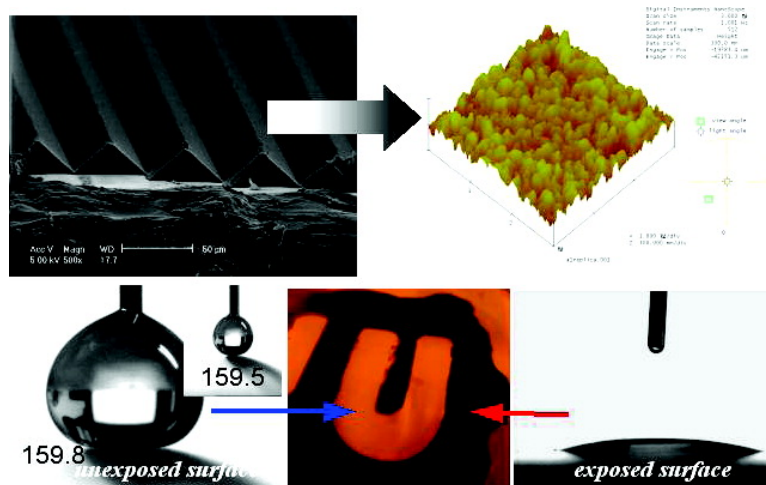


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## Direct UV-Replica Molding of Biomimetic Hierarchical Structure for Selective Wetting

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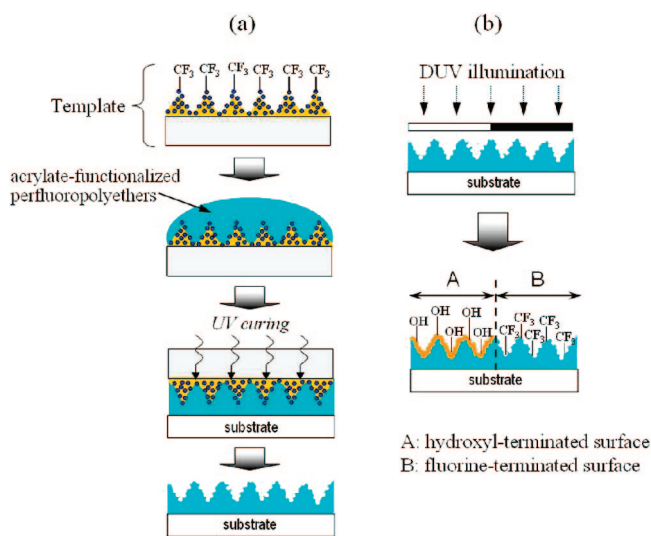
The wettability of solid surfaces can be controlled by surface topography and/or surface chemistry. With this controllability, many useful methods<sup>1</sup> have been introduced to produce superhydrophobic surfaces. Among these, an approach for artificial superhydrophobic surfaces<sup>2,3</sup> that mimic lotus leaves, in which the surface is covered by branch-like nanostructure on top of micropapillae, has drawn much interest because the multiscale hierarchical structure observed in nature could be effective in manipulating important surface properties such as wettability, friction, and adhesion for electronic, optical, and biological applications.<sup>4</sup> However, most methods for constructing biomimetic hierarchical structure usually require specialized equipment and/or complicated processing (temperature, substrate, and chemicals), which limits widespread utilization of the methods for large-scale production.

The wettability of the multiscale hierarchical structure can be alternated between superhydrophobicity and superhydrophilicity by a change in surface chemistry.<sup>5</sup> Wettability-switching surfaces have also been realized by applying an external stimulus, such as light irradiation,<sup>6</sup> electrical potential,<sup>7</sup> temperature,<sup>8</sup> and solvent.<sup>9</sup> While the reversibility is desirable in certain applications, the methods cannot be used for selective transformation of the wettability.<sup>7–9</sup> In the case of light irradiation, the wettability control is realized only in the absence of visible light or ultraviolet light.<sup>6</sup> A permanent change of wettability<sup>10</sup> has been shown to be realized through topographical feature or surface chemistry, although the processing involved is not simple.

In this communication, we introduce a direct ultraviolet (UV)-assisted replica molding method for creating a biomimetic hierarchical structure and its use for selectively transforming the superhydrophobic surface to a superhydrophilically patterned surface on large area, regardless of the type of substrate. The method yields an environmentally and chemically stable surface, and the processing is simple. Only one step is involved for obtaining a multiscale hierarchical structure from a prepared template with micro/nano dual-scale roughness: direct UV-assisted replica molding from the template with a UV-curable, fluoro-functionalized prepolymer. This method allows for selective wetting when predefined regions are exposed to deep ultraviolet (DUV) through an optical mask or shadow mask.

Shown in Scheme 1 are the procedures for one-step fabrication of the hierarchical, superhydrophobic surface and for its utilization for selective wetting. Our previous work<sup>11</sup> demonstrated that the template for the replication can be prepared using an ultraviolet (UV)-curable liquid precursor dispersed with nanoparticles and a rigiflex poly(urethane acrylate) (PUA) mold<sup>12</sup> with a desired pattern. With this template of dual-scale roughness, the same hierarchical structure can be replicated by one-step UV-assisted molding using the template as a master (Scheme 1a). In this method, a UV-curable liquid precursor with low surface energy is first drop-dispensed onto the prepared template pattern, and then a flexible or rigid substrate is brought into contact with the coated liquid layer. After conformal

**Scheme 1.** Schematic Illustrations: (a) Fabrication of a Biomimetic Dual-Scale Hierarchical Structure by Direct UV-Replica Molding with the Template and (b) Fabrication of Selectively Wetting Surface



contact of the template with the liquid precursor layer, UV light ( $\lambda = 250\text{--}400\text{ nm}$ ) is illuminated for 20 s (dose =  $200\text{ mJ/cm}^2$ ) through the backside of the transparent template for curing by cross-linking. After the UV curing, the template is removed from the cured, low surface energy layer by peeling.

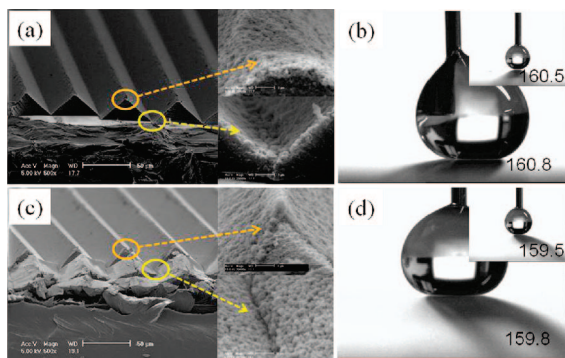
The UV-curable precursor that was used for the direct replication is a mixture of photoinitiator and UV-curable acrylate-functionalized perfluoropolyether (PFPE). Its high solvent resistance and low surface energy characteristics<sup>13</sup> have recently been utilized for microfluidic device fabrication and high-resolution soft lithography. Acrylate-functionalized prepolymer with a perfluoropolyether backbone can be photochemically cross-linked by UV exposure, exhibiting a low surface energy after UV curing due to the fluorine moiety in the backbone. Therefore, the surface does not require further chemical surface modification with a low surface energy molecule for superhydrophobicity after it is replicated. Furthermore, the patterned PFPE layer has a transmittance higher than 90% in the visible range between 450 and 750 nm (see Supporting Information).

To prepare a superhydrophilically patterned superhydrophobic surface, the micro/nanoscale patterned surface is exposed in air to DUV illumination having two beams at wavelengths of 254 and 185 nm (Scheme 1b). A shadow mask is used for the desired pattern. Deep UV illumination causes the cross-linked PFPE backbone chain to be photochemically altered to a polar, hydrophilic chain including carbonyl species such as carboxylic acid at the surface (see Supporting Information).

Figure 1 shows scanning electron microscopy (SEM) images and CAs of the template and replicated surfaces. The replicated structure obtained by one-step UV-assisted replica molding in Figure 1c

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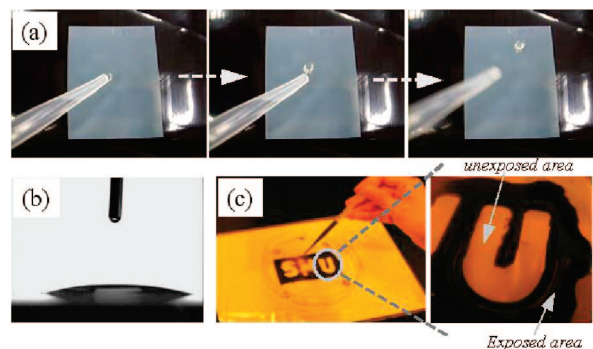


**Figure 1.** SEM images and CAs of the patterned surfaces (inset images in the right column show receding CAs): (a) SEM image of the template with dual-scale roughness; (b) CA on the template; (c) SEM image of the replicated surface by direct UV molding with the template; (d) CA on the replicated surface. Thickness of patterned PFPE layer is around 20  $\mu\text{m}$ .

resembles the original template pattern in Figure 1a, exhibiting almost the same surface morphology in terms of overall geometrical shape (micropattern) and the nanoscale roughness that was created uniformly on the entire microstructure with high fidelity (a quantitative analysis of the multiscale surface by AFM is given in Supporting Information). Therefore, both surfaces have the same superhydrophobic characteristics with water CA as high as  $160^\circ$  and CA hysteresis as low as  $1^\circ$ , as shown in Figure 1b,d. It is notable that the replicated surface obtained directly from the template is superhydrophobic without any further surface treatment for low surface energy. Remarkably, this superhydrophobic surface was extremely stable for a long period of time such that the contact angle and sliding-off property of a water droplet did not change even after exposure to ambient conditions for 3 months. In addition, the replicated surface shows excellent inertness to chemicals and solvents, which can cause deformation or swelling problems, because of the presence of the cross-linked fluorine backbone (see Supporting Information).

One notable feature of this method is that it allows for local definition of wettability through rapid, permanent change of surface wetting from superhydrophobic to superhydrophilic without complex time-consuming processing. When the replicated superhydrophobic surface was illuminated with DUV, the CA was dramatically decreased below  $10^\circ$  due to the transformation of surface chemistry. During the DUV exposure, conversion of the hydrophobic to hydrophilic surface as a result of photochemical change in surface chemistry causes wetting behavior to change from the Cassie mode to Wenzel mode,<sup>5</sup> resulting in a decrease in the apparent CA such that the liquid droplet will fill the grooves of the rough substrate.

To demonstrate the capability of selective wetting, we fabricated a pattern consisting of superhydrophobic and superhydrophilic regions on the same substrate surface by selective DUV illumination through a stainless steel (SUS) mask (with “SNU” letters). As shown in Figure 2a,b, the superhydrophobic PFPE surface is water-repellent with a sliding angle as low as  $1^\circ$  prior to DUV illumination, but the exposed surface exhibits a superhydrophilic property with CA below  $10^\circ$ . For visualization, dyestuffs-dissolved water was dispensed onto the DUV-modified surface. The masked area maintains its superhydrophobic behavior of complete dewetting, while dyestuffs-dissolved water selectively wets the surface that was exposed to DUV, clearly revealing SNU letters as shown in Figure 2c.



**Figure 2.** (a) Time-lapse photographs of rolling off of a water droplet on a water-repellent superhydrophobic surface obtained by one-step UV-replica molding. (b) Photograph of wetting on a superhydrophilic substrate after DUV illumination. (c) Selective wetting of dyestuffs-dissolved water on the DUV-modified surface obtained with a SUS mask.

In summary, this communication describes a template-based one-step fabrication of dual-scale hierarchical structure with superhydrophobic characteristics, providing a low-cost and environment-friendly approach to fabricating superhydrophobic surface on a large scale. The biomimetic hierarchical structure with a photo-cross-linked PFPE is stable and inert to solvents and chemicals. Furthermore, any parts of the hydrophobic surface can be transformed selectively to a hydrophilic surface by simply exposing the surface to DUV through a shadow mask, requiring no complex time-consuming processing steps.

**Supporting Information Available:** Experimental details on the formulations and chemical resistance, AFM analysis and transmittance for hierarchical surface, and FT-IR analysis for exposed surface by DUV. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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