

Columnar Self-Assembly of Colloidal Nanodisks

Aaron E. Saunders,^{†,‡} Ali Ghezelbash,^{†,‡} Detlef-M. Smilgies,[§]
Michael B. Sigman, Jr.,[‡] and Brian A. Korgel^{*,‡}

Department of Chemical Engineering, Texas Materials Institute, Center for Nano- and Molecular Science and Technology, The University of Texas at Austin, Austin, Texas 78712, and Cornell High Energy Synchrotron Source (CHESS), Cornell University, Ithaca, New York 14853

Received October 13, 2006; Revised Manuscript Received November 13, 2006

ABSTRACT

The self-assembly of sterically stabilized colloidal copper sulfide nanodisks, 14–20 nm in diameter and 5–7 nm thick, was studied. The nanodisks were observed by electron microscopy and small-angle X-ray scattering to form columnar arrays when evaporated as thin films from concentrated dispersions. These superstructured nanomaterials might give rise to technologically useful properties, such as anisotropic electrical transport and electrorheological and optical properties.

With current synthetic capability to make a variety of colloidal nanocrystals of different materials, including metals, magnets, semiconductors, and ferroelectrics, with controlled size (<10 nm) and in many cases shape, efforts are underway to develop their modular assembly as a general strategy to build nanostructured materials with new properties.^{1–9} Inorganic “building blocks” are synthesized with well-defined size, shape, and composition and then self-assembled into periodically ordered superlattices with characteristic dimensions much smaller than what is possible from conventional lithographic patterning and fabrication approaches. The nanocrystals are typically coated with a thin (1–2 nm) organic layer that provides dispersibility, stabilizes their size (and shape), and determines the interparticle separation when the solvent is removed. These nanocrystal superlattice composites may exhibit a wide range of new properties as a result of the size-tunable physical properties of the nanocrystals and the controllable (interparticle separation dependent) collective interactions between nanocrystals in the assembly. Therefore, nanocrystal superlattices have been proposed as the basis for a wide range of new technologies, including thermoelectrics,¹⁰ photovoltaics,¹¹ photodetectors,¹² light-emitting diodes,^{13,14} transistors,^{15,16} memory storage,^{17–19} and chemical sensing.^{20,21}

Inorganic colloidal nanocrystals with anisotropic shape not only are interesting building blocks for superlattices but also may form the basis for a new class of mineral liquid crystal materials.^{22–25} The majority of liquid crystalline materials studied to date are composed of flexible organic molecules, and these are an extremely versatile and useful class of materials.²⁶ However, liquid crystals of inorganic “mesogens” could have some unique and important properties such as high thermal stability, a well-defined rigid structure with weak interparticle attractions and a very short range soft repulsion that might give rise to unique rheological properties. Nanocrystals can be made with a wide range of compositions, including those with magnetic and light-emitting properties, providing the opportunity to design in variable responses to different kinds of applied external fields, including electric, magnetic, and optical. In comparison to micrometer or submicrometer colloidal particles, nanocrystals do not settle under gravity and their fast diffusion rates should make for very fast equilibration and switching times.

Liquid crystalline order has been observed from collections of rod-shaped nanocrystals in concentrated dispersions,^{22–24} at the air–water interface of a Langmuir–Blodgett trough,²⁷ and in evaporated films.^{9,28–33} For example, concentrated dispersions of CdSe nanorods have exhibited both nematic and smectic order.²⁴ Collections of disk-shaped nanocrystals should also exhibit orientational order with sufficient concentration (and sufficiently narrow size and shape distributions),^{34–36} as has been observed in dispersions and films of larger submicrometer-size colloidal disks of Al(OH)₃ (gibb-

* Corresponding author: e-mail, korgel@che.utexas.edu; telephone, (512) 471-5633; fax, (512) 471-7060.

[†] These authors contributed equally to this work.

[‡] Department of Chemical Engineering, Texas Materials Institute, Center for Nano- and Molecular Science and Technology, The University of Texas at Austin.

[§] Cornell High Energy Synchrotron Source (CHESS), Cornell University.

site) and $\text{Ni}(\text{OH})_2$.^{37–40} Indeed, electron microscopy images of evaporated films of nanodisks in the literature have hinted at long-range orientational order.^{41–46} In this Letter, we show transmission and scanning electron microscopy (TEM and SEM) images of copper sulfide (CuS and Cu_2S) nanodisks that appear to have columnar order. Small-angle X-ray scattering (SAXS) is then employed to study CuS nanodisk self-assembly and confirms their organization into columnar superlattices. High-intensity synchrotron radiation was used for these studies, which enabled time-dependent SAXS data to be acquired that revealed the isotropic \rightarrow columnar phase transition of the CuS nanodisks during solvent evaporation. It is noteworthy that the colloidal copper sulfide nanodisks studied here have diameters that are an order of magnitude smaller than those of other colloidal disk-shaped particles observed with columnar order in concentrated dispersions and evaporated films in the recent past, such as gibbsite ($\text{Al}(\text{OH})_3$)⁴⁷ and $\text{Ni}(\text{OH})_2$.⁴⁸

Copper sulfide nanodisks with two different compositions, Cu_2S and CuS , were synthesized by two different approaches: a solventless synthesis^{42,49} and a solution-based arrested precipitation.⁴⁶ The solventless synthesis yields nanodisks of high chalcocite Cu_2S , which has a hexagonal crystal structure.^{42,49} The arrested precipitation in a hot solvent produces under certain reaction conditions nanodisks of covellite CuS , which also has hexagonal crystal structure.⁴⁶ Both methods provide relatively size- and shape-monodisperse nanodisks with diameters ranging from 14 to 20 nm and thicknesses between 5 and 7 nm, with the Cu_2S nanodisks tending to be slightly thinner than the CuS nanodisks. Both CuS and Cu_2S nanodisks are readily dispersible in nonpolar organic solvents and can be evaporated as thin films and studied by TEM and SEM. The Cu_2S nanodisks, however, are not as stable in solution as the CuS nanodisks and the amount of Cu_2S product obtained by the solventless synthesis is smaller than the CuS nanodisks obtained by arrested precipitation. Therefore, only the CuS nanodisks were studied by SAXS.

Figures 1 and 2 show TEM and SEM images of CuS and Cu_2S nanodisks evaporated from concentrated dispersions onto various substrates. The data show that the disks tend to stack face-to-face with a variety of orientations with respect to the substrate—either face-down on the substrate (sometimes as a monolayer), face-to-face in rows with their edges perpendicular to the substrate, or into supercrystals that are not apparently associated with the substrate. Although the shape of the Cu_2S and CuS disks is very similar—the only difference being that the Cu_2S disks are slightly thinner—there are observable differences in their assembly with respect to orientation with the substrate. The CuS nanodisks tend to lay face-down on the substrate, whereas the Cu_2S nanodisks generally orient edge-down unless isolated from other nanodisks. For example, Figure 1A shows CuS nanodisks oriented face-down in a monolayer (as illustrated in Figure 1E(i)). In contrast, Cu_2S nanodisks tend not to orient face-down on the substrate. Instead, Cu_2S nanodisks tend to align face-to-face, forming linear ribbons as they have in Figure 1B. Extended linear ribbon assemblies

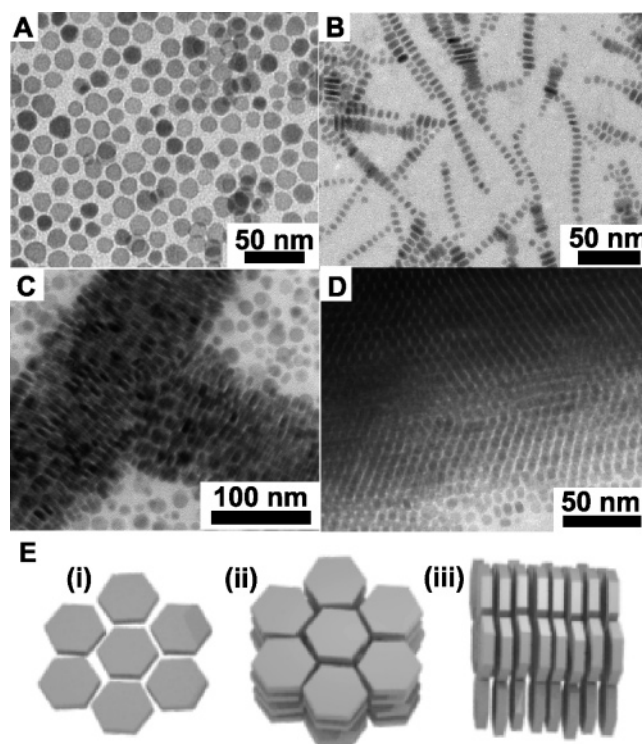


Figure 1. TEM images of CuS and Cu_2S nanodisks. (A) CuS nanodisks in a monolayer on their faces. (B) Linear chains of stacked Cu_2S nanodisks. (C) CuS nanodisks crystallized into a “T”-shaped structure. (D) Ordered Cu_2S nanodisk assembly oriented parallel to the substrate. (E) Illustrations of different nanodisk assemblies and orientations on the substrate: (i) a monolayer; (ii) columnar assembly with columns oriented perpendicular to the substrate; (iii) columnar assembly with columns oriented parallel to the substrate.

like these are typical for Cu_2S nanodisks but are rarely formed by CuS nanodisks. At higher concentrations, Cu_2S nanodisks crystallize into three-dimensional supercrystals as shown in the TEM image in Figure 1D and in the SEM images in panels B and C of Figure 2. In contrast, CuS nanodisks tend to orient face-down on the substrate even at high concentrations when superlattices form. For example, Figure 2A shows an SEM image of CuS nanodisks that have formed close-packed columns of disks extending from the surface (as illustrated in Figure 1E(ii)). There are, however, instances when CuS nanodisks do not assemble face-down on the substrate. Figure 1C shows CuS nanodisks that have crystallized into a “T”-shaped aggregate oriented with the disks edge-down on the substrate. These “T”-shaped structures are observed quite regularly in TEM images, especially in the corners of the copper grid, and it appears that the base of the “T” nucleates off the edge of the top of the “T”, perhaps in solution toward the end of the evaporation process.

Although the orientation of the nanodisks with respect to the substrate depends strongly on the nanodisk composition, with CuS tending to orient face-down on the substrate and Cu_2S orienting edge-down, there does appear to be some influence of the substrate on the orientation of the evaporated CuS nanodisks as well. Although the CuS disks were observed to favor deposition with their faces in contact with the substrate, there was a much higher tendency for the disks

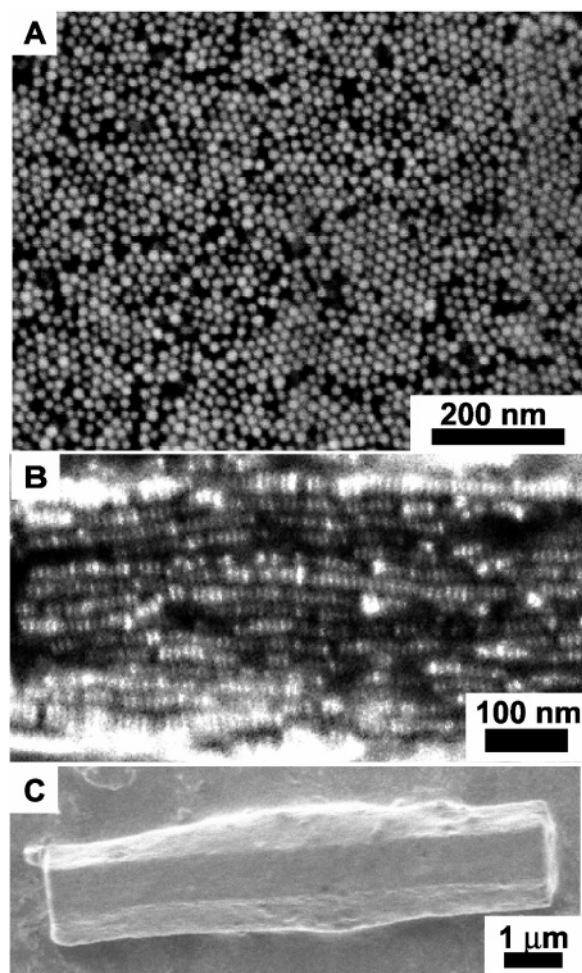


Figure 2. SEM images of CuS and Cu₂S nanodisks on Si substrates with a native oxide layer. (A) CuS nanodisks evaporated from toluene, assembled into close-packed columns (a columnar phase) with the columns oriented perpendicular to the substrate. (B) Cu₂S nanodisks evaporated from toluene assembled in a columnar phase with the columns oriented parallel to the substrate. (C) Low-resolution image of the nanodisks in (B): they are packed together to form a faceted colloidal crystal of Cu₂S nanodisks.

to orient face-down on the oxide-coated Si substrates (imaged by SEM) than on the carbon-coated TEM grids. It is unclear why the substrate influences the nanodisk orientation in this way, but the oxide-coated Si substrates are more polar than the carbon coating of the TEM substrates. Similar substrate-dependent nanodisk orientation was observed by Shevchenko and co-workers with LaF₃ disks as well.⁶ The orientation of deposited Cu₂S did not appear to be influenced by the substrate and always assembled edge-down on both TEM substrates and oxide-coated Si. Although more data are needed to be certain, it appears that nanodisks of Cu₂S have stronger attractive forces between disk faces than CuS, perhaps as a result of stronger electric dipole coupling, as hexagonal Cu₂S has been reported to be ferroelectric.^{50,51}

TEM and SEM images provide excellent snapshots of nanodisk order, but only on very small local length scales (micrometers). Scattering techniques, such as SAXS, supplement TEM and SEM imaging techniques by probing very large sample volumes (~mm³) to give an average description of average structural organization in the material. Since the

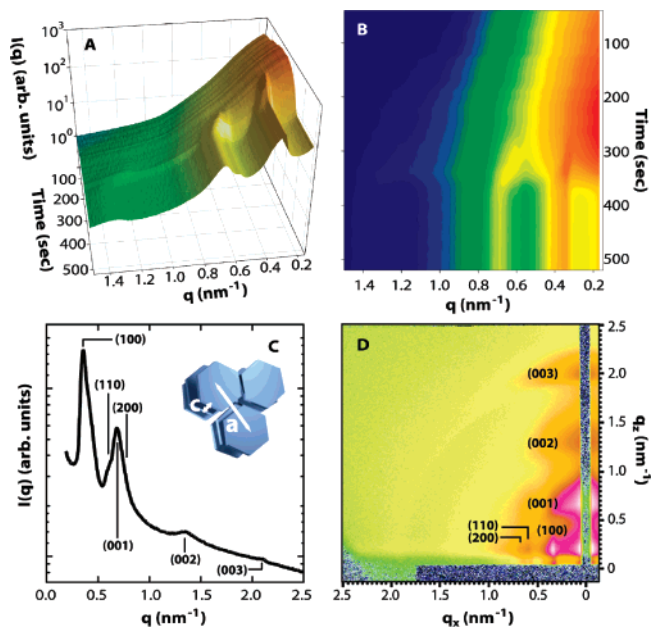


Figure 3. (A) Background-subtracted time-resolved synchrotron SAXS from an evaporating toluene dispersion of CuS nanodisks on a Kapton substrate. The initial featureless scattering profiles indicate that the nanodisks are well-dispersed in solution. As toluene evaporates, the nanodisks begin to crystallize and give rise to sharp diffraction peaks. (B) Scattering data in (A) replotted as a contour plot; the intensity scale is logarithmic with red corresponding to the most intense and blue to the least intense. (C) The final scattering profile ($t > 500$ s) indexed to a columnar structure with unit cell dimensions $a = b = 15.7$ nm, $c = 9.2$ nm; $c/a = 0.59$. (D) GISAXS obtained from a nanodisk film on a silicon substrate. The horizontal streaks of the (00 l) reflections indicate that the columns are oriented perpendicular to the substrate.

nanodisks and their interparticle spacings are on the order of nanometers, SAXS is an ideal tool for probing their structure and characterizing superlattice order.^{1–3,52–56} With high-intensity X-rays, nanodisk assembly can even be followed in real time from an evaporating droplet of nanocrystal dispersion on a substrate.^{54–56} The use of two different SAXS configurations—SAXS taken in a transmission mode configuration and grazing-incidence SAXS (GISAXS)—provides extensive information about nanodisk assembly. Both techniques are nondestructive, and GISAXS provides characterization of the structure of thin films in both the in-plane and perpendicular directions of the film.^{57,58}

Figure 3A shows time-resolved SAXS data acquired as ~200 μ L of toluene-dispersed CuS nanodisks evaporated on a Kapton window. Initially (at $t < 250$ s), the nanodisk volume fraction is small, and the scattering profile is typical of well-dispersed colloidal particles. After ~280 s, three sharp scattering peaks appear, indicating structural ordering of the nanodisks. With further solvent evaporation, interparticle scattering (i.e., diffraction) begins to dominate the scattering profile—the intensity of the initial isotropic scattering decreases, and the diffraction peaks become increasingly pronounced. The final scattering profile from the evaporated nanodisk film is replotted in Figure 3C.

The scattering peaks in Figure 3C index to a columnar structure,⁴⁴ as summarized in Table 1. All of the expected

Table 1. Indexing of the SAXS Diffraction Peaks in Figure 3C^a

assignment	q_{hkl} (nm ⁻¹)		d_{hkl} (nm)	
	expected	observed	expected	observed
(100)	0.347	0.347	18.13	18.11
		0.377		16.67
(110)	0.600	0.604	10.47	10.40
(001)	0.683	0.684	9.20	9.19
(200)	0.693	0.701	9.06	8.96
(002)	1.366	1.380	4.60	4.55
(003)	2.049	2.100	3.07	2.99

^a The measured peak positions ($d_{hkl} = 2\pi/q_{hkl}$) match the expected lattice spacings of a columnar structure with unit cell dimensions $a = 15.7$ nm and $c = 9.2$ nm.

peaks appear in the diffraction pattern with lattice spacings corresponding to unit cell dimensions $a = 15.7$ nm and $c = 9.2$ nm. The $(hk0)$ diffraction peaks correspond to inter-column distances. The center-to-center nearest neighbor column-to-column separation of 15.7 nm indicates that the columns are close packed and separated by the nanodisk capping ligands. The $(00l)$ reflections correspond to intra-column spacings, indicating that the face-to-face separation between disks is 9.2 nm. Both lattice constants, a and c , agree closely with the expected values based on TEM data.

After the diffraction peaks appear at ~ 280 s, the (100) peak and the grouping of (110), (001), and (200) peaks shift gradually to higher q with time, indicating a relatively slow, yet perceptible decrease in the interparticle spacing as residual solvent associated with the capping ligands evaporates. The (100) peak shifts from $q = 0.316$ nm⁻¹ at $t = 280$ s to $q = 0.347$ nm⁻¹ at $t = 360$ s, corresponding to a change in d_{100} spacing of almost 2 nm, from 19.9 to 18.1 nm. Three hundred sixty seconds after casting the drop, the peaks did not noticeably shift, indicating that solvent evaporation was complete.

Figure 3D shows GISAXS data collected at a grazing incidence angle of 0.15° where the diffraction peaks have been indexed. GISAXS provides information about the columnar structure of the nanodisks and their orientation with respect to the substrate. The reflections parallel to the substrate (along the q_x direction) correspond to reflections between columns, while the peaks out of the plane of the substrate correspond to reflections from layers of disks. The small spread in the width of the peaks along the q_z directions indicates that the disks all lay at approximately the same angle with respect to one another, and the presence of well-defined diffraction peaks (rather than diffraction rings) indicates that the columns have a strongly preferred orientation in the sample. From these data, it can be deduced that the columns are oriented perpendicular to the substrate, as in the structure imaged by SEM in Figure 2A and illustrated in Figure 1E(ii).

The range of order can be determined by examining the diffraction peak widths. Analysis of the (100) peak width using the Scherrer equation indicates that the average “crystallite” size within the columnar nanodisk film is approximately 370 nm, corresponding to about 20 disks. The

range of order in the direction perpendicular from the substrate is indicated from the (001) peak breadth: the Scherrer equation indicates a domain size of approximately 200 nm, indicating that the ordered domains in the film extend up about 21 disks. On average, there are approximately 9000 to 10000 disks per ordered columnar domain. This range of order is consistent with the observed occurrence of peaks up to third order, which suggest independently that at least third-nearest and fourth-nearest neighboring columns are still quite well ordered (in discotic polymer films from the spin coater there is often only nearest-neighbor order). It is also worth noting that the GISAXS data indicate that the in-plane structure is powder-like.

In conclusion, the structure of self-assembled copper sulfide nanodisks was examined by TEM, SEM, SAXS, and GISAXS. The nanodisks were observed to spontaneously assemble with face-to-face close packing when the solvent is evaporated from concentrated dispersions. Columnar self-assembly of CuS nanodisks, with long range orientational order, was confirmed by SAXS and GISAXS. With time-resolved SAXS, the isotropic-to-columnar phase transition was observed during solvent evaporation and GISAXS revealed that the columns orient perpendicular to the substrate. Hexagonal close-packed ordering of the columns is relatively extensive, but the disks within the columns are not periodically ordered with respect to other disks.

Acknowledgment. We thank Dayne Fanfair and Danielle Smith for assistance with the measurements at CHESS. We acknowledge funding from the Robert A. Welch Foundation, the National Science Foundation through their STC program (CHE-9876674) and a NIRT grant (DMR-0210383), the Office of Naval Research (N000N-05-1-0857), and DARPA through the Advanced Processing and Prototyping (AP2C) Program (HR0011-06-1-0005). CHESS is a national user facility supported by NSF and NIH-NIGMS by NSF Grant DMR-0225180.

References

- (1) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, *270*, 1335–1338.
- (2) Korgel, B. A.; Fullam, S.; Connolly, S.; Fitzmaurice, D. J. *Phys. Chem. B* **1998**, *102*, 8379–8388.
- (3) Whetten, R. L.; Shafigullin, M. N.; Khoury, J. T.; Schaaff, T. G.; Vezmar, I.; Alvarez, M. M.; Wilkinson, A. *Acc. Chem. Res.* **1999**, *32*, 397–406.
- (4) Markovich, G.; Collier, P.; Henrichs, S. E.; Remacle, F.; Levine, R. D.; Heath, J. R. *Acc. Chem. Res.* **1999**, *32*, 415–423.
- (5) Redl, F. X.; Cho, K. S.; Murray, C. B.; O'Brien, S. *Nature* **2003**, *423*, 968–971.
- (6) Shevchenko, E. V.; Talapin, D. V.; Kotov, N. A.; O'Brien, S.; Murray, C. B. *Nature* **2006**, *439*, 55–59.
- (7) Shevchenko, E. V.; Talapin, D. V.; O'Brien, S.; Murray, C. B. *J. Am. Chem. Soc.* **2005**, *127*, 8741–8747.
- (8) Saunders, A. E.; Korgel, B. A. *ChemPhysChem* **2005**, *6*, 61–65.
- (9) Talapin, C. V.; Shevchenko, E. V.; Murray, C. B.; Kornowski, A.; Forster, S.; Weller, H. *J. Am. Chem. Soc.* **2004**, *126*, 12984–12988.
- (10) Harman, T. C.; Taylor, P. J.; Walsh, M. P.; LaForge, B. E. *Science* **2002**, *297*, 2229–2232.
- (11) Gur, I.; Fromer, N. A.; Geier, M. L.; Alivisatos, A. P. *Science* **2005**, *310*, 462–465.
- (12) Konstantatos, G.; Howard, I.; Fischer, A.; Hoogland, S.; Clifford, J.; Klem, E.; Levina, L.; Sargent, E. H. *Science* **2006**, *442*, 180–183.
- (13) Coe, S.; Woo, W. K.; Bawendi, M.; Bulovic, V. *Nature* **2002**, *420*, 800–803.

- (14) Achermann, M.; Petruska, M. A.; Koleske, D. D.; Crawford, M. H.; Klimov, V. I. *Nano Lett.* **2006**, *6*, 1396–1400.
- (15) Ridley, B. A.; Nivi, B.; Jacobson, J. M. *Science* **1999**, *286*, 746–749.
- (16) Talapin, D. V.; Murray, C. B. *Science* **2005**, *310*, 86–89.
- (17) Hanafi, H. I.; Tiwari, S.; Khan, I. *IEEE Trans. Electron Devices* **1996**, *43*, 1553–1558.
- (18) Liu, Z. T.; Lee, C.; Narayanan, V.; Pei, G.; Kan, E. C. *IEEE Trans. Electron Devices* **2002**, *49*, 1606–1613.
- (19) Sun, S. H.; Murray, C. B. *J. Appl. Phys.* **1999**, *85*, 4325–4330.
- (20) Shipway, A. N.; Katz, E.; Willner, I. *ChemPhysChem* **2000**, *1*, 18–52.
- (21) Wohltjen, H.; Snow, A. W. *Anal. Chem.* **1998**, *70*, 2856–2859.
- (22) Li, L.-S.; Walda, J.; Manna, L.; Alivisatos, A. P. *Nano Lett.* **2002**, *2*, 557–560.
- (23) Li, L.-S.; Alivisatos, A. P. *Adv. Mater.* **2003**, *15*, 408–411.
- (24) Li, L.-S.; Marjanska, M.; Park, G. H. J.; Pines, A.; Alivisatos, A. P. *J. Chem. Phys.* **2004**, *120*, 1149–1152.
- (25) Lozano, K.; Hernandez, C.; Petty, T. W.; Sigman, M. B.; Korgel, B. A. *J. Colloid Interface Sci.* **2006**, *297*, 618–624.
- (26) Chandrasekhar, S. *Liquid Crystals*, 2nd ed.; Cambridge University Press: New York, 1992.
- (27) Kim, F.; Kwan, S.; Akana, J.; Yang, P. *J. Am. Chem. Soc.* **2001**, *123*, 4360–4361.
- (28) Korgel, B. A.; Fitzmaurice, D. *Adv. Mater.* **1998**, *10*, 661–665.
- (29) Li, M.; Schnablegger, H.; Mann, S. *Nature* **1999**, *402*, 393–395.
- (30) Nikoobakht, B.; Wang, Z. L.; El-Sayed, M. A. *J. Phys. Chem. B* **2000**, *104*, 8635–8640.
- (31) Sau, T. K.; Murphy, C. J. *Langmuir* **2005**, *21*, 2923–2929.
- (32) Janan, N. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1536–1540.
- (33) Dumestre, F.; Chaudret, B.; Amiens, C.; Respaud, M.; Fejes, P.; Renaud, P.; Zurcher, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 5213–5216.
- (34) Onsager, L. *Ann. N. Y. Acad. Sci. U.S.A.* **1949**, *51*, 627.
- (35) Veerman, J. A. C.; Frenkel, D. *Phys. Rev. A* **1992**, *45*, 5632–5648.
- (36) Zhang, S. D.; Reynolds, P. A.; van Dujneveldt, J. S. *J. Chem. Phys.* **2002**, *117*, 9947–9958.
- (37) Brown, A. B. D.; Clarke, S. M.; Rennie, A. R. *Langmuir* **1998**, *14*, 3129–3132.
- (38) Van der Kooij, F. M.; Lekkerkerker, N. W. *J. Phys. Chem. B* **1998**, *102*, 7829–7832.
- (39) Van der Kooij, F. M.; Kassapidou, K.; Lekkerkerker, H. N. W. *Nature* **2000**, *406*, 868–871.
- (40) Davidson, P.; Gabriel, J.-C. P. *Curr. Opin. Colloid Interface Sci.* **2005**, *9*, 377–383.
- (41) Puentes, V. F.; Zanchet, D.; Erdonmez, C. K.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2002**, *124*, 12874–12880.
- (42) Sigman, M. B.; Ghezelbash, A.; Hanrath, T.; Saunders, A. E.; Lee, F.; Korgel, B. A. *J. Am. Chem. Soc.* **2003**, *125*, 16050–16057.
- (43) Park, K. H.; Jang, K.; Son, S. U. *Angew. Chem., Int. Ed.* **2006**, *45*, 4608–4612.
- (44) Zhang, H.-T.; Wu, G.; Chen, X.-H. *Langmuir* **2005**, *21*, 4281–4282.
- (45) Zhang, Y.-W.; Sun, X.; Si, R.; You, L.-P.; Yan, C.-H. *J. Am. Chem. Soc.* **2005**, *127*, 3260–3261.
- (46) Ghezelbash, A.; Korgel, B. A. *Langmuir* **2005**, *21*, 9451–9456.
- (47) Van der Beek, D.; Petukhov, A. V.; Oversteegen, S. M.; Vroege, G. J.; Lekkerkerker, H. N. W. *Eur. Phys. J. E* **2005**, *16*, 253–258.
- (48) Brown, A. B. D.; Ferrero, C.; Narayanan, T.; Rennie, A. R. *Eur. Phys. J. B* **1999**, *11*, 481–489.
- (49) Larsen, T. H.; Sigman, M.; Ghezelbash, A.; Doty, R. C.; Korgel, B. A. *J. Am. Chem. Soc.* **2003**, *125*, 5638–5639.
- (50) Corry, C. E. *J. Appl. Geophys.* **1994**, *32*, 55–72.
- (51) Bieniulis, M. Z.; Corry, C. E.; Hoskins, E. R. *Geophys. Res. Lett.* **1987**, *14*, 135.
- (52) Korgel, B. A.; Fitzmaurice, D. *Phys. Rev. B* **1999**, *59*, 14191–14201.
- (53) Korgel, B. A. *Phys. Rev. Lett.* **2001**, *86*, 127–130.
- (54) Connolly, S.; Fullam, S.; Korgel, B.; Fitzmaurice, D. *J. Am. Chem. Soc.* **1998**, *120*, 2969–2970.
- (55) Narayanan, S.; Wang, J.; Lin, X. M. *Phys. Rev. Lett.* **2004**, *93*, 135503.
- (56) Bigioni, T. P.; Lin, X. M.; Nguyen, T. T.; Corwin, E. I.; Witten, T. A.; Jaeger, H. M. *Nat. Mater.* **2006**, *4*, 265–270.
- (57) Smilgies, D.-M.; Busch, P.; Posselt, D.; Papadakis, C. M. *Synchrotron Radiat. News* **2002**, Issue 15 (5), 35–41.
- (58) Du, P.; Li, M.; Douki, K.; Li, X.; Garcia, C. B. W.; Jain, A.; Smilgies, D.-M.; Fetters, L. J.; Gruner, S. M.; Wiesner, U.; Ober, C. *Adv. Mater.* **2004**, *16*, 953–957.

NL062419E