

Fabrication of Patterned Superhydrophobic Polybenzoxazine Hybrid Surfaces

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The hydrophilicity of bis(3-allyl-3,4-dihydro-2H-1,3-benzoxazinyl)isopropane(B-ala) polybenzoxazine film and superhydrophobic polybenzoxazine-hybrid surface can be controlled through UV exposure to change the ratio of intra- to intermolecular hydrogen bonds. A fraction of the intramolecular hydrogen bonding of the as-cured sample will convert into intermolecular hydrogen bonding upon UV exposure and thus results in an increase of hydrophilicity. This simple method allows for manipulating the hydrophilicity at selected regions on a superhydrophobic polybenzoxazine hybrid surface to create a patterned surface with superhydrophobic and superhydrophilic regions. Additionally, we have found that the superhydrophobic polybenzoxazine–silica hybrid surface exhibits good adhesion of water droplets after UV exposure, which can be served as a “mechanical hand” to transfer water droplets from a superhydrophobic surface to a hydrophilic one.

Introduction

A solid surface's water repellency is one of the most important characteristics in both theoretical research and industrial applications. The wettability of solid surfaces can be controlled by surface topography and/or surface chemistry. With this controllability, many useful methods¹ have been developed to produce numerous superhydrophobic surfaces. Among these, an approach toward artificial superhydrophobic surfaces^{2,3} such as mimic lotus leaves has drawn great interest where the surface is covered by branch-like nanostructures on top of micropapillae. 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.⁴ The wettability of the multiscale hierarchical structure can also be alternated between superhydrophobicity and superhydrophilicity by a change in surface chemistry.⁵ Wettability-switching surfaces have also been realized by applying an external stimulus, such as light irradiation,⁶ electrical potential,⁷

temperature,⁸ and solvent.⁹ While the reversibility is desirable in certain applications, this approach cannot be used for selective transformation of the wettability.^{7–9}

Patterned surfaces with dissimilar wetting properties have been achieved using techniques such as microcontact printing,^{10,11} chemical vapor deposition,¹² and photolithography.^{13–15} However, these approaches often involve complicated procedures to introduce functional groups to the patterned areas. Therefore, a simple and more effective route to generate arrays of patterns with different wetting properties and chemical functionalities is highly desirable. Furthermore, surfaces with extreme wetting properties such as superhydrophilic patterns on a superhydrophobic surface offer new possibilities in the fabrication of novel devices such as planar microchannels (open-air microfluidic channels).¹⁶ Open-air microfluidic channels offer advantages such as the facile handling of small amount of liquids, the possibility of massive parallel processing, direct accessibility, and ease of cleaning.^{16–18} The availability of patterned surfaces with superhydrophobic and superhydrophilic regions can greatly enhance the utility and function of such devices and move us beyond nature's impressive accomplishment with the Namib beetle.

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In our previous study, we discovered that polybenzoxazine (PBZ) is a new class of nonfluorine, nonsilicon low surface free energy polymeric material, and the superhydrophobic PBZ hybrid surface with excellent environmental stability can be carried out by an easy two-step coating process.¹⁹ We are unaware of any previously available methods by which superhydrophilic regions can be created on the superhydrophobic PBZ hybrid surface. In this communication, we introduce a direct ultraviolet (UV)-assisted replica molding method to create superhydrophilic regions on the superhydrophobic PBZ hybrid surface. This method allows for selective wetting on PBZ thin films or superhydrophobic PBZ hybrid surfaces by exposing to UV light through an optical mask or shadow mask.

Experimental Section

All the chemicals were used as received. Bisphenol A and paraformaldehyde (95%) were supplied by the Showa Chemical Company of Japan. The synthesis of bis(3-allyl-3,4-dihydro-2*H*-1,3-benzoxazinyl)isopropane (B-ala) was based on the reaction of bisphenol A with allylamine and paraformaldehyde according to the previously reported procedure.²⁰ Column chromatography eluting with ethylacetate–hexane (2:1) was used to separate the impurities, which were identified as unreacted phenols, amines, and benzoxazine oligomers. Silica nanoparticles (Tokusil 233G) were kindly provided by the Oriental Silicas Corporation. The nanoparticle is a 22 nm precipitated hydrated silica. One-half gram of the B-ala monomer was dissolved in 10 mL of tetrahydrofuran (THF) at room temperature. The solution was then filtered through a 0.2 μm syringe filter before spin coating onto a glass slide (50 \times 50 \times 1 mm³). One milliliter of the appropriate monomer solution was spin-coated onto a glass slide using a photoresist spinner operating at 1500 rpm for 45 s, then the sample was cured in an oven at 210 $^{\circ}\text{C}$. Superhydrophobic coating on a glass slide based on PBZ and silica nanoparticles was performed through a two-step process. First, B-ala benzoxazine (0.5 g) was mixed with nanoparticles (0.75 g) in THF (10 mL). After keeping the solutions in an ultrasound bath for 2 h, the mixture was spin-coated onto a glass slide (50 \times 50 \times 1 mm³) at 1500 rpm for 45 s and then cured in an oven at 210 $^{\circ}\text{C}$ for 1 h. Subsequently, the PBZ–silica hybrid surface was modified with 0.1% (w/v) B-ala PBZ film. The B-ala benzoxazine solution was spin coated onto a rough surface for 45 s at 1500 rpm and then cured at 210 $^{\circ}\text{C}$ for 1 h.

Results and Discussion

The resulting water contact angle was about 111.3 $^{\circ}$ for the B-ala PBZ thin film, and the contact angle for the superhydrophobic PBZ–silica hybrid surface was 161.1 $^{\circ}$, while the sliding angle was smaller than 3 $^{\circ}$.

PBZs feature strong intramolecular hydrogen bonds that result in extremely low surface free energies, even lower than that of pure Teflon.¹⁹ In PBZ systems, strong intramolecular hydrogen bonding between the hydroxyl groups and the amino groups in the Mannich bridges tends to decrease the surface free energy, whereas intermolecular hydrogen bonding between hydroxyl groups results in higher surface free energies. The destruction portion of intramolecular hydrogen bonding by switching into intermolecular hydrogen bonding in PBZ system tends to increase its surface free energy and higher hydrophilicity.

Ishida et al.^{21,22} determined that C=O-containing species are formed when a bisphenol A-based PBZ resin is exposed to UV

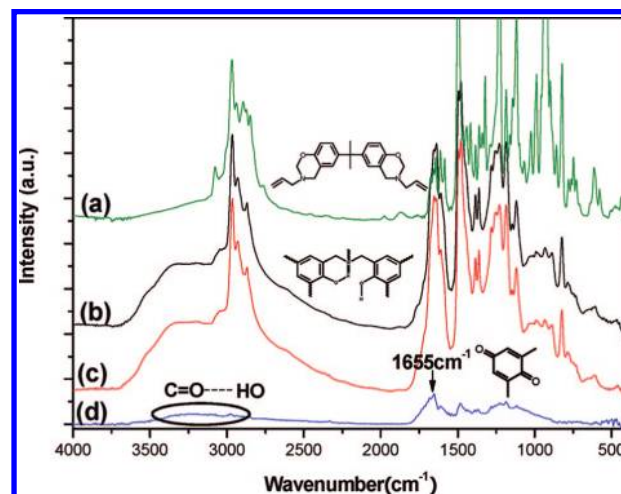


Figure 1. FTIR spectrum and structure of (a) the B-ala monomer, (b) the unirradiated B-ala PBZ, (c) the B-ala PBZ irradiated for 60 min, and (d) the difference spectrum of (b) and (c).

radiation under ambient conditions. The isopropylidene linkages of PBZ are the reactive sites where oxidation and cleavage occur upon UV exposure, forming 2,6-disubstituted benzoquinone units. The presence of these benzoquinone moieties decreases the extent of intramolecular hydrogen bonding while increasing the extent of intermolecular hydrogen bonding. Figure 1 shows FTIR spectra and structures of (a) the unirradiated B-ala PBZ, (b) B-ala PBZ irradiated for 60 min, and (c) the differential spectrum of (a) and (b). There are two important changes evident in the differential spectrum (Figure 1c): the growth of the band at 1655 cm^{-1} assigned to the 2,6-disubstituted benzoquinone and a slight increase in intermolecular hydrogen bonding in the range 3550–3100 cm^{-1} . The reason for this difference is the reduction in intramolecular hydrogen bond by converting the hydroxyl group to carbonyl group. Table S1 reveals that the atomic fraction of oxygen, an indication of the degree of photo-oxidation of the surface, increases after UV exposure. From Figure S1, the growth of the minor peak at 294.3 eV can be assigned to the hydrogen bonding between benzoquinone and the hydroxyl group by comparing with Figure S2a,b,c. According to these results, the photo-oxidation reaction in the B-ala PBZ system can be illustrated in Scheme S1.

Since the radical formation and oxidation reactions induced by UV radiation are usually concentrated at polymer surfaces, we anticipated that the surface properties of PBZ thin films would be greatly affected by their length of UV exposure. Figure 2 reveals that the contact angles of water decrease upon increasing the UV exposure time of B-ala PBZ films and superhydrophobic PBZ–silica hybrid surfaces. In the B-ala PBZ thin film (cured for 1 h at 210 $^{\circ}\text{C}$) system, the contact angle of water decreases with increasing UV exposure time, from 111.3 $^{\circ}$ to 18.6 $^{\circ}$ after 60 min of UV exposure. The contact angle of water for the superhydrophobic PBZ–silica hybrid surface decreases rapidly upon increasing the UV exposure time, from 161.1 $^{\circ}$ to 0 $^{\circ}$ after 60 min of UV exposure. This behavior is consistent with a partial destruction of intramolecular hydrogen bonding and the increase in the extent of intermolecular hydrogen bonding after UV exposure and the result of higher surface free energies and higher hydrophilicity.

However, the contact angle of water is affected by surface properties, the energy of materials, and surface morphology. Figure 3 shows scanning electron microscopy (SEM) images and the corresponding contact angles of the PBZ–silica hybrid surface with different treatments. The surface topography of the

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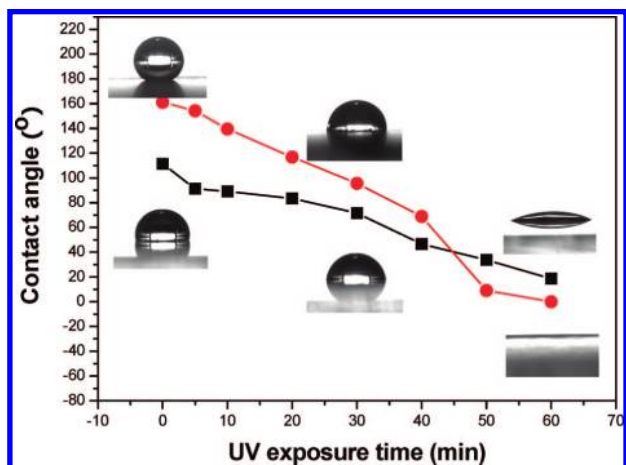


Figure 2. Water contact angles for (■) PBZ thin films and (●) superhydrophobic PBZ-silica hybrid surfaces with different UV exposure times.

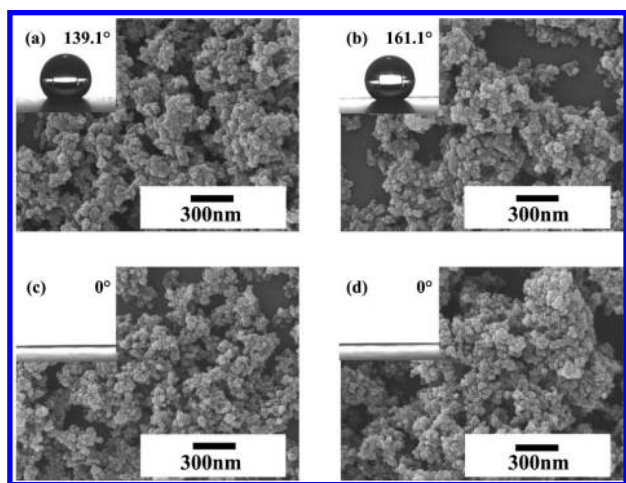


Figure 3. SEM images and the corresponding contact angles of (a) a polybenzoxazine-silica hybrid surface, (b) a polybenzoxazine-silica hybrid surface modified with 0.1% pure B-ala PBZ thin film, (c) b after 60 min of UV irradiation, and (d) c washed with acetone and methanol.

PBZ-silica hybrid surface with different treatments remains unchanged, but the changes in the contact angles of water are dramatic. The surface topography of the B-ala PBZ thin film is also unchanged after UV irradiation exposure (Figure S3). The reason for the contact angle decrease upon increasing the UV exposure time of the B-ala PBZ film and the superhydrophobic PBZ-silica hybrid surface is the change of chemical composition on the surface. Therefore, we can manipulate the wettability at selected regions merely by varying the UV exposure time to create patterned surfaces containing superhydrophobic and superhydrophilic regions. Figure 4a,b presents photographic images of superhydrophilic patterns upon a superhydrophobic PBZ-silica hybrid surface. In addition, good adhesion of the water droplet placed on the superhydrophobic PBZ-silica hybrid surface after 5 min of UV exposure was observed. For

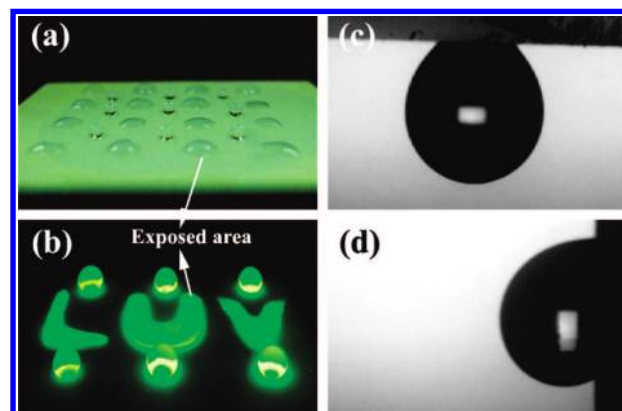


Figure 4. (a) Water drops on a selective wetting PBZ-silica hybrid surface. (b) CdTe quantum dot containing solution drops on the UV-modified PBZ-silica hybrid surface obtained with a large unilamellar vesicle (LUV) mask. Shapes of 5 μ L water droplets on the superhydrophobic PBZ-silica hybrid surface after 5 min of UV exposure with different tilt angles: (c) 180° and (d) 90°.

example, even when we tilted the surfaces vertically or flipped them upside down, as shown in Figure 4d,c, the water droplet did not slide from the surface. The adhesion force of surface was found to depend strongly on its chemical composition²³ and topography.²⁴ For the superhydrophobic PBZ-silica hybrid surface, the change of chemical composition of the surface is the major factor to increase the adhesion force because its surface topography remains unchanged after UV exposure. Furthermore, we have reported²⁵ that the presence of new polar quinone C=O functional groups on the irradiated surface led to stronger polar forces between the B-ala PBZ film and polar liquids. We have measured the adhesion force of B-ala PBZ thin films with silicon cantilevers before and after UV irradiation. The mean adhesion force for B-ala PBZ thin films before and after 5 min of UV irradiation were 2.66 nN and 8.12 nN, respectively. It is expected that a surface with a sufficiently high adhesive force to a liquid will have many potential applications, such as in liquid transportation without loss and in the analysis of very small volumes of liquid samples. The superhydrophobic PBZ-silica hybrid surface after 5 min of UV exposure can be used as a “mechanical hand” to transfer small water droplets from a superhydrophobic surface to a hydrophilic one. As seen in Figure S9a, we started with a water droplet on an ordinary superhydrophobic surface with a water contact angle as high as 161.1°. Then, we used the superhydrophobic PBZ-silica hybrid surfaces that had been UV irradiated for 5 min to touch and adhere to this water droplet (b) until it was transferred from the ordinary superhydrophobic surface. Finally, this water droplet was released on a hydrophilic surface (poly(4-vinylphenol) thin film). We found that the droplet could be completely transferred from the ordinary superhydrophobic surface to the superhydrophobic PBZ-silica hybrid surface that had been UV irradiated for 5 min, but a little volume was lost when the water droplet was released on a hydrophilic surface. We believe the water droplet could be completely released on a hydrophilic surface without any loss by optimizing the process condition or applying external force such as magnetic force.²⁵

Conclusions

The superhydrophobic PBZ-silica hybrid surface can be prepared by an easy two-step coating process, and the hydro-

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philicity of a superhydrophobic PBZ–silica hybrid surface can be controlled through UV exposure to change the ratio of intra- to intermolecular hydrogen bonds.

This simple method allows superhydrophilic regions to be produced on superhydrophobic PBZ hybrid surfaces. Additionally, good adhesion of the water droplet on the superhydrophobic PBZ–silica hybrid surface can be obtained after 5 min of UV

exposure, and we apply this surface as a “mechanical hand” to transfer small water droplets from a superhydrophobic surface to a hydrophilic one.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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