Stimuli-Responsive Surfaces for Tunable and Reversible Control of Wettability

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Designing a solid surface with specific wettability is important for many applications such as for self-cleaning, antifouling, antifogging, separation, printing, and many biomedical applications.[1–6] In addition, it is desirable to control the wettability of a solid surface reversibly from hydrophilic to hydrophobic via an external stimulus such as pH, light, temperature, electrical potential, and different types of solvents.[7–10] Responsive materials with controllable wettability have applications in many different technological fields; some interesting examples include programmable operations in microfluidic devices,[11] site-specific delivery of drugs,[12] switchable surfaces for capturing and releasing of circulating tumor cells (CTCs),[13] controllable separation of water and oil,[1] detection of biomolecules, and bioseparation.[14] A number of methods have been proposed in previous studies to fabricate materials with such controllable wettability. Some of them involve complicated structures that can be technically challenging to make (e.g., a stress-responsive material that consists of micrometer-sized polyamide fibers tied together in a triangular network).[15] More common methods of fabrication involve a unique type of material that has the ability to change its wettability under the influence of a particular external stimulus. For example, wettability can be controlled for certain inorganic materials (e.g., TiO_2, ZnO, SnO_2, WO_3, V_2O_5, and Ga_2O_3) under the influence of light, and for certain polymeric materials (e.g., poly(-isopropylacrylamide) (PNIPAm)) with a change in temperature.[9,10] However, the range at which the wettability can be controlled is usually limited for a smooth, unprocessed material; this limitation applies to many materials, including both inorganic and polymeric materials. A smooth PNIPAm surface, for example, exhibits a controllable range of contact angle from only 63.5° to 93.2° (i.e., slightly hydrophilic to slightly hydrophobic) when the temperature is changed.[16] In order to control wettability over a larger range, a general method involves modifying the material with a particular type of surface roughness. It is well known that surface roughness can enhance both hydrophilicity and hydrophobicity, thus a wider range of wettability can be controlled. Many methods have been proposed to create surfaces with micro- to nanoscale structures to enhance surface roughness, specifically for the purpose of controlling a wider range of wettability;[16,17] examples include electrodeposition[18] and electrospinning.[19] Through engineering surface roughness, it is possible to fabricate many types of surfaces with a controllable range that extends from superhydrophobicity (defined as having a contact angle of >150°) to superhydrophilicity (defined as having a contact angle of ≈0°). The modification of surfaces with specific micro- to nanoscale structures, however, can be technically difficult. An additional requirement is that in order to use surface roughness to enhance both the hydrophobicity and hydrophilicity of the surface, the material must inherently have the ability to switch between both hydrophobic and hydrophilic states before any surface modification. Since this characteristic is rather unique, only a limited selection of these materials is available. Furthermore, these methods of fabrication are usually different for materials that respond to different stimuli. It would be convenient to establish a technically simple and general method that allows the fabrication of different types of stimuli-responsive surfaces. A general method will be especially useful for building an integrated system that uses a combination of these stimuli-responsive surfaces in order to respond to different external stimuli simultaneously.

This study describes a novel general procedure for fabricating surfaces that can vary from superhydrophobicity to superhydrophilicity reversibly under the influence of different types of external stimuli. The method is simple: it involves coating silanized particles into a stimuli-responsive hydrogel (**Figure 1**a). Stimuli-responsive hydrogels are a class of materials that expands or contracts under the influence of a specific external stimulus. These hydrogels have been widely studied; they can be fabricated to be responsive to a large variety of stimuli such as temperature, pH, electric field, magnetic field, light, pressure, gases, ions, alcohol, and many different types of biomolecules.[12,20,21] Because of their affinity for water, hydrogels are typically superhydrophilic: when a drop of water is placed on the surface of a hydrogel, it spreads out quickly, and exhibits negligible contact angle. Another reason for choosing to work with these stimuli-responsive hydrogels is because they have many desirable properties, and have been used widely in many scientific fields (e.g., biomedical).[22–24] We propose to coat a stimuli-responsive hydrogel with silanized particles, which are known to be superhydrophobic. Thus, when the hydrogel is in its contracted state, it is superhydrophobic; when it expands, we found experimentally that it is superhydrophilic (Figure 1a). In this way, it is possible to control the wettability by regulating the amount of the external stimulus. Therefore, instead of relying on materials that have the inherent ability to switch between hydrophobic and hydrophilic states under the influence of a stimulus, we use stimuli-responsive hydrogels as the medium that responds to the stimulus.

Our method has several advantages: (1) it is a general method that is compatible with different types of stimuli-responsive macromolecules, and can produce surfaces that

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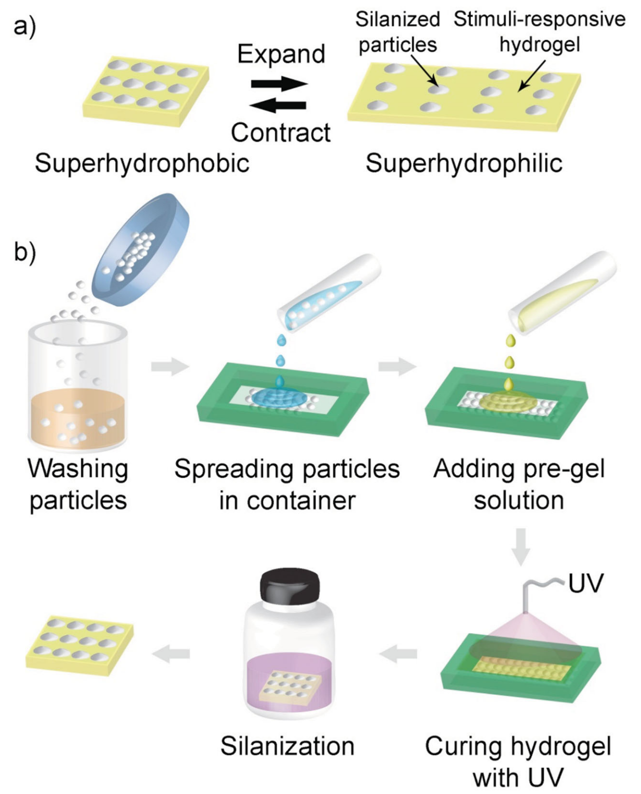

Figure 1. A stimuli-responsive composite material that can vary its wettability from superhydrophobicity to superhydrophilicity reversibly. a) The surface consists of a stimuli-responsive hydrogel and micrometer-sized glass particles. The particles are made superhydrophobic by silanization. Thus, in its contracted state, the surface is superhydrophobic due to the layers of silanized particles. When the hydrogel expands under the influence of a specific external stimulus, the surface becomes superhydrophilic. b) Experimental procedure for fabricating the stimuli-responsive composite material.

are responsive to a wide variety of external stimuli (since it is known that hydrogels can be made to respond to many different types of stimuli); (2) it offers a wide range of control from superhydrophobicity to superhydrophilicity; (3) the control is reversible; (4) the control is tunable; and (5) it is relatively simple to implement. Subsequently, we demonstrated an application of this composite material: we used it as a responsive membrane that allows the permeability of chemicals through it to be controlled by varying an external stimulus. We also assembled a pH-responsive, a temperature-responsive, and a stress-responsive membrane together into an integrated system; this system demonstrates that it is possible to construct a device that responds to multiple stimuli simultaneously by using a combination of these stimuli-responsive composite materials.

The scheme in Figure 1b illustrates the process of fabricating the composite material. Glass particles were first washed with a piranha solution for 40 min in order to remove any organic contaminant on their surfaces. They were then rinsed with ethanol and deionized water, and dried in an oven. After cleaning the particles, we re-dissolved some of the particles (0.2 g) in deionized water, and poured the mixture into a rectangular glass container. The spontaneous spreading of water allowed the bottom of the container to be covered with layers of particles. The mixture was then dried in an oven, leaving only the layers of particles at the bottom of the container (see Section 1, Supporting Information, for more details on the experimental procedure).

In a separate step, we prepared the pregel solution of the stimuli-responsive hydrogel. We used three types of hydrogels: a stretchable hydrogel (or a stress-responsive hydrogel), a pH-responsive hydrogel (i.e., a hydrogel that expands when it is immersed in a basic solution), and a temperature-responsive hydrogel (i.e., a hydrogel that expands when temperature is increased). The surfaces of these three hydrogels were found to be superhydrophilic. For the fabrication of the stretchable hydrogel, we used a procedure discussed in a previous study;[25] the hydrogel reported is found to be highly stretchable, and has superior mechanical properties. Briefly, we mixed alginate, acrylamide (the weight ratio of alginate: acrylamide at 1:6), ammonium persulfate as the photo-initiator (at a fraction of 0.0025 the weight of acrylamide), *N*,*N*′-methylenebisacrylamide as the cross-linker (at a fraction of 0.0006 the weight of acrylamide), and deionized water (86 wt%). The mixture was degassed in a vacuum chamber for 10 min. Subsequently, we added *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (at a fraction of 0.0025 the weight of acrylamide) as the accelerator for the crosslinking of polyacrylamide, and calcium sulfate dehydrate ($CaSO_4 \cdot 2H_2O$) (at a fraction of 0.1328 the weight of alginate) as the ionic cross-linker for alginate. This pregel solution was then poured into the glass container covered with the layers of glass particles. After 10 min, the solution was cured with an UV light (at an intensity of 10 mW cm^{-2} and a wavelength of 254 nm) at 50 °C for 1 h. The product—the composite material that consisted of both the stretchable hydrogel and the glass particles—was left in a chamber with high humidity for a day in order for the reaction to go to completion. It was then dried in an oven at 80 °C for 5 min. The pH-responsive hydrogel was made by following the procedure of another study.[26] The pregel solution was prepared by mixing acrylic acid (4.3 wt%), 2-hydroxyethyl methacrylate (64.3 wt%), ethylene glycol dimethacrylate (0.7 wt%) as the cross-linker, 2,2-dimethoxy-2-phenylacetophenone (2.1 wt%) as the photoinitiator, and deionized water (28.6 wt%). (The composition of this hydrogel has been modified slightly from its original reference. See Section 2, Supporting Information, for details and reasons of the modification.) The mixture was poured into the glass container covered with the layers of glass particles. After 10 min, it was cured under UV light (intensity of 10 mW cm^{-2}, and a wavelength of 365 nm), for 20 min, and dried in an oven at 80 °C for 5 min. The temperature-responsive pregel solution was prepared by mixing acrylamide (3.31 wt%), acrylic acid (3.36 wt%), *N*,*N*′-methylenebisacrylamide (0.15 wt%) as the cross-linker, α-ketoglutaric acid (0.04 wt%) as the photoinitiator, and deionized water (93.14 wt%).[27] Similarly, this mixture was poured into the glass container, and was cured under UV light (intensity of 10 mW cm^{-2}, and a wavelength of 365 nm) for 2 h. It was then dried in the same way as the pH-responsive hydrogel.

After fabricating the composite material, we silanized the glass particles in order to make them superhydrophobic. Previous studies have reported that it is possible to make glass

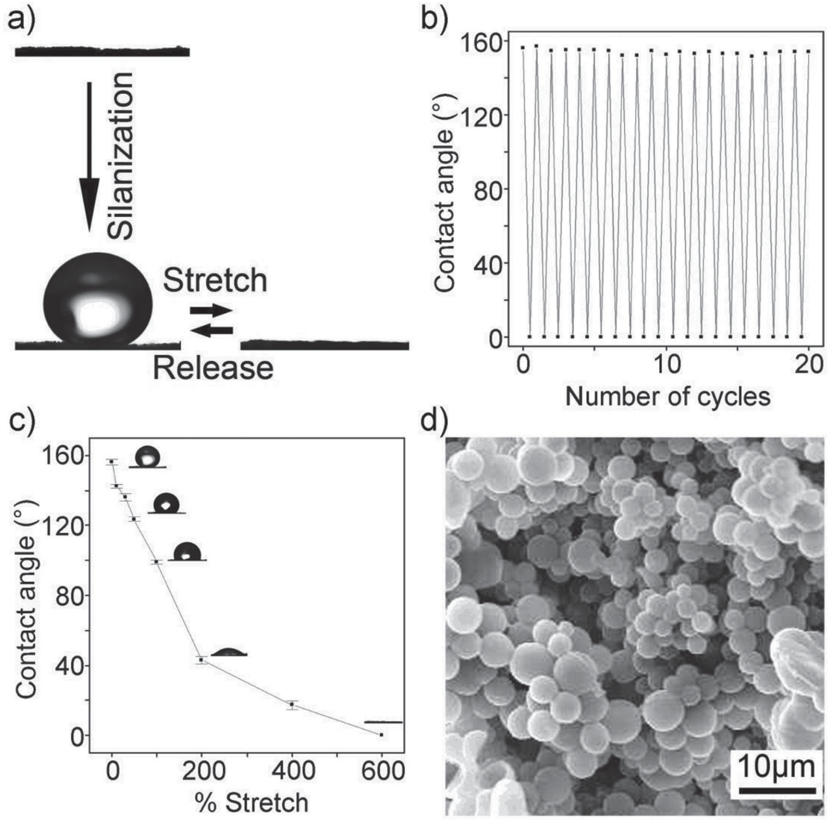

Figure 2. Controlling the wettability of the stretch-responsive composite material. a) When the glass particles are not silanized, a drop of water spreads quickly across the surface, and exhibits negligible contact angle. After silanization, the surface becomes superhydrophobic. When the material is stretched, the surface becomes superhydrophilic. b) The switch from superhydrophobicity to superhydrophilicity is reversible. The material is stretched and released for 20 times; the contact angle maintained ≈0° when stretched, and >150° when released for 20 times. c) The contact angle can be tuned by the stretching the material to different extents. d) An SEM image of the glass particles on the surface of the material.

surfaces superhydrophobic through silanization.[28] A piece of the composite material (10 × 10 × 2 mm) was placed in a gas-tight vial containing 10 mL of toluene and 95 µL of methyltrichlorosilane. Another 0.25 mL of concentrated hydrochloric acid (12 M) was added to the vial, and the reaction was allowed to go to completion for 48 h. In a separate set of experiments, we found that the hydrochloric acid did not affect the performance of the stimuli-responsive hydrogel (see Section 3, Supporting Information). In addition, we found that this method of silanization effectively silanized all the particles in the composite material (see Section 4, Supporting Information, for the set of experiments in which we observed directly the extent of silanization by coating the particles with fluorescent molecules). After silanization, the material was rinsed three times in toluene, three times in ethanol, and three times in deionized water. It was then dried in an oven at 100 °C before use. The thickness of the layers of silanized glass particles was ≈100 µm for all the three types of composite materials. The mean size of the original glass particles purchased from Sigma-Aldrich was measured by a Laser Diffraction Particle Size Analyzer to be 8.2 ± 4.7 µm. After cleaning the particles with the piranha solution and silanizing them, their sizes reduced; this reduction may be due to the acids used (see Section 5, Supporting Information, for a fuller description of the effects and causes of the reduction in size).

After fabrication, we first measured the contact angle of a drop of water (10 µL) on the stretch-responsive composite material; this drop of water was in contact with the surface coated with the silanized glass particles. **Figure 2**a shows the experimental images of the droplet on the substrate. When the composite material was not silanized, water spread quickly across the surface, and penetrated into the material. After silanization, the droplet maintained a contact angle of more than 150° with the surface; thus, the surface is superhydrophobic. This contact angle is similar to that reported for silanized glass particles in a previous study.[28] The surface roughness (root mean square) of this surface is 25 µm (see Section 6, Supporting Information, for the height profile measured by a profilometer). When we stretched the material to 600% and then placed a drop of water on it, we observed that the droplet spread across the substrate with a contact angle of ≈0°; thus, the surface is superhydrophilic (see Section 7, Supporting Information, for the top-down images of the surface). At the same time, we also observed that the water penetrated into the material. Penetration was possible because stretching created spaces between the glass particles such that water came into direct contact with the stretchable hydrogel. This type of superhydrophilic material is reminiscent of certain surfaces of plants (e.g., mosses) in which the surface is able to absorb water.[4,29] The effect is reversible: when the stretched material was allowed to return to its relaxed state, the contact angle was again measured to be more than 150°. In order to test the integrity of the material, we repeated the process of stretching (600%) and relaxing (0%) for 20 times, and found that the contact angle switched from ≈0° to more than 150° repeatedly (Figure 2b). Although water always penetrated into the material when it was stretched, we could measure the contact angle at a specific time. Figure 2c shows the case in which a drop of water was left on the substrate (stretched or not stretched) for 90 s before the contact angle was measured. Importantly, this contact angle was tunable with respect to the extent at which the composite material was stretched. The SEM image of the surface containing the glass particles is shown in Figure 2d (an additional SEM image is shown in Section 8, Supporting Information). The size of the particles used to coat the hydrogels can affect the wettability of the surface. If the size of the unprocessed particles is too big (e.g., 500 µm), the composite material is not superhydrophobic in its contracted state (see Section 9, Supporting Information).

We also performed similar sets of experiments for the pH-responsive composite material (**Figure 3**), and the

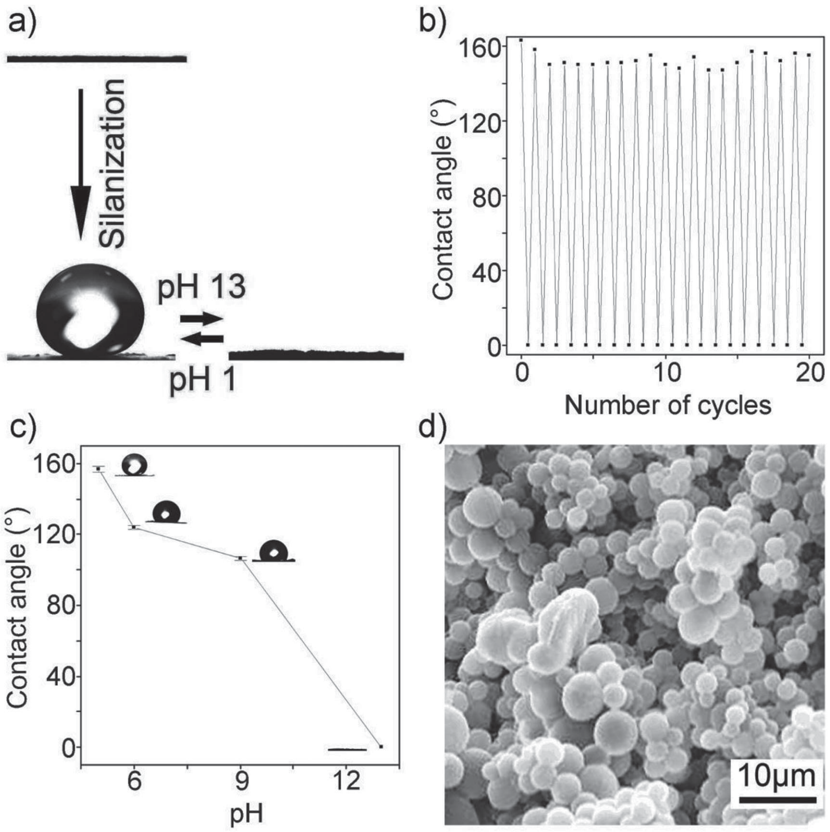

Figure 3. Controlling the wettability of the pH-responsive composite material. a) When the glass particles are not silanized, the contact angle of a drop of water on the surface is negligible. After silanization, the surface becomes superhydrophobic. When the material is expanded by a solution of pH 13, the surface becomes superhydrophilic. b) The switch from superhydrophobicity to superhydrophilicity is reversible as demonstrated by expanding and contracting the material in solutions of pH 13 and pH 1, respectively, for 20 times. c) The contact angle can be tuned by immersing the material in solutions of different pH. d) An SEM image of the glass particles on the surface of the material.

temperature-responsive composite material (**Figure 4**). After silanizing the particles in both these materials, we found that the contact angles of droplets of water on their surfaces were more than 150°. The surface roughnesses of the pH-responsive and temperature-responsive composite materials are 12 and 14 µm, respectively (see Section 6, Supporting Information). In order to expand the material, we placed the pH-responsive composite material into a basic solution (i.e., sodium hydroxide at pH 13) for around 2 h; for temperature-responsive composite material, we placed it in a water bath maintained at 40 °C for around 1 h (see Section 7, Supporting Information, for the top-down images of the expanded surfaces). Unlike the case of the stretch-responsive composite material in which it was stretched in one dimension, the surfaces of these materials expanded in two dimensions. The surface area of the pH-responsive composite material expanded around four times, and the surface area of the temperature-responsive composite material expanded around six times. After soaking and expanding the composite materials, the materials were quickly dried by a stream of nitrogen, and a droplet of water (10 µL) was placed on each of the two surfaces. For both these materials, the droplets spread quickly across the surface and exhibited negligible contact angles (Figures 3a and 4a). When the pH-responsive composite material expanded, we noticed that it tended to bend slightly. For the temperature-responsive composite material, however, it did not bend (see Section 10, Supporting Information). The effect is again reversible: we expanded and contracted the materials for 20 times, and found that the surfaces switched from superhydrophobic to superhydrophilic states repeatedly (Figures 3b and 4b). We contracted the pH-responsive composite material by immersing it in a solution of pH 1 hydrochloric acid, and expanded it with a basic solution at pH 13. The temperature-responsive composite material was contracted by immersing it in a water bath at room temperature, and expanded by immersing it in a water bath at 40 °C. Subsequently, we also measured the contact angles of droplets of water that rested on the surface for 90 s under different conditions. For the pH-responsive composite material, we expanded it to different extents by soaking it in solutions of different pH. For the temperature-responsive composite material, it was expanded to different amounts by soaking it in water of different temperatures. Similar to the case of the stretch-responsive composite material, it is possible to obtain a range of contact angles (Figures 3c and 4c). Figures 3d and 4d show the SEM images of the particles (additional SEM images of these surfaces can be found in Section 8, Supporting Information). All these demonstrations show that coating silanized glass particles into a stimuli-responsive hydrogel is a general method to obtain surfaces with tunable and reversible wettability (i.e., from superhydrophobic and superhydrophilic) for different types of external stimuli.

A potential application of these composite materials is to use them as stimuli-responsive (or "smart") membranes. Specifically, the switch between hydrophobic and hydrophilic gives the material the ability to control whether the chemicals can penetrate into, and through, the material, or not. We demonstrated for the case of the stretch-responsive composite material that when it was in the relaxed state (superhydrophobic), no penetration was observed; when it was stretched, molecules penetrated into the material. In addition, it is possible to control the rate of penetration of chemicals by varying the extent at which the material was stretched. Experimentally, we made six samples; one of them was not stretched (or, 0% stretched), while the other five were stretched to different percentages: 10%, 30%, 50%, 200%, and 600%. A drop of Ponceau 4R red dye (100 µL) was placed on each surface, which was coated with the layers of silanized glass particles as described (**Figure 5**a). The experiment was carried out in a chamber with high humidity (≈100%) in order to minimize the evaporation of the droplets. After two days, we cut through the center of the material, and imaged the cross section of the material. Figure 5b shows that the amount

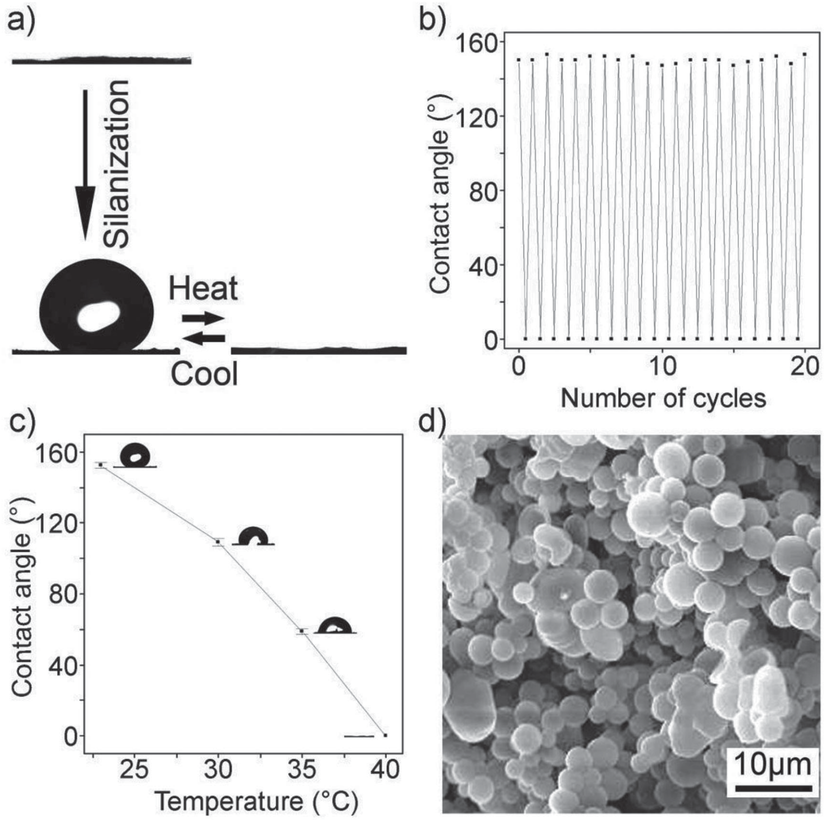

Figure 4. Controlling the wettability of the temperature-responsive composite material. a) When the glass particles are not silanized, the contact angle of a drop of water on the surface is negligible. After silanization, the surface becomes superhydrophobic. When the material is expanded by an increase in temperature (40 °C), the surface becomes superhydrophilic. b) The switch from superhydrophobicity to superhydrophilicity is reversible as demonstrated by expanding and contracting the material under different temperatures (i.e., 40 °C and room temperature respectively) for 20 times. c) The contact angle can be tuned by exposing the material to different temperatures. d) An SEM image of the glass particles on the surface of the material.

of penetration of the dye increased when the stretch-responsive composite material was stretched to a higher percentage. When the material was not stretched, we did not observe any penetration of the dye. According to the color distribution of the dye in the material, we could quantify the amount of dye that penetrated through the layers of particles with respect to the percentage at which the material was stretched (Figure 5c). A control experiment was also conducted in which we fabricated a stretch-responsive composite material in the same way as described in Figure 1b, but without silanizing the glass particles; in this case, the dye penetrated the material even when it was not stretched. This control experiment illustrates that it is necessary for the surface of the material to be hydrophobic in order to prevent the penetration of chemicals.

Since the method proposed in this study can be compatible with different types of stimuli-responsive hydrogels, it is possible to construct a system that responds to multiple types of stimuli by using a combination of these composite materials (**Figure 6**). As a demonstration, we made a container that consisted of four reservoirs; three of them were on the outside, and one of them was in the center. Each of the three reservoirs on the outside contained a dye of a different color, and was separated from the center reservoir by a specific type of stimuli-responsive composite material. More specifically, the reservoir on the right (containing a blue dye) was separated from the reservoir in the center by a temperature-responsive composite material; the reservoir on the left (containing an orange dye) was separated by a pH-responsive composite material; the reservoir on top (containing a red dye) was separated by a stretch-responsive composite material (Figure 6a). When the stretch-responsive composite materials was not stretched, and when the reservoir in the center contained only deionized water at room temperature, we did not observe any diffusion of dye from the reservoirs on the outside to the reservoir in the center (Figure 6b). When we placed warm deionized water (40 °C) into the center reservoir, the temperature-responsive composite material on the right expanded; thus, the blue dye diffused into the center reservoir (Figure 6c). When we placed a basic solution of pH 13 into the center reservoir, both the pH-responsive composite materials on the left and the temperature-responsive composite material on the right expanded (Figure 6d). This outcome is not surprising since the temperature-responsive hydrogel we used was polymerized with acrylic acid as one of the monomers. In fact, acrylic acid is also one of the monomers used for fabricating the pH-responsive hydrogel used in this study. Poly(acrylic acid) is known to be the component that is responsible for the change in size of the hydrogel under the influence of different pH.[30] When we stretched the stretch-responsive composite material (200%), the red dye from the top reservoir diffused into the center reservoir. Therefore, we have fabricated a system that is responsive to multiple external stimuli.

To conclude, we are introducing a general procedure for fabricating surfaces that can vary their wettability in response to specific types of external stimuli. Essentially, these materials consist of a stimuli-responsive hydrogel coated with silanized glass particles. The method is general because the same procedure can potentially be used to fabricate surfaces that respond to many different types of external stimuli, such as temperature, pH, electric field, magnetic field, light, and different types of biomolecules. In this way, the fabrication does not need to involve a unique (and limited) class of materials that vary their wettability from hydrophobic to hydrophilic under the influence of a stimulus (e.g., inorganic oxides as photoresponsive surfaces). There is also no need to introduce an additional step that involves the modification of the surface with a certain type of surface roughness (e.g., micro- or nano-structures) in order to achieve superhydrophobicity and superhydrophilicity.

We found in our experiments that the wettability is tunable and reversible by controlling the amount of external stimulus

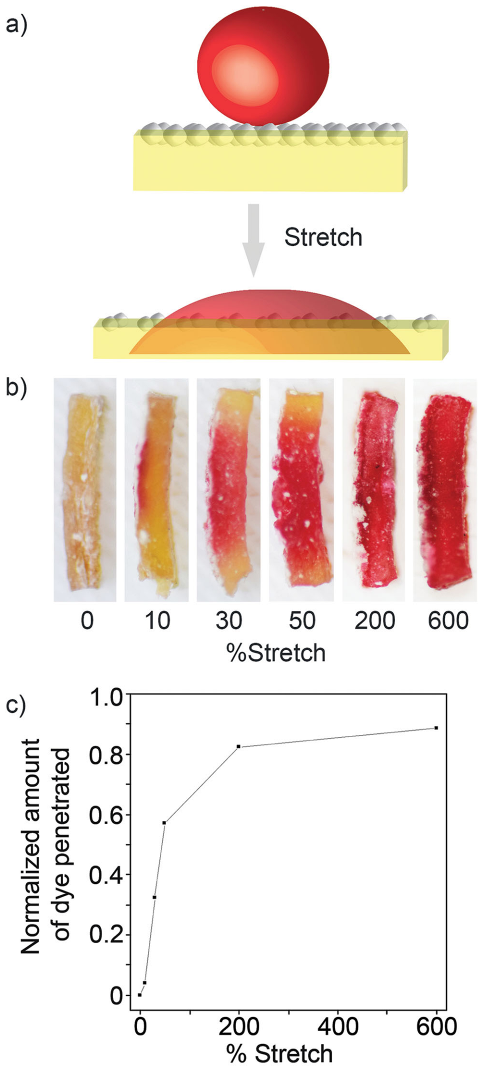

Figure 5. Controlling the rate of penetration of a dye into the stretch-responsive composite material. a) Scheme illustrating the experiment conducted: a red dye was placed on the surface, and then the material was stretched. After the experiment, the material was cut in the middle in order to observe the amount of penetration of the dye into the material. b) Images showing the cross sections of the materials. When the material was not stretched, the dye did not penetrate. For increasing amount of stretch, the dye penetrated more. c) Plot showing the amount of dye penetrated with respect to the percentage stretched.

(e.g., stress, pH, or temperature) applied to the material. The method allows a wide range of control of wettability: from superhydrophobic to superhydrophilic. Unlike other surfaces (e.g., impermeable solid surfaces, such as the light-responsive inorganic materials) that also switches from superhydrophobic to superhydrophilic, one feature of this composite responsive material is that it is permeable to chemicals when expanded. It is thus possible to use them as "smart membranes" with controllable rate of permeability in response to a specific stimulus of interest. We have demonstrated this feature with a stretch-responsive hydrogel. When it was not stretched, the dye did not penetrate into the material; when it was stretched to increasing amounts, the amount of penetration increased.

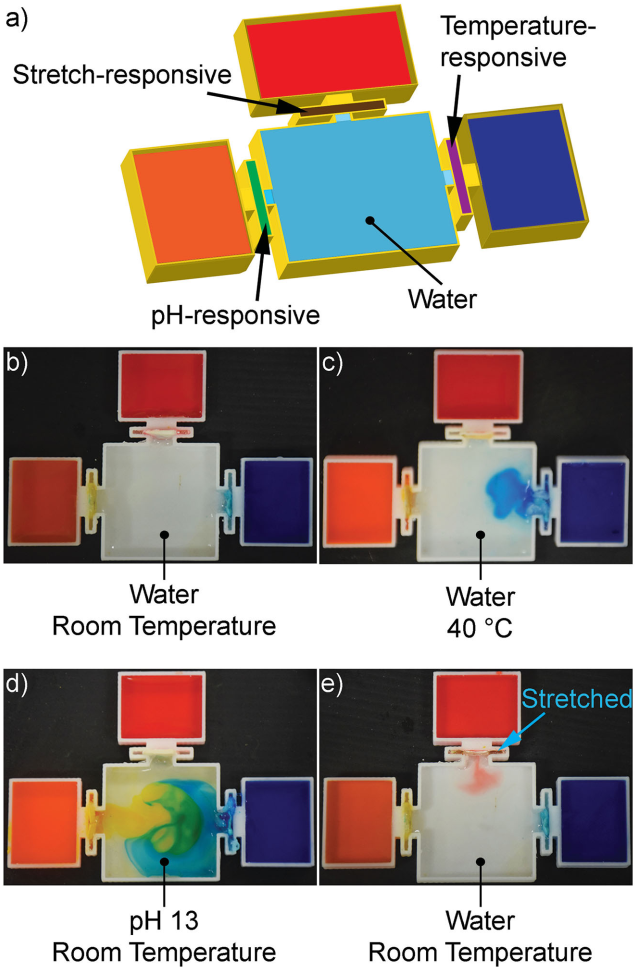

Figure 6. System that responds to multiple stimuli. Through using a combination of stretch-responsive, pH-responsive, and temperature-responsive composite materials, it is possible to construct a system that responds to these three types of stimuli simultaneously. a) Scheme showing the system in which the three reservoirs on the outside contain dyes of different colors. These reservoirs are separated from the reservoir in the center by the three different types of stimuli-responsive composite materials. b) Without the influence of any stimulus, the dyes stayed in their respective reservoirs. c) When water at 40 °C was placed in the center reservoir, the temperature-responsive material expanded, and allowed the blue dye from the reservoir on the right to diffuse into the reservoir in the center. d) When a solution of pH 13 was placed in the center reservoir, the orange dye from the reservoir on the left and the blue dye from the reservoir on the right diffuse into the reservoir in the center. e) When the stretch-responsive material was stretched (200%), the red dye from the top reservoir diffuses into the reservoir in the center.

Since the method of fabrication is similar for all types of stimuli-responsive surfaces, we believe that it is a technically convenient strategy for building systems that respond to multiple stimuli simultaneously using a combination of these stimuli-responsive materials. We have fabricated a system that can respond to stress (or stretch), pH, and temperature. In general, this method of fabricating surfaces with controllable wettability may be useful for constructing different types of smart, responsive systems.

Supporting Information

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

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