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Droplet and Fluid Gating by Biomimetic Janus Membranes

Xuelin Tian, Hua Jin, Jani Sainio, Robin H. A. Ras,* and Olli Ikkala*

The ability to gate (i.e., allow or block) droplet and fluid transport in a directional manner represents an important form of liquid manipulation and has tremendous application potential in fields involving intelligent liquid management. Inspired by passive transport across cell membranes which regulate permeability by transmembrane hydrophilic/hydrophobic interactions, macroscopic hydrophilic/hydrophobic Janus-type membranes are prepared by facile vapor diffusion or plasma treatments for liquid gating. The resultant Janus membrane shows directional water droplet gating behavior in air-water systems. Furthermore, membrane-based directional gating of continuous water flow is demonstrated for the first time, enabling Janus membranes to act as facile fluid diodes for one-way flow regulation. Additionally, in oil-water systems, the Janus membranes show directional gating of droplets with integrated selectivity for either oil or water. The above remarkable gating properties of the Janus membranes could bring about novel applications in fluid rectifying, microchemical reaction manipulation, advanced separation, biomedical materials and smart textiles.

1. Introduction

Liquid droplets are among the most commonplace objects in our daily life. Their behavior and manipulation have recently attracted considerable fundamental curiosity as well as technical interest for, e.g., liquid repellant surfaces,[1] droplet translocation,[2] anisotropic spreading or sliding,[3] coalescence and bouncing,[4] digital microfluidics,[5] microchemical reactors,[6] droplet logics,[7] and even visualizing routes for static and dynamic self-assemblies.[8] Despite recent progress, developing facile methods that can directionally gate droplet and fluid transport in different environments is still challenging and in high demand for intelligent liquid management.[9] Here we show droplet and fluid manipulation via particularly simple routes that lead to directional and selective liquid gating by a membrane in liquid-liquid and liquid-air systems. This is achieved by specific hydrophilic/hydrophobic asymmetries across the membrane, which allow transport or blockage of liquid depending on the membrane direction and whether the liquid droplets are aqueous or oily.

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DOI: 10.1002/adfm.201400714

Our work is inspired by passive transport across cell membranes, which offer an intriguing example of regulating membrane permeability based on transmembrane hydrophilic/hydrophobic interactions.[10] The cell membrane has a lipid bilayer structure consisting of hydrophilic phosphate outer layers and hydrophobic hydrocarbon core layer. This structure allows spontaneous diffusion of hydrophobic molecules from the hydrophilic outer side across the hydrophobic core layer whereas hydrophilic polar molecules show reduced permeation. The cell membrane thus passively controls the permeation of molecular-sized entities, and it inspires us to apply hydrophilic/hydrophobic membrane designs to rectify gating of liquids. Instead of a membrane of nanoscale thickness, we selected technically relevant porous membranes of submillimeter-thickness to construct hydrophobic/hydrophilic asymmetry across it. Taken water transport as an example, such membrane might preferentially allow water to penetrate from the hydrophobic side, but tend to hinder its penetration from the hydrophilic side. Accordingly, we prepare two types of hydrophilic/hydrophobic Janus membranes by facile vapor diffusion or plasma treatments and demonstrate directional gating of water droplets as well as continuous water flow in air-water system. More generally, our membranes show directional gating of droplets in oil-water systems with integrated selectivity for either oil or water. Such membranes possessing both selectivity and directionality in liquid gating represent a new concept of intelligent materials. We also demonstrate the construction of "Janus trapper" to collect water droplets from oil or oil droplets from water.

2. Results and Discussion

In order to demonstrate the tunability of gating properties in Janus membranes, two approaches were incorporated, i.e., (1) to hydrophobize selectively one side of an initially hydrophilic membrane, (2) to hydrophilize selectively one side of an initially hydrophobic membrane. These approaches led to a different hydrophilic/hydrophobic balance across the membranes, which allowed complementary liquid gating properties. In the first approach, vapor of 1*H*,1*H*,2*H*,2*H*-perfluorooctyltrichlorosilane (POTS), which previously had been used to hydrophobize cellulose[11] and silica[12] aerogels, was allowed to topochemically react on one side of hydrophilic cotton fabric membrane (**Figure 1**a and Supporting Information, Figure S1). Cotton

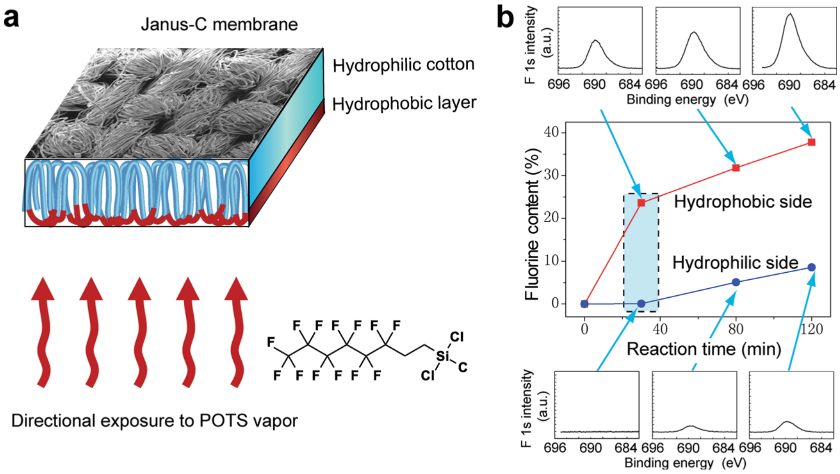

Figure 1. Preparation of Janus-C. a) Schematic illustration of the preparation method where vapor of POTS diffuses towards a cotton membrane and reacts with its surface hydroxyl groups, creating a through-plane chemical gradient. Careful control of reaction conditions renders the exposed side hydrophobic and the other side hydrophilic. b) XPS analysis of F 1s peaks on both sides of the Janus membranes with different reaction time. The green rectangle indicates Janus-C.

fabric was selected because of its easy availability and abundance of reactive hydroxyl groups, which allows hydrophobization through silanization reaction with POTS. The membrane has a thickness of ≈380 μm, composed of nearly cylindrical fiber bundles with pore size up to 200 μm (Supporting Information, Figure S2). Through control of the reaction conditions, the exposed side could become hydrophobic while the opposite shaded side remained hydrophilic. The surface compositions on both sides of the membranes prepared with different reaction times from 30 to 120 min were analyzed by X-ray photoelectron spectroscopy (XPS), which confirmed asymmetric fluorination of the membrane (Figure 1b). While the exposed side exhibits high fluorine concentration from 23.6 to 37.8 atomic% depending on the reaction time, the shaded side shows no or low fluorine content (XPS analyses of other elements are shown in Supporting Information, Figure S3 and Table S1). Notably, although the membrane prepared with 30 min reaction shows on the exposed side fluorine content of ≈23.6 atomic%, an indication of effective hydrophobic modification, the fluorine content on the shaded side remains below the detection limit, suggesting preservation of hydrophilic character. This sample thus possesses a hydrophilic/hydrophobic Janus feature (denoted as Janus-C) and is used to investigate liquid gating behaviors. An advantage of the employed vapor diffusion technique is its extreme simplicity, which had been used to produce an in-plane chemical gradient on silicon wafer,[2a] and here we show it is also effective to create a through-plane chemical gradient across membranes. In the second approach, a hydrophilic skin layer was produced by treating one side of a pristine hydrophobic teflon fabric membrane with O_2/H_2 plasma (Supporting Information, Figure S4), where the membrane was denoted as Janus-T. The membrane has a thickness of ≈134 μm with pore size of tens of micrometers. XPS shows that the plasma-treated side is enriched in oxygen, leading to hydrophilic surface properties (Supporting Information, Table S2).

The anisotropic surface chemistry across Janus-C brings out directional water gating behavior in air-water systems. As shown in **Figure 2**a, water droplets penetrate spontaneously from the hydrophobic to the hydrophilic side (the positive direction) whereas when the membrane is turned over (the reverse direction), water droplets are blocked and spread on the hydrophilic side (see also Supporting Information, Movies 1, 2). Beyond water droplets, Janus-C importantly shows directional gating for continuous water flow (Figure 2b and Supporting Information, Movie 3). The directional water penetration across Janus-C can be attributed to its anisotropic critical breakthrough pressure (P_c). Recently we demonstrated theoretically[13] that a hydrophilic/hydrophobic Janus gradient membrane possesses a larger P_c to water in the reverse direction than in the positive direction because of the coupling effect between local geometrical angle

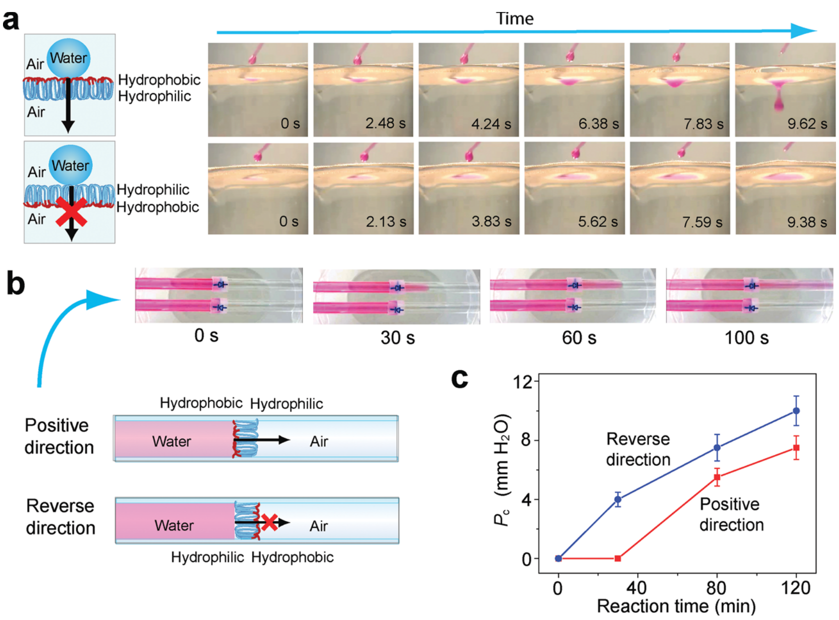

Figure 2. Directional water droplet and flow penetration across Janus-C in air-water systems. a) Unidirectional droplet penetration demonstrated by dropwise addition of water droplets (≈20 μL per droplet, dyed red with rhodamine 101) onto hydrophobic side (top) and hydrophilic side (bottom) of Janus-C. b) Schematics and sequential snapshots showing unidirectional water flow penetration through Janus-C. The membrane was sandwiched between two glass tubes (tube volume of ≈10 mL and inner diameter ≈1 cm), and water (3.5 mL) was loaded respectively on the hydrophobic (upper) and hydrophilic sides (lower) of Janus-C. c) Anisotropic critical breakthrough pressure (P_c) of Janus membranes prepared with different reaction time.

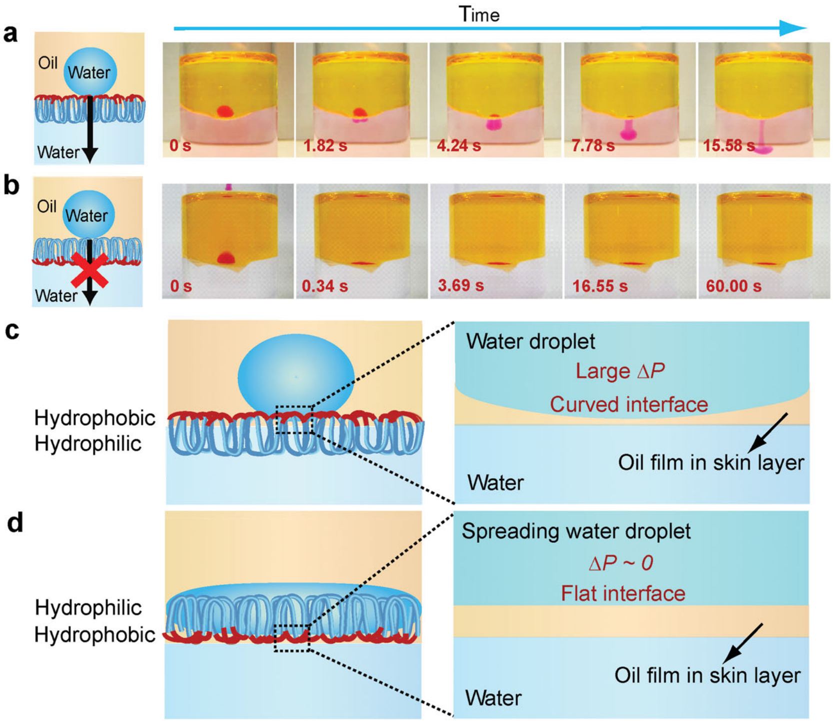

Figure 3. Directional water droplet penetration across Janus-C in oil-water systems. a) Janus-C allows penetration of water droplet (dyed red) when the hydrophobic side is towards oil (hexadecane dyed yellow by Nile red), b) and prevents droplet penetration when reversely aligned. c) For positively aligned Janus-C, a water droplet touching the hydrophobic side exerts a larger Laplace pressure (ΔP), creating a larger driving force for penetration. Consequently, the water droplet can penetrate through the thin oil-infused skin layer and further across the whole membrane. d) For reversely aligned Janus-C, a water droplet touching the hydrophilic side tends to spread, exerting limited Laplace pressure. The oil-infused skin layer is thus able to block its penetration.

and contact angle, and this anisotropy in P_c results in anisotropic penetration resistance to liquid, thus causing directional liquid penetration. It should be noted that directional droplet penetration does not ensure directional flow penetration, as the former does not necessarily require anisotropic P_c, although it is a prerequisite to the latter (see Supporting Information). The nearly cylindrical components with gradient surface chemistry of our asymmetric membranes facilitate the acquisition of anisotropic P_c,[13] which is confirmed by measuring P_c on their both sides (Figure 2c). Janus-C shows a P_c of ≈4 mm H_2O in the reverse direction, whereas in the positive direction its P_c is vanishingly small and any height of water column appears to penetrate easily through it. The moderate P_c values suggest that only a relatively thin skin layer on the hydrophobic side of Janus-C is effectively fluorinated, and the major part of the membrane gets limited or no fluorination because a highly fluorinated membrane with a pore size of ≈200 µm is estimated to give a much higher P_c (≈4γ/L, γ is water surface tension and L the pore size) at around 10 cm H_2O.

Importantly, the directional gating of continuous water flow shown here, as far as we know, is its first demonstration with a chemically asymmetric membrane, which is very desirable as it enables Janus membranes to act as a fluid diode for one-way flow regulation. The previously reported fluid diodes are generally based on intricate designs of asymmetric topologies and some of them require auxiliary channels or moving parts to gain anisotropic flow control.[14] Tedious fabrication procedures are required for such fluid diodes. Our chemically asymmetric Janus membrane provides an easy-to-prepare, scalable, and low-cost alternative for rectifying fluid diodes. Additionally, based on our theoretical work,[13] Janus membranes would allow convenient adjusting of anisotropic ratio (i.e., the ratio of P_c in the two different directions) by changing the chemical gradient, pore size, or the two layer thicknesses of the membrane. Moreover, the membrane-based configuration facilitates preparation of fluid diodes with thin and flexible structures, which can hardly be acquired on conventional fluid diodes and is important for construction of complex fluid controlling circuits.

It is interesting to consider the response of fluid gating behaviors when the membrane is stretched since stretching of fabrics would increase the spacing ratio, causing modification of wetting properties, including macroscopic contact angles and liquid breakthrough pressures. For example, wetting properties of homogeneous polyester fabrics were shown to vary considerably upon stretching, leading to switching between oleophobicity and oleophilicity.[15] In our case, anisotropic liquid breakthrough pressure is crucial for the fluid gating behaviors. As we indicated before, the anisotropic ratio of Janus membrane decreases with increased spacing ratio and can even approach 1 (i.e., anisotropy vanishes) at much larger spacing ratio.[13] Therefore, the directional liquid gating behavior is expected to become less obvious if the membrane is markedly stretched. However, unlike polyester fabric which can be largely stretched due to the high flexibility of polyester fibers, the cotton fabric we used can only be stretched to a limited extent (less than 10%) because of the poor flexibility of cellulose fibers. In this stretching range, we did not observe apparent variation of fluid gating property of the Janus membrane. Nevertheless, if more stretchable membrane materials would be employed, stretching could potentially provide a convenient way to tune the fluid gating behaviors.

Having shown the working principle for air-water system, we next investigate the liquid gating of Janus-C at the oil-water interface, using hexadecane as a model oil. When Janus-C is aligned in the positive direction (hydrophobic side towards oil), a water droplet penetrates easily through it (**Figure 3**a and Supporting Information, Movie 4). In contrast, when Janus-C is reversely aligned, the water droplet is blocked from the hydrophilic side (Figure 3b and Supporting Information, Movie 5). The unidirectional water droplet penetration through a membrane in oil-water systems has never been reported before, and it is even more intriguing than unidirectional water droplet penetration in liquid-air systems[13,16] as the former involves two liquid-liquid interfaces (i.e., droplet-oil and oil-water interfaces) whereas the latter involves only one liquid-air interface (i.e., droplet-air interface).

Accurate understanding of the unidirectional penetration behavior in the oil-water system requires the determination of the wettability profile across Janus-C (i.e., the variation of local water-in-oil contact angle across the fiber bundle surface), which is challenging to assess experimentally. The problem is further complicated by its complex surface structure and the deformation of the flexible membrane in the oil-water system as the configuration of the oil-membrane-water interface significantly affects liquid penetration. Nevertheless, this behavior could be preliminarily understood by considering the Laplace pressure of the liquid droplet and its hydrophilic/hydrophobic interaction with Janus-C. In the oil-water system, a thin oil film should be adsorbed into the fluorinated hydrophobic skin layer of Janus-C due to their similar polarity, forming a barrier for water droplet penetration. When Janus-C is positively aligned at the oil-water interface, a water droplet contacting the hydrophobic side exerts a larger Laplace pressure, creating a larger driving force for penetration (Figure 3c). Moreover, as the oil-infused hydrophobic skin layer is thin, the water droplet with large Laplace pressure can thus break through this layer and reach the underlying hydrophilic matrix layer, which then "pulls" the liquid of the same polarity across the whole membrane. In contrast, for reversely aligned Janus-C, a water droplet contacting the hydrophilic matrix layer tends to spread, giving negligible Laplace pressure, close to zero (Figure 3d). This limits the driving force for penetration, and consequently the underlying oil-infused hydrophobic skin layer is able to block the further transport of the collapsed water droplet.

Turning now to the penetration of oil droplets through Janus-C, we use dichloromethane as the model oil phase as it has higher density than water, thus allowing facile demonstration of the phenomena. Consequently, oil droplets are blocked by both positively and reversely aligned Janus-C at the oil-water interface as they bead up on both sides of the membrane (Supporting Information, Figure S5). We consider that this behavior is due to the hydrophilic/hydrophobic balance within Janus-C, where only a thin skin layer is hydrophobic and the major matrix layer keeps hydrophilic, thus preventing the penetration of oil droplets.

Hence, to facilitate unidirectional penetration of oil droplets, predominantly hydrophobic membranes with thin hydrophilic skin layers are suggested. Indeed, Janus-T having such a structural characteristic as prepared by hydrophilizing one surface of a teflon membrane, shows selective and unidirectional permeability to oil droplets in liquid-liquid system. An oil droplet penetrates from the hydrophilic side across Janus-T (Supporting Information, Figure S6a and Movie 6) and is blocked from the hydrophobic side (Supporting Information, Figure S6b and Movie 7). In contrast, water droplets are blocked by both positively and reversely aligned Janus-T at oil-water interface (Supporting Information, Figure S7), in accordance with its hydrophilic skin layer/hydrophobic matrix layer structure. Therefore, selecting a hydrophilic or hydrophobic skin layer in an oppositely-polar bulk membrane provides a feasible principle to design smart membranes with selective and unidirectional permeability to oil or water droplets in liquid-liquid systems upon proper regulation of the through-plane hydrophilic/hydrophobic profiles.

Notably, our hydrophilic/hydrophobic Janus membranes involving skin layers are conceptually different from the much studied asymmetric membranes used in desalination and the asymmetric self-assembled block copolymer membranes. The reported desalination membranes[17] have a characteristic asymmetry in physical structure (i.e., porosity and density), consisting of a dense skin layer for salt-rejection supported by a porous matrix layer, instead of the present polarity difference. The asymmetric block copolymer membranes[18] consist of a thin layer of self-assembled porosity on top of a non-ordered sponge-like supporting layer. Our Janus membranes keep a uniform physical structure, though they importantly are based on asymmetric surface chemistry with a strong polarity difference between the surface layer and the underlying part. The latter component also plays an active role in inducing the smart permeability through creating anisotropic hydrophilic/hydrophobic interfacial interaction in conjunction with the surface layer, not just as a supporting layer.

The selective and directional water droplet permeability of Janus-C in oil-water systems facilitates the collection of water droplets from oil. One version of "Janus-trapper" involves Janus-C with its hydrophobic side outside towards the oil medium containing water droplets, and its hydrophilic side towards a tube that collects the scavenged water droplets (**Figure 4**a). As Janus-C allows water droplet penetration from hydrophobic to hydrophilic side, water droplets dispersed in oil medium should be able to penetrate through the membrane and then become trapped in the hydrophilic interior. Indeed, the Janus trapper effectively scavenges water droplets from the oil/water mixture (Figure 4b and Supporting Information, Movie 8). Note that the hydrophilic side of the membrane should be wetted by water

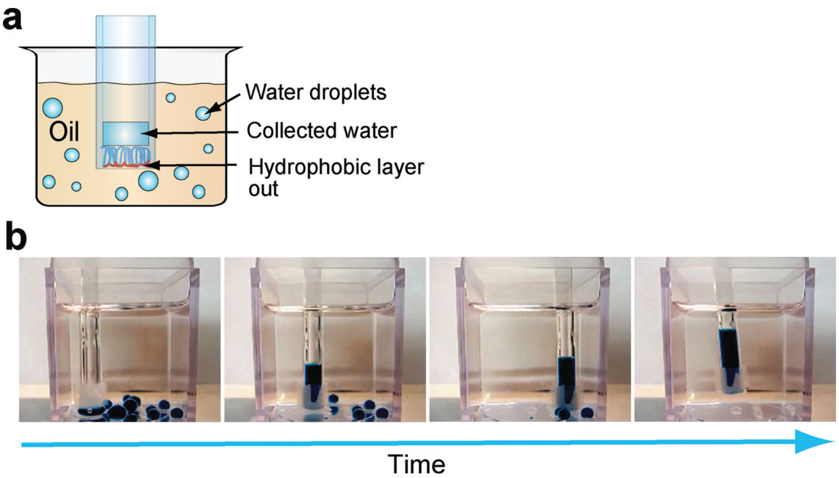

Figure 4. Water droplet scavenging using Janus-C. (a) Scheme showing the construction of "Janus trapper" for water droplet collection from oil. (b) Sequential snapshots showing effective collection of water droplets (dyed blue by methylene green) from oil (hexadecane) by the Janus trapper.

prior to the collection, otherwise the oil would enter into the tube when the device contacts the oil reservoir. In comparison with a homogeneous hydrophilic membrane, the Janus membrane provides a superior choice for collecting water droplets from oil because it allows a larger Laplace pressure to be exerted on the hydrophobic side, thus favoring through-plane penetration rather than in-plane spreading of water droplets. Another advantage of the Janus trapper is that in principle it can prevent oil from entering into the collected water as well as simultaneously preventing the collected water from returning to the oil phase, whereas a homogeneous membrane usually prevents occurrence of only one adverse event (see Supporting Information).

Water droplet collection from oil with Janus trapper provides an effective way for manipulation of samples, for example in droplet-based chemical reaction. Water droplets dispersed in a continuous oil phase can act as microreactor for biochemical reactions,[19] and the Janus trapper capable of droplet collection is thus useful for on-demand removal of intermediate products or collection of final products. The Janus trapper could also have implication for fluid purification. Besides Janus-C, Janus-T with selective and directional permeability to oil droplets could be selected to construct another form of Janus trapper with its hydrophilic side towards outside, which can effectively collect oil droplets from water (Supporting Information, Figure S8 and Movie 9).

3. Conclusion

Hydrophilic/hydrophobic Janus-type membranes involving chemically asymmetric skin-layer structures are prepared by facile vapor diffusion or plasma treatments. The resultant membranes show directional gating to water droplets as well as continuous water flow in air-water system. Furthermore, the membranes exhibit directional gating to droplets in oil-water systems with integrated selectivity to oil or water. The directional and selective liquid gating behaviors of the membranes are useful for development of various applications involving liquid transport and manipulation in air-liquid and liquid-liquid environments, including fluid diodes, microchemical reaction manipulation, advanced separation, biomedical materials, and smart textiles. We believe that many opportunities remain to be explored based on amphiphilic Janus structures, and new attractive properties, gatings, and functionalities are expected on artificial Janus membranes through further modulation of the membrane structure and characteristic size as well as its through-plane chemical profile.

4. Experimental Section

Materials Preparation: Cotton fabric membrane material was purchased from Eurokangas Oy, Finland. The topochemical fluorination of one surface was conducted in a fume hood at ambient temperature. Optical image of the experimental set-up is shown in the Supporting Information (Figure S1, Supporting Information). POTS (800 μL, 97%, Sigma-Aldrich) contained in an open petri-dish was placed inside a crystallizing dish (500 mL, Duran). The cotton fabric membrane was positioned to cover the crystallizing dish. The crystallization dish was used here because it had no spout and could thus be better covered by the fabric. The distance between the POTS liquid and the membrane is about 6 cm. The membrane was pressed by a glass plate, which helped to keep the membrane straight and prevented the rapid escape of POTS vapor from the crystallizing dish. POTS vapor was allowed to diffuse and react on the bottom side of cotton fabric membrane through silanization reaction between POTS and hydroxyl groups on the cotton fabric. After the silanization reaction, the exposed bottom side of the cotton fabric became hydrophobic whereas the shady upper side remained hydrophilic. The treated membrane was then removed from the crystallizing dish, and kept overnight in a vacuum oven to remove unreacted and loosely adsorbed POTS molecules. A set of membranes was made by varying the reaction time.

To prepare Janus-T membranes, a piece of fabric woven of teflon (polytetrafluoroethylene) fibers (T-187, Stern & Stern Industries, Inc.) was put at the bottom of the chamber of a Solarus 950 Gatan Advanced Plasma System. The membrane was then treated with O_2 and H_2 mixture plasma for 30 min with one side exposed to the plasma flux. The gas flow of both O_2 and H_2 was set at 20 SCCM, and the forward RF Target power was 65 W.

Characterization: X-ray photoelectron spectroscopy analysis was performed with a Surface Science Instruments SSX-100 ESCA spectrometer using monochromatic Al K_α X-rays and an electrostatic hemispherical analyzer. The spectra were recorded with a pass energy of 160 eV, X-ray spot size of 1 mm and step size of 0.05 eV. The base pressure in the analysis chamber was around 10^{-9} mbar. Scanning electron microscope investigation was performed on a Zeiss Sigma VP microscope. The breakthrough pressure of membranes was obtained through measuring the maximum height of water column that the membranes could support. Hexadecane (99%, Sigma Aldrich)-water interfacial tension was measured at ambient conditions using pendant drop method on a Biolin Scientific Theta Optical Tensiometer. The videos on liquid penetration, droplet collecting and interface stability were recorded using a Canon IXUS 115 HS digital camera.

To demonstrate anisotropic water flow penetration, two devices were made. For each device, a Janus-C membrane was sandwiched between two glass tubes (with a volume of ≈10 mL and inner diameter of ≈1 cm). Water (3.5 mL, dyed red with rhodamine 101) was loaded into one tube of each device which was placed horizontally on a stage. In the first device, the water was loaded on the hydrophobic side of Janus-C, whereas for the second one, the water was loaded on the hydrophilic side. For water droplet penetration experiment in oil-water system, the hydrophilic membrane used was a pristine cotton fabric membrane and the hydrophobic membrane was a cotton membrane with both sides treated with POTS vapor for more than 30 min. For water droplet collection experiment, bulk hexadecane was first put into a transparent plastic vessel, and then water droplet spills (dyed blue by methylene green) were deposited into the oil. The droplet collecting device was made by attaching a Janus-C membrane to the bottom end of a two open-ended glass tube with an inner diameter of ≈6 mm. The hydrophobic side of the membrane was towards outside and the hydrophilic side was towards inside of the tube. The hydrophilic side was wetted first by water before collecting droplets. The oil droplet collection experiment was performed in a similar way using Janus-T as the collection component with its hydrophilic side towards outside and hydrophobic side towards inside of the tube.

Supporting Information

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

Acknowledgements

This work was supported by the European Research Council and the Academy of Finland through its Centres of Excellence Programme (2014-2019). This work made use of the Aalto University Nanomicroscopy

Center premises. The authors thank Dr. Juan Li and Dr. Antti Soininen for helpful discussion, and Stern & Stern Industries, Inc. for kindly providing teflon fabric sample.

Received: March 3, 2014
Revised: April 24, 2014
Published online: July 28, 2014

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