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Completely Superhydrophobic PDMS Surfaces for Microfluidics

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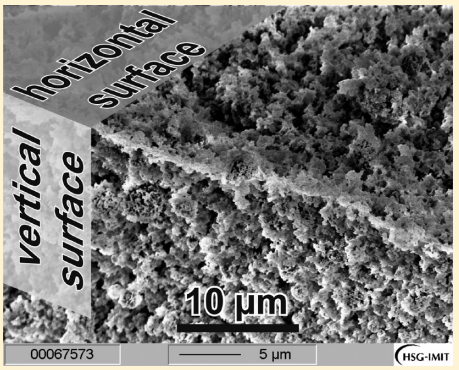
Supporting Information

ABSTRACT: This study presents a straightforward two-step fabrication process of durable, completely superhydrophobic microchannels in PDMS. First, a composite material of PDMS/PTFE particles is prepared and used to replicate a master microstructure. Superhydrophobic surfaces are formed by subsequent plasma treatment, in which the PDMS is isotropically etched and PTFE particles are excavated. We compare the advancing and receding contact angles of intrinsic PDMS samples and composite PTFE/PDMS samples (1 wt %, 8 wt %, and 15 wt % PTFE particle concentration) and demonstrate that both the horizontal and vertical surfaces are indeed superhydrophobic. The best superhydrophobicity is observed for samples with a PTFE particle concentration of 15 wt %, which have advancing and receding contact angles of 159° ± 4° and 158° ± 3°, respectively.



INTRODUCTION

Superhydrophobic surfaces are of great interest in various research fields. They not only are interesting because of their working principle, but also have a great impact on applications which demand antisoiling or water-repellent surfaces.[1,2] Further, microfluidic applications may be operable with particularly low pressures for liquid flow, as long as all channels in a microfluidic chip feature superhydrophobic walls. The accompanying boundary conditions include slip conditions along the channel walls, decreased shear stress in the flow, and therefore reduced pressure losses.[3,4] Generally, superhydrophobicity comprises a combination of multiscale roughness in the micrometer and nanometer ranges and an intrinsic low surface energy of the materials used.[5−8] For example, polytetrafluorethylene (PTFE) is known for its very low surface energy.

Contact-free dosage applications may require superhydrophobic nozzles to prevent pinning of water-based liquid droplets at the nozzle outlet. An accumulation of small amounts of liquid near the nozzle outlet due to pinning effects may result in further liquid accumulation or deflection of the droplet flight direction. Completely superhydrophobic nozzles (i.e., where all surfaces are superhydrophobic) could prevent these effects. Capillary stops on microfluidic chips are also of great interest and can be used as integrated and pressure-regulated valves for liquids in specific applications, such as pressure-dependent breakthrough of channel cross sections in *Lab-on-Chip* platforms.[9]

Polydimethylsiloxane (PDMS) is one of the most frequently used materials in microfluidic applications and Lab-on-Chip solutions. Contact angles for intrinsic PDMS have values of 110°, and this material does not exhibit low sliding angles, so it can be declared to be hydrophobic at most. During the past decade, several successful approaches have been taken to produce superhydrophobic PDMS surfaces.

Tserepi et al. (2006)[10] treated PDMS (Sylgard 184, Dow Corning) with SF6 plasma within an inductively coupled plasma (ICP) to generate structures of high aspect ratio. These structures were coated by fluorocarbon deposition using C_4F_8 plasma in the same setup. At this point, we want to emphasize that the generated structures with high aspect ratios were created by a highly anisotropic process of PDMS etching, as pointed out by the authors. Cortese and Manca et al. (2008)[11] used SU-8 masters to emboss micropillars onto the PDMS sample. The PDMS sample was subsequently pretreated with argon plasma (200W, 5.3 Pa) within an ICP. According to the publication of one of the authors, argon plasma was used to enhance the fluorination rate of the PDMS surface. Subsequent CF_4 plasma was then used to generate nanoposts on top of the micropillars by preferential etching of certain PDMS components.[12] The presented SEM images[11] clearly show that CF_4 plasma treatment in fact generates nanoroughness on top of the PDMS pillars but does not affect the side walls of these micropillars, which remain smooth. According to the authors, measured contact angles on their treated PDMS samples ranged from 155° to 170° with a contact angle hysteresis of less than 7°. Cordeiro et al. (2009)[13] also studied the fluorination of PDMS surfaces in CF_4 plasmas but pointed out that PDMS was rather more hydrophilic after plasma treatment. We believe that the different configurations of the plasma chamber, gas pressure, and generator power result in different etching rates and thus different water contact angles. Givenchy et al. (2009)[14] used acidic treatment (sulfuric acid or hydrofluoric acid) of PDMS samples to roughen the surface. After exposure to acid, covalent grafting of a highly fluorinated

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monolayer was performed. Xiu et al. (2007)[15] published a study that used a composite coating material consisting of PDMS and PTFE particles. A silicon wafer was used as a substrate. The composite (PDMS/PTFE) was then applied on top of the silicon wafer via dip-coating, bar-coating, or spin-coating. The authors observed different water contact angles depending on the coating procedure, with spin-coating showing the best results in terms of hydrophobicity (water contact angle 161°, contact angle hysteresis 7°). The authors stated that the different shear forces of the coating procedures used led to different surface morphologies. In the case of spin-coating, PTFE particles are forced to float nearer to the air/PDMS interface, resulting in appropriate roughness for superhydrophobicity. The authors have shown that this approach works well for smooth surfaces, but we believe that their method is not suitable for casting of microfluidic channels with high aspect ratios, where spin-coating procedures cannot be employed. Finally, Liu et al. (2010)[16] presented an approach where a PDMS film was patterned with micropillars (diameter = 5 μm, aspect ratio up to 2.7) using an SU-8 mold. The PDMS sheets were subsequently used to form 1 × 1 mm^2 channels with a hot embossing process.

This study presents a new and simple process for the fabrication of PDMS chips with completely superhydrophobic channel walls (vertical and horizontal surfaces). Microchannels are formed in a composite of PTFE nanoparticles and PDMS as the matrix material. Afterward, the fabricated chips are exposed to a 4 kHz CF_4/O_2 plasma to obtain superhydrophobic surfaces by isotropic PDMS etching. The fabricated chips are then used for a potential application of contact free dosage of liquids.

MATERIALS AND METHODS

Fabrication of a Composite Material of PDMS/PTFE Particles. First, a mixture of PDMS (Sylgard 184, Dow Corning) and a curing agent with a weight ratio of 10:1 is prepared. The mixture is stirred manually for at least 5 min, additionally mixed, and defoamed with a centrifugal mixer (Thinky Mixer ARE-250) for 3 and 2 min, respectively, and subsequently degassed for 30 min in a low-pressure chamber. Afterward, three samples of different PTFE nanoparticle/PDMS composition with PTFE nanoparticle (200 nm, Polysciences) weight ratios of 1 wt %, 8 wt %, and 15 wt % are prepared. After adding PTFE nanoparticles to the PDMS mixture, each of the samples is stirred manually for at least 10 min and mixed and defoamed with the centrifugal mixer, as described above, to ensure a good distribution of the PTFE nanoparticles within the PDMS. After subsequent degassing for 30 min, all samples are cured in an oven at 70 °C for about 12 h. Next, three composite samples containing PTFE and one intrinsic PDMS sample are treated with CF_4/O_2 plasma in a commercially available Diener Tetra30 plasma chamber. The CF_4/O_2 gases are introduced to a pressure-regulated plasma chamber at a 50%/50% mass flow ratio using integrated mass flow controllers which are situated upstream of the plasma chamber and regulate the CF_4 and O_2 mass flows to 29 and 36 sccm, respectively. The mass flow controllers regulate the chamber pressure to 60 Pa (pascal), whereas the roots pump evacuates the chamber downstream at a constant flow rate. The plasma chamber walls serve as the negative electrode, whereas the substrate-bearing surface acts as the positive electrode. After a constant chamber pressure is reached, the plasma is ignited using a 4 kHz generator at a power of 900 W. The samples are plasma-treated for 90 min. Afterward, the prepared samples are stored for about 1 h in ambient atmosphere before the contact angles are measured.

Fabrication of PDMS/PTFE Sample with Microchannels. To demonstrate that all surfaces of the microfluidic channels are superhydrophobic, we prepared a PDMS/PTFE composite chip which is an exact replica of a star-shaped silicon nozzle (Figure 1a). The star-shaped nozzle is fabricated by deep reactive-ion etching. The replication is done by a double-casting process. The first fabrication step

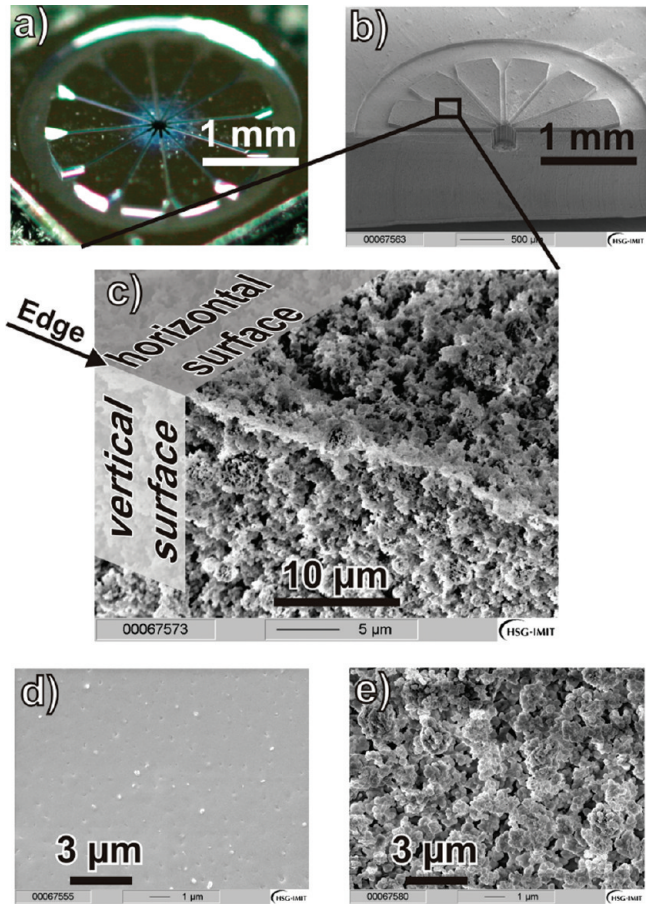

Figure 1. (a) Star-shaped structure fabricated in silicon. (b) The cut chip of PTFE/PDMS composite. (c) SEM picture of an edge showing horizontal and vertical surface. (d) Untreated surface of sample with 15 wt % PTFE particles. (e) Plasma-treated surface of sample with 15 wt % PTFE particles.

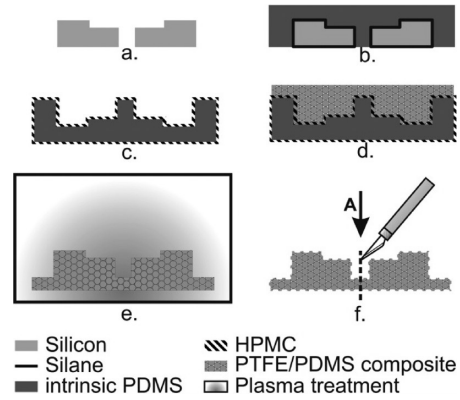

Figure 2. Fabrication steps of a completely superhydrophobic PDMS chip.

uses the star-shaped silicon nozzle as a master structure to form a negative PDMS structure (Figure 2a). Beforehand, a silane monolayer is deposited onto the silicon structure, a process which takes about 24 h. An intrinsic PDMS/curing agent mixture (10:1 ratio) is prepared as described earlier, and poured onto the silicon nozzle (Figure 2b). After degassing for 30 min and curing for 12 h at 70 °C, the PDMS structure is easily removed from the star-shaped silicon structure. This PDMS

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structure now serves as a microstructured negative master for the following casting process, leading to a positive structure again. As casting PDMS from a PDMS mold is difficult due to the good adhesion between the PDMS layers, we employed a simple method for casting PDMS on PDMS, which was introduced by Gitlin et al. (2009).[17] The process requires pretreatment of the PDMS master with a dilute aqueous solution of hydroxypropyl methyl cellulose (HPMC) (Figure 2c). The thin HPMC layer prevents adhesion and does not impede removal of the structures from the mold. After deposition of the thin HPMC layer onto the PDMS master, the prepared dispersion of 15 wt % PDMS and PTFE particles (see previous section for preparation details) is poured onto the PDMS master (Figure 2d). After degassing and 12 h of curing at 70 °C, the PDMS/PTFE composite chip can be easily removed from the mold. The resulting PDMS/PTFE structure is now a positive copy of the star-shaped silicon chip structure. It is covered solely by a thin PDMS/PTFE layer and is processed in the plasma chamber as described in the previous section (Figure 2e). We want to emphasize that the PDMS/PTFE chip was lying flat in the plasma chamber, i.e., it was not flipped, rotated, or placed diagonally within the plasma chamber.

EXPERIMENTAL SECTION

Demonstration of the Superhydrophobicity of Vertical Surfaces. The superhydrophobicity of vertical walls is demonstrated by cutting the entirely processed PDMS/PTFE composite chip in half (Figure 2f). This PDMS/PTFE chip (Figure 1b) is positioned upright, so that water droplets can be deposited onto the cavity which previously formed the vertical walls of the PDMS/PTFE composite chip. The cavity structure is about 180 μm in diameter and 300 μm in depth and thus does not allow the deposition of small droplets via the sessile drop method. Instead, a contact-free, drop-on-demand dispenser (PipeJet,[18] BioFluidix GmbH) is used to shoot single drops onto the previously vertical structure. A series of photos (Figure 3a) shows a single flying droplet as it approaches and leaves the cavity. The droplet impinges directly on the cavity and bounces back without any pinning or sticking effects (see Supporting Information for video capture). Furthermore, SEM images of casted channels show the nanoroughness near an edge where horizontal as well as vertical surfaces are visible (Figure 1c). To exclude the option that the observed superhydrophobicity is related to the microstructure of the cavity itself, the experiment is repeated with an identical microstructure in intrinsic PDMS. Figure 3b shows that the droplet sticks to the structure in intrinsic PDMS, thus demonstrating that the introduced fabrication process for the PDMS/PTFE composite is responsible for the complete superhydrophobicity of the surfaces.

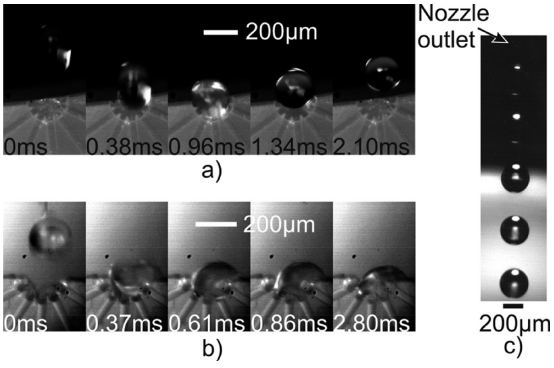

Figure 3. (a) Water droplet dispensed onto the cut structure of the completely superhydrophobic PDMS/PTFE chip, viewed from direction A (refer to Figure 2f). (b) Water droplet dispensed onto an identical structure in an intrinsic PDMS chip. (c) Application of the completely superhydrophobic nozzle for continuous dispensing of water drops.

Application of Completely Superhydrophobic Nozzles for Continuous Liquid Droplet Generation. Metz et al. (2008)[19] introduced a tubing design with a star-shaped cross section for multiphase flow that minimizes gas bubble resistance and therefore prevents clogging of tubes by gas bubbles. The star-shaped cross section of the tube features so-called grooves and fingers. Clogging is prevented by centering the gas bubble within the fingers of the star-shaped cross-section geometry so that liquids flow past the bubble within the tube grooves (detailed information available in Metz's study[19]). Based on this work, we inverted the working principle of these star-shaped tubes, applied them to silicon nozzles (Figure 1a) and introduced a method for the pneumatic dispensing of nano- to picoliter droplets of molten metal with the so-called StarJet method where liquid metal is centered between the nozzle fingers and gas flows through the nozzle grooves.[20] In the case of molten metals, the liquid is centered within the silicon nozzles by the intrinsic high contact angle between liquid metal and silicon substrate. The high advancing and receding contact angles (typically above 140°[21]) prevent pinning of molten metal within the structure. However, while liquid metals are not pinning to the star-shaped cross-section geometry, aqueous liquids generally pin within the nozzle structures when the receding contact angle is not sufficiently high. This leads to clogging of the nozzle and accumulation of the aqueous liquid at nozzle outlet and prevents any dispensing of single droplets. Therefore, a completely superhydrophobic star-shaped nozzle from PDMS is fabricated and used to dispense single droplets by applying a constant pneumatic gas pressure. Figure 3c demonstrates the continuous drop generation of deionized water with a constant actuation pressure of 1000 Pa without any pinning and accumulation of liquid at the nozzle outlet. More information on the dispensing performance can be found in the Supporting Information.

Contact Angle Measurements. The previously fabricated samples were characterized by their advancing (CA_{adv}) and receding contact angles (CA_{rec}) for deionized water. In the case of samples which had not been modified by plasma treatment, the results of the contact angle measurements (Figure 4) do not show any significant dependence on the PTFE particle concentration. Their mean advancing and receding contact angles are 116° ± 6° and 94° ± 8°, respectively. This indicates that the PTFE particles are almost completely covered by the PDMS matrix material, suppressing any superhydrophobicity (Figure 1d). By contrast, plasma modification has a significant effect on the advancing and receding contact angles because the plasma etching of PDMS uncovers the PTFE particles which cause superhydrophobicity (Figure

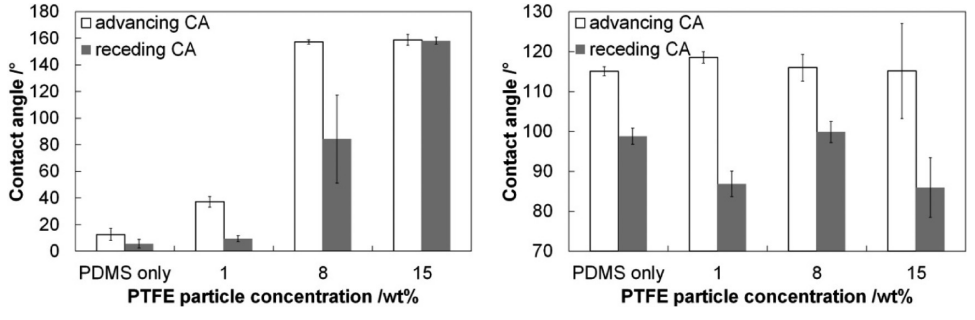

Figure 4. Contact angle measurements on the plasma-modified samples (left) and untreated samples (right).

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1e). For low PTFE particle concentration (0 wt % and 1 wt %), the advancing and the receding contact angles are both less than 40°. Thus, the PTFE particle concentration is too low to form multiscale roughness and the plasma treatment just activates the PDMS surface, leading to hydrophilic PDMS surfaces. In the case of 8 wt % PTFE particle concentration, the surface exhibits $CA_{adv} = 157° \pm 2°$ and $CA_{rec} = 84° \pm 33°$, resulting in a contact angle hysteresis of around $CA_{hys} = 73°$. If the PTFE particle concentration is increased to 15 wt %, the contact angle hysteresis drops to $CA_{hys} = 1°$ as the advancing and receding CAs are $CA_{adv} = 159° \pm 4°$ and $CA_{rec} = 158° \pm 3°$, respectively. Samples with 15 wt % PTFE concentration also exhibit long-term superhydrophobicity, which was tested for samples that were stored for 3 months in ambient atmosphere. Although PTFE particles lead to superhydrophobicity of the prepared PDMS/PTFE samples, they also become opaque. Details on light transmission of the 15 wt % PTFE sample can be found in the Supporting Information.

CONCLUSIONS

This study presents an approach to fabricate completely superhydrophobic PDMS microchannels. In contrast to previous studies, the method enables superhydrophobicity to be achieved on both horizontal and vertical surfaces. The straightforward fabrication of such microchannels consists of two main steps: (1) casting a microstructure with the composite material of PDMS/PTFE particles and (2) CF_4/O_2 plasma treatment for isotropic PDMS etching to uncover the hydrophobic multiscale roughness of the PTFE particles (compare Figure 1d and e). As the plasma treatment is responsible for isotropic etching of PDMS, it is possible to generate horizontal and vertical superhydrophobic surfaces in one processing step. This is demonstrated by the microstructure in Figure 3, which is 180 μm in diameter and 300 μm in depth (aspect ratio of 1.6), and by Figure 1c displaying both the horizontal and vertical surface. In particular, this approach enables the fabrication of superhydrophobic nozzles for any contact-free dosage application. If the plasma is applied using plasma stamps, it is possible to generate superhydrophobic spots on the PDMS surfaces and channels. These can be applied as self-organizing surfaces, and in the case of superhydrophobic channels, they can be used to reduce drag and viscous forces in microfluidic applications.

ASSOCIATED CONTENT

Supporting Information

Pictures of the dispensing performance of water and measurements on light transmission of the PDMS/PTFE composite material. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

PTFE, polytetrafluorethylene; PDMS, polydimethylsiloxane; HPMC, hydroxypropyl methyl cellulose; CA, contact angle

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