hcp) as compared to the final dried state (bcc) and thus reveal the role of complex ligand–solvent interactions in the self-assembly process. In addition, cross-correlations of Bragg reflections provide access to structures beyond standard SAXS analysis intriguingly indicating the formation of bcc substructures already in the vapor saturated hcp superlattice. This method could be extended to study the real-time organization of a wide range of colloidal particles and other soft materials, such as polymers and proteins.

2. Results and Discussion

For the investigation of the self-assembly in real time we have synthesized nearly spherical oleic acid-capped PbS nanocrystals with an absorption peak at 1020 nm (**Figure 1a,b**). By fitting the SAXS curve from the colloidal solution using the Schulz–Flory distribution for polydisperse spheres, we obtained an average nanocrystal radius R of 1.96 nm with a polydispersity of 8 % (**Figure 1c**). This number represents the radius of the inorganic core, since the organic ligand shell consisting of low scattering light elements has very low contrast with the solvent and cannot be detected by SAXS. The size of the nanocrystals determined from absorbance is in good agreement with the diameter determined from solution SAXS (see Supporting Information, **Equation S1**). The PbS NCs are capped with oleic acid ligands with the grafting density σ of approximately $4.6 \text{ chains nm}^{-2}$ as estimated from thermogravimetric analysis (TGA) (for more details see Supporting Information, **Figure S1, Equation S2**). We studied the self-assembly of NC solutions in heptane and toluene to elucidate the possible difference between aliphatic and aromatic solvent molecules during the evaporative self-assembly since it was reported that different solvents result in different PbS superlattices.^[18] Heptane was chosen instead of commonly used hexane due to its higher boiling point, which is closer to the boiling point of toluene and thus enables a better comparison.

To observe the time-resolved assembly of PbS nanocrystals during solvent evaporation, we used a custom-built sample chamber allowing for in situ SAXS measurements in transmission mode.^[25] Before the sample was filled in, the chamber was evacuated and purged with helium twice to ensure oxygen- and water-free environment, although at this size PbS nanocrystals were reported to exhibit stability in air.^[26] Subsequently, pure solvent (heptane or toluene) was added to the chamber to raise the solvent partial pressure, after which the chamber was sealed. After that, approximately 21–24 μl of 10 mg ml^{-1} or 25 mg ml^{-1} PbS nanocrystal suspension in heptane or toluene was injected through a thin capillary from outside of the chamber into the sample cell with two silicon nitride windows (**Figure 2a**). The helium flow through the chamber was turned on to evaporate the solvent in a controlled manner over the course of 2–4 hours. Due to combined influence of convective flow and capillary forces, colloidal particles accumulated and self-organized at the edge of the meniscus thus forming highly ordered superlattice films along the cell windows (Figure 2a).

Two experimental protocols have been performed: (1) The silicon nitride windows were scanned so that 27 points were measured (3 horizontally at a distance of 0.5 mm and 9 vertically at a distance of 0.4 mm) and each point was recorded approximately every 2 minutes (**Figure 2b**); (2) Scattering patterns were collected every 3 seconds at a single point for the whole duration of a measurement.

First, we concentrate on protocol (1). The results of the real-time measurements of PbS NC suspension in heptane at the upper middle point of the membrane window (point A, Figure 2b) are shown in **Figure 2c,d**. It can be seen that in the beginning of the experiment the SAXS curves show the form factor of spherical nanocrystals in heptane. Upon controlled solvent evaporation, the PbS NC concentration in the close proximity to the silicon nitride windows increases very slowly with time due to movement of the liquid meniscus from the top to the bottom of the cell, thus inducing the crystallization of nanoparticles into

superlattices (Figure 2c,d). As PbS NCs start to form ordered assemblies along the silicon nitride windows upon movement of the evaporation front, Bragg peaks appear in the SAXS patterns. The detailed evolution of SAXS curves from the colloidal suspension state to the first formation of crystalline structure is shown in **Figure S2** (obtained using measurement protocol (2)).

From Figure 2c,d it can be seen that highly ordered superstructures are obtained during the evaporative self-assembly. The first assembled crystallographic structure (at approximately 22 min of elapsed time) shows peak position ratios of $q_n/q_1 = 1, \sqrt{3}, \sqrt{4}, \sqrt{7}, \sqrt{9}, \sqrt{12}$ (where q_n refers to the position of the n^{th} peak), which correspond to a hexagonal close-packed (hcp) lattice. Additionally, the observation of $\{100\}_{\text{hcp}}$, $\{002\}_{\text{hcp}}$, and $\{110\}_{\text{hcp}}$ reflections corresponding to different crystallographic directions in the unit cell confirms the formation of a three dimensional superstructure. During further drying, the Bragg peaks continuously shift to larger q -values indicating lattice contraction. At 80 min of elapsed time, the crystallographic structure undergoes a transformation into a bcc superlattice with the peak positions relative to the first peak of $q_n/q_1 = 1, \sqrt{2}, \sqrt{4}, \sqrt{6}, \sqrt{8}$. While the thermodynamically favored superlattice structures are fcc and hcp due to the highest packing of the spheres, the bcc structure is often observed in lead chalcogenide NC superlattices.^[14,18,23,27] It is believed that the bcc structure is formed due to anisotropic NC interactions caused by preferential ligand coverage on certain facets or because the bcc structure allows for more uniform distribution of ligands around the NC core.^[17,28,29] In our system, the core radius is $R = 1.96$ nm and the fully extended length of oleic acid (OA) is $L_{\text{OA}} = 2.29$ nm (for calculations of ligand length see Ref. [30]), so the ligand length to nanocrystal radius ratio is $L_{\text{OA}}/R = 1.17$. At this ratio, the repulsive interactions of the ligand shells become significant compared to the van der Waals attraction between inorganic cores and the minimization of the ligand packing frustration results in the bcc structure.^[29,31]

The same transformation of the superstructure from hcp to the bcc phase was observed for NC solution in toluene (**Figure S3**). Thus, in our experiment the assembled superstructures showed the same transitions with the same lattice constants for both aliphatic and aromatic solvents, i.e., heptane and toluene. The only difference was the evaporation time at the same helium flow rate, which was longer for toluene. Further in this paper we will focus on the results obtained in heptane.

Up to now, time-resolved SAXS data measured only at one point of the silicon nitride windows were presented. However, our sample cell design allows for monitoring of the real-time structures self-assembled along the silicon nitride membranes at different vertical positions simultaneously and, consequently, various stages of the crystallization process can be captured and compared. **Figure 3a** summarizes the temporal evolution of the Bragg peak positions for the measurement points A, B, C, D and E (Figure 2b). At point A the self-assembly begins at 20 min after start of solvent evaporation, when the liquid meniscus reaches the corresponding vertical position, and takes approximately 10 min longer at each subsequent point (B–E). Independent of the vertical position, the PbS NCs arrange themselves into ordered structures with hcp symmetry from the top to the bottom of the cell along the silicon nitride membranes. In the beginning of the self-assembly, all the points present the same Bragg peak positions, so the same supercrystalline hcp organization. The only difference between the points is the time that is necessary for the crystallization to start. Additionally, the hcp superlattices exhibit the same lattice constant upon crystallization independent of the vertical position in the cell. Continuously, during further drying the hcp superlattice undergoes contraction which is evident by the shift of Bragg peaks towards larger q -values. It should be noted that the observed hcp lattice is almost undistorted, so the theoretical values of the c -axis lattice constant calculated as $c_{\text{hcp}} = \sqrt{\frac{8}{3}} a_{\text{hcp}}$, where a_{hcp} was determined from the $\{100\}_{\text{hcp}}$ reflection, are very close to the experimental values calculated from the $\{002\}_{\text{hcp}}$

reflection as $c_{\text{hcp}} = 4\pi/q_{002}$ (see **Figure 3b** for point A). Furthermore, the superlattice contracts isotropically along the a - and c -axes during solvent evaporation. We model the hcp superlattice densification by an exponential decay with a time constant of 18–21 min for points A, B and C. Thus, for different points the lattice densification rate is constant and due to various assembly times the superlattice reaches different contraction states at each vertical position before the following transformation into the bcc phase (Figure 3a).

It is interesting that the transformation into the bcc crystal structure occurs at approximately 80 min of elapsed time for all vertical positions simultaneously (Figure 3a). This indicates that the residual solvent molecules that were present in the self-assembled superlattices evaporate fast when the chamber is not anymore saturated by solvent vapor, which leads to a rearrangement of the crystal structure. A similar result was reported by Bian et al., who observed by in situ GISAXS that under ambient conditions PbS and PbSe NCs formed superlattices with a body-centered tetragonal (bct) structure, which showed reversible transformation to an fcc structure after exposing the NC film to a subsaturated solvent vapor atmosphere.^[23] The authors attributed the 34 % increase in fcc unit cell volume relative to the initial bct NC superlattice to solvent swelling and capillary condensation of vapor in the interstitial spaces of the NC film. Weidman et al. also reported the transition of an fcc superlattice structure present at the early stages of evaporative self-assembly of PbS NCs in a real-time GISAXS experiment to final bcc through intermediate bct superlattice.^[16] The authors suggested that the fcc structure is initially favored due to the solvent molecules within the superlattice that filled the voids between neighboring NCs and the bcc structure became entropically favored as the solvent continued to evaporate. In our experiment, we observe an hcp to bcc superlattice transformation that, to the best of our knowledge, was not reported earlier for this system. The detailed transformation of the hcp into the bcc superlattice for the measurement where SAXS patterns were collected every 3 seconds (measurement protocol

(2)) is shown in **Figure S4**. The hcp-bcc transformation is known as the Burgers mechanism in the martensitic transformation and proceeds via the common orthorhombic subgroup.^[32] In the presence of solvent its molecules penetrate the ligand shell and swell the ligand corona, making the NC more spherical. The NCs behave as interacting spheres and, therefore, have an energetic preference for the higher lattice symmetry. Although calculations have shown small entropic preference of around $10^{-3} k_B T$ per sphere for fcc over hcp lattice,^[33] both packings are observed in NC assembly. It has been hypothesized that solvent flow through the interstitial sites of close-packed spheres may play a role in favoring the formation of specific colloidal crystal structures.^[34,35] In our study, we observe the formation of the hcp superlattice in a swollen state and not fcc. Whether this is an intrinsic property of the presented system being in the equilibrium state or caused by conditions of the bulk-sensitive SAXS experiment used for the evaporative assembly, where the solvent flow is different compared to previously reported surface-sensitive GISAXS experiments,^[16,23] needs to be further investigated. **Figure S5** shows the calculated peak positions for both hcp and fcc structures for points A and C (see Figure 2b) in order to rule out the coexistence of the fcc phase. It has to be noted that the two-dimensional scattering patterns of the assembled superlattices do not show the complete Debye-Scherrer rings, which is why some reflections that would be expected in a powder sample are not observed. Since the lattice densification rate in the hcp phase is similar for all vertical positions, we assume that in a vapor saturated atmosphere the slow evaporation of solvent molecules occurs both from the bulk solution, as long as it is still present in the cell, and from the wet NC solid assembled along the silicon nitride windows. Apparently, at the point when the whole bulk solution evaporates and the chamber is not any more solvent vapor saturated, the residual solvent molecules leave the superlattice voids in the self-assembled NC superstructures formed along the cell windows leading to the rearrangement of NC organization. Post-assembly scanning electron microscopy (SEM) reveals micrometer-sized

three-dimensional films formed on the silicon nitride membranes with a thickness of several hundred nanometers, which possess cracks as a result of contraction of superlattice dimensions upon solvent loss (**Figure S6**).

For point A, during the lattice densification we observe a decrease of hcp unit cell volume

($V_{\text{hcp}} = \frac{3\sqrt{3}a_{\text{hcp}}^2c_{\text{hcp}}}{2}$) of about 29.8 % (Figure 3b). After abrupt transformation to the bcc

lattice at 80 min of elapsed time, the bcc lattice constant a_{bcc} becomes 7.28 nm and slightly decreases to 7.05 nm during further measurements. The change of interparticle separation

between closest neighbor NCs with time for both hcp ($\delta_{\text{hcp}} = d_{002(\text{hcp})}\sqrt{\frac{3}{2}} - d_{\text{core}}$) and bcc

structures ($\delta_{\text{bcc}} = d_{110(\text{bcc})}\sqrt{\frac{3}{2}} - d_{\text{core}}$), where $d_{\text{core}} = 3.92$ nm is the NC diameter, is shown

in **Figure 3c**. The gray area in Figure 3c indicates the region, where hcp phase is still coexisting together with the predominant bcc phase. The time-resolved SAXS curves of this region are shown in Figure 2d (80.78 – 84.77 min). The formation of the bcc superlattice can be observed at 80.78 min of elapsed time evident by the main $\{110\}_{\text{bcc}}$ reflection at 1.22 nm^{-1} (Figure 2d). The hcp phase is coexisting until approximately 85 min of elapsed time.

It can be seen from Figure 3c that upon crystallization the gap between closest NCs in the hexagonal unit cell is 3.66 nm and continuously reduces to 2.72 nm during further drying and reaches 2.38 nm after rearrangement in the bcc lattice. The final interparticle spacing in the dry bcc superlattice of 2.18 nm is in a good agreement with the optimal packing model (OPM)^[36] that predicts the minimum distance between one-component nanoparticles in superlattices taking into account their softness parameter and ligand grafting density. Thus, the effective NC radius, which is the radius of the core plus the length of the constrained ligand, was calculated from the OPM for our system to be approximately 3.09 nm, whereas the experimentally obtained effective radius in the final bcc lattice is 3.05 nm (**Figure S7**). The details of this calculation can be found in the Supporting Information (**Equation S3**).

According to the OPM, the hydrocarbon-capped monodisperse spheres, like their hard-sphere counterparts, close pack at 74 % density in the fcc lattice^[36,37] and 68% density in the bcc lattice (for details see Supporting Information, **Equation S4**) for all softness values. Boles and Talapin confirmed the 74 % packing efficiency in the fcc structure by analyzing TEM images of nanoparticles with different softness values.^[37] The packing efficiency of soft nanoparticles in our assembled three-dimensional superlattices is shown in Figure 3c (for calculations see Supporting Information). In particular, it is interesting to observe the rapid increase in the packing efficiency in the bcc superlattice upon its formation from the hcp structure due to the solvent loss. Moreover, the evolution of the packing efficiency at the final stages of self-assembly towards 71 % is intriguingly indicating that the superlattices of NCs with soft dense corona exhibit higher packing fraction than hard spheres with 68 % of packing efficiency in the bcc lattice. This observation is consistent with mechanism proposed by Boles and Talapin that in a low-coordination lattice, soft NCs fill space more efficiently than hard NCs because the organic coating can deform from the spherical core/shell structure observed in the solvated state to a Voronoi polyhedron (Wigner–Seitz cell) in the solid state, yielding a higher packing fraction.^[37] Additionally, our results corroborate previous findings that soft NCs prefer to pack in low-coordination lattices since this geometry allows for the densest packing of ligands between inorganic cores.^[31,37]

In order to study the self-assembly process in more detail, we performed an X-ray cross-correlation analysis (XCCA) of the Bragg peaks observed for the 10 mg/ml PbS NC suspension in heptane following the measurement protocol (2). It has to be noted that this measurement was carried out at the vertical point located on the silicon nitride window between points A and B as depicted in Figure 2b. Due to small variations in the sample volume and the solvent amount needed for chamber saturation, the absolute time differs from that shown in Figure 3a. Cross-correlations of Bragg reflections have been recently

demonstrated as a valuable tool to access structural information beyond conventional pair-correlation^[38–40] as probed in the standard SAXS analysis. Here, Fourier coefficients of the correlation function $C(q, \Delta) = \frac{\langle I(q, \phi)I(q, \phi + \Delta) \rangle_\phi - \langle I(q, \phi) \rangle_\phi^2}{\langle I(q, \phi) \rangle_\phi^2}$ are calculated from the two-dimensional diffraction patterns. Therein, ϕ denotes the azimuth angle of the two-dimensional scattering pattern at fixed q , and Δ the correlation angle. To obtain qualitative measure of the symmetry of the diffraction pattern, Fourier coefficients of $C(q, \Delta)$ are typically studied. More details of the analysis procedures can be found in Ref. [41]. The fourth (c_4) and sixth (c_6) Fourier coefficients of C are shown in **Figure 4** as a function of scattering vector q and time t after start of solvent evaporation. As demonstrated in previous publications, these are sensitive to four- and sixfold symmetries of the diffraction pattern, respectively. For crystalline materials, correlations of Bragg reflections dominate^[38,39]. In particular, C is found to peak for Δ corresponding to angles between equivalent lattice planes. Three different time ranges can be identified: (I) For $t < 30$ min no significant correlation can be observed before self-assembly sets in. (II) At $t \approx 30$ min, strong correlations appear at the q -values that correspond to the $\{100\}_{\text{hcp}}$ and $\{110\}_{\text{hcp}}$ reflections. The correlations shift to larger q with time following the Bragg reflections as discussed above. It is important to note that both 4- and 6-fold symmetries are observed as expected for the corresponding hcp reflections.^[38] For instance, C calculated for $\{110\}_{\text{hcp}}$, shows peaks for $\Delta = 60^\circ$ and $\Delta = 90^\circ$,^[38] which results in high values of c_4 and c_6 . Likewise, for the $\{100\}_{\text{hcp}}$ reflections C shows multiple peaks at different Δ and consequently contributions to c_4 and c_6 . $\{111\}_{\text{fcc}}$ is expected at a similar q -value and would result in a strong c_6 and low c_4 values. Therefore, this XCCA results strongly support the formation of an hcp structure. (III) For $t > 96$ min, c_4 disappears while a broad contribution around $q \approx 1.23 \text{ nm}^{-1}$ appears in c_6 . This coincides with the transition to the bcc superlattice, where the correlations are observed at the $\{110\}_{\text{bcc}}$ reflection. Since

equivalent lattice planes of this reflection show an angle of multiples of 60° , only correlations with a 6-fold symmetry are expected.^[39] Thus, the absence of c_4 supports the formation of the bcc structure. Furthermore, the most intriguing feature can be observed in region (II) in c_6 . While the $\{100\}_{\text{hcp}}$ reflection sets in at $q \approx 0.94 \text{ nm}^{-1}$ and shifts to $q \approx 1.08 \text{ nm}^{-1}$ at $t = 96 \text{ min}$, a broad weak feature appears at slightly larger q . As this transfers continuously to the $\{110\}_{\text{bcc}}$ correlation in range (III) and is absent in c_4 , the formation of small amounts or precursors of bcc crystallites is suggested in range (II). In contrast, bcc reflections do not manifest in the SAXS curves shown in Figure 2c,d, apart from asymmetries of the $\{100\}_{\text{hcp}}$ reflections.

3. Conclusion

In this study, we use in situ SAXS in transmission mode to investigate the evaporative self-assembly of PbS nanoparticles in a bulk colloidal solution in real time. The main appealing observation is that, during the slow solvent evaporation, PbS nanocrystals first form an hcp superlattice in a swollen state along the cell windows before rearranging into a bcc one upon drying. The hcp superlattice that was not observed in previous studies for this system may be caused by the very slow evaporation of a small amount of the colloidal solution located in the confined environment between cell windows, which allows to achieve quasi-equilibrium states. Using transmission geometry, we are able to access any desired point in the relative time of the assembly process by scanning over different vertical positions on the silicon nitride windows at the same absolute elapsed time after start of evaporation. Our experimental data and quantitative analysis allow to access real-time information on precursor structures during the nucleation and growth of highly ordered superlattices and clearly reveal the role of ligand–solvent interactions during the assembly process. Transformation of the superstructure during the solvent-mediated crystallization from hcp to bcc and the corresponding values of lattice constants were found to be independent of the solvent used (heptane or toluene). The only difference was the evaporation time at the same helium flow rate, which was longer for

toluene. Thus, whereas this study provides direct evidence for the importance of solvent molecules during the crystallization process of colloidal nanoparticles, we do not observe any difference between aliphatic and aromatic solvent molecules. Additionally, our results showed a space filling fraction of soft particles in the bcc superlattice of 71 %, which confirms previous observations that soft nanocrystals can fill space more efficiently than hard ones. Intriguingly, the cross-correlation results demonstrate that the self-assembly is more complex than observed solely from SAXS analysis and that the precursors of the bcc superlattice are initiated already within the hcp phase of the swollen superstructure. This in situ method of characterization can be applied to study the self-organization of other types of soft materials, including various colloidal nanoparticles, micelles and polymers.

4. Experimental Section

4.1. Nanocrystal Synthesis

The PbS nanocrystals used for the self-assembly experiments in this study were prepared using the method described in Ref. [42]. The synthesis was performed using a standard Schlenk line technique. Lead acetate trihydrate (0.759 g, 99.999 % Sigma Aldrich), oleic acid (OA, 2.25 ml, 90 %, Sigma Aldrich) and octadecene (ODE, 20 ml, 90 % Sigma Aldrich) were heated in a three-neck round-bottom flask to 120 °C under reduced pressure ($10^{-1} - 10^{-2}$ mbar) for 1 h. Subsequently, the solution was purged with nitrogen and heated up to 130 °C, where an injection solution containing bis(trimethylsilyl)sulfide ((TMS)₂S, 0.210 ml, Sigma Aldrich) dissolved in ODE (10 ml) was rapidly injected with a G14 needle under constant stirring. The heating mantle was removed during the injection and further growth. After 3 min of growth, the reaction was quenched by a cold water bath and the solution was cooled down to room temperature. The colloidal suspension was mixed with hexane and the particles were precipitated by ethanol in a centrifuge at 7,000 rpm for 5 min. Afterwards, the supernatant was removed and the particles were redispersed in hexane. The purifying procedure was

repeated one more time and the washed particles were redispersed in anhydrous heptane or toluene (Sigma Aldrich). The nanoparticle suspensions were stored in a dry nitrogen glove box.

4.2. In Situ Small-Angle X-ray Scattering

The in situ SAXS measurements were performed at beamline ID02 of the European Synchrotron Radiation Facility (ESRF), Grenoble. The energy of the incident X-ray beam was set at 12.46 keV and the beam size was 100 μm (vertical) x 200 μm (horizontal). The SAXS data were recorded by a Rayonix MX-170HS charge-coupled device (CCD) area detector, positioned at 1.245 m from the sample, and were automatically corrected for transmission. Images were collected with exposure times ranging from 0.02 to 0.05 seconds. Two-dimensional SAXS data were radially integrated into one-dimensional scattering curves $I(q)$ presented as a function of scattering vector $q = \frac{4\pi}{\lambda} \sin(\frac{\theta}{2})$, where λ is the wavelength of the incident X-ray beam and θ is the scattering angle. Background scattering of the solvent and the experimental setup was subtracted from data. It has to be noted that no radiation damage of the sample was observed for the chosen exposure times.

The real-time self-assembly of PbS nanocrystals was monitored during controlled solvent evaporation in a custom-built chamber.^[25] Briefly, the solvent vapor chamber used for in situ SAXS measurements was equipped with two Kapton windows for the incident and scattered X-ray beam. The inner liquid sample cell consisted of two silicon nitride membranes at 0.5 mm separation. The size of X-ray transparent silicon nitride windows was 5 mm x 5 mm with a membrane thickness of 0.5 or 1 μm . The overall nanoparticle solution volume was in the range of 21–24 μl depending on the filling level. The typical helium flow rate was kept as low as 1–2 $\text{cm}^3 \text{min}^{-1}$ to ensure slow solvent evaporation. Thus, the evaporation rate was approximately 0.25–0.30 $\mu\text{l min}^{-1}$ for the solution in heptane and 0.20–0.25 $\mu\text{l min}^{-1}$ for toluene. During all measurements the cell temperature was kept constant at 25 $^{\circ}\text{C}$.

4.3. Nanoparticle Characterization

Transmission Electron Microscopy (TEM) measurements were performed using a JEOL JEM-1011 instrument operating at 100 kV. To prepare the sample, a drop of the diluted NC solution in hexane was deposited on a carbon-coated copper grid and dried in air.

UV-Vis-NIR absorbance spectra were recorded using a Varian Cary 5000 spectrophotometer. PbS NCs were dissolved in tetrachloroethylene for absorption measurements.

Thermogravimetric analysis (TGA) was carried out on a Netzsch TG 209 F1 Iris instrument. For the measurement, 7.7 mg of PbS NCs were used, obtained by drying of a concentrated NC solution in heptane. The sample was heated up to 600 °C at a rate of 10 °C min⁻¹ under nitrogen atmosphere.

Scanning electron microscopy (SEM) imaging was carried out at DESY Nanolab^[43] using a FEI Nova Nano SEM 450 instrument. Parts of silicon nitride membranes with assembled superlattices after in situ SAXS measurements were placed on top of conductive substrates.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figures

Figure 1. (a) Absorption spectrum of PbS nanocrystals in a colloidal solution. (b) TEM image of PbS nanoparticles. (c) SAXS curve of a 10 mg ml^{-1} colloidal suspension of PbS nanocrystals in heptane with the corresponding form factor fit.

Figure 2. (a) Illustration of the sample cell used for *in situ* SAXS measurements, where colloidal PbS nanocrystals self-organize into highly ordered superstructures along cell windows upon controlled solvent evaporation; (a) left: schematic representation of the beginning of the experiment (3 min of elapsed time); (a) right: intermediate stage of the self-assembly process, where part of the solvent has already evaporated (40 min of elapsed time in this particular measurement). (b) Scheme of the measurement points on the silicon nitride windows; points A, B, C, D and E shown in (b) are depicted as well in (a). (c) Time-resolved SAXS curves of 25 mg ml^{-1} PbS nanocrystals in heptane recorded every 2 min at point A. (d) 2D representation of selected SAXS curves from (c) for better visualization of the crystal structure evolution.

Figure 3. (a) Evolution of the positions of Bragg peaks from PbS nanocrystal superstructures during evaporative self-assembly for different vertical points on the silicon nitride windows (points A to E, see Figure 2b) monitored using in situ SAXS. The following data are shown for the measurement point A: (b) time dependence of lattice constants for both hcp and bcc superlattices; (c) interparticle separation and filling fraction of soft nanocrystals as a function of time during the observed crystal structure evolution. Transition of hcp into bcc superlattice occurs at approximately 80 min of elapsed time. The gray region in (c) depicts the coexistence of both hcp and bcc phases with the predominant bcc superlattice.

Figure 4. (a) The fourth c_4 and (b) the sixth c_6 Fourier coefficients of the cross-correlation function determined from different Bragg reflections during in situ self-assembly. Dashed lines and corresponding regions (I) colloidal suspension, (II) swollen hcp superlattice, and (III) dried bcc superlattice are displayed for eye guidance.

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Monitoring Nanocrystal Self-Assembly in Real Time Using In Situ Small-Angle X-ray Scattering

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Time-resolved self-assembly of colloidal PbS nanocrystals upon controlled solvent evaporation is studied using in situ synchrotron small-angle X-ray scattering (SAXS) and X-ray cross correlation analysis (XCCA). PbS nanocrystals first form highly ordered hexagonal closed-packed (hcp) superlattice in a solvent vapor saturated atmosphere, followed by a transition into the final body-centered cubic (bcc) superlattice upon complete evaporation of the solvent.

Supporting Information

Monitoring Nanocrystal Self-Assembly in Real Time Using In Situ Small-Angle X-ray Scattering

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Comparison of PbS NC diameter determined from solution SAXS and from absorbance spectra

By fitting the SAXS curve obtained from colloidal solution of PbS NCs using the Schulz-Flory distribution for spheres, the average nanocrystal diameter was determined to be 3.92 nm with a polydispersity of 8 % (Figure 1c).

For the calculation of nanoparticle size from absorbance we used the empirical equation reported by Maes et al.:^[1]

$$d = \alpha \cdot \lambda^3 + \beta \cdot \lambda^2 + \gamma \cdot \lambda + \delta \quad (\text{S1})$$

where d is the particle diameter in nm, λ is the position of the first excitonic transition in nm, $\alpha = 7.32 \cdot 10^{-10} \text{ nm}^{-2}$, $\beta = -1.68 \cdot 10^{-6} \text{ nm}^{-1}$, $\gamma = 5.60 \cdot 10^{-3}$, and $\delta = -9.57 \cdot 10^{-1} \text{ nm}$ are the empirical fitting parameters of SAXS-based sizing curves for PbS nanocrystals.

From this equation, for PbS nanocrystals synthesized in this study with the first excitonic transition at 1020 nm we obtain the diameter of 3.78 nm, which is in good agreement with the size obtained from solution SAXS.

Calculation of ligand grafting density from thermogravimetric analysis (TGA)

Figure S1. Thermogravimetric analysis (TGA) of oleic acid-capped 3.9 nm diameter PbS NCs.

The observed weight loss due to strongly bound oleic acid molecules is 30 %. The small step in the weight loss before 200 °C is attributed to the unbound surface ligands (see Ref. [2]).

The grafting density was calculated from TGA analysis using the following equation

$$\sigma_{\text{TGA}} = \frac{\frac{\text{wt \%}_{\text{shell}}}{\text{wt \%}_{\text{core}}} \rho_{\text{core}} \frac{4}{3} \pi R_{\text{core}}^3 \cdot N_A}{MW_{\text{OA}} \cdot 4 \pi R_{\text{core}}^2} \approx 4.6 \text{ chains nm}^{-2} \quad (\text{S2})$$

where $\text{wt \%}_{\text{shell}}$ is the relative mass of the organic shell corresponding to bound oleic acid ligands (30 %), $\text{wt \%}_{\text{core}}$ is the residual mass of pure inorganic core (68.7 %), $\rho_{\text{core}} = 7.6 \text{ g cm}^{-3}$ is the density of bulk lead sulfide, MW_{OA} is the molecular weight of oleic acid, $R_{\text{core}} = 1.96 \text{ nm}$ is the radius of inorganic core (determined from solution SAXS), and N_A is Avogadro's number.

Monitoring of the formation of nanocrystal superlattice from the colloidal solution

In order to observe the smallest transition steps during the crystallization process, the SAXS data were acquired at one point on the silicon nitride membrane every 3 seconds for the whole duration of evaporation (measurement protocol (2)). Chosen SAXS curves are represented in Figure S2. It is important to note that this measurement was carried out at the point located on the silicon nitride window between points A and B as depicted in Figure 2b. Due to small variations in the sample volume and the solvent amount needed for chamber saturation, the absolute time differs from that in the measurement shown in Figure 2c,d.

Figure S2. Formation of superlattice during *in situ* self-assembly of PbS nanocrystals from a colloidal solution (10 mg ml^{-1} in heptane) by real-time SAXS.

In the very beginning of the self-assembly, at 29.55 min of elapsed time for this measurement, a weak diffraction peak at scattering vector $q = 1.635 \text{ nm}^{-1}$ starts to appear, indicating formation of an ordered crystalline phase (Figure S2). Within 27 s after this peak appears, it shifts to the scattering vector $q = 1.64 \text{ nm}^{-1}$ and becomes more pronounced. Simultaneously, a broad peak at $q = 0.961 \text{ nm}^{-1}$ is formed and continues to grow. During further assembly at 31.70 min of elapsed time, the broad peak evolves into two peaks at $q = 0.963 \text{ nm}^{-1}$ and $q = 1.01 \text{ nm}^{-1}$ and the third peak appears at $q = 2.867 \text{ nm}^{-1}$. In the following 93 s, the sharp peak at $q = 0.963 \text{ nm}^{-1}$ continues to grow and shifts to $q = 0.965 \text{ nm}^{-1}$, whereas the broad shoulder $q = 1.015 \text{ nm}^{-1}$ slowly decreases. At the same time, the peak at $q = 1.646 \text{ nm}^{-1}$ shifts to $q = 1.673 \text{ nm}^{-1}$ and the peak at $q = 2.867 \text{ nm}^{-1}$ shifts to $q = 2.91 \text{ nm}^{-1}$. At 34.30 min of the elapsed time, one additional peak appears and altogether the four peaks are observed at $q = 0.974 \text{ nm}^{-1}$, $q = 1.691 \text{ nm}^{-1}$, $q = 1.951 \text{ nm}^{-1}$ and $q = 2.935 \text{ nm}^{-1}$. The peak positions show ratios of $q_n/q_1 = 1, \sqrt{3}, \sqrt{4}, \sqrt{9}$ (where q_n refers to the position of the n^{th} peak), which correspond to a hexagonal closed-packed (hcp) lattice.

Self-assembly of PbS nanocrystals from solution in toluene

The formation of PbS nanocrystal superlattices from toluene solutions underwent the same transitions as from heptane solutions (Figure S3). Thus, the superstructures with the same lattice symmetry and the same lattice constants were observed. The only difference was the evaporation time at the same helium flow rate, which was longer for toluene. Figure S3 has lower intensity of the SAXS signal than that in Figure 2c because of the lower NC concentration, i.e., 10 mg ml^{-1} instead of 25 mg ml^{-1} .

Figure S3. Time-resolved SAXS curves recorded during in situ self-assembly of PbS NCs from 10 mg ml^{-1} solution in toluene. This plot represents data obtained at point C (see Figure 2b) approximately every 2 min following measurement protocol (1).

Monitoring of the superlattice transformation from hcp to bcc structure upon solvent loss

Figure S4 represents further evolution of the superlattice during the hcp to bcc transformation as shown in Figure S2. In this measurement, the SAXS patterns were collected every 3 s at one point on the silicon nitride window (located between points A and B, see Figure 2b) according to the measurement protocol (2). The chosen patterns during the transition from hcp to bcc superlattice are shown in Figure S4. It can be seen that the superlattice transition occurs on a very fast time scale.

Figure S4. SAXS curves during the transformation of the superlattice from hcp to bcc structure.

Figure S5. Calculated hcp and fcc peak positions (hcp: red, solid line; fcc: blue, dashed line) for the superlattice observed at (a) point A at 24.03 min and (b) point C at 47.35 min of elapsed time. These SAXS curves correspond to the same measurement in Figures 2 and 3.

Scanning electron microscopy (SEM) imaging of superlattice films formed along the cell windows

Figure S6. Post-assembly SEM images of PbS nanocrystal films obtained on the silicon nitride membranes from 25 mg ml⁻¹ solution in heptane.

Calculation of the effective radius for close-packed soft spheres using the Optimal Packing Model (OPM)

According to the OPM the effective radius for soft particles in a close packing can be expressed as

$$R_{\text{eff}}^{\text{OPM}} = R \left(1 + 3 \cdot \sigma A_0 \frac{L}{R} \right)^{1/3} \approx 3.09 \text{ nm} \quad (\text{S3})$$

where $R = 1.96 \text{ nm}$ is the radius of inorganic core (determined from solution SAXS), $L = 2.29 \text{ nm}$ is the length of fully extended oleic acid molecule, $\sigma = 4.6 \text{ chains nm}^{-2}$ is the grafting density (determined from TGA), $A_0 = 0.182 \text{ nm}^2$ is the cross-sectional area of one ligand molecule.^[3]

The length of an oleic acid molecule was calculated using Ref. [4] as

$$L \approx \left((n - 1)r_0 \cos\left(\frac{\alpha}{2}\right) + r_1 \right) \cos(\omega) + r_{\text{dd}},$$

where $n = 18$ is the number of carbon atoms, $r_0 = 0.154 \text{ nm}$ is the C–C bond distance, $\alpha = 68^\circ$ is the C–C angle, $r_1 = 0.2 \text{ nm}$ is the radius for the end-carbon, $\omega = \frac{\pi}{3} - \frac{\alpha}{2} = 24.5^\circ$, $r_{\text{dd}} = 0.133 \text{ nm}$ is the double bond length.

The temporal evolution of the experimentally obtained effective radius, determined from the lattice constant in the bcc superlattice as $R_{\text{eff}} = a_{110(\text{bcc})} \cdot \frac{\sqrt{3}}{4}$, is shown in Figure S7.

Figure S7. Effective radius of soft densely packed PbS nanocrystals as a function of time in the bcc superlattice observed at point A (see Figure 2b).

Space filling fraction of soft particles in a bcc superlattice predicted by the Optimal Packing Model (OPM)

The theoretical space-filling efficiency for close-packed soft spheres in a bcc cell can be calculated as:

$$\rho_{ss} = \frac{N_{\text{NCS}}^{\text{bcc}} \cdot V_{\text{NC}}}{V_{\text{unit cell}}^{\text{bcc}}} = \frac{2 \cdot (V_{\text{core}} + V_{\text{ligands}})}{\frac{64\sqrt{3}}{9} \cdot R_{\text{eff}}^3}$$

Plugging the OPM solution for effective radius $R_{\text{eff}}^{\text{OPM}} = R \left(1 + 3 \cdot \sigma A_0 \frac{L}{R}\right)^{1/3}$ into the expression for soft-sphere packing efficiency ρ_{ss} yields:

$$\rho_{ss}^{\text{OPM}} = \frac{2 \cdot \left(\frac{4}{3}\pi R^3 + 4\pi R^2 \cdot \sigma A_0 L\right)}{\frac{64\sqrt{3}}{9} \left(R \left(1 + 3 \cdot \sigma A_0 \frac{L}{R}\right)^{1/3}\right)^3} = \frac{\frac{4}{3}\pi R^3 \cdot \left(1 + 3 \cdot \sigma A_0 \frac{L}{R}\right)}{\frac{32\sqrt{3}}{9} R^3 \cdot \left(1 + 3 \cdot \sigma A_0 \frac{L}{R}\right)} = \frac{\sqrt{3}\pi}{8} \approx 0.68 \quad (\text{S4})$$

Calculation of the packing fraction of soft particles in the hcp and bcc superlattices

For the hcp and bcc NC superlattices observed in our experiment, we calculated the packing efficiency of soft nanoparticles as follows.

The volume of one nanoparticle with a dense soft corona is given by:

$$V_{\text{NC}} = V_{\text{core}} + V_{\text{ligands}} = \frac{4}{3}\pi R^3 + 4\pi R^2 \sigma A_0 L,$$

where R is the core diameter ($R = 1.96$ nm, determined from solution SAXS), L is the fully extended ligand length ($L = 2.29$ nm for oleic acid), σ is the ligand grafting density ($\sigma = 4.6$ chains nm^{-2} , determined from TGA), A_0 is the cross-sectional area of a ligand molecule approximated as a cylinder ($A_0 = 0.182$ nm^2 for oleic acid). Thus, the volume of one soft nanocrystal was calculated to be $V_{\text{NC}} = 124.1$ nm^3 . The total volume of nanoparticles in each unit cell is calculated as $V_{\text{NCs}} = N_{\text{NCs}} V_{\text{NC}}$, where N_{NCs} is the number of nanoparticles in each cell. $N_{\text{NCs}} = 6$ for the hcp lattice and $N_{\text{NCs}} = 2$ for the bcc lattice. Thus, the volume of soft nanoparticles in each hcp unit cell is $V_{\text{NCs(hcp)}} = 744.6$ nm^3 and in each bcc unit cell is $V_{\text{NCs(bcc)}} = 248.2$ nm^3 .

The volume of the hcp unit cell is defined as $V_{\text{hcp}} = \frac{3\sqrt{3}a_{\text{hcp}}^2 c_{\text{hcp}}}{2}$ and the volume of the bcc cell as $V_{\text{bcc}} = \alpha_{\text{bcc}}^3$. Consequently, the nanoparticle space filling fraction can be calculated from the ratio $V_{\text{NCs(hcp)}}/V_{\text{hcp}}$ or $V_{\text{NCs(bcc)}}/V_{\text{bcc}}$ for hcp and bcc lattices, respectively.

For the final bcc unit cell, $\alpha_{\text{bcc}} = 7.05$ nm and $V_{\text{bcc}} = \alpha_{\text{bcc}}^3 = 349.8$ nm^3 . Thus, the space filling fraction of nanoparticles in the final bcc unit cell $V_{\text{NCs(bcc)}}/V_{\text{bcc}} = 248.2/349.8 \approx 71$ %.

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