Competing Interactions between Various Entropic Forces toward Assembly of Pt₃Ni Octahedra into a Body-Centered Cubic Superlattice

Ruipeng Li,† Jun Zhang,‡ Rui Tan,§ Frauke Gerdes,∇ Zhiping Luo,∥ Hongwu Xu,⊥ Jennifer A. Hollingsworth,#, Christian Klinke,∇ Ou Chen,§ and Zhongwu Wang*†

†Cornell High Energy Synchrotron Source, Cornell University, Ithaca, New York 14850, United States
‡State Key Laboratory of Heavy Oil Processing, College of Chemical Engineering, China University of Petroleum, Qingdao 266580, China
§Department of Chemistry, Brown University, Providence, Rhode Island 02912, United States
∥Department of Chemistry and Physics, Fayetteville State University, Fayetteville, North Carolina 28301, United States
⊥Earth and Environmental Sciences Division and #Materials Physics and Applications Division: Center for Integrated Nanotechnology, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States
∇Institute of Physical Chemistry, University of Hamburg, 20146 Hamburg, Germany

Supporting Information

ABSTRACT: Anisotropic nanocrystal assembled supercrystals with open superlattices (SLs) manifest novel and unique properties, but poor understanding of the nucleation/growth mechanisms limits their design and fabrication for practical applications. Using highly anisotropic Pt₃Ni octahedral nanocrystals, we have grown large single supercrystals with an open body-centered cubic (bcc) superlattice that has a low filling factor of 26.8%. Synchrotron-based X-ray structural reconstruction fully revealed the coherence of translational and orientational orderings and determined that the constituent octahedra arrange themselves with the vertex-to-vertex and face-to-face configurations along the SL[100] and SL[111] directions, respectively. The large face-to-face separation and flexible vertex-to-vertex elastic contact provided the rattle space and supporting axis for local rotations of Pt₃Ni octahedra within the bcc superlattice. Development of orientational disordering along with robust preservation of translational ordering during the heating process of a supercrystal in the oleic acid wetting environment confirmed the dominance of rotational entropy of hard octahedra in the formation of the open bcc superlattice. Ultimate achievement of dynamic equilibrium between the vertex-oriented elastic repulsions and the face-oriented attractions of surface-coating ligands governs the structural and mechanical stability of the supercrystal. This discovery provides significant insights into the design and control of geometrical shapes for the fabrication of highly anisotropic nanocrystals into desired open superlattices with tailored optical and electronic properties.

KEYWORDS: Pt₃Ni Octahedron, nanocrystal assembly, body-centered cubic, open superlattice, rotational and translational entropies, repulsive and attractive forces

Octahedron, one of the five platonic shapes, is composed of six vertices, 12 edges and eight equilateral triangle faces. For such anisotropically and geometrically shaped particles, burgeoning interests have been developing theoretically and experimentally to perform a series of in-depth examinations on how octahedra interact with surrounding environments and spontaneously self-assemble into the random or periodically ordered superlattices (SLs). As recognized long time ago, octahedra optimize their unique geometrical shape and pack into the densest superlattice known so far, the Minkowski superlattice,¹ in which the space filling factor (i.e., packing density) is as large as \( \varphi \approx 18/19 \). Using Monte Carlo simulations, Glotzer and her colleagues²–⁴ revealed a rhombohedral superlattice, which has a reduced space filling factor of \( \varphi \approx 0.605 \). These pioneering studies suggest that the spontaneous assemblies of octahedra into dense superlattices are largely driven by the directional entropic forces, which arise from a shape-induced increase of the excluded volume through parallel face-to-face alignment of the octahedra. Additional computations performed by Torquato and colleagues⁵–⁷

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revealed the primary assembly of a body-centered cubic (bcc) superlattice, which represents for an open superlattice and has a very low space filling factor of \( \varphi \approx 0.33 \). Recently, a two-dimensional (2D) Kagome superlattice was observed in a colloidal assembly of chemically shaped particles.\(^8,9\) Investigations of the nucleation and growth mechanisms suggest the governing role of the rotational entropic forces toward the formation of such an open superlattice.\(^9,9\) The geometrically shaped octahedra can be alternatively treated as the chemically patched anisotropic particles used in the above-described 2D assembly. Therefore, the rotational entropic forces could play an analogous role, leading to the large three-dimensional (3D) assembly of octahedra into open superlattices with reduced space filling factors.

Recent advances in wet synthetic chemistry have enabled the fabrication of highly monodispersive octahedral colloidal particles with excellent control of particle size over a broad range of length scales.\(^10\)–\(^13\) Yang and his colleagues made the large silver octahedra with dimensions in the submicron range.\(^10,13\) Using a gravity-induced sedimentation approach, they grew the millimeter-sized supercrystals, which possess a Minkowski superlattice.\(^10\) At the early stage of nucleation and growth, several hexagonal monolayers, which have a simple hexagonal superlattice (\( \varphi \approx 8/9 \)), nucleated, and then these monolayers quickly grew into a Minkowski superlattice.\(^10\) In parallel, Fang and his colleagues fabricated the small octahedra of metallic alloys with an edge length of \( \sim 10 \) nm.\(^11,12\) Through the control of solvent evaporation, they discovered the exclusive assemblies with the bcc superlattice, which has a low space filling factor of \( \varphi \approx 0.33 \). Besides investigations of 3D assemblies of octahedra made of variable compositions,\(^14\)–\(^20\) the three 2D superlattices, which led to the space filling factors of \( \varphi \approx 1/3, 2/3, \) and \( 8/9, \) were discovered in an air–liquid interface assembly.\(^21\)

Both experiments and simulations have revealed the shape-directed structural diversity of octahedral colloid assemblies.\(^22\)–\(^24\) It is well accepted that spherical particles favor the assembly of either a face-centered cubic (fcc) or a hexagonal close-packed (hcp) superlattice,\(^25\) both of which have a space filling factor of \( \varphi = 0.74 \). However, upon development of a geometrical shape with increased crystallographic anisotropy, octahedra prefer the parallel alignment of their triangular surface faces to increase the excluded volume and thus to maximize the directional entropy.\(^24,26\) Once the molecular decorations are chemically made on the octahedral surface faces, dramatic increase of excluded areas or volumes between neighboring octahedra enhances the molecular interactions. Upon size reduction of the inorganic octahedral cores, the relatively increased amounts of molecular decorations behave much like the anisotropically chemical patches and facilitate a local dense packing that contains a large degree of disorder. In the meantime, the resultant increase of the rattle space inside an assembly allows for easy rotation of the hard octahedra and local vibration of the soft ligands. In addition to the contributions of the rotational entropy from hard inorganic octahedra and the conformational entropy from surface-coating soft organic molecules, the directional entropy appears to enhance the interfacet coupling and the orientational ordering of octahedra, whereas the translational entropy continues to play an important role and increase the number of octahedral occupations per unit volume. Extensive investigations have documented the diversity and complexity of driving forces, which include not only the relatively simple colloidal assemblies with single components\(^27\)–\(^7,10\)–\(^12,13,22\)–\(^25\) but also the more complex assemblies with binary and ternary systems.\(^27\)–\(^31\)

Despite experimental and theoretical investigations, very little is known about how various driving forces interact with each other in either a coupling or a competing way, which drives the assembly of octahedra into an unanticipated open superlattice through a rational minimization of the total free energy. Of particular interest is to understand how a thermodynamic or/and kinetic balance is achieved between the shape-dependent orientational and rotational entropies and the traditionally known translational and configurational entropies in order to form an open-packing low-density superlattice rather than a close-packing high-density superlattice.

Current developments in the large supercrystal growth and synchrotron-based X-ray single supercrystallography at CHESS provide a unique base for the precise structural reconstruction of nanocrystal (NC) assemblies at unprecedented levels from atomic through nanometric to mesoscopic scale.\(^32\)–\(^35\) Aimed at in-depth understanding of the open superlattice formation through intricate interactions between various driving forces, we have continued to make efforts in the synthesis of highly anisotropic Pt\(_3\)Ni octahedra with subsequent design and conduction of unique experiments to achieve the above goals, particularly determining the shape-dependent effects. Our achievements include (1) controlled growth of the large single supercrystals of Pt\(_3\)Ni octahedra, (2) full reconstruction of the supercrystal structure with coherence of translational and orientational orderings, and (3) synchrotron-based in situ small and wide-angle X-ray scattering (SAXS/WAXS) measurements of the supercrystals in real environments of drying, solvent wetting, heating, and pressurizing. The structural reconstruction of the assembled bcc superlattice and the systematic analysis of in situ SAXS/WAXS data sets provide a lucid view of how Pt\(_3\)Ni octahedra coordinate in terms of both geometrical and chemical shapes and interact with surrounding environments and thus undertake effective optimization of translational, directional, and rotational entropies to form the novel open superlattice with a low packing density.

**Experimental Section. Synthesis of Pt\(_3\)Ni Octahedra.** Octahedral Pt\(_3\)Ni NCs were synthesized using a previously developed protocol.\(^11\) Briefly, a mixture of 0.04 g of Pt(Ac)_2, 0.02 g of NiCl\(_2\)·6H\(_2\)O, 18.0 mL of oleylamine, and 2.0 mL of oleic acid (OA) were loaded into a three-neck flask and heated to 150 °C under vacuum. After 0.1 g of tungsten hexacarbonyl [W(CO)\(_6\)] was added to the solution under a nitrogen flow, the temperature was raised to 190 °C, which was kept under mild stirring for 60 min. Subsequently, the reaction solution was chilled using water cooling. By adding 20 mL of ethanol to the solution, the products were isolated via centrifugation. The resultant Pt\(_3\)Ni octahedra were dispersed into toluene to form a colloidal suspension for storage.

**Assembly of Large Single Supercrystals.** A 300 μL toluene-dispersed octahedral Pt\(_3\)Ni NC solution with a particle concentration of 10 mg/mL was transferred into a small glass vial. The vial was sealed and stabilized to maintain a slow evaporation rate for the NC assembly. The entire assembly process took about 3 weeks, and the formed supercrystals were preserved in the vial for additional investigations.

**Electron Microscopy Characterization.** Toluene-dispersed suspensions of Pt\(_3\)Ni octahedra were drop casted onto a carbon coated 200 mesh copper grid for transmission electron microscopy (TEM) characterization. TEM images were taken using a JEOL 2100F microscope operated at 200 kV. Another small portion of assembled supercrystals were transferred to a
Si wafer for scanning electron microscopic (SEM) characterization. SEM images with variable magnifications were recorded using a LEO-1530 microscope operated at 10 kV.

**Synchrotron-Based X-ray Scattering Measurements.** Both SAXS and WAXS images were collected from supercrystals at the B1 station of CHESS, Cornell University. Using a double circular pinhole aligned tube, monochromatic X-rays at a collimated energy of 25.514 keV were reduced to a small beam with a diameter of 100 μm. Ag behenate and CeO2 powders were used to calibrate the sample-to-detector distances and detector seating parameters for SAXS and WAXS analyses, respectively. One supercrystal grain was loaded onto a MiTeGen mesh grid, which was subsequently mounted on the two-circle diffractometer. Upon X-ray illumination, both SAXS and WAXS images were collected from the same volume of the supercrystal with an angular rotation step of 1°.

**In Situ Experiments of Supercrystals under Drying, Wetting, Heating, and Pressurizing Environments.** A small hole was made on the stainless gasket and served as the sample chamber. One supercrystal grain with or without oleic acid (OA) liquid (wetting/drying) was loaded into the gasket hole with subsequent sealing by Kapton tape for simultaneous collections of both SAXS and WAXS images. After sealing both sides of the gasket, the assembly was moved into a heating cell mounted on the sample stage at the B1 station. Upon increase of temperature from room temperature to 150 °C, both SAXS and WAXS images were simultaneously collected from the same volume of the supercrystal. A diamond anvil cell (DAC) was used for in situ SAXS and WAXS experiments at high pressure. One stainless gasket was preindented from 250 μm down to ~100 μm, and a 200 μm diameter hole was drilled to serve as the sample chamber. The supercrystal samples were loaded into the gasket hole, and then several ruby chips were distributed randomly on the top of the samples as the pressure marker. The pressure was monitored using a laser-excited ruby fluorescence technique. After closure of the gasket hole by DAC, in situ SAXS and WAXS measurements were conducted upon compression of the samples from atmospheric pressure to 6 GPa and then decompression back to the atmospheric pressure.

**Results and Discussions.** Careful control of the solvent evaporation allowed the growth of large 3D single supercrystals. Such large and high-quality supercrystals enabled subsequent conduction of an unprecedented structural study to determine not only the overall superlattice structure but also the crystallographic orientation and relative positioning of constituent NC building blocks. The as-synthesized Pt3Ni NCs display an octahedral morphology and have an edge length of 9.26 nm, on average (Figures 1a,b and S1−4). During the evaporation of octahedra suspensions, the mechanism of self-focusing for the octahedra with similar sizes and sharp shape was operating, which enabled simultaneous assembly of Pt3Ni octahedra into order (Inset Figure 1a). Optical microscopic characterization shows that the supercrystals have a grain size of >60 μm (Figures 1c). One typical high-resolution SEM image (Figures 1d) reveals the single crystal nature of individual supercrystals. The supercrystals possess a bcc superstructure (1m3m) with a superlattice cell constant of dSL = 14.13 nm (Figure 1e), whereas the constituent octahedra crystallize in a fcc structure (Fm3m) with an atomic cell constant of aPt3Ni = 3.852 Å (Figure 1f).

Use of the synchrotron-based X-ray single supercrystallography allowed the reconstruction of the structural details of Pt3Ni supercrystal with the full coherence of translational and orientational orderings (Figures 2, S5−7, and Video S1). Single supercrystal SAXS images shown in Figure 2 (left) represent the three typical superlattice orientations of SL[111], SL[110], and SL[100], where the corresponding WAXS images (Figure 2, right) reveal the atomic crystallographic orientations of Pt3Ni[111], Pt3Ni[110], and Pt3Ni[100] of Pt3Ni octahedron. Such structural correlations indicate that the constituent building blocks of octahedra arrange themselves in a bcc superlattice with vertex-to-vertex and face-to-face configurations along SL[100] and SL[111] (Figure 2, middle), respectively.

The space filling factor of Pt3Ni octahedra in the bcc superlattice is calculated to be 26.8%, which is somewhat smaller than 33.4% estimated based on a perfect hard tip-to-tip touch of octahedra (Table S2). The inter-NC distances of octahedra along the SL[100] and SL[111] directions are determined to be 14.09 and 12.20 nm, respectively, giving rise to the corresponding vertex-to-vertex and face-to-face separations of 1.0 and 4.64 nm (Figure 3; Table S2). These two separations are correspondingly much shorter and somewhat longer than the total length of 4 nm for the two extended OA molecules. Therefore, the intercalation of OA molecules may occur in the vertex-to-vertex separation space. In contrast, the face-to-face separation is about 0.64 nm larger than the two OA molecules. Therefore, the intercalation of OA molecules may occur in the vertex-to-vertex separation space.
(i.e., 13.1 nm), the rotating freedom is apparently reduced in nonaxial directions of the superlattice. If solvents could penetrate into or partially remain inside the supercrystal during the nucleation and growth process, an expected superlattice expansion, as compared with a corresponding dry supercrystal, provides extra room and freedom for the local rotation of Pt$_3$Ni octahedra (see later discussion). Accordingly, a rotational entropic term is developed as an additional driving force to guide the formation of the bcc superlattice.

In our previous studies on the molecular crystals of OA and lead oleate [Pb(Ac)$_2$], we observed the interlamellar distances of 4.0 and 4.65 nm, respectively, which represent a compromise of intermolecular interactions between steric repulsions and van der Waals (vdW) attractions. In the Pt$_3$Ni octahedral assembly, the face-to-face separation along SL[111] is larger than the interlamellar distances observed in the two OA-dominant molecular crystals. In good solvent environments such as toluene used in this work, the surface coating OA molecules interact with solvents and develop purely the steric repulsions between NCs, which gradually enhance along with slow solvent evaporation. Upon drying of the supercrystal, the two monolayers of OA molecules between the parallel flat faces of two neighboring octahedra behave much like lamellar molecules arranged in the OA and Pb(Ac)$_2$ solids to approach an intermolecular equilibrium state for structural stability. The intermolecular distance for the ultimately achieved equilibrium should fall in a similar range of 4.0–4.65 nm. Instead of the strong steric repulsions between surface-coating molecules in solvent environments, the ultimately dried supercrystal gives rise to strong intermolecular vdW attractions, which drive Pt$_3$Ni octahedra to approach the equilibrium distance, such as the upper limit of 4.65 nm. On the other hand, the vertex-to-vertex separation of 1.0 nm falls much shorter than the two extended OA lengths of 4.0 nm, so the OA molecules from two oppositely vertex-localized surface faces have a large ratio of inter-OA overlapping. Taking a close look at the packing configurations of OA molecules inside the superlattice shown in Figure 3, we notice that the OA molecules between the two SL[100]-aligned vertices can be contacted only through their hydrocarbon tails (Figure S9). Upon projection of the face-standing OAs along the vertex direction (see SI), the estimated length of 2.31 nm is dramatically larger than the vertex-to-vertex separation of 1.0 nm. Apparently, the vertex-localized stiff OA molecules are highly strained, giving rise to strong elastic repulsions through the OA ligands located at the tips of the vertices. Such highly strained ligands in the vertices (illustrated in Figures 3d,e) also result in an apparent morphological modification of the octahedron (Figure S10). For each octahedron in the bcc superlattice, the eight triangle surface faces develop via vdW attractions, whereas the six opposite types of intermolecular interaction forces take action over a long-range of the supercrystal to reach an overall equilibrium state, which accordingly maintains the structural and mechanical stability of the supercrystal.

Landau theory predicts that all atomic crystals eventually transform into a bcc lattice. Analogously, this prediction may be used to understand the superlattice change of NC assemblies. Previous investigation on 3.5 nm PbS NC assemblies revealed a fcc-to-bcc superlattice transformation upon long-term air aging and heating of supercrystals. In combination with a recent report that PbS NCs with size below 4.0 nm adopt an octahedral shape, it is reasonable to assume that the bcc

Figure 2. Structural reconstruction of the NC translation and atomic orientation in a bcc supercrystal made of Pt$_3$Ni octahedra. (Left) SAXS patterns of the supercrystal along the SL[111], SL[100], and SL[110] directions; (right) WAXS images collected along the corresponding superlattice orientations; and (middle) reconstructed structural projections along the three directions based on the collected SAXS and WAXS images (left and right).

Figure 3. (a) Random rotating model of Pt$_3$Ni octahedra in the bcc superlattice and illustrations of (b) OA and contacting configurations of the surface-coating OA molecules in (c) the face-to-face and (d,e) vertex-to-vertex configurations. The OA ligands in solid color in (d,e) display the direct contacts of OAs through their tips.

lengths of 4 nm, excluding the possibility of OA intercalation in the face-to-face orientation (Figure 3c). If OA molecules are flexibly connected between two neighboring vertices, octahedra are certainly able to rotate locally without much resistance along any of the three superlattice axes (Figure 3a). Because the observed inter-NC distance of 12.2 nm is somewhat smaller than the diameter of the circumscribed sphere of an octahedron...
superlattice represents a stable and favorable supercrystal phase in the assembly of octahedral NCs.

To verify the above argument and our hypothesis about the local rotation of octahedra in the bcc superlattice and also to estimate the magnitude of resultant rotational entropic contribution, in situ SAXS and WAXS measurements were performed on a Pt_{3}Ni NC supercrystal in the real environments of OA-wetting and heating (Figure 4). Upon soaking of the superlattice in an OA liquid, we observed slight azimuthal broadening of the WAXS spots and apparent superlattice expansion but no noticeable change in the SAXS spotty feature. The OA wetting caused an increase in the SL(110) d-spacing of the supercrystal from 9.96 to 10.59 nm, equivalent to a volumetric expansion of 17.3%. These observations indicate that the OA wetting did not change the translational positioning of octahedra in the superlattice but provided extra room to facilitate their local rotation. As a direct indication for the random particle distribution by powder-like WAXS rings, the slight azimuthal broadening of WAXS spots undoubtedly revealed the appearance of local rotation of octahedra and the development of slight orientational disordering. These results allow us to claim the imminent play of rotational entropy in the nucleation and growth process of the bcc supercrystals.

In situ SAXS and WAXS measurements provided similar results upon heating the supercrystal at relatively low temperatures (Figure S8). At temperatures above 120 °C, the supercrystal continuously maintained its bcc superlattice as shown in the SAXS pattern with good preservation of its spotty textures, but the original WAXS spots quickly increased their azimuthal widths from ~12° to 30° at the peak temperature of 150 °C and subsequently retained to the annealing conditions (Figure 4). Such dramatic variations of X-ray scattering features imply robust preservation of the translational positioning but primary loss of the orientational ordering of the constituent octahedra in the superlattice. In linkage with the heating-induced superlattice contraction and associated development of the orientational disordering, the thermal treatment appears to facilitate the increase of the magnitudes of not only the rotational entropy but also the configurational entropy. On the basis of the temperature-dependent structural changes, the magnitude of the rotational entropic contribution can be reasonably estimated to be in the order of ~0.5kT. Differently, the supercrystal without experiencing the OA wetting did not display an apparent temperature-induced change of either the translational or the orientational ordering (Figure 4, left).

To better illustrate the temperature-induced structural changes of the supercrystals and thus to understand the underlying mechanism of the octahedral rotation in the superlattice, we plotted the variations of the SL(110) d-spacing and the azimuthal width of the Pt_{3}Ni (111) spot as a function of temperature in Figure 5. For the supercrystal without OA-wetting, the SL(110) d-spacing displayed a temperature-dependent linear expansion upon increasing temperature, and interestingly this expansion trend continued to maintain upon decrease of temperature. Surprisingly, the SL(110) d-spacings during cooling are similar to those of the OA-wetted supercrystal. In the whole cycle of thermal treatment from initial heating to subsequent cooling, the Pt_{3}Ni(111) WAXS spot remained constant in azimuthal width, indicative of the orientational ordering stability of the octahedra in the supercrystal. In contrast, for the supercrystal with OA-wetting its SL(110) d-spacing displayed a temperature-induced negative expansion, and a decrease in temperature caused its complete bouncing back along the heating-developed path. Correspond-
ingly, the Pt₃Ni(111) WAXS spot remained constant in azimuthal width upon increasing temperature to 120 °C, then changed dramatically at 140 °C, and eventually developed into a powder-like ring at 150 °C. Decreasing temperature did not change much of the Pt₃Ni(111) scattering feature. These results demonstrate that a heating-induced orientational disordering occurs only in a solvent environment, indicative of the particular requirement of both heating and OA wetting toward the development of orientational disordering in the supercrystal. Such solid experimental evidence not only reveals but also strengthens the governing role of rotational entropic forces in the formation of the open bcc superlattice in solvent environments.

In situ high-pressure SAXS and WAXS measurements provided additional information for understanding the elastic response of surface-coating OA molecules and associated influence on the structural stability of the supercrystals. As shown in Figure 6, the interoctahedron distance in the SL[100] direction displays a similar linear compressibility to those of the PbS NC assembled supercrystal with a fcc superlattice. 34

Figure 6. Pressure-dependent inter-NC separations of the octahedra in the vertex-to-vertex SL[100] and the face-to-face SL[111] orientations of the bcc superlattice.

direction displays a similar linear compressibility to those of the PbS NC assembled supercrystal with a fcc superlattice. 34 Although the SL[111]-oriented face-to-face separation is five times greater than the SL[100]-oriented vertex-to-vertex separation, the reduced magnitude of the face-to-face separation during compression to 6 GPa is slightly smaller than that of the vertex-to-vertex separation. Such different linear compressibilities imply that the OA molecules filled in the SL[100]-oriented vertex-to-vertex separation spaces provide a dominant support to the bcc superlattice against the external loading forces. This further confirms the existence of strong inter-OA repulsions in the SL[100]-oriented vertex-to-vertex direction, which counter the SL[111]-oriented intermolecular attractions. Therefore, an overall balance between the repulsive and attractive interactions is achieved over a long-range of the supercrystal to stabilize its superlattice structure.

NC assembly originates from multiple interactions, which involve not only the hard inorganic cores and associated geometrical shape but also the surface-coating organic molecules and resultant chemical shapes. 39−42 In the physical processing of NCs in solvent environments, different levels of interacting competitions between various driving forces balance with each other to achieve overall equilibria and thus the formation of various superlattices in NC assembly. 22,25,44,47 In the case of octahedra, the geometrical shape contributes to the increase of directional degrees of freedom and thus to maximize the directional entropy. 4,15 Basically, the shape-dependent interaction consequence arises from the enhancement of the steric force (depletion attraction) between parallel aligned surface faces through the face-to-face interactions and the relative increase of the ligand/solvent ratio. On the basis of the hard sphere packing theory that favors the primary packing of NCs into a dense superlattice, it is expected that the octahedra maximize the configuration entropy and spontaneously self-assembly into a dense close packing superlattice. In principle, the increased occupation numbers of octahedra are achieved in one volumetric unit so that octahedra efficiently optimize the arrangement of the geometrical shape not only to maximize the face-to-face interacting areas but also to minimize the inter-NC separation distances. As a result, a high density Minkowski lattice is strongly preferred110 rather than the open bcc superlattice observed in this work.

To interpret the formation of the low-density bcc superlattice, one additional term of driving forces is required to dominate the interactions over the configuration entropy. Taking into consideration of the geometrical shape and surface-coating OA molecules of Pt₃Ni octahedra, the short vertex-to-vertex distance and the frustration of OA molecules inside the superlattice allow for an increase in the rotational degree of hard octahedra and the disordering ratio of surface molecules. As a consequence, the two driving forces including the rotational and conformational entropies arise from the hard octahedra and soft surface-coating molecules, respectively. They both compete with the translational entropy of hard octahedra and thus control the overall assembly process. These two terms of entropic forces appear to operate in an assembly of the low-density open superlattice and compensate the loss of both the translational and the directional entropies during the formation of the high-density close-packed superlattice. Therefore, alternative development of the new equilibrium state with a slightly lower free energy leads to the unique formation of the bcc superlattice, rather than a close-packed superlattice.

From the mechanical dynamics point of view, the mechanical equilibrium is achieved in a supercrystal through an overall balancing between the vertex-oriented elastic repulsions and the face-oriented vdW attractions. This mechanical equilibrium state eventually extends over the entire range of the assembled bcc supercrystal, thereby maintaining its structural and mechanical stability. Recent studies on PbS and PbSe NC assemblies revealed the formation of both bcc and fcc superlattices. 46−49 However, their assembling mechanism remains largely unresolved. If we consider the size-dependent development of NC shape, the mechanism derived in this work can be also used to interpret the formation and transformation of the bcc and fcc superlattices in PbS and PbSe NC systems. 46−50 In perspective, our discovery, together with the recent experimental and computational studies of binary and ternary systems, 57−61,47,65 provides valuable information to design either anisotropic or multiple component NCs with consideration of both the geometrical and chemical shapes and with subsequent control of the driving forces. The detailed studies will lay the foundation for fabrication of desired superlattices, such as large bandgap diamond superlattices, for photonic applications. 25−53
Conclusions. Through the control of solvent evaporation at a slow rate, large single supercrystals were grown from the toluene-dispersed suspensions of Pt$_2$Ni octahedral NCs. Using synchrotron-based X-ray supercrystallography, the structure of supercrystals has been fully reconstructed to be an open bcc superlattice, which has a low space filling factor of 26.8% and displays coherence of both translational and orientational orderings. The constituent building blocks of octahedra orient their atomic planes of Pt$_2$Ni(111), Pt$_2$Ni(110), and Pt$_2$Ni(100) parallel to the superlattice planes of SL(111), SL(110), and SL(100), respectively, giving rise to the vertex-to-vertex and the face-to-face configurations along the major bcc superlattice axes and the SL[111] directions accordingly. The inter-NC separations in the two directions are 1.0 and 4.64 nm, respectively. In situ SAXS and WAXS measurements of supercrystals under heating and solvent wetting as well as pressurizing environments reveal the local rotation of Pt$_2$Ni octahedra under solvent environments and the dominance of rotational entropic forces through multiple competitions between various types of driving forces. Beyond the leading role of translational and directional entropies in the formation of close-packing superlattices, the increased rotational entropies compete with the translational entropy and play a governing role in the formation of the low-density open bcc superlattice. In addition, an overall mechanical equilibrium, which is achieved between the intermolecular attractions through face-to-face coupling and the elastic repulsions through vertex-to-vertex molecular contacts, maintains the structural stability of assembled bcc supercrystals. Our experimental data sets and quantitative analysis not only provide insights into spontaneous nucleation and growth of the supercrystals but also help find feasible ways to design and fabricate supercrystals with tailored open superlattices and desired properties for technological applications.

REFERENCES

(9) Mao, X.; Chen, Q.; Granick, S. Nat. Mater. 2013, 12, 217–222.