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Patterning and Impregnation of Superhydrophobic Surfaces Using Aqueous Solutions

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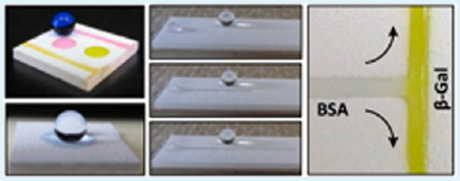
Supporting Information

ABSTRACT: We report a solvent-assisted approach to the patterning and impregnation of porous superhydrophobic coatings that permits the use of entirely aqueous solutions. This approach permits immobilization of proteins and enzymes, creating opportunities to decorate superhydrophobic surfaces with hydrophilic domains and channels that can capture aliquots of aqueous media, guide and mix aqueous solutions, and chemically process streams of organic molecules. Because this approach does not require destruction of non-wetting features, it can also be used to transfer highly water-soluble polymers and small molecules without compromising superhydrophobicity, providing methods for post-fabrication loading of water-soluble agents into protective non-wetting coatings that are difficult to achieve using other approaches.



KEYWORDS: *layer-by-layer, superhydrophobic, hydrophilic, patterning, proteins, enzymes*

INTRODUCTION

Many emerging applications of superhydrophobic materials, including approaches to water harvesting and the design of surfaces for the guided transfer of water, require non-wetting surfaces with hydrophilic domains that can collect, confine, or transport small volumes of aqueous solutions.[1−9] Other potential applications could benefit substantially from methods for the immobilization or loading of biologically active agents into or onto superhydrophobic coatings.[10−13] Although several physical/chemical methods can be used to create hydrophilic domains[14−16] or transfer hydrophilic materials[10,17,18] to superhydrophobic surfaces, methods that permit this to be accomplished using entirely aqueous solutions are rare.[19−21] The reason for this, of course, is that superhydrophobic materials are, by definition, extremely non-wetting to water − they have water contact angles >150°, and water placed on their surfaces generally beads up and rolls off.[22,23] Many superhydrophobic surfaces also remain jacketed by a layer of air when submerged in water (i.e., in the Cassie-Baxter state),[24] further complicating approaches to the transfer, loading, or immobilization of water-soluble materials. Water-soluble agents that are also soluble in organic solvents or alcohol/water mixtures can be transferred using solvent-based methods,[10,17,18] but for highly charged agents that are only soluble in water − or for proteins, enzymes, and other bioactive agents that are readily denatured or inactivated in non-aqueous solvents − the use of non-aqueous solvents is either ineffective or impractical. The transfer of water-soluble agents onto or into extremely water repellant materials using entirely aqueous solutions creates several intellectual and practical design challenges.

Hatton and Aizenberg recently reported the precipitation and deposition of $CaCO_3$ and polyvinyl alcohol on the surfaces of superhydrophobic nano-post arrays using entirely aqueous solutions of these agents.[21] These methods were restricted, however, to deposition on the top-most, water-contacting tips of the arrays, and the modified arrays retained their superhydrophobic properties after functionalization.[21] Other studies have demonstrated that the tips of superhydrophobic post arrays can be decorated with colloids and other compounds by the drying of aqueous solutions in contact with the surface.[25−28] Approaches to the creation of protein-patterned regions in and within superhydrophobic materials have typically made use of methods that first require the selective destruction of superhydrophobicity (e.g., using photolithography) to create permanently hydrophilic, water-wetting domains that can then absorb proteins from aqueous media.[12,29] As an alternative to that approach, we reported chemically reactive superhydrophobic surfaces that permit the transfer and covalent attachment of proteins and other water-soluble agents by direct contact with aqueous solutions.[20] That approach permitted the design of superhydrophobic coatings having defined hydrophilic domains and protein-patterned surfaces, but was restricted to the immobilization of agents containing reactive primary amine groups.

Here, we report a simple and direct approach to the patterning and impregnation of porous superhydrophobic surfaces with proteins and other highly charged agents dissolved in entirely aqueous media. Because this process makes use of aqueous solutions that are non-denaturing to proteins, it can be used to transfer and immobilize active enzymes and create hydrophilic, catalytically active domains on the surfaces and in the bulk of these materials. This approach

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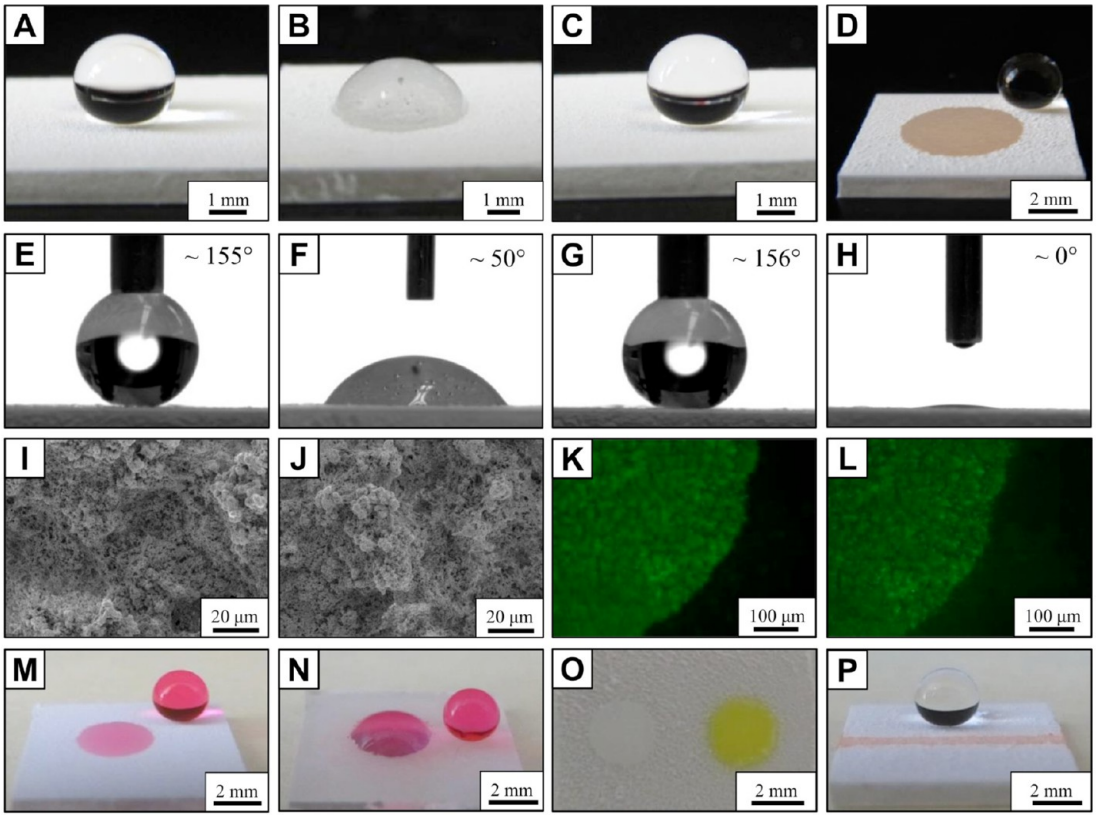

Figure 1. (A–H) Beading and selective wetting of water, and corresponding contact angles, on PEI/PVDMA films. Images were acquired after placing aqueous droplets on: (A, E) a dry film, (B, F) the film in A treated with DCM before placement of the drop, and (C, G) the film in B after removal of the aqueous drop and drying. (D, H) Wetting of water on a film patterned by placing a droplet containing FITC-BSA on a DCM-saturated film; the protein-patterned region appears brown. (I, J) SEM images of PEI/PVDMA films (I) before and (J) after patterning with FITC-BSA. (K, L) Fluorescence microscopy images of PEI/PVDMA films patterned with FITC-BSA (K) before and (L) after rinsing with surfactant solution; FITC-BSA appears green. (M, N) PEI/PVDMA film patterned with BSA (M) before and (N) after sonication to fracture the film (see text); the location of the protein-treated spot is revealed by the wetting of red-colored water. (O) Film with two spots containing BSA (left) and β-gal (right), shown after capture of samples of aqueous solution containing ONPG. (P) Film patterned with a linear hydrophilic feature by contact with a cotton thread soaked in FITC-BSA.

also creates opportunities to decorate superhydrophobic surfaces with patterned features and open channels that can capture and confine aliquots of aqueous media, guide and mix aqueous solutions, and chemically process aqueous streams containing enzyme substrates. However, because these methods do not require the destruction of nonwetting features, they can also be used to pattern or load other water-soluble species (including highly charged synthetic polymers and water-soluble small molecules) without compromising the nonwetting behavior of the original superhydrophobic matrix (providing methods for the postfabrication loading of water-soluble agents into protective superhydrophobic coatings that are difficult to achieve using other approaches). These approaches can be implemented using a variety of low-cost pattern transfer methods. Our approach exploits transient and reversible changes in the wettability of porous, polymer-based superhydrophobic coatings that occur upon exposure to water-immiscible organic solvents.

RESULTS AND DISCUSSION

The work reported here makes use of porous superhydrophobic coatings (~80 μm thick) fabricated by the reactive/covalent layer-by-layer assembly of poly(ethyleneimine) (PEI) and the amine-reactive polymer poly(4,4-dimethylazlactone) (PVDMA).[20,30−32] Our past studies demonstrate that treatment of reactive PEI/PVDMA multilayers with the hydrophobic amine *n*-decylamine yields internally superhydrophobic coatings that remain superhydrophobic (e.g., in the Cassie-Baxter state: advancing water contact angle $\theta \approx 155°$, with roll-off angles of ~1°; Figure 1A, E) upon prolonged submersion in water or upon physical removal of surface layers.[20,30−32] During the course of those past studies, we discovered that the superhydrophobic properties of these coatings could be compromised − transiently and reversibly − by saturating them with the volatile and water-immiscible solvent dichloromethane (DCM). Images B and F in Figure 1 show a droplet of water placed on a DCM-saturated PEI/PVDMA film. Droplets of water applied in this manner readily wet the surface when DCM was present in the films and remained pinned in location (e.g., in the Wenzel state,[24] $\theta \approx 50°$) after the DCM evaporated − they did not spread or expand in size for up to 2 h, and the superhydrophobic properties of the underlying substrates returned completely after the droplets were removed (Figure 1C,G; $\theta \approx 156°$). Schematic illustrations showing individual steps of this solvent-treatment process are shown in Figure 2A–D.

We hypothesized that this solvent-induced change in wettability could be exploited to transfer water-soluble compounds onto and into these materials by direct contact with water droplets containing dissolved agents (a process

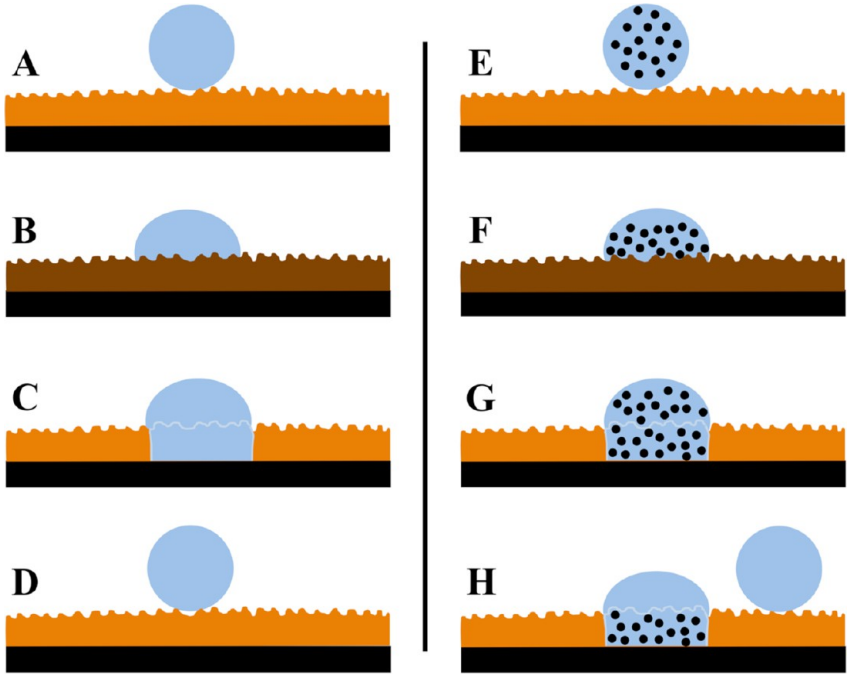

Figure 2. Schematic illustration depicting the solvent-assisted wetting of aqueous droplets on porous superhydrophobic PEI/PVDMA films. (A–D) Transient and reversible wetting of water on DCM-saturated coatings. (A) Droplets of water (blue) placed on the surface of a dry superhydrophobic film (as-fabricated; shown as orange) bead up and do not wet the surface ($\theta \approx 155°$). (B) Droplets of water do wet the surfaces of DCM-saturated films (shown as brown; ($\theta \approx 50°$). (C) Aqueous droplets remain pinned in place after evaporation of DCM; evaporation of DCM also results in water being drawn into the interior of the film, confined to regions below the footprint of the aqueous drop placed on the surface. (D) Removal of the aqueous droplet and drying of the coating results in restoration of superhydrophobicity. (E–H) Solvent-assisted transfer and patterning of water-soluble species (e.g., proteins) from aqueous solutions placed on DCM-saturated coatings. Steps and conditions shown in (E–G) are similar to those shown in (A–C), but the use of aqueous solutions (as opposed to pure water) results in the transfer and immobilization of solutes (black dots) to the surface and into the interior of these porous films. (H) Patterning using protein solutions results in the immobilization of protein on/in the films and a corresponding change in wettability from superhydrophobic to very hydrophilic in the patterned region; adjacent regions of the film that were not treated with aqueous solutions remain superhydrophobic. Treatment with highly charged synthetic polymers and hydrophilic small molecules can also be patterned and loaded using this approach, but do not result in a change in wetting behavior in impregnated regions of the film (see text).

illustrated schematically in Figure 2E–H). To explore the feasibility of this approach, we conducted a first series of experiments using solutions of the model protein bovine serum albumin (BSA) fluorescently labeled with fluorescein isothiocyanate (FITC-BSA). Droplets of FITC-BSA in water (10 mg/mL) beaded up instantly ($\theta > 150°$) on dry films but, similar to the behavior described above, readily wet the surfaces of DCM-saturated films (see Figure S1 in the Supporting Information). In these experiments, FITC-BSA was transferred uniformly to the films in a circular pattern defined by the footprint of the aqueous droplet [as determined by visual inspection (Figure 1D) and fluorescence microscopy (Figure 1K); these images were acquired after removal of the droplet, washing, and drying; see Experimental Section)]. Interestingly, these patterned regions were found to be very hydrophilic – droplets of water rapidly wet these protein-treated areas ($\theta \approx 0°$; Figure 1H), but did not spread or wick into surrounding superhydrophobic (untreated) regions. Our past studies suggest that the superhydrophobic properties of these decylamine-functionalized PEI/PVDMA films arise from a combination of micro- and nanoscale surface roughness.[20,30] Images I and J in Figure 1 show SEM images of films acquired (I) before and (J) after the immobilization of FITC-labeled BSA. We did not observe large changes in the micro/nanoscale features of these covalently cross-linked films after treatment, suggesting that the substantial change in the wettability of protein-patterned regions arises from the presence of immobilized protein, and not from solvent-induced changes in surface morphology.

Figure 1L shows a fluorescence microscopy image of the same film shown in 1K after rigorous washing with surfactant solutions. These results demonstrate that protein is strongly bound, likely through a combination of electrostatic, hydrogen-bonding, and hydrophobic interactions with structural motifs (e.g., amine groups, amide functionality, or alkyl groups) present in these PEI/PVDMA films. It is highly unlikely that protein is immobilized covalently through the reaction of surface-exposed lysine groups with residual azlactone groups (as demonstrated in our past studies),[20,33] because the films used here were exhaustively functionalized with decylamine before use and do not contain residual azlactones (as determined by FTIR spectroscopy).

Other experiments demonstrated that this solvent-assisted process results in the transfer of protein deep into the bulk of these porous coatings. Figure 1M shows a superhydrophobic surface displaying a circular pattern of unlabeled BSA; the patterned spot is hydrophilic, as revealed by the wetting of a droplet of red-colored water. Figure 1N shows the same surface after ultrasound-induced cleavage to fracture the film and expose underlying layers (as described in our past studies;[20] the film in Figure 1M is ~80 μm thick, and the film in Figure 1N, after fracture, is ~0.5 μm thick). Inspection of the film in Figure 1N reveals a hydrophilic pattern with a size and location similar to that observed in Figure 1M (prior to fracture),

demonstrating that aqueous solutions used to transfer protein are delivered into the bulk and throughout the thickness of these materials. These results are consistent with a process in which aqueous solutions that wet DCM-saturated surfaces are drawn into the interiors of these porous materials as the DCM evaporates (see also schematic illustrations in Figure 2F–G). A key feature of this bulk-patterning process is that features defined by the placement of aqueous solutions at the surfaces of these films are transferred faithfully into the bulk and do not spread or wick substantially in the interior, a result of the rapid evaporation of DCM and the fact that these porous films are internally superhydrophobic.[20]

An additional series of experiments using aqueous solutions of active enzymes demonstrated that this approach can be used to create superhydrophobic surfaces with hydrophilic, water-wettable domains that are catalytically active and capable of processing enzyme substrates. Figure 1O shows a surface patterned with a circular spot of BSA (left) and a spot patterned using an aqueous solution of β-galactosidase (β-gal; right), an enzyme that converts the colorless, small-molecule substrate ortho-nitrophenyl-β-D-galactopyranoside (ONPG) to a highly colored yellow product. This patterned superhydrophobic substrate was then immersed briefly into, and then immediately removed from, an aqueous solution of ONPG. Aliquots of solution were selectively captured by both hydrophilic protein-patterned spots, but ONPG was converted rapidly to yellow product (within 30 s) only on the feature displaying immobilized β-gal. It is possible that brief contact with DCM during patterning, or the adsorption of protein to the hydrophobic polymer matrix itself, could result in changes in protein structure that inactivate some fraction of the protein that is immobilized. Our results, however, demonstrate that enzymes can be immobilized on these materials with substantial retention of catalytic function, and that this approach can be used to design surfaces that report the presence of enzyme substrates in ways that can be identified by the unaided eye. Results discussed below demonstrate that this approach can also be used to process and report on the presence of enzyme substrates in aqueous streams.

The methods reported here can be used to pattern more complex hydrophilic features, such as networks of channels and junctions useful for the guided transport of water, on superhydrophobic backgrounds using other contact-transfer methods (including contact with cotton thread or shaped patterns of filter paper soaked in protein solutions). Figure 1P shows a PEI/PVDMA film patterned with a linear hydrophilic channel by contact with a cotton thread soaked in aqueous FITC-BSA. Images A and B in Figure 3 show a similar film with a hydrophilic channel patterned using unlabeled BSA. Placement of a droplet of water at one end of this feature (left) resulted in spreading and transport along the channel (at a rate of ~3.4 cm/min; substrates were held horizontally) without measurable wicking, breaching of the channel/boundary interface, or compromising the superhydrophobicity of surrounding areas (intermediate images from this sequence are shown in Figure S2 in the Supporting Information). Figure 3C–N shows images of thick (~80 μm) and thin (~0.5 μm; refined by sonication as described above) superhydrophobic films with hydrophilic Y-junctions contact-printed using Y-shaped samples of protein-soaked paper. These patterns provide features that can guide and split the flow of water (Figure 3C–J; flow is from left to right) or promote the passive mixing of two aqueous streams (Figure 3K–N). Figure 3O–Q shows the flow of a colorless solution of ONPG (left to right) through a BSA-patterned channel (Figure 3O) to a T-junction designed to transport this enzyme substrate to two channels containing immobilized β-gal (see formation of yellow color in Figure 3P, Q), demonstrating a basis for the design of open, surface-fluidic channels that can guide, mix, and chemically process streams containing organic analytes. Other features that can be patterned using this approach are shown in Figure S3 in the Supporting Information.

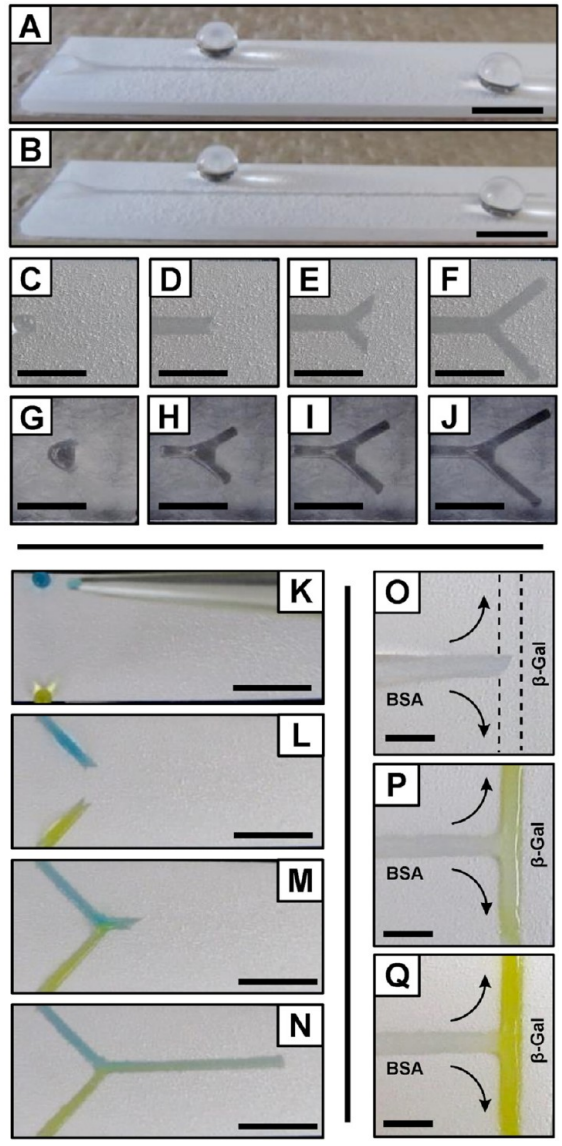

Figure 3. (A, B) Superhydrophobic film patterned with a linear hydrophilic channel by contacting a DCM-saturated film with a thread soaked in aqueous BSA. Placing a droplet of water (3 μL) at one end of this feature (A; shown after 20 s) resulted in passive transport along the channel (B; after 60 s). (C–N) Transport of water on films patterned with BSA-functionalized Y-junctions. (C–J) Transport and splitting of aqueous streams on thicker (~80 μm; C–F, flow is from left to right) and thinner (~0.5 μm; G–J, flow is from center outward) films. (K–N) Mixing of two aqueous streams (containing blue and yellow dyes; flow is from left to right). (O–Q) Flow of a solution of ONPG (left to right) through a BSA-patterned channel (O) to a T-junction leading to channels containing immobilized β-gal (P, Q; indicated by dotted lines in O); enzymatic processing of ONPG is revealed by the formation of yellow color. Scale bars are 5 mm.

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The results above demonstrate that adsorption of protein directly onto/into these PEI/PVDMA coatings creates regions that are hydrophilic. We emphasize here, however, that this solvent-assisted approach permits the infusion of aqueous solutions and the loading of water-soluble agents using benign processes that do not inherently destroy superhydrophobicity (e.g., see Figure 1A–C and accompanying discussion above). This useful feature creates opportunities to pattern or load other types of water-soluble agents, including highly charged polyelectrolytes, into coatings that remain superhydrophobic after loading. Images A and B in Figure 4 show droplets of aqueous solutions of (A) labeled poly(styrenesulfonate) (an anionic polymer; red) and (B) labeled poly(ethyleneimine) (a cationic polymer; yellow) wetting two PEI/PVDMA films (droplets were patterned and pinned in location using methods described above). Inspection of the colored patterns in the corresponding images D and E in Figure 4, acquired after removal of the droplets and rinsing/drying, demonstrates that these water-soluble polymers were transferred to the films; images C and F in Figure 4 show a similar sequence of images for films patterned using a droplet containing the small molecule methyl blue. In contrast to the results above using solutions of protein, the patterning/loading of these highly charged species can be achieved *without* compromising the nonwetting properties of the coatings (e.g., Figure 4D–F; $\theta \approx 155°$, roll-off angles of ~3° in patterned regions). Although the reasons for this behavior are not yet completely understood, our results are consistent with the transport of these materials deep enough into the films that their surfaces do not display residual loaded material. These results provide a basis for the loading of highly water-soluble species into coatings that can prevent or delay exposure to water or, possibly, sustain and prolong release when placed in aqueous media.

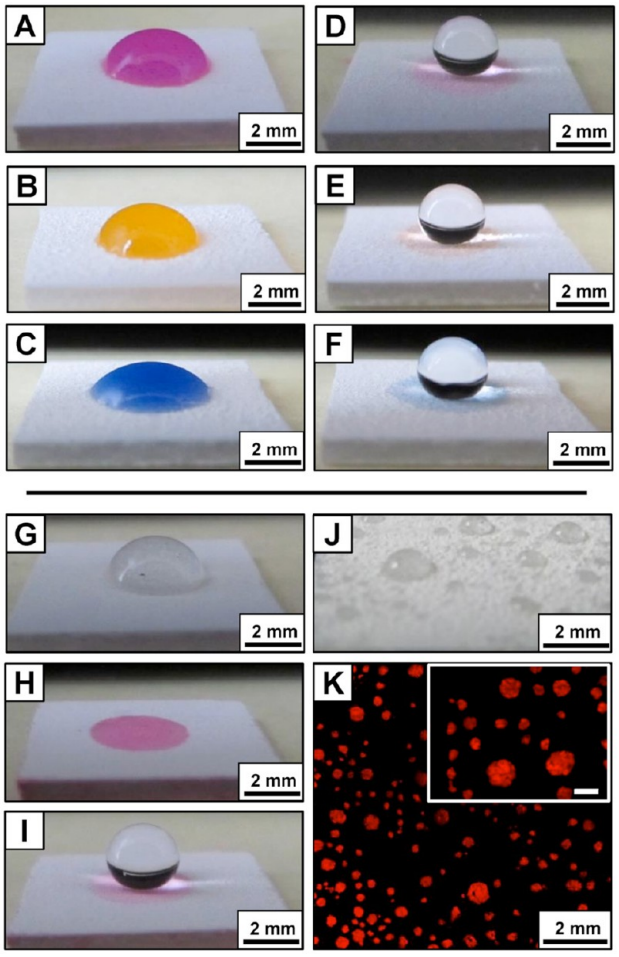

Figure 4. (A–C) Droplets of solutions of (A) labeled poly(styrene sulfonate) (red), (B) labeled poly(ethyleneimine) (yellow), and (C) methyl blue wetting the surfaces of DCM-saturated films. (D–F) The same surfaces shown in A–C after removal of the droplets and rinsing/drying; treated regions remained superhydrophobic ($\theta \approx 155°$; roll-off angle ~3°). (G,H,I) Images of a film patterned by solvent-assisted placement of a droplet of water (G) before and (H) after immersion into aqueous TMR. TMR was transferred selectively to the water-patterned region; the loaded/patterned region remained superhydrophobic after drying (I). (J) Array of small droplets pinned on a PEI/PVDMA coating by spraying water at a DCM-saturated film. Immersion of this water-patterned surface into aqueous BSA yielded an irregular array of hydrophilic spots (K; substrate was immersed in TMR before imaging to aid identification of hydrophilic spots using fluorescence microscopy). Inset scale is 200 μm.

Finally, this solvent-assisted approach provides opportunities to pattern or load agents into transiently "wet" (or water-logged) domains of these materials by subsequent diffusion-based accumulation/transfer of water-soluble agents from secondary aqueous solutions. Figure 4G–I shows an image of a film patterned by the solvent-assisted placement and pinning of a droplet of pure water (no dissolved solutes) (G) before and (H) after immersion of the entire substrate into an aqueous solution of tetramethylrhodamine (TMR) for 1 min. The image in 3H demonstrates that TMR was transferred from the surrounding solution selectively to the "wet" patterned region of the film (the remaining superhydrophobic regions of the film remained free of adsorbed TMR after immersion). The image in Figure 3I shows, again, that the loading of this small molecule can be achieved without compromising superhydrophobicity in treated regions ($\theta \approx 155°$). Figure 4J shows an irregular array of small droplets of pure water pinned on a superhydrophobic PEI/PVDMA coating, created by spraying a mist of water at a DCM-saturated film. Immersion of this patterned surface into a solution of BSA resulted in the transfer of protein to create an irregular array of small, isolated hydrophilic spots (Figure 4K; this substrate was further processed, before imaging, by immersion in aqueous TMR to aid identification of hydrophilic spots using microscopy).

The sizes of the hydrophilic spots here ranged from ~75 μm to ~600 μm as a result of the method used to spray the pattern of pinned droplets. The sizes, juxtaposition, and dispersity of these features, however, is similar in some respects to the irregular hydrophilic/hydrophobic patterns found on the backs of desert beetles,[34] a natural example often cited as inspiration for the design of synthetic materials for the harvesting of water in arid environments. In this case, the ability of the beetle's back to assist in the harvesting of drinkable water is believed to be aided by the presence of those patterned motifs on larger, raised topographic features (although the mechanism through which collection occurs, and the specific species in which it is used, remain a topic of debate).[35] Past studies have demonstrated, however, that flatter synthetic superhydrophobic surfaces decorated with hydrophilic features can also be used to condense and harvest water.[4,36] Studies to explore the potential of this approach for the capture and collection of water and other separations-based applications are currently underway.

In conclusion, we have reported a solvent-assisted approach to the patterning and impregnation of superhydrophobic

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surfaces that permits the use of entirely aqueous solutions. This approach enables direct immobilization of proteins and thus permits patterning of hydrophilic domains and channels decorated with these agents on superhydrophobic backgrounds; the resulting protein-containing features can capture and confine aqueous solutions, guide and mix aqueous streams, and enzymatically process solutions of organic molecules. Because this solvent-assisted approach itself does not inherently destroy features needed to maintain superhydrophobicity, it can also be used to transfer other highly charged water-soluble polymers and small molecules into these coatings without compromising non-wetting behavior. Surfaces with extreme contrasts in wettability or the ability to sequester and protect water-soluble agents in aqueous environments are of interest in a broad range of emerging applications. The work reported here introduces nondestructive methods to create such surfaces using (i) functional materials (proteins and enzymes) that could expand the scope and utility of superhydrophobic materials in these applications and (ii) benign and convenient processing conditions (aqueous solutions and contact printing) that are otherwise challenging to employ in this context.

EXPERIMENTAL SECTION

A detailed description of experimental procedures can be found in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

Details of experimental procedures and additional characterization and control experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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