

Formation of Thick, Large-Area Nanoparticle Superlattices in Lithographically Defined Geometries

Austin Akey,^{†,§} Chenguang Lu,^{†,§} Lin Yang,[‡] and Irving P. Herman^{*†}

[†]Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York 10027 and

[‡]National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York 11973

ABSTRACT Superlattices of colloidal nanocrystals hold the promise of new nanomaterials with tunable properties. The positioning and size of these structures are often poorly controlled after self-assembly from the solution phase, making studies of their properties difficult. We report the fabrication of ~ 100 layer thick, three-dimensional superlattices on a substrate with controlled lateral placement. This novel fabrication technique generates long-range order over the micrometer scale and controlled placement by employing lithographic patterning and microfluidic flow.

KEYWORDS Nanoparticles, superlattice, self assembly, microfluidics, ordered array

The formation of varied types of ordered films of colloidal nanoparticles (NPs)^{1–7} holds the promise of new materials with tunable properties that differ from those of disordered assemblies; however, the careful measurement of their properties, including potential collective properties,^{8–10} and analysis of potential applications^{11,12} has been limited by the difficulty in fabricating thick superlattices with controllable dimensions and placement. Controlled drying of solutions of monodisperse nanoparticles has produced single- or several-layer superlattices with lateral dimensions up to the millimeter range.^{13–19} Many micrometer-dimension, 3D supercrystals of monodisperse nanoparticles have been reported, formed by extended drying of nanoparticle solutions in beakers (and sometimes collected on substrates).^{20–22}

We form large 3D supercrystals of nanoparticles by controlling solvent evaporation in a lithographically defined structure in which solution is entrained into capillary channels. A drop of a solution containing either CdSe or Fe₂O₃ nanoparticles dispersed in a high-boiling-point/low-boiling-point two-solvent system¹³ is placed into a central reservoir well and entrained into a series of long, narrow channels by the capillary effect as the solvents evaporate; this motion into the channels also concentrates the nanoparticles. Ordered growth of supercrystals occurs during high boiling point (bp) solvent evaporation assisted by vacuum pumping over several hours. The presence of a high boiling point solvent slows drying sufficiently to allow crystallization. The ability to fabricate ~ 100 layer superlattices with $\sim 1\ \mu\text{m}$ lateral dimensions opens up opportunities for diverse optical,

electronic, magnetic, and mechanical investigations of their emergent collective properties and potential applications.

The synthesis of the colloidal crystalline CdSe and γ -Fe₂O₃ nanoparticles is described in the Supporting Information. Silicon $\langle 100 \rangle$ wafers were patterned using electron-beam lithography (see Supporting Information) to form a large reservoir ($\sim 500\ \mu\text{m}$ diameter) connected to several capillary channels of the same depth ($1\text{--}8\ \mu\text{m}$ wide, $10\text{--}100\ \mu\text{m}$ long, $1\text{--}3\ \mu\text{m}$ deep) radially extending from the reservoir perimeter (Figure 1a), all confined by a $15\ \mu\text{m}$ wide wall. The wafers were stored in a drybox after fabrication and used without further surface treatment.

Under ambient conditions, $5.5\ \text{nm}$ CdSe or $8.0\ \text{nm}$ Fe₂O₃ nanoparticles (core diameters given), dispersed in a 3% decanol in xylene solution ($\sim 10^{15}$ NPs/mL), were injected to fill the reservoir. After ~ 20 min, the low boiling point solvent xylene (bp $140\ ^\circ\text{C}$) evaporated and the wafer was pumped for ~ 12 h in a vacuum chamber with base pressure typically below 100 mTorr (for the channel configuration in Figure 1a) to assist and control removal of the decanol (bp $230\ ^\circ\text{C}$).

Very thick nanoparticle films of ~ 100 layers were observed in the $1200\ \text{nm}$ deep and $3\ \mu\text{m}$ wide channels (Figure 2) and $1\text{--}3$ layers were seen in the central reservoir, along with multilayer lips about the reservoir periphery. Atomic force microscopy (AFM) (DI Instrument) showed the $5.5\ \text{nm}$ CdSe nanoparticle films in Figure 2a were $\sim 790\ \text{nm}$ thick and the $8.0\ \text{nm}$ Fe₂O₃ nanoparticle films in Figure 2b were $\sim 950\ \text{nm}$ thick.

The film in the channels was found to be a highly ordered, multilayer, nanoparticle superlattice, by using scanning electron microscopy (SEM) (Hitachi 4700). The high degree of order in the top layer is seen across the entire film, as in Figures 2 and 3. Figure 3b shows a terrace structure with

* To whom correspondence should be addressed.

§ These authors contributed equally.

Received for review: 01/14/2010

Published on Web: 03/31/2010

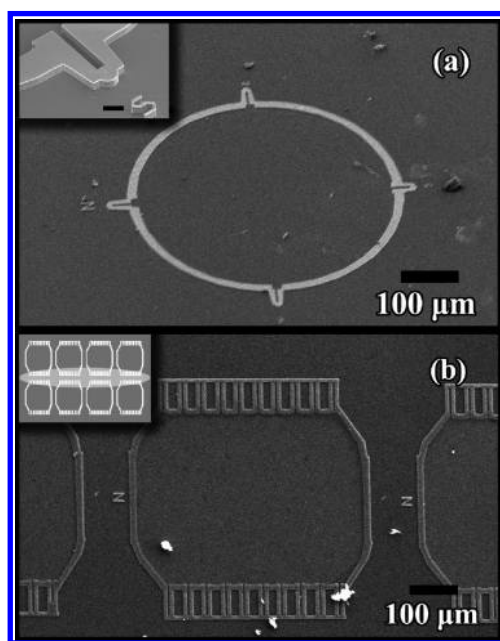


FIGURE 1. (a) SEM micrograph of a typical reservoir/channel pattern, consisting of a $\sim 500\ \mu\text{m}$ central reservoir with several capillary channels (typically 4–8) extending radially from the perimeter, with the channel magnified in the inset (scale bar of $10\ \mu\text{m}$). (b) SEM of alternative geometry used for small-angle X-ray scattering measurements which places large numbers of channels in parallel to improve signal-to-noise, with an inset showing the region typically analyzed by X-ray scattering (schematic, not drawn to scale).

ordered layers and apparent single nanoparticle high steps every ~ 8 nanoparticles. The superlattices extend across the width of the channel, often with long cracks running parallel to the channel walls (Figures 2c and 2d) and sometimes as contiguous domains of slightly different heights (Figure 2d), leading to grains of highly ordered nanoparticles with lateral dimensions typically $\sim 1\ \mu\text{m}$.

The channels contain a much thicker film of nanoparticles than the reservoir, which suggests that many nanoparticles were entrained into the channels from the reservoir and the lip about it by the capillary effect; this occurs during evaporation of the solvents in air and under vacuum. Such flow continues as the drying proceeds because only an $\sim 25\ \text{nm}$ thick film would form for a channel filled to the top with the initial solution of nanoparticles after xylene evaporation. Flow into the channels is self-limited to a fraction of the channel height due to the lessening exposed wall, and this avoids overfilling of the channels.

SEM of the top surface of the superlattice suggests hexagonal packing of nanoparticles. Some defects and dislocations are observed on the top surface, including point defects (Figures 2b and 3), edge dislocations, and screw dislocations (Figure 3a), which should affect “bulk” collective optical, electronic, and magnetic properties little, but could affect mechanical properties. Several samples had small fractional areas with what appears to be hcp $\langle 110 \rangle$ planes on the top surface ($< 5\%$) (Figure 3c) or a herringbone type reconstruction ($< 1\%$).²³

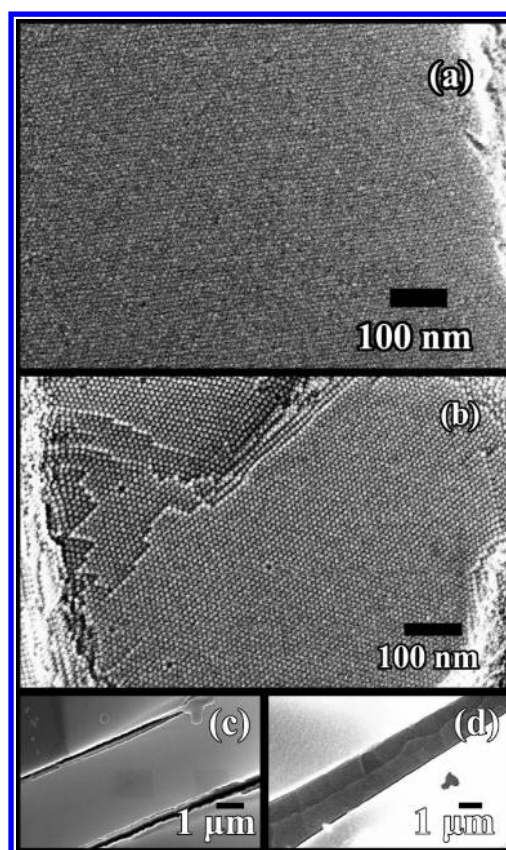


FIGURE 2. (a) SEM micrograph of the top surface of a thick nanoparticle superlattice, composed of $5.5\ \text{nm}$ CdSe nanoparticles. Hexagonal order of the top surface is evident. (b) SEM micrograph of the top surface of a superlattice composed of $8.0\ \text{nm}$ Fe_2O_3 maghemite nanoparticles. Hexagonal order is observed again, along with a number of point defects. Lower magnification SEM micrographs of the (c) CdSe and (d) Fe_2O_3 nanoparticle superlattices, show fracture near the walls in the former and micrometer-dimension regions in the latter.

Examination of the terraces on the Fe_2O_3 nanoparticle superlattice surface, across as many as 20 layers, suggests hexagonal AB-stacking ordering with a $\langle 001 \rangle$ top surface. Longer range order below the surface of the Fe_2O_3 nanoparticle superlattices was also assessed by cleaving, in which the channels were scribed across with a diamond wafer scribe (Figure 4a). A very high degree of order through the film thickness is seen to within 1–2 layers of the bottom of the nanoparticle film (where disorder was due either to film growth or the cleaving procedure).

The superlattices of Fe_2O_3 nanoparticles were characterized by small-angle X-ray scattering (SAXS) in reflection mode using $14.5\ \text{keV}$ photons (X9 beamline at the National Synchrotron Light Source) (Figure 4b). To obtain an adequate signal-to-noise ratio, samples with many (~ 160) parallel channels (Figure 1b) filled with supercrystals were probed by the $\sim 0.2\ \text{mm} \times 0.3\ \text{mm}$ beam. The thick superlattice is highly ordered, and has hexagonal AB-stacking structure (space group $P6_3/mmc$) with $a = b = 9.7 \pm 0.1\ \text{nm}$ and $c = 14.0 \pm 0.1\ \text{nm}$ lattice constants (which is consistent with the SEMs). This is similar to hcp but with uniaxial lattice

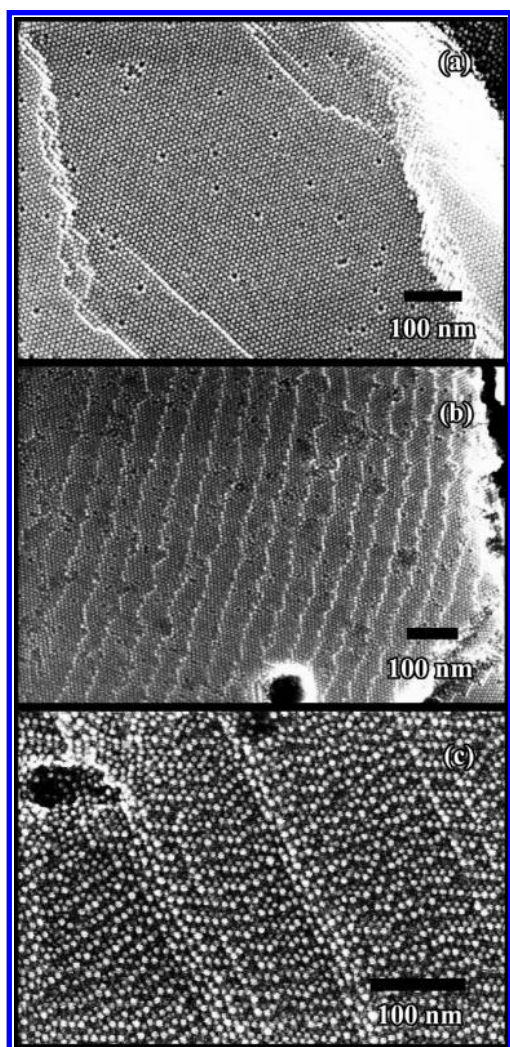


FIGURE 3. SEM micrographs of top surfaces of 8.0 nm Fe_2O_3 nanoparticle superlattices. (a) Showing a screw dislocation as well as several point defects. (b) Showing a terraced structure. Each step corresponds to one layer of nanoparticles. Order is maintained through several visible layers. (c) Showing a section exposing what appears to be a hexagonal AB-stacking $\langle 110 \rangle$ facet.

compression (11 %) in the c -axis; the deviation from hcp may be due to volume loss during solvent evaporation. In addition to rings expected from a sample of randomly oriented crystal grains, peaks were observed indicating preferential alignment of the supercrystals with their $\langle 001 \rangle$ planes parallel to the substrate. Transmission scattering confirmed the high degree of transverse hexagonal ordering (Figure S1, Supporting Information). Though the hcp structure is energetically less favored than fcc for hard sphere packing,²⁴ hcp-type AB stacking has been observed in other studies of nanoparticle superlattice formation, likely because of interactions between the nanoparticle cores, including dipole–dipole interactions.^{25,26} Uniaxial compression has also been observed in binary nanoparticle superlattices.²⁷

Control of the design of the channels, drying rate, and nanoparticle concentration in the solution provides an opportunity to control fluid flow into the capillary channels and

the growth kinetics that determine the degree of order. For Fe_2O_3 nanoparticle structures, increasing the channel width beyond $\sim 4 \mu\text{m}$ led to very small polycrystalline grains, while increasing it beyond $\sim 8 \mu\text{m}$ led to little fluid entrainment into the channels. Slowing the rate of decanol evaporation by increasing the pressure in the chamber improved the degree of order, for the channel configuration in Figure 1b, from amorphous assembly (Figure 5a) at lower pressures (~ 100 mTorr) to ordered assembly (Figure 5b) at higher pressures (~ 25 Torr). Increasing the nanoparticle concentration in the solution changed the film structure, for the channel configuration in Figure 1a, from one with no long-range order [disordered (amorphous) or locally ordered (polycrystalline) regions] (Figure 5c) for $\sim 10^{14}$ NPs/mL (in the 3% decanol/xylene solution), to one with a very high degree of hexagonal AB-stacking order for $\sim 10^{15}$ NPs/mL (Figures 2b, 3, 4a), and then to one with columnar structures of locally hexagonal AB-stacking ordered regions (Figure 5d) for $\sim 10^{16}$ NPs/mL. Films formed using $\sim 10^{14}$ Fe_2O_3 NPs/mL (Figure 5c) were almost as thick (790 nm), though less densely packed, as those formed with $\sim 10^{15}$ NPs/mL (and the lip of nanoparticles was significantly narrower), which is further evidence for self-limiting flow during drying.

In Figure 2c (and Supporting Information Figure S2), long cracks can be seen between the walls of the lithographically defined capillary channel and the supercrystal. These cracks run along the length of the channel, and are believed to have been caused by volume contraction of the supercrystal during solvent evaporation. They are observed to always run parallel to the wall of the confining channel, closely copying the local morphology of the wall, independent of the local superlattice crystal plane. This suggests that the energy required to cleave the supercrystal is higher than the energy of adhesion between the supercrystal and the channel wall. The channel geometry determines the shape and position of the supercrystal by confining the solvent and nanoparticles during drying, but the final size of the supercrystal is smaller than the channel and is determined by the volume contraction during the final stage of solvent evaporation.

In previous studies, the formation of superlattices of colloidal nanoparticles has been found to be sensitive to many parameters,^{13,14,16} including temperature, pressure, addition of extra polar molecules/ligands, nanoparticle concentration, etc. This has resulted in poor repeatability and has made control of formation difficult, due to the complexity and sensitivity of superlattice formation to the local environment. Our versatile microfluidics technique provides the direct control of the immediate environment necessary to probe the superlattice formation mechanism and improve repeatability; it localizes superlattice formation in a lithographically defined structure whose design parameters determine nanoparticle concentration as well as solvent flow and evaporation conditions. In addition, the two-solvent system partially separates the nanoparticle concentration step from the crystallization step, permitting some control

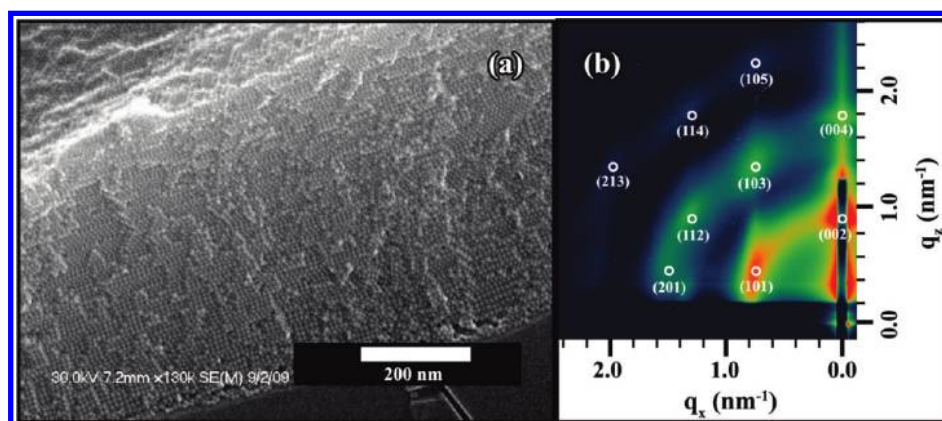


FIGURE 4. (a) SEM micrograph of a cross-sectional view of 8.0 nm Fe_2O_3 nanoparticle superlattice, showing a high degree of nanoparticle ordering through the thickness of the film. The top of the film has been damaged or flaked during cross-sectioning. (b) SAXS data with crystal planes corresponding to hexagonal AB-stacking structure with $a = b = 9.7$ nm and $c = 14.0$ nm lattice constants overlaid. The presence of rings indicates long-range order, while the presence of spots shows preferential orientation of individual crystal grains (in this case, ordering so that the $\langle 001 \rangle$ planes are parallel to the substrate).

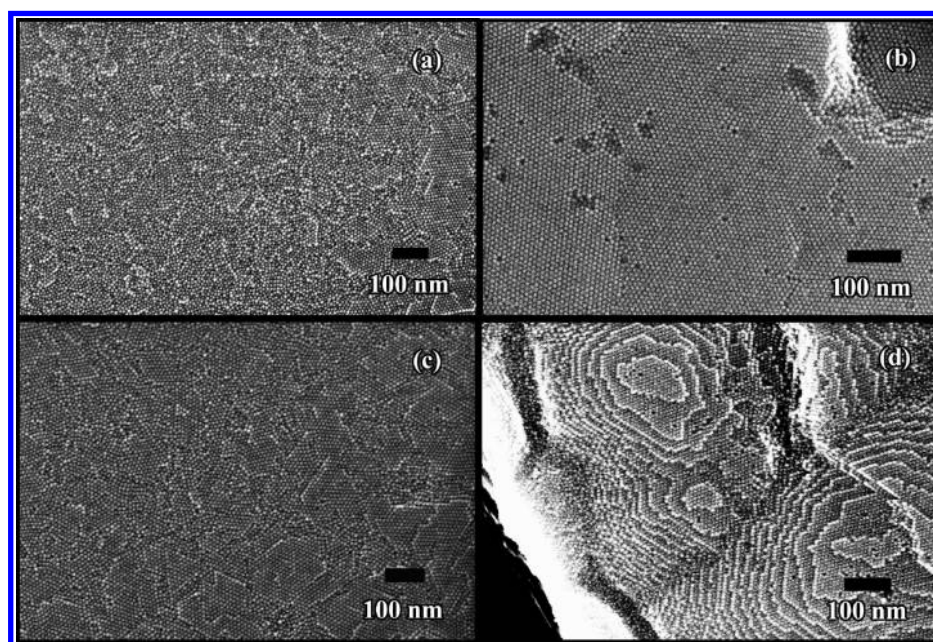


FIGURE 5. SEM micrographs of top surface of thick 8.0 nm Fe_2O_3 superlattices formed under different conditions. (a) Lower base pressure during drying (100 mTorr), 10^{15} NPs/mL, which leads to polycrystalline/amorphous order, (b) higher base pressure during drying (25 Torr air), 10^{15} NPs/mL, which leads to large supercrystal grains, (c) initial nanoparticle concentration, $\sim 10^{14}$ NPs/mL (much lower than the $\sim 10^{15}$ NPs/mL standard in Figures 2b,d, 3, and 4), which leads to polycrystalline order, (d) initial nanoparticle concentration, $\sim 10^{16}$ NPs/mL (much higher than the $\sim 10^{15}$ NPs/mL standard), which leads to columnar grains that are highly ordered.

over both. In Figure 5, we demonstrate our ability to adjust and analyze the impact of two key formation parameters: the solvent evaporation rate and the starting nanoparticle concentration. These results are highly repeatable, making systematic optimization and investigation of the formation mechanism possibilities for future research.

Acknowledgment. The authors thank Stephen O'Brien for use of his synthesis facilities. This work was supported primarily by the MRSEC program of the National Science Foundation (DMR-0213574), the NSEC program of the NSF

(CHE-0641523), and by the New York State Office of Science, Technology, and Academic Research (NYSTAR). Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

Supporting Information Available. Detailed descriptions of nanoparticle and substrate preparation, nanoparticle deposition, and small-angle X-ray scattering. This material is available free of charge via the Internet at <http://pubs.acs.org>.

REFERENCES AND NOTES

- (1) Talapin, D. V.; Lee, J.-S.; Kovalenko, M. V.; Shevchenko, E. V. *Chem. Rev.* **2010**, *110* (1), 389–458.
- (2) Park, S. Y.; Lytton-Jean, A. K. R.; Lee, B.; Weigand, S.; Schatz, G. C.; Mirkin, C. A. *Nature* **2008**, *451* (7178), 553–556.
- (3) Nykypanchuk, D.; Maye, M. M.; van der Lelie, D.; Gang, O. *Nature* **2008**, *451* (7178), 549–552.
- (4) Kalsin, A. M.; Fialkowski, M.; Paszewski, M.; Smoukov, S. K.; Bishop, K. J. M.; Grzybowski, B. A. *Science* **2006**, *312* (5772), 420–424.
- (5) Rogach, A. L.; Talapin, D. V.; Shevchenko, E. V.; Kornowski, A.; Haase, M.; Weller, H. *Adv. Funct. Mater.* **2002**, *12* (10), 653–664.
- (6) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545–610.
- (7) Baker, J. L.; Widmer-Cooper, A.; Toney, M. F.; Geissler, P. L.; Alivisatos, A. P. *Nano Lett.* **2010**, *10* (1), 195–201.
- (8) Chen, C.-F.; Tzeng, S.-D.; Chen, H.-Y.; Lin, K.-J.; Gwo, S. *J. Am. Chem. Soc.* **2008**, *130* (3), 824–826.
- (9) Black, C. T.; Murray, C. B.; Sandstrom, R. L.; Sun, S. H. *Science* **2000**, *290* (5494), 1131–1134.
- (10) Chen, M.; Kim, J.; Liu, J. P.; Fan, H.; Sun, S. *J. Am. Chem. Soc.* **2006**, *128* (22), 7132–7133.
- (11) Urban, J. J.; Talapin, D. V.; Shevchenko, E. V.; Kagan, C. R.; Murray, C. B. *Nat. Mater.* **2007**, *6* (2), 115–121.
- (12) Talapin, D. V.; Murray, C. B. *Science* **2005**, *310* (5745), 86–89.
- (13) Lu, C.; Chen, Z.; O'Brien, S. *Chem. Mater.* **2008**, *20* (11), 3594–3600.
- (14) Shevchenko, E. V.; Talapin, D. V.; Kotov, N. A.; O'Brien, S.; Murray, C. B. *Nature* **2006**, *439* (7072), 55–59.
- (15) Bigioni, T. P.; Lin, X. M.; Nguyen, T. T.; Corwin, E. I.; Witten, T. A.; Jaeger, H. M. *Nat. Mater.* **2006**, *5* (4), 265–270.
- (16) Redl, F. X.; Cho, K. S.; Murray, C. B.; O'Brien, S. *Nature* **2003**, *423* (6943), 968–971.
- (17) Overgaag, K.; Evers, W.; de Nijs, B.; Koole, R.; Meeldijk, J.; Vanmaekelbergh, D. *J. Am. Chem. Soc.* **2008**, *130* (25), 7833–7835.
- (18) Shevchenko, E. V.; Talapin, D. V.; O'Brien, S.; Murray, C. B. *J. Am. Chem. Soc.* **2005**, *127* (24), 8741–8747.
- (19) Chen, Z. Y.; Moore, J.; Radtke, G.; Sirringhaus, H.; O'Brien, S. *J. Am. Chem. Soc.* **2007**, *129* (50), 15702–15709.
- (20) Shevchenko, E.; Talapin, D.; Kornowski, A.; Wiekhorst, F.; Kotzler, J.; Haase, M.; Rogach, A.; Weller, H. *Adv. Mater.* **2002**, *14* (4), 287–290.
- (21) Talapin, D. V.; Shevchenko, E. V.; Kornowski, A.; Gaponik, N.; Haase, M.; Rogach, A. L.; Weller, H. *Adv. Mater.* **2001**, *13* (24), 1868–1871.
- (22) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, *270* (5240), 1335–1338.
- (23) Chambliss, D. D.; Wilson, R. J.; Chiang, S. *Phys. Rev. Lett.* **1991**, *66* (13), 1721–1724.
- (24) Norris, D. J.; Arlinghaus, E. G.; Meng, L. L.; Heiny, R.; Scriven, L. E. *Adv. Mater.* **2004**, *16* (16), 1393–1399.
- (25) Talapin, D. V.; Shevchenko, E. V.; Murray, C. B.; Titov, A. V.; Kral, P. *Nano Lett.* **2007**, *7* (5), 1213–1219.
- (26) Hynninen, A.-P.; Dijkstra, M. *Phys. Rev. Lett.* **2005**, *94* (13), 138303.
- (27) Smith, D. K.; Goodfellow, B.; Smilgies, D. M.; Korgel, B. A. *J. Am. Chem. Soc.* **2009**, *131* (9), 3281–3290.