

A Facile Approach to Superhydrophilic–Superhydrophobic Patterns in Porous Polymer Films

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Superhydrophobic surfaces showing extreme water-repellency have been eagerly investigated during the last years.^[1–3] Their possible applications range from self-cleaning surfaces, as seen in nature on lotus leaves,^[5] to microcondensation^[6,7] and even droplet manipulation.^[8] For many of these uses (super)hydrophilic patterns on superhydrophobic surfaces are required, but only a few examples for creating such patterns have been published. Zhai et al. used a multilayer of polymers, where silicon nanoparticles were added, which were then made superhydrophobic using a perfluorosilane. A hydrophilic pattern was then created by micropipetting another polymer onto the surface.^[6] Superhydrophilic patterns on superhydrophobic surfaces were also created with the help of plasma treatment or photodegradation of hydrophobic surface functionality.^[7–9] Pastine et al. used photoinduced modification of carbon nanotube “forests” with hydrophilic azides to create superhydrophilic patterns.^[10] Recently, Kang et al. reported a method for creating superhydrophilic patterns on a superhydrophobic surface through a mussel-mimetic deposition of dopamine in combination with soft-lithography.^[11] The difference in wettability of such patterns has been used for confining liquid inside channels for creating so-called surface-tension-confined (STC) microchannels in two dimensions^[12] or even in three dimensions using two-photon lithography.^[13]

In this paper, we present a facile method for the preparation of superhydrophilic patterns in superhydrophobic microporous and in hydrophobic nanoporous polymer films. The method is based on the preparation of a (super)hydrophobic thin porous polymer film, which is then modified by UV-initiated surface photografting^[14,15] through a photomask in order to create a superhydrophilic micropattern with defined geometry. The

produced patterns can be used, for example, as microfluidic channels, where water solutions are confined in the channels solely by the difference in surface tension. We recently have shown an application of such virtual microfluidic channels for two-dimensional peptide separation.^[16] Herein, we demonstrate the versatility of the approach by using two hydrophilic monomers to produce superhydrophilic patterns with positively or negatively charged surface functional groups, different pattern geometries, and with feature sizes down to several micrometers. STC microchannels have been prepared inside porous polymer films with different thicknesses and with both micro- and nanoporous structures.

Superhydrophobic, microporous^[17] poly(butyl methacrylate-co-ethylene dimethacrylate) (BMA-EDMA) films have been prepared by UV-initiated radical polymerization of a prepolymer mixture containing monomers, crosslinkers, porogens, and a UV initiator.^[18,19] The top part of the produced porous polymer film is covered with a flat and less porous micrometer-thin polymer layer and is removed either mechanically in the case of the microporous polymer or by plasma etching in the case of a nanoporous polymer. An additional photografting step is required for the nanoporous material to regain hydrophobicity. The rough porous surface, which is exposed during this fabrication step, is essential for achieving both the superhydrophobic and superhydrophilic effect (Figure 1A). The thickness of the porous polymer layer can be controlled between ≈ 12 and $100 \mu\text{m}$ by using Teflon strips of different thicknesses as spacers between two glass plates (Figure 2F, Figure 3). The

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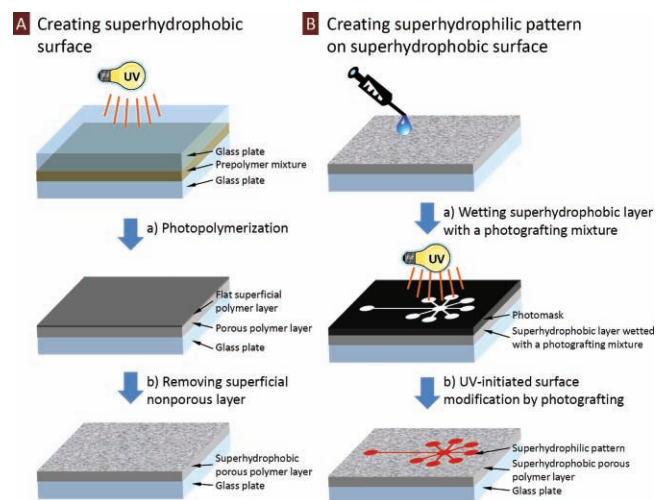


Figure 1. Schematic representation of the method for A) making superhydrophobic porous polymer films on a glass support and for B) creating superhydrophilic micropatterns by UV-initiated photografting.

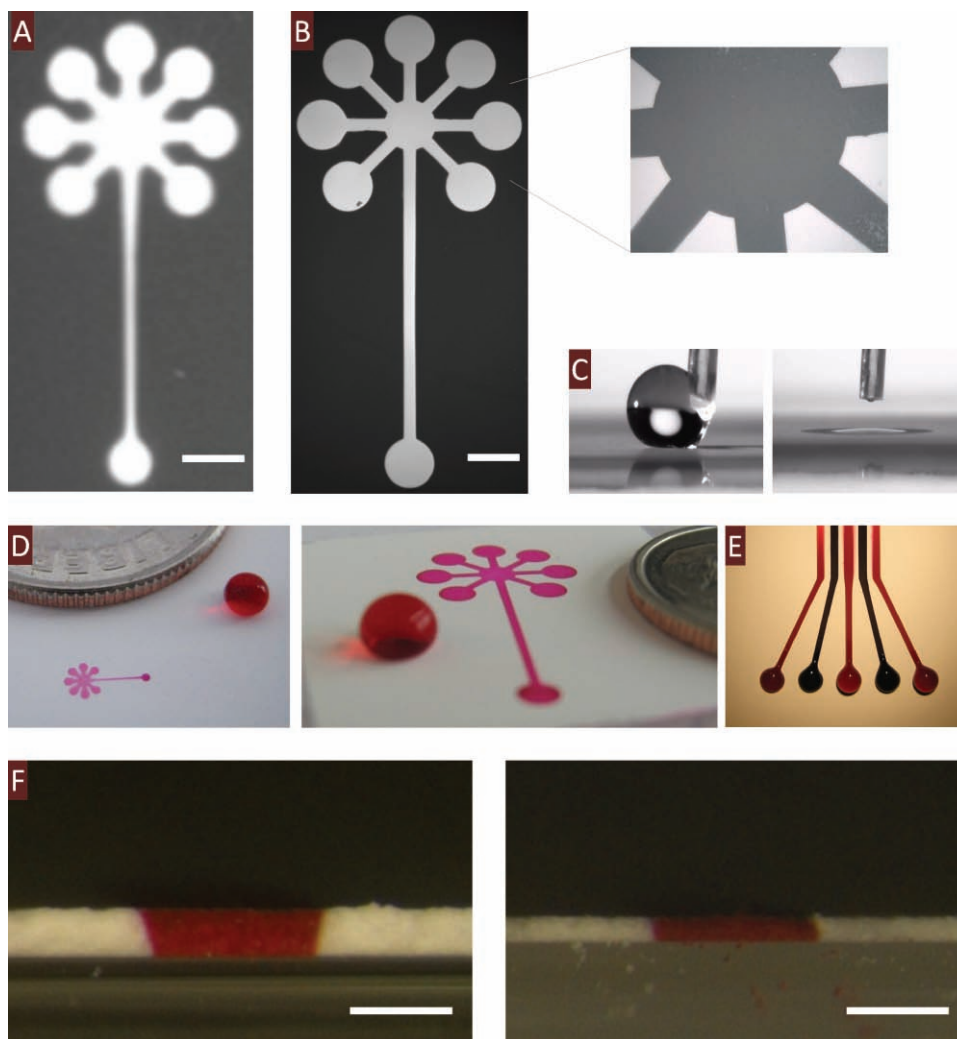


Figure 2. A,B) Optical microscopy images of a superhydrophilic pattern (photografted with AMPS) on a superhydrophobic porous polymer. Scale bars in (A) are 500 μm and in (B) are 2 mm. The patterns were wetted with water making the hydrophilic areas more transparent. C) Water droplets on the superhydrophobic microporous poly(butyl methacrylate-co-ethylene dimethacrylate) (left) and on the same surface after photografting with AMPS (right). D,E) Superhydrophilic patterns with different geometries and sizes filled with water dye solutions. F) Cross-sections of 200- μm -wide superhydrophilic microchannels (photografted with AMPS) colored with a water solution of neutral red. Polymer films: 50- and 25- μm -thick microporous poly(butyl methacrylate-co-ethylene dimethacrylate) films. Scale bars are 100 μm .

superhydrophobic property of the BMA-EDMA layer is a result of the combination of its porous surface, possessing double-scale roughness, and the hydrophobic nature of butyl methacrylate monomers.^[18]

To create a superhydrophilic pattern on the superhydrophobic polymer background we used a single-step surface modification method based on UV-initiated photografting.^[18,19] According to this method (Figure 1B), a porous BMA-EDMA film is wetted with a photografting mixture composed of a methacrylate monomer, benzophenone as the initiator, and a mixture of *tert*-butanol/water. Then, the polymer surface is irradiated with UV light through a photomask (Figure 1B). If a hydrophilic methacrylate (e.g., [2-(methacryloyloxy)ethyl]trimethylammonium hydrochloride (META) or 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS)) is used in the photografting mixture, the irradiated superhydrophobic surface transforms

into a highly wettable superhydrophilic surface with a static water contact angle close to zero. The reason for the transformation is the growth of polymethacrylate brushes from the surface of the porous polymer matrix irradiated with UV light. The surface modification is confirmed by X-ray photoelectron spectroscopy (XPS) analysis (Figure S1, Supporting Information).

This method can be used to create superhydrophilic patterns with feature sizes as small as a few micrometers. Figure 2 shows examples of superhydrophilic patterns of different sizes and geometries prepared on a superhydrophobic surface. Because of the extreme difference in wettability between superhydrophilic and superhydrophobic areas, such patterns work as microfluidic channels and can be filled with different water solutions as shown in Figure 2E and Video S1 (Supporting Information). Figure 2F shows the shape of cross-sections of such microfluidic channels prepared in polymers with different

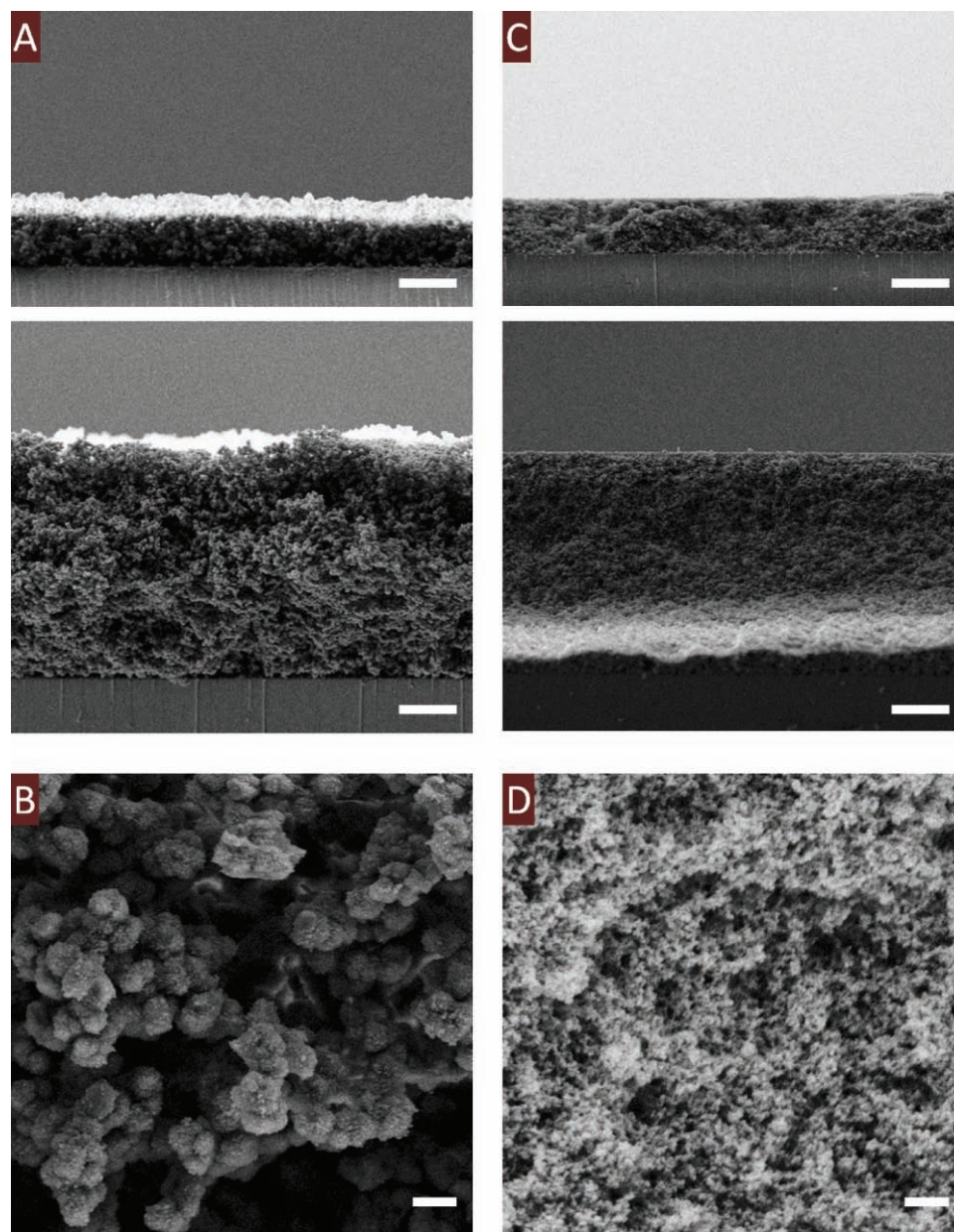


Figure 3. SEM images of the cross-sections of A,B) microporous and C,D) nanoporous poly(butyl methacrylate-co-ethylene dimethacrylate) films. Scale bars in (A,C) are 10 μm and in (B,D) are 1 μm .

thicknesses, which confirms that the surface modification by photografting takes place throughout the whole thickness of the used porous polymers. The trapezoidal shape of the cross-section is a result of the decrease in photografting efficiency caused by scattering of UV light passing through the porous polymer film. Nevertheless, the sharp edges of the microchannel's virtual walls show that there is a threshold of the grafting efficiency below which the porous polymer is non-wettable and above which the polymer becomes fully wettable. This also means that photografting of relatively thick polymer films or photografting for shorter times can result in 3D superhydrophilic structures lying on the surface of a superhydrophobic film (Figure S2, Supporting Information).

Figure 3 and Figure S3 (Supporting Information) show scanning electron microscopy (SEM) images of the cross-sections of the polymer films with different thicknesses. The morphology of the porous structure of polymer films was controlled by varying the composition of the polymerization mixture.^[18] Thus, the use of a 2:1 mixture of 1-decanol:cyclohexanol as a porogen in the polymerization mixture leads to the formation of a microporous polymer (pore size: 1–4 μm ; Figure 3B), while the use of excess of cyclohexanol (1:2 mixture of 1-decanol:cyclohexanol) leads to a nanoporous structure (pore size: 100–200 nm; Figure 3D).

The morphology of the porous polymers influences other properties of the materials. Thus, the produced microporous

BMA-EDMA polymer is superhydrophobic and non-transparent (although translucent), with static, advancing, and receding water contact angles (WCAs) of $163^\circ \pm 4^\circ$, $166^\circ \pm 3^\circ$, and $164^\circ \pm 2^\circ$, respectively (Table S1, Supporting Information). The nanoporous BMA-EDMA polymer layers are significantly more transparent as seen from UV-vis-NIR spectra (Figure S4, Supporting Information), however, at the same time significantly less hydrophobic with static, advancing, and receding WCAs of 124° , 136° , and 0° , respectively. The low receding WCA is a result of oxidation caused by the plasma etching used for removing the superficial polymer layer. Nevertheless, despite the loss of superhydrophobicity the nanoporous polymer remains non-wettable for water solutions and, thus, it is applicable for making transparent surface-tension-confined microfluidic channels.

An important parameter for applications of superhydrophilic/superhydrophobic patterns as microfluidic channels is the velocity of an aqueous solution propagating through a channel. We tested the flow velocity for different water/acetonitrile mixtures through a microchannel with the length, depth, and width of 11.6 mm, 40 μm , and 500 μm , respectively. The microchannel was created by photografting BMA-EDMA surfaces with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS). The microporous microchannels were in general easier to wet than the nanoporous ones. The flow velocity increased gradually with an increase in the amount of acetonitrile in water and reached an overall maximum of $\approx 5 \text{ mm s}^{-1}$ at 10% (v/v) acetonitrile in water for the microporous polymer and 20% (v/v) for the nanoporous polymer (Table S2, Supporting Information).

In conclusion, we have shown a facile method for creating superhydrophilic micropatterns on superhydrophobic porous polymer surfaces using photoinitiated surface grafting. Due to the extreme difference in wettability between the patterned and non-patterned areas and because of the three dimensionality of the produced superhydrophilic structures, such patterns can be used as microfluidic channels, for example, for separation purposes. We believe that the simple two-step approach presented here for making superhydrophilic patterns on superhydrophobic surfaces will find numerous applications for biological, medical, and diagnostic purposes.

Experimental Section

An OAI model 30 deep-UV collimated light source (San Jose, CA, USA) fitted with a 500 W HgXe lamp was used for UV irradiation. The lamp was calibrated to 12 mW cm^{-2} at 260 nm (intensity after a modified glass plate: 4.6 mW cm^{-2} ; after fluorinated glass plate: 5.1 mW cm^{-2} ; after 75- μm -thick Teflon film (American Durafilm Co.): 9.51 mW cm^{-2}) with the OAI 306 UV power meter. SEM images were obtained with a LEO 1530 scanning electron microscope (Zeiss, Germany). The samples were platinum-sputtered for the SEM measurements using a Cressington Sputter Coater 108 auto, with an average thickness of 28 nm measured by a Cressington Thickness Monitor mtm 10. The UV-vis spectra were obtained using a Micropack DH-2000-BAL UV-VIS-NIR-Lightsource, and the XPS spectra were recorded with a Leybold-Heraeus MAX200 with an EA200 hemispheric energy analyzer as the energy-dispersive element and a 300 W magnesium anode as the X-ray source without a monochromator (pass energy 48 eV, step size 0.2 eV). For taking pictures and videos of the water droplets, a DSA 100 from Krüss GmbH (Germany) was used. The WCAs were determined using ImageJ software with a DropSnake plugin. The images of the patterns and surfaces were

taken with a Leica MZ10 F microscope with a Leica DFC 360 FX camera; the images of the cross-sections were taken with a Wild M10 microscope from Leica using an AxioCam HRC from Zeiss. The plasma cleaner was a Harrick-Plasma cleaner/sterilizer PDC 326. The UV-transmitting glass plates were Nexterion B glass from Schott (Germany), and the non-UV-transmitting plates were J. Melvin Freed brand microscope slides. The pore size of the polymers was determined from the SEM images. Butyl methacrylate was purchased from Fluka (Germany) and methyl green was purchased from Merck (Germany); all other chemicals were purchased from Sigma-Aldrich (Germany). Monomers containing an inhibitor were purified using a short column filled with basic aluminum oxide.

Polymerization Mixture for Making Microporous BMA-EDMA: The mixture contained butyl methacrylate (BMA) (24 wt%), ethylene dimethacrylate (EDMA) (16 wt%), 1-decanol (40 wt%), cyclohexanol (20 wt%), and 2,2-dimethoxy-2-phenylacetophenone (DMPAP) (1 wt% with respect to monomers).

Polymerization Mixture for Making Nanoporous BMA-EDMA: The mixture contained BMA (24 wt%), EDMA (16 wt%), 1-decanol (20 wt%), cyclohexanol (40 wt%), and DMPAP (1 wt% with respect to monomers).

Butyl Methacrylate Photografting Mixture: The mixture contained BMA (15 wt%) and benzophenone (0.25 wt%) in a solution of *tert*-butanol:water (3:1, v/v).

AMPS Photografting Mixture: The mixture contained AMPS (15 wt%) and benzophenone (0.25 wt%) in a solution of *tert*-butanol:water (3:1, v/v).

META Photografting Mixture: The mixture contained a solution of 80 wt% META in water (18.75 wt%) and benzophenone (0.25 wt%) in a solution of *tert*-butanol:water (3.52:1, v/v).

Activation of Glass Plates: To activate the glass plates, they were washed with water, dried with a stream of nitrogen, and immersed in a 1 M sodium hydroxide solution for 0.5 h. The plates were then washed again with water and dried. After that they were immersed in a 1 M hydrochloric acid solution for 0.5 h, washed with water, and dried extensively with a stream of nitrogen.

Functionalization of the Glass Plates: The activated glass plates were functionalized with 3-(trimethoxysilyl)propyl methacrylate as an anchor group for the polymerization. A few droplets of 20 vol% 3-(trimethoxysilyl)propyl methacrylate in ethanol adjusted to apparent pH = 5 with acetic acid were applied to the activated glass plates and covered with another activated glass plate. The solution was renewed after 30 min and retained on the glass plates for additional 30 min. Then the glass plates were washed with acetone and dried with a stream of nitrogen.

Fluorination of the Glass Plates: To create inert, fluorinated glass slides, the activated glass plates were placed in a desiccator together with an open vial containing several droplets of trichloro(1H,1H,2H,2H-perfluorooctyl)silane. The desiccator was evacuated and left under vacuum overnight, followed by washing the fluorinated glass plates with acetone.

Making Microporous BMA-EDMA Films: The polymerization mixture was applied between two methacrylated glass plates, which were separated by two thin strips of Teflon film (American Durafilm Co.). Various Teflon film thicknesses were used to adjust the thickness of the polymer film. The glass slides were fixed with multiple clamps and put under the UV lamp for 15 min of irradiation. The upper glass slide needed to be a UV-transmitting one, while the bottom glass slide could be a non-UV-transmitting one. After irradiation, the glass slides were carefully opened with a scalpel. The polymer film stuck to the upper glass plate, while there was only a very thin polymer layer left on the lower glass plate. The polymer was washed extensively with methanol, immersed into methanol for at least 1 h, and then dried with a stream of nitrogen.

In an alternative approach, one fluorinated and one modified glass plate were used. In this case, a flat and significantly less porous superficial polymer layer was formed on the surface of the porous polymer film attached to the modified glass slide. This flat, dense layer could be easily removed by attaching conventional pressure-sensitive (Scotch) tape to the polymer film and then peeling it off.

Making Nanoporous BMA-EDMA Films: The polymerization mixture was applied between a modified, UV-transmitting glass plate and a fluorinated glass plate, which were separated by two thin strips of Teflon film (American Durafilm Co.) with different thicknesses to adjust the thickness of the polymer film. The glass slides were fixed with multiple clamps and placed under a UV lamp for 15 min of radiation, where the modified glass plate was on top. After irradiation, the glass slides were carefully opened with a scalpel. In this case, the polymer stuck completely to the modified glass plate. The polymer was then washed extensively with methanol, immersed into methanol for at least 1 h, and then dried with a stream of nitrogen.

Since the fluorinated glass plate was used in this case, the flat superficial polymer layer was formed. Because of the higher mechanical stability of the nanoporous polymer, the flat polymer layer could not be removed using the method with pressure-sensitive tape. Therefore, a method based on plasma treatment was used. The surface of the polymer film was treated with oxygen plasma using a plasma cleaner for 10 min (Harrick-Plasma cleaner/sterilizer PDC 326 (USA)). Then, the polymer was washed with methanol and dried again with a stream of nitrogen. However, the polymer treated with plasma became hydrophilic. To restore the hydrophobicity, the polymer was modified with a poly(butyl methacrylate) using the photografting technique: the porous polymer was wetted with a corresponding photografting mixture and then irradiated with UV light for 3 min, followed by washing the plate with methanol and drying.

Photografting: The surface of a porous polymer film was wetted with a photografting solution, and the substrate was covered with a 75- μm -thick Teflon film (American Durafilm Co.) and with a photomask. The plate was irradiated with UV light (260 nm) either for 3 min (for the nanoporous polymers) or for 15 min (for the microporous polymers). After this process, the polymer film was washed with methanol and dried with a stream of nitrogen.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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