A Shape-Induced Orientation Phase within 3D Nanocrystal Solids

Max Burian, Carina Karner, Maksym Yarema, Wolfgang Heiss, Heinz Amenitsch, Christoph Dellago, and Rainer T. Lechner*

When nanocrystals self assemble into ordered superstructures they form functional solids that may inherit the electronic properties of the single nanocrystals. To what extent these properties are enhanced depends on the positional and orientational order of the nanocrystals within the superstructure. Here, the formation of micrometer-sized free-standing supercrystals of faceted 20 nm Bi nanocrystals is investigated. The self-assembly process, induced by nonsolvent into solvent diffusion, is probed in situ by synchrotron X-ray scattering. The diffusion-gradient is identified as the critical parameter for controlling the supercrystal-structure as well as the alignment of the supercrystals with respect to the substrate. Monte Carlo simulations confirm the positional order of the nanocrystals within these superstructures and reveal a unique orientation phase: the nanocrystal shape, determined by the atomic Bi crystal structure, induces a total of 6 global orientations based on facet-to-facet alignment. This parallel alignment of facets is a prerequisite for optimized electronic and optical properties within designed nanocrystal solids.

Design of nanocrystal (NC) solid materials seeks to obtain superlattices that mimic the atomic structure of crystalline solids to enable new functionalities. In atomic systems, spatially anisotropic orbitals determine the crystalline lattice type. Similarly, in NC systems the building block anisotropy defines the order of the final solid: here, the NC shape, a property that can be altered by synthetic means, governs the final superlattice structure. Yet, in contrast to atomic systems, NC anisotropy induces not only positional, but also orientational order, such that either no orientation relation exists (plastic crystal), or a stable, fixed alignment of all NCs is found (crystal). This orientational relation, in particular parallel alignment of neighboring NC facets, was recently found instrumental to obtain atomically coherent connections between NCs, possibly enabling complete wave function delocalization within the NC solid. Optimization of such new NC materials hence requires prediction of the final positional and orientational order based only on the shape of the building blocks.

The realization of NC materials demands a controllable fabrication process such that the designed order can be produced. Generally, such highly ordered NC superstructures are achieved through solvent evaporation induced self-assembly on hard substrates, liquid–air interfaces or due to sedimentation. 2D substrate templating has been employed for building superlattice structures however, the planar nature of the process is limiting if 3D supercrystals are desired. Nonsolvent into solvent diffusion, a technique commonly used to grow single crystals of dissolved molecules, overcomes these limitations, and is also applicable to NC systems. Several works including ours have followed this strategy to form free-standing micrometer-sized supercrystals, yet parameters controlling this self-assembly process have so far only been addressed once. In particular, the precise effect of diffusion speed and gradient as well as the influence of heterogeneous nucleation remain unknown for controlling, e.g., the influence of the container walls on the final superlattice structure.

In this work, we pose two closely related questions: 1) how can the self-assembly process be controlled to yield highly ordered free-standing supercrystals and 2) what is the detailed...
NC positional and orientational order within the NC solid? We approach these questions by studying the self-assembly of 20 nm sized Bi NCs into highly ordered supercrystals by means of in situ transmission and small-angle X-ray scattering (SAXS) experiments as well as Monte Carlo (MC) simulations.

We synthesized monodisperse Bi NCs according to our previous work and stabilized them in toluene using oleic acid ligands.[24] To obtain information on the nanocrystal shape and size as well as on the stability of the colloidal system, we performed SAXS measurements of the initial dispersion. Fits of elliptical and spherical models to the integrated SAXS data (see SFigure S1a, Supporting Information) result in an approximate oblate shape with ±3.2% Gaussian size distribution, allowing the use of model free shape reconstruction with DAMMIN.[26,27] This computational technique uses artificial dummy atoms of 0.6 nm, which arrange into a 3D shape such that its scattering pattern best fits the experimental SAXS data. This method allows for full pattern refinement of the experimental data (see Figure 1a and Figure S2, Supporting Information).

The fitted 3D dummy atom model (see Figure 1b) displays two long and one short axis with diameters of 21.5 and 16.8 nm, respectively. The derived measurement accuracy is even better than one dummy atom and hence in the range of 1–2 monolayers of Bi surface atoms (see Figure S3, Supporting Information). Along the short direction, two pronounced facets are visible (black arrows in Figure 1b), which would not be captured by a simple ellipsoidal shape model. Similar surface facets are also visible in a high resolution transmission electron microscope (HR-TEM) image, but in this case the image only shows a 2D cut through the 3D shape of a single Bi NC (see Figure 1c and Figure S1b, Supporting Information).

This NC shape is linked to the rhombohedral crystal structure of Bi (space group R3m, \(a_{\text{Bi}} = 0.456\) nm, \(c_{\text{Bi}} = 1.186\) nm). The two most densely packed hexagonal \(\{001\}_{\text{Bi}}\) planes form the apparent short axis. Consequently, the high packing density along these facets causes enhanced surface passivation and therefore hindered growth during the NC synthesis.[28] Hence, faster NC growth is observed along the perpendicular hexagonal \(\{100\}_{\text{Bi}}\) directions resulting in longer in-plane dimensions. Closing the surface using only \(\{113\}_{\text{Bi}}\) facets results in an idealized crystal shape in agreement with the reconstructed dummy atom model, as shown in Figure 1d. To validate the proposed model, scattering curves of this ideal crystal shape and other feasible crystallographic models were calculated and compared to the experimental data (see Figure S4 in the Supporting Information). Best agreement (see Model 1) is found for the model presented above, which corresponds to a truncated hexagonal (thhp) geometry with an aspect ratio (long-axis/short-axis) of 1.3.

In order to study the self-assembly process in situ, we filled a quartz capillary with the stable toluene-nanocrystal solution and added the nonsolvent ethanol on top. We placed the sample into the incident X-ray beam and recorded series of 2D scattering images as well as the transmitted intensity at positions from 1 mm down to 7 mm below the initial interface (positions 1–7). A schematic representation of the experimental setup is shown in Figure 2a. The size of the X-ray beam is 75 \(\mu\)m × 75 \(\mu\)m. We probe the supercrystal growth either in the middle of the capillary (see Figure 2b,e) or the edge (see Figure 2c,f). In the middle we get the pure SAXS in-plane scattering signal, i.e., perpendicular to the transmitting X-ray beam, from the back and the front capillary wall. By scanning in 50 \(\mu\)m steps across, we can find the position just above the right (and left) edge of the capillary wall. Due to the curvature of the capillary we record grazing incidence SAXS (GISAXS) and transmission SAXS patterns, simultaneously. This allows now to probe additionally the supercrystal structure perpendicular to the substrate wall (see Figure 2c,f). With this setup we tracked the self-assembly process from dispersed NCs to the formation of supercrystals, as indicated by pronounced Bragg peaks in the scattering patterns (see Figure 2 and Figures S3 and S6 in the Supporting Information). In the following, we discuss the differences in the scattering images at positions 1 and 7 at the final state (see Figure 2b,c,e,f).

At position 1 we find a face centered cubic (fcc) lattice with hexagonally close packed (hcp) stacking faults. This lattice type can be deduced from distinct diffraction spots and pronounced streaks in the reciprocal space map (RSM) within the \(q_x = q_y\) plane measured near the capillary wall, where \(q_x\) is the scattering vector parallel to the capillary wall and \(q_y\) the vector perpendicular to it (see Figure 2c). The corresponding fcc lattice has a cubic lattice constant \(a_{\text{fcc}}\) of 33.7 nm, equal to a 2D hexagonal in-plane constant of \(a_{\text{hex}} = 23.8\) nm (see Figure S7 of the Supporting Information for indexing). The scattering
streaks only along $q_z$ indicate hcp stacking faults along the [111] fcc superlattice direction. \[29\] The unique [111] streak direction reveals that the vast majority of supercrystals are aligned with their in-plane hexagonal 2D planes parallel to the capillary wall, as illustrated in Figure 2d.

Parallel to the wall, in the $q_x - q_y$ in-plane RSM of position 1, we find strong and homogeneous diffraction rings of the hexagonal in-plane lattice and no out-of-plane scattering features (see Figure 2b). These ring patterns are common for small grained powder samples, indicating that in-plane the supercrystals are randomly oriented with respect to each other. Through the in-plane (110) reflection, which is least sensitive to lattice defects, \[29,30\] we estimate the in-plane supercrystal size at position 1 to be around 450 nm.

At position 7, close to the bottom of the capillary, we also find a fcc lattice with the same lattice constant, but, in contrast to position 1, with little to no hcp stacking faults. In the $q_x - q_y$ plane several single diffraction spots (see Figure 2e) indicate fewer and bigger supercrystals than above. In the $q_y - q_z$ plane (see Figure 2f) the strong scattering streaks have vanished, evidencing a better crystalline quality (absence of stacking faults). We observe several short and sharp streaks directly connected with single diffraction peaks pointing in various directions, especially visible in Figure 2e around $q_y = 0.5$ nm$^{-1}$. These streaks indicate that the global supercrystal-to-wall alignment from above has turned into a random orientation of individual large supercrystals as sketched in Figure 2g. Hence, the direction templating effect of the capillary surface on the supercrystal growth is diminished. Using peak width analysis, we estimate a mean supercrystal radius of at least 770 nm at position 7. The derived picture of large, individual supercrystals is supported by an additional ex situ study on free standing ≈10 µm sized supercrystals formed by 17 nm Bi NCs, \[24\] where optical microscopy images are combined with SAXS measurements at a laboratory source. The recorded 2D scattering patterns show again only pronounced single diffraction peaks (see Figure S17 in the Supporting Information).

Heterogenous nucleation at the wall has one advantage: While free moving supercrystals sediment to the bottom once they reach a critical size, NCs nucleating and growing at the...
wall remain at their initial position over a longer time period. Hence, we can correlate the local supercrystal properties with local solvent conditions that govern the self-assembly process. When and how fast the NCs reach a critical sedimentation size can be estimated through the relative NC, toluene and ethanol volume fractions (see sections “Non-solvent into solvent diffusion” and “In-situ X-ray transmission,” as well as Figures S8 and S9 of the Supporting Information for details).

We find that the critical nonsolvent concentration required for initiating self-assembly is between vol. 35% and vol. 42% for all measured positions 1, 4, 7 (see Figure S9 of the Supporting Information for details). The only difference between top and bottom solvent conditions is how fast the nonsolvent diffuses into the nanocrystal-solvent dispersion: once a critical concentration of 35 vol% is reached, the nonsolvent concentration changes by 47 vol% h⁻¹ at position 1, while at positions 4 and 7 the gradient value is only 5 and 4 vol% h⁻¹ (see Figure S9 of the Supporting Information). We hence argue that it is the concentration gradient that acts as driving force in the self-assembly process. While the steep concentration gradient at the top leads to templated crystallization of a defect rich, hcp/fcc stacking process. When and how fast the NCs reach a critical sedimentation size can be estimated through the relative NC, toluene and ethanol volume fractions (see sections “Non-solvent into solvent diffusion” and “In-situ X-ray transmission,” as well as Figures S8 and S9 of the Supporting Information for details).

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In all of the 30 performed simulations, we directly observe a phase transition at packing fractions of $\phi = 0.55$–0.59 from the isotropic liquid to a plastic crystal. This plastic crystal at $\phi = 0.6$ possesses fcc order with few hcp stacking faults (see Figure 3a), but, at visual inspection, appears to lack orientational ordering such that building blocks are allowed to rotate freely. To compare simulation with experiment, we calculated the radial structure factors from the building block positions in the simulation box and from the recorded scattering intensities (scattering intensity divided by form factor) for the same volume fraction. We find excellent agreement between them as shown in Figure 3b. Both structure factors show strong cubic fcc peaks with faint additional hcp peaks (visible as shoulders), indicating only minor stacking faults also for the experiment.

This overall agreement confirms that the experimentally used Bi NCs can in fact be approximated as hard colloids, to the extent that no influence of the soft ligands is visible. In the following we analyze the degree and nature of orientational order in the plastic crystalline phase of thhp Bi NCs. We start with defining the building block director as the vector connecting the two parallel [001]tr truncation planes (see short axis in Figure 1d and Figure S10 of the Supporting Information). Subsequently, the global orientation of each building block is described using two solid angles between the director and the simulation box vector, similar to a spherical coordinate system. Hence, for each configuration a solid angle distribution (SAD) can be calculated and gives an intuitive measure of the found orientational order, as shown in Figure 3c. At packing fractions above the liquid-fcc crystallization ($\phi = 0.60$) we find the SAD to be not perfectly isotropic (see Figure S11 of the Supporting Information for liquid reference SAD). Instead, we observe orientation clusters indicating that some building block orientations occur more frequently than others (see Figure 3c). As we expect this orientational anisotropy to become more prevalent at higher packing fractions, we increased the pressure stepwise until $\phi = 0.74$. As the packing fraction increases, 12 distinct orientation clusters emerge, and—as by shape symmetry—we find that these correspond to six unique global orientations. We highlighted this observation in Figure 4a by

![Figure 3. Comparison of MC simulation and experiment: a) Simulation snapshot at packing fraction $\phi = 0.60$. The lines indicate the hexagonal lattice symmetry. b) Comparison of the experimental structure factor $S(q)$ at $\phi = 0.60$ with the simulated structure factor calculated from positional data (a). Both yield the same fcc superlattice structure. c) Solid angle distribution (SAD) of the building block directors in configuration (a). The SAD shows emerging peaks, indicating that some solid angles occur more frequently than others.](image-url)
coloring building blocks according to their orientation (see Figure S12 of the Supporting Information for a larger version). Note that even if the specific SAD peak positions vary from simulation run to simulation run, the number of peaks always stays $2 \times 6$. The angular variance of these global orientations in the SAD is calculated to be less than $3^\circ$ for packing fractions of $\phi = 0.74$ (see Figure 4b,c).

We explain this initially unexpected occurrence of a discrete number of global orientations in a plastic crystal as follows: At higher packing fraction the free orientational movement of the positionally ordered NCs becomes increasingly hindered by the presence of their neighbors. To maintain equilibrium in this state, the system needs to maximize its entropy. Analogous to the prominent case of hard rods described in Onsager theory\cite{35} and as observed in other systems of anisotropic polyhedra,\cite{10,32,36–39} truncated hexapyramids achieve this by mutual alignment with their respective largest faces. In all possible building block pairs of Figure 4a, we find one of the three motives depicted in Figure 4d, that is: i) $\{001\}_a \parallel \{001\}_b$, ii) $\{001\}_a \parallel \{113\}_b$, or iii) $\{113\}_a \parallel \{113\}_b$.

Note that since it is possible for the building blocks to stay aligned while rotating around one axis, in principle more than $6$ global orientation peaks are possible. We argue that building block rotations are limited to this particular set of six global orientations by the underlying fcc lattice. Indeed, calculating the SAD of the building block directors with respect to the [111] fcc superlattice direction reveals that the set of global orientations is identical in all simulations with respect to the lattice [111] direction (see Figure 4c,e). The $2 \times 6$ global orientations now correspond to an invariant set of solid angle coordinates $\theta_{[111]}$ and $\varphi_{[111]}$ (see Figure 4c): 3 of the 6 global orientations are orthogonal to the [111] direction with solid angles $(90^\circ, 0^\circ)$, $(90^\circ, 60^\circ)$, and $(90^\circ, 120^\circ)$, while the other 3 are tilted $30^\circ$ degrees from the [111] direction with solid angles $(30^\circ, 30^\circ)$, $(30^\circ, 90^\circ)$, and $(30^\circ, 150^\circ)$ as illustrated in Figure 4e. A corresponding $180^\circ$ inversion results in the 12 orientation peaks shown in Figure 4b,c.

To test whether this orientation phase is stable, within a simulation box, we artificially aligned all thbp building blocks parallel to each other such that their directors are orthogonal to the [111] lattice direction. Upon equilibration for $3 \times 10^5$ MC sweeps at constant volume for packing fractions $0.6 < \phi < 0.71$ this uniform alignment always decomposes into the six stable global orientations within $10^5$ MC sweeps (see Figure S13 of the Supporting Information). Only at $\phi > 0.71$ the predefined parallel orientation alignment persists. From this we conclude that the found mixed $\{001\}_a$ or $\{113\}_b$ facet-to-facet alignment is a stable orientation phase at least for packing fractions $0.6 < \phi < 0.71$. At a packing fraction $\phi > 0.71$ a quantitative analysis over all building blocks yields that at least

Figure 4. Relationship between orientational and positional order: a) Simulation snapshot of 2016 individual building blocks inside the simulation box at packing fraction $\phi = 0.74$. The building blocks are colored according to their orientation as determined by the SAD in (b). The colors are: red, green, blue, yellow, orange, and ice-blue. White represents building blocks not detected by the coloring algorithm. b) Solid angle distribution (SAD) in angular space ($\theta_{\text{box}}$, $\varphi_{\text{box}}$) with respect to the simulation box. The colors correspond to (a) and denote the 6 distinct global orientations. c) SAD in angular space ($\theta_{[111]}$, $\varphi_{[111]}$) with respect to the [111] direction of the fcc superlattice. d) Sketch of all possible facet-to-facet alignments as found in (a). Note: full set of aligned pair orientations arises through axis rotation of the sketched motives. e) Sketch illustrating the $2 \times 6$ possible building block orientations with respect to the fcc [111] direction.
locally, building blocks prefer parallel over nonparallel facet-to-facet alignment as can be observed also visually in Figure 4a (see Figure S14 of the Supporting Information for quantitative details). This indicates that at packing fraction \( \phi > 0.71 \), a global parallel alignment might be more stable. Over a simulation time of \( 2 \times 10^6 \) MC sweeps we did however not observe any of the global orientations to grow at the cost of the others (see Figure S15 of the Supporting Information). The reason for this might be that at packing fractions \( \phi > 0.71 \) the orientational dynamics becomes glassy: For \( \phi > 0.71 \) the orientational mean squared displacement shows subdiffusive behavior typical of glassy systems whereas for \( \phi < 0.68 \) the orientational dynamics exhibits normal diffusion (see Figure S16 of the Supporting Information for MSD plots).

Relating our experimental and theoretical findings now allows us to answer the posed questions posed at the beginning. First, we identify the diffusion-gradient as key parameter to obtain template- and defect free 3D NC solids. Second, the particular position and orientation order within these highly ordered solids is closely related to the detailed NC shape: We find that local facet-to-facet alignment of neighboring NCs in fact results in a global orientation phase, as each NC can only align according to a limited number of orientations. Since the observed crystal facet formation is determined by the atomic Bi crystal structure we have established a partial epitaxial relation between the atomic lattice and the colloidal supercrystal structure via the NC shape. In a general context, we provide evidence that orientational and positional order within NC solids can be achieved without the help of surface ligands,[40–42] making the technique of nonsolvent into solvent diffusion an attractive option for the controlled fabrication of various NC solids. Further, the parallel alignment of atomically defined nanocrystal facets offers a new possibility for transferring atomic properties of the individual NCs to the entire supercrystal structure. Hence our findings offer a recipe to push nanocrystal solids toward their full electronic potential and inspire more detailed studies toward orientation phases within colloidal solids.

**Experimental Section**

**NC Synthesis:** The Bi NCs used in this work were synthesized according to the method described in ref. [24]. To dry the base solution, hexadecylamine (HDA, 20 g) inside a three-neck flask was heated to 100 °C under vacuum for 30 min. Simultaneously, a precursor solution was prepared in glovebox by combining bismuth(III)tris[bis(trimethylsilyl) amide], \( \text{Bi}([\text{N}(\text{SiMe}_3)_2]_3 \) (0.2 mmol, 0.14 g), and \( \text{Li}([\text{N}(\text{SiMe}_3)_2]_3 \) (1 mmol, 0.17 g) in 2 mL of toluene. After heating HDA up to 140 °C, the Bi precursor solution was injected and rapidly cooled to room-temperature after \( \sim 15 \) s. Solidification of HDA was inhibited by addition of 20 mL anhydrous toluene at 50 °C. The NCs were isolated by adding ethanol and subsequent centrifugation. Finally, the NCs were dispersed in tetrachloroethylene together with oleic acid and again precipitated using ethanol. This precipitate was dispersed in toluene such that the final solution was used for the experiments presented in this work.

**X-Ray Scattering:** The in situ small angle X-ray scattering experiments of the NC self-assembly were conducted at the Austrian SAXS beamline, at the Synchrotron Elettra, Trieste[43] using a photon energy of 8 keV. The beamline setup was adjusted to a sample to detector-distance of 1.810 m to result in an accessible \( q \)-range of 0.09–2.00 nm\(^{-1}\). All images were recorded using the Pilatus 100k detector (Dectris, Switzerland), whereas for each image an exposure time of 60 s was used. The calibration of the \( q \)-scale was based on diffraction patterns of silver-benenate (\( d \)-spacings of 5.838 nm). The radial averaging and the image calibration were conducted using the FIT2D software.[44] The liquid samples were filled into standard 1.5 mm quartz capillaries which were sealed using commercial epoxy glue. For each static measurement at least 4 images were taken to check for radiation damage in the sample. All presented data was corrected for fluctuations of the primary intensity transmission and the corresponding background has been subtracted from each solution scattering pattern. For the in situ experiments, the X-ray beam-size was 800 × 800 µm. For the horizontal capillary scan, the beam was reduced to 75 × 75 µm for better spatial resolution. Throughout the experiment, the temperature at the sample position was continuously monitored and remained between 25 and 28 °C.

**Monte Carlo Simulations:** A hard particle potential is used to describe the interactions between building blocks, such that the potential is either infinity or zero if they do or do not overlap, respectively. This enables the use of a collision detection scheme based on the separating axis theorem.[45] In total, 30 NPT-Monte-Carlo simulations, each consisting of 2016 building-blocks, were carried out. Every system used a different configuration and was initialized at a packing fraction of \( \phi = 0.05 \). After equilibration (\( 10^5 \) MC-sweeps), the pressure was increased until the visual onset of crystallization. During the crystallization process the pressure was kept constant.

**Supporting Information**

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

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**Conflicts of Interest**

The authors declare no conflicts of interest.

**Keywords**

colloidal nanocrystals, in situ SAXS, MC-simulation, self-assembly, supercrystal

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