Template-Directed Self-Assembly of 10-μm-Sized Hexagonal Plates

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Abstract: This article presents a strategy for the fabrication of ordered microstructures using concepts of design inspired by molecular self-assembly and template-directed synthesis. The self-assembling components are 4-μm-thick hexagonal metal plates having sides 10 μm in length (“hexagons”), and each template consists of a 4-μm-thick circular metal plate surrounding a central cavity, the perimeter of which is complementary in shape to the external edges of a two-dimensional, close-packed array of hexagons. The hexagons and templates (collectively, “pieces”) were fabricated via standard procedures and patterned into hydrophobic and hydrophilic regions using self-assembled monolayers (SAMs). Templated self-assembly occurs in water through capillary interactions between thin films of a nonpolar liquid adhesive coating the hydrophobic faces of the pieces. The hexagons tile the cavities enclosed by the templates, and the boundaries of the cavities determine the sizes and shapes of the assemblies. Curing the adhesive with ultraviolet light furnishes mechanically stable arrays having well-defined morphologies. By allowing control over the structures of the resulting aggregates, this work represents a step toward the development of practical methods for microfabrication based on self-assembly.

Introduction

In this paper we describe the template-directed self-assembly of 10-μm-sized hexagonal metal plates (“hexagons”) into ordered arrays having predetermined sizes and shapes. These studies build upon our previous work in mesoscale self-assembly (MESA): self-assembly using forces that operate over distances similar to the dimensions of the components being assembled.1 MESA based on capillary interactions can form crystalline arrays of nonspherical components with largest dimensions of 10—30 μm;2 we are developing this general strategy in the belief that it may prove useful in the fabrication of functional devices such as photonic band gap materials3—6 and self-assembling microelectronic systems.7—10 The realization of these goals will, however, require control over several attributes of the resulting assemblies, including the final dimensions and morphologies of the aggregates, the number of component pieces that comprise them, and the spatial arrangement of these pieces with respect to one another. Here, we address these challenges by using appropriately designed templates to direct the self-assembly process.

Template is a general term for a scaffold or guide that is used to arrange objects with the aim of influencing the outcome of a subsequent process. For example, a chemical template is a species that organizes an assembly of atoms with respect to one or more geometric loci in order to achieve a particular linking or arrangement of the atoms.11 The replication of DNA is an example of chemical templateing by a molecular species,12 and emulsion-templated synthesis of porous solids is an instance of templating by a supramolecular assembly.13 Oriented single crystals template the deposition of thin crystalline layers in molecular beam epitaxy,14 and colloidal crystals can function as sacrificial templates in the synthesis of inverse opaline materials.15

In recent years, several groups have applied the concepts of chemical templating to the self-assembly of components much larger than individual atoms or molecules. Wiltzius and van...
Blaaderen employed lithographically fabricated reliefs to direct the formation of bulk colloidal crystals with predetermined sizes and lattice structures.\textsuperscript{16} and Pouliquen et al. extended this strategy to the crystallization of 2-mm-sized spheres.\textsuperscript{17} Xia used holes in flat substrates, designed to accommodate a discrete number of spherical colloids, to generate aggregates with defined sizes and structures.\textsuperscript{18,19} Smith demonstrated shape-selective integration of microelectronic device elements into textured substrates via fluidic self-assembly (FSA).\textsuperscript{20,21} Velev has exploited the spatial confinement afforded by liquid droplets to direct the crystallization of colloidal spheres,\textsuperscript{22–24} and we have used a related method—templated MESA based on capillary interactions at the interface between two liquids—to generate spherical\textsuperscript{25} and quasi-two-dimensional structures.\textsuperscript{26,27} Similar approaches by Xia, Ozin, and others have included the crystallization of spherical colloids through confinement in microchannels,\textsuperscript{15,28,29} and the selective placement of small objects on patterned surfaces using chemical,\textsuperscript{30,31} magnetic,\textsuperscript{32} electrostatic,\textsuperscript{33} and capillary\textsuperscript{34} interactions.

Previously, we used capillarity to generate untemplated arrays from 10-\(\mu\)m-sized metallic plates.\textsuperscript{2} We patterned the surfaces of the plates into hydrophobic and hydrophilic regions using self-assembled monolayers (SAMs) and coated the hydrophobic regions with thin films of a nonpolar liquid adhesive; in water, capillary forces between the adhesive films provided the attractive forces necessary for assembly. Although the resulting aggregates were internally well ordered, our inability to control their external morphologies represented a potential limitation to this method (Figure 1a). Here, we explore an approach to overcoming this limitation that employs templates to control the sizes and shapes of the structures formed by the self-assembly of 10-\(\mu\)m-sized hexagons (Figure 1b).

### Experimental Design

Each template consists of a 4-\(\mu\)m-thick circular metal plate enclosing a central cavity intended to accommodate a discrete number of 4-\(\mu\)m-thick hexagonal metal plates having sides 10-\(\mu\)m-long; the scale bar is the same for the two images. In both cases, the components self-assemble in water through capillary interactions between thin layers of a nonpolar liquid adhesive precipitated selectively onto their hydrophobic surfaces.\textsuperscript{2} (a) In the absence of a template, the hexagons self-assemble into arrays that are internally well-ordered but irregular in size and shape. (b) In templated self-assembly, the hexagons tile the cavity enclosed by a circular template. The edges of the cavity present “binding sites” for the attachment of hexagons, and the boundaries of the cavity define the sizes and shapes of the resulting assemblies.

We fabricated the hexagons and templates (collectively, “pieces”) using photolithography and electrodeposition as previously reported (Figure 2a).\textsuperscript{2} Starting with a silicon wafer coated sequentially with a thin film of Cr, Ag, Cr, and Au, photolithography generated molds for the electrodeposition of Cr oxide (Cr/Cr\(\textsubscript{2}O\textsubscript{3}\)), \textsuperscript{35} and we rendered the exposed Au surfaces hydrophobic by treatment with an ethanolic solution of hexadecanethiol (HDT) to generate alkanethiolate SAMs.\textsuperscript{16}

![Figure 1](image_url)  
**Figure 1.** Comparison of untemplated and templated self-assembly of 4-\(\mu\)m-thick hexagonal metal plates having sides 10-\(\mu\)m-long; the scale bar is the same for the two images. In both cases, the components self-assemble in water through capillary interactions between thin layers of a nonpolar liquid adhesive precipitated selectively onto their hydrophobic surfaces. (a) In the absence of a template, the hexagons self-assemble into arrays that are internally well-ordered but irregular in size and shape. (b) In templated self-assembly, the hexagons tile the cavity enclosed by a circular template. The edges of the cavity present “binding sites” for the attachment of hexagons, and the boundaries of the cavity define the sizes and shapes of the resulting assemblies.
Figure 2. (a) Fabrication of the templates and 10-μm-sized hexagons (collectively, “pieces”). (i) Electrodeposition through patterned photoresist on a Si/SiO2/Cr/Au electrode formed 4-μm-thick gold pieces. (ii) We evaporated chromium (50 nm) onto the pieces. (iii) Dissolution of the silver film with nitric acid released the pieces and (iv) sonication in ethanol removed the residual thin films of chromium extending from their edges. (v) Treatment with a 10 mM ethanolic solution of HS(CH2)15CH3 formed a hydrophobic SAM on the gold surfaces; the chromium surfaces formed a hydrophilic native oxide layer (Cr/Cr2O3). (vi) We placed ~10^3 templates and ~3 × 10^5 hexagons in a 3 mL glass cuvette containing 50 μL of a ~0.1% ethanolic solution of nonpolar photocurable adhesive. Slow addition of water diluted the ethanol, precipitated the lubricant selectively onto the hydrophobic faces of the pieces, and caused the pieces to aggregate. The adhesive-coated pieces and 3 mL of water remained in the cuvette. (vii) We rotated the cuvette axially at 100–200 rpm for 12–24 h; this rotation provided the annealing force that allowed the initially formed aggregates to coalesce into ordered arrays. (viii) After assembly, exposure to UV radiation (λ ~ 254 nm) furnished mechanically stable arrays that could be removed for examination.

A typical experiment began by placing ~10^3 templates and an approximately 100-fold stoichiometric excess of hexagons together in a glass cuvette and treating them with an ethanolic solution of a nonpolar liquid adhesive (Figure 2b; the details of this procedure are described in the Experimental Section). Dilution of the ethanol with water caused the adhesive to precipitate and selectively coat the hydrophobic faces of the pieces; axial rotation of the cuvette provided the agitation that allowed the self-assembly to proceed. When two adhesive-coated faces contacted each other, the liquid films merged, prompting the pieces to align through capillarity in order to minimize the area of the resulting adhesive–water interface. The self-assembly typically reached completion within 12–24 h. After curing the adhesive with ultraviolet light, we confirmed the structures of the aggregates using optical and scanning electron microscopy (SEM). The yields of the assemblies were determined by dividing the number of full templates by the total number of templates observed; to avoid skewing the results through additional handling, we did not attempt to purify the assemblies.

Results

We focused our initial efforts on optimizing the fit of the hexagons to the templates. According to our fabrication scheme, the sizes of the pieces are determined by the sizes of the molds used for electrodeposition (Figure 2a). We began, therefore, by adjusting the photolithographic conditions used to generate the molds, and then tested the resulting pieces in self-assembly experiments. Because the tolerance of the features on our photomasks was only ±0.5 μm,37 we were unable to adjust the absolute sizes of the pieces arbitrarily by simply designing new masks. Instead, we adjusted the relative sizes of the pieces by varying other photolithographic conditions, including the tone of photoresist used and the parameters of exposure and development,38–40 until we obtained hexagons and templates that were appropriately matched in size—that is, the linear dimensions of the templates were a few percent larger than those of the hexagons. A representative example of this refinement process is shown in Figure 3.

Figure 4 presents schematic and SEM images of four templated assemblies prepared using optimized photolithographic conditions as described in the Experimental Section. The simplest template was intended to accommodate a single hexagon and consists of a solid circle surrounding a hexagonal cavity (1); we also designed templates for trimeric (2), heptameric (3), and nonadecameric (4) assemblies. In all cases, the pieces self-assembled to give well-ordered arrays in good yields (Figure 4). By contrast, we obtained less ordered aggregates in significantly lower yields when the pieces were mismatched in size.

We explored the self-assembly process by using optical microscopy to examine the “reaction mixtures” at various times during the course of a single experiment. Within a few seconds after precipitating the adhesive onto the pieces, most of the hexagons organized themselves into small, untemplated arrays oriented randomly with respect to each other; these arrays were single-layered and contained ~10–100 hexagons each. The templates had bound few hexagons by this point and contained many vacancies. As the assembly proceeded, the untemplated arrays coalesced into larger, multilayered assemblies, each containing ~10^4–10^5 hexagons, and the vacancies in the templates began to fill. These observations suggest the following mechanism for the templated self-assembly. In the early stages of an experiment, the hexagons aggregate quickly to produce arrays that are too large and irregularly shaped to bind stably.

37 The chrome/soda lime glass photomasks employed in this study were fabricated using a laser imager and wet development and etch procedures; the nominal overall resolution of these processes is ±0.5 μm. Advance Reproductions, Inc., North Andover, MA (www.advancerepro.com). Personal communication, 2001.
38 Over-exposure and/or over-development of a positive photoresist can broaden features relative to the photomask. This broadening increases the size of the hexagons while decreasing the size of the binding sites on the templates. (b) Negative photoresists such as SU-8 that rely upon cross-linking reactions tend to yield features that are slightly smaller than those on the photomask due to shrinkage of the photoresist following exposure.39
to the templates; this aggregation also rapidly decreases the concentration of free hexagons and small assemblies capable of filling the binding cavities. As they grow in size, the untemplated assemblies experience increasingly forceful collisions with their surroundings. These collisions dislodge single hexagons and small aggregates, which in turn bind to vacant sites on the templates.

The results presented in Figure 4 demonstrate the success of our strategy for producing aggregates of defined sizes and shapes. Although we made no attempt to purify the templated assemblies, we expect that the use of techniques such as sizing and differential sedimentation will allow us to isolate the desired products and recycle the untemplated arrays and defective aggregates.

Defects in the templated assemblies consisted of two types: assemblies containing vacancies (Figures 1b and 6a) and assemblies containing extra hexagons (Figure 6b). Vacancies were more common in larger assemblies (e.g., 4a and 5a) than in smaller ones; we believe that this trend reflects, in part, the greater susceptibility of larger assemblies to mechanical damage under the agitation conditions used. Many templated assemblies, however, contained only one or a small number of vacant sites; we believe that such vacancies are unlikely to have arisen from mechanical damage, and may have been caused by the low concentration of free hexagons during the self-assembly process.

In an effort to reduce the number of vacancies in the templated assemblies, we examined two methods intended to

(41) We were unable to obtain 1a in quantitative yield even after extended "reaction" times (~4 days), possibly due to slow polymerization of the adhesive layer during the course of the experiments.
increase the concentration of free hexagons. For the first method, we precipitated the adhesive simultaneously onto the hexagons and templates, allowed the pieces to self-assemble for some time, and then added fresh hexagons; for the second method, we precipitated the adhesive onto the templates only, and then added fresh hexagons and allowed the pieces to assemble. In both cases, the course of the self-assembly was indistinguishable from that observed previously: the hexagons aggregated quickly into untemplated arrays with few unassociated hexagons remaining, and the binding cavities on the templates filled slowly and incompletely. The failure of these methods may have resulted from the persistence of excess adhesive in the reaction vessels, perhaps in the form of microscopic droplets adventitiously attached to the walls of the cuvette, which then coated the hexagons and allowed them to assemble. In both cases, the course of the self-assembly was indistinguishable from that observed previously: the hexagons aggregated quickly into untemplated arrays with few unassociated hexagons remaining, and the binding cavities on the templates filled slowly and incompletely. The failure of these methods may have resulted from the persistence of excess adhesive in the reaction vessels, perhaps in the form of microscopic droplets adventitiously attached to the walls of the cuvette, which then coated the hexagons and allowed them to assemble. The complete elimination of vacancies will likely require pieces that self-assemble only in the presence of a template; we are currently examining ways of designing such pieces.

The second type of defect—arrays containing one or more extra hexagons attached at unintended locations—likely arises from small differences in thickness among the pieces. In our earlier study, we found that electrodedeposited Au typically varies in thickness by \( \pm 10\% \) over the surface of a wafer; here, this variation produces hexagons and templates having hydrophobic faces that differ in height from piece to piece. When the pieces assemble, portions of their adhesive-coated faces remain exposed to water, presenting partial binding sites to which extra hexagons may adhere weakly. We minimized these defects by employing vigorous agitation to remove the extra hexagons. Under these conditions, this type of defect occurred in only \( \sim 5\% \) of the templated assemblies; for the purpose of calculating yields, we considered these assemblies full. Complete elimination of these defects would require either that the pieces be uniformly thick or that the thickness of the hydrophilic layers on the top and bottom of each piece be greater than or equal to the variation in thickness among the pieces. For example, we expect that pieces bearing a \( \geq 0.8\-\mu\text{m} \) thick layer of Cr on their top and bottom faces would produce arrays free from this type of defect.

The results presented in Figures 4 and 5 suggest that the structures of the templates can strongly influence the stabilities of the corresponding assemblies. For example, the yields of assemblies \( 1a-4a \) \( (1a \approx 2a > 3a > 4a) \) correlate inversely with the number of hexagons that comprise them. We believe that this correlation indicates that the small assemblies are more stable than the large ones under the agitation conditions used. The yield of assembly \( 5a \) is, however, greater than that of \( 4a \) (67% vs 53%), even though the former contains more hexagons (30 vs 19). We rationalize this observation by considering not only the number of hexagons in the assemblies but also the number of binding sites on the templates. In this context, we define a “binding site” as an edge in the binding cavity of a template to which one edge of a hexagon binds. For example, template 1 (Figure 4) contains 6 binding sites, which together bind a single hexagon. Figure 7 shows a plot of the ratio (number of binding sites on the templates/number of hexagons in the resulting assemblies) vs the yields of the assemblies. The observed positive correlation suggests that the stability of the assemblies increases with increasing number of binding sites per hexagon. We note that, because the yields shown in Figures...
fabrication of micro- and nanostructured devices such as microelectromechanical systems (MEMS)\textsuperscript{44−50} and photonic band gap crystals.\textsuperscript{3−6}

Experimental Section

Chemicals. All chemicals and solvents were used as supplied from the indicated vendors. Cr and Ag evaporation sources were purchased from Alfa Aesar, and Au evaporation sources from Materials Research Corp. We obtained 453 developer and SJR5440 and SU-8-5 photoresists from Microchem Corp. (Newton, MA). Propylene glycol methyl ether acetate (PGMEA), benzoin isobutyl ether, 1,6-hexanediol diacrylate, mercaptohexadecanoic acid (MHA), and hexadecanethiol (HDT) were acquired from Aldrich. Dodecyl mercaptan was purchased from Polysciences, Inc. (Warrington, PA). Gold electroplating solutions (Techni-25E) were obtained from Technic, Inc. (Cranston, RI). We purchased concentrated nitric acid and acetone from VWR Scientific, and absolute EtOH from Pharmco (Brookfield, CT).

Fabrication of the Substrates. Substrates for use with the positive photoresist SJR-5440 were primed by immersion for 5 min in a 0.02 M ethanolic solution of 85:15 mol % HDT/MHA to promote adhesion of the photoresist. We rinsed the substrates with ethanol, sonicated them for 1 min in clean-room-grade acetone, and rinsed them with acetone followed by 18 MΩ water. Residual water was removed under a stream of nitrogen, and the wafers were dried by placing them for 30 s on a digital hotplate set at 105 °C. We spin-coated\textsuperscript{39} the wafers with SJR5440 photoresist at 500 rpm for 5 s, accelerated them to 3200 rpm at 2000 rpm s\textsuperscript{−1}, and spun them an additional 30 s to give a 4.5-μm-thick film. The wafers were placed directly onto a digital hotplate set at 105 °C, baked for 1 min, then promptly removed and held under ambient conditions for ±30 min before exposure.

We primed the substrates for use with the negative photoresist SU-8-5 by immersion for 5 min in a 2 mM ethanol solution of 90:10 mol % MHA/HDT to promote adhesion of the photoresist; substrates were cleaned and dried as above. We spin-coated\textsuperscript{39} the wafers with SU-8-5 at 500 rpm for 5 s, accelerated them to 3500 rpm at 2000 rpm s\textsuperscript{−1}, and spun them an additional 15 s to give a 5-μm-thick film. The wafers were baked for 1 min on a digital hotplate set at 65 °C, then transferred promptly to another hotplate set at 90 °C. After 3 min at 90 °C, we turned off the heating element and allowed the wafers to reach room temperature slowly over ~15 min.

Fabrication of the Photomasks. The photomasks were fabricated from chromium and soda lime glass by Advance Reproductions, Inc. (North Andover, MA).\textsuperscript{37} Masks for use with positive and negative photoresists were fabricated in dark and clear field, respectively,\textsuperscript{39} and patterns for the hexagons and each of the templates were produced on separate masks. We generated the patterns for the photomasks using a CAD program (AutoSketch 6.0, Autodesk, Inc.). As provided to the mask manufacturer, the features consisted of regular hexagons having sides 10.0 μm in length and templates having corresponding linear dimensions 5% larger; for example, we designed the cavity of template 1 to be a regular hexagon having sides 10.5-μm-long.

Conclusion

Using principles of design inspired by template-directed chemical synthesis, we have developed a strategy for the fabrication of ordered microstructures having well-defined sizes and shapes. Our approach separates the fabrication into two distinct steps: preparation of the components and their self-assembly into larger structures. Although the pieces described here are composed of gold and chromium, we anticipate that this method will extend to components prepared from a variety of materials; one potential application lies in the integration of micro-device elements made from incompatible substances. In this context, we note that a related process—fluidic self-assembly (FSA)—is currently being developed for the incorporation of optoelectronic elements into flexible polymeric substrates.\textsuperscript{20,21}

This work represents a step toward the realization of practical methods for microfabrication based on self-assembly. Because capillary interactions become stronger at smaller size scales relative to other forces,\textsuperscript{43} we anticipate that these techniques will also prove useful in preparing structures at the nanoscale. Our ultimate goal is to develop efficient methods for the fabrication of small, functional devices. In other work, we have already used capillarity to form electrical contacts in the millimeter\textsuperscript{−9} and 280-μm-size regimes,\textsuperscript{10} and Howe and co-workers reported a similar strategy for the attachment of micromachined silicon parts to patterned substrates.\textsuperscript{34} We are currently working to extend the strategy described here to the

\begin{figure}[ht]
\centering
\includegraphics[width=0.5\textwidth]{figure7.png}
\caption{Plot of the ratio (no. of binding sites on a template/no. of hexagons in the corresponding assembly) vs the yields of the templated assemblies: 4a (•), 5a (○), 3a (△), 2a (□), and 1a (rotated triangle) (Figures 4 and 5; see text for the definition of “binding site”). The error bars were constructed by using a conservative estimate of the error in the percentage yields of these assemblies (a fixed error of ±5% yield). The observed positive correlation suggests that increasing the number of binding sites per hexagon increases the stability of the templated assemblies. This correlation must be considered tentative, however, because the yields determined for these assemblies represent results from single experiments.}
\end{figure}
Photolithography. Photolithography\textsuperscript{30} was performed in a class-100 clean room in the absence of ambient ultraviolet light using a Suss MJF 3 mask aligner in contact mode, with a 350 W mercury lamp set at 10 mW cm\(^{-2}\) (\(\lambda = 405\) nm).

(a) Photolithography for Monomeric Assembly 1a. For template 1, we exposed a 4.5-\(\mu\)m-thick film of SJR5440 photoresist for 18 s using a dark-field photomask. We then immersed the wafer in fresh 453 developer contained in a 100-mm-diameter glass Petri dish. Using a pair of tweezers, we gently agitated the wafer. Within 3 min, the exposed regions began to exude a red color, indicating that development of the photoresist had begun. The agitation was continued until formation of the red color ceased and the resulting pattern attained a uniform appearance (~10 min total). After rinsing thoroughly with 18 M\(\Omega\) water, we dried the wafer under a stream of \(N_2\).

For the hexagons, the use of SJR5440 photoresist resulted in hexagons that were too large for the binding sites,\textsuperscript{34a} but the use of SU-8-5 gave hexagons that were appropriately matched to the binding sites.\textsuperscript{30} We exposed at 5-\(\mu\)m-thick film of SU-8-5 photoresist for 12 s using a clear-field photomask. We then placed the wafer directly onto a digital hotplate set at 65 °C with a platinum anode. We then placed the wafer directly onto a digital hotplate set at 65 °C; under these conditions, a 1-\(\mu\)m-thick film of Au formed in 16 min. We continued the electrodeposition for a 2 ; under these conditions, a 1-\(\mu\)m-thick film of Au and an approximately 100-fold stoichiometric excess of hexagons to a 1 x 1 x 3 cm glass cuvette. After rinsing the pieces thoroughly with EtOH and dried it under a stream of \(N_2\).

(b) Photolithography for Trimeric Assembly 2a. We performed the photolithography used to fabricate both the hexagons and templates using SJR5440 photoresist as described above for template 1.

(c) Photolithography for Heptameric Assembly 3a. We performed the photolithography used to fabricate both the hexagons and templates using SJR5440 photoresist as described above for template 1.

(d) Photolithography for Nonadecameric Assembly 4a. We performed the photolithography used to fabricate both the hexagons and templates using SJR5440 photoresist as described above for template 1.

(e) Photolithography for V-Shaped Assembly 5a. For template 5, we over-exposed a 4.5-\(\mu\)m-thick film of SJR5440 photoresist for 30 s using a dark-field photomask in order to decrease the size of the binding sites relative to the features on the photomask.\textsuperscript{34a} The wafer was developed as described above for template 1.

We performed the photolithography for the hexagons using SU-8-5 photoresist as described above for the hexagons used to generate assembly 1a.\textsuperscript{38b}

Electrodeposition. Prior to electrodeposition, we cleaned the substrates for 5 min in a UV/ozone cleaner to remove the SAM primer and any residual photoresist. We electrodeposited Au from a gold sulfate bath (Techni-2SE, 1 Tr oz Au gal)\(^{-1}\)) at 60 °C with a platinum anode. The solution was stirred at 300 rpm, and the current density was 200 rpm for 12 h. This rotation enabled the initially formed aggregates to contact one another and coalesce into ordered arrays. After thoroughly rinsing away the piranha with water, we incubated the pieces in EtOH for 30 min at room temperature to reduce any AuO\(_2\) that had formed on the Au surfaces.\textsuperscript{33–36} Subsequent treatment with 10 mM HDT in EtOH for several hours generated hydrophobic alkanethiolate SAMs on the Au faces.\textsuperscript{36} Formation of the native oxide (CrO\(_3\))\textsuperscript{35} rendered the Cr faces hydrophilic.

Self-Assembly. Using a pasteur pipet, we transferred ~10 \(^3\) templates and an approximately 100-fold stoichiometric excess of hexagons to a 1 x 1 x 3 cm glass cuvette. After rinsing the pieces thoroughly with EtOH to remove excess thiol, we filled the cuvette with 3 mL of EtOH, added ~30 \(\mu\)L of a photocurable adhesive (96:2:2 w/w/w dodecyl methacrylate/benzoin isobutyl ether/1,6-hexanediol diacrylate), and stirred the EtOH until the adhesive had fully dissolved. We then allowed the pieces to settle into one corner of the cuvette and, using a pasteur pipet, withdrew nearly all of the ethanol/adhesive solution, leaving only enough to cover the pieces (~50 \(\mu\)L). The slow addition of water precipitated the adhesive mixture selectively onto the hydrophobic surfaces, overflowed the cuvette, and caused the pieces to aggregate. We continued to add water (~50 \(\mu\)L total) in order to rinse away all of the excess ethanol and adhesive. The cuvette then contained the liquid-coated pieces and 3 mL of water, to which we added ~50 \(\mu\)L of concentrated NH\(_4\)OH to promote ionization of the glass surface and discourage the pieces from adhering to the walls of the cuvette.

The cuvette was then attached to a rotor, with the long axis of the cuvette at a ~10° angle relative to the horizon, and rotated at 100–200 rpm for 12–24 h. This rotation enabled the initially formed aggregates to contact one another and coalesce into ordered arrays. After the self-assembly reached completion, the suspension of pieces was deoxygenated by sparging with N\(_2\) and exposed to UV radiation (\(\lambda \approx 254\) nm) for ~1 h to polymerize the adhesive. Using a pasteur pipet, we removed a droplet of water containing ~10% of the reaction mixture and placed it onto carbon tape. After drying in air, we examined the sample by optical microscopy and estimated the yield of the experiment by counting ~100 templates and dividing the number of fully formed assemblies by the total number of templates observed. The samples were then sputtered with a thin film of Au and examined using a scanning electron microscope.

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