J|A|C|S
A R T I C L E S

Using Hierarchical Self-Assembly To Form Three-Dimensional Lattices of Spheres

Hongkai Wu,[†] Venkat R. Thalladi,[†] Sue Whitesides,[‡] and George M. Whitesides*,[†]

Contribution from the Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, and School of Computer Science, McGill University, 3480 University Street #318, Montreal, Quebec, H3A 2A7, Canada

Received July 31, 2002

Abstract: This paper describes an approach to the fabrication of three-dimensional (3-D) structures of millimeter-scale spherical beads having a range of lattices—tetragonal, cubic, and hexagonal—using hierarchical self-assembly. The process has five steps: (i) metal-coated beads are packed in a rod-shaped cavity in an elastomeric polymer (poly(dimethylsiloxane), PDMS); (ii) the beads are embedded in a second polymer (PDMS or polyurethane, PU) using a procedure that leaves the parts of the beads in contact with the PDMS exposed; (iii) the exposed areas of the beads are coated with a solder having a low melting point; (iv) the polymer rods—with embedded beads and exposed solder drops—are suspended in an approximately isodense medium (an aqueous solution of KBr) and allowed to self-assemble by capillary interactions between the drops of molten solder; and (v) the assembly is finished by several procedures, including removing the beads from the polymer matrix by dissolution, filling the voids left with another material, and dissolving the matrix. The confinement of the beads in regular structures in polymer rods makes it possible to generate self-assembled structures with a variety of 3-D lattices; the type of the lattice formed can be controlled by varying the size of the beads, and the size and shape of the cross-section of the rods.

Introduction

This work uses hierarchical self-assembly to generate three-dimensional (3-D) ordered arrays of millimeter-scale spherical beads with a range of space lattices. Its ultimate objective is to develop a strategy that can generate ordered 3-D structures of smaller (micron- and nanometer-scale) objects; such structures could function, inter alia, as photonic band gap (PBG) materials,[1−4] and they might also be useful in 3-D microelectronic devices,[5,6] and as matrixes for tissue culture.[7−9] The original work of Yablonovich and John established the potential of 3-D lattices as PBG materials,[2,3] but the fabrication of arbitrary 3-D lattices using the methods of planar lithography remains difficult.[10−14] Self-assembly of colloidal beads provides an alternative route to PBG materials, but the beads tend to form face-centered-cubic (fcc) or hexagonal-close-packed (hcp) structures, or structures by random stacking of hexagonal planes.[15−18] Templating the self-assembly expands the types of accessible lattices, but the range of structures that can be prepared this way remains to be established.[19−23] Procedures that begin by forming structurally defined aggregates of beads may also lead to new solids. Routes leading to lattices of beads other than fcc or hcp, and to lattices of nonspherical objects, would be useful.[24,25]

Here, we explore a new method for making regular lattices of beads. This method is based on hierarchical self-assembly.

---

* To whom correspondence should be addressed. E-mail: gwhitesides@gmwgroup.harvard.edu.

[†] Harvard University.

[‡] McGill University.

(1) Joannopoulos, J. D.; Meade, R. D.; Winn, J. N. *Photonic Crystals*; Princeton University Press: New Jersey, 1995.

(2) John, S. *Phys. Rev. Lett.* **1987**, *58*, 2486−2489.

(3) Yablonovitch, E. *Phys. Rev. Lett.* **1987**, *58*, 2059−2062.

(4) Soukoulis, C. M. *Photonic Band Gap Materials*; Kluwer Academic Publishers: Boston, 1995; Vol. 315.

(5) Varadan, V. K.; Varadan, V. V. *Proc. SPIE-Int. Soc. Opt. Eng.* **1999**, *3879*, 116−123.

(6) Gracias, D. H.; Tien, J.; Breen, T. L.; Hsu, C.; Whitesides, G. M. *Science* **2000**, *289*, 1170−1172.

(7) Yang, S.; Leong, K.-F.; Du, Z.; Chua, C.-K. *Tissue Eng.* **2002**, *8*, 1−11.

(8) Bellamkonda, R.; Ranieri, J. P.; Bouche, N.; Aebischer, P. *J. Biomed. Mater. Res.* **1995**, *29*, 663−671.

(9) Widmer, M. S.; Mikos, A. G. In *Frontiers in Tissue Engineering*; Patrick, C. W., Jr., A. G. M., Mcintire, L. V., Eds.; Pergamon: New York, 1998; p 107.

(10) Cheng, C. C.; Scherer, A. *J. Vac. Sci. Technol., B* **1995**, *13*, 2696−2700.

(11) Lin, S. Y.; Fleming, J. G.; Hetherington, D. L.; Smith, B. K.; Biswas, R.; Ho, K. M.; Sigalas, M. M.; Zubrzycki, W.; Kurtz, S. R.; Bur, J. *Nature* **1998**, *394*, 251−253.

(12) Leung, K. M. *Phys. Rev. B* **1997**, *56*, 3517−3519.

(13) Lin, S. Y.; Fleming, J. G.; Chow, E. *MRS Bull.* **2001**, *26*, 627−631.

(14) Noda, S.; Tomoda, K.; Yamamoto, N.; Chutinan, A. *Science* **2000**, *289*, 604−606.

(15) Wijnhoven, J. E. G. J.; Vos, W. L. *Science* **1998**, *281*, 802−804.

(16) Blanco, A.; Chomski, E.; Grabtchak, S.; Ibisate, M.; John, S.; Leonard, S. W.; Lopez, C.; Meseguer, F.; Miguez, H.; Mondia, J. P.; Ozin, G. A.; Toader, O.; van Driel, H. M. *Nature* **2000**, *405,* 437−440.

(17) Muller, M.; Zentel, R.; Maka, T.; Romanov, S. G.; Sotomayor-Torres, C. M. *Adv. Mater.* **2000**, *12*, 1499−1503.

(18) Lu, Y.; Yin, Y.; Gates, B.; Xia, Y. *Langmuir* **2001**, *17*, 6344−6350.

(19) Vlasov, Y. A.; Bo, X.-Z.; Sturm, J. C.; Norris, D. J. *Nature* **2001**, *414*, 289−293.

(20) van Blaaderen, A.; Rue, R.; Wiltzius, P. *Nature* **1997**, *385*, 321−324.

(21) Cheng, Z.; Russel, W. B.; Chaikin, P. M. *Nature* **1999**, *401*, 893−895.

(22) Velikov, K. P.; Christova, C. G.; Dullens, R. P. A.; van Blaaderen, A. *Science* **2002**, *296*, 106−109.

(23) Yin, Y.; Xia, Y. *Adv. Mater.* **2002**, *14*, 605−608.

(24) Li, Z.-Y.; Gu, B.-Y.; Yang, G.-Z. *Phys. Rev. Lett.* **1998**, *81*, 2574−2577.

(25) Toader, O.; John, S. *Science* **2001**, *292*, 1133−1135.

10.1021/ja0210446 CCC: $22.00 © 2002 American Chemical Society

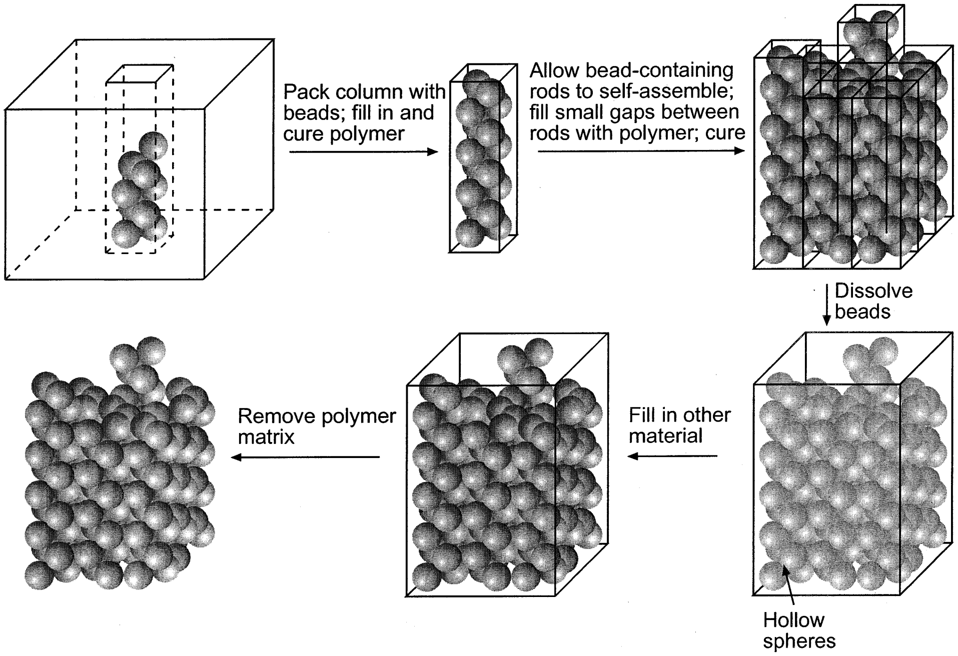

Figure 1. Schematic illustration of the method to form different lattices of spherical beads. Four steps are involved: (1) packing the beads into channels and fixing them in a rod-shaped matrix; (2) allowing the rods with embedded beads to self-assemble; (3) removing the beads to reveal a lattice of air spheres in the matrix; and (4) filling the voids to transform the structure into other materials.

The beads are first packed into rods in which the space between the beads is filled with an organic polymer; the polymer rods are then allowed to self-assemble. The beads in adjacent rods are caused to connect with one another, and either the beads or the polymer is removed from the assembled structure (Figure 1). The polymer matrix is important in the process: it supports the beads so that the self-assembled structures are stable and do not collapse. The cross-sectional shapes and areas of the rods play a crucial role in determining the structures that form on both stages of self-assembly.

This method of self-assembly can generate ordered 3-D arrays of beads. Because of the influence of confinement during packing on the configuration of the beads in the rods, and of the patterns of solder dots on rods on the structures of the 3-D solids, the beads can generate a wide variety of geometries and structures. The results described in the paper demonstrate that 1 mm beads can be formed into arrays using this method, and initial results suggest that it can also be used to form arrays of 100 μm beads. The experiments here are proofs-of-concept and use large (1 mm) beads to facilitate the characterization of the resulting assemblies. Whether the method can be extended to the smaller beads (0.1−10 μm) required for PBG materials in the IR/visible range is a subject for future research.

Design Rules for Packing Beads in Columns

Ratio of the Diameters of Spherical Beads to the Size of Square Columns. We choose the relative size of beads and columns, and the shape of the columns, to allow beads to pack into structures having the desired geometries (Figure 2). This packing of beads in columns of different shapes and sizes provides a route to a range of starting structures. In general, the beads pack into the array that has the highest filling factor (i.e., the ratio of the volume of the beads to the volume of the column). We use square columns as an example to show the dependence of the structure formed on the dimensions of the beads and of the column into which they pack. In Figure 2, L is the length of the square cross-section of the column, and D is the diameter of the beads. In the stage of design, we consider the molds and beads to be incompressible. When the beads are too big ($D/L > 1$), they cannot fit into the column. When the beads exactly fit the column ($D/L = 1$), they pack in a line, centered in the column. Bead-to-bead contact in neighboring columns after self-assembly causes the final structure to be a simple cubic lattice. As the beads become smaller relative to the column ($0.59 < D/L < 1$), they form a zigzag chain; this packing, after self-assembly, generates a body-centered-tetragonal lattice with four neighboring beads as its repeat unit.[26] A further decrease in the size of the beads ($0.5 < D/L < 0.59$) allows two beads to fit diagonally in a cross-sectional plane of the column; the next layer of two beads occupies the orthogonal diagonal direction. Although the final lattice of beads derived from this structure remains body-centered-tetragonal, the filling factors and the dimensions of the lattice (c/a) are different from those of the previous lattice and are dependent on D/L. For even smaller beads ($D/L < 0.5$), packing in the columns becomes more complicated, and the self-assembly becomes more complex; we do not discuss these cases here. If the cross-sectional area of the column is much larger than the diameter of the beads ($D/L < 0.2$), the beads start to form close-packed arrays within the column.

Shape of the Column. The shape (i.e., the cross-section) of the column also influences the symmetry of the sub- and final lattices. Triangles, parallelograms (including rectangles and squares), and regular hexagons are the only shapes that can repeat themselves periodically to cover a planar surface without overlap (that is, to "tile" the surface); thus, only those columns with cross-sections of these shapes can self-assemble to fill the 3-D space. Close-packing of the rods is not the only arrangement

---

(26) A repeat unit is the unit that can reconstruct a structure by repeating itself translationally in the Bravais lattice of the structure.

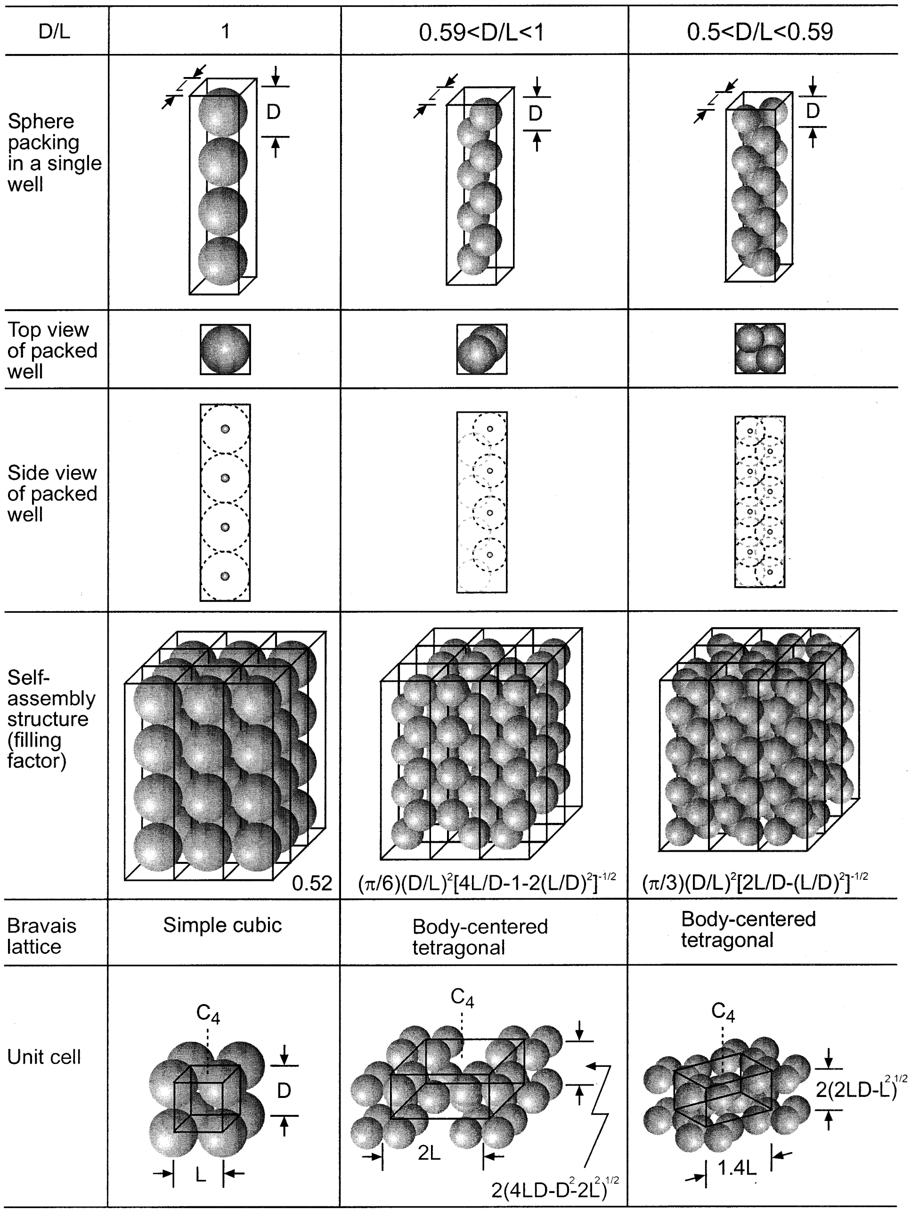

Figure 2. Beads pack into square columns in different ways as their size (relative to the size and shape of the column) changes from 1.00 to 0.59 (diameter of bead, *D*/side of square, *L*). The structure resulting from self-assembly of these bead-containing rods changes from a simple cubic lattice to a body-centered-tetragonal lattice over this range. Other properties—the filling factor of the solid by the spheres and the dimension of the lattice—also change.

possible in self-assembly, but it tends to be the most dense, most stable, and best ordered. Figure 3 lists the structures that can be formed by packing columns of triangular, hexagonal, or rectangular cross-sections. Beads in triangular columns or hexagonal columns both form hexagonal lattices; the repeat units of these lattices are, however, different, as are the dimensions (c/a) of the lattice. The triangular columns direct the beads to form a graphite-type structure. Beads in the hexagonal columns form an array that vertically stacks planar, close-packed sheets of beads. If the columns have a rectangular cross-section, the beads form orthorhombic lattices. Zigzag packing of beads in single columns results in a final lattice that is body-centered-orthorhombic; if the cross-section of the rectangle is just big enough to accommodate two beads, the final structure becomes face-centered. The beads in a column having the cross-section of a parallelogram cannot self-assemble into an ordered continuous structure (Figure 4), because the beads do not contact one another.

There are other shapes (e.g., circles) and polygons (e.g., octagons) that do not tile a planar surface, but that still, in principle, might allow the formation of columns that would pack into ordered structures or quasi-ordered structures (e.g., a Penrose tiling). These structures still must satisfy the requirement of self-assembly that the beads contact one another between columns. These and other shapes broaden the number of structures we can, in principle, generate using this procedure. Figure 3 (last column) shows an example of rods with a circular cross-section. With beads packed in them, the rods can generate an ordered structure in which the beads form a simple cubic lattice with a distinct repeat unit.

Results and Discussion

Preparation of Beads and Filling the Beads into Rods Prior to Self-Assembly. The starting point for the hierarchical self-assembly described in this work was polymer (polymethyl methacrylate (PMMA)) beads (Figure 5). These beads were first

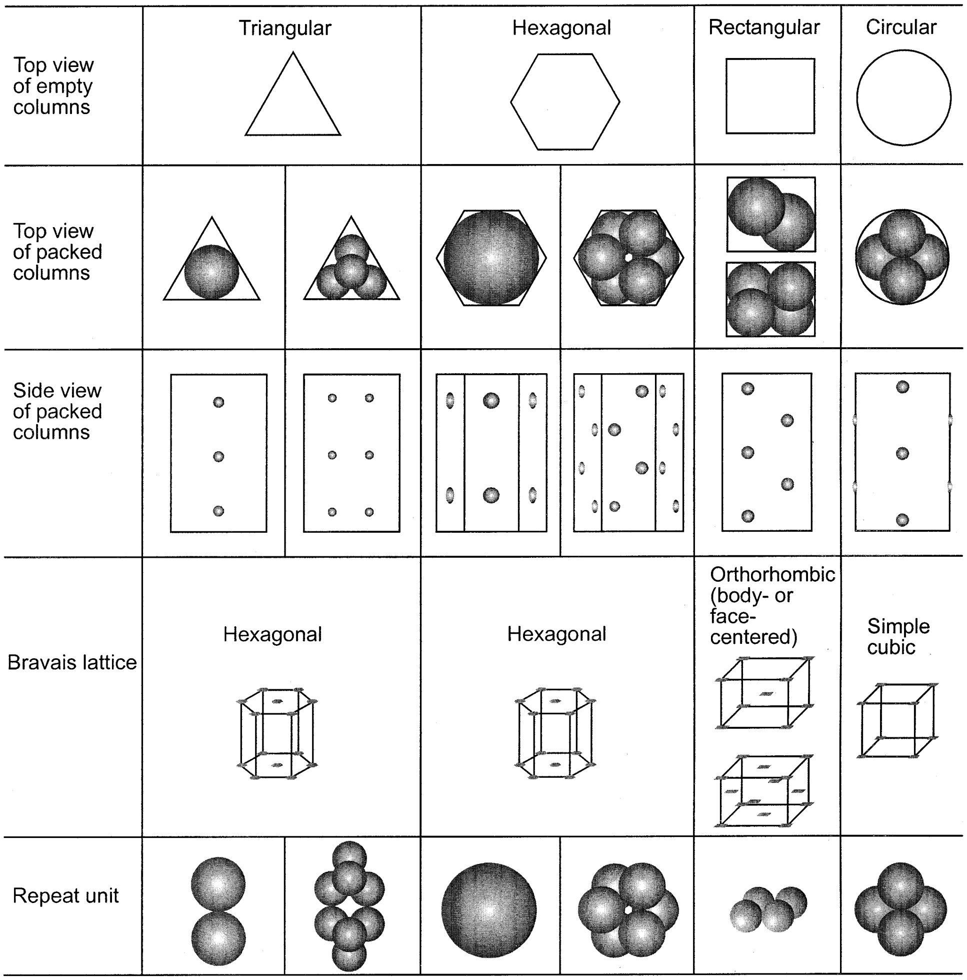

Figure 3. Packing of spheres into columns with cross-sections other than square results in a range of structures for the lattice of beads.

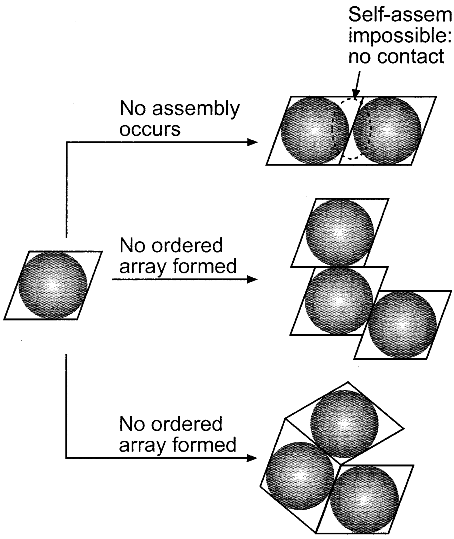

Figure 4. Beads packed in rods having a cross-section of a parallelogram cannot assemble into ordered, continuous structures.

coated with a thin film of copper by electroless deposition; this coating made the beads wettable by a low melting-point solder (mp 47 °C, Small Parts, Inc.). A PDMS column for the self-assembly of the beads was prepared by casting the prepolymer of PDMS around a suitable template (commonly a brass rod), curing the PDMS, and removing the template. We added a few drops of ethanol as lubricant to the PDMS column and positioned the column so that its long axis was vertical; copper-coated beads, added to the column, packed by gravity.

When the beads filled the column to the top, we allowed the ethanol to evaporate, and then we filled the rest of the space in the column with a polyurethane (PU) precursor. After curing this PU precursor under UV light for 2 h, we removed the resulting, bead-packed PU rods from the PDMS molds. The columns were designed to be slightly (~5%) smaller than the geometrical size suggested in the Design section. This slight mismatch in size guaranteed that the parts of the beads in contact with the walls of the PDMS column were *not* covered by PU. We then coated the exposed surfaces of the copper-coated beads with solder by dipping the PU rods into, and withdrawing them from, a heated bath of liquid solder.

Self-Assembly of the Rods Containing Beads. We have previously described the procedure of self-assembly with solder that was used here for the millimeter-scale rods.[6,27,28] Briefly, approximately 4-cm-long rods were suspended in a roughly isodense, aqueous solution of potassium bromide (KBr) at 60 °C in a Morton flask; the pH of this solution was adjusted to 4 with 1 N HCl solution to prevent the oxidation of solder. When the rods were agitated by rotation of the flask, the drops of liquid solder merged. The resulting capillary interactions held the rods

---

(27) Breen, T. L.; Tien, J.; Oliver, S. R. J.; Hadzic, T.; Whitesides, G. M. *Science* **1999**, *284*, 948−951.
(28) Jacobs, H. O.; Tao, A. R.; Schwartz, A.; Gracias, D. H.; Whitesides, G. M. *Science* **2002**, *296*, 323−325.

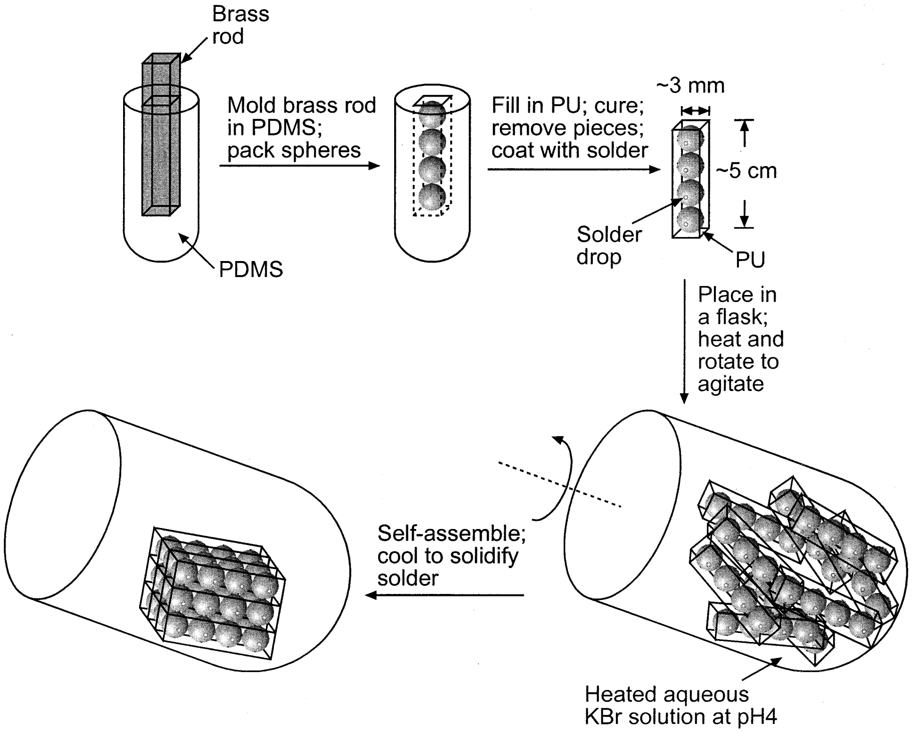

Figure 5. Schematic procedure used to pack spheres in columns and to allow self-assembly of these columns in a heated aqueous KBr solution at pH 4.

together. After self-assembly was complete, the suspension was allowed to cool to room temperature. The solder solidified and rendered the resulting structures mechanically stable. The rotation speed and the KBr concentration (and, thus, the density of the solution) controlled the intensity of agitation.[27] During the rotational agitation, all of the rods aligned with their long axes parallel to the axis of rotation of the flask within the first few minutes. Small aggregates comprising from two to four rods formed first, and these small aggregates combined further into a large array. The whole self-assembly process usually required about 30 min to form the array (e.g., 20 square rods, each with dimensions of ∼3 mm on a side and ∼4 cm in length).

Figure 6 shows two self-assembled structures. For the hexagonal lattice shown in Figure 6a, beads were assembled in a triangular polymer column (see inset) before self-assembly. The beads packed in the triangular column with their centers along the axis of the column. Each column had about 15 beads; a group of 21 columns self-assembled into an array containing more than 300 beads. The beads in the final structure formed a hexagonal lattice with the *c* axis of the lattice along the axis of the columns with two neighboring beads as the repeat unit of the structure. In Figure 6b, the size of the square column and the beads were designed so that two beads just fit in the square (see inset). Each layer of packed beads in a column had a 90° rotation relative to its neighboring layer. Each column had around 40 beads; all of the 13 columns in a batch self-assembled into a structure that had the beads in a body-centered-tetragonal lattice. The repeat unit of the bead array was an aggregate of four neighboring beads. This structure corresponds to the lattice shown in the last column of Figure 2.

The relative density of the rods and the solution is important in determining the outcome of the self-assembly. If the rods are too heavy, aggregates fall through the solution, collide, and break apart during agitation. We used PMMA beads ($d = 1.34$ g/cm^3) because it was easy to match that density by adding KBr to water. We also surveyed heavier beads. If the beads were made of glass ($d = \sim 2.6$ g/cm^3), the aggregates were small and consisted of three or four rods. Carefully slowing the agitation (from 50 to 20 rpm) helped bigger aggregates to form, but these aggregates were usually smaller than 10 rods. When we used brass beads ($d = 8.47$ g/cm^3), no stable aggregates

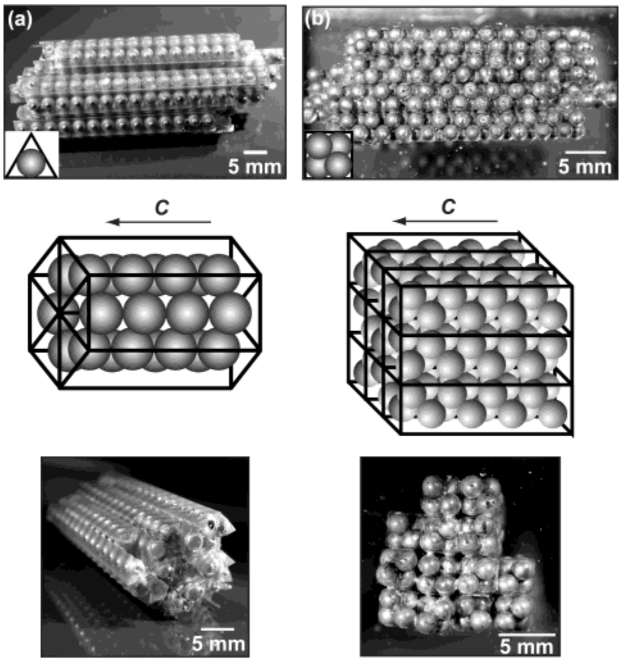

Figure 6. (a) Left column: a self-assembled hexagonal lattice of metal-coated, polymer beads. (b) Right column: a self-assembled body-centered-tetragonal lattice of polymer beads. For both columns, the top photographs are the side view of the self-assembled structures (the insets are schematic top view of packed columns); the middle ones are the schematic illustration of the structures; and the bottom photographs are the top view of the structures.

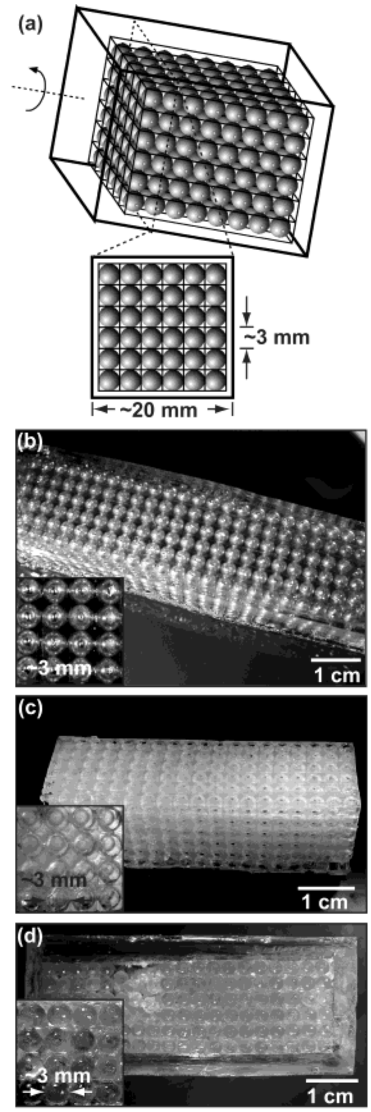

Figure 7. Template effect of the container on the self-assembly of rods. (a) Schematic outline of self-assembly in a container that acted as a template for the final, desired structure. (b) Photograph of a self-assembled simple-cubic lattice of brass beads. (c) Photograph of a PDMS structure generated by dissolving the brass beads and solder in the structure shown in (b); the slight rough shape of the edges of the structure was caused by cutting with a razor blade to expose the brass beads to their etchant. (d) Photograph of a simple-cubic lattice of epoxy beads formed by filling and curing epoxy in the structure shown in (c), and removing PDMS; a few beads were removed on the top layers to examine the inner structure. In (b), (c), and (d), an inset shows the details of each structure.

were formed in a standard Morton flask having a cross-section that was much larger than the largest possible aggregate.

Template Effect of the Size of the Container on Self-Assembly. The aggregates of the heavy beads can be stabilized by controlling the size and shape of the container in which the assembly takes place. In Figure 7a, 36 square rods of PDMS containing brass beads were arranged and placed in a square cylinder; the cross-section of the cylinder was only ~15% larger than that of the aggregate of the 36 rods. The small size of this container (i.e., only slightly larger than that of the aggregate) limited the free space available to the rods during the assembly and decreased the possibility that the aggregates, as they formed, would break apart. The use of a small container thus greatly facilitated the self-assembly of large aggregates. We chose the square shape for the container because (i) it provided agitation when rotated during the self-assembly (in comparison, a circular cylinder generates little or no agitation, and the rods simply slid along the walls of the container during its rotation), and (ii) a square cross-section assisted the system of square rods to self-assemble into the desired, square structure. Using this procedure, we generated an aggregate of $\sim 10^3$ beads arranged in a simple cubic lattice. After the self-assembly was completed, we dried the aggregate and molded it into PDMS (Figure 7b); the PDMS glued the structure together even after the beads and solder were removed (see the next section).

Conversion of the Self-Assembled Structures into Other Materials. Once a structure of beads had been formed, the PDMS was cut to expose the metal beads, which were removed by chemical wet etching or by dissolution in appropriate solvents; this process leaves a PDMS matrix incorporating the complementary structure of air spheres. Figure 7c shows an optical photograph of the structure of PDMS with spherical voids obtained by dissolving the brass beads and solder drops (of the structure shown in Figure 7b) in nitric acid. This structure of PDMS can be used as a template to transform the voids into other materials. For example, a UV-curable epoxy was filled into the vacant space in the structure in Figure 7c. After it had been cured with UV light, the PDMS was removed by dissolution in a tetrahydrofuran solution (1.0 M) of tetrabutylammonium fluoride. Figure 7d shows that the simple cubic structure of brass beads had been converted into the lattice of the epoxy; this faithful conversion of the PDMS structures of voids into plastic verified that all of the hollow space in PDMS (Figure 7c) was interconnected. Many previous studies have demonstrated that voids in a structure of the types generated here can be filled with a wide variety of materials;[15,16,19,29−32] these self-assembled structures can, thus, in principle, be transformed into corresponding structures based on materials for which beads are not available.

Extension to 100-μm Beads. Xia, Ozin, and others demonstrated previously the use of patterned substrates as templates to grow colloidal crystals with specific crystalline orientations[20,23,33−36] and to form small, uniform structures of colloidal beads with sizes as small as a few hundred nanometers.[37−40] Although these methods have fully shown the ability to control crystalline orientation, geometric shape, and size, their capability to generate nonclose-packed arrays of colloids still needs to be demonstrated.

To begin to test the applicability of the protocol in this paper to beads having smaller sizes, we examined the packing of small (100 μm) beads in microfluidic channels (Figure 8), and we

---

(29) Braun, P. V.; Zehner, R. W.; White, C. A.; Weldon, M. K.; Kloc, C.; Patel, S. S.; Wiltzius, P. *Adv. Mater.* **2001**, *13*, 721−724.

(30) Jiang, P.; Cizeron, J.; Bertone, J. F.; Colvin, V. L. *J. Am. Chem. Soc.* **1999**, *121*, 7957−7958.

(31) Braun, P. V.; Wiltzius, P. *Nature* **1999**, *402*, 603−604.

(32) Zakhidov, A. A.; Baughman, R. H.; Iqbal, Z.; Cui, C.; Khayrullin, I.; Dantas, S. O.; Marti, J.; Ralchenko, V. G. *Science* **1998**, *282*, 897−901.

(33) Ozin, G. A.; Yang, S. M. *Adv. Funct. Mater.* **2001**, *11*, 95−104.

(34) Lin, K.-H.; Crocker, J. C.; Prasad, V.; Schofield, A.; Weitz, D. A.; Lubensky, T. C.; Yodh, A. G. *Phys. Rev. Lett.* **2000**, *85*, 1770−1773.

(35) Kim, E.; Xia, Y.; Whitesides, G. M. *Adv. Mater.* **1996**, *8*, 245−247.

(36) Yang, S. M.; Ozin, G. A. *Chem. Commun.* **2000**, 2507−2508.

(37) Yin, Y.; Lu, Y.; Gates, B.; Xia, Y. *J. Am. Chem. Soc.* **2001**, *123*, 8718−8729.

(38) Yin, Y.; Lu, Y.; Xia, Y. *J. Am. Chem. Soc.* **2001**, *123*, 771−772.

(39) Velev, O. D.; Lenhoff, A. M.; Kaler, E. W. *Science* **2000**, *287*, 2240−2243.

(40) Velev, O. D.; Furusawa, K.; Nagayama, K. *Langmuir* **1996**, *12*, 2374−2384.

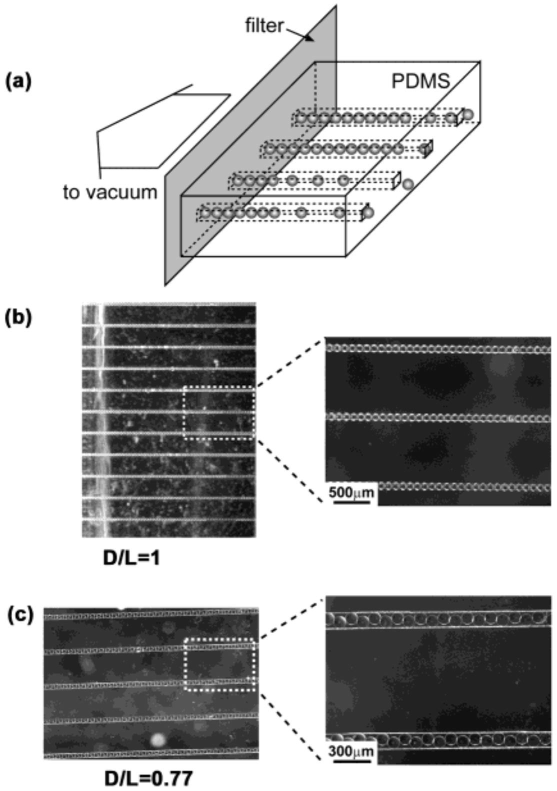

Figure 8. (a) Scheme of the process used to pack small beads into microfluidic channels. Straight channels in PDMS with open ends were fabricated by soft lithography. A filter was placed at one end of the channels, and vacuum was applied across the filter. When an aqueous solution containing small, suspended beads was added at the other end, the vacuum pulled water and the beads into the channels. The beads packed regularly in the channels. (b) and (c): Optical photographs of packed beads in these channels. The beads were 100 μm in diameter, and channels had a square cross-section. In (b), the sides of the channel opening were 100 μm ($D/L = 1$), and beads lined up their centers along the channels; in (c), the sides were 130 μm ($D/L = 0.77$), and beads formed a zigzag chain.

found that the beads packed in the channels as designed. The channels shown in Figure 8 were fabricated in PDMS by soft lithography and related techniques.[41,42] These channels had a square or rectangular cross-section. The lateral dimensions of the channels were determined by photomasks, and the height of the channels was controlled by the rate and duration of spin-coating photoresist during photolithography. We focused on polystyrene beads with 100 μm diameter. With beads of this size in aqueous solution, gravity is not effective in causing packing. Instead, we used air pressure or capillarity to pack beads in the channels. We filled in channels with beads of matching size under a house vacuum. The beads flowed into the channels and stopped at a filter that was placed at the outlet of the channels. Using this procedure, we formed centimeter-long (on the order of 10^3 beads) straight or zigzag chains depending on the relative cross-section of the channels with respect to that of the beads.

This work demonstrates (as expected from the work of others[20,23,33−36,43,44]) that it is possible to pack 100-μm sized beads into long channels in a way analogous to the procedure used to pack the millimeter-scale beads used in most of this paper. Work from other groups[20,23,33−36,43,44] suggests that this method can be extended to beads and channels in the submicron region. The hierarchical self-assembly of beads of 1−100 μm dimensions will be carried out in future work.

Conclusion

We have demonstrated a new strategy for generating regular 3-D arrays of beads by hierarchical self-assembly. In this strategy, beads pack in confined columnar wells; the orientation of the beads within the columns can be controlled by changing the shape and the size of the cross-section of the columns. The columns were filled with a polymer to form rods containing the beads; self-assembly of the rods formed extended 3-D lattices. Although Bravais lattices with low symmetry (triclinic, monoclinic) cannot be generated with this method (at least as developed here), the technique provides a practical way to form structures having lattices with high symmetry (cubic, hexagonal, tetragonal, or orthorhombic). It may be possible to extend this approach to systems having beads with more than one size. These millimeter-size structures with different lattices could be useful as resonance materials in the microwave range and for acoustic waves;[45] both have wavelengths in the range of millimeters.

The method described in this work can generate lattices that have not been accessible, or cannot be easily fabricated, by previously developed methods.[11,13,15,18,23,46,47] The applicability of the current method, however, has been demonstrated only at the millimeter-scale and to structures containing a few hundreds of spheres; its extension to micron-scale structures containing millions of beads remains to be established.

Experimental Section

Materials. All commercially obtained materials were used as received. PMMA beads, brass beads, and metal meshes were purchased from Small Parts, Inc., Miami Lakes, FL. Polystyrene beads were obtained from Duke Scientific Corp., Palo Alto, CA. The silver sensitizing agent, silver electroless solutions A, B, and C, and copper electroless solutions A and B were purchased from Peacock Corp., Philadelphia, PA. The PDMS prepolymer (Sylgard 184), the PU precursor (Norland optical adhesive 73), the negative photoresist (NANO XP SU-8) and the UV-curable epoxy (UVO-114) were from Dow Corning, Midland, MI, Norland Products Inc., Cranbury, NJ, MicroChem Corp., Newton, MA, and EPO-TEK, Billerica, MA, respectively.

Electroless Deposition of Cu/Ag on Plastic Beads. Polymethyl methacrylate (PMMA) beads were rinsed with ethanol and blown dry. These beads were arranged in the form of a monolayer in a Petri dish and oxidized for 1 min in an oxygen plasma using a plasma cleaner (Harrick PDC-23G). After being rinsed with the silver sensitizing agent and dried, the beads were immersed in a 1:1:1 mixture of the silver electroless solutions A, B, and C for 2 min; a thin layer of silver (∼0.5 μm) formed at the surface of the beads and served as a promoter for the subsequent copper coating. The silver-coated beads were rinsed with deionized water and immersed in a mixture of a 1:1 copper electroless solutions A and B for 2−3 h to be coated with a copper layer (∼5 μm). These copper-coated beads were rinsed with deionized water and blown dry for use in self-assembly.

---

(41) Xia, Y.; Whitesides, G. M. *Annu. Rev. Mater. Sci.* **1998**, *28*, 153−184.
(42) Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 550−575.
(43) Yin, Y.; Lu, Y.; Xia, Y. *J. Mater. Chem.* **2001**, *11*, 987−989.
(44) Xia, Y.; Gates, B.; Yin, Y.; Lu, Y. *Adv. Mater.* **2000**, *12*, 693−713.
(45) Liu, Z.; Zhang, X.; Mao, Y.; Zhu, Y. Y.; Yang, Z.; Chan, C. T.; Sheng, P. *Science* **2000**, *289*, 1734−1736.
(46) Holland, B. T.; Blanford, F.; Stein, A. *Science* **1998**, *281*, 538−540.
(47) Campbell, M.; Sharp, D. N.; Harrison, M. T.; Denning, R. G.; Turberfield, A. J. *Nature* **2000**, *404*, 53−56.

Fabrication of Bead-Filled Rods. Brass rods (standard sizes from Small Parts, Inc., or machined locally) were placed in plastic tubes, and PDMS was molded around them. After PDMS prepolymer was cured at 60 °C for 2 h, the brass rods were removed to give PDMS molds with columnar wells. The columns were positioned with their long axis vertical and filled with the copper-coated beads (or brass beads) manually with a pair of tweezers. A few drops of ethanol lubricated the filling process. When the beads filled the wells to the top, the ethanol was allowed to evaporate under house vacuum for 2 h. Liquid polyurethane (PU) precursor (or PDMS) was allowed to fill the void space in the bead-packed columns and was cured under UV light for 3 h (or at 60 °C for 3 h). These PU (or PDMS) rods with embedded beads were taken out from the PDMS columns, and dipped into and withdrawn from liquid solder at ∼80 °C under an acidic aqueous solution (pH 4 adjusted with 1 N HCl; this solution removed oxide from the surface of the solder). The liquid solder wetted and coated the exposed copper surfaces of the beads.

Self-Assembly. The rods filled with beads were placed in a 100 mL Morton flask (for the brass beads, a homemade cylindrical tube with a square cross-section was used instead) containing concentrated KBr solution. The flask was mounted on a rotary evaporator at a tilt angle of 10° relative to the horizontal and was rotated to agitate the mixture of rods. During the agitation, we kept the temperature of the solution at 75 °C using a heat gun. Once the self-assembled structures had formed and were stable, we stopped the agitation and let the solution cool to room temperature. The structures were removed from the flask and imaged.

Conversion of the Self-Assembled Structures into Other Materials. The self-assembled aggregate of brass beads in PDMS rods was rinsed with water and ethanol, and then dried in a stream of nitrogen. PDMS prepolymer was poured on the structure and cured at 50 °C for over 5 h. After cutting the PDMS with a razor blade to expose the brass beads on each side, we immersed the structure in 20% nitric acid to dissolve the brass beads and solder. The resulting structure of hollow spheres in PDMS was rinsed in water and dried in a stream of nitrogen. A UV-curable epoxy was poured onto this PDMS structure and degassed under a house vacuum. After being cured under UV light (Model B 100 AP, UVP, Upland, CA) overnight, the structure was immersed in a 1.0 M tetrahydrofuran solution of tetrabutylammonium fluoride (TBAF) (Aldrich) for 3 h to dissolve the PDMS. ***Caution:*** *Solutions containing fluoride ions are very toxic to skin and bones and should be handled with appropriate precautions, and with counter measures available.* This overall procedure had the effect of converting a simple cubic lattice of brass beads into a corresponding lattice of epoxy beads.

Fabrication of Microfluidic Channels and Packing the Beads in the Channels. The photomasks for photolithography were generated using rapid prototyping.[48] The pattern was designed using a CAD program (Macromedia Freehand 8.0); files containing these patterns were sent to a commercial high-resolution printer (5000 dpi) and printed onto transparencies.[48] Using the transparencies as photomasks, we fabricated masters in SU-8 photoresist on silicon wafers by 1:1 contact photolithography.

Microfluidic channels in PDMS were fabricated by molding against the SU-8 master.[49−51] The surface of the SU-8 master was made hydrophobic by exposing it to a vapor of perfluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (United Chemical Technologies, Inc., Bristol, PA) in a vacuum desiccator to prevent the adhesion of the PDMS to the SU-8 structure. The PDMS structure was peeled from the master and placed onto a flat slab of PDMS to form fluidic channels. The resultant PDMS channels were cut open at both ends.

A metal mesh with openings of ∼50 μm was pressed at one end of the PDMS channels, and a house vacuum was applied on the backside of the mesh through a tube. Drops of aqueous solution containing suspended polystyrene beads were added with a pipet at the other end of the channels. The beads flowed into the channels under the vacuum and packed. The packed channels were imaged using an optical microscope.

Acknowledgment. This work was supported by the National Science Foundation (CHE-9901358) and the Defense Advanced Research Projects Agency (DARPA). S.W. thanks NSERC (Canada) for support.

JA0210446

---

(48) Qin, D.; Xia, Y.; Whitesides, G. M. *Adv. Mater.* **1996**, *8*, 917−919.
(49) Duffy, D. C.; Mcdonald, J. C.; Schueller, O. J. A.; Whitesides, G. M. *Anal. Chem.* **1998**, *70*, 4974−4984.
(50) McDonald, J. C.; Whitesides, G. M. *Acc. Chem. Res.* **2002**, *35*, 491−499.
(51) McDonald, J. C.; Duffy, D. C.; Anderson, J. R.; Chiu, D. T.; Wu, H.; Schueller, O. J. A.; Whitesides, G. M. *Electrophoresis* **2000**, *21*, 27−40.