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Self-Assembly of Hexagonal Rod Arrays Based on Capillary Forces

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A series of well-ordered, extended mesostructures has been generated from hexagonal polyurethane rods (15 × 3.2 mm) by self-assembly using capillary forces. The surface of one or more sides of the rods was rendered hydrophilic by exposure to an oxygen plasma. This modification determined the pattern of hydrophobic and hydrophilic faces; the hydrophobic sides were coated with a thin film of a hydrophobic lubricant. Agitation of the rods in an approximately isodense aqueous environment resulted in their self-assembly, in a process reflecting the action of capillary forces, into an array whose structure depends on the pattern of hydrophobic sides; capillarity also aligned the ends of the rods. We also carried out experiments in reaction chambers that restricted the motion of the rods; this restriction served to increase the size and regularity of the assemblies.

Key Words: **self-assembly; capillarity; mesostructures.**

INTRODUCTION

This report describes the formation of two-dimensional (2D) and three-dimensional (3D) arrays from hexagonal rods. The objective of this work was to demonstrate the generation of a range of 3D structures by mesoscale self-assembly (MESA) using a common component: a hexagonal rod. We have accomplished this objective by controlling hydrophobicity/hydrophilicity of the rods: by coating hydrophobic faces with a hydrophobic liquid that serves both as a lubricant and as a photocurable adhesive, it is possible to generate ordered, structurally stable 3D arrays by MESA. Hydrophobic faces come into contact and align; this process forms a series of arrays: slabs, sheets, and close-packed and open 3D aggregates. These studies are models for other work focused on the self-assembly of components with 1- to 100-μm dimensions.

This work is an extension of previous work in 2D and 3D MESA (1–13). We have shown that patterning the hydrophobicity/hydrophilicity of the sides of millimeter-sized hexagonal polymeric plates, agitated at a liquid–liquid interface, leads to a series of 2D arrays (1–3). This degree of structural control, however, has not been displayed, and is experimentally more difficult to accomplish, for 3D arrays; in the 3D systems that we have studied, the topography of the array can be changed only by modifying the shape of the self-assembling component (4–6) or by forcing the pieces to assemble on, and therefore assume the shape of, a liquid–liquid interface (7). One exception is corner-truncated cubes: two arrays are possible, depending on whether the pieces connect through four or eight truncated sides (6). In order to expand the strategies available for 3D MESA, we wished to construct a larger range of structures from one shape of building block.

We selected hexagonal rods as the component structure in this work for three reasons: (i) at the millimeter scale, they are easily fabricated and examined, and observation of their behavior allows us to test strategies for self-assembly rapidly; (ii) we have studied two-dimensional self-assembly of hexagonal *plates* extensively (1–3); (iii) the functionalization of the faces of the rods into hydrophobic and hydrophilic sets is relatively straightforward experimentally. This functionalization determines the pattern of interaction of faces on different objects and thus the structure of the array.

RESULTS AND DISCUSSION

Fabrication of Hexagonal Rods

Molds were prepared by filling a polypropylene tube with a polydimethylsiloxane prepolymer and inserting an aluminum or brass hexagonal rod (width, 3.2 mm; Fig. 1). After curing at 70°C for at least 30 min, the rod was removed. The resulting mold was filled with a polyurethane prepolymer (J-91, Summers Laboratories) and cured under ultraviolet light for 2 h. The polyurethane replica rods were then removed and cut into lengths of 15 mm using a razor blade.

To generate rods with patterns of hydrophobic sides, those sides were protected with tape (Scotch Brand, 3M Corp.) and the pieces were oxidized in an oxygen plasma for 10 min. Hollow rods were constructed by inserting a capillary melting point tube (i.d. 1.3 mm, VWR Scientific) through two hollow PDMS plugs that were placed on both ends of the mold.

Procedure for Self-Assembly

An indented, single-necked, round-bottomed flask (250 mL capacity, Lab Glass) was used for these studies. Approximately 100 hexagonal rods were added to a separate flask and 240 μL of a hydrophobic photocurable liquid adhesive was added to

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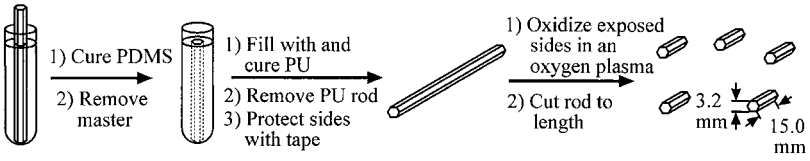

FIG. 1. Schematic diagram of the fabrication of the hexagonal rods.

coat the rods.[2] The liquid adhesive coated all of the faces of the rods. The rods were then added to the round-bottomed flask, and the flask was completely filled with water. The liquid adhesive spontaneously dewet from the hydrophilic faces, and any excess adhesive floated to the top of the flask, where it was removed. For experiments where n sides of the rods were oxidized, the amount of photocurable lubricant was reduced by a factor of $n/6$, in order to account for the reduction in the number of hydrophobic sides relative to unmodified pieces. Air bubbles on the pieces or walls of the flask were eliminated by agitation and/or extracted with a pipet. The flask was rotated at a constant rate of approximately 20 rpm. The final product was permanently bound by purging the solution with nitrogen and curing under UV light for at least 2 h to set the photocurable adhesive.

A rectangular-shaped reaction chamber, used for some experiments, was made by affixing a glass slide onto the bottom of a water-tight polypropylene container. The container was filled with PDMS prepolymer and cured, and a rectangular cavity (7×3 cm) was cut out by hand. The chamber was filled with deionized water, and 20 hexagonal rods that had been precoated with the photocurable adhesive were added, followed by the lid of the water-tight container. The liquid adhesive coated the entire surface of the objects in air. When the objects were added to the water, the liquid adhesive spontaneously dewet from the hydrophilic faces and remained only on the hydrophobic faces. A rotary platform shaker set at an oscillation of approximately 50 rpm was used for agitation.

Self-Assembly of a Close-Packed Array

We used polyurethane pieces for four reasons: (i) the polymer is not dissolved by the solution or lubricant;[3] (ii) the low viscosity of the prepolymer allows the mold to fill readily; (iii) the cured polymer is hard and does not fracture easily; (iv) the pieces are hydrophobic ($\theta_a(H_2O) = 76^\circ$, $\theta_r(H_2O) = 49^\circ$) and can be coated with a thin film of a hydrophobic lubricant. This film is necessary for the formation of an aligned, extended array: it allows the pieces to adhere and also to move laterally relative to one another.[4] The pieces collided with the walls of the flask and with one another when the flask rotated: complete assembly required approximately 30 min (Fig. 2a).

We also wished to introduce additional structure into these close-packed arrays. As a demonstration, we selected the formation of a solid object containing a hexagonal array of channels by using hollow polyurethane hexagonal rods (Fig. 2b).

Oligomeric and Open Arrays

We describe the pattern of hydrophobic faces by numbering them (see Fig. 3), using a system analogous to that employed in the study of the 2D mesoscale self-assembly of hexagonal plates (1–3). For example, [1]-rods formed exclusively dimers (Fig. 3a); [1,2]-rods resulted in a mixture of trimers and bilayer structures [Fig. 3b; these structures are analogous to the 2D structures seen with hexagonal plates (1–3)].

Similar experiments with [1,4]-rods resulted in sheets of rods that are a single layer thick. The maximum number of rods in a given aggregate was typically only five units; due to their

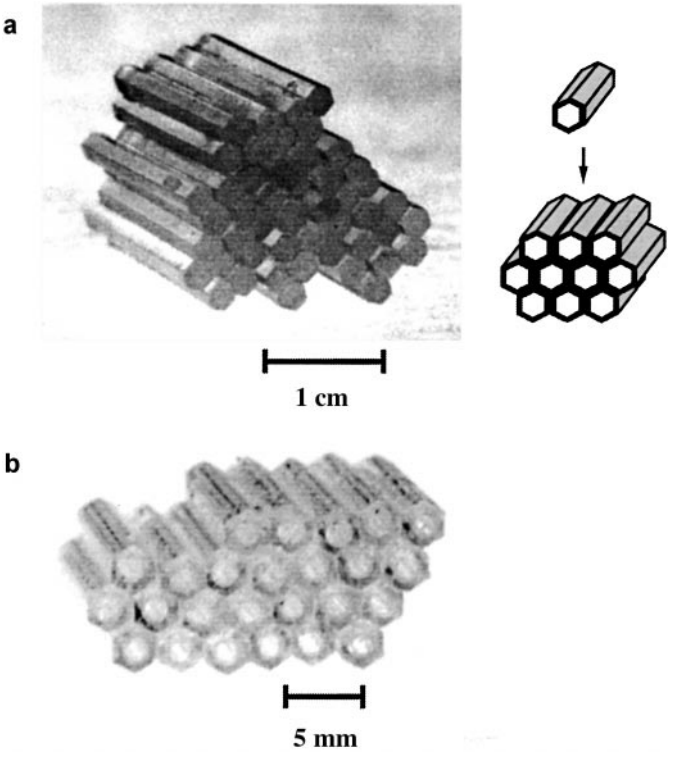

FIG. 2. Unmodified, all-hydrophobic rods formed extended, close-packed arrays. (a) Solid hexagonal rods. (b) Hollow hexagonal rods.

[2] Photocurable adhesive: 96.0 wt% lauryl methacrylate, 2.0 wt% benzoin isobutyl ether, and 2.0 wt% 1,6-hexanediol diacrylate. See A. Terfort and G. M. Whitesides, *Adv. Mater.* **10**, 470 (1998).

[3] Dissolution of the polymer by the lubricant did occur for other polymers we used, such as polystyrene average MW 45,000 or polystyrene average MW 280,000.

[4] PDMS pieces, for example, connect irreversibly and no lateral movement between pieces occurs. The aggregates formed are therefore random and unordered.

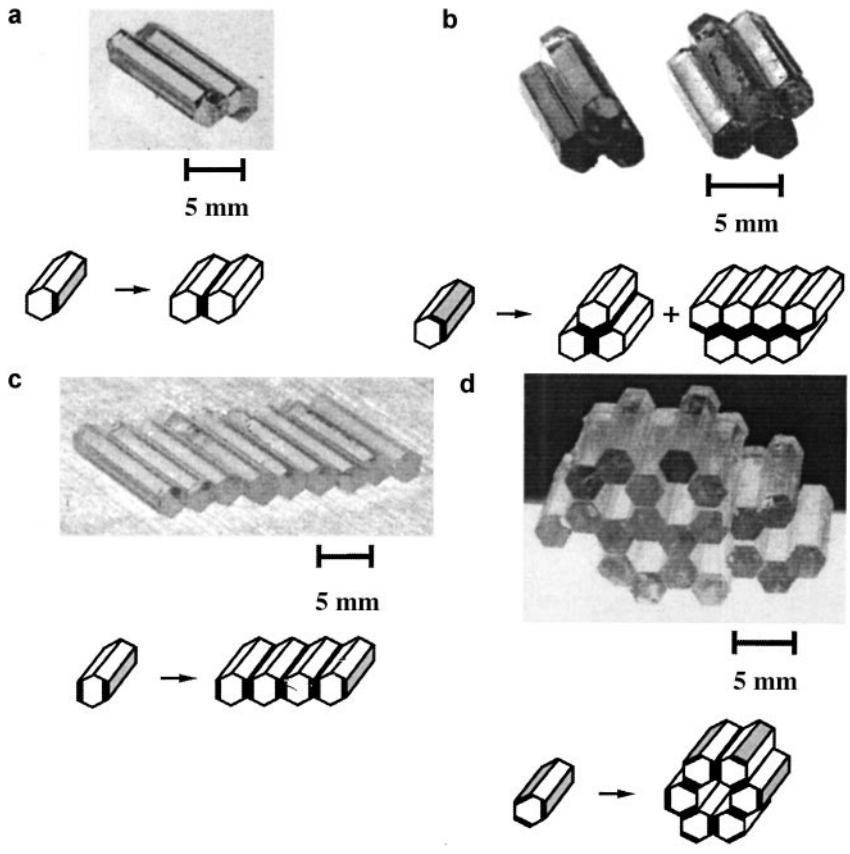

FIG. 3. Various oligomeric arrays are formed by pieces with specific sides patterned hydrophilic. For clarity, schematic diagrams of the arrays are also shown (hydrophilic sides, nonshaded (white) and thin lines; hydrophobic sides, shaded (grey) sides and thick lines). (a) [1]-rods in a spherical flask resulted exclusively in dimers. One such dimer is shown. (b) [1,2]-rods formed a mixture of trimers and bilayers, also using a spherical flask. (c) A rectangular chamber was used for [1,4]-rods; this more restricted container yielded an extended flat array. (d) Tumbling [1,3,5]-rods in a cylindrical flask induced the formation of an open array.

flat shape, larger aggregates broke apart upon collisions, during tumbling, with the round sides of the spherical flask. In order to form more extended arrays, we used a reaction chamber with a shape that was closer to that of the desired aggregate. For example, a reaction chamber having rectangular shape, used with [1,4]-rods, acted as a template and increased the average aggregate size from 5 pieces to 10 pieces (Fig. 3c). The stability of this assembly is underlined by the fact that it is the vertices of the rods that contact the bottom of the reaction chamber, rather than their faces; the latter is observed for a single, unattached piece.

When [1,3,5]-rods ($\rho_{\text{measured}} = 1.35$ g cm^{-3}) were allowed to tumble in water ($\rho = 1.00$ g cm^{-3}), they formed small sections (3 or 4 pieces) of an open hexagonal array. These small aggregates broke apart readily upon collision with the walls of the flask during tumbling. Less rigorous agitation was achieved by using a 36.0 wt% KBr solution ($\rho_{\text{soln}} = 1.33$ g cm^{-3}) in place of water. This value allowed the pieces to descend more slowly in the flask and therefore to contact the walls of the flask more gently. These less rigorous conditions allowed formation of the open array (Fig. 3d).

CONCLUSIONS

This work has four implications for MESA: (i) It demonstrates that a simple structure—a hexagonal rod—can be used as a common building block in the generation of a variety of structures by 3D MESA. We have not explored the influence of the dimensions of the hexagonal rods on the structures of the aggregates that they form. (ii) It confirms again that modifying the surface properties of the self-assembling object—a procedure already demonstrated for the 2D MESA of hexagonal plates—provides a very useful strategy for generating and controlling capillary forces between objects and that these forces strongly influence the shape of the final 3D aggregate. (iii) This work suggests that at least some of the patterns of aggregation observed with thin hexagonal *plates* at an interface can be extended to long hexagonal *rods* in suspension. (iv) We have demonstrated that the size and shape of the aggregate can be controlled, to some extent, by the shape of the chamber in which the agitation is carried out and in which the self-assembly occurs. This templating effect will, we believe, be broadly practical in MESA.

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