Crystallization of Millimeter-Scale Objects with Use of Capillary Forces

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This communication describes the use of self-assembly as a technique for making large, ordered, three-dimensional (3D) arrays of mesoscopic[1] (~1 mm scale) objects. Its objective is to identify processes and motifs at the mesoscale that can be applied at the micro- and perhaps nanoscale, and ultimately, to develop processes that can generate functional 3D structures that consist of micro- and nanoscale components. Three-dimensional structures suggest new interconnect architectures for electronic and optical systems.[2] Existing technologies for making 3D microstructures are limited stereolithography[3] and free-form laser sintering[4] are slow, and traditional casting, machining, and assembly are difficult with small, complex structures or with porous ones. We believe that self-assembly can become a practical strategy for the assembly of large numbers of individual components into ordered aggregates: self-assembling processes operate in parallel, take advantage of cooperative phenomena, and tend to produce structures that are thermodynamic minima and therefore relatively free of defects.[5]

We used capillary forces between thin liquid films coating mm-sized hydrophobic objects to assemble these objects into ordered 3D aggregates ("crystals"). We chose capillarity as the basis for crystallization because it (i) can easily be tailored by varying the interfacial free energy of the liquid–liquid interfaces, (ii) is well-understood theoretically,[6] and (iii) has successfully organized polymeric objects into extended 2D arrays[7] and small 3D structures.[8,9] We used mm-scale objects because their sizes are comparable to the range of capillary forces, and because they are relatively easy to fabricate and observe.

Figure 1 diagrams the assembly process. We cast polymeric objects from silicone molds of the desired shape.[10] The polymer used[11] was hydrophobic: $\theta_a(H_2O) \sim 50°$. Introduction of these objects, together with a small amount of hydrophobic liquid (1–10 μL for every cm² of polymer surface area), into a Morton flask and subsequent filling of the flask with water coated each object with a thin (10–100 μm) film of liquid.[12] This film acted as a lubricant and allowed the pieces to slide laterally when in contact. Rotation of the flask caused the pieces to collide and aggregate. Addition of KBr tailored the density of the aqueous phase and, thus, controlled how rapidly the pieces fell and collided in the rotating flask. Changing the density and/or the speed of rotation varied the intensity of agitation.[13] To assemble arrays
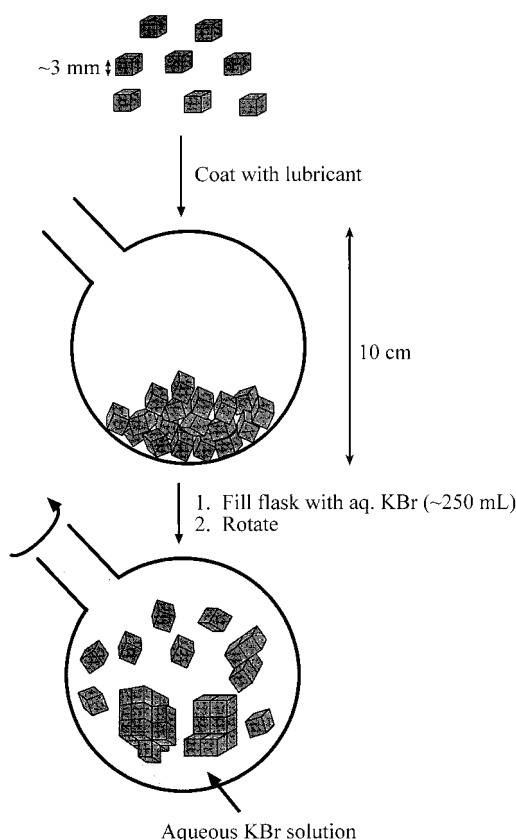
Figure 1. Schematic diagram of fabrication of shapes and assembly into aggregates. We made the polymeric shapes by molding or machining.

that were free-standing, we used a photocurable adhesive as lubricant, allowed assembly to proceed to completion, and irradiated the structures without stopping the agitation or removing the assemblies from the aqueous solution.[14]

Assemblies of 8 and 27 cubes formed rapidly: several cubes reproducibly combined into a "nucleus" within a few minutes, and the remaining cubes attached to this nucleus quickly thereafter (Figure 2). Arrays of larger (>50) numbers of cubes formed in two distinct stages: they first condensed into a few small arrays, and then further combined into a large array. This second stage required >1 day, and weak agitation (that is, agitation carried out with the aqueous phase nearly isodense with the cubes and/or with a low rotation frequency). With strong agitation, the system stabilized as two or three small blocks. In both stages of assembly, the size distribution of arrays remained relatively uniform. The arrays in Figure 2 are internally crystalline; a fraction (~10%) of the arrays we made, however, showed a substantial slip (that is, misalignment on the order of half the width of a cube). We never observed amorphous arrays. Even with very weak agitation, the cubes packed as crystals.

(1) We define "mesoscopic" as the length scale on the order of the phenomena being observed. In our experiments, capillary forces between liquid films coating polymeric objects decrease with a decay length of ~1 mm; thus, we consider mm-scale objects mesoscale.

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(4) DeAngelis, F. E. *Proc. SPIE* **1991,** *1598,* 61–70.

(5) Whitesides, G. M. *Sci. Am.* **1995,** *273,* 146–149.

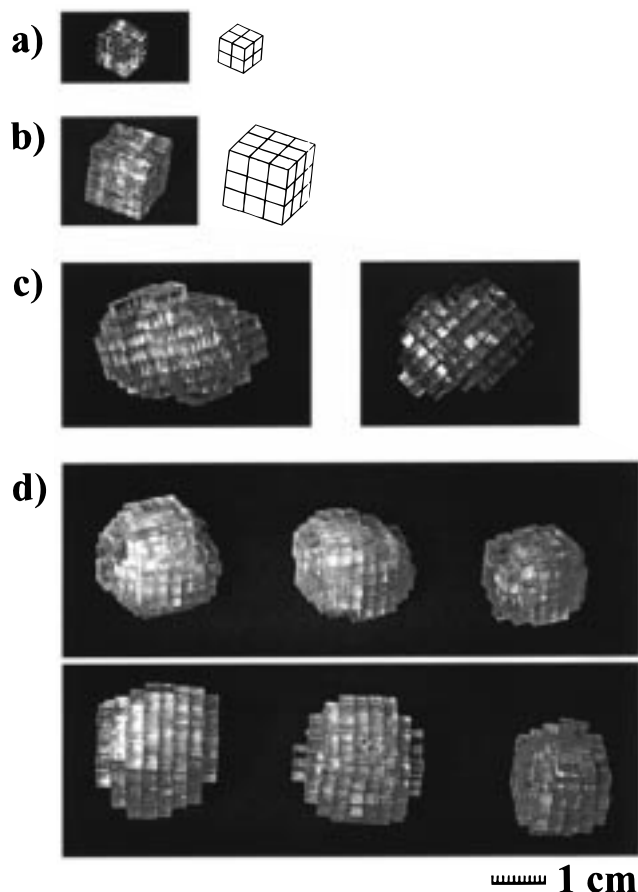(6) Kralchevsky, P. A.; Nagayama, K. *Langmuir* **1994,** *10,* 23–36.

(7) Bowden, N.; Terfort, A.; Carbeck, J.; Whitesides, G. M. *Science* **1997,** *276,* 233–235.

(8) Terfort, A.; Bowden, N.; Whitesides, G. M. *Nature* **1997,** *386,* 162–164.

(9) Terfort, A.; Whitesides, G. M. *Adv. Mater.* **1998,** *10,* 470–473.

(10) Machined aluminum cubes and hexagons were placed in a Petri dish with sufficient poly(dimethylsiloxane) prepolymer (Sylgard 184, DuPont) to cover. Heat (~60 °C, 1 h) cured the prepolymer into a silicone mold; removal of the aluminum shapes created a mold that we filled to make polymeric cubes and hexagons.

(11) A UV-curable polyurethane (J-91; Summers Laboratories; Fort Washington, PA) were used. Cubes with holes were machined from polycarbonate; three perpendicular channels run through each piece.

(12) Each Morton flask (250 mL) was cleaned thoroughly in a KOH/*i*-PrOH bath. A stir-bar in a 20-mL glass vial provided agitation for very small assemblies (<30 pieces). We first coated the polymeric objects with lubricant—either heptane or photocurable adhesive—and then added water to fill the flask entirely.

(13) The photocurable adhesive consisted of dodecyl methacrylate (96 wt %), 1.6-hexanediol diacrylate (2%), and benzoin isobutyl ether (2%). All components were used as received from Aldrich. Curing of the adhesive required degassing of the aqueous phase with N_2 and irradiation with UV light (~2 h with a 100 W bulb). See ref 9.

(14) Densities for the aqueous phase ranged from 1.1 to 1.2 g/cm³; we used a rotation speed of ~25 rpm.

(15) If we allowed the assembly process to go to completion, we obtained an oblate assembly of 1000 cubes. This assembly was structurally similar to the assembly in Figure 2c.

Figure 2. Assemblies of 3-mm-sized cubes. (a) A 2 × 2 × 2 array of 8 cubes. (b) A 3 × 3 × 3 array of 27 cubes. (c) An array of 300 cubes (front and side views). (d) Three ∼300-cube arrays, assembled from 1000 cubes (front and side views).

Figure 3. Arrays of shapes designed to reduce or eliminate slip. (a) An array of 36 hexagons. (b) An array of 90 cubes with holes. Each cube possesses three holes drilled through it.
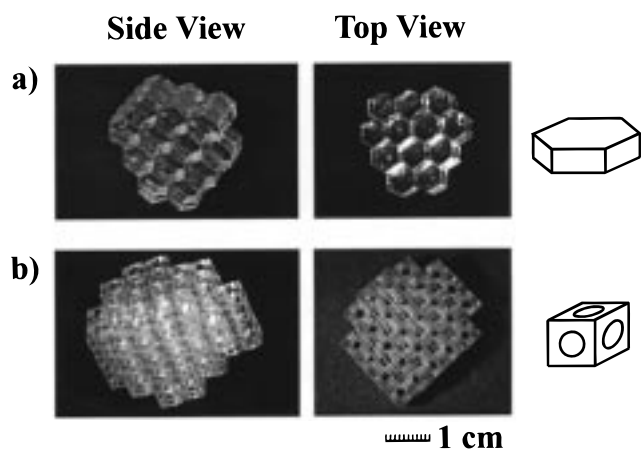
While the internal structure of the arrays remained crystalline, the external shape of these crystals changed with the nature of agitation (Figures 2c and 2d). These images show four aggregates, with each containing ∼300 cubes. The trio of aggregates in Figure 2d resulted from an experiment in which we placed 1000 cubes in a flask with the appropriate amount of lubricant and intentionally *stopped* the assembly before the cubes combined into one monolithic array.[17] The solitary aggregate in Figure 2c formed from an experiment that started with just 300 cubes, and all 300 of those cubes are present in the pictured array. The front and side views show that the three aggregates that formed from 1000 cubes are closer to rectangular than the lone aggregate assembled from 300 cubes. The outlines of rectangular blocks can be seen in the profile of the three aggregates in Figure 2d, with axes coincident with the axes of the cubes. The surfaces of these arrays exhibit large flat areas separated by one-cube-high steps. In contrast, arrays crystallized from 300 cubes were consistently oblate, and axes obtained from the external shape of the arrays do not coincide with the axes of the constituent cubes.[15]

We hypothesized that this oblate shape reflects the axial agitation provided by the rotating flask. During assembly, the array tumbled with its long axis parallel to the axis of rotation. When several arrays are crystallized simultaneously in one flask, collisions between arrays provide shear forces that could order the aggregates. These shear forces could suffice to "polish" the arrays into nearly rectangular blocks. To test this hypothesis, we placed a large (∼1 cm³) polymeric cube together with 300 small (∼27 mm³ each) cubes in a flask and allowed the mixture to assemble with rotation.[16] During assembly, collisions between the aggregate and the large cube added a shear component to the agitation, and as predicted, the array of 300 cubes that resulted was rectangular rather than oblate.

Slip within these arrays—the misalignment of layers—depended on the shape of the constituent pieces. Arrays of cubes have several slip planes (3 translational, 3 rotational for each crystal layer). One strategy to minimize slip is to create arrays that have few slip planes: arrays of hexagons have half as many slip planes (2 translational, 1 rotational) as cubes. A complementary approach is to force the desired structure to be energetically minimal by forming arrays made of cubes with three orthogonal channels drilled through each. Although these arrays have slip planes, the presence of water-filled channels in every cube and the minimization of this additional lubricant/water interfacial free energy forces the aggregate to adopt a structure with all channels aligned. Figure 3 shows that nearly perfect arrays can be obtained from hexagons and from cubes with holes. Under the *same* experimental conditions, arrays of cubes with holes exhibited less slip than arrays of hexagons, which in turn exhibited less slip than arrays of cubes.

We draw four inferences from these results: First, with this procedure, it is possible to form aggregates of cubes that are internally well-ordered and externally roughly rectangular. Second, aggregation is driven by minimization of the lubricant/water interfacial area, for which cubic arrays are energetically minimal.[17] Third, as arrays made from cubes with holes and those made from hexagons show, deliberate design of internal structure into the assembling pieces can practically eliminate slip within assembled arrays. Fourth, the mechanism for annealing these structures into their final form involves movement of components within an aggregate, rather than dissociation/reassociation. As such, "polishing" is a more accurate description of this type of assembly than is "crystallization". We believe that these inferences will also apply to assembly of microscale objects[18] and will eventually lead to fabrication of microstructures that cannot easily be created by conventional means.

(16) We oxidized the large polymeric cube in an O₂ plasma for ∼5 min. to render its surface hydrophilic. This treatment prevented the lubricant from coating the large cube and stopped the small cubes from sticking to the large one.

(17) For a given number of cubes, a cubic array possesses the smallest surface area.

(18) Capillary forces are the dominant force at the microscale and should be strong enough to form ordered assemblies of microscale objects, provided the agitation is sufficient.