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Autonomous Control of Fluids in a Wide Surface Tension Range in Microfluidics

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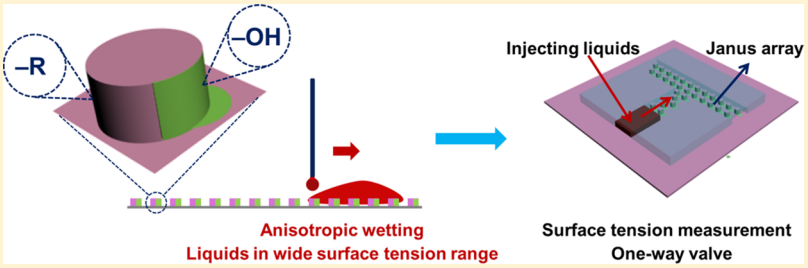
Supporting Information



ABSTRACT: In this paper, we report the preparation of anisotropic wetting surfaces that could control various wetting behaviors of liquids in a wide surface tension range (from water to oil), which could be employed as a platform for controlling the flow of liquids in microfluidics (MFs). The anisotropic wetting surfaces are chemistry-asymmetric "Janus" silicon cylinder arrays, which are fabricated via selecting and regulating the functional groups on the surface of each cylinder unit. Liquids (in a wide surface tension range) wet in a unidirectional manner along the direction that was modified by the group with large surface energy. Through introducing the Janus structure into a T-shaped pattern and integrating it with an identical T-shaped poly(dimethylsiloxane) microchannel, the as-prepared chips can be utilized to perform as a surface tension admeasuring apparatus or a one-way valve for liquids in a wide surface tension range, even oil. Furthermore, because of the excellent ability in controlling the flowing behavior of liquids in a wide surface tension range in an open system or a microchannel, the anisotropic wetting surfaces are potential candidates to be applied both in open MFs and conventional MFs, which would broaden the application fields of MFs.

INTRODUCTION

In recent years, microfluidics (MFs) have gained popularity owing to the shortened analysis time, portability, low cost, and reduced sample volume. MFs have been applied to a variety of research fields such as chemistry, biochemistry, and medical detection.[1−8] In MF systems, flow control of the fluids in microchannels is important, and the functions such as timing reaction, metering samples, and pumping liquids are usually realized with the assistance of additional microvalves. Conventional microvalves utilizing the stumbling-block mode including mechanical[9−12] and stimuli-responsive hydrogel-based valves[13−15] require external control parts in the channels or changes in the physical/chemical environment of fluids, which limit the applications. In microchannels, because of the large surface-to-volume ratio, the inner walls have a great effect on the flow behaviors of liquids. Therefore, researchers fabricated passive microchannels with surface modification to achieve fluid control and microvalve simplification.[16,17]

Among the passive channels prepared by the surface modification method, employment of asymmetric structures to manipulate the fluid flow has become a promising alternative.[18−22] For example, the asymmetric ratchet structures, Janus silicon elliptical pillar arrays, and stooped nanohairs within microchannels could finely control the fluid flow in MFs.[19,21,22] In these cases, fluid was directed to flow in a desirable direction, which was ascribed to the anisotropic wetting surfaces that possess inhomogeneous energy barrier distribution in different directions. Moreover, most of the prepared passive microchannels were utilized to control the flow behavior of water, while controlling the oil flow in microchannels is still difficult to achieve because of the low surface tension of oil compared with water. Actually, in addition to water, surface tension is quite different in various kinds of liquids, such as oil, ethanol aqueous solution, and other functional liquids, which are frequently used. Manipulating the flow behavior of liquids with different surface tensions would

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further broaden the application fields of MFs. Although an electrokinetically controlled oil droplet valve for sequential MF operations was prepared to detect pathogens, it still needs complicated external control parts, which greatly increases the cost.[23] Therefore, fabricating passive microvalves that could manipulate the flow behavior of liquids is an urgent need. Furthermore, with the development of MFs, open MF systems that worked on planar chips offer a promising mode of digital MFs, which minimizes the contact between the microchannel walls and the fluids, thus eliminating the risk of nonspecific surface absorption of reagents and air-bubble clogging.[24−27] In a word, it is highly desirable to prepare a multifunctional anisotropic wetting surface, which could achieve fluid control in a wide surface tension range (especially from water to oil) in both open MFs and microchannels of conventional MFs.

In recent years, many anisotropic wetting surfaces have been fabricated and investigated with the help of introducing asymmetric morphology,[22,28−31] groove structures,[32−36] or chemical heterogeneity.[37−41] Recently, we have reported the anisotropic wetting surfaces through employing Janus systems, which could induce unidirectional wetting in certain liquids (water or oil), and proposed a preparation strategy.[42] In the present work, we combined Janus systems with some typical groups (−COOH, −OH, −F, and $-CH_3$) to exploit and fabricate anisotropic wetting surfaces, which could manipulate the wetting behavior of liquids in a wide surface tension range (from water to oil). The results showed that the liquids in a wide surface tension range all wet in a unidirectional manner on the as-prepared Janus 1-hexadecanethiol (HDT)−OH silicon cylinder arrays (Si-CAs). We proposed the preparation strategy and further report that the Janus arrays are an excellent flow control device for both open and conventional MF systems. After introducing the Janus structure into a T-shaped pattern and coupling the as-prepared surface with a T-shaped poly(dimethylsiloxane) (PDMS) channel, MF chips with different functions were prepared. Through regulating the surface properties of the PDMS channel, typical PDMS (large interaction between the liquids and the channel) or oleophobic molecule-blended PDMS channels (weak interaction between the liquids and the channel) were introduced to prepare a surface tension admeasuring apparatus or one-way valve for liquids in a wide surface tension range.

EXPERIMENTAL SECTION

Materials. Silicon wafers (100) were cut into small pieces with the size of 2.0 cm × 2.0 cm and immersed in piranha solution (7:3 concentrated H_2SO_4/30% H_2O_2) for 2 h at 70 °C to create hydrophilic surfaces and then rinsed with ethanol and Milli-Q water (18.2 MΩ cm^{-1}) repeatedly. Before use, the substrates were dried in a nitrogen flow. The initial wafer for mold fabrication was borosilicate glass (SG-2506; with a 145 nm thick chrome film and a 570 nm thick S-1805-type positive photoresist, Changsha Shaoguang Chrome Blank Co. Ltd.). A curing agent for PDMS and a SYLGARD 184 elastomer base were purchased from Dow Corning (Midland, MI). BP212-37S positive photoresist was purchased from Kempur Microelectronics, Inc., Beijing, China. Polystyrene microspheres (1 μm in diameter), trichloro(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silane (PFS), 16-mercaptohexadecanoic acid (MHA), and HDT were all purchased from Aldrich. Chromium etchant was purchased from Transene Company Inc., USA. Ethylene, diiodomethane, sulfuric acid, hydrogen peroxide, absolute ethanol, sodium hydroxide, toluene, hydrofluoric acid, nitric acid, ammonium fluoride, 1,2-dichloroethane, rapeseed oil, and hexadecane were used as received. Water used in the experiments was deionized.

Preparation of Janus HDT−OH-Modified Si-CAs. Si-CAs were prepared by the combination of interfacial self-assembly and colloidal lithography (the detailed fabrication process can be seen in Supporting Information "Process 1").[43] Then, the as-prepared Si-CAs were treated in oxygen plasma cleaner for 5 min. After that, Cr (3 nm in thickness, to improve the adhesion between Au and the substrate) followed by Au (20 nm in thickness) was selectively deposited on one side of the cylinders via oblique 45° thermal evaporation. After immersing the Janus arrays into an ethanol solution of HDT with a concentration of 3 mM for 10 min, Janus HDT−OH-modified Si-CAs were obtained.[42]

Flow Behavior of Liquids with Different Surface Tensions in the Microchannel upon the Janus Surface. Preparation of glass mold was carried out as reported before.[44] Here, two types of PDMS-based microchannels were fabricated. Microchannel 1: typical PDMS, which was prepared by mixing the PDMS precursor and curing agent (10:1).[44] Sample 2: PFS-blended PDMS.[45] PFS was first added into the typical PDMS mixture with a PFS/PDMS weight percentage of 1.00%. The two kinds of mixtures were stirred and fully degassed. After casting the two kinds of mixtures onto the glass molds, the molds were put into an oven to cure at 100 °C for 30 min. After being detached from the glass molds, the two PDMS microchannels were compressed onto the Janus surfaces and connected to a microfluidic flow control system (MFCS and Flowell, Fluigent) using a poly(tetrafluoroethylene) (PTFE) pipe. The liquids in the microchannels were pressure-driven. The liquids of different surface tension values were obtained as follows: for 70−40 mN/m, the liquids were prepared by mixing water and ethanol with different mass fractions of ethanol, and for 30−20 mN/m, frequently used oils were selected (rapeseed oil, 1,2-dichloroethane, and hexadecane).

Characterization. A JEOL FESEM 6700F electron microscope was used to take scanning electron microscopy (SEM) images with an acceleration electron energy of 3 kV, and the surface was sputter-coated with 2 nm Pt before testing. Chemical compositions of the Janus arrays were confirmed by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250). Wetting behavior of the liquids on the surfaces ("Sessile drop " mode) and the surface tension of the liquids were measured via DataPhysics OCA20 ("Pendant drop" mode). An Olympus fluorescence microscope was employed to record the flow behavior of the liquids and to take the optical microscopy images.

RESULTS AND DISCUSSION

Preparation of Janus HDT−OH-Modified Si-CAs. Wetting Behavior of Liquids on Janus HDT−OH-Modified Si-CAs. Janus HDT−OH-modified Si-CAs were prepared through colloidal lithography and asymmetric modification. As shown in the schematic of the Janus HDT−OH-modified Si-CAs (Figure 1a), two sides of the Si-CAs were modified by −OH and $-CH_3$ asymmetrically. Si-CAs were first prepared through colloidal lithography. The cross-sectional SEM image of the as-prepared Si-CAs shows the silicon cylinder with an average diameter of about 685 nm and a height of about 375 nm (Figure S1a). We found the uniformity over a

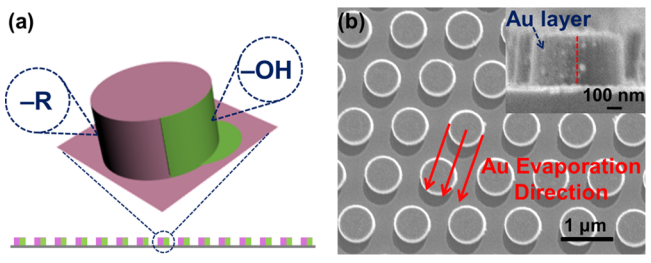

Figure 1. (a) Schematic of the as-prepared asymmetric surface. (b) Top-view SEM image of the Janus HDT−OH Si-CAs, the red arrows represent the direction of Au deposition. The inset image shows the cross section of the asymmetric Si-CAs.

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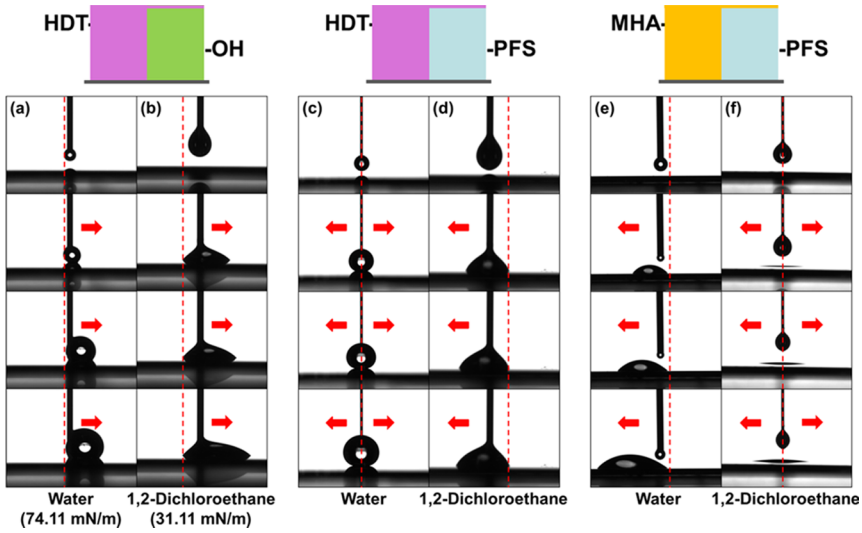

Figure 2. Time-lapse photographs of wetting behavior of 10 μL water and 1,2-dichloroethane on Janus HDT−OH (a,b), HDT−PFS (c,d), and MHA−PFS Si-CAs (e,f). The surface tension values of water and 1,2-dichloroethane are 74.11 and 31.11 mN/m, respectively. The red dotted lines represent the center axis of the syringe needle (c,f) and right (d,e) and left (a,b) positions of the liquid droplets when they are in contact with the asymmetric surface. The red arrows indicate the moving direction of liquids. The PFS- and −OH-modified directions were all placed on the right side when taking photographs.

large area is well (Figure S2). The red arrows in the top-view SEM image of the Janus surface present the direction of Au deposition (Figure 1b). The dark crescent-shaped shadows showed the asymmetric nature of the arrays because one side of the Si-CAs was Au (modified by HDT), whereas nearly no Au was deposited on the other side. The inset image in Figure 1b shows the cross section of the Janus surface, which clearly shows the asymmetric structure. Further detailed characterizations of the Janus surfaces are shown in Figure S1.

It is well-known that water possesses large surface tension, whereas typical oils possess low surface tension (about 30 mN/m).[46] Thus, we first evaluated the wetting behavior of water (74.11 mN/m measured by DataPhysics OCA20, Figure S3) and 1,2-dichloroethane (31.11 mN/m, measured by DataPhysics OCA20, Figure S3, which was selected as an experimental oil) on the Janus HDT−OH Si-CAs. Figure 2a,b shows the time-lapse photographs of the wetting behavior of 10 μL water and 1,2-dichloroethane on the Janus HDT−OH-modified Si-CAs. The −OH-modified direction was placed on the right side when taking photographs. The red dotted lines in Figure 2a,b represent the left positions of the liquid droplets when they are in contact with the asymmetric surface. Indicated by the red dotted lines in the photographs, we found that Janus HDT−OH Si-CAs direct both water and oil wet in a unidirectional manner toward the −OH-modified direction. Similar phenomena were not found based on other asymmetric surfaces, such as Janus HDT−PFS or MHA−PFS Si-CAs (Supporting "Process 2" and Figure S1). Among them, Janus HDT−PFS Si-CAs direct isotropic movement in water (Figure 2c), whereas they induce unidirectional wetting in oil toward the HDT-modified direction (Figure 2d). Opposite results were found on Janus MHA−PFS Si-CAs, which manipulate unidirectional wetting in water along the MHA-modified direction (Figure 2e) but isotropic wetting in oil (Figure 2f). Therefore, Janus HDT−OH Si-CAs possess the potentiality to manipulate the wetting behavior of liquids in a wide surface tension range. Meanwhile, other oils such as rapeseed oil (32.86 mN/m, measured by DataPhysics OCA20) and hexadecane (with a lower surface tension, 27.75 mN/m measured by DataPhysics OCA20) were selected to investigate the universality of the Janus HDT−OH Si-CAs for oil. As shown in Figure 3a,b, similar results were found as mentioned before. The Janus

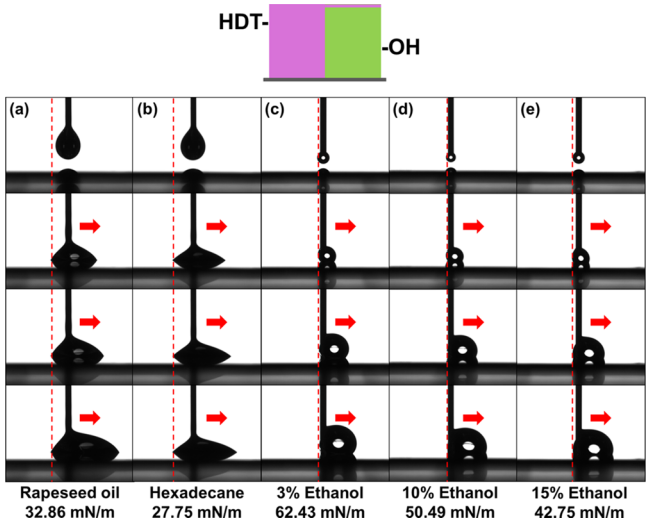

Figure 3. Time-lapse photographs of wetting behavior of 10 μL rapeseed oil (a), hexadecane (b), and solutions of different mass fractions of ethanol on the Janus HDT−OH Si-CAs (c−e). Liquids possess different surface tension values that are 32.86 (a), 27.75 (b), 62.43 (c), 50.49 (d), and 42.75 mN/m (e). The red dotted lines represent the left positions of the liquid droplets when they come in contact with the asymmetric surface. The red arrows indicate the moving direction of liquids. The −OH-modified direction was placed on the right side when taking photographs.

HDT−OH Si-CAs also controlled unidirectional wetting in rapeseed oil and hexadecane toward the −OH-modified direction.

The size of the Si-CAs is critical to the wetting behavior of liquids. We fixed the height of the Si-CAs (375 nm) and prepared another three Si-CAs with diameters of about 840, 705, and 465 nm(Figure S4a−c). The wetting behavior of

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rapeseed oil on Janus HDT−OH-modified Si-CAs was selected as an example. We modified the three kinds of Si-CAs with HDT−OH and tested the wetting behavior of the oil on them. Results are shown in Figure S4e−g, and the −OH-modified direction was placed on the right side. We found that the three kinds of asymmetric Si-CAs all induced unidirectional wetting in oil toward −the OH-modified direction. Therefore, we conclude that the distance between pillars does not influence the anisotropic property of the asymmetric Si-CAs. The only difference found was that the oil contact angle (CA) on the three surfaces was different, as shown in Figure S4e−g, a larger diameter of the Janus Si-CAs and a smaller oil CA on it. This is attributed to the change in the roughness of the surface. It is known that the wettability can be enhanced greatly by increasing the roughness of the surface.[46] In our experiment, the oil CA on the Janus Si-CAs was oleophilic (Figure S4e−g); thus, when the roughness of the surface was increased (Si-CAs with larger diameter), the oil CA would be more oleophilic (a smaller oil CA on it). Moreover, we also prepared Si-CAs with a different cycle (500 nm). As shown in Figure S4d, the size of the as-prepared Si-CAs was 315 nm in diameter and 245 nm in height. After asymmetric modification, oil also showed unidirectional wetting on it (Figure S4h). Therefore, in the following experiments, we used the original size of the Si-CAs with a diameter of 675 nm and a height of 375 nm.

If surfaces possess the ability to direct anisotropic wetting in liquids (in a wide surface tension range), it would be excited. It would broaden the application ranges of the surfaces. The Janus HDT−OH Si-CAs could control the wetting behavior of liquids with both large and low surface tension. We suspect that the wetting behavior of liquids with surface tension between water and typical oils may also be controlled by the Janus HDT−OH Si-CAs. Therefore, to prove our assumption, we investigated the wetting behaviors of liquids with different surface tensions on the as-prepared Janus HDT−OH Si-CAs. First, we prepared ethanol aqueous solution with different mass fractions and measured their surface tension values using the pendant drop method (DataPhysics OCA20). As shown in Table 1, the surface tension of liquids increases with the decrease in the ethanol fraction. When the mass fractions of ethanol are 3, 10, and 15%, the surface tension values of liquids are 62.43, 50.49, and 42.75 mN/m, respectively. After characterizing the wetting behaviors of the ethanol aqueous solutions on the asymmetric surfaces, we summarized the results as shown in Figure 3c−e. It is evident that the Janus surface could induce unidirectional wetting in the above three types of solutions toward the −OH-modified direction. We also investigated the wetting behavior of other liquids with moderate surface tension, such as ethylene glycol (47.90 mN/m, Figure S5a) and diiodomethane (50.43 mN/m, Figure S5b). We found that Janus HDT−OH Si-CAs direct both ethylene glycol and diiodomethane wet in a unidirectional manner toward the −OH-modified direction indicated by the red dotted lines in the photographs (Figure S5c,d).

Table 1. Surface Tension Values of Solutions of Different Mass Fractions of Ethanol, and Their Detailed Wetting Parameters on the Janus HDT−OH Si-CAs

wt %	surface tension (mN/m)	wetting characteristic
0.0	74.11	unidirectional
3.0	62.43	unidirectional
10.0	50.49	unidirectional
15.0	42.75	unidirectional

In air, the surface with larger surface energy is easy for wetting the liquids.[47] The surface energies of HDT-, −OH-, PFS-, and MHA-modified flat silicon surfaces are 23.32, 120.22, 12.77, and 76.69 mN/m, respectively.[42] Comparison of HDT−PFS-modified Si-CAs and MHA−PFS-modified Si-CAs shows the difference in the upper surface of the two asymmetric surfaces. The upper surfaces are modified by HDT and MHA molecules, which result in different surface tension differences in the two asymmetric surfaces. The small surface tension difference in Janus HDT−PFS Si-CAs nearly plays no effect on the wetting behavior of water, resulting in isotropic movement of water on it; meanwhile, the small surface energy of HDT- and PFS-modified regions helps the water droplet to maintain a hydrophobic state. However, for the MHA−PFS-modified asymmetric surface, water moves toward the MHA-modified direction owing to the relatively large surface tension difference. Moreover, liquids with lower surface tension (like oil) are easier to wet on the same surface compared with water,[47] which results in the oleophilic state of HDT- and MHA-modified regions in air.[42] However, the extreme low surface tension of the PFS-modified region results in the oleophobic state. Note that compared with HDT, the MHA-modified region possesses ultrafast wetting speed for oil. In this case, for Janus MHA−PFS Si-CAs, when oil is dropped onto the surface, the PFS-modified region could be neglected, causing isotropic wetting in oil, while oil shows unidirectional wetting on Janus HDT−PFS Si-CAs. For Janus HDT−OH Si-CAs, compared with Janus HDT−PFS Si-CAs, the upper surface is retained, and the surface energy difference is enlarged. Hence, we ascribe the excellent property of the Janus HDT−OH Si-CAs to the considerable surface tension difference between the two sides of the Si-CAs and the upper surface that possesses a slow wetting speed for liquids with low surface tension. Whether liquids with high (water), moderate (ethanol aqueous solution), or low surface tension (hexadecane), when they are gradually dropped onto the Janus HDT−OH surface, air−liquid−solid three-phase contact line would move from a low surface tension region (HDT) to a high surface tension region (−OH) at every silicon cylinder, which caused unidirectional wetting in liquids toward the −OH-modified direction. Therefore, a strategy for preparing anisotropic wetting surfaces that could manipulate the wetting of liquids in a wide surface tension range is proposed. Two factors need to be taken into consideration. One is finding two molecules with a relatively large surface energy difference to be modified asymmetrically onto Si-CAs and the other is that the upper surface should possess a slow wetting speed for oil.

Unlike the anisotropic wetting surfaces with an asymmetric morphology, such as line-patterned surfaces, liquids with low surface tension have low wetting anisotropy when they are dropped onto the patterns.[38] The chemistry-asymmetric Janus surface is excellent owing to the strong capacity of controlling unidirectional wetting (from water to oil) in liquids, which could be applied in open MFs for guidance and operation of fluids. In addition, because of the wide range of regulation, the Janus surface may meet more applications of open MFs that require different kinds of liquids as microfluids.

Microfluid Manipulation in a Wide Surface Tension Range Based on the Asymmetric Si-CAs. *Fabrication of a Surface Tension Admeasuring Apparatus for Liquids Based on the Asymmetric Si-CAs.* As shown before, the Janus HDT−

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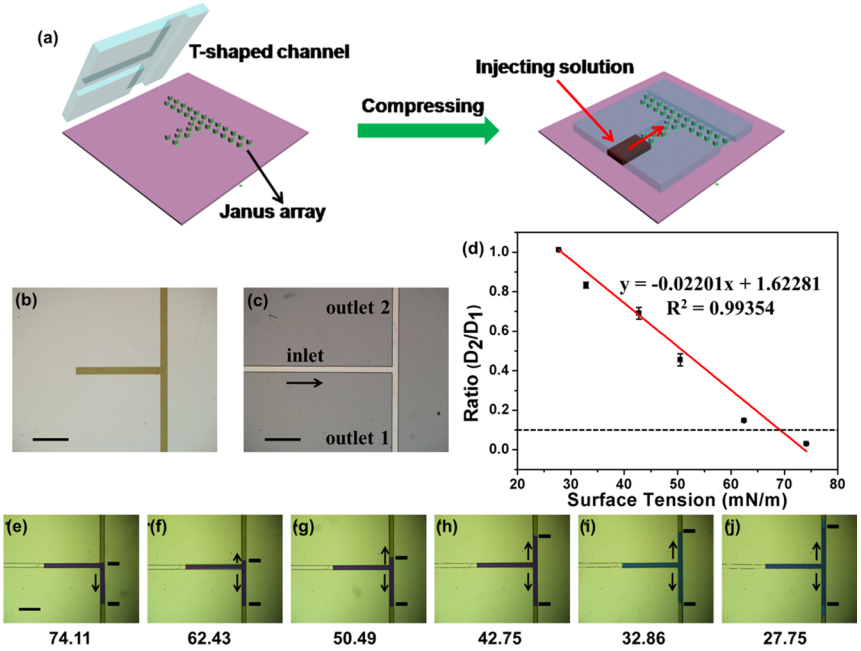

Figure 4. (a) Schematic illustration of the fabrication of a T-shaped microchannel upon the Janus HDT−OH Si-CAs in a T-shaped pattern. (b) Optical microscopy image of the Si-CAs employed in a T-shaped pattern, and the width of the pattern is 200 μm. (c) Optical microscopy image of the T-shaped microchannel (top = 146 μm, bottom = 200 μm, and height = 25 μm). The black arrow represents the injection direction of liquids. (d) Plots of the ratio (D_2/D_1) as a function of the surface tension of the liquids. The microchannel is fabricated from a typical PDMS. D_1 and D_2 represent the flow distances in outlets 1 and 2, respectively. (e−j) Flow behavior of liquids (with diminishing surface tension) in the T-shaped typical PDMS microchannel bonding Janus HDT−OH Si-CAs. The black lines represent the position of liquids, and the arrows represent the moving direction of liquids in the two outlets. The scale bars are 1 mm, and the flow speed is ∼0.25 mm/s.

OH Si-CAs presented strong ability of inducing the movement of liquids (unidirectional wetting). We speculate that the as-prepared asymmetric surface possesses the ability to manipulate the liquid motion in MF channels. To evaluate the microfluid manipulation ability of the Janus HDT−OH Si-CAs, we integrated the asymmetric structure into a T-shaped pattern and compressed a T-shaped typical PDMS microchannel with the same width upon the surface (Figure 4a, schematic illustration). The Si-CA-based T-shaped pattern was prepared by the combination of photolithography and colloidal lithography (see Supporting "Process 3"). Figure 4b shows the optical microscopy image of the Si-CAs employed in a T-shaped pattern. The optical microscopy image of the T-shaped microchannel is shown in Figure 4c, while the black arrow represents the injection direction of liquids. The widths of the T-shaped pattern and microchannel are both 200 μm. In our MF chip, outlet 1 is along the −OH-modified direction, whereas outlet 2 is along the HDT-modified direction, and the two outlets were both connected to the surrounding atmosphere. Liquids were injected into the inlet microchannel through a PTFE pipe, and the flow speed was kept at ∼0.25 mm/s by adjusting the applied pressure. Figure 4e−j shows the flow behavior of liquids with diminishing surface tension in the T-shaped typical PDMS microchannel bonding Janus HDT−OH Si-CAs. The black lines represent the position of liquids in the two outlet microchannels, and the arrows represent the direction of liquid movement in the two outlets. For water (liquid with a large surface tension, 74.11 mN/m), as shown in Figure 4e, it only flows into outlet 1 while pins at the beginning of outlet 2. In other words, water shows a unidirectional flow behavior in the microchannel, and the fluid motion into outlet 2 is largely suppressed. When the surface tension of the liquids (ethanol aqueous solution, 62.43 mN/m) decreased, as shown in Figure 4f, the solution was directed into outlet 1; meanwhile, just a little amount of the solution flowed into outlet 2. With further decrease in the surface tension of the liquids (the liquids in Figure 4g,h are ethanol aqueous solution with surface tension values of 50.49 and 42.75 mN/m and rapeseed oil in Figure 4i with a surface tension value of 32.86 mN/m), an increase in the amount of liquids was induced into outlet 2. Once the surface tension of the liquid reached to 27.75 mN/m (Figure 4j, hexadecane), the liquid flowed freely toward two microchannels without any differences. In conclusion, the ability of the Janus surface of inducing movement of liquids decreases with the decrease in the surface tension of the liquids. The above phenomena presented that the Janus HDT−OH Si-CAs could induce unidirectional wetting in liquids in a wide surface tension range in an open system, but it could not work in a microchannel. This should be ascribed to the interaction between the liquids and the PDMS microchannel. Actually, in MF systems, the flow behavior of fluids strongly depends on the surface property of the microchannel owing to the high surface-to-volume ratio. In previous MF systems that combine anisotropic wetting surfaces with a typical PDMS microchannel to fabricate a one-way valve for water, the interaction between water and the hydrophobic PDMS microchannel wall is negligible.[20,21] Therefore, the flow behavior of water simply depends on the wetting property of the underlying anisotropic wetting surface. However, because liquids with lower surface tension are easier to wet on the same surface,[47] in our MF system which involves liquids in a wide surface tension range, the interaction between the liquids and the PDMS microchannel should be taken into consideration. Thus, the flow behavior is not just influenced by the Janus surface, but the channel also plays an important role. As the surface tension of the liquids decreases, it becomes easier for liquids to wet the

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PDMS microchannel. When liquids with low surface tension were injected into the chip, the anisotropic wetting property would weaken. Once the surface tension of the liquid was decreased to 27.75 mN/m (Figure 4j, hexadecane), the PDMS microchannel dominated the flow behavior of the liquid while the underlying Janus surface could be neglected. That is to say, lower surface tension results in weaker anisotropic wetting property, which could explain the phenomena shown in Figure 4e–j.

Detection of the surface tension of liquids in MF systems could be applied to monitor the chemical reaction process, which contributes to the development of the future MFs. In our work, as shown in Figure 4e–j, the flow behavior of liquids with different surface tensions in the chip was different. Therefore, we can utilize the phenomena to estimate the surface tension of liquids. Table 2 shows detailed flowing parameters of liquids in a wide surface tension range in the T-shaped microchannel upon the Janus HDT–OH Si-CAs. Figure 4d shows the plots of the ratio (D_2/D_1) as a function of the surface tension of liquids. We obtain a functional relationship between D_2/D_1 value and surface tension of liquids, as shown below

$$y = -0.02201x + 1.62281$$

where y represents D_2/D_1 and x represents the surface tension of the liquids. D_1 and D_2 represent the flow distances in outlets 1 and 2, respectively. Here, we fixed D_1 to 1.8 mm. The linear relationship is in agreement with "R^2 = 0.99354". Therefore, when unknown liquids were injected into the chip, the ratio (D_2/D_1) could be measured, and the surface tension of liquids could be estimated utilizing the function.

Table 2. Flow Distance Values of Liquids in a Wide Surface Tension Range in the T-Shaped Microchannel upon the Janus HDT–OH Si-CAs[a]

surface tension (mN/m)	D_2 (mm)	D_1 (mm)	D_2/D_1
74.11	0.055 ± 0.005	1.800	0.031 ± 0.003
62.43	0.265 ± 0.007	1.800	0.147 ± 0.004
50.49	0.820 ± 0.055	1.800	0.456 ± 0.031
42.75	1.244 ± 0.053	1.800	0.691 ± 0.029
32.86	1.500 ± 0.026	1.800	0.833 ± 0.014
27.75	1.822 ± 0.000	1.800	1.012 ± 0.000

[a]Microchannel is fabricated from typical PDMS. D_1 and D_2 represent the flow distances in outlets 1 and 2, respectively. Outlet 1 is along the –OH-modified direction. Here, we fixed D_1 to 1.8 mm.

Fabrication of a One-Way Valve for Liquids in a Wide Surface Tension Range Based on the Asymmetric Si-CAs. As we all know, controlling the motion of liquids in MFs is one of the critical issues. Furthermore, MF chips possessing the ability of manipulating the flow behavior of liquids with low surface tension (especially oil) are inspiring because it would broaden the application fields. As mentioned before, although the Janus HDT–OH Si-CAs could induce unidirectional wetting in liquids in a wide surface tension range (from water oil) in an open system, the chip prepared by combining the Janus HDT–OH Si-CAs with a typical PDMS microchannel could not control the unidirectional flow of liquids inside the microchannel, which is caused by the strong interaction between the microchannel and the liquids with low surface tension. To obtain a chip that could direct liquids with a wide surface tension range in a unidirectional flow in the microchannel, the interaction between the PDMS microchannel and the liquids should be weakened, namely, oleophobic channels are needed. Zhao et al. prepared PFS-blended PDMS micropillared surfaces that exhibit the oleophobic property with an oil CA of ∼141°.[45] Following this method, we prepared a flat PFS-blended PDMS surface. Rapeseed oil was selected as an example. Figure 5a,b shows rapeseed oil CA on a flat typical PDMS and PFS-blended PDMS surface. The oil shows the oleophilic state on a typical PDMS surface with an oil CA of 62.4 ± 2.1° (Figure 5a). However, after blending PFS, the PDMS surface changes to an oleophobic state with an oil CA of 100.2 ± 1.7°. Note that the oil CA on PFS-coated PDMS surfaces was nearly the same (70°) as that on the flat typical PDMS surface (see Figure S6 and "Process 4"). Therefore, we prepared a T-shaped PFS-blended PDMS microchannel and combined the channel with the T-shaped Janus HDT–OH Si-CAs to fabricate a one-way valve for liquids in a wide surface tension range. Figure 5c–h shows the flow behavior of liquids (in a wide surface tension range) in the chip. The flow speed was kept at ∼0.25 mm/s. We found that liquids with surface tension from 74.11 to 32.86 mN/m were directed into outlet 1 (Figure 5c–g), resulting in a unidirectional flow behavior. The compatibility between the rapeseed oil and the PDMS-based channels is well. When the liquid was changed to hexadecane with very low surface tension (27.75 mN/m), our chip induced the liquid anisotropic flow in the channel (Figure 5h). Table 3 shows detailed flowing parameters of liquids in a wide surface tension range in the T-shaped microchannel upon the Janus HDT–OH Si-CAs. The microchannel is fabricated from PFS-blended PDMS. We plotted the ratio (D_2/D_1) as a function of the surface tension of

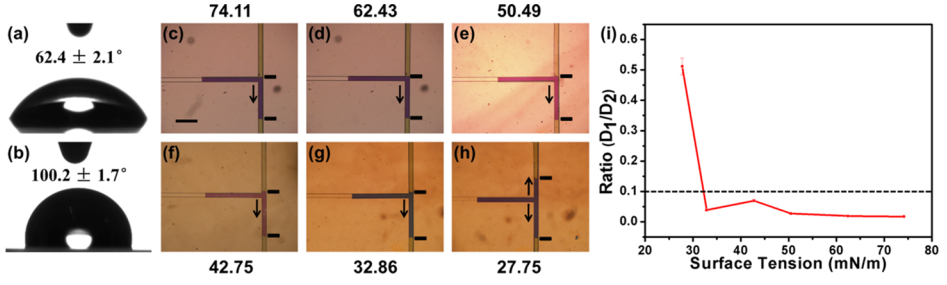

Figure 5. Rapeseed oil CA on flat typical (a) and PFS-blended (b) PDMS surfaces. (c–h) Flow behavior of liquids (in a wide surface tension range) in the T-shaped PFS-blended PDMS microchannel bonding Janus HDT–OH Si-CAs. The black lines represent the position of liquids, and the arrows represent the moving distance of liquids in the two outlets. The scale bar is 1 mm, and the flow speed is ∼0.25 mm/s. (i) Plots of the ratio (D_2/D_1) as a function of the surface tension of the liquids. The microchannel is fabricated from PFS-blended PDMS. D_1 and D_2 represent the flow distances in outlets 1 and 2, respectively. Here, we fixed D_1 to 1.8 mm.

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Table 3. Flow Distance Values of Liquids in a Wide Surface Tension Range in the T-Shaped Microchannel upon the Janus HDT−OH Si-CAs[a]

surface tension (mN/m)	D_2 (mm)	D_1 (mm)	D_2/D_1
74.11	0.031 ± 0.002	1.800	0.017 ± 0.001
62.43	0.035 ± 0.002	1.800	0.019 ± 0.001
50.49	0.049 ± 0.002	1.800	0.027 ± 0.000
42.75	0.125 ± 0.006	1.800	0.069 ± 0.001
32.86	0.070 ± 0.006	1.800	0.039 ± 0.003
27.75	0.921 ± 0.050	1.800	0.512 ± 0.028

[a]Microchannel is fabricated from PFS-blended PDMS. D_1 and D_2 represent the flow distances in outlets 1 and 2, respectively. Outlet 1 is along the −OH-modified direction. Here, we fixed D_1 to 1.8 mm.

the liquids, as shown in Figure 5i. We found that liquids with surface tension from 74.11 to 32.86 mN/m possess relatively small D_2/D_1 (<0.1) but hexadecane (27.75 mN/m) with $D_2/D_1 \approx 0.52$. In short, the chip combining a PFS-blended PDMS microchannel and Janus HDT−OH Si-CAs could be utilized as a one-way valve in MF systems for liquids in a wide surface tension range. Although the incompatibility between some organic solvents (such as hexadecane) and PDMS-based channels still exists, it just limits the working time of our microchannel for part of the organic solvents. Because of the excellent ability of the Janus surface for inducing unidirectional wetting in liquids in a wide surface tension range, we will search for a microchannel possessing lower surface energy and good compatibility with organic solvents, which may direct the liquids with relatively small surface tension in the unidirectional flow in MF systems.

CONCLUSIONS

In summary, "Janus" systems were utilized to investigate and prepare an anisotropic wetting surface, which could manipulate the wetting behavior of liquids in a wide surface tension range (from water to oil). Through colloidal lithography and asymmetric modification, the obtained asymmetric Si-CAs possess an extraordinary ability of fluid control, which directs the unidirectional wetting of liquids in a wide surface tension range. The preparation strategy is proposed, which requires two factors. One is finding two molecules with considerable large surface energy difference to modify two sides of the cylinders asymmetrically and the other is the upper surface of the Janus Si-CA needs to possess a slow wetting speed for oil. Then, the "Janus" Si-CAs were utilized to develop a platform for flowing control of liquids in a wide surface tension range in MFs. Through coupling the asymmetric surface with a T-shaped PDMS microchannel, different functional MF chips were obtained. When a typical PDMS channel was chosen, a surface tension admeasuring apparatus for liquids was prepared, and the chip could be used to estimate the surface tension of unknown liquids. If the microchannel was fabricated from PFS-blended PDMS, the as-prepared chip showed great abilities to manipulate the liquids in a wide surface tension range (even oil) in the unidirectional flow in MFs. Therefore, because of the large range of fluid control in MFs (open or conventional system), the Janus surface is a great tool to be applied in MFs and would show a broad range of applications in the future MF systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.7b01934.

Preparation of the Si-CAs and T-shaped Si-CAs; preparation of Janus HDT−PFS and MHA−PFS Si-CAs; water CA on the Si-CAs before and after −OH modification; XPS during the preparation process; surface tension measurement process; wetting behavior of ethylene, diiodomethane, and rapeseed oil on the Janus HDT−OH Si-CAs; SEM images of Si-CAs with different diameters; preparation of flat PFS-coated PDMS surfaces; and rapeseed oil CA on PFS-coated PDMS surfaces (PDF)

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Notes

The authors declare no competing financial interest.

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