Published in final edited form as:

J Phys Chem C Nanomater Interfaces. 2011 April 14; 115(14): 6397–6404. doi:10.1021/jp2004908.

Melting and Sintering of a Body-Centered Cubic Superlattice of PbSe Nanocrystals Followed by Small Angle X-ray Scattering

Brian W. Goodfellow^a, Reken N. Patel^a, Matthew G. Panthani^a, Detlef-M. Smilgies^b, and Brian A. Korgel^{a,*}

^aDepartment of Chemical Engineering, Texas Materials Institute, Center for Nano- and Molecular Science and Technology, The University of Texas at Austin, Austin, Texas 78712-1062

^bCornell High Energy Synchrotron Source (CHESS), Cornell University, Ithaca, New York 14853

Abstract

The structural evolution of a body-centered cubic (bcc) superlattice of 6.6 nm diameter organic ligand-coated PbSe nanocrystals was studied in situ by small angle X-ray scattering (SAXS) as it was heated in air from room temperature to 350°C. As it was heated above room temperature, the superlattice contracted slightly, but maintained bcc structure up to 110°C. Once the temperature rose above 110°C, the superlattice began to disorder, by first losing long-range translational order and then local positional order. At temperatures exceeding 168°C, the nanocrystals sintered and oxidized, transforming into PbSeO₃ nanorods.

Keywords

nanocrystals; lead selenide; lead chalcogenide; self-assembly; nanocrystal superlattice; thermal stability; in situ structural characterization; small angle x-ray scattering

Introduction

Colloidal nanocrystals with precisely controlled size and shape represent a unique class of materials with significantly different properties than their bulk analogs.^{1,2} Nanocrystal assemblies have been explored for a variety of applications, including solar cells,^{3–14} field effect transistors,^{8, 15–18} light emitting diodes,^{19–22} thermoelectric devices,^{17, 23, 24} photodetectors,^{13, 25} and chemical sensors.²⁶ The deposition of nanocrystals on substrates by solution-based processes also provides a low-cost route to forming inorganic films without the use of high temperature or vacuum.^{3,14,27,28} Lead chalcogenide (i.e. PbS, PbSe, PbTe) nanocrystals, in particular, have received considerable attention,^{29–41} due in part to a large Bohr exciton radius, a narrow and size-tunable^{29–31} band gap, symmetric conduction and valence bands,⁴² and significant electronic coupling between neighboring nanocrystals in superlattices due to their relatively low effective electron and hole masses.⁴³ These properties make them interesting candidates for a variety of electronic and optoelectronic applications.^{6–13,17,18,22–25}

*Corresponding author: korgel@che.utexas.edu; (T) 512-471-5633; (F) 512-471-7060.

Supporting Information Available

Comparison of superlattice d-spacings measured by TEM and SAXS; TGA and DSC of oleic acid-capped PbSe nanocrystals and neat oleic acid as they are heated from room temperature to 400°C in air; TEM images of PbSe nanocrystal superlattice before and after heating to 300°C in air; High resolution TEM images and corresponding FFTs of bcc superlattice of PbSe nanocrystals.

Many applications of nanocrystal films will require device operation or processing at elevated temperature. The impacts of nanocrystal size,^{12,44,45} arrangement,^{15,46} surface chemistry,^{13,18,47–50} and separation^{18,44,48,49} on the electronic and optoelectronic properties of lead chalcogenide nanocrystal thin films have been extensively studied; however, the influence of heating on the structure and composition of the nanocrystal films has largely been overlooked. Several reports have shown that thermal processing can change significantly the electronic properties of PbSe nanocrystal films. For example, Law et. al.⁴⁹ observed a dramatic increase in the electrical conductivity of PbSe nanocrystal films, of nearly 10 orders of magnitude, after heating above 250°C. Based on scanning electron microscopy (SEM), small angle x-ray scattering (SAXS), and wide angle x-ray scattering (WAXS) data, they suggested that this was due to nanocrystal sintering; however, a detailed analysis of the structural changes of the heated PbSe nanocrystal assemblies was not provided. Similarly, Baik et. al.⁵¹ reported significant increases in the electrical conductivity of ethanedithiol-treated PbSe and PbS nanocrystals when heated to an even lower temperature of 170°C, and Klem et. al.⁵² observed improvements in both electrical conductivity and mobility of ethanedithiol-treated PbS nanocrystal films annealed at still lower temperature of only 90°C in air, which they attributed to surface oxidation and corresponding increases in hole concentration. Van Huis et. al.⁵³ directly observed nanocrystal fusion in PbSe nanocrystal assemblies by in situ high resolution transmission electron microscopy (TEM) of hexylamine-capped PbSe nanocrystal monolayers heated just above 100°C. One of the problems, however, with in situ TEM to study the structural changes of a heated superlattice is the presence of the energetic electron beam. The beam can induce melting of the inorganic cores, which may prematurely destabilize the superlattice, or decompose the hydrocarbon ligands into a graphitic carbon layer between particles that stabilizes the superlattice to unusually high temperature.^{54,55} Clearly, there is still much uncertainty about how heating changes the structure of PbSe nanocrystal superlattices.

Here, we report a detailed study of how the structure and composition of a body-centered cubic (bcc) superlattice of oleic acid-capped PbSe nanocrystals changes as it is heated in air to 350°C, relying on real time SAXS measurements with synchrotron radiation to provide statistically-appropriate structural data with sub-Ångstrom spatial resolution. Complementary X-ray diffraction (XRD), TEM, and SEM measurements of the heated superlattices were also carried out to provide additional information about the structural transitions observed by SAXS. In the cases of Ag^{56,57} and Au^{58,59} nanocrystal superlattices, in situ SAXS measurements of heated superlattices have provided new insight, for example, revealing that the temperature-dependence of the structural transitions can be quite complicated and interesting.^{60–63} In the case here of a PbSe nanocrystal superlattice, the SAXS data show that the bcc superlattice is stable up to only 110°C, and then above this temperature the periodic superlattice order collapses. There is first a loss of long-range translational order between 110°C and 150°C and then a loss of local positional order at 168°C. Above 168°C, the nanocrystals undergo a gradual sintering process accompanied by an oxidative conversion of the PbSe nanocrystals to PbSeO₃ nanorods, which has not been previously observed.

Experimental Methods

Chemicals

Lead acetate trihydrate (Pb(ac)₂·H₂O, 99.999%), oleic acid (OA, >99%), diphenyl ether (Fluka, >99.9%), selenium powder (Se, 100 mesh, 99.99%), and trioctylphosphine (TOP, tech., 90%) were purchased from Aldrich and used as received. TOP was stored in a N₂-filled glovebox. A stock solution of 1M Se in TOP was prepared by dissolving 20 mmol Se powder in 20 mL TOP overnight in a glovebox.

PbSe Nanocrystal Synthesis and Purification

PbSe nanocrystals were prepared following an adaptation of a procedure described by Cho et.al.³² In a 25 mL 3-neck flask, 10 mL phenyl ether, 2.5 mL oleic acid, and 0.76 g $\text{Pb}(\text{ac})_2 \cdot \text{H}_2\text{O}$ were combined. The flask was attached to a Schlenk line, heated to 75°C under vacuum, and held there for one hour to begin the formation of a lead oleate precursor and to completely remove the acetic acid and water byproducts from the reaction flask. The flask was then heated to 150°C under a N_2 atmosphere and held there for 30 minutes to complete the formation of the lead oleate complex. The flask was then cooled to 60°C and 6 mL of the TOP-Se stock solution was injected into the flask. Separately, in a 50 mL three neck flask, 15 mL of phenyl ether was dried and degassed by heating to 75°C under vacuum for one hour. This flask was then heated to 150°C under N_2 flow. At this point, 13 mL of the lead-oleate and TOP-Se mixture in phenyl ether was rapidly injected into the hot flask. Once the temperature in the flask regained 120°C, the remaining 5.5 mL was injected dropwise over the course of 4 minutes. The temperature was then increased to 150°C, where it was allowed to react for 10 minutes. The heating mantle was then removed and the flask was allowed to cool to room temperature.

Excess ligand and unreacted precursors were removed from the crude reaction product by redispersion and precipitation of the nanocrystals using toluene and ethanol as a solvent/antisolvent pair. Initially, ethanol was added to the crude reaction solution to precipitate the nanocrystals. The mixture was centrifuged at 8000 rpm for 5 min to isolate the nanocrystals as a precipitate. The supernatant was discarded and the precipitate was redispersed in toluene. This procedure was repeated once more. After redispersing the nanocrystals in toluene, the dispersion was centrifuged at 8000 rpm for 5 minutes to separate any poorly-capped nanocrystals or agglomerates. The precipitate was discarded and the supernatant was collected and used for the experiments in this study.

PbSe Nanocrystal Film Preparation

PbSe nanocrystals were dispersed in hexane and then diluted with an equal volume of toluene. It is important to point out that the choice of solvent used for deposition can significantly affect the microstructure of the nanocrystal film.^{64,65} The dispersion was drop-cast onto a TEM grid (carbon-coated copper 200 mesh, Electron Microscopy Sciences) for TEM imaging or a soda-lime glass cover slide (Fisherfinest Premium, 25mm × 25mm, 0.13 to 0.17mm thick, Fisher Scientific) for SAXS. The nanocrystal films were stored under ambient atmosphere at room temperature for approximately 5 days prior to characterization by in situ SAXS.

Materials Characterization

TEM was performed on a Phillips EM208 TEM with 80 kV accelerating voltage. Images were acquired digitally. Small angle x-ray scattering (SAXS) was performed on dilute dispersions (~0.5 mg/mL) of PbSe nanocrystals in hexane in a stainless steel cell with kapton windows using a Molecular Metrology instrument with a rotating copper anode X-ray generator (Bruker Nonius; $\lambda = 1.54 \text{ \AA}$) operating at 3.0 kW. The scattered X-rays were collected on a 2D multiwire gas-filled detector (Molecular Metrology, Inc.). A silver behenate ($\text{CH}_3(\text{CH}_2)_{20}\text{COOAg}$) standard was used to calibrate the scattering angle of scattered photons. Radial integrations of scattering intensity were performed using Datasqueeze.⁶⁶ Background scattering of the hexane solvent and the experimental setup were subtracted from the data.

In situ SAXS of a heated PbSe film

A glass cover slide containing a PbSe nanocrystal film was placed into a Mettler Toledo FP82HT hot stage between 2 aluminum spacers specifically fabricated for this experiment. The hot stage was then placed into the D1 beam line at the Cornell High Energy Synchrotron (CHESS) in transmission mode with the side containing the nanocrystal film facing the detector. While much of the beamline is under vacuum or helium atmosphere, the x-ray beam transmits through a 10 cm section of ambient atmosphere and that this section was used to mount the hot stage. The hot stage was controlled with a Mettler Toledo FP80 processing unit to heat the sample from 28°C to 350°C at a rate of 3°C/min. SAXS measurements were performed using monochromatic radiation of wavelength $\lambda=1252$ Å with a bandwidth $\Delta\lambda/\lambda$ of 1.5%. The x-ray beam was produced by a hard-bent dipole magnet in the Cornell storage ring and monochromatized with Mo:B₄C multilayers with a period of 30 Å. The D1 area detector (MedOptics) is a fiber coupled CCD camera with a pixel size of 46.9 μm by 46.9 μm and a total of 1024 × 1024 pixels with a 14-bit dynamical range per pixel. Typical readout time per image was below 5 sec. The images were dark current corrected, distortion-corrected, and flat-field corrected by the acquisition software. The sample to detector distance was 852 mm, as determined using a silver behenate powder standard. The exposure time for each collected scattering image was 4 seconds and was followed by a 16 second delay (including detector readout). Considering the heating rate, this resulted in the collection of a scattering image about every 1°C. Scattering images were calibrated and integrated using the Fit2D software.⁶⁷

Results and Discussion

PbSe nanocrystals and bcc superlattice formation

Figure 1 shows TEM images of oleic acid-capped PbSe nanocrystals drop-cast from 1:1 hexane:toluene dispersions. The nanocrystals are sufficiently monodisperse to order into superlattices. The inorganic PbSe cores of the nanocrystals remain separated by the oleic acid capping ligand layer coating each particle. The superlattice structure was observed to vary depending on the concentration of the nanocrystals in the dispersion deposited on the substrate. Nanocrystals deposited from relatively dilute dispersions to form monolayers assembled with hexagonal order as shown in Figure 1a. In contrast, nanocrystals deposited from more concentrated dispersions as thicker superlattice films—as in Figure 1b— assembled into superlattices with bcc structure. Some regions of the sample showed the coexistence of thin monolayers with hexagonal order and thicker superlattices with bcc structure. The origin of this difference in superlattice symmetry and its dependence on the layer thickness is presently not understood and is under investigation. The thicker nanocrystal superlattice films with bcc structure were the focus of this study and were heated and probed by in situ SAXS.

Figure 2 shows transmission SAXS data for a sample of PbSe nanocrystal superlattice. The radial X-ray scattering intensity profile is obtained by integrating the experimentally-measured 2D scattering pattern in the inset. The observation of relatively sharp Bragg peaks confirms that there is long-range periodic superlattice ordering of the nanocrystals, as was observed by TEM. Most commonly, monodisperse nanocrystals have been observed to assemble into superlattices with face centered cubic (fcc) structure;^{68,69} however, in this case, the diffraction peaks appear with relative positions of $q/q^* = \sqrt{1} : \sqrt{2} : \sqrt{3} : \sqrt{4}$, where $q^* = 0.825 \text{ nm}^{-1}$ is the location of the lowest order reflection, indicating that the superlattice has either bcc or simple cubic (sc) symmetry. An independent measure of the superlattice d -spacings by TEM confirmed that the superlattice is bcc and not sc. As illustrated in Figure 3, the d -spacings observed by TEM between (100), (110), and (210) planes of 10.57 nm, 7.63 nm, and 4.71 nm, respectively, correspond to an average lattice constant of $a_{bcc,TEM} = 10.63$

nm, which is very close to the bcc lattice constant determined from SAXS of $a_{bcc,SAXS} = 10.79$ nm. If the superlattice had sc symmetry, the lattice constant determined by SAXS would be $a_{sc,SAXS} = 7.63$ nm, which is not consistent with the lattice constant determined by TEM—i.e., $a_{sc,TEM} = 10.63$ nm. A full comparison of the d -spacings measured by SAXS and TEM is provided in the Supporting Information.

The center-to-center interparticle separation between nearest neighbor PbSe nanocrystals in the bcc superlattice measured by SAXS and TEM are $D_{eff,SAXS} = 934$ nm and $D_{eff,TEM} = 9.21$ nm. This separation corresponds to a “soft sphere” nanocrystal diameter that includes the inorganic PbSe core of the nanocrystals and part of the ligand shell.⁷⁰ To obtain an estimate of the volume that is excluded in the superlattice by the ligands, the diameter of the inorganic PbSe cores was determined independently from solution SAXS measurements of the nanocrystals dispersed in hexane, shown in Figure 4. By fitting the data to a model for the X-ray scattering intensity, $I(q)$, from a dilute dispersion of non-interacting spherical particles,^{69,70}

$$I(q) \propto \int_0^\infty N(R)P(qR)R^6 dR \quad (1)$$

the average radius of the inorganic PbSe cores $\bar{R}$, can be determined. In Eqn (1), q is the scattering vector, which depends on the X-ray wavelength ($\lambda = 1.54$ Å) and the scattering angle θ : $q = (4\pi/\lambda)\sin(\theta/2)$. Since the scattering intensity depends on the nanocrystal radius R , the data are very sensitive to the size distribution, $N(R)$, which is the number fraction of nanocrystals of radius R , in the sample. $P(qR)$ is the form factor for a solid homogeneous sphere:^{71, 72}

$$P(qR) = \left[3 \frac{\sin(qR) - qR \cos(qR)}{(qR)^3} \right]^2. \quad (2)$$

Relatively monodisperse nanocrystals prepared by arrested precipitation, such as the PbSe nanocrystals studied here, typically exhibit a Gaussian size distribution with an average nanocrystal radius $\bar{R}$ and standard deviation of σ about the mean,⁷⁰

$$N(R) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left[-\frac{(R - \bar{R})^2}{2\sigma^2} \right]. \quad (3)$$

The average diameter (i.e., $2\bar{R}$) of the crystalline PbSe cores of the nanocrystals determined by fitting Eqns (1–3) to the data in Figure 4 is $D_{core,SAXS} = 6.60$ nm $\pm$ 0.79 nm ($\pm$ 12%). Therefore, the corresponding “soft sphere” ligand shell thickness is $\delta = \frac{1}{2}(D_{eff,SAXS} - D_{core,SAXS}) = 1.37$ nm.

The interstitial void space between the soft sphere particles in the superlattice—corresponding to 32% of the total volume for a bcc superlattice—is also filled by ligand. Therefore, by knowing the lattice constant of the bcc unit cell and the PbSe core diameter independently, the total volume in the superlattice that must be occupied by the capping ligands can be compared to the ligand excluded volume that is expected for each nanocrystal. The total volume excluded by the adsorbed oleic acid chains on each nanocrystal can be estimated by assuming that each ligand molecule attaches to the PbSe surface with a circular footprint of 0.16 nm² with a close-packed density on the surface of 91%, and taking an excluded volume of 0.5116 nm³ for each oleic acid molecule.⁶⁵ Based

on the total surface area of a 6.6 nm diameter PbSe nanocrystals, the total volume excluded by the capping ligand layer around each nanocrystals is $V_{\text{ligand}}/\text{particle} = 398 \text{ nm}^3$. There are two nanocrystals per bcc unit cell, where the volume of the bcc unit cell is $V_{\text{cell}} = a_{\text{bcc,SAXS}}^3 = 1256 \text{ nm}^3$. The inorganic PbSe cores occupy only $2 \times V_{\text{core}} = 301 \text{ nm}^3$, or 24% of the unit cell. The remaining volume in the superlattice of 955 nm^3 is higher than the estimated excluded volume occupied by the capping ligands ($2 \times V_{\text{ligand}}/\text{particle} = 796 \text{ nm}^3$). This leaves a remainder of 159 nm^3 , or 13% of the unit cell, that is not accounted for by the nanocrystal cores or their capping ligands. This space is most likely occupied by unbound oleic acid or trapped solvent, as discussed later.

Film heating and in situ SAXS

Figure 5 shows in situ transmission SAXS data collected from a bcc superlattice of PbSe nanocrystals as it was heated at $3^\circ\text{C}/\text{min}$ from 28°C to 350°C . Figure 6 shows a radial integration of the data at select temperatures. The data reveal four predominant transitions as the superlattice was heated from room temperature: (1) a contraction of the superlattice until reaching about 140°C ; (2) a loss of long-range translational order (i.e. amorphization) between about 110°C and 150°C ; (3) a loss of local, short-range, positional order at around 168°C ; and (4) nanocrystal sintering above 168°C .

Figure 7 shows the center-to-center nearest neighbor spacing in the superlattice determined from SAXS as it was heated from room temperature up to 160°C . In this temperature range, the superlattice contracts upon heating, while maintaining the bcc structure. The data in Figure 7 show that the lattice contraction became more significant when the temperature reached the boiling points of hexane (69°C) and toluene (110°C)—the solvents used to disperse the nanocrystals. Therefore, it would appear that the superlattice contraction is related to the evaporation of solvent trapped in the superlattice after deposition. In previous reports of heated superlattices, heating has either increased,^{56,73} decreased,^{8,59,73} or left unaffected,⁵⁹ the interparticle spacing; the lattice expansion or contraction of a nanocrystal superlattice in this temperature range appears to depend on the details of the system, such as the presence of trapped solvent and the thermal expansion of the ligands. In our case, TGA of a sample of oleic acid-capped PbSe nanocrystals (9 nm diameter) confirmed that there was indeed significant solvent trapped in the superlattice, equivalent to about 2% of the total sample weight after heating from room temperature to 190°C . The amount of superlattice contraction that is actually observed corresponds to an amount of trapped solvent that would be about 4–5 times higher than this.⁷⁴ Therefore, it appears that solvent evaporation is indeed partly responsible for the superlattice contraction, but cannot completely explain it. Perhaps there is a cooperative effect between the ligand packing density (i.e. conformational changes or interdigitation) in the superlattice and the amount of residual solvent between particles. This issue requires further study, but it is clear that in this case of oleic acid-capped PbSe nanocrystals, the superlattice contracts significantly as it is heated from room temperature to its disordering transition, by more than 20%, and that this is somehow related to solvent trapped in the superlattice during solvent deposition.

When the temperature is increased to just above 110°C , a broad diffraction ring begins to appear at slightly lower q than the position of the bcc (220) Bragg ring (labeled in Figure 5 by a star). This diffraction ring is a second order reflection corresponding to an average nearest neighbor distance in an amorphous assembly and signifies the loss of long-range translational order of the superlattice. As shown in Figure 6, the Bragg peaks have disappeared completely by 150°C and the diffraction pattern consists of two broad diffraction peaks characteristic of an amorphous assembly of nanocrystals.⁶⁹ The two diffraction rings associated with the amorphous assembly are present in the scattering data up to 168°C , indicating that the nanocrystals have not sintered and remain intact, but are no longer ordered in a periodic superlattice.

At 168°C, the scattering rings disappear, which indicates that complete disordering of the nanocrystals has occurred and marks the onset of the sintering process. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of oleic acid-capped PbSe nanocrystals (see Supporting Information) showed no observable transitions below 168°C aside from the evaporation of some residual solvent. This suggests that structural transformations of the PbSe nanocrystal superlattice below 168°C are not directly influenced by the thermal behavior of the capping ligand. However, TGA of pure oleic acid showed that oleic acid begins to evaporate at around 150°C, so it is possible that superlattice disordering and nanocrystal sintering may be related to the evaporation of “free”, or unbound, oleic acid from the superlattice.

There is also a noticeable increase in scattering intensity at lower q -values as the temperature increased above 168°C. This is a signature of sintering and grain growth. We found that heating PbSe nanocrystals in air led to oxidation and the formation of lead selenite (PbSeO₃) nanorods (see Supporting Information). Figure 8 shows XRD profiles and TEM images of PbSe nanocrystal films heated in air. There is no evidence of PbSeO₃ in the initial sample, but at 200°C, a mixture of PbSe and PbSeO₃ is clearly present. By 300°C, all of the PbSe has oxidized to PbSeO₃. TEM of PbSe nanocrystal films heated to 300°C in air revealed that the PbSe nanocrystals had transformed into PbSeO₃ nanorods. A transformation from spherical nanocrystals into nanorods, with an elongation of the nanocrystal size in one direction, is consistent with the observed increase in scattering intensity at low q after the temperature was increased from 200°C to 250°C. Micrometer-size PbSe particles have also been observed to oxidize to PbSeO₃ when annealed in an oxygen-containing atmosphere.⁷⁵

Conclusions

The heating-induced structural changes of a PbSe nanocrystal superlattice with bcc structure were followed by in situ SAXS. The bcc superlattice is stable up to a temperature of 110°C with a slight lattice contraction. At 110°C, the lattice contraction becomes more pronounced and is accompanied by disordering of the superlattice. By 150°C, the nanocrystal film has lost long-range translational order and is completely amorphous. The amorphous assembly of nanocrystals persists to a temperature of 168°C, at which point the weak diffraction peaks from the amorphous nanocrystal assembly disappear, indicating loss of local, short-range, positional order. Above 168°C, the nanocrystals sinter. XRD revealed that the sintering of neighboring nanocrystals is accompanied by the oxidative transformation of the PbSe nanocrystals to PbSeO₃ nanorods when the superlattice is heated in air. These results are valuable as many practical applications of semiconductor nanocrystal superlattices will require operation at elevated temperatures.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This research was supported by funding from the Robert A. Welch Foundation (Grant no. F-1464) and the National Science Foundation (DMR-0807065). In situ SAXS measurements were conducted at the Cornell High Energy Synchrotron Source (CHESS), which is supported by the National Science Foundation and the National Institute of Health/National Institute of General Medical Sciences under NSF award DMR-0936384. B.W.G. acknowledges financial support under the NSF IGERT program DGE-054917. We thank Andrew Heitsch, Vince Holmberg, and Vahid Akhavan for their assistance with collecting SAXS measurements and fruitful discussions and Landry Khounlavong for his assistance with Matlab in producing the contour plot of the in situ SAXS profiles. We also thank Marleen Kamperman, Marvin Paik, and the Ober group (MSE, Cornell University) for the use of their heating stage for the in situ heating experiments.

References

1. Brus L. Appl. Phys. A: Mater. Sci. Process. 1991; 53:465–474.
2. Alivisatos AP. J. Phys. Chem. 1996; 100:13226–13239.
3. Gur I, Fromer NA, Geier ML, Alivisatos AP. Science. 2005; 310:462–465. [PubMed: 16239470]
4. Wu Y, Wadia C, Ma W, Sadtler B, Alivisatos AP. Nano Lett. 2008; 8:2551–2555. [PubMed: 18651779]
5. Panthani MG, Akhavan V, Goodfellow B, Schmidtke JP, Dunn L, Dodabalapur A, Barbara PF, Korgel BA. J. Am. Chem. Soc. 2008; 130:16770–16777. [PubMed: 19049468]
6. Zhao N, Osedach TP, Chang L-Y, Geyer SM, Wanger D, Binda MT, Arango AC, Bawendi MG, Bulovic V. ACS Nano. 2010; 4:3743–3752. [PubMed: 20590129]
7. Johnston KW, Pattantyus-Abraham AG, Clifford JP, Myrskog SH, MacNeil DD, Levina L, Sargent EH. Appl. Phys. Lett. 2008; 92:151115.
8. Mentzel TS, Porter VJ, Geyer S, MacLean K, Bawendi MG, Kastner MA. Phys. Rev. B. 2008; 77:075316.
9. Choi JJ, Lim Y-F, Santiago-Berrios MEB, Oh M, Hyun B-R, Sun L, Bartnik AC, Goedhart A, Malliaras GG, Abruña HD, Wise FW, Hanrath T. Nano Lett. 2009; 9:3749–3755. [PubMed: 19719095]
10. Ma W, Luther JM, Zheng H, Wu Y, Alivisatos AP. Nano Lett. 2009; 9:1699–1703. [PubMed: 19351196]
11. Luther JM, Law M, Beard MC, Song Q, Reese MO, Ellingson RJ, Nozik AJ. Nano Lett. 2008; 8:3488–3492. [PubMed: 18729414]
12. Leschkies KS, Beatty TJ, Kang MS, Norris DJ, Aydil ES. ACS Nano. 2009; 3:3638–3648. [PubMed: 19842707]
13. McDonald SA, Konstantatos G, Zhang S, Cyr PW, Klem EJD, Levina L, Sargent EH. Nature Mater. 2005; 4:138–142. [PubMed: 15640806]
14. Akhavan VA, Goodfellow BW, Panthani MG, Reid DK, Hellebusch DJ, Adachi T, Korgel BA. Energy Environ. Sci. 2010; 3:1600–1606.
15. Urban JJ, Talapin DV, Shevchenko EV, Kagan CR, Murray CB. Nature Mater. 2007; 6:115–121. [PubMed: 17237786]
16. Sun B, Sirringhaus H. Nano Lett. 2005; 5:2408–2413. [PubMed: 16351187]
17. Lin Y-M, Dresselhaus MS. Phys. Rev. B. 2003; 68:075304.
18. Talapin DV, Murray CB. Science. 2005; 310:86–89. [PubMed: 16210533]
19. Coe S, Woo W-K, Bawendi M, Bulovic V. Nature. 2002; 420:800–803. [PubMed: 12490945]
20. Cho K-S, Lee EK, Joo W-J, Jang E, Kim T-H, Lee SJ, Kwon S-J, Han JY, Kim B-K, Choi BL, Kim JM. Nature Photon. 2009; 3:341–345.
21. Mueller AH, Petruska MA, Achermann M, Werder DJ, Akhador EA, Koleske DD, Hoffbauer MA, Klimov VI. Nano Lett. 2005; 5:1039–1044. [PubMed: 15943439]
22. Steckel JS, Coe-Sullivan S, Bulovic V, Bawendi MG. Adv. Mater. 2003; 15:1862–1866.
23. Harman TC, Taylor PJ, Walsh MP, LaForge BE. Science. 2002; 297:2229–2232. [PubMed: 12351781]
24. Wang RY, Feser JP, Lee J-S, Talapin DV, Segalman R, Majumdar A. Nano Lett. 2008; 8:2283–2288. [PubMed: 18597536]
25. Sarasqueta G, Choudhury KR, So F. Chem. Mat. 2010; 22:3496–3501.
26. Shipway AN, Katz E, Willner I. ChemPhysChem. 2000; 1:18–52.
27. Ridley BA, Nivi B, Jacobson JM. Science. 1999; 286:746–749. [PubMed: 10531054]
28. Akhavan VA, Goodfellow BW, Panthani MG, Korgel BA. Modern Energy Review. 2010; 2:25–27.
29. Murray CB, Sun S, Gaschler W, Doyle H, Betley TA, Kagan CR. IBM J. Res. & Dev. 2001; 45:47–56.
30. Du H, Chen C, Krishnan R, Krauss TD, Harbold JM, Wise FW, Thomas MG, Silcox J. Nano Lett. 2002; 2:1321–1324.

31. Wehrenberg BL, Wang C, Guyot-Sionnest P. *J. Phys. Chem. B.* 2002; 106:10634–10640.
32. Cho K-S, Talapin DV, Gaschler W, Murray CB. *J. Am. Chem. Soc.* 2005; 127:7140–7147. [PubMed: 15884956]
33. Wang N, Cao X, Guo L, Yang S, Wu Z. *ACS Nano.* 2008; 2:184–190. [PubMed: 19206617]
34. Talapin DV, Yu H, Shevchenko EV, Lobo A, Murray CB. *J. Phys. Chem. C.* 2007; 111:14049–14054.
35. Hines MA, Scholes GD. *Adv. Mater.* 2003; 15:1844–1849.
36. Lifshitz E, Bashouti M, Kloper V, Kigel A, Eisen MS, Berger S. *Nano Lett.* 2003; 3:857–862.
37. Houtepen AJ, Koole R, Vanmaekelbergh D, Meeldijk J, Hickey SG. *J. Am. Chem. Soc.* 2006; 128:6792–6793. [PubMed: 16719451]
38. Lu W, Fang J, Ding Y, Wang ZL. *J. Phys. Chem. B.* 2005; 109:19219–19222. [PubMed: 16853481]
39. Lee S-M, Jun Y-w, Cho S-N, Cheon J. *J. Am. Chem. Soc.* 2002; 124:11244–11245. [PubMed: 12236719]
40. Zhao Z, Zhang K, Zhang J, Yang K, He C, Dong F, Yang B. *Collids surf., A.* 2010; 355:114–120.
41. Smith DK, Luther JM, Semonin OE, Nozik AJ, Beard MC. *ACS Nano.* 2011; 5:183–190. [PubMed: 21141910]
42. Kang I, Wise FW. *J. Opt. Soc. Am. B.* 1997; 14:1632–1646.
43. Liljeroth P, Overgaag K, Urbiet A, Grandidier B, Hickey SG, Vanmaekelbergh D. *Phys. Rev. Lett.* 2006; 97:096803. [PubMed: 17026390]
44. Liu Y, Gibbs M, Puthussery J, Gaik S, Ihly R, Hillhouse HW, Law M. *Nano Lett.* 2010; 10:1960–1969. [PubMed: 20405957]
45. Kigel A, Brumer M, Maikov G, Sashchiuk A, Lifshitz E. *Superlattices Microstruct.* 2009; 46:272–276.
46. Fischbein MD, Puster M, Drndic M. *Nano Lett.* 2010; 10:2155–2161. [PubMed: 20469842]
47. Sykora M, Koposov AY, McGuire JA, Schulze RK, Tretiak O, Pietryga JM, Klimov VI. *ACS Nano.* 2010; 4:2021–2034. [PubMed: 20369900]
48. Choi JJ, Luria J, Hyun B-R, Bartnik AC, Sun L, Lim Y-F, Marohn JA, Wise FW, Hanrath T. *Nano Lett.* 2010; 10:1805–1811. [PubMed: 20420458]
49. Law M, Luther JM, Song Q, Hughes BK, Perkins CL, Nozik AJ. *J. Am. Chem. Soc.* 2008; 130:5974–5985. [PubMed: 18396872]
50. Barkhouse DAR, Pattantyus-Abraham AG, Levina L, Sargent EH. *ACS Nano.* 2008; 2:2356–2362. [PubMed: 19206403]
51. Baik SJ, Kim K, Lim KS, Jung S, Park Y-C, Han DG, Lim S, Yoo S, Jeong S. *J. Phys. Chem. C.* 2011; 115:607–612.
52. Klem EJD, Shukla H, Hinds S, MacNeil DD, Levina L, Sargent EH. *Appl. Phys. Lett.* 2008; 92:212105.
53. van Huis MA, Kunneman LT, Overgaag K, Xu Q, Pandraud G, Zandbergen HW, Vanmaekelbergh D. *Nano Lett.* 2008; 8:3959–3963. [PubMed: 18816148]
54. Xu BS, Tanaka SI. *Acta Mater.* 1998; 46:5249–5257.
55. Sutter E, Sutter P, Zhu Y. *Nano Lett.* 2005; 5:2092–2096. [PubMed: 16218744]
56. Korgel BA, Zaccheroni N, Fitzmaurice D. *J. Am. Chem. Soc.* 1999; 121:3533–3534.
57. Sandhyarani N, Antony MP, Selvam GP, Pradeep T. *J. Chem. Phys.* 2000; 113:9794–9794.
58. Constantinides MG, Jaeger HM, Li X, Wang J, Lin X-M. *Z. Kristallogr.* 2007; 222:595–600.
59. Robel I, Lin X-M, Sprung M, Wang J. *J. Phys.: Condens. Matter.* 2009; 21:264011–264011.
60. Luedtke WD, Landman U. *J. Phys. Chem.* 1996; 100:13323–13329.
61. Pérez-Dieste V, Castellini OM, Crain JN, Eriksson MA, Kirakosian A, Lin JL, McChesney JL, Himpel FJ, Black CT, Murray CB. *Appl. Phys. Lett.* 2003; 83:5053–5053.
62. Takagi M. *J. Phys. Soc. Jpn.* 1954; 9:359–363.
63. Goldstein AN, Echer CM, Alivisatos AP. *Science.* 1992; 256:1425–1427. [PubMed: 17791609]
64. Sigman MB, Saunders AE, Korgel BA. *Langmuir.* 2004; 20:978–983. [PubMed: 15773133]

65. Smith DK, Goodfellow B, Smilgies D-M, Korgel BA. J. Am. Chem. Soc. 2009; 131:3281–3290. [PubMed: 19216526]
66. Heiney, P. Datasqueeze Software. <http://www.datasqueezesoftware.com/>
67. Hammersley, AP. ESRF Internal Report; ESRF97HA02T. 1997.
68. Murray CB, Kagan CR, Bawendi MG. Science. 1995; 270:1335–1338.
69. Korgel BA, Fitzmaurice D. Phys. Rev. B. 1999; 59:14191–14191.
70. Korgel BA, Fullam S, Connolly S, Fitzmaurice D. J. Phys. Chem. B. 1998; 102:8379–8388.
71. Guinier, A.; Fournet, G. Small-Angle Scattering of X-Rays. New York: Wiley; 1955.
72. Glatter, O.; Kratky, O. Small-Angle X-Ray Scattering. New York: Academic Press Inc.; 1982.
73. Lee B, Podsiadlo P, Rupich S, Talapin DV, Rajh T, Shevchenko EV. J. Am. Chem. Soc. 2009; 131:16386–16388. [PubMed: 19863066]
74. The density of PbSe, oleic acid, hexane, and toluene are 8.27 g/cm³, 0.895 g/cm³, 0.6548 g/cm³, and 0.8669 g/cm³, respectively. The relative weight fractions of PbSe, oleic acid, and solvent in the bcc superlattice at room temperature were calculated by assuming that the volume (and weight) of 6.6 nm diameter PbSe nanocrystal cores is fixed in the bcc unit cell and that the volume contraction of the superlattice as it was heated to 140°C was due to the evaporation of the solvent ($V_{bcc}^{RT} = (a_{bcc, SAXS}^{RT})^3 = 1256 \text{ nm}^3$; $V_{bcc}^{140C} = (a_{bcc, SAXS}^{140C})^3 = 979 \text{ nm}^3$). The remainder of the unit cell volume (e.g., $V_{bcc, cell} - V_{cores} - V_{solvent}$) was assumed to be filled by a constant volume of ligands. The exact ratio of hexane to toluene trapped in the superlattice is not known, so the expected weight fraction of solvent in the superlattice at room temperature was calculated for the two extreme cases of pure hexane and pure toluene, expecting that the actual case lies somewhere in between. If all of the trapped solvent is hexane, the superlattice at room temperature would consist of 76.0 wt% PbSe, 18.5 wt% oleic acid, and 5.5 wt% hexane. If all the trapped solvent is toluene, the superlattice would consist of 74.6 wt% PbSe, 18.2 wt% oleic acid, and 7.2 wt% toluene.
75. Tomaev VV, Makarov LL, Tikhonov PA, Solomennikov AA. Glass Phys. Chem. 2004; 30:349–355.

Figure 1.

TEM images of PbSe nanocrystals drop-cast from relatively (a) dilute or (b–c) concentrated dispersions in 1:1 mixture by volume of hexane and toluene. (a) A monolayer of PbSe nanocrystals with hexagonal order; (b) a PbSe nanocrystal superlattice film of several nanocrystals thick (~20 nm) with bcc symmetry. (c) A region of sample with the coexistence of thicker bcc superlattice films and monolayers of hexagonally ordered nanocrystals.

Figure 2.

Transmission SAXS of a PbSe nanocrystal superlattice. The peak positions $q/q^* = \sqrt{1}, \sqrt{2}, \sqrt{3}, \sqrt{4}$ are consistent with reflections from the (110), (200), (211), and (220) lattice planes of a bcc superlattice. The inset shows the experimentally measured 2D scattering pattern. The d -spacings of the first four diffraction peaks correspond to $d = 2\pi/q = 7.61$ nm, 5.44 nm, 4.40 nm and 3.80 nm, for an average lattice constant of $a_{bcc,SAXS} = 10.79$ nm.

Figure 3.

(Left) TEM image of a PbSe nanocrystal superlattice. A (100) superlattice plane has been imaged. The body-centered positions were also observed at different focal depths with high-resolution TEM (see Supporting Information). (Right) Schematic that shows how certain d-spacings can be directly measured from the TEM image. The measured lattice spacings of 10.57 nm, 7.63 nm, and 4.71 nm, correspond to the (100), (110), and (210) d-spacings of a bcc superlattice. The corresponding lattice constant of $a_{TEM} = 10.63 \text{ nm}$ is close to that measured by SAXS, $a_{SAXS} = 10.79 \text{ nm}$.

Figure 4.

SAXS of PbSe nanocrystals dispersed in hexane. The radially integrated 2D scattering intensity (inset) is plotted as (a) $I(q)$ vs. q and (b) $I(q) \times q^4$ vs. q (Porod plot), with the data normalized to the scattering intensity of the first peak maximum in the Porod plot at $q = 0.81 \text{ nm}^{-1}$. The best fit of Eqn (1) (solid line) to the scattering data ($\circ$) gives an average diameter of $6.60 \text{ nm} \pm 0.79 \text{ nm}$.

Figure 5.

Contour plot of the SAXS intensity obtained from a PbSe nanocrystal superlattice with an initial bcc structure as it was heated from 28°C to 350°C. Each slice of the contour plot is a radial integration of 2D scattering profiles (representative patterns shown in upper panel). Between 25°C and 110°C, the superlattice exhibits bcc structure, with the diffraction peaks shifting to slightly larger q —indicating a slight lattice contraction upon heating. Above 110°C, the superlattice contracts more significantly with a gradual loss of order as indicated by the appearance of a second order diffraction peak (denoted by star) associated with an amorphous assembly. At 150°C, the superlattice structure has completely disappeared as indicated by the loss of the bcc (200), (211) and (220) diffraction peaks. At 168°C, all of the diffraction rings have disappeared, indicating the complete loss of local positional order and the onset of sintering. Above 168°C, sintered grains grow in size, as indicated by the shift in scattering intensity to lower q . Between 200°C and 250°C, the scattering intensity increases at low q values, which is consistent with oxidation of the PbSe nanocrystals into PbSeO₃ nanorods.

Figure 6.

Radial integration of the 2D scattering profiles in Figure 5 of the PbSe nanocrystal superlattice at selected temperatures. The bcc peak indexing is provided. The two diffraction peaks in the blue curve at 150°C indicate that the superlattice has disordered to an amorphous structure.

Figure 7. Center-to-center nearest-neighbor spacing and the bcc superlattice constant a , calculated from the bcc (110) Bragg ring plotted as a function of temperature. The boiling temperatures (b.p.) of hexane and toluene are indicated. Note that when the temperature exceeds 110 $^{\circ}\text{C}$, the superlattice begins to lose order.

Figure 8.

a) XRD profiles of 9 nm PbSe nanocrystal films heated in air from room temperature to the indicated temperature. Oxidation of the PbSe nanocrystals to PbSeO₃ begins to occur at around 200°C. Complete transformation of PbSe to PbSeO₃ has occurred after heating to 300°C in air. TEM images at b) 25°C and c) 300°C indicate that the PbSe nanocrystals transform to nanorods upon oxidation.