Integrating *in situ* high pressure small and wide angle synchrotron x-ray scattering for exploiting new physics of nanoparticle supercrystals

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Combined small and wide angle synchrotron x-ray scattering (SAXS and WAXS) techniques have been developed for *in situ* high pressure samples, enabling exploration of the atomic structure and nanoscale superstructure phase relations. These studies can then be used to find connections between nanoparticle surfaces and internal atomic arrangements. We developed a four-axis control system for the detector, which we then employed for the study of two supercrystals assembled from 5 nm Fe₃O₄ and 10 nm Au nanoparticles. We optimized the x-ray energy and the sample-to-detector distance to facilitate simultaneous collection of both SAXS and WAXS. We further performed *in situ* high pressure SAXS and WAXS on a cubic supercrystal assembled from 4 nm wurtzite-structure CdSe nanoparticles. While wurtzite-structure CdSe nanoparticles transform into a rocksalt structure at 6.2 GPa, the cubic superstructure develops into a lamellarlike mesostructure at 9.6 GPa. Nanoparticle coupling and interaction could be enhanced, thus reducing the compressibility of the interparticle spacing above ~3 GPa. At ~6.2 GPa, the wurtzite-to-rocksalt phase transformation results in a noticeable drop of interparticle spacing. Above 6.2 GPa, a combined effect from denser CdSe nanoparticle causes the interparticle spacing to expand. These findings could be related to a series of changes including the surface structure, electronic and mechanical properties, and strain distribution of CdSe under pressure. This technique opens the way for exploring the new physics of nanoparticles and self-assembled superlattices. © 2010 American Institute of Physics.

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I. INTRODUCTION

Superlattices built from self-assembled nanoparticles (NPs) combine the size-dependent unique properties of single crystals with the collective properties of newly created (one-, two-, and three-dimensional) ordered arrays and promise the next generation of devices spanning a variety of applications.^{1–4} Many excellent examples have been discovered in nature, such as the colorless opal, which is a disordered aggregate of silica particles. When the silica particles become ordered, the opal manifests interference colors correlated with both the size and the ordering of the self-assembled particles.³ In laboratory, approaches based on templating, soft lithography, or supramolecular chemistry have enabled creation of numerous NP superlattices that cover a wide range of compositions.^{3,5–7} These superlattices comprising NP nanobuilding blocks mostly fall into three types of periodic arrangements with variable packing densities and properties: *face-centered-cubic* (fcc), *hexagonal-*

closed-packed (hcp), and *body-centered-cubic* (bcc) or *body-centered-tetragonal* (Fig. 1).⁴

Transformation from one ordered NP superlattice to another can be influenced by changing the inter-NP spacing. These superstructure transition and NP interactions at various length scales can either enhance the mechanical and optical performance or manifest novel properties.⁸ An example is found in the DNA-assembled gold NP superlattice in which a slight modification in the length scale of the DNA chains directs the self-assembly of gold NPs into diverse superlattice structures.^{9,10} When the nearby NPs inside a supercrystal are brought close enough, multiple interactions and communications between NPs are initiated and consequently enhance the intensity of plasmonic emission.¹¹ Numerous engineering and technological applications can be thus enabled, such as what has been found in photovoltaic devices, nonlinear and nanofocusing optics, and biological sensors.^{12,13} Of fundamental interests, such as high pressure physics, extensive investigations have clarified the size- and morphology-tuned enhancement of mechanical strength and structural stability of materials,^{1,7,14–16} but a gap still remains for understanding how the pressure-tuned variation of the NP

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FIG. 1. (Color online) Schematic illustrating the positioning of nanobuilding blocks into periodic crystallographic arrays. Bottom: the three common superlattice structures. Top left: a superlattice comprising nanobuilding blocks located at bcc lattice points, Top right: a spherical nanobuilding block.

surface structure and inter-NP interaction forces could be correlated with the atomic scale structural transition inside the nanoparticle core.

Facilitating custom engineering and technological applications of NP superlattices requires finding pathways capable of exploiting the interaction and communication between NPs, and thus to identify scaling laws for correlating inter-NP spacing changes to NP superlattice phase and newly manifested properties. To this end, we developed an *in situ* high pressure synchrotron x-ray scattering technique. Our technique utilizes both small and wide angle x-ray scattering (SAXS and WAXS) to explore the puzzling nanoworld, uncovering new physics and chemistry in a wide range of NP supercrystals.

II. INSTRUMENTALS

Probing a wide spectrum of information concerning NP superlattice formation requires sensitivity from the atomic scale to the nanoscale via monitoring the x-ray scattering from the wide to the small angle scattering ranges. The application of pressure increases the experimental complexity that mostly involves three components: (1) pressure cell with transparent x-ray window, (2) x-ray energy tuning, and (3) position control of a large area Mar345 detector. The diamond anvil cell (DAC) is certainly the primary option to reach extreme pressure, but diamond causes strong attenuation of low energy x-rays that reduce x-ray scattering intensity. To circumvent this problem, we devised a double tuning protocol to optimize the x-ray energy and the sample-to-detector distance. Compromising between these two factors not only effectively avoids weakening of x-ray beam intensity but also allows the collection of images with clean first-order SAXS rings. Detecting the first-order SAXS rings is critical for precise refinements of NP superlattice structures and the determination of the inter-NP distance.

The DAC used in this study has a large downstream angular opening that provides good coverage in both the SAXS and WAXS ranges. For a supercrystal assembled from nanoparticles with known size, it is desirable to estimate the x-ray scattering angles for the first-order rings with the largest inter-NP distance at a set x-ray energy. In practical selection of the experimental settings, the detector is first moved

FIG. 2. (Color online) Four-axis control system for a Mar345 detector used for tuning the sample-to-detector distance at an optimized x-ray wavelength. The components include (1) Mar345 detector, (2) horizontal (x), (3) backward-forward (y), (4) vertical (z), (5) rotational (x - y), and (6) moving tracks.

to an intermediate distance normally used for the WAXS measurement of bulk materials in the hard x-ray range (e.g., 25.5 keV). Using the NP size characterized by transmission electron microscopy, we tuned the incident x-ray beam by adjusting the germanium (111) monochromator crystals to an optimum x-ray energy that is most likely suitable for the samples. We monitored the quality of the first-order SAXS rings using short exposures and then moved the detector downstream until we achieved the best results. After the x-ray energy and sample-to-detector distance meet the requirements, a *Ag-behenate* (e.g., $d_{(001)}=58.3$ Å) standard is used to calibrate the sample-to-detector distance.

As for NPs with large size, one image collected from a single exposure but covering both the SAXS and WAXS rings requires (1) placement of the beam stop as close as possible in front of the detector and (2) adjustment of the detector vertically or horizontally on one side to cover the scattering angle as wide as possible. Particular care must be taken to prevent the x-ray beam from hitting the detector directly due to the beam divergence. Before integrating the collected x-ray scattering image to produce the two-dimensional pattern, an additional calibration of the beam center is required to revise the old parameters, thus ensuring the accuracy and reliability of the reduced data.

Reaching an optimum experimental condition for collecting high quality images at relatively short exposure time requires setting three important parameters: (1) x-ray energy (higher is better), (2) beam stop size (smaller is better), and (3) sample-to-detector distance (shorter is generally better). Our key instrumental development is a four-axis control system for moving the detector. Figure 2 shows the details for the installation and operation of the Mar345 detector. By fastening the detector on the solid roof, the vibration of the detector during x-ray exposure can be effectively reduced or eliminated. Two buttons (2 and 3) control moving the detector horizontally (x) and parallel (y) to the x-ray beam and

FIG. 3. (Color online) SAXS images of a hexagonal supercrystal assembled by Fe_3O_4 nanoparticles with a uniform particle size of ~ 5 nm. Top: three images [(a)–(c)] collected at a fixed sample-to-detector distance of ~ 0.5 m, but at different x-ray energies. Bottom: two x-ray scattering images [(d) and (e)] collected at a set x-ray energy of 17 keV, but at different sample-to-detector distances as indicated.

two knobs (4 and 5) allow adjustment of the detector in the vertical (z) and angular (x - y) positions, respectively.

III. DOUBLE TUNING FOR OPTIMIZING THE SAMPLE-TO-DETECTOR DISTANCE AND THE X-RAY ENERGY

For a NP supercrystal, we need to optimize the x-ray energy and the sample-to-detector distance to fully expose the first-order SAXS rings for unambiguous refinement of the superlattice structure. To show the practical details and give better understanding, a Fe_3O_4 NP supercrystal was used for this double tuning procedure. The Fe_3O_4 NP supercrystal was made of the highly uniform spherical NPs with a particle size of ~ 5 nm, on average. Figure 3 shows a series of x-ray scattering images of the Fe_3O_4 NP supercrystal collected at each tuning step.

When the detector is set at a sample-to-detector distance of ~ 480 mm, the SAXS rings from the Fe_3O_4 NP supercrystals are partially blocked by the beam stop [Figs. 3(a) and 3(b)] using an x-ray beam with energies of 25.5 and 20.0 keV, respectively. Tuning the x-ray energy at 17 keV yields first-order SAXS rings that are fully observed [Fig. 3(c)]; however, the nearby peaks still overlap seriously. Tuning the sample-to-detector distance to ~ 1000 and ~ 1600 mm allows us to separate the nearby x-ray scattering rings from each other [Figs. 3(d) and 3(e)]. The integration of the two-dimensional SAXS pattern collected at 17 keV is presented in Fig. 4.

The x-ray scattering vector q has a length of $q = 4\pi \sin \theta / \lambda$, where 2θ is the scattering angle and λ is the x-ray wavelength. Using the observed peaks, the calculated q/q_0 displays a developing sequence of $1/\sqrt{3}/\sqrt{4}/\sqrt{7}/\sqrt{9}/\sqrt{12}/\sqrt{13}/\sqrt{14}$, where q_0 denotes the first-order scattering peak with the largest interparticle distance. Hence, the Fe_3O_4 NPs form a *hexagonal-closed-packed* superlattice structure.

FIG. 4. (Color online) The integrated two-dimensional SAXS pattern of the Fe_3O_4 NP supercrystals, indicative of a hcp superlattice structure.

For supercrystals assembled from larger NPs, a collection of an image fully revealing both SAXS and WAXS rings through one single x-ray exposure can be achieved by sliding the detector either horizontally (x) or vertically (z). While the x-ray beam is off the detector center, one part of the collected image that covers a wider angle can be integrated to provide the SAXS and WAXS information. Figure 5 shows one image collected from the gold supercrystals assembled from relatively large NPs (~ 10 nm).¹⁷ The three WAXS rings on the right side of Fig. 5 allow one to define the atomic ordered cubic structure of the inside of gold NPs; the SAXS rings shown in Fig. 5 (e.g., the enlarged inset) reveal the periodic order of the gold supercrystals.

IV. A CASE STUDY OF WURTZITE-TYPE CdSe NPS FORMING A SELF-ASSEMBLED FCC SUPERCRYSTAL

The supercrystals assembled from ~ 4 nm wurtzite-type CdSe NPs were employed to test the availability and reliability of the *in situ* high pressure technique described above. The combination of SAXS and WAXS not only helps effectively construct the pressure-tuned phase relationships at both the atomic and mesoscale (or nanoscale) but also facilitates the detection of NP surface structure development and inter-NP driving forces during pressurization and upon atomic structural transformation inside NP.

FIG. 5. (Color online) X-ray scattering image collected at the beam off-detector center from Au NP superlattice self-assembled by ~ 10 nm spherical NPs, indicating that both the SAXS and WAXS rings can be simply obtained from one single x-ray exposure on the samples.

FIG. 6. (Color online) Demonstration of the CdSe NP with a hexagonal lattice, the self-assembled NP supercrystal, and the corresponding SAXS and WAXS images collected through a DAC.

Bulk CdSe is stable in the wurtzite and zincblende structures at ambient conditions. Upon reducing particle size, wurtzite-structure CdSe becomes slightly more stable than the zincblende form,^{14–16} but when deviatoric strains (i.e., *nonhydrostatic pressure across the samples*) are introduced, the nanoparticle tends to favor a zincblende structure. This study employed wurtzite CdSe NPs with an average size of ~ 4 nm synthesized by a chemical approach.¹⁸ *van der Waals* forces drive CdSe NP self-assembly into periodic order with NP supercrystals that have fcc superlattice structure (No. 216: $Fd3m$). The atomic structure and NP superlattice structure of CdSe with the corresponding WAXS and SAXS images are shown in Fig. 6.

V. IN SITU WAXS UNDER PRESSURE

The WAXS image and the integrated two-dimensional pattern indicate that the 4 nm CdSe NPs have a hexagonal atomic structure. Upon compression, the wurtzite CdSe NPs transform into a rocksalt structure at 6.2 GPa (Fig. 7). This atomic scale transition pressure is greater than the bulk transition pressure of 2.5 GPa, consistent with the previous studies on wurtzite CdSe NPs with a similar particle size.¹⁴

FIG. 7. (Color online) The WAXS patterns of wurtzite CdSe NPs, indicating that the wurtzite CdSe transforms into a rocksalt structure at 6.2 GPa. The sharp peaks marked by * are possibly due to a crystallization of the remnant organic materials during drying.

FIG. 8. (Color online) Representative *in situ* pressure SAXS pattern of the CdSe NP supercrystals. The marked values at SAXS peaks are the calculated q/q_0 . The change in q/q_0 indicates that the fcc CdSe NP supercrystals develop into a lamellarlike mesostructure at 9.6 GPa.

VI. IN SITU SAXS UNDER PRESSURE

The representative high pressure SAXS patterns shown in Fig. 8 for CdSe NP supercrystals follow $q/q_0 = 1/\sqrt{8/3}/\sqrt{11/3}$, confirming that the wurtzite CdSe NPs form a fcc superlattice structure. Increasing pressure to 9.6 GPa, the peak positions display a dramatic change in q/q_0 , roughly equivalent to 1:2:3, indicating that the fcc NP supercrystal develops into a lamellarlike mesostructure.

VII. RELATING ATOMIC SCALE PERIODIC CHANGE TO MESOSCALE (NANOSCALE) STRUCTURE OF CDSE AS A FUNCTION OF PRESSURE

Even though the *in situ* SAXS and WAXS measurements reveal the structural transformations at atomic scale and mesoscale, respectively, the observed transition pressures are quite different, i.e., 6.2 GPa versus 9.6 GPa. This observation appears to conflict with the existence of a close correlation between these two types of structural transformations. However, plotting the inter-NP spacing as a function of pressure (Fig. 9) allows one to easily recognize that the observed atomic scale structural transformation inside NP is responsible for the multiple NP interactions and associated inter-NP spacing fluctuation. Below 3 GPa, the inter-NP spacings display a pressure-induced large compression similar to the bulk, but upon compression from 3 GPa to the atomic scale transition pressure of 6.2 GPa, a much lower compressibility of inter-NP spacing was observed. Upon wurtzite-to-rocksalt phase transformation at 6.2 GPa, a noticeable reduction of the inter-NP spacing appears and then a noticeable expansion dominates at pressures above 6.2 GPa. The noticeable reduction of the inter-NP spacing at 6.2 GPa can be reasonably explained by an 18% volumetric decrease from wurtzite to rocksalt upon phase transformation.^{14–16} The other observed subtle fluctuations of inter-NP spacing could be related to the pressure-induced changes of surface structure and atomic scale transition-tuned variation of optical and physical prop-

FIG. 9. (Color online) Inter-NP spacing of wurtzite CdSe supercrystals as a function of pressure, showing a series of interparticle spacing fluctuations upon pressurizing.

erties. These could include inter-NP driving forces, multiple NP coupling and interaction, stress distribution, particle size, and surface morphology.¹⁹ However, a full understanding of these observations and the resulting mechanisms still need further and detailed experimental and theoretical explorations including a series of *in situ* pressure measurements of mechanical and optical properties, electrical conductivity, and theoretical modeling.²⁰

VIII. CONCLUSIONS

We have developed a technique that allows an *in situ* collection of SAXS and WAXS images of NP supercrystals under pressure. Using the newly constructed four-axis control system for manipulating the detector, we are able to easily optimize the x-ray energy and the sample-to-detector distance for the particular application of NP supercrystals in a DAC and then collect the SAXS and WAXS images through one single x-ray exposure. Measurements on wurtzite CdSe NP supercrystals reveal a series of novel phenomena such as the correlation between atomic and mesoscale structural transformation. This unique technique opens a way for exploring new phenomena and tuning mechanisms for a wide spectrum of NPs and NP building blocks, as well as their mechanical strength, structural stability, and the nature of interparticle interactions.

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²⁰A series of *in situ* measurements of mechanical and optical properties as well as electrical conductivities of self-assembled CdSe nanoparticle supercrystals is undergoing. Meanwhile, theoretical simulations with different considerations are performed in parallel as well.