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Surface Modification

One-Step Modification of Superhydrophobic Surfaces by a Mussel-Inspired Polymer Coating**

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Mussels, which are promiscuous, underwater fouling organisms, attach to virtually any natural or synthetic organic/inorganic substrate. The major components of mussels' adhesive pads include proteins that contain the unusual amino acid 3,4-dihydroxy-L-phenylalanine (DOPA).[1] In particular, *Mytilus edulis* foot protein-5 (Mefp-5), a protein located at a distal side of adhesive pads that attaches to opposing substrates, shows an exhaustive repeat of DOPA-lysine.[1c,d] Recently, Lee, Messersmith, and co-workers identified dopamine that contains both side chain functionalities of DOPA and lysine and reported new surface chemical method, called polydopamine coating.[2] Polydopamine modified a wide variety of material surfaces, including noble metals, metal oxides, ceramics, and synthetic polymers on which protein immobilization, metallization, biomineralization, and cell adhesion were demonstrated.[2] Despite the unparalleled capability of polydopamine, the functionalization of superhydrophobic surfaces remains unexplored.

Superhydrophobic surfaces have received significant attention because of their extraordinary surface properties. A great deal of effort has been made to fabricate such surfaces.[3] The well-known biological model system of superhydrophobicity is the lotus leaf, which exhibits a static contact angle for water of greater than 150°. Most superhydrophobic surfaces have been prepared by various lithographic techniques: photolithography,[4] e-beam lithography,[5] assembly of colloidal particles,[6] capillary lithography and others.[7] The nonwetting properties of superhydrophobic surfaces have allowed a variety of applications, such as antireflectivity,[8] self-cleaning,[9] anti-fouling,[10] and in a long lifetime microfluidic valves.[11] Despite the large effort to develop methods to prepare superhydrophobic surfaces and to seek useful applications, few strategies to tailor the superhydrophobic surface properties have been developed. In particular, a facile strategy to modify superhydrophobic surfaces that can be integrated with widely implemented soft-lithographic techniques has not been achieved.

Herein, we report a one-step, solution-based surface chemical method that modifies superhydrophobic surfaces (Figure 1). The surface chemistry to enable this innovation is inspired by adhesion mechanisms of marine mussels and is compatible with established soft-lithographic techniques. By immersing substrates into a solution containing dopamine, a mussel-mimetic adhesive molecule, the superhydrophobic surface is immediately transformed into a hydrophilic substrate. By partial exposure of the substrate by a soft-lithographic technique, micromolding in capillaries (MIMIC),[12] the micropatterned surface remained superhydrophobic but was found to be adhesive to water. Similar to the mechanism of water collection by a desert beetle, *Stenocara sp.*, the modified surface can be used to capture, guide, and collect water droplets.[13]

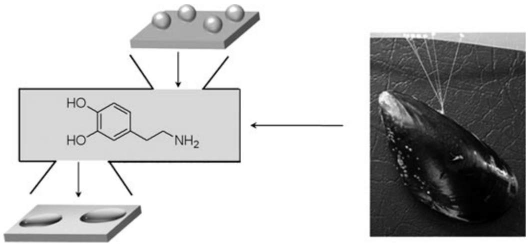

Figure 1. Mussel-inspired superhydrophobic surface modification. One-step immersion of a superhydrophobic surface into a solution of dopamine—a functional mimic of mussel adhesive proteins—modifies superhydrophobic surfaces.

We hypothesized that polydopamine formed by oxidative self-polymerization of dopamine could modify superhydrophobic surfaces, as it demonstrated functionalization of all other tested surfaces. For the preparation of superhydropho-

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bic surfaces, anodic aluminum oxide (AAO) membranes were utilized as templates on which fluorosilane was coated by gas-phase deposition.[14] The resulting AAO superhydrophobic surfaces were immersed into the dopamime solution to test the hypothesis. The superhydrophobic surface became hydrophilic with a dramatic decrease in contact angle from (158.5 ± 2.8)° to (37.3 ± 2.6)° after polydopamine functionalization for 18 h (Figure 2 A). A partially modified surface prepared by half immersion of the superhydrophobic substrate into the dopamine solution showed drastic differences in the behavior of water droplets on the surface (Figure 2 B). This conversion of surface properties supported the hypothesis, clearly demonstrating that polydopamine can control surface hydrophobicity. The surface was characterized by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). SEM images showed that polydopamine was coated on the top and side walls of porous AAO nanostructures (Figure 2 C). The XPS spectra revealed the change in surface chemical compositions caused by the polydopamine coating; the photoelectron peaks detected in the unmodified surface originated from the AAO substrate, Al 2s (119.9 eV), Al 2p (74.5 eV), and O 1s (529.9 eV), and from the fluorosilane, F 1s (685.6 eV) and C 1s (290.5 eV for C-F). In addition to the observed peaks, a newly appeared N 1s peak was observed in the polydopamine-modified surface (Figure 2 D, right).

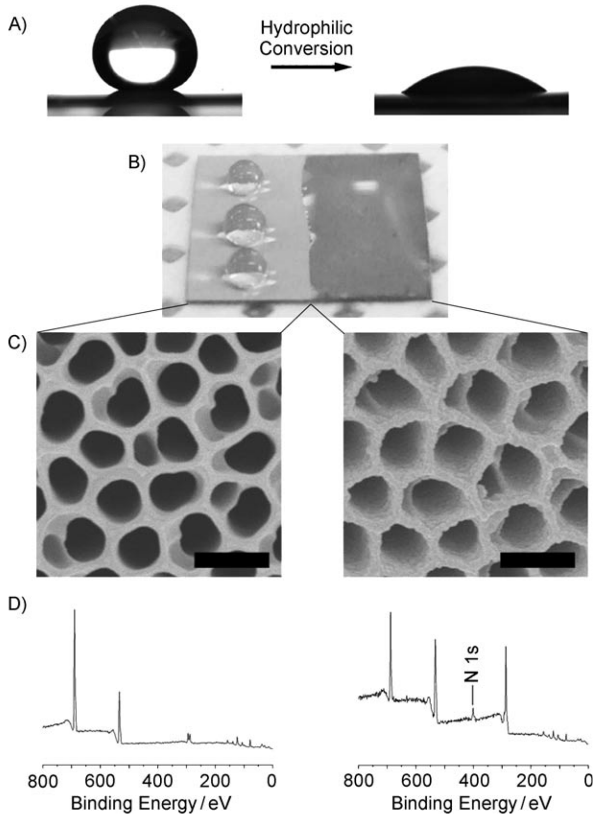

Figure 2. Characterization of the polydopamine-functionalized superhydrophobic surface. A) Contact angle images of superhydrophobic surface before and after polydopamine coating. B) A photograph of wetting properties of water droplets on the partially modified superhydrophobic AAO surface. C) SEM images of the unmodified superhydrophobic AAO surface (left) and the modified surface (right). The scale bar is 500 nm. D) XPS spectra of the unmodified (left) and polydopamine-functionalized surface (right).

Quantitative analysis of the surface chemical composition unambiguously supported polydopamine functionalization; nitrogen and carbon content was increased owing to the presence of polydopamine (N 1s: 0.98→3.74 %, C 1s: 6.56→48.2 %) and aluminum and fluorine content from the underlying layer decreased (Al 2p: 14.26→5.26 %, F 1s: 41.2→14.09 %).

The demonstrated one-step, in-solution functionalization of superhydrophobic surface can be easily combined with widely used soft-lithographic techniques. MIMIC can be a suitable technique to control the properties of the AAO superhydrophobic surfaces at a micrometer scale. MIMIC was chosen among a number of other soft-lithographic techniques because it involves a solution process in which the solution is injected into microcapillaries. Thus, it can be expected that the solution of interest (i.e. polydopamine) in the capillaries can create microscale patterns on the superhydrophobic surfaces with ease.

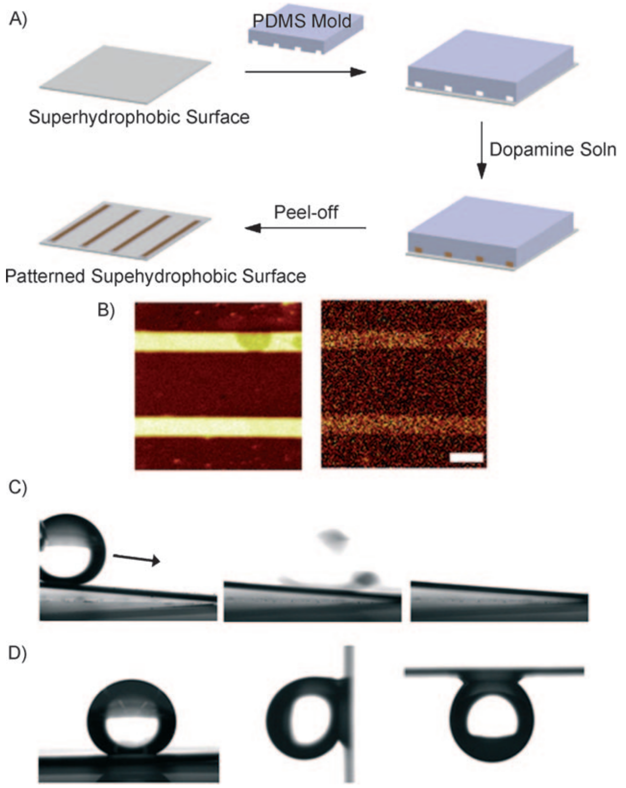

Figure 3. Micropatterning of superhydrophobic surfaces and wetting properties. A) Schematic description for preparing polydopamine-patterned superhydrophobic surface (PDMS = polydimethylsiloxane) and B) ToF-SIMS images of the polydopamine-patterned superhydrophobic surface: CN^- (left) and $C_8H_5N_2O^-$ (right). The scale bar is 100 μm. C,D) Rolling vs. stationary water droplets: the water droplet on the unmodified superhydrophobic rapidly rolled down when the surface was tilted (4°) (C); however, the water droplet on the polydopamine-micropatterned superhydrophobic surface remained attached even when the surface was tilted at 90° and 180° (D).

Applying an alkaline dopamine solution (2 mg mL^{-1}) into the microchannels followed by incubation for 18 h generated line patterns with 50 µm width (Figure 3 A). These superhydrophobic (unmodified AAO)—hydrophilic (polydopamine) alternating micropatterns were characterized by time-of-flight secondary ion mass spectrometry (ToF-SIMS) (Figure 3 B). ToF-SIMS provided images that exhibited clear 50 µm-width line patterns in which a strong nitrogen-containing CN$^-$ fragment (m/z 26) was detected from the polydopamine-modified area (Figure 3 B, left). Detection of nitrogen in ToF-SIMS experiments from the modified area is consistent with the XPS result in which the N 1s photoelectron peak appeared (Figure 2 D, right). Another characteristic mass fragment from the polydopamine-modified region was $C_8H_5N_2O^-$ (m/z 145; Figure 3 B, right). The exact chemical structure of the ion fragment is not yet clear, but may be an indole-like structure originating from the polydopamine layer.[2] The micropatterned surface remained superhydrophobic with a slight decrease in contact angle from $(158.5 \pm 2.8)°$ to $(151.4 \pm 1.2)°$ (Figure 3 C, lower, left). Interestingly, however, the wetting property of the functionalized superhydrophobic surfaces was considerably different. In contrast to the water droplet on the unmodified superhydrophobic surfaces, which rapidly roll down an incline under gravity (Figure 3 C, upper), a droplet placed on the patterned surface did not roll even when the surface was tilted vertically (90° tilt, Figure 3 C, lower, middle) or was inverted (180° tilt, Figure 3 C, lower, right). The 90° tilted surface could hold up to a 20 mg water droplet. The alternating superhydrophobic and hydrophilic areas on the surface created capillary interactions (i.e. surface tension) between the droplet and the polydopamine-modified area. This interfacial surface energy is a key contributor to the observed adhesion of water droplets. Determination of surface energy created by the alternating micropatterns on the superhydrophobic surface is a challenging task. We utilized the law of energy conservation. The law states that the amount of energy in a system remains constant. The falling water droplet loses energy by interacting (i.e. collision) with the unmodified superhydrophobic surface (Figure 4 B). The difference in height (h_1-h_2) indicated the energy lost, which can be calculated by potential energy difference: $(h_1-h_2)gm$, where h_1 is 1.73×10^{-2} m, h_2 is 5.76×10^{-3} m, g is 9.8 m s^{-2}, and m is 1.25×10^{-5} kg. However, the falling water droplet with the same initial height (h_1) onto the modified superhydrophobic remains attached on the surface. Thus, to safely hold the

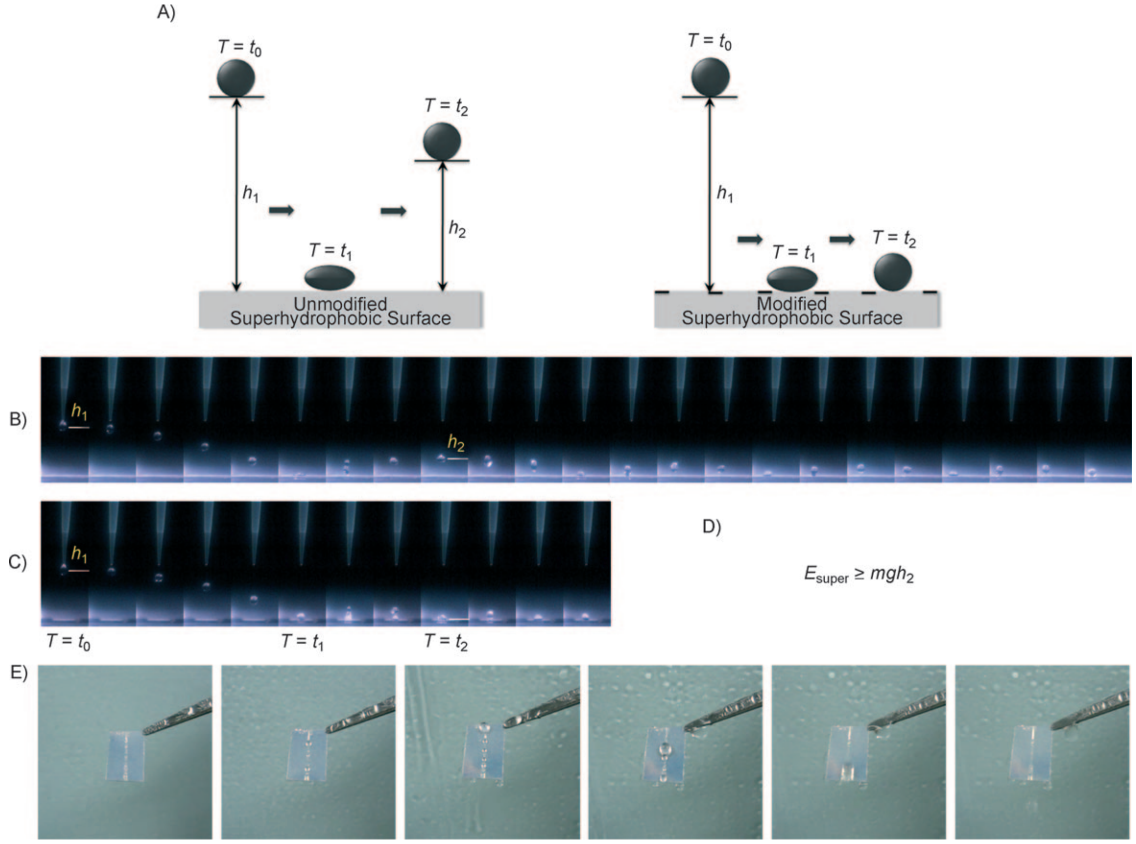

Figure 4. Determination of the surface energy of the micropatterned superhydrophobic surface. A) Schematic description of the behavior of a falling water droplet on the unmodified superhydrophobic and patterned superhydrophobic/hydrophilic surfaces. Sequences of time-resolved high-speed camera images (12 ms interval) of the falling water droplet on B) the superhydrophobic surface and C) the micropatterned superhydrophobic surface. D) Equation for calculating the surface energy generated by polydopamine micropatterns. E) Demonstration of the ability to capture and collect water by the micropatterned superhydrophobic surface. Water droplets approaching to the surface from air were collected in the modified area. As the size of water droplets increases, the droplet started to roll down along the track of polydopamine, resulting in the collection of water.

droplet, the surface energy (E_{super}) contributed by the micropatterns should be equal to or greater than the potential energy after collision (mgh_2), otherwise the water droplet would be detached from the modified surface. Time-resolved observation of the falling water droplets using a high-speed camera enabled us to reveal the surface energy. The calculated E_{super} is equal to or greater than mgh_2, which is 706 nJ. Considering the contact surface area (1.81×10^{-5} m^2) of the water droplet, the calculated surface tension of the patterned superhydrophobic surface was 39 mN m^{-1}, which is similar to the surface energy of synthetic polymers for example poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA).[15] Other causes for energy loss, such as interactions between water molecules and friction at the air–water interface, were excluded.

The polydopamine-modified superhydrophobic surface could be used as a water-capturing device. When vaporlike fine water was continuously sprayed on the modified superhydrophobic surface (400 μm in width at center), water was concentrated and rolled specifically down along the polydopamine-coated area (Figure 4E). The ability to collect water by utilizing hydrophilic micropatterns on superhydrophobic surface mimics the primary water collection mechanism utilized by the Namib desert beetle, which lives in an extremely dry environment.[13]

In conclusion, we demonstrated a facile, one-step superhydrophobic surface modification strategy utilizing the adhesion mechanism of mussels. Hydrophilic conversion of a superhydrophobic surface was easily achieved by polydopamine, a functional polymeric mimic of the mussel adhesive protein *Mytilus edulis* foot protein-5 (Mefp-5). This superhydrophobic surface modification is compatible with widely used soft-lithographic techniques such as MIMIC to enable facile functionalization of superhydrophobic surfaces. The modified surface remained superhydrophobic but showed high-water adhesion properties. A general approach to determine surface energy of the modified superhydrophobic surface was demonstrated. Finally, the modified superhydrophobic surface can be used as a part of a water-capturing device that mimics the mechanism of collecting water shown in the cuticle of the Namib dessert beetle. This new superhydrophobic surface chemistry can be applied to potentially advance superhydrophobic surface engineering for a variety of applications.

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