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Polydopamine Circle-Patterns on a Superhydrophobic AAO Surface: Water-Capturing Property

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The water-collecting and -guiding ability of Namib desert beetles has recently gained a great deal of attention because of its potential applications, such as efficient water-capture from the humid air and loss-free transport of the captured water.[1,2] It has been known that the hydrophilic bumps on the beetle's superhydrophobic back play a crucial role in the achievement of this special ability:[1] the superhydrophobicity of the background surface is achieved by the microstructure coated with a wax, and the wax-free hydrophilic bumps (about 0.5 mm in diameter) are distributed randomly on the superhydrophobic background with 0.5-1.5 mm apart. Since the essential surface-features of the beetle's back were identified, various approaches including selective deposition/removal of hydrophilic[2-4] and hydrophobic materials[5,6] have been attempted to mimic the surface structure and properties of the beetle and to apply the patterned surfaces to many different areas. For example, the circular, (super)hydrophilic patterns on a (super)hydrophobic background provide useful tools for establishing droplet-based microarray, microreservoirs, and high-throughput screening (HTS).[7-10] Butler *et al.* reported *in situ* synthesis of oligonucleotide arrays on a glass surface by differentiating surface wettability:[7] the fluorinated background acted as a wetting boundary, which enabled the localized synthesis of oligonucleotide onto the aminosilated hydrophilic sites. Superhydrophilic circular micropatterns on the superhydrophobic surface were also generated by microwave plasma-enhanced chemical vapor deposition and subsequent irradiation of ultraviolet light through a photomask.[8] By tuning the distance between the superhydrophilic spots, the adhesion and proliferation behavior of NIH3T3 cells were investigated. Levkin *et al.* fabricated superhydrophilic circular patterns for cell screening and cell-to-cell communication studies.[9,10] Although many interesting applications can be envisioned based on Namib desert beetle's back patterns, most of the reported techniques relied on photolithographic processes, which require a special equipment and handling. In this work, we used a simple soft lithographic technique, micromembrane deposition, to generate hydrophilic circle-patterns on a superhydrophobic surface. Specifically, hydrophilic polydopamine (pD) was spatio-

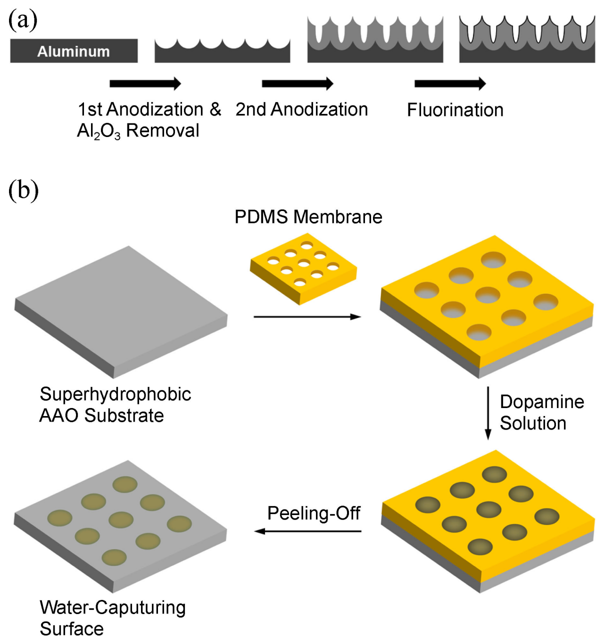

Figure 1. Schematic description for (a) the preparation of superhydrophobic AAO surfaces and (b) the generation of polydopamine circle-patterns.

selectively deposited onto a superhydrophobic anodized aluminum oxide (AAO) surface. As one of the applications of the patterns generated, a water-capturing ability was demonstrated.

Superhydrophobic surfaces were fabricated using fluorinated AAO surfaces based on the previous report (Figure 1(a)).[11] The resulting superhydrophobic surfaces showed nanoporous structures and the static water contact angle was measured to be 156.0°.

The hydrophilic conversion of the superhydrophobic surface was achieved by pD coating (Figure 1(b)). Dopamine undergoes polymerization under slightly basic conditions, and pD has been reported to coat virtually any type of surfaces, even in the case of poly(tetrafluoroethylene) that has adhesion-resistant properties as well as low surface energy.[12] For the achievement of selective pD coating onto

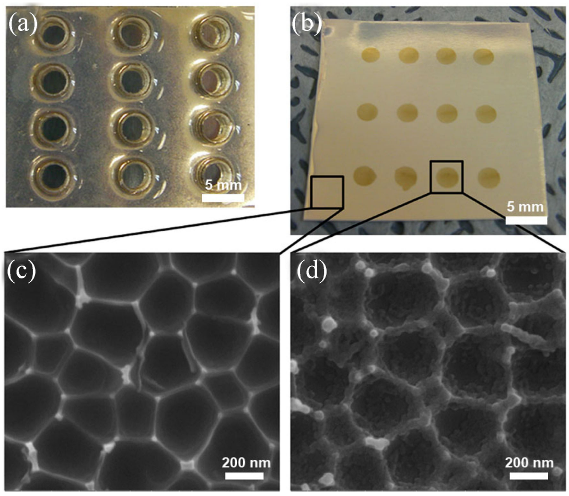

Figure 2. (a) An optical image of a PDMS membrane. (b) A photograph of the pD-coated superhydrophobic surface. SEM images of (c) unmodified and (d) pD-coated areas.

the superhydrophobic AAO surface, a poly(dimethylsiloxane) (PDMS) membrane with centimeter-scale holes (0.23 cm in diameter) was fabricated (Figure 2(a)). The PDMS membrane was placed on the AAO surface to make a conformal contact, and the holes of the PDMS membrane were filled with the dopamine solution (10 mM). Methanol and Tris buffer solution (pH 8.5) (CH_3OH:Tris buffer = 2:3 in volume ration) were used as a co-solvent for dopamine to increase coating efficiency by enhancing the wetting property of the dopamine solution onto the superhydrophobic surface. After 18-h pD coating, the PDMS membrane was carefully peeled off, and the surface was rinsed with water. The resulting surface showed a visible change in color only at the pD-modified circle region (Figure 2(b)), and showed remarkable change in the contact angles from 156.0^o to 57.6^o. The pD-deposited area lost the original self-cleaning property from superhydrophobicity and kept the water droplets. These results confirmed that the membrane-based pD deposition spatio-selectively changed the superhydrophobic AAO surface to the hydrophilic one. Further surface characterizations were carried out by scanning electron microscopy (SEM). The SEM images showed that the nanostructure of the AAO surface was fully covered by the pD layer after overnight coating (Figure 2(c), 2(d)).

The pD-patterned superhydrophobic surface possessed a water-capturing ability. When water was randomly sprayed onto the surface with a sprayer, water droplets were captured selectively and exclusively on the pD-modified region (Figure 3). The captured water rolled down with tilting of the surface when sufficient amount of water was captured, which mimics the water-collecting and -guiding property of the beetles. Quantitatively, up to 145 mL of water droplet was captured and collected at one pD-coated circle: the maximum volume was defined as the volume of the water droplet that did not touch the neighboring hydrophilic spots on its hydrophobic region, and rolled down when the surface was tilted slightly, while staying.

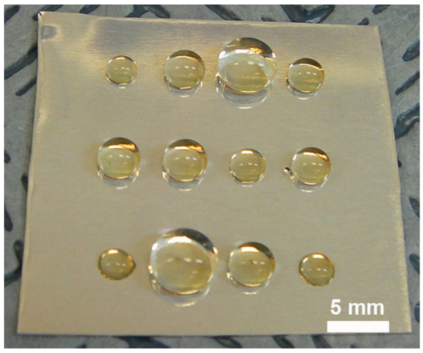

Figure 3. A photograph of water droplets captured on the pD circle patterns on the superhydrophobic AAO surface.

In summary, the hydrophilic/superhydrophobic hybrid patterns were fabricated with the inspiration from the structure of Namib desert beetle's back. The superhydrophobic surface was fabricated by fluorosilane-coating of AAO, and pD was spatio-selectively deposited onto the superhydrophobic AAO surface by using a PDMS membrane with centimeter-scale holes. The process is simple compared with photolithographic techniques and enables the generation of discontinuous patterns that cannot be formed with ease by microfluidic devices. In addition, the circle size can be tuned and various sizes and shapes be generated on a single substrate. The investigation of cell behaviors on microdroplets will be our next research thrust.

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