Controlled switching of the wetting behavior of biomimetic surfaces with hydrogel-supported nanostructures†

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An important feature of biological systems is their response to external stimuli with subsequent changes in properties and function. The ability to "engineer" adaptiveness into next-generation materials is becoming a key requirement and challenge in chemistry, materials science and engineering. Recently we have described new hybrid nano/microstructures capable of dynamic actuation by a hydrogel "muscle". Here we demonstrate the application of a variation of such biomimetic surfaces in controlled reversible switching of the surface wetting behavior. Arrays of rigid nanostructures were integrated with responsive hydrogel films by performing *in situ* polymerization in microscopic confinement of two surfaces. The attachment of hydrogel was achieved through a multifunctional polymeric anchoring layer. Using two different attachment strategies, several designs involving an array of either attached or free-standing nanocolumns embedded in the hydrogel film are described. We demonstrate a superhydrophobic–hydrophilic transition (so-called "direct response") or a hydrophilic–superhydrophobic transition ("reverse response"), respectively, upon the exposure of these two structures to water. We show that all the changes in the wetting behavior are reversible and the structures return to their original superhydrophobic or hydrophilic state upon drying. The ability to design surfaces with reversible changes in their wetting behavior may have exciting applications as "smart," responsive materials with tunable water-repelling or water-attracting properties.

Introduction

Responsive materials are the focus of recent studies in different fields, from medicine and biology to microfluidics, electrical engineering and sensors.[1] Many examples of artificial responsive surfaces have been reported. In most cases, polymeric materials were used.[2] The dynamic rearrangement of polymer chains in different solvents was demonstrated for a binary polymer brush attached to a solid surface.[3] A novel and unexpected "contra-philic" wetting behavior was reported for block copolymer surfaces, when a water-induced increase of hydrophobicity of the polymer coatings was caused by the dynamic rearrangement of the fluorinated polymer segments.[4]

The ability to induce adaptive behavior based on the mechanical rearrangement of microscopic structures has been explored using hydrogel or gel-like polymer materials. Hydrogels are responsive materials composed of cross-linked flexible polymeric hydrophilic chains, whose elastic networks can swell in water to the desired degree of hydration. The shape-memory characteristic of hydrogels[5] gives the advantage of the repeatability and reversibility of the response. A variety of stimuli (humidity, pH, temperature, ionic strength, electric field, *etc.*) that cause the swelling of the specially designed hydrogels have been studied.[6] Such diversity of response mechanisms makes hydrogels promising candidates for actuation, sensor and drug delivery applications. Hydrogel posts embedded into microchannel valves were shown to redirect the fluid flow.[7]

The intrinsic flexibility of polymers is, on the one hand, advantageous for the design of the responsive materials. For example, a device consisting of moveable polydimethylsiloxane (PDMS) pins that change aspect ratio by external signalling has been reported.[8] Fabrication approaches for generating complex micro- and nanopatterns on polymeric surfaces are reviewed in ref. 9. On the other hand, however, features composed of soft materials are mechanically unstable and often irreversibly collapse.[10] Recently, we described a method of fabricating Si nanostructured surfaces with high-aspect-ratio features (Fig. 1A).[11] When a hydrophobic coating is applied (either using self-assembled silane monolayers or CVD deposition of a hydrophobic layer), the nanostructured surfaces demonstrate remarkable superhydrophobicity and eventually superlyophobicity.[12,13] We define the term "superhydrophobicity" as a combination of two wetting parameters: a very high water droplet contact angle and a very small advancing–receding hysteresis. In other words, a water droplet deposited on a superhydrophobic surface maintains its almost spherical shape and easily slides over the surface (Fig. 1B). We have shown that the infiltration of such nanostructured surfaces with a hydrogel layer leads to the ability to actuate the nanostructures in response to changes in humidity and allows the fabrication of stable,

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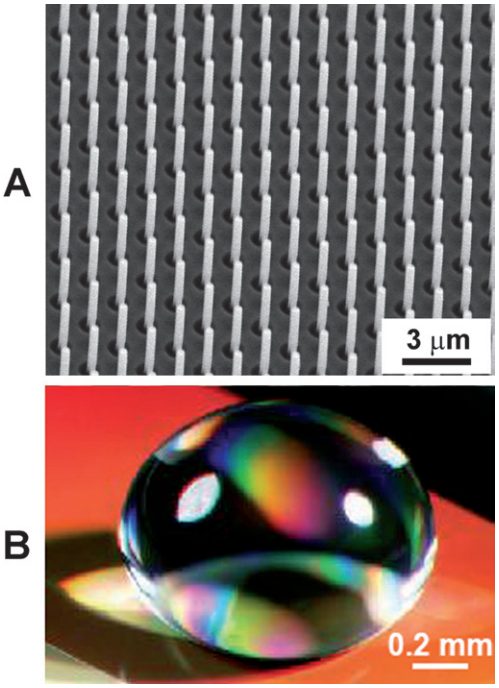

Fig. 1 Superhydrophobic high-aspect-ratio silicon nanostructures. (A) Scanning electron micrograph (SEM) of the array of isolated rigid setae (AIRS); (B) water droplet on the superhydrophobic surface shown in (A).

non-collapsing nanoarrays capable of controlled geometrical rearrangements.[14]

Here, we report on the synthesis of new designs that explore the concept of combining hydrogels with an array of high-aspect-ratio nanostructures. We demonstrate the application of these structures in controlling surface wetting behavior. The synthesis of these hybrid surfaces was inspired by a variety of biological materials that are naturally optimized to provide the hydrophilic/hydrophobic behavior.[15] For example, arrays of microcolumns (setae) cover the surface of a gecko's toe. These superhydrophobic structures allow extraordinarily high adhesion of the gecko's feet to different surfaces.[16] Another interesting example is a well-defined array of nanoscopic columns developed on cicadas' wings, and the legs of water spiders and beetles; these nanostructures offer the organisms the required superhydrophobic property used for water repellence, movement and water capture.[17] The similar structure and properties of lotus leaves are a classical example of superhydrophobic, self-cleaning surfaces in nature.[18] The fabrication of synthetic superhydrophobic surfaces has been a hot topic in materials science recently, and a variety of approaches have been described.[19] We show that two designs reported in the current paper offer the ability of controlled, dynamic switching of the surface wetting properties—an extremely important quality of next-generation synthetic surfaces. The first surface type acts in a "direct" response mode and undergoes reversible transitions from a superhydrophobic state to a hydrophilic state before/after exposure to water, whereas the second surface design acts in a "reverse" response mode and undergoes reversible transitions from a hydrophilic state to a superhydrophobic state before/after exposure to water.

Results and discussion

Covalent attachment of hydrogel layers for integration into silicon-based nanostructures

The backbone of the hydrogel-infiltrated surfaces designed for controlled switching of the surface wetting behavior is composed of an array of isolated rigid setae (AIRS) etched in silicon using the Bosch process (Fig. 1A).[11,14] Reliable and robust attachment of microscopically thick hydrogel films to solid substrates is an extremely important step for the successful integration of soft and hard materials into a responsive, hybrid device. Recently, several approaches have been proposed to graft water-soluble cross-linked polymers to solid substrates.[20] Generally, the strategy of hydrogel film fabrication involves polymerization of a monomer solution in the confinement of two solid substrates divided by a spacer of the desired thickness. The surface of one of the substrates (*e.g.* Si wafer) is modified with a self-assembled monolayer (SAM) of a functionalized silane, which introduces reactive moieties, such as vinyl or (meth)acryl groups. The polymerization can then be either thermally or photo-initiated. The approach was applied with great success to attach submicroscopically thick films of linear and hyperbranched polymer brushes and polymer gels.[20,21] The surface attachment using single bonds of silane SAMs fails, however, if exploited in the case of highly swellable hydrogels reaching several microns in thickness. The tangential stresses along the plane of the film/substrate surface result in delamination of the films during multiple drying/swelling cycles. Therefore, a novel platform of substrate modification that allows a simple, robust and permanent introduction of active groups on the surface has been proposed.[22] It has been shown that the chemisorbed layer of poly(glycidyl methacrylate) (PGMA) forms multiple bonds between glycidyl groups of PGMA and silanol groups of a native silica layer of silicon or glass. Moreover, chemisorbed PGMA builds the anchoring interface rich in reactive epoxy groups available for further chemical modifications.

We used this approach for grafting poly(acrylamide) gel (PAAmG) and preparing microscopically thick films of hydrogel. The "bottom-up" synthesis procedure consists of four steps (Fig. 2). First, a PGMA layer was deposited on the substrate (Fig. 2A). About 1 h of annealing at elevated temperatures allowed covalent bonding of glycidyls of PGMA with silanol groups of the silicon/silica substrate (Fig. 2B). At the next step, the substrate was immersed into acrylic acid (AcA) to introduce the double C=C bonds on the PGMA surface by reaction of free glycidyl groups of PGMA with AcA (Fig. 2C). As a result, we fabricated a multi-site anchoring chemisorbed PGMA layer with reactive acrylic C=C bonds. Finally, we performed the *in situ* radical copolymerization of acrylamide (AAm) and *N*,*N*′-methylenebisacrylamide (bis-AAm) as a cross-linking agent. The polymerization was initiated by either a water-soluble photoinitiator (PI) upon exposure to UV light or a convenient thermoinitiator. The polymerization was performed by a "grafting through" technique. The free radicals were generated in the bulk of the polymerization solution. The radical growth propagates and includes acrylic C=C bonds exposed at the PGMA surface into the growing polymer chain. The multiple bond formation between the anchoring layer, substrate, and newly grown

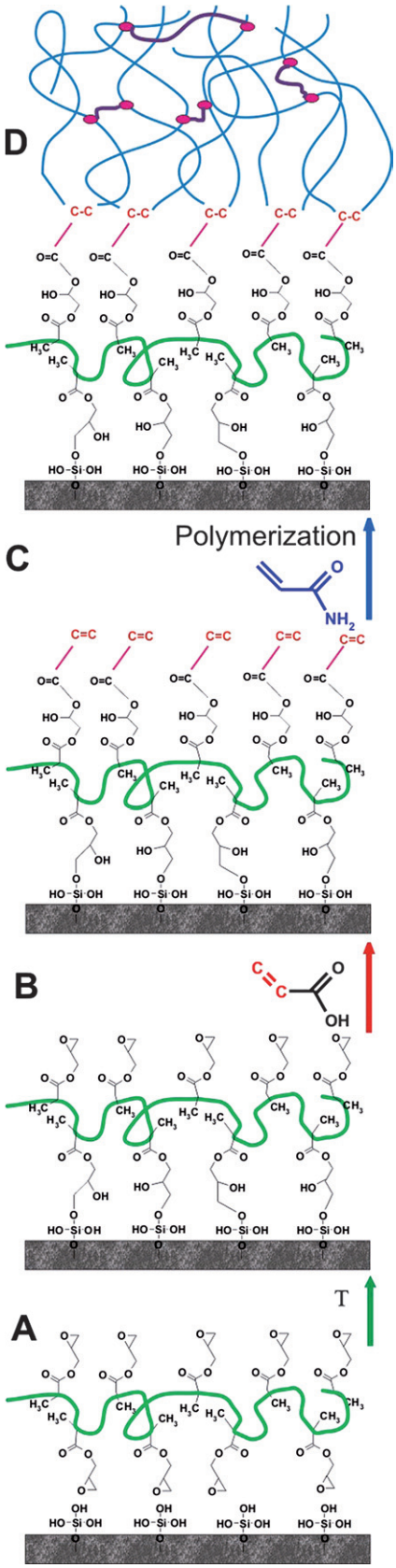

Fig. 2 Synthetic steps of the covalent attachment of hydrogel layers to a substrate for integration into AIRS. See text for details.

cross-linked polymer, *i.e.* PAAmG, ensures robust and reliable hydrogel attachment to the solid substrate (Fig. 2D).

Surfaces with "direct response"

Fig. 3 shows the scheme of integration of microscopically thick hydrogel film with AIRS to fabricate the hybrid device (HAIRS) (Fig. 3A). We have shown earlier that the drying cycle of the hydrogel film in such a hybrid structure induces bending of high-aspect-ratio nanocolumns.[14] We have demonstrated that the extent of bending can be controlled by regulating the aspect ratio of the AIRS. In our current design, we choose relatively low aspect ratio (~20) setae that cannot be moved by the drying hydrogel and remain straight on the surface. In this case, when exposed to water, the hydrogel film will flood the nanostructures. We anticipated that such architecture will lead to switching from the *superhydrophobic* to the *hydrophilic* state upon exposure to water (Fig. 3B). We therefore name the HAIRS as a surface with "direct response," in the sense that both natural and artificial[23] surfaces demonstrate the capability to mimic the environment, *i.e.* to switch from the hydrophobic to the hydrophilic state in water or humid conditions.

There are several specific requirements for the hydrogel films used to realize the design. First, the film has to be reliably attached to the bottom of the AIRS. Second, the film should preserve the capability of sufficient swelling. Finally, the amount of the hydrogel material should be commensurate with the height of the setae and the swelling ratio. The latter is required to achieve the most prominent response of the assembly. To produce a PAAmG film covalently attached to the sample, a droplet of polymerization solution (μL of 60% AAm, 3% of bis-AAm, and 1% solution of PI in water) was deposited on the sample with PGMA/AcA anchoring layer. This amount of polymerization solution was calculated to fill the working volume of the sample defined by the patterned area of 1×10^{-4} m^2 and setae heights of 5×10^{-6} m. The droplet of the polymerization solution spread over the patterned area within several seconds. The wet sample surface was then covered with n-decane (Fig. 3A). The layer of n-decane played the role of a liquid confining surface. We chose n-decane as an alternative to a solid confinement for three reasons: (i) being immiscible with an aqueous polymerizate, it prevented further evaporation of water that would otherwise lead to undesired crystallization of AAm; (ii) the liquid layer provided better, more conformal contact with the tips of the nano-structured array; (iii) n-decane did not interfere with the UV-light initiation of radical polymerization. The samples filled with the polymerizate and covered with n-decane were exposed to UV light. Upon proper washing and drying, submicron films of PAAmG covalently grafted to the bottom of the AIRS were obtained. In most experiments described in this paper, the thickness of the films was about 0.5 μm.

Fig. 3C shows the HAIRS fabricated as described. The grafted hydrogel film forms uniform onion-like features surrounding every seta. The onion-like features presumably reflect the pinning of the retracting hydrogel layer around the seta upon drying. To view the HAIRS samples swollen in water, we have applied a novel technology—WETSEM™ capsules—that allows the SEM analysis of wet samples under atmospheric pressure in the back-scattered electrons mode. The depth of focus for imaging

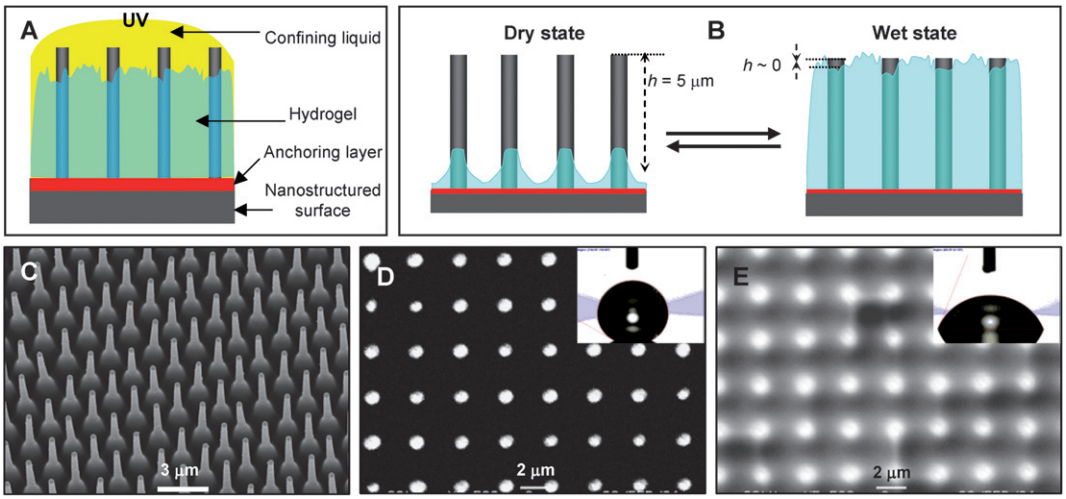

Fig. 3 Hybrid device for a direct response to exposure to water (HAIRS). (A) Schematic of the hydrogel attachment to the AIRS substrate during UV-light-induced *in situ* synthesis in a liquid confinement. (B) Schematic illustration of the dynamic rearrangement of the HAIRS in the dry and wet states. (C) Representative SEM image of the hybrid surface. (D,E) WETSEM images of dry (D) and wet (E) HAIRS with the corresponding water contact angles (red lines in insets). The dry HAIRS surface reveals superhydrophobic behavior (D, inset), whereas the wet HAIRS surface is hydrophilic (E, inset).

organic materials using WETSEM is <1–2 μm.[24] The absence of the polymer signal in the dry state (Fig. 3D) and clear detection of the hydrogel film in the wet state (Fig. 3E) imply that the polymer swells and floods the setae at least within a micron from the tips of the nanocolumns. To study the wetting behavior of the assembly, we have applied a monolayer of hydrophobic fluoroalkyl silane (FOS) onto the tips of the dry setae. Completeness of the SAM was monitored by contact-angle measurements using the flat part of the silicon sample (Table 1). The hybrid HAIRS surface showed superhydrophobicity (Fig. 3D, inset) similar to that described for AIRS.[12] In a wet state, however, the swollen hydrogel film expanded and became exposed to the probing water droplet. As a result, the entire surface turned hydrophilic (Fig. 3E, inset). The specific feature of the HAIRS is its switching from the *superhydrophobic* to the *hydrophilic* state upon exposure to water.[25] The change in the wetting behavior is reversible and the surfaces return to their original superhydrophobic state upon drying.

Surfaces with "reverse response"

Materials with a "reverse response" to changes in humidity that reveal hydrophilic properties in the dry state and turn hydrophobic in the wet state may find application as "smart" cloths that attract moisture in a dry atmosphere and repel water when exposed to a humid environment.

Table 1 Water contact angles (degrees) upon successive preparation steps[a]

	Flat surface (frame)	AIRS surface
Initial surface (AIRS)	<10	<10
PGMA chemisorbed	55 ± 2	80 ± 5[a]
PGMA + acrylic acid	27 ± 3	<10
Grafted hydrogel	N/A	<10
SAM modified (wet)	105 ± 2	<10 (130–150 for GEARS)

[a] The water droplet is unstable.

Our approach to the design of surfaces with reverse response consists of the transfer of AIRS setae on the confining surface (Fig. 4A). The synthesis of a gel-embedded array of rigid setae (GEARS) is outlined below. A droplet of the polymerization solution is deposited between AIRS and the solid confining surface. The confining surface is modified with an anchoring layer, *i.e.* chemisorbed PGMA followed by an AcA modification. The thermo-induced "grafting through" polymerization results in PAAmG. The assembly is cleaved by tangential stress. The procedure breaks the nanostructures from the Si surface and allows complete transfer of the setae onto the confining surface. As a result, the hydrogel film is covalently grafted to the flat, confining surface and the setae are partially embedded into the film. In most experiments described in this paper, the thickness of the film in the dry state was about 5 μm. Due to the contraction of the polymer film upon drying, nanocolumns redirect the tensile forces from the gel into a lateral actuation that results in the tilt of the partially exposed nanostructures. The tilt angle is controlled by the volume change of the gel and can be therefore regulated by the appropriate choice of the polymer. If v_w and v_d are the volumes of the gel in the wet and the dry state, respectively, then $\cos\alpha = v_d/v_w$. Re-hydration of the sample leads to swelling and relaxation of the hydrogel. This results in the normal orientation of the bristles (Fig. 4B). The microscopy observation along the surface normal shows the tilted nanostructures in the dry sample (Fig. 4C, D). The tilt angle can be directly measured from the micrographs viewed normal to the surface: $\sin\alpha = a/l$, where l is the length of the emerging portion of the nanocolumns and a is the length of the column projections. With the materials typically used in this study, the tilt angle from the surface normal was 60–75°. The same nanostructures appear as an array of dots when a water droplet is applied, confirming their reorientation normal to the surface (Fig. 4E). The specific feature of the GEARS is its switching from the *hydrophilic* to the

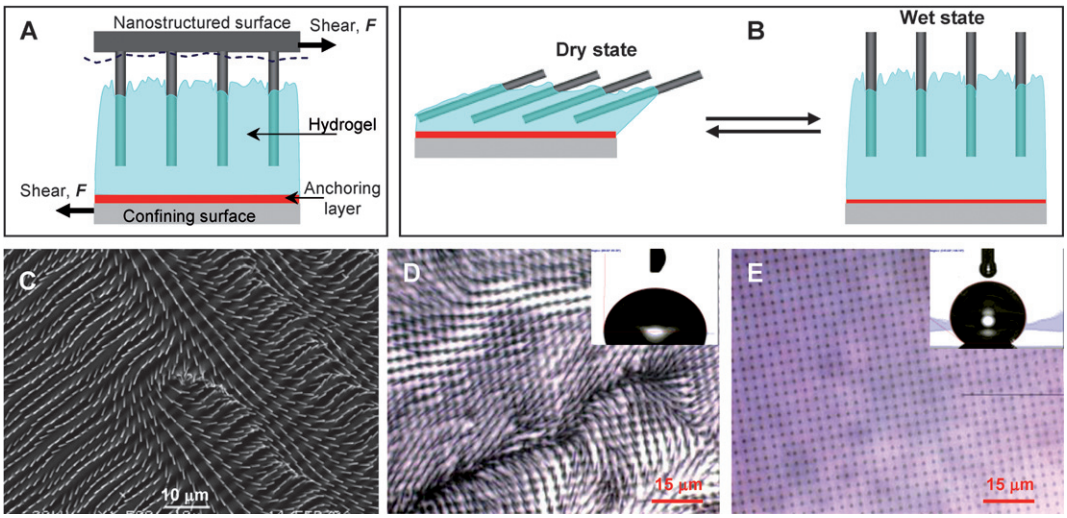

Fig. 4 Gel-embedded array of rigid setae (GEARS) designed to provide a reverse response to exposure to water. (A) Schematic of the setae transfer into the hydrogel layer attached to the confining solid surface modified with the PGMA anchoring layer upon *in situ* synthesis. (B) Schematic illustration of the dynamic rearrangement of the GEARS in the dry and wet states. (C) Representative SEM image of the GEARS bristle in the dry state. (D) Optical microscopy analysis of the dry GEARS surface reveals highly tilted setae. The surface is relatively hydrophilic (D, inset). (E) Optical microscopy analysis of the same region as in (D) in a humid atmosphere reveals setae standing perpendicular to the surface and its hydrophobic character (E, inset).

superhydrophobic state upon exposure to water.[25] The change in the wetting behavior is reversible and the structures return to their original tilted orientation and the corresponding hydrophilic state upon drying.

In conclusion, we report the synthesis of new biomimetic responsive surfaces that explore the concept of combining hydrogels with an array of high-aspect-ratio nanostructures. We propose two designs that offer the capability of controlled, reversible, dynamic switching of the surface wetting properties. We demonstrate both the direct and reverse responses of these "smart" surfaces; that is, superhydrophobic/hydrophilic and hydrophilic/hydrophobic transitions before/after exposure to water.

Experimental

Materials

Acrylamide (AAm), *N*,*N*′-methylenebisacrylamide (bis-AAm), ammonium persulfate (APS), 2-hydroxy-4-(2-hydroxyethoxy)-2-methylpropiophenone as photoinitiator (PI), azobisisobutyronitrile (AIBN), glycidyl methacrylate (GMA), acrylic acid (AcA) and methyl ethyl ketone (MEK) were purchased from Sigma-Aldrich, all of grade "purum." Poly(glycidyl methacrylate) (PGMA) was synthesized from GMA by radical polymerization with AIBN in MEK as solvent. The mixture of 30% GMA and 1% of AIBN in MEK was purged with argon and placed in a water bath at 60 °C for 6 h. Upon polymerization, PGMA was purified by multiple precipitation in diethyl ether and dried under vacuum for 24 h. (Tridecafluoro-1,1,2,2-tetrahydrooctyl)triethoxysilane (FOS) was purchased from Gelest, Inc., and used for hydrophobization of silicon.

Sample preparation

The samples of square arrays of well-defined setae with diameters of 300–350 nm, heights of 3–8 μm, and periodicities of 2–4 μm (AIRS) were formed on silicon wafers using the Bosch process. The AIRS samples were then cleaned by Ar plasma and matured at normal conditions at least overnight to allow the formation of silanol groups. More details on the preparation can be found elsewhere.[11] The attachment of the hydrogel layer to form hydrogel-AIRS hybrids was performed in three steps. First, an anchoring layer of PGMA was deposited from 1% solution in MEK. The thickness of the PGMA layer was 1.3–1.8 nm, as revealed by ellipsometry. The samples were annealed for 60 min at 110 °C to ensure the formation of covalent bonding of epoxy groups of PGMA to silanol groups on the sample surface. Second, the introduction of reactive acrylic groups was accomplished by immersing the samples in pure AcA. The reaction completed in 10 min, as monitored by contact-angle measurements (Table 1).

The final step is the radical polymerization of AAm in a water solution with cross-linking agent bis-AAm and an initiator, in the confinement of two surfaces. We used photo- and thermo-initiated polymerization for HAIRS and GEARS, respectively. For the HAIRS design, the PGMA/AcA anchoring layer was applied to the AIRS surface. A droplet of 0.8 μL of 60% AAm, 3% bis-AAm, and 1% solution of PI in water was deposited onto the sample with a microsyringe. The droplet of polymerization solution spread over the patterned area within several seconds. The wet sample surface was then covered with a layer of n-decane deposited dropwise on the wet sample. The samples were illuminated with a UV lamp (Black-Ray B-100 mercury lamp, 365 nm) for 1 h. Upon rinsing with an abundant amount of water, a submicron film of hydrogel covalently grafted to the bottom of the AIRS was obtained.

For the fabrication of GEARS, we used a solid confining surface, *i.e.* a flat silicon wafer. The anchoring PGMA/AcA layer was applied to the confining surface as described above. Then a polymerizate solution containing 40% of AAm, 2% of bis-AAm and 2% of APS in water was deposited onto the AIRS surface.

The "sandwich" consisting of the AIRS sample, the polymerizate solution, and the functionalized confining surface was clamped and placed in an oven at 40 °C for 1 h for polymerization. The sample was then additionally dried under vacuum for 2 h. By applying shear stress, the two confining surfaces were separated.

The hydrophobization of dried samples of HAIRS and GEARS was performed in a 5% solution of FOS in toluene for 5 min, followed by an abundant rinse in toluene. The completeness of the hydrophobization was monitored by contact-angle measurements on the flat part of the samples (frame) (Table 1).

Characterization

The thickness of adsorbed PGMA layers was measured with a Sentech 800 ellipsometer at 70° incident angle and 633 nm laser wavelength. Optical microscopy investigations were carried out with a Nikon Optishot microscope. Contact-angle measurements were performed using the sitting-droplet method with a home-made optical goniometer. High-resolution surface imaging was performed using a JEOL 5600 scanning electron microscope. The WETSEM™ capsules were used to observe the morphology of the wet samples with SEM microscopy.

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