Controlled Arrangement of Colloidal Crystal Strips

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Received May 25, 2005

Colloidal crystals or opals have potential applications in photonics,[1,2] optics,[3,4] and sensing.[5] For these applications, synthetic opal crystals should be arranged into special architectures or have to be integrated into microdevices, which can then behave as photonic circuits, switches, mirrors, filters, waveguides, superprisms, or sensors. Several promising methods have been developed for the preparation of planar colloidal crystals;[6−8] however, the normal opal films are difficult to use or integrate into photonic crystal circuits without a post-structuring process. Recently, several methods based on micromolding,[9,10] microcontact printing,[11] and other template-directed growth processes[5,12,13] have been used to mold the architecture of colloidal crystals, and different opal microstructures have been obtained. In these processes, well-defined microstructured templates have been combined with a self-assembly process, leading to colloidal crystals in different shapes[14,15] and optical circuit-like arrangements;[16] however, the template fabrication itself is a very complicated process.

Capillary forces are very often exploited in the self-assembly of colloidal crystals.[17,18] The vertical deposition method,[7] one of the most applied opal deposition methods, uses the adsorption affinity between the solvent and a vertically positioned hydrophilic substrate to adsorb the suspension and utilizes the capillarity between spheres to deposit the crystals.[17,19−21] Even though large area opal films of single composition can be efficiently fabricated with this simple method, more complex architectures are difficult to realize without a previous lithographic structuring step.[13] Up to now, layered structures of differently sized silica microspheres[22,23] and binary opal structures[24,25] have been achieved by the vertical deposition method,[22,24,25] by a simple stepwise spin-coating method,[26] or by combining the vertical deposition method with the Langmuir−Blodgett technique.[23] These examples represent vertical opal heterostructures where the type of photonic crystals is changed perpendicular to the film plane. The arrangement of the colloidal crystals into more complex structures using a simple self-assembly without templates has not been reported up to now.

In this communication, we are reporting on an approach to alternating strip opal heterostructures based on a simple capillary-assisted deposition method developed recently in our group.[27] We show that alternating opal strips and bended opal strips can be realized on smooth substrates. This method uses a capillary tube to convey polystyrene (PS) suspensions into a planar capillary cell where controllable assembly of the opal is taking place. Two normal glass slides or two glass slides with special shape (in both cases, one of the slides with a 1-mm hole) and a thin polymer layer (e.g., Teflon, 16 mm × 5 mm) were used to construct the planar capillary cell. The polymer spacer is placed at one end between the two parallel slides fixed with a clip, forming the planar capillary cell with three open edges.[27] The capillary tube with an external diameter of 1 mm is inserted into the hole in the bottom slide of the cell. When the other end of this tube is inserted into a PS aqueous suspension (287 nm), the suspension is delivered from the container to the edges of the planar capillary cell by capillary forces. Solvent evaporation leads to the deposition of PS spheres along the open sides, where a colloidal crystal is formed within several hours (Supporting Information Figure S1a). Thereafter, the capillary tube is connected with pure water which is infiltrated for several hours until the residual PS suspension is deposited at the already formed opal strip (Supporting Information Figure S1b). Then, the capillary tube is connected with another suspension of 345-nm PS spheres, leading to the growth of a further colloidal crystal strip of bigger-sized PS spheres beside the previous one. After that, infiltration cycles of water and the different suspensions are repeated until the capillary cell is completely filled by alternating opal strips. Pictures A−D of Figure 1 show opal films consisting of alternating strips with different widths obtained inside normal-shaped capillary cells with the capillary deposition method. These images show the reflection of daylight under

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(1) Xia, Y.; Gates, B.; Yin Y.; Lu, Y. *Adv. Mater.* **2000**, *12*, 693.
(2) Lopez, C. *Adv. Mater*. **2003**, *15*, 1679.
(3) Dowling, J. P. *Science* **1998**, *282*, 1841.
(4) Painter, O.; Lee, R. K.; Scherer, A.; Yariv, A.; O'Brien, J. D.; Dapkus P. D.; Kim, I. *Science* **1999**, *284*, 1819.
(5) Blaaderen, A. V.; Ruel R.; Wiltzius, P. *Nature* **1997**, *385*, 321.
(6) Park, S. H.; Qin D.; Xia, Y. *Adv. Mater.* **1998**, *10*, 1028.
(7) Jiang, P.; Bertone, J. F.; Hwang K. S.; Colvin, V. L. *Chem. Mater.* **1999**, *11*, 2132.
(8) Jiang, P.; McFarland, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 13778.
(9) Kim, E.; Xia Y.; Whitesides, G. M. *Adv. Mater.* **1996**, *8*, 245.
(10) Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 550.
(11) Yan, X.; Yao, J.; Lu, G.; Chen, X.; Zhang, K.; Yang, B. *J. Am. Chem. Soc.* **2004**, *126*, 10510.
(12) Shiu, J. Y.; Kuo, C. W.; Chen, P. *J. Am. Chem. Soc*. **2004**, *126*, 8096.
(13) Wang, D.; Möhwald, H. *J. Mater. Chem.* **2004**, *14*, 459.
(14) Yang, S. M.; Ozin, G. A. *Chem. Commun.* **2000**, *24*, 2507.
(15) Yin, Y.; Li, Z. Y.; Xia, Y. *Langmuir* **2003**, *19*, 622.
(16) Yang, S. M.; Miguez, H.; Ozin, G. A. *Adv. Funct. Mater.* **2002**, *12*, 425.
(17) Kralchevsky, P. A.; Denkov, N. D. *Curr. Opin. Colloid Interface Sci.* **2001**, *6*, 383.
(18) Denkov, N. D.; Velev, O. D.; Kralchevsky, P. A.; Ivanov, I. B.; Yoshimura, H.; Nagayama, K. *Nature* **1993**, *361*, 26.
(19) Norris, D. J.; Arlinghaus, E. G.; Meng, L.; Heiny, R.; Scriven, L. E. *Adv. Mater.* **2004**, *16*, 1393.
(20) Vlasov, Y. A.; Bo, X. Z.; Sturm, J. C.; Norris, J. *Nature* **2001**, *414*, 289.
(21) Wong, S.; Kitaev, V.; Ozin, G. A. *J. Am. Chem. Soc.* **2003**, *125*, 15589.
(22) Jiang, P.; Ostojic, G. N.; Narat, R.; Mittleman, D. M.; Colvin, V. L. *Adv. Mater.* **2001**, *13*, 389.
(23) Zhao, Y. X.; Wostyn, K.; Schaetzen, G. D.; Clays, K.; Hellemans, L.; Persoons, A.; Szekeres, M.; Schoonheydt, R. A. *Appl. Phys. Lett.* **2003**, *82*, 3764.
(24) Velikov, K. P.; Christova, C. G.; Dullens, R. P. A.; Blaaderen, A. V. *Science* **2002**, *296*, 106.
(25) Kitaev, V.; Ozin, G. A. *Adv. Mater*. **2003**, *15*, 75.
(26) Wang, D.; Möhwald, H. *Adv. Mater*. **2004**, *16*, 244.
(27) Li, H. L.; Dong, W.; Bongard, H. J.; Marlow, F. *J. Phys. Chem. B* **2005**, *109*, 9939.

10.1021/cm051114i CCC: $30.25
Published on Web 06/18/2005

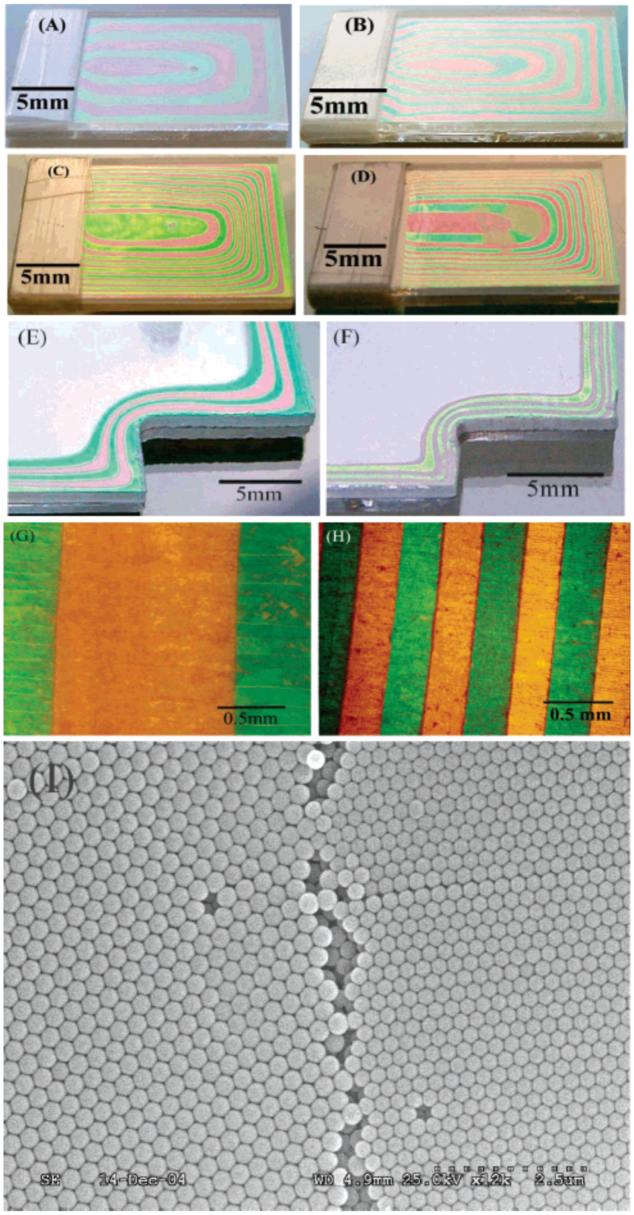

Figure 1. (A−D) Alternating strip opal heterostructures consisting of 4, 9, 18, and 20 colloidal crystal strips obtained inside rectangular capillary cells. (E and F) Alternating strip opal heterostructures obtained inside capillary cells with special shape. (G and H) Optical microscopy images of opal films in transmission with halogen lamp illumination (Orthoplan microscope, Leitz). (I) SEM image of a boundary region of two adjacent colloidal crystal strips (S3500N scanning electron microscope, Hitachi).

an observation angle of about 60°, resulting in a good color contrast between different strips. The observation angle influences the color appearance of the opal film sensitively; therefore, the colors of the four samples are slightly different. The bright (green) and dark (reddish) strips correspond to the colloidal crystals consisting of 287- and 345-nm PS spheres, respectively. The 4, 9, 18, and 20 near-n-shaped loops can be observed in images A−D, respectively. Pictures E and F show alternating arrangements of strips inside specially shaped capillary cells (two corners of the slides were cut). Here, the orientations of the opal strips were modified due to the changing of the shape of the capillary cells, forming more complex opal heterostructures. To our knowledge, the possibility of bending opal strips without a complicated template has not been achieved. As demon-

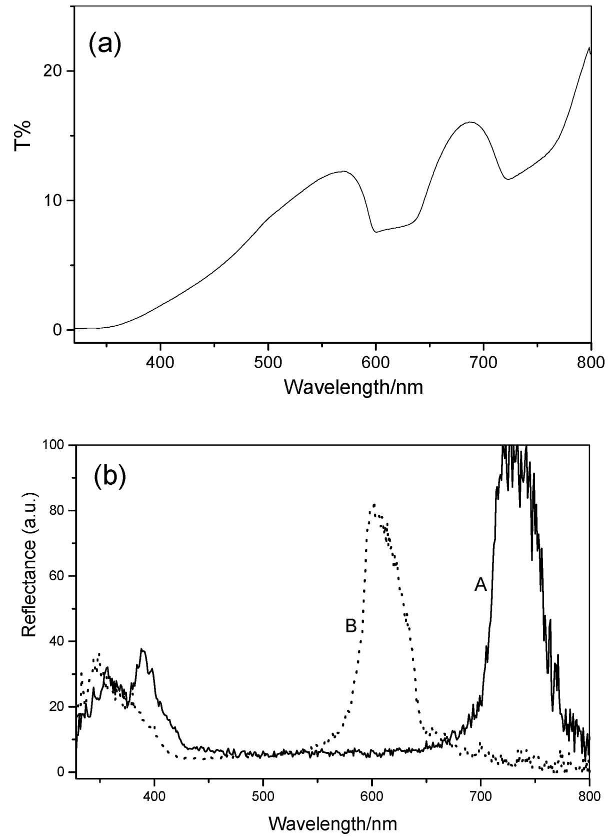

Figure 2. (a) UV−vis spectrum obtained by a transmission measurement (Cary 500 spectrometer). (b) Reflection spectra obtained from individual opal strips of (A) 345-nm PS and (B) 287-nm PS (Orthoplan microscope, Zeiss).

strated by these heterostructures, the capillary deposition method offers useful deposition controllability but differs decisively in setup and working principle from the vertical deposition method[7] and the confined cell deposition method.[6] Our method does not have special requirements with respect to the type of substrates and spacers; therefore, the heterostructures can be easily combined with silicon or other semiconductors. More complex structures, such as ternary or quaternary components, can also be derived from this deposition method. It is also very useful for preparing homogeneous large-area opal films (Supporting Information, Figure S2). Figure 1G−H shows optical microscopy images of opal strips with different widths. The green-blue color arises from the opal strips made of 287-nm PS, and the brilliant yellow color corresponds to the strips consisting of 345-nm PS spheres. The thickness of the opal film is determined by the spacer, while the width of the strips can be tuned by changing the PS concentration and the infiltration time. Opal films with a thickness from 25 to 75 μm and a strip width down to 50 μm have been fabricated in our experiments. The boundary between adjacent strips can be very sharp, and a boundary width less than 1 μm has been observed in the scanning electron microscopy (SEM) image (Figure 1I). Our opal deposition method enables also possibilities for influencing the interface between the two photonic crystal strips, for example, by introducing buffer layers or dissolvable layers leading to gaps. Narrow and well-defined boundary regions are necessary for the exploration of specific optical boundary effects.

Transmission spectra with two stop bands have been observed from these strip-structured opal heterostructures. Figure 2a shows a typical spectrum obtained from an opal film with a thickness of about 25 μm and a measurement area of about 12 mm^2. The intensities of the two peaks are slightly dependent on the adjustment of the sample. The peak at about 618 nm is the stop band of the 287-nm PS colloidal crystals, while the peak at about 721 nm arises from the colloidal crystals of 345-nm PS spheres. The peak assignments have been verified by a microfocus reflection measurement (Figure 2b), which confirms further that the two peaks in the spectrum of Figure 2a arise from two different crystals.

In summary, opal films consisting of different colloidal crystal strips have been fabricated based on the capillary deposition method. This method offers controllability for photonic crystal strip arrangements without templates, the possibility to bend the strips by using differently shaped capillary cells, and also possibilities to control the interface between different photonic crystal strips. Combinations with other structuring techniques such as the use of etched or microcontact printed substrates seem to be possible. The prepared opal heterostructures show multiple stop bands in optical transmission and reflection.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie and the DFG under Grant Ma 1745/7-1. We are grateful to Prof. F. Schüth for constructive criticism.

Supporting Information Available: Figures depicting the real setup used for the deposition process and two infiltration steps (Figure S1) and a single compositional opal film (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

CM051114I