

Fabrication of Ordered Macroporous Cylinders by Colloidal Templating in Microcapillaries

Jun Hyuk Moon,[†] Sarah Kim,[†] Gi-Ra Yi,[†]
Yong-Hee Lee,[‡] and Seung-Man Yang^{*,†}

Department of Chemical and Biomolecular Engineering and
Department of Physics, Korea Advanced Institute of Science
and Technology, 373-1 Guseong-dong, Yuseong-gu,
Daejeon 305-701, Korea

Received September 26, 2003.

In Final Form: December 10, 2003

Introduction

For many years, researchers of materials have been keenly interested in porous materials with three-dimensional periodicity for their potential applications in photonic crystals,¹ chemical sensors,² catalysts,³ and membranes.⁴ For example, periodic porous structures with feature dimensions on the order of a fraction of an optical wavelength have photonic band gap properties. In addition, macroporous structures enhance mass transport and efficiency of catalysts. Increasing attention in these areas has driven extensive research toward the synthesis of novel materials. Two different fabrication techniques have been demonstrated experimentally: microlithography⁵ and colloidal self-assembly.⁶ Colloidal assemblies are a typical bottom-up approach, wherein monodisperse particles are used as building blocks, and convective assemblies during evaporation of a solvent induce ordered arrays of particles, resulting in coexisting randomly stacked hexagonal close-packed (hcp) or face-centered cubic (fcc) lattices.⁷ Generally, colloidal crystals have been used as templates to form organic, inorganic, or metallic porous structures depending on the nature of the applications.^{8–11} Unlike lithography-based techniques that have shown mostly two-dimensional features, a colloidal self-assembly approach can produce complex and regular three-dimensional structures including channel-like,¹² spherical,¹³ ellipsoidal,¹⁴ and rectangular shapes as well as more complex forms such as star-shaped assemblies.¹⁵ Such shape-controlled colloidal crystals are of critical importance for practical use of bulk

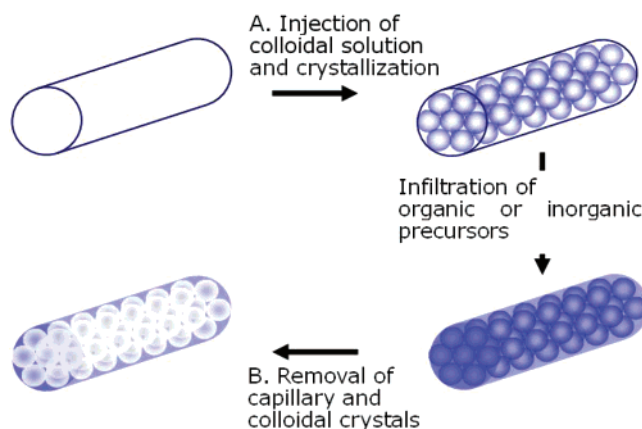


Figure 1. Schematic diagram for fabrication of the CylCC (A) and inverted structures from the CylCC template (B).



Figure 2. (a) Optical microscope image of colloidal assemblies inside a 50 μm diameter silica microcapillary. (b) Optical microscope image of colloidal assemblies inside a 65 μm diameter polymeric microcapillary.

colloidal crystals. Here, we present a facile route for the fabrication of cylindrical colloidal crystals (CylCCs) by self-assembly inside a microcapillary and their inverted replica with ordered macropores by using the colloidal crystals as templates. Our strategy for the fabrication of CylCCs commenced with filling a microcapillary with an aqueous dispersion containing monodisperse colloidal particles, as shown in Figure 1A. Capillary forces then drove the aqueous colloidal dispersion to penetrate into a microcapillary tube. The particles subsequently arranged into a hexagonally ordered array of cylindrical shape as water was removed slowly by evaporation inside the microcapillary. The CylCCs were used as templates for the fabrication of ordered macroporous cylinders (Figure 1B).

Experimental Section

Monodisperse submicron-sized polystyrene (PS) beads (250 and 500 nm in diameter) were prepared by emulsifier-free emulsion polymerization using a styrene monomer (styrene, 98%, Showa), 2,2'-azo-bis-isobutyronitrile (AIBN, 98%, Junsei Chemical), and divinylbenzene (DVB, 80%, Aldrich). Micron-sized PS spheres (1 and 3 μm in diameter) were purchased from Interfacial Dynamics. Monodisperse silica spheres (700 nm in diameter) were synthesized by the Stöber–Fink–Bohn method.¹⁶ Fused silica (10, 50, and 100 μm in diameter) and poly(methyl methacrylate) (PMMA) microcapillaries (65 and 125 μm in

(15) Yang, P.; Deng, T.; Zhao, D.; Feng, P.; Pine, D. J.; Chmelka, B. F.; Whitesides, G. M.; Stucky, G. D. *Science* **1998**, *282*, 2244.

* To whom correspondence should be addressed. E-mail: smyang@kaist.ac.kr. Phone: +82-42-869-3962. Fax: +82-42-869-5962.

[†] Department of Chemical and Biomolecular Engineering.

[‡] Department of Physics.

(1) Iwayama, Y.; Yamanaka, J.; Takiguchi, Y.; Takasaka, M.; Ito, K.; Shinohara, T.; Sawada, T.; Yonese, M. *Langmuir* **2003**, *19*, 977.

(2) Li, Y. Y.; Cunin, F.; Link, J. R.; Gao, T.; Betts, R. E.; Reiver, S. H.; Chin, V.; Bhatia, S. N.; Sailor, M. J. *Science* **2003**, *299*, 2045.

(3) Al-Daous, M. A.; Stein, A. *Chem. Mater.* **2003**, *15*, 2638.

(4) Mitchell, D. T.; Lee, S. B.; Trofin, L.; Li, N.; Nevanen, T. K.; Soderlund, H.; Martin, C. R. *J. Am. Chem. Soc.* **2002**, *124*, 11864.

(5) Cheng, C. C.; Scherer, A.; Fainman, T. Y.; Witzgall, G.; Yablono-vitch, E. *J. Vac. Sci. Technol., B* **1997**, *15*, 2764.

(6) van Blaaderen, A.; Ruel, R.; Wiltzius, P. *Nature* **1997**, *385*, 321.

(7) Dimitrov, A. S.; Nagayama, K. *Langmuir* **1996**, *12*, 1303.

(8) Bertone, J. F.; Jiang, P.; Hwang, K. S.; Mittleman, D. M.; Colvin, V. L. *Phys. Rev. Lett.* **1999**, *83*, 300.

(9) Dong, A.; Wang, Y.; Tang, Y.; Zhang, Y.; Ren, N.; Gao, Z. *Adv. Mater.* **2002**, *14*, 1506.

(10) Ye, Y.-H.; Badilescu, S.; Truong, V.-V. *Appl. Phys. Lett.* **2002**, *81*, 616.

(11) Kulinowski, K. M.; Jiang, P.; Vaswani, H.; Colvin, V. L. *Adv. Mater.* **2002**, *12*, 833.

(12) Yang, S. M.; Miguez, H.; Ozin, G. A. *Adv. Funct. Mater.* **2002**, *12*, 425.

(13) Velev, O. D.; Lenhoff, A. M.; Kaler, E. W. *Science* **2000**, *287*, 2240.

(14) Yi, G.-R.; Moon, J. H.; Yang, S.-M. *Adv. Mater.* **2001**, *13*, 1186.

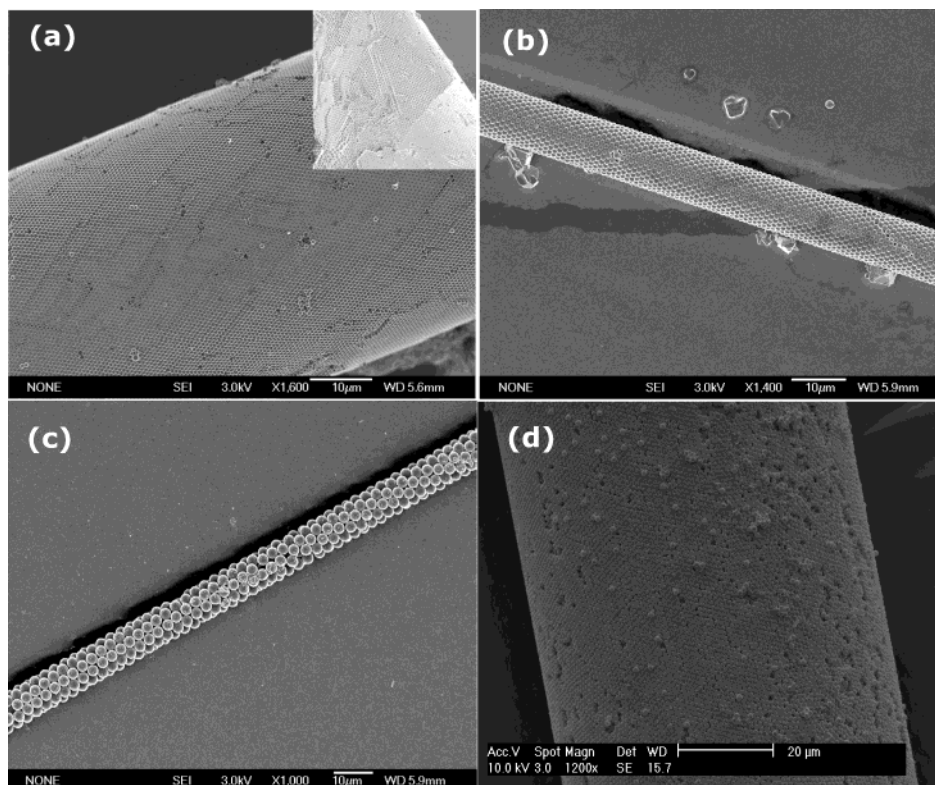


Figure 3. SEM images of CylCCs of PS particles for various ratios of capillary to particle diameter: (a) $50\ \mu\text{m}/0.6\ \mu\text{m}$, (b) $10\ \mu\text{m}/1\ \mu\text{m}$, and (c) $10\ \mu\text{m}/3\ \mu\text{m}$. The inset of panel (a) shows the colloidal assemblies inside the CylCC. (d) SEM image of a CylCC of silica particles. The ratio of capillary to particle diameter is $65\ \mu\text{m}/0.7\ \mu\text{m}$.

diameter) were purchased from Polymicro Technologies and Paradigm Optics, respectively. Photochemically curable polyurethane (PU) prepolymer (NOA60) was purchased from Norland, and nanometer-sized silica particles (Ludox, HS-40) were purchased from Aldrich. The aqueous colloid, HS-40, had a mean particle size of 30 nm at 40 wt % solid fraction. Images of the colloidal dispersions inside the microcapillaries were taken using an optical microscope (Nikon, TE2000). Images of the prepared colloidal crystals and their inverted structures were taken by scanning electron microscopy (SEM) (Philips XL30). The samples for SEM were coated with Au to make them conductive. An acceleration voltage of 3–5 kV was typically used. Particle size and size distribution were measured by photon correlation spectroscopy (Brookhaven with BI200SM goniometer) or directly from the SEM images.

Results and Discussion

The aqueous dispersion of monodisperse particles was injected by soaking a microcapillary in silica or a PS colloidal dispersion (1–10 wt %). To control the direction of water evaporation, we immersed one end of the capillary tube in the colloidal dispersion for several minutes until evaporation-induced colloidal crystallization started from the other end. Then, as the colloidal crystallization proceeded, the length of the colloidal dispersion column was shortened due to evaporation through the open end. Finally, colloidal assemblies of cylindrical shape were obtained inside the capillaries after drying for 4–6 h. Free-standing CylCCs of polymer latex and silica were prepared by using silica and polymeric microcapillaries, respectively. Then, the silica and polymeric capillaries were removed selectively by etching with diluted hydrofluoric (HF) acid and by calcinations at $500\ ^\circ\text{C}$ for 3 h, respectively. (Caution: HF solution is extremely hazardous; use only with adequate ventilation and wear protective clothing and safety goggles.)

The colloidal particles were not adsorbed on the tube wall during colloidal crystallization inside the capillary, unlike the previous evaporation-induced colloidal deposition.¹⁷ Theoretically, in an evaporation-induced colloidal self-assembly, the thickness (or the number of layers) of deposited colloidal crystals on a substrate is proportional to the meniscus height. Meanwhile, the meniscus height increases with Bond number ($B_o = \rho g r^2 / \sigma$), which is the ratio of gravity (g) to surface tension (σ) contribution.¹⁸ Here, ρ is the density and r is the capillary radius. Therefore, a smaller capillary radius or higher surface tension yields a proportionally shallower meniscus, that is, fewer deposited colloidal crystal layers. Under these conditions, a hollow cylinder colloidal crystal is not likely to form on a very narrow microcapillary wall. For the case of a polymeric microcapillary tube, the meniscus height is indiscernibly much smaller because of the poor wettability of the aqueous colloidal dispersion on the polymer. This can be seen from Figure 2a,b, which shows the shapes of menisci formed on the silica and polymeric microcapillaries, respectively. Moreover, our aqueous colloidal suspension has a larger surface tension than the ethanol–water mixture of a previous report,¹⁷ which also lowers the meniscus height. Consequently, our colloidal crystal assembled from a colloidal suspension inside a microcapillary did not possess a hollow core but was homogeneous in structure. The scanning electron micrographs reproduced in Figure 3 show CylCCs after the microcapillaries were decorticated. The length and diameter of the CylCC can be controlled by changing the particle concentration and the diameter of the microcapillary. Figure 3a shows a CylCC, where the PS beads were arranged into an fcc lattice throughout the capillary without forming

(16) Stober, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.

(17) Wang, H.; Li, X.; Nakamura, H.; Miyazaki, M.; Maeda, M. *Adv. Mater.* **2002**, *14*, 1662.

(18) Middleman, S. *An introduction to fluid dynamics*; John Wiley & Sons: New York, 1998.

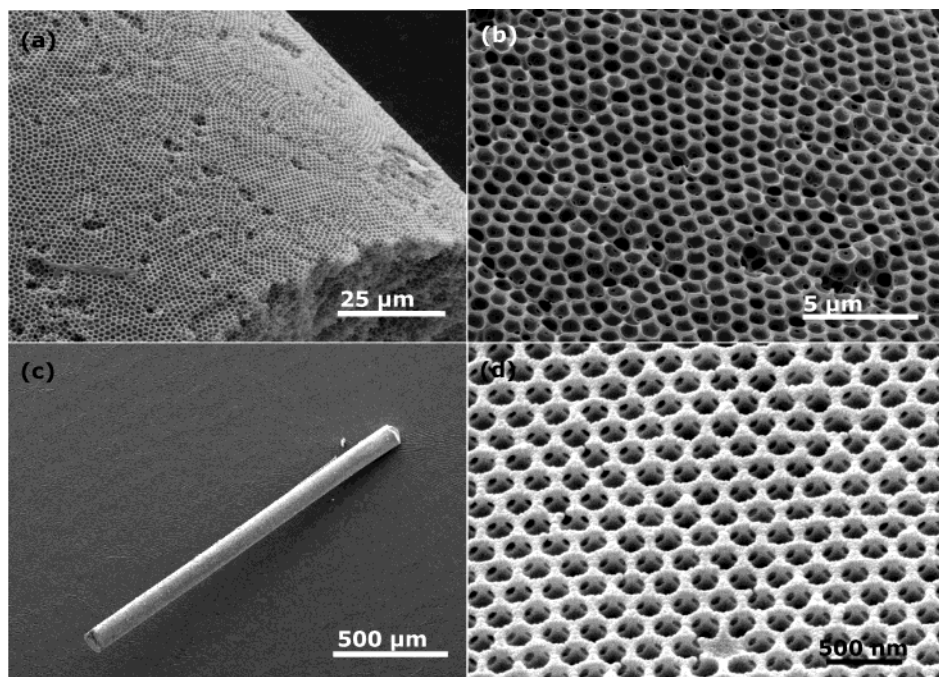


Figure 4. (a) SEM image of an ordered macroporous cylinder of polyurethane substrate and (b) surface morphology. Silica particles of $0.7 \mu\text{m}$ in diameter and a silica capillary of $100 \mu\text{m}$ in diameter were used to fabricate the colloidal crystal template. (c) SEM image of an ordered macroporous cylinder of silica substrate and (d) surface morphology. PS beads of $0.25 \mu\text{m}$ in diameter and a PMMA capillary of $125 \mu\text{m}$ in diameter were used for the colloidal crystal template.

a hollow core. This is clearly seen from the inset of Figure 3a. As noted from Figure 3c, colloidal crystals assembled inside a capillary exhibited helically ordered arrays, when the capillary was comparable to the particles in size.^{19,20} This structural deviation from usual colloidal self-assemblies of fcc or hcp symmetry was induced by particle packing on the nonplanar surface.²¹ It can be noted from the SEM images that the colloidal crystal of cylindrical shape was a single crystal when the sacrificial microcapillary was comparable in size to the building block spheres. However, when the microcapillary was much larger than the spheres, the crystal grain boundaries were observed. We also successfully fabricated self-organized CylCCs with silica beads ($0.7 \mu\text{m}$ in diameter) using PMMA microcapillaries ($65 \mu\text{m}$ in diameter), as shown in the SEM image of Figure 3d.

As we noted previously, colloidal crystals have been used as templates for macroporous structures of tailored materials. In the present study, ordered macroporous cylinders were produced by using colloidal crystals as templates, which were assembled inside the microcapillaries. The PU prepolymer (NOA60) was infiltrated into a microcapillary containing colloidal crystals and then photopolymerization proceeded to capture the preformed structure of CylCC. Figure 4a,b shows SEM images of the polymeric inverted replica after the silica beads and microcapillaries were removed by HF etching.

Ordered macroporous cylinders of an inorganic substrate have also been fabricated as shown in Figure 4c,d. The process involves mixing nanometer-sized silica particles (Ludox, HS-40) into a submicrometer-sized PS colloidal dispersion. The concentrations of PS beads and silica nanoparticles in water were 10 vol %, and the mixture was prepared with the same volume ratio. Then,

the mixture dispersion was infiltrated into a PMMA microcapillary. The ultrafine silica particles were consolidated at the interstices between the larger PS beads that were undergoing self-organization during evaporation of water. By using silica nanoparticles instead of a sol-gel synthetic route from silica precursors, we could minimize vacancies, which are common defects in colloidal crystals.²² Furthermore, the volume shrinkage of the consolidated silica nanoparticles during heat treatment was about $\sim 6\%$, which was less than that of silica gel. Therefore, the present method provided enhanced thermal stability.²³ Eventually, the polymeric colloidal crystal template and microcapillary were removed by thermal decomposition leaving behind silica inverted CylCC with ordered macropores. The inverted silica CylCC also exhibited a hexagonal arrangement of air voids with interconnected windows, which is clearly seen from Figure 4d.

Conclusions

In conclusion, polymeric and inorganic CylCCs were obtained by using different types of particles and microcapillaries. Further, the shaped colloidal crystals were used as templates for inorganic and polymeric inverted replicas of the CylCCs. These cylinders with ordered macropores can be applied to photonic devices such as a fiber Bragg grating²⁴ for optical communications and as supporting materials for catalysis, separation, and chromatography.

Acknowledgment. This work was supported by the Brain Korea 21 Program, CUPS-ERC, and the "National R&D Project for Nano Science and Technology" of the Ministry of Science and Technology.

LA0358015

(19) Pickett, G. T.; Gross, M.; Okuyama, H. *Phys. Rev. Lett.* **2000**, *85*, 3652.

(20) Xia, Y.; Yin, Y. *J. Am. Chem. Soc.* **2003**, *125*, 2048.

(21) Bausch, A. R.; Bowick, M. J.; Cacciuto, A.; Dinsmore, A. D.; Hsu, M. F.; Nelson, D. R.; Nikolaides, M. G.; Travasset, A.; Weitz, D. A. *Science* **2003**, *299*, 1716.

(22) Meng, Q.-B.; Fu, C.-H.; Einaga, Y.; Gu, Z.-Z.; Fujishima, A.; Sato, O. *Chem. Mater.* **2002**, *14*, 83.

(23) Subramanian, G.; Manoharan, V. N.; Thorne, J. D.; Pine, D. J. *Adv. Mater.* **1999**, *11*, 1261.

(24) Hill, K. O.; Meltz, G. *J. Lightwave Technol.* **1997**, *15*, 1263.