Cucurbit[8]uril-Regulated Nanopatterning of Binary Polymer Brushes via Colloidal Templating

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Interest in the fabrication of micro-/nanopatterned polymer surfaces with high precision has grown substantially in recent years, on account of potential applications in surface-based technologies including photovoltaic devices, semiconductors, photonic crystals, nanofluidic devices and platforms for tissue engineering. In particular, development of less stringent alternative approaches to traditional nanoimprint lithography methods, which use photons or electrons to modify the chemical and physical properties of surface-bound resins, is crucial in many areas, for example, photonics, chip-based sensors, and most biological applications. Patterned polymer brushes have attracted considerable interest not only in a myriad of applications, ranging from semiconductors to biomaterials, but also as useful tools to study fundamental questions of surface-tethered polymer films, such as swelling behavior or molecular organization. Despite numerous strategies such as microcontact printing, electron beam, or UV irradiation, assisted nanolithography techniques for both laboratory and industrial use to prepare patterned polymer surfaces, few approaches have been reported for the preparation of laterally patterned binary brushes on the sub-micrometer scale under ambient conditions.

The monolayer colloidal crystal (MCC) templated self-assembly process has proven to be a promising alternative strategy to fabricate ordered arrays with well-defined micro and nanostructures because of its flexibility and controllable morphologies. Since Deckman et al. reported the formation of identical sub-micrometer microlumbar structures in 1982, the MCC templating approach has been employed to prepare various ordered micro-/nanostructures such as nanosphere arrays and hierarchical polymer surfaces by different methods including dip coating, spin coating, electrochemical deposition, etc. A main challenge that remains in the area of MCC templating is the controllable and reversible immobilization of colloidal particles on surfaces. For example, in the fabrication of hierarchical binary structures, the surface-attachment should be strong enough so the colloids do not fall off the surface during the assembly of the first required material, yet need to be easily removed from the surface on demand to leave void spaces available for subsequent material deposition.

We herein demonstrate a solely supramolecular route as a promising alternative process for the preparation of sub-micrometer and nanopatterned brush surfaces. Cucurbit[8]uril (CB[8]) is a pumpkin-shaped macrocyclic host that has received tremendous interest in the supramolecular community, on account of its ability to simultaneously incorporate two guest molecules (e.g., viologen (MV) as the first guest and azobenzene (Azo) or naphthol (Np) as the second guest) and their exceptional recognition properties in aqueous medium. Recently, our group reported a CB[8]-based rotaxane structure on Au surfaces, where CB[8] is threaded onto a MV$_2^{2+}$ core and prevented from dissociation away from the surfaces. The reversible formation of colloidal monolayers on Au surfaces through the host–guest interaction between these surface-bound CB[8] rotaxanes and Azo functionalized silica microspheres (Azo-Si) was also described.

We now further explore the application of these supramolecularly assembled colloidal monolayers in the MCC templated formation of sub-micrometer and nanopatterned polymer brushes.

The four-step protocol for the patterning of binary brush surfaces is illustrated in Figure 1. First, a trans-Azo-Si colloidal crystal monolayer was assembled on a CB[8]-rotaxane functionalized Au surface using a dip coating technique, which allows the monolayer deposition of particles in hexagonal arrangement on the substrate (Figure 1A). The Azo-Si colloids were prepared by postmodification of bare silica microspheres with 4-hydroxyazobenzene-functionalized silane with a hydrodynamic diameter of 455 nm (polydispersity, PD = 0.046) as measured by dynamic light scattering (see Figure S1B in the Supporting Information). The ordered hexagonal arrangement of Azo-Si on the surface was verified by both scanning electron microscopy (SEM) and atomic force microscopy (AFM) (Figure 2), which showed a diameter of 333 nm for the particles. This MCC serves as a template in the next step for the supramolecular assembly of the first polymer, a naphthol functionalized poly(ethylene glycol) (M$_n$ = 2000 g mol$^{-1}$, Np-PEG$_{30}$), on the surface.

In the second step, as illustrated in Figure 1B, Np-PEG$_{30}$ was used to fill in the interstitial vacancies between the Azo-Si colloids leading to polymer brush structures through the formation of heteroternary complexes (Np-PEG · MV$_2$) ⊂ CB[8].

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The SEM and AFM topography images do not exhibit much difference before (Figure 2) or after (Figure 3) the grafting of Np-PEG$_{2k}$ brushes, because the Azo-Si particles are much larger compared to the height of the Np-PEG brushes. The advantage of using the supramolecular chemistry to attach brushes on the surface in a “grafting to” fashion is its ability to carry out the brush assembly in ambient conditions without the requirement of further chemical reactions and any special instruments, e.g., cyclic voltammetry (CV) for electropolymerization.

The high hexagonal ordering of the colloidal particles on the surface was well-preserved after the assembly of Np-PEG$_{2k}$ brushes (Figure 3); the assembly process involves the immersion of the substrate in an aqueous solution of Np-PEG$_{2k}$ ($5 \times 10^{-3}$ M) for 30 min on a shaker (200 rpm). Note, this robust immobilization of the Azo-Si colloids to the surface is only made possible by employing the CB[8]-mediated host–guest interaction at the interface to “stick” the particles onto the surface. In an analogous control
It is noteworthy that although Np exhibits a higher binding sacrificing template for the preparation of ordered Np-PEG2 brushes. The Azo-Si colloids serve as a "free" surface-bound CB[8]-rotaxanes, capable of further com-

removed from the surface to expose a dotted pattern with experiment where Azo-Si colloids were dip coated on an unfunctionalized Au substrate, the Azo-Si particles fell off the surface during the assembly process of the Np-PEG2k brushes as water washes off the particles and destroys the ordering. It is noteworthy that although Np exhibits a higher binding constant ($6.1 \times 10^5 \text{ m}^{-1}$) to MV$^{2+} \subset \text{CB}[8]$ than Azo derivatives ($1.4 \times 10^4 \text{ m}^{-1}$), the MCC structure of the Azo-Si microspheres was well-maintained during the assembly of Np-PEG2k brushes. This is likely on account of the multivalent nature of the binding between the Azo-Si colloids and the CB[8]-functionalized substrate.\textsuperscript{33,34,39}

In the third step (see Figure 1C), the Azo-Si particles were removed from the surface to expose a dotted pattern with “free” surface-bound CB[8]-rotaxanes, capable of further complexation with second guests. The Azo-Si colloids serve as a sacrificial template for the preparation of ordered Np-PEG2k brushes and their controlled removal was achieved by the trans-to-cis isomerization of the Azo functionalities on the periphery of the particle surfaces upon UV light irradiation ($350 \text{ nm}, 1 \text{ min}$). While the trans-Azo can be incorporated into the CB[8]-rotaxane structure via hetero-eroternary complex formation and “stick” the Azo-Si colloids onto the surface, the cis-Azo will dissociate from the CB[8] cavity, resulting in the release of the Azo-Si colloids from the surface. SEM analysis (Figure 4A) confirmed that the Np-PEG2k brushes were retained as a monolayer array on the surface and self-assembled not only in-between but also at the interstitial void spaces underneath the Azo-Si. As shown in Figure 4B,C, AFM topography measurements of the ordered Np-PEG2k network depict a periodical cavity of 333 nm in diameter, which matches the size of the Azo-Si colloidal template. The AFM line profile as shown in Figure 4D reported an average height of the cavity equivalent to 10 nm. Surfaces modified with ethylene glycol units have shown to resist nonspecific adsorption of proteins and cells, thus may find potential applications as biomedical coatings.\textsuperscript{40–43}

In order to prepare ordered dual polymer brushes, as schematically illustrated in Figure 1D, the cavities created by removing the Azo-Si colloids were back-filled with a second polymer Azo-PEG5k. Azo-PEG5k is a poly(ethylene glycol) ($M_n = 5000 \text{ g mol}^{-1}$) end-functionalized with an azobenzene group. A longer PEG chain was used in Azo-PEG5k compared to Np-PEG2k to provide a contrast in heights between the two polymer brushes, in order to obtain a visible pattern. After immersing the substrate in a solution of Azo-PEG5k ($5 \times 10^{-3} \text{ m}$) for 30 min on a shaker (200 rpm), the adsorption of the Azo-PEG5k brushes into the cavities via CB[8]-directed heteroternary complex formation can be clearly seen. As shown by the SEM and AFM topography images in Figure 5A–C, the periodical patterning is well-maintained after the assembly of the second polymer Azo-PEG5k. An average increase of $\approx 30 \text{ nm}$ in height of the inside cavities after grafting Azo-PEG5k brushes was determined in the line profile obtained from a zoomed-in scan with AFM (see Figure 5D,F).

Force-distance curves of Np-PEG2k and Azo-PEG5k were recorded by approaching a bare Si$_3$N$_4$ AFM tip to different areas of the surface (Figure 5D), to further confirm the existence of dual polymer brushes on the surface and their difference in terms of brush height. The brown force spectroscopy curve in Figure 5E was taken on the dark area and exhibited a brush height of 9 nm for the Np-PEG5k brushes, while the yellow curve was obtained on the bright area and resulted in a thickness of 26 nm for the Azo-PEG5k brushes. Note that the slight inconsistency in brush height between AFM topography and force spectroscopy is due to the fact that the topography images were taken in tapping mode, while the force–distance curves were measured in contact mode.

Figure 3. Microscopy images showing the ordered monolayer Azo-Si particles with their gaps filled with Np-PEG2k brushes. A) SEM image, B) AFM 2D topography image (3 $\mu$m $\times$ 3 $\mu$m), and C) AFM 3D topography image (3 $\mu$m $\times$ 3 $\mu$m).

Figure 4. Microscopy images showing the inverse pattern of Np-PEG2k brushes after the removal of Azo-Si colloids. A) SEM image, B) AFM 2D topography image (3 $\mu$m $\times$ 3 $\mu$m), and C) AFM 3D topography image (3 $\mu$m $\times$ 3 $\mu$m). D) The line profile taken along the blue line as indicated by arrow in (B).
Importantly, the patterned supramolecular Np-PEG \( k \) brushes (Figure 1D) remained stable on the CB[8]-functionalized surface during the subsequent assembly of the longer Azo-PEG \( k \) brushes. Previously, we have shown that Np-PEG brushes did not exhibit any significant decrease in height after 5 h of continuous washing with an aqueous solution of a small molecule Np derivative (\([Np] = 1 \times 10^{-3} \text{ M}\)).\(^{38}\) Here, the stability of the Np-PEG \( k \) brushes in the presence of a solution of Azo-PEG \( k \) is even greater as the likelihood of competitive surface displacement with end-functionalized Azo-PEG \( k \) “polymer chains” is substantially lower. The observed robust nature of the supramolecular PEG brushes is likely due to a multivalent “carpet effect” created by the presence of multiple \( N\text{H}_2\text{O} \) bridges exploiting hydrogen bonds between oxygen atoms of neighboring PEG chains.\(^{44}\) These \( N\text{H}_2\text{O} \) bridges are only possible when the distance between two adjacent PEG polymer chains is necessarily low.

CV was employed to evaluate the accessible area (\( A_{\text{surf}} \)) of the modified gold substrates at the different stages of the self-assembly process outlined in Figure 1 of the binary polymer brushes. Figure 6 shows typical voltammograms for the \( \text{Fe(CN)}_6^{3−}/\text{Fe(CN)}_6^{4−} \) oxidation at the modified gold electrode. The CB[8]-functionalized gold electrode is redox-responsive as indicated by the black curve in Figure 6, the current (\( i_p \)) decreased from 90 to 31 \( \mu \text{A} \) (a reduction of 66%) after assembly of the Azo-Si colloids on the electrode (blue curve).\(^{45}\) As \( i_p \) is directly proportional to \( A_{\text{surf}} \), this significant decrease in \( i_p \) can be attributed to the fact that the well-ordered Azo-Si colloidal crystal blocks the electron-transfer event thereby reducing \( A_{\text{surf}} \).\(^{46}\) A further decrease in \( i_p \) to only 3 \( \mu \text{A} \) (90% overall decrease in current) was observed (red curve) after the assembly of Np-PEG\( k \) brushes; the electrochemically inactive PEG polymer brushes cover the remaining, accessible gold surface, further reducing \( A_{\text{surf}} \). The removal of Azo-Si colloids by UV light irradiation exposed spherically patterned CB[8]-functionalized surfaces causing an increase in \( A_{\text{surf}} \) and resulting in a boost in \( i_p \) to 39 \( \mu \text{A} \) (a 12-fold increase in current, brown curve). Finally, a gold electrode modified with patterned binary polymer brushes containing both Np-PEG\( k \) and Azo-PEG\( k \) exhibited a negligible \( i_p \) (green curve), as the dense layer of polymer brushes rendered the gold electrode completely insulating and stopped the flow of electrons to the surface.

In this stepwise approach to prepare nanopatterned dual polymer brushes, the changes in the composition of

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**Figure 5.** Nanopatterned dual brushes of Np-PEG\( k \) and Azo-PEG\( k \). A) SEM image, B) low-magnification AFM 2D topography image (3 \( \mu \text{m} \times 3 \mu \text{m} \)) and C) AFM 3D topography image (1.3 \( \mu \text{m} \times 1.3 \mu \text{m} \)). D) High-magnification AFM 2D topography image (1.3 \( \mu \text{m} \times 1.3 \mu \text{m} \)). E) Approach force–distance curves of the Np-PEG\( k \) brushes (brown line, taken on the dark areas in (D)) and the Azo-PEG\( k \) brushes (yellow line, taken on the bright areas in (D)) on the dual brush pattern. F) The line profile taken along the blue line as indicated by arrow in (B).

**Figure 6.** Cyclic voltammograms of \( \text{Fe(CN)}_6^{3−}/\text{Fe(CN)}_6^{4−} \) (0.5 \( \times 10^{-3} \text{ M} \)) in 0.5 \( \text{M} \) KCl solution obtained using the modified gold substrate as the working electrode, a silver chloride electrode as the reference electrode. Scans start from −0.2 to 0.6 V, with a scan rate of 50 \( \text{mV} \cdot \text{s}^{-1} \).
surface-bound materials can also be followed by water contact angle measurements. As shown in Figure 7, a contact angle (CA) of 98° was measured on the substrate with hexagonally ordered Azo-Si colloids. After filling the gaps with Np-PEG₂₈° (CA) of 98°, the CA decreased slightly to 94°. The CA was further reduced to 66° after removal of Azo-Si colloids with UV irradiation. Note that this value is higher than the CA for both the CB[8]-rotaxane functionalized surface (43°) and the homogeneous Np-PEG₂₈ brush-modified surface (61°). The CA increased to 74° after back-filling the void spaces on the surface vacated by the Azo-Si spheres, and again this value is higher than the CA for either the Np-PEG₂₈ brushes (61°) or Azo-PEG₂₈ (61°) brushes grafted to the surface. This slight increase in hydrophobicity (61° to 74°) is likely because the nanopatterned structures on the surface make it more hydrophobic. The observed phenomena that the nanopatterned composite materials make more hydrophobic than surfaces modified with either of the individual components opens up opportunities to fabricate superhydrophobic surfaces using our supramolecular assembly strategy.

In conclusion, we have developed a facile and lithography-free approach to creating topologically and chemically defined polymer surfaces under mild and ambient conditions by combining the techniques of MCC-templated patterning, host–guest complexation and orthogonally controlled supramolecular self-assembly. Dual composition nanopatterned brushes have been prepared by employing CB[8] rotaxanes as supramolecular linking agents on gold surfaces to controllably “stick” trans-Azo functionalized silica colloids onto the surface in a hexagonal arrangement, which serve as a template for the assembly of short polymer brushes. The formed MCC is photosensitive and can be reversibly disassembled upon UV light irradiation to create void spaces for the grafting of a second, longer polymer brush to form a dual pattern on the nanoscale. To the best of our knowledge, this is the first example of host–guest recognition directed sub-micrometer nanopatterning of binary brushes using MCC as a template. This facile supramolecular approach provides a platform to prepare nanopatterned composite brushes with sophisticated structures under mild conditions, and may prove useful in a number of potential applications including dual responsive sensor films and biomedical coatings.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 7. Water contact angle measurements for the four stages in the stepwise preparation of nanopatterned dual polymer brushes.
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