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Fabrication of Active Surfaces with Metastable Microgel Layers Formed during Breath Figure Templating

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KEYWORDS: responsive patterned polymer surfaces; breath figure method; interfacial assembly of microgels; morphological transitions; wettability variations

ABSTRACT: Patterned porous surfaces with responsive functionalities are fabricated by a thermo-responsive microgel-assisted breath figure (BF) process. When water droplets submerge into a polystyrene (PS) solution during formation of a porous surface by the bottom-up BF process, poly(N-isopropylacrylamide)-co-acrylic acid (PNIPAm-co-AA) microgels dispersed in the solution spontaneously assemble at the water-organic interfaces like “Pickering emulsions”, reinforced by capillary flow. The conformal layer of PNIPAm-co-AA microgels lining the pores appears in images of scanning electron microscope (SEM) either as a smooth surface layer (L) or as an array of dome-like protrusions (D), depending on the conditions at which the sample was dried for SEM. The change between L and D morphology correlates with the volume phase transition behavior of the microgels freely suspended: drying at a temperature below the Volume Phase Transition Temperature (VPTT) gives L, and the D morphology is formed by drying at a temperature greater than the VPTT of PNIPAm-co-AA microgels. The morphological transition is shown to accompany a significant change in surface contact angle (CA) relative to a corresponding pore layer made of PS, with L having a CA that is reduced by 85° relative to PS, while the decrease is only 22° for D. Porous structures with morphologically responsive surfaces could find application in biocatalysis or tissue engineering, for example, with functional enzymes sequestered when microgels are collapsed and accessible when the microgels are swollen.

1. Introduction

Responsive polymers undergo physical changes, such as altering color, transparency, conductivity, permeability or shape, triggered by changes in their environment, e.g., variations in temperature, humidity, pH, light intensity, *etc.*¹⁻³ Introducing responsive polymers on patterned surfaces with regular micro-, nano- or molecular-scale morphologies can create active patterned polymer surfaces (APPS) that have diverse proposed applications, including self-cleaning and water-resistant devices,⁴⁻⁵ electro-wetting devices,⁶⁻⁸ switching wettability surfaces⁹⁻¹⁴ or water/ oil purification films.¹⁵

Routes to APPS include physical or chemical modification of surfaces. Physical methods normally include procedures involving electrical fields,¹⁶⁻¹⁹ self-assembly of nanoparticles,²⁰⁻²⁵ interfacial instabilities,²⁶⁻³⁰ soft lithography,³¹⁻³⁴ *etc.* On the other hand, chemical approaches are mainly achieved by chemically grafting responsive self-assembled monolayers (SAMs) or polymer brushes onto surfaces to obtain responsive wettability and conductivity, *etc.*⁹⁻¹⁴ For example, Sun and co-workers⁹ grafted poly(N-isopropylacrylamide) (PNIPAM) brushes onto a silica surface, to confer switchable wetting characteristics to and from super-hydrophobic and super-hydrophilic as a function of temperature relative to the Lower Critical Solution Temperature (LCST) of PNIPAM.

The transient presence of water/organic interfaces during breath figure (BF) templating can be used to fabricate APPS in the water-templated pores through a bottom-up, self-assembly method. In brief, the BF method uses the condensation of water from humid air flowing over

the surface of a polymer solution in a volatile solvent.³⁵⁻³⁸ Conditions are controlled such that the water droplets grow with uniform size until they largely obstruct transport of solvent vapor away from the interface; at that point, the high interfacial energy of water drives them to submerge beneath the organic-air interface. After evaporation of the solvent, honeycomb-like arrays of pores remain at the surface of the polymer. During the evaporation process, water-organic interfaces can induce assembly of interfacially-active, functional building blocks present in the casting solution. Nanoparticles, block copolymers and other components containing hydrophilic parts can diffuse to and spontaneously assemble at the water/organic interfaces between the templating water droplets and casting solution.³⁹⁻⁴³ Simple, yet novel strategies, either focusing on establishing different functionality by directly adding functional components into the casting solution or developing novel ways to further functionalize the chemically patterned BF templates, were adopted to endow the BF pore arrays with functionalities.⁴⁴⁻⁴⁹ Among all the types of functionalities brought by employing the BF method, the reports on the stimuli-responsive BF surfaces are rather limited.

This “one-step” pore formation and functionalization method was used by Cui and Han²⁸ to produce a predominantly polystyrene (PS) quasi-honeycomb structure with pores lined by poly-(2-vinylpyridine) (P2VP), which preferentially segregated to the water droplets when solvent evaporation caused P2VP to phase separate from PS. The resulting surfaces exhibited reversible changes in response to different solvent vapors, switching between a honeycomb pattern of pores and a hexagonal island-like pattern of PVP protrusions. In addition, Billon

and co-workers⁵⁰ fabricated a hierarchically ordered honeycomb surface with pH-responsive wettability by self-assembling a pH-sensitive polystyrene-*b*-poly(4-vinylpyridine) diblock copolymer (PS-P4VP) via the “one-step” BF method. In relation to these prior methods, we show that microgels can be used in the “one-step” BF method to provide a relatively simple and robust route to active surfaces without the need for precision control of phase separation or the synthesis of block copolymers.

Although microgels are not amphiphilic, they can assemble at the water/organic interface in the “one-step” BF method. Pioneered by Ngai and Behrens,⁵¹ the stimuli-sensitive microgel stabilized emulsion has been under extensive study in the past ten years. Microgels such as poly(*N*-isopropylacrylamide)-co-acrylic acid (PNIPAm-co-AA) have been shown to be able to segregate to the water/organic interface, reminiscent of particles in a Pickering emulsion.⁵²⁻

⁵⁴ While in our work, simply including PNIPAm-co-AA microgels in the solution of matrix polymer used for BF fabrication—using as little as 1:40 mass ratio of PNIPAm-co-AA to matrix—was sufficient to create densely microgel-decorated BF pores. The as-prepared microgel functionalized surfaces exhibit, both wettability and water absorption. Exposing the film to water and drying at temperatures above the volume phase transition temperature (VPTT) of the PNIPAm-co-AA triggers a morphological transition that renders the surface relatively hydrophobic. As illustrated in Scheme 1, microgels were involved in the BF assembling process to achieve the facile fabrication of APPS. To our knowledge, this is the first report of microgel-functionalized BF pores.

2. Experimental Section

2.1. Materials

Monocarboxylic acid terminated polystyrene (PS-COOH, $M_w=2.0 \times 10^5$ g/mol⁻¹), N-isopropylacrylamide (NIPAm monomer), acrylic acid (AA), N,N-methylenebisacrylamide, potassium persulfate and ethanol (99.5%) were purchased from Sigma-Aldrich Co. Ltd. (U.S.); chloroform (99.8%) was purchased from VWR Co. Ltd. (U.S.), respectively.

2.2. Synthesis of PNIPAm-co-AA microgels

Poly (N-isopropylacrylamide)-co-acrylic acid (PNIPAm-co-AA) microgels were prepared by precipitation polymerization. NIPAm monomer (0.475 g), AA (0.024 g), and N,N-methylenebisacrylamide (0.052 g) dissolved in water (98 g) at room temperature were stirred at 400 rpm under N₂ for 30 min and then heated to 70 °C. After equilibrating at 70 °C for 15 min, polymerization was initiated by addition of potassium persulfate (0.060 g)/water (2 g) solution and the reaction was allowed to proceed under stirring at 70 °C for 4 h. The resulting microgel particles were dialyzed for 1 week against deionized water (changed twice daily) to remove surfactant and unreacted molecules. After dialysis, PNIPAm-co-AA microgels were concentrated by ultracentrifugation at 10,000 rpm for 1 hour and re-dispersed in deionized water. The microgels were then collected by lyophilization.

2.3. Fabrication of microgel-functionalized surfaces in the BF method

Dry PNIPAM-co-AA microgels were dispersed to form a 20 mg/mL suspension in ethanol, which acts like an amphiphilic surfactant to subsequently disperse the hydrophilic microgels in chloroform. A solution of the matrix polymer, PS-COOH, was prepared by dissolving 20 mg PS-COOH in 1 mL chloroform. A mixed casting solution at 40:1 weight ratio of PS-COOH to PNIPAm-co-AA microgel was prepared by adding 25 μ L of 20 mg/mL PNIPAM-co-AA suspension (above) per mL of 20 mg/mL PS-COOH solution. The typical procedure for the BF method was firstly described by François.³⁵ To be specific, the as-prepared casting solution was introduced onto a substrate using a syringe to form a liquid thin film under the environmental condition of high humidity. Rapid evaporation of the volatile chloroform solvent cools the humidified air above the casting solution to its dew point, leading to nucleation of water droplets in the atmosphere above the solution. The latent heat of condensation of water reduces the subcooling, allowing droplets to grow without further nucleation. In the end, after full evaporation of both solvent and water, a surface with regular porous arrays was made.

2.4. Characterization

The size of PNIPAm-co-AA microgels was characterized as a function of temperature from 25°C-50°C using dynamic light scattering (DLS, Zeta PALS, Brookhaven Instruments Co. Ltd). Data acquisition was performed 11 times at each temperature. After each change of the

temperature, five minutes of equilibration was allowed after reaching the desired temperature for microgels to reach their equilibrium size.

The contact angle was measured using a contact angle goniometer (CA goniometer, equipped with an AmScope Microscope 3.0 MP Camera) at room temperature with 3 μ L droplet volume. Qualitative observation of water absorption was also made in the same apparatus.

The surfaces and cross-sectional structures of BF-templated pores were characterized with a field emission scanning electron microscope (1550VP Field Emission SEM, ZEISS Co. Ltd.), all samples were completely dried in a vacuum oven at ambient temperature and coated with gold before imaging on SEM. For cross-sectional SEM imaging, samples were fractured.

3. Results

The volume phase transition temperature (VPTT) of the PNIPAm-co-AA microgels is manifested by an abrupt change in their hydrodynamic diameter from approximately 825 nm at temperatures from 25 to 40 $^{\circ}$ C to approximately 510 nm from 47 to 57 $^{\circ}$ C, indicating the VPTT is in the range of 40 $^{\circ}$ C~45 $^{\circ}$ C (Figure 1). This transition coincides with a change from transparent to cloudy as a result of the increase in refractive index contrast between the microgel and water when the volume of each microgel decreases by approximately one half (Figure 1 inset).

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4 A monolayer of highly ordered pores was fabricated from chloroform solutions of PS-
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6 COOH with and without PNIPAm-co-AA microgels by the BF method under relative
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8 humidity of 65%-75% at 25 °C (Figure 2). Carboxyl-terminated PS was used as the matrix
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10 polymer for the obtained BF films. The presence of hydrophilic/polar terminal groups in
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12 linear polystyrenes has been proved to be able to promote the stabilization of the templating
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14 water droplets during the BF formation, thus increasing the regularity of the honeycomb
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16 structures.⁵⁵⁻⁵⁷ Pores made from the mixed solution show ruffled edges on the rim of each
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18 pore, which are absent for pores produced from the PS-COOH solution. Immediately after the
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20 BF process, the inner surfaces of the pores are almost equally smooth for pores made from the
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22 mixed solution as from the PS-COOH solution.
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34 The cross-sectional SEM images were taken to get a close look into the interior of the pores
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36 made from microgel-containing samples (Figure S1). It shows the morphological details of
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38 the microgel layers covering the polymer matrix (see the caption of Figure S1). Interestingly,
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40 images of the fracture surfaces sometimes revealed an overhang of an intact microgel-made
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42 replica of the pore surface (Figure S1c). In order to obtain the fracture, the sample of the
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44 porous film was immersed in liquid nitrogen for a few minutes and then broken into halves
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46 with hand. During such handling, the polymer of PS, being brittle in nature, was easy to be
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48 shattered into pieces at the region close to the fracture. While the “soft” microgels were kept
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50 intact as free-standing layers. The ability of free-standing layers of PNIPAm-co-AA microgels
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4 to peel off the polymer matrix during handling suggests there is only weak adhesion between
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6 the microgels and the PS-COOH.
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10 To characterize the thermoresponsive behavior of the PNIPAm-co-AA microgel layer on
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12 the solid PS-COOH matrix, samples were soaked in deionized water at 47 °C (above the
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14 VPTT) to trigger the size transition from swollen to compact. After 3h of treatment, the
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16 sample was dried in a vacuum oven at 47 °C for 12 hours and then characterized using SEM.
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19 After this treatment, microgel-lined pores show arrays of protrusions (Figure 3). The
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21 diameters of the domes are around 500 nm (Figure 3), which corresponds well to the size of
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23 the compact state of the microgels observed by DLS. We did the control experiment with PS
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25 only samples, following the same protocol. And they did not show any thermoresponsive
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27 behavior. To distinguish different types of the samples, the three porous surfaces are denoted
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29 by P0 (made from PS-COOH solution), L (as prepared, made from mixed solution, with
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31 layered-like morphology), and D (made from mixed solution, after treatment with 47 °C water
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33 and drying at 47 °C, with dome-like protrusions in pores). Figure 4 shows the morphologies
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35 of both L and D, which were derived from a pair of counter parts from the same surface. The
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37 geometrically matched pair shows completely different structural features after one part was
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39 treated by 47 °C water, changing from L to D. One could see that microgels protrusion of the
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41 D (Figure 4b) were so close to form honeycomb-like arrays.
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The morphological transition is accompanied by a significant change in contact angle (CA). In contrast to BF templated pores made from PS-COOH solutions, which are hydrophobic, the contact angle drops dramatically in a transient manner after the droplet was deposited onto the surface of the as-prepared pore structure made from the mixed solution of PS-COOH and microgels (Figure 5a). After the 47°C water and drying treatment, the pore structure again becomes quite hydrophobic (D in Figure 5a). Over time, the water was absorbed into the pores (Figure 5b), which required approximately 25 minutes for P0 and D, but only 15 minutes for L.

4. Discussion

The free-standing microgel layers prove that PNIPAm-co-AA microgels at high surface density line each pore—and the surface where the volatile solution was in contact with air (Figure S1c). The lining of the pores was expected, due to affinity of the hydrogel for the water-organic interface. The accumulation of PNIPAm-co-AA microgels at the air-organic was not expected, given the low interfacial energy of chloroform (ca. 27 mJ/m²) and polystyrene (41 mJ/m²). This suggests that the microgel is able to preferentially expose its isopropyl groups to air at the solution-air interface, much as it preferentially exposes its hydrogen bonding groups to water at the solution-water interface. This conformational rearrangement would also occur during drying (i.e., the isopropyl groups would present

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3 themselves to the air at the hydrogel-air interface during drying), explaining the initially
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6 hydrophobic character of all of samples (Figure 5a).
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10 The distinctive transient behavior of the contact angle and water adsorption for the as
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12 prepared BF structure indicates that the dense microgel layer on the pore walls retains a
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14 memory of the expanded state. During the early stage of the BF templating, microgels that
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16 diffuse to the surface of the templating water droplets become irreversibly bound and expand
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18 by absorbing water. The relatively slow evaporation of water during the time when the water
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20 droplets are fully submerged in the chloroform solution provides microgels at the solution-
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22 water interface sufficient time to swell fully prior to evaporation of water. Our working
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24 hypothesis is that amide groups of PNIPAm-co-AA microgels remain relatively accessible
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26 after the water evaporates, trapped in a metastable state by rapid solidification of PS-COOH
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28 during the final stages of drying at a temperature below VPTT (i.e., expanded microgels,
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30 having extensive hydrogen bonding with water).¹³ Indeed, the memory of the expanded state
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32 appears to be necessary: the microgel layer on the plateau surface does not show signs of
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34 restructuring, apparently because the microgels were in a collapsed state at the air-solution
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36 interface when the structure solidified.
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52 The distinct morphological transition of PNIPAm-co-AA microgels on the solid walls of a
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54 BF substrate, as well as switchable wettability and water absorption, accord with the behavior
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56 of thermoresponsive microgels on pore surfaces formed from an oil/water emulsion.⁵²
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4 Richtering gave microgel-stabilized emulsion the name “Mickering emulsion” due to their
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6 distinctive properties relative to Pickering emulsions.⁵² In a classic Pickering emulsion,
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8 water/oil interfaces are stabilized by a monolayer of particles that have a stronger affinity to
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10 one of the two phases and have a relatively low interfacial energy when in contact with the
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12 less favorable phase. In the case of a “Mickering emulsion”, microgels form a thick,
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14 continuous layer at the water/organic interface, with microgels preferentially protruding into
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16 the water phase. After the water has evaporated, the walls of pores left by water droplets are
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18 lined with microgel layers that retain the ability to respond to changes in temperature.
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28 Similarly, on the pore walls of the present BF structures, only a small portion of each
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30 microgel is fixed in the polymer matrix (PS-COOH). The major portions, then, can restructure
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32 in the presence of water, which gives the chains mobility, allowing the morphological
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34 transition of the microgels layers when exposed to water at a temperature above VPTT. This
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36 change in structure also explains the corresponding changes in wettability: the portion of each
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38 microgel that protrudes from the solid pore walls have sufficient mobility in water that the
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40 amide groups can reorient to the interior of the microgel when the volume collapse transition
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42 occurs.
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52 Initially, we were surprised that dome-like features were not present on the walls of as-
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54 prepared BF structures. In retrospect, it is clear that the swollen state of the protruding portion
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56 of the microgels crowds them together, providing a smooth surface. When immersed in water
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4 at a temperature of 47 °C (above the VPTT), microgels undergo a transition from swollen
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6 status to collapsed status. The most compact shape they can adopt is dome-like. The switch of
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8 hydrogen bonding from intermolecular hydrogen bonds (between the microgel's amide groups
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10 and water) to intramolecular hydrogen bonds (C=O and N-H groups) explains the observed
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12 volumetric and morphological transition.¹⁵ The accompanying change in wettability of the
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14 pores from hydrophilicity to hydrophobicity after being treated at 47°C is enabled by the
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16 dense coverage of microgels on the pore walls.
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25 Moreover, although the expanded microgels (hydrophilic) in pores enable the L to absorb
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27 water, the initial contact angle (CA) of L was still hydrophobic. We believe this results from
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29 the microgel layer being in contact with air during evaporation of the water from the hydrogel
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31 layer. The apparent change of the contact angle occurs without movement of the contact line,
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33 so it may simply reflect contact line pinning combined with adsorption of water into the
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35 hydrophilic pores below the plateau surface of the BF structure. In contrast, the D samples
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37 retain hydrophobic character for a much longer time, since the microgels are trapped in a state
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39 with the backbones and isopropyl side groups of PNIPAm-co-AA microgels exposed. Thus, a
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41 relatively long time was required for the microgels to resturcture and provide a water-
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43 absorptive surface, even though the CA test was processed under room temperature (at which
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45 the expanded state is stable).
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After we obtained the active pattered surface which could be switched from the microgel morphology of L to D, we have further tried to reverse the morphology from D back to L. We put the samples with morphology of D in water at room temperature (around 20°C), hoping to activate the volume transition once again, only from collapsed status to swollen status for this time. After we dried the samples in a vacuum oven at room temperature, the reversible morphological transition was not observed. Before we discuss the reason, one needs to know that such morphological transition was accomplished with the microgels trapping into the polymer matrix, which is quite different from the cases of solution-based manipulation with responsive microgels. We assume that after the first round of hot water treatment, which turned the decorated arrays of microgels from swollen status to collapsed status, the microgels have further pressed themselves into the polymer matrix, and it compromised the mobility of the molecular chains for restructuring. Moreover, after the morphological transition of L to D, the decorated microgels also changed from being hydrophilic to hydrophobic. As evidenced by the data of Figure 5, water penetration is more difficult for sample D than L, which gives less chance of morphological transition in aqueous environment.

5. Conclusions

A simple modification of the BF method, adding a small concentration of PNIPAm-co-AA microgels to the polymer solution, allows the pore surfaces to be densely functionalized with

responsive PNIPAm-co-AA microgels: even when they are adsorbed on the polymer matrix, the microgels undergo their volume transitions at the VPTT. Compact assembly of microgels through BF process translates the volume transition into a larger-scale morphological transition from a relatively uniform layer (L) morphology to an array of dome-like protrusions (D), which produce changes in wettability and water absorption. In turn, the spontaneously assembled layer on the pore walls has the potential to encapsulate components for subsequent release from responsive microgels on the surface. For example, in relation to tissue engineering, encapsulation and release of desired amounts of cytokines or enzymes could be used to modify micromechanical and biochemical niches in a programmable, responsive manner.

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ASSOCIATED CONTENT

Supporting Information

SEM images showing detailed L morphology of PNIPAm-co-AA microgel decorating the polymer pore arrays.

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Scheme 1. During a BF process, water droplets condense from humid air flow due to supersaturation in the cool region created by evaporative cooling at the solution-air interface (a), these droplets grow to the point that they nearly obstruct the evaporation of solvent and then submerge into the organic solution, creating water-organic interfacial. And microgels, at the same time, are spontaneously migrating onto w/o interfaces (b). After fully evaporation of the solvent, continuous arrays appear on the upper surface of polymer matrix (c). Also, because of intensive assembly of microgels through BF process, morphological variations on wall of pores, which integrate individual volume transitions of each microgels at temperatures around VPTT, are exhibited distinctly (d).

Figure 1. Effective diameter of PNIPAm-co-AA microgels in aqueous suspension at 0.2 mg/mL measured by dynamic light scattering (DLS). Inserted photos on lower left show a phenomenon that status of microgels suspension changes from transparent to opaque when temperature increases from the region below VPTT to the region above VPTT.

Figure 2. Scanning electron micrographs of ordered porous structures made by breath figure templating of (a, b) the mixed solution (with PNIPAm-co-AA microgels and (c, d) the PS-COOH solution (without PNIPAm-co-AA microgels). The morphologies show rough edges of the pore openings prepared from mixed solution, in contrast to smooth pore edges and walls prepared from the PS-COOH solution.

Figure 3. Cross sectional SEM image clearly shows typical morphology of dome-like protrusions arrays at wall of pores.

Figure 4. Cross-sectional SEM images of surfaces (a) and (b) is a pair of counter parts from the same surface, (b) was treated by 47 °C water, while (a) was not; microgels protrusion on (b) were so close to form honeycomb-like arrays.

Figure 5. (a) Graph of contact angle as a function of time after a 3 μL drop of water was placed on the surface. Straight lines are linear regressions through the data for P0 and L. The red lines simply connect the data points for D. Inset indicates time at which the water is fully absorbed, t_{abs} . The three porous surfaces are denoted by P0 (made from PS-COOH solution), L (as prepared, made from mixed solution), and D (made from mixed solution, after treatment with 47 $^{\circ}\text{C}$ water and drying at 47 $^{\circ}\text{C}$). (b) Images of CA tests of P0, L and D and correspondent cross-sectional images of pores on three types of surfaces; initial CA of P0, L and D are all around 100 $^{\circ}$. After 10 min, CA of L drops to 12 $^{\circ}$, indicating a hydrophilic status, however, CA of P0 and D keep in values above 90 $^{\circ}$, presenting a hydrophobic condition of the surface.

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