

Array Patterns of Binary Colloidal Crystals

Hailin Cong and Weixiao Cao*

College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Received: April 21, 2004; In Final Form: October 10, 2004

Binary colloidal crystals (BCCs) were prepared from two kinds of poly(styrene-methyl methacrylate-acrylic acid) colloids ~ 190 and ~ 380 nm in diameter by the codeposition method. A variety of array patterns of BCCs were observed and characterized by AFM and SEM. The significance of these colloidal arrays in crystallography has been discussed preliminarily.

Introduction

The three-dimensional order structures from monodispersed spheres (particles), both organic and inorganic, have attracted more and more attention.^{1–8} The order array from micrometer and submicrometer spheres represents an important and interesting approach for fabrication of colloidal crystals.^{9–11} Many macroporous materials of various types including inorganic, organic, metallic, ceramic, etc. have been successfully made by using colloidal crystals as a template.^{12–18} And it is believed that this technique will play a key role in the photonic research field.^{19–22}

The array and packing of the real crystals made from ions, atoms, and molecules are hard to observe because of the size of these crystalline elements usually at the nanometer and angstrom scales. This makes the study of crystallography difficult. But in colloidal crystals, the crystalline elements are micrometer and submicrometer colloids, and their array and packing can be observed conveniently with optical and electron microscopes. Therefore, the colloidal crystals have been utilized as a model for the research of crystallography.^{23–26} Dosho et al. reported that the point defect, grain boundary, dislocation, recrystallization, annealing, etc. could be shown accurately and vividly in the crystalline process of the colloids.²⁷ Velikov and Kitaev et al. reported recently that the binary colloidal crystals (BCCs) formed by strictly controlling the proportion of two kinds of colloids can mimic the real crystals in both process and structure.^{28,29}

In this study, two kinds of poly(styrene-methyl methacrylate-acrylic acid) (P(St-MMA-AA)) colloids with diameters of ~ 190 and ~ 380 nm were synthesized, and the BCCs from them as well as their array patterns were studied. The significance of BCCs to mimic the real crystals has been discussed preliminarily.

Experimental Section

Synthesis of Monodispersed Colloids. Styrene (St), methyl methacrylate (MMA), and acrylic acid (AA) were distilled before use. Sodium dodecyl sulfate (SDS) was purified by recrystallization in ethanol. Ammonium persulfate and ammonium bicarbonate are chemical reagents and were used as received. The monodispersed P(St-MMA-AA) colloids ~ 190 nm in diameter were synthesized by emulsion polymerization. A typi-

cal sample was prepared as follows: A 120 mL sample of an aqueous solution (A) containing $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.4 g), NH_4HCO_3 (0.8 g), and SDS (0.08 g) in a funnel and 25 mL of a monomer mixture (B) consisting of St/MMA/AA (90:5:5 v/v/v) in another funnel were added at the same time to a 250 mL flask, the mixture was stirred at 70 °C in a N_2 atmosphere for 5 h to obtain a homogeneous latex with a particle size of ~ 190 nm diameter, and the particles were almost monodispersed. Monodispersed P(St-MMA-AA) colloids ~ 380 nm in diameter were synthesized by a soap-free emulsion polymerization described elsewhere.³⁰

Preparation of Colloidal Crystals. The colloidal crystals and BCCs were fabricated by deposition of the colloids (~ 380 nm in diameter) and codeposition of the two kinds of colloids (~ 190 and ~ 380 nm in diameter) on inclined silicon substrates, respectively. The procedure was depicted as follows: Two silicon wafers (10 mm \times 30 mm \times 1 mm) were pretreated in a $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (7:3 v/v) mixture for 30 min at 70–75 °C to create a clean and hydrophilic surface. The pretreated wafers with a 45° incline were dipped into two 10 mL vessels, one containing 8 mL of ~ 380 nm P(St-MMA-AA) latex (3.4 $\text{mg}\cdot\text{mL}^{-1}$) and the other containing 4 mL of ~ 190 nm (0.2 $\text{mg}\cdot\text{mL}^{-1}$) and 4 mL of ~ 380 nm (1.6 $\text{mg}\cdot\text{mL}^{-1}$) P(St-MMA-AA) latex. Following the water being vaporized at ~ 25 °C, the colloids induced by capillary force³⁰ were orderly deposited onto the wafers to assemble into colloidal crystals and BCCs. After deposition for 8–10 days, the colloidal crystals and BCCs (both ~ 2 cm^2) were acquired on the respective silicon wafer.

Characterization. The size and distribution of the colloids were visualized by a transmission electron microscope (JEM-100CX, Japan) and scanning electron microscope (Amray-1910FE). An atomic force microscope (Nanoscope III A) was used to observe the structure and array pattern of the formed crystals.

Results and Discussion

Colloidal Particles. The size and distribution of the two kinds of P(St-MMA-AA) colloids visualized by a transmission electron microscope are shown in Figure 1. We can see that the large particles (~ 380 nm) are rightly 1 time larger than the small ones (~ 190 nm). Both kinds of colloids are almost monodispersed.

Array Patterns of the Colloidal Crystals and BCCs. Figure 2 shows the AFM images of the colloidal crystals and BCCs

* To whom correspondence should be addressed. Fax: +86-10-6275-1708. E-mail: wxcao@pku.edu.cn.

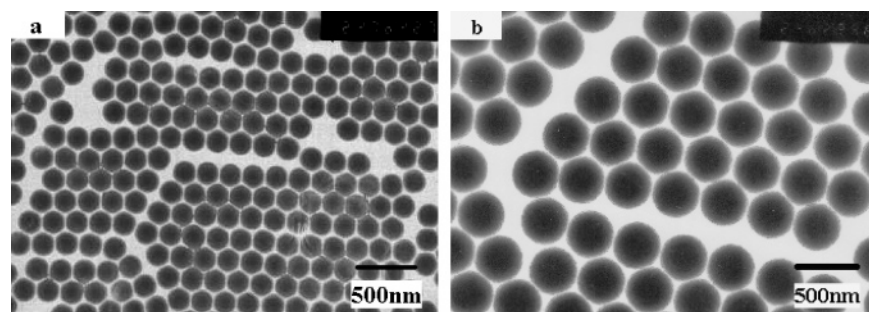


Figure 1. TEM micrographs of the P(St-MMA-AA) colloids with different sizes. Diameter (nm): (a) ~ 190 , (b) ~ 380 .

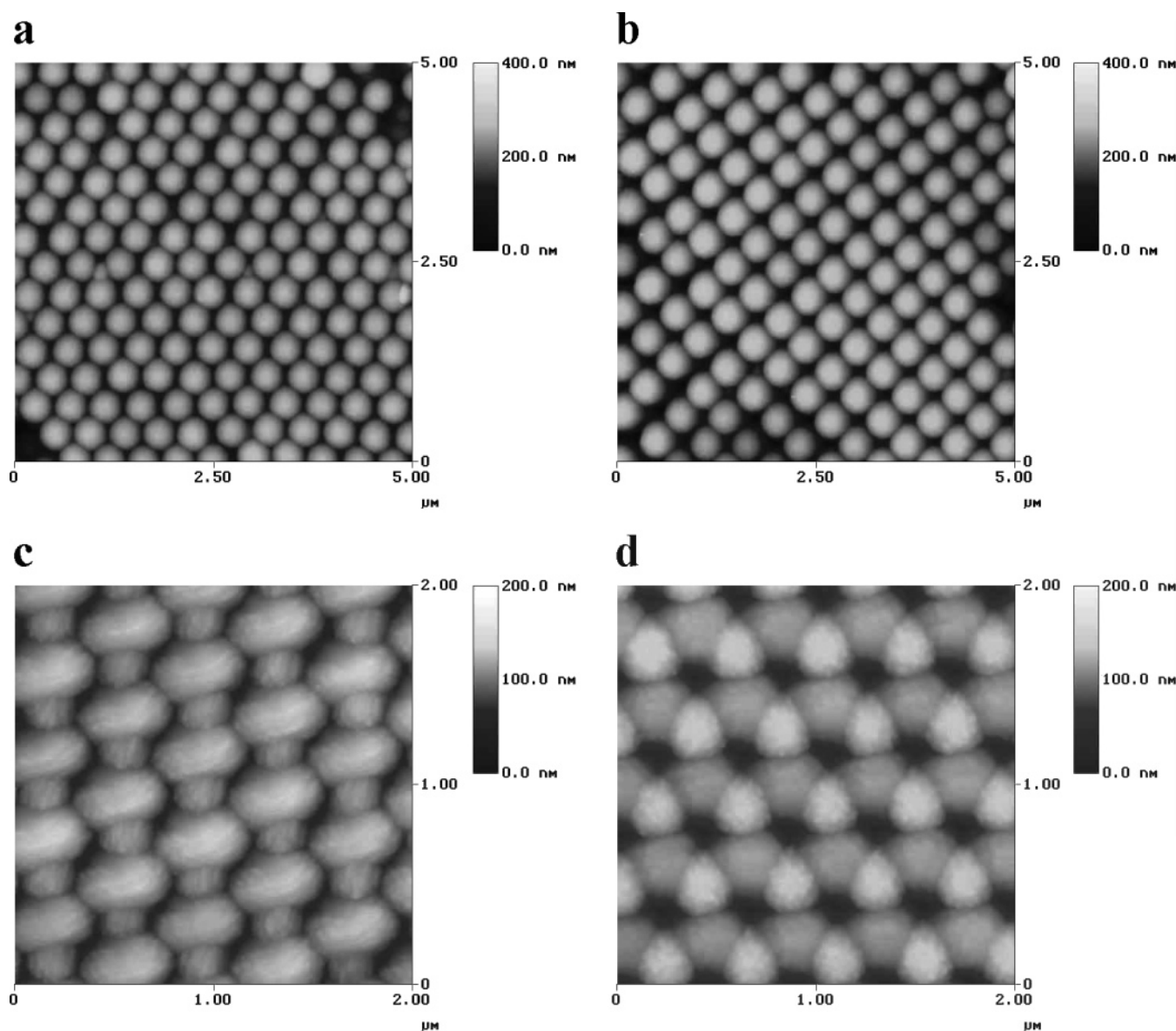


Figure 2. AFM images of array patterns for the colloidal crystals and BCCs. Colloidal crystals: (a) hexagonal array, (b) square array. BCCs: (c) L_4S_4 array, (d) L_3S_3 array.

obtained in the tapping mode. The hexagonal array (Figure 2a) and square array (Figure 2b) for the colloidal crystals and two coarray patterns, i.e., L_4S_4 and L_3S_3 arrays (Figure 2c,d), for BCCs were observed. From Figure 2c, we can see that there are four small particles (S) around each large particle (L), and there are also four L particles around each S particle, which is the L_4S_4 array mode. This is the first time that the L_4S_4 array pattern has been observed in binary colloidal crystals. In Figure

2d, one L particle is surrounded by three S particles, and one S particle is surrounded by three L particles, which is the L_3S_3 array mode.

The SEM images in Figure 3 show the colloidal crystals having hexagonal (Figure 3a) and square (Figure 3b) arrays, and the BCCs having L_4S_4 (Figure 3c) and L_3S_3 (Figure 3d) arrays. Compared with the AFM images shown in Figure 2, we can see that the shapes of the colloids in AFM are usually

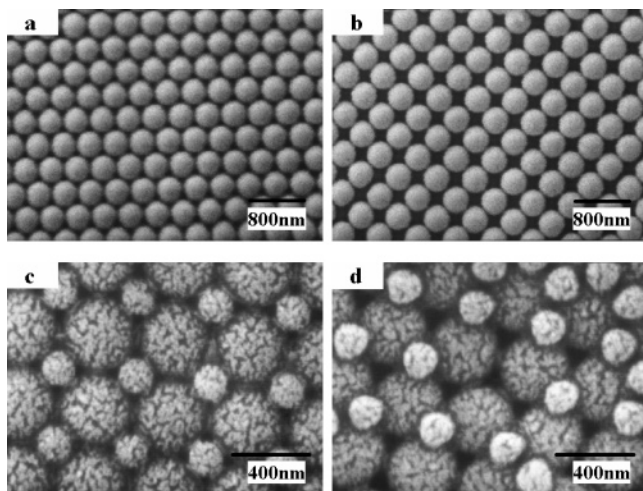


Figure 3. SEM images of array patterns for the colloidal crystals and BCCs. Colloidal crystals: (a) hexagonal array, (b) square array. BCCs: (c) L_4S_4 array, (d) L_3S_3 array.

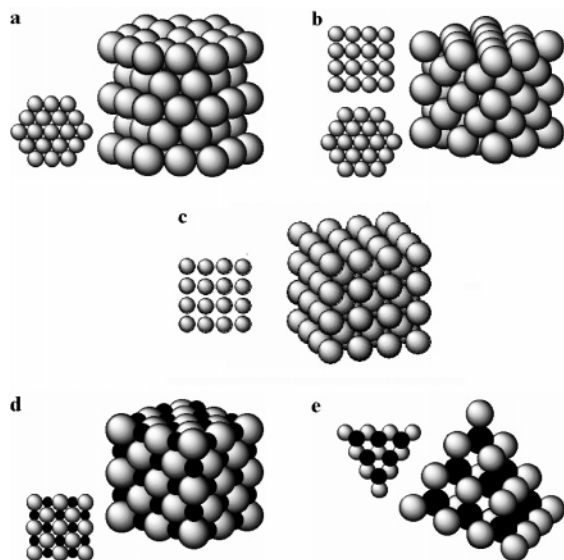


Figure 4. Schematic illustration of five packing modes from the four arrays of the colloids: (a) hcp, (b) fcc packing, (c) bcc packing, (d) NaCl packing, (e) ZnS packing.

deformed, which may be caused by signal distortion when the AFM needle point moves along the surfaces of such large colloids (~ 190 – 380 nm).

The five crystallographic forms of real crystals mimicked by the colloids are illustrated schematically in Figure 4. The hexagonal and square arrays of the colloids can mimic the hexagonal closed packing (hcp), face-centered cubic (fcc) packing, and body-centered cubic (bcc) packing of the atoms in metal crystals, while the L_4S_4 and L_3S_3 arrays of the colloids in BCCs can mimic the packing of the ions in NaCl and ZnS ionic crystals, respectively. It is worth mentioning that the hexagonal array can form either an hcp (Figure 4a) or an fcc (Figure 4b) crystal, while the square array can form either an fcc (Figure 4b) or a bcc (Figure 4c) crystal.

Moreover, the other coarray patterns were also observed in the BCCs (Figure 5). Figure 5a shows the L_3S_6 array pattern; i.e., one L particle is surrounded by six S particles, but one S particle is only surrounded by three L particles. It is interesting that there are two isomeric array patterns (L_2S_6 -1 and L_2S_6 -2). One is where the L and S particles are both in a hexagonal array (Figure 5b), and the other is where the S particles are in

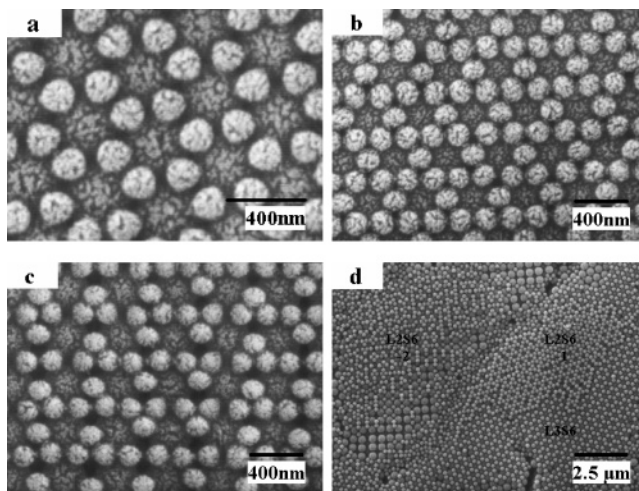


Figure 5. SEM images of other array patterns from two kinds of colloids (~ 190 and ~ 380 nm): (a) L_3S_6 array, (b) L_2S_6 -1 array, (c) L_2S_6 -2 array, (d) SEM image with lower resolution.

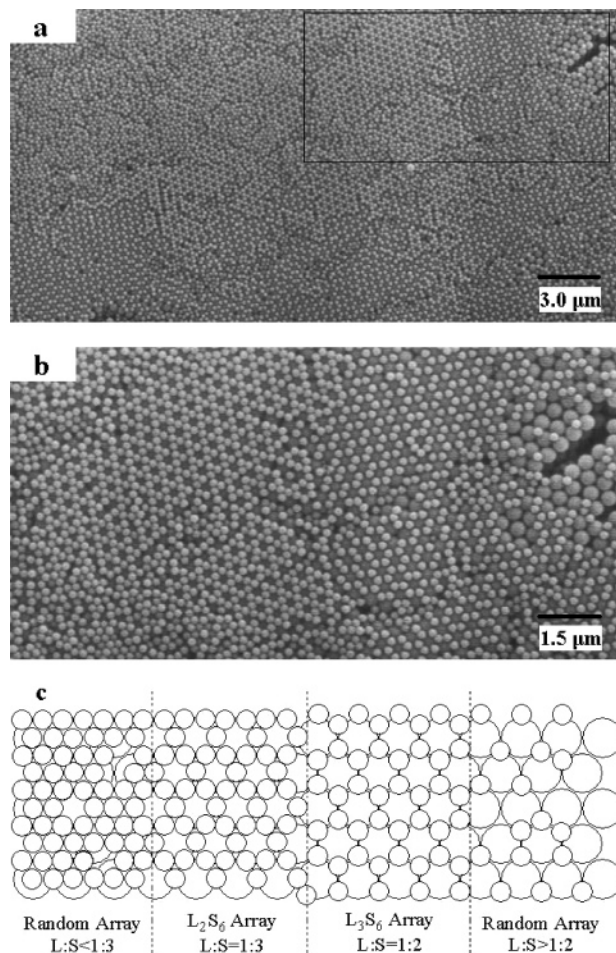


Figure 6. SEM images (a, b) and the schematic illustration (c) of the BCCs formed by codeposition of two kinds of colloids.

a hexagonal array but the L particles are in a square array (Figure 5c). This is the first time that isomeric L_2S_6 array patterns have been observed in binary colloidal crystals. Figure 5d is a lower resolution SEM image of the array patterns, which shows a larger area of the crystal.

Figure 6 shows the SEM images and the schematic illustration of the BCCs formed by codeposition of two kinds of colloids. Figure 6a is a lower resolution SEM image, and Figure 6b is the detailed image of the marked rectangular area of Figure 6a.

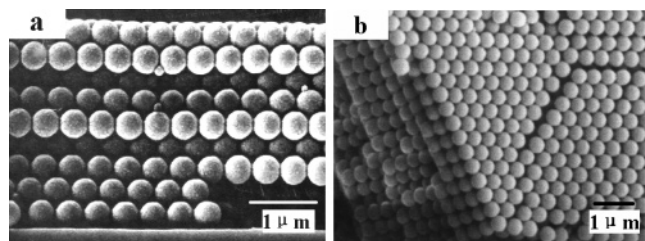


Figure 7. SEM images of two packing modes of the ~ 380 nm colloids: (a) hexagonal packing, (b) face-centered cubic packing.

We can see that various array patterns are involved in the formed BCCs. Figure 6c is a schematic illustration, from which we can see that the various array patterns are composed of different proportions of L and S spheres. This should originate from the difference in free motion rate as well as the capillary force of the L and S particles in the codeposition process.

Packing Modes of the Colloidal Crystals and BCCs. The hcp and fcc packing can be found easily in the colloidal crystals formed by ~ 380 nm colloids (Figure 7). The bcc packing has a higher void ratio ($\sim 32\%$) than the hcp ($\sim 26\%$) and fcc packing ($\sim 26\%$); therefore, it should be an unstable packing. In fact, it has not been observed in the colloidal crystals of our experiments. The ordered coarray packing of L_4S_4 (the type found in NaCl) and L_3S_3 (the type found in ZnS) of colloids is very hard to find in the BCCs. It is reasonable to consider that the crystals of NaCl and ZnS are built up from the ions with opposite charges, which are difficult to mimic by the P(St-MMA-AA) colloids carrying same charge.

Conclusions

The colloidal crystals formed only from ~ 380 nm colloids and BCCs from two kinds (~ 190 and ~ 380 nm) of colloids have been investigated. The former have hexagonal and square arrays, and the latter have a variety of arrays including L_4S_4 , L_3S_3 , L_3S_6 , and L_2S_6 patterns. The L_4S_4 and L_3S_3 arrays can mimic the NaCl and ZnS ionic crystals, while the hexagonal and square arrays can mimic the hcp, fcc, and bcc structures of metal crystals. And two isomeric array patterns were also observed in the L_2S_6 colloidal arrays. All these arrays may be interesting in the research of crystallography.

Acknowledgment. We are grateful to the NSFC for financial support of this work (Contract No. 20274002).

Supporting Information Available: AFM 3D images of the array patterns and lower resolution SEM images of array patterns for the BCCs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Velev, O. D.; Lenhoff, A. M.; Kaler, E. W. *Science* **2000**, *287*, 2240–2243.
- (2) Velikov, K. P.; Christova, C. G.; Dullens, R. P. A.; Blaaderen, A. *Science* **2002**, *296*, 106–109.
- (3) Jiang, P.; Bertone, J. F.; Colvin, V. L. *Science* **2001**, *291*, 453–457.
- (4) Takeoka, Y.; Watanabe, M. *Langmuir* **2003**, *19*, 9104–.
- (5) Zeng, F.; Sun, Z.; Wang, C.; Ren, B.; Liu, X.; Tong, Z. *Langmuir* **2002**, *18*, 9116–9120.
- (6) Gu, Z.; Fujishima, A.; Sato, O. *Chem. Mater.* **2002**, *14*, 760–765.
- (7) Yin, Y.; Li, Z.; Xia, Y. *Langmuir* **2003**, *19*, 622–631.
- (8) Reculosa, S.; Ravaine, S. *Chem. Mater.* **2003**, *15*, 598–605.
- (9) Liang, Z.; Susha, A. S.; Caruso, F. *Adv. Mater.* **2002**, *14*, 1160–1164.
- (10) Cardoso, A. H.; Leite, C. A. P.; Zaniquelli, M. E. D.; Galembeck, F. *Colloids Surf., A* **1998**, *144*, 207–217.
- (11) Bardosova, M.; Tredgold, R. H. *J. Mater. Chem.* **2002**, *12*, 2835–2842.
- (12) Dinsmore, A. D.; Hsu, M. F.; Nikolaides, M. G.; Marquez, M.; Bausch, A. R.; Weitz, D. A. *Science* **2002**, *298*, 1006–1009.
- (13) Wang, D. Y.; Rogach, A. L.; Caruso, F. *Chem. Mater.* **2003**, *15*, 2724–2729.
- (14) Yi, G.; Moon, J. H.; Yang, S. *Chem. Mater.* **2001**, *13*, 2613–2618.
- (15) Meng, Q. B.; Fu, C. H.; Einaga, Y.; Gu, Z. Z.; Fujishima, A.; Sato, O. *Chem. Mater.* **2002**, *14*, 83–88.
- (16) Chi, E. K.; Kim, Y. N.; Kim, J. C.; Hur, N. H. *Chem. Mater.* **2003**, *15*, 1929–1931.
- (17) Yi, D. K.; Kim, D. *Chem. Commun.* **2003**, 982–983.
- (18) Valtchev, V. J. *Mater. Chem.* **2002**, *12*, 1914–1918.
- (19) Hillebrand, R.; Senz, S.; Hergert, W.; Gosele, U. *J. Appl. Phys.* **2003**, *94*, 2758–2760.
- (20) Blanco, A.; Chomski, E.; Grubbs, S.; Ibbett, M.; John, S.; Leonard, S. W.; Lopez, C.; Meseguer, F.; Miguez, H.; Mondia, J. P.; Ozin, G. A.; Toader, O.; vanDriel, H. M. *Nature* **2000**, *405*, 437–440.
- (21) Wijnhoven, J. E. G. J.; Vos, W. L. *Science* **1998**, *281*, 802–804.
- (22) Harkins, P.; Eustace, D.; Gallagher, J.; McComb, D. W. J. *J. Mater. Chem.* **2002**, *12*, 1247–1249.
- (23) Ackerson, B. J.; Schatzel, K. *Phys. Rev. E* **1995**, *52*, 6448.
- (24) Harland, J. L.; Henderson, S. I.; Underwood, S. M.; van Megen, W. *Phys. Rev. Lett.* **1995**, *75*, 3572.
- (25) Imhof, A.; Pine, D. J. *Nature* **1997**, *389*, 948.
- (26) Larsen, A. E.; Grier, D. G. *Nature* **1997**, *385*, 230.
- (27) Dosho, S.; Norio, I.; Ito, K. *Langmuir* **1995**, *9*, 394.
- (28) Velikov, K. P.; Christova, C. G.; Dullens, R. P. A.; Blaaderen, A. *Science* **2002**, *296*, 106–109.
- (29) Kitaev V.; Ozin, G. A. *Adv. Mater.* **2003**, *15*, 75–78.
- (30) Cong, H.; Cao, W. *Langmuir* **2003**, *19*, 8177–8181.