Directional Liquid Gating by Hydrophilic/Hydrophobic Janus Membranes

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ABSTRACT

Controlling 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. We have shown theoretically that a hydrophilic/hydrophobic Janus membrane with a transmembrane chemical gradient can induce directional liquid gating due to its anisotropic liquid critical breakthrough pressure. We further experimentally prepare hydrophilic/hydrophobic Janus membranes by facile vapor diffusion method. The resultant Janus membrane evidences directional water droplet gating behavior in air-water systems. Moreover, membrane-based directional gating of continuous water flow is demonstrated, 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 remarkable gating properties of the Janus membranes open new perspectives for fluid rectifying, advanced separation, biomedical materials and smart textiles.

Keywords: wetting, hydrophilic/hydrophobic, Janus membrane, fluid diode, liquid separation

TEXT

Developing smart materials with direction-dependent solid-liquid interactions is of great interest for a wide range of applications, such as microfluidic control [1-2], heat exchange [3], fog collection [4-5] and aquatic device [6]. Although a number of materials with anisotropic wetting properties have been reported, particularly in the past decade, the majority of them have concentrated on achieving *in-plane* directional solid-liquid interactions, i.e., anisotropic liquid spreading, adhesion and transport on a surface. In contrast, much less effort has been devoted to study porous materials with *through-plane* directional liquid transport properties [7].

Functional membranes play indispensable roles in every aspect of our lives [8], and endowing membranes with direction-specific transport properties may open up promising applications in advanced separation, selective delivery and medical one-way valves [9-10]. Using a simplified membrane model composed of spaced microcylinders, we have show theorectcially that through-membrane wettability gradient direction can induce anisotropic liquid penetration behavior (Figure 1), which is attributed to the couple effect of local geometrical angle and contact angle on the critical breakthrough pressure (P_c). When the liquid penetrates from the reverse direction (hydrophilic → hydrophobic side), a relative small geometrical angle and large contact angle are obtained at the back side of the membrane, which leads to a large critical breakthrough pressure ($P_{c\text{-}r}$). Whereas when the liquid penetrates from the positive direction (hydrophobic → hydrophilic side), a large contact angle and small geometrical angle would not be coupled and thus a limited critical breakthrough pressure ($P_{c\text{-}p}$) is obtained. We have further demonstrated that the anisotropic ratio of the Janus membrane (i.e., the ratio of critical breakthrough pressure in the two different directions, $P_{c\text{-}p}/P_{c\text{-}r}$) can be improved by reducing the spacing ratio of the cylinder membrane apart from increasing the magnitude of wettability gradient (Figure 2).

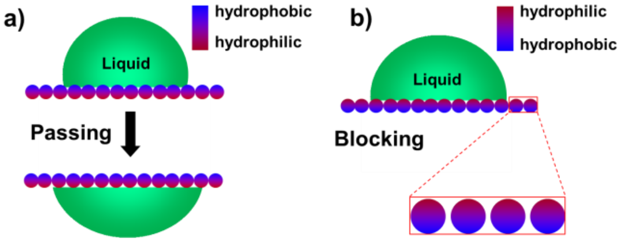

Figure 1: Directional liquid gating through a porous membrane with through-membrane wettability gradient. a) Liquid penetrates in the positive direction (hydrophobic → hydrophilic side), and is blocked b) in the reverse direction.

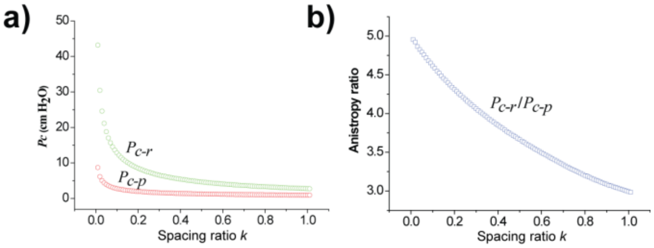

Figure 2: (a) Relationship between critical breakthrough pressure (P_c) and spacing ratio (k) of Janus gradient membrane. (b) Relationship between anisotropic ratio ($P_{c\text{-}r}/P_{c\text{-}p}$) and k.

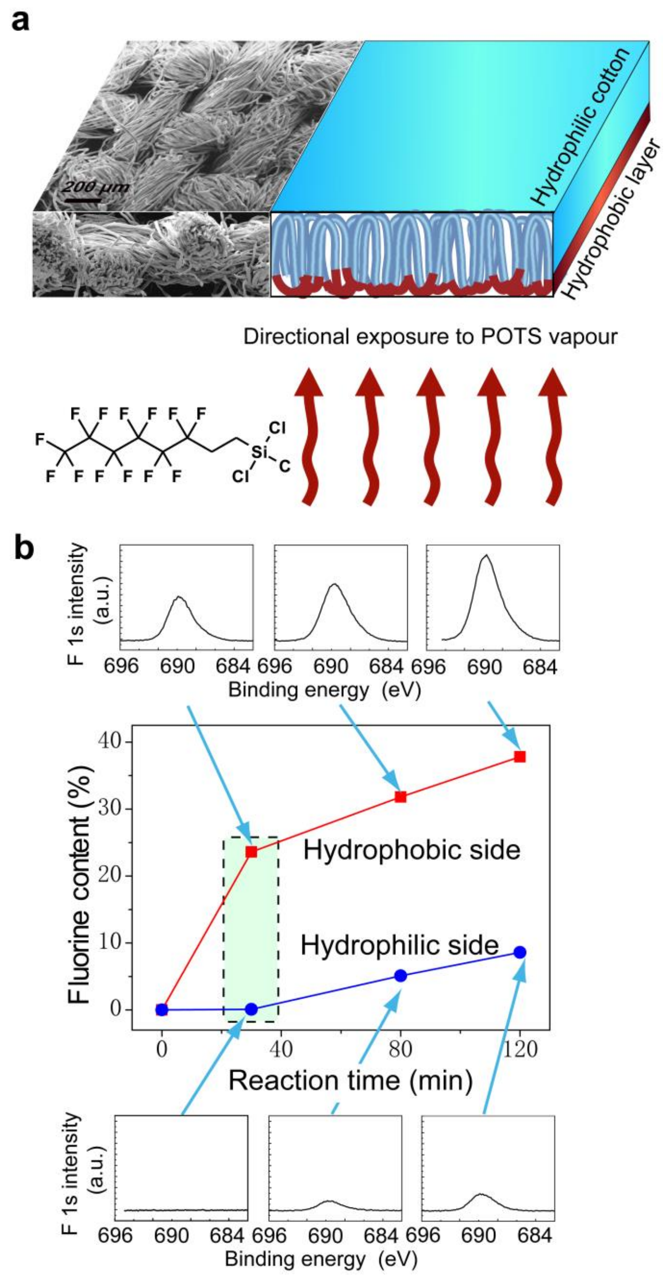

Figure 3: Experimental preparation of Janus membranes. (a) Schematic illustration of the preparation method and (b) XPS analysis of asymmetric elelmental F modification on the two sides of Janus membranes.

To experimentally prepare Janus membranes, vapor of 1*H*,1*H*,2*H*,2*H*-Perfluorooctyltrichlorosilane (POTS) was allowed to diffuse across and react with hydrophilic cotton fabric membranes (Figure 3a) [11]. The fabric membrane has a thickness of ~ 380 μm and is composed of nearly cylindrical bundles which further comprise secondary fibers. The POTS molecules react with surface hydroxyl groups on the membrane and thus create a chemical gradient along its thickness. A prominent advantage of the vapor diffusion technique lies in its extreme simplicity. This technique was used by Chaudhury et al. [12] to produce an in-plane chemical gradient, and we find it is also effective to create a through-plane chemical gradient. Through careful control of the reaction conditions and time, the exposed side of the membrane could become hydrophobic while the shady side remained hydrophilic. The surface composition on both sides of the membranes prepared under different reaction time was analyzed by X-ray photoelectron spectroscopy (XPS), which confirmed that asymmetric fluorination was achieved across the membrane (Figure 3b). Notably, although the exposed side of the membrane prepared with 30 min shows high fluorine content of ~ 23.6 at %, an indication of effective hydrophobic modification, almost no fluorine is detected on the shady side, suggesting the preservation of hydrophilic character of that side. The 30 min sample is used in our further studies to study the liquid gating properties.

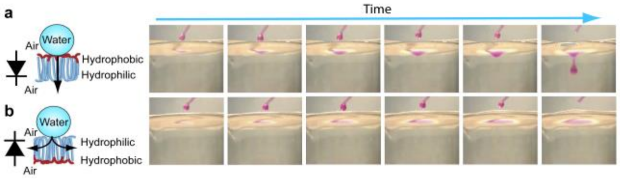

Figure 4: Directional water droplet penetration across the Janus membrane.

The directional water droplets penetration through the Janus membrane is shown in Figure 4. Water drops penetrate easily in the positive direction (Figure 4a) whereas when the same membrane is turned over water water droplets just spread on the hydrophilic side but do not penetrate (Figure 4b).

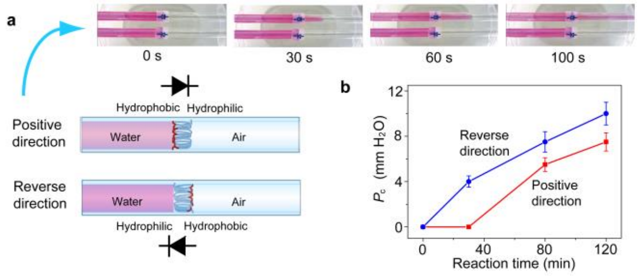

Figure 5: (a) Directional water flow penetration across the Janus membrane. (b) Anisotropic critical breakthrough pressure (P_c) of Janus membranes prepared with different reaction time.

In addition to water droplets, the Janus membrane shows directional gating for continuous water flow (Figure 5a). The directional water penetration across the Janus membrane can be attributed to its anisotropic critical breakthrough pressure P_c (Figure 5b). The Janus membrane shows a P_c of ~ 4 mmH_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 the Janus membrane is effectively fluorinated, and the major part of the membrane gets limited or no fluorination because a highly fluorinated membrane is estimated to give much higher P_c.

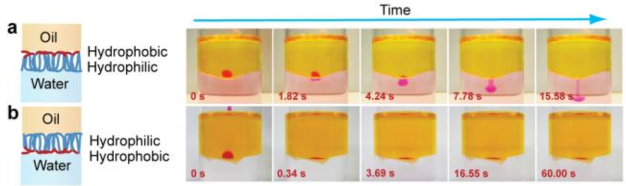

Figure 6: Directional water droplet penetration across the Janus membrane in the oil-water system.

We further investigate the liquid permeability of the Janus membrane in oil-water systems. When the Janus membrane is aligned in the positive direction (hydrophobic side towards oil), a water droplet penetrates easily through it (Figure 6a). In contrast, when the membrane is reversely aligned, the water droplet is blocked from the hydrophilic side (Figure 6b). The unidirectional water droplet penetration in the oil-water system is even more intriguing than unidirectional water droplet penetration in liquid-air systems 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). This phenomenon can be preliminarily understood by considering the Laplace pressure of the liquid droplet and its hydrophilic-hydrophobic interaction with the Janus membrane. In the oil-water system, a thin oil film should be adsorbed into the fluorinated hydrophobic skin layer of the Janus membrane due to their similar polarity, forming a barrier for water droplet penetration. When the membrane is positively aligned, a water droplet contacting the hydrophobic side exerts a larger Laplace pressure, creating a larger driving force for penetration. 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 membrane, a water droplet contacting the hydrophilic matrix layer tends to spread, giving negligible Laplace pressure. 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.

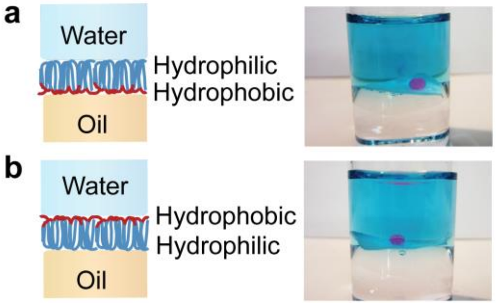

Figure 7: Prevention of oil droplet penetration across the Janus membrane in the oil-water system. Oil droplets are blocked by both (a) positively- and (b) reversely-aligned Janus membrane.

Regarding the penetration of oil droplets, the Janus membrane shows remarkedly different gating behavior compared to that of water droplets. Dichloromethane was used as the model oil phase here 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 membrane in the oil-water system as they bead up on both sides of the membrane (Figure 7). This behavior is due to the hydrophilic/hydrophobic balance within the Janus membrane, where only a thin skin layer is hydrophobic and the major matrix layer keeps hydrophilic, thus preventing the penetration of oil droplets in the oil-water systems.

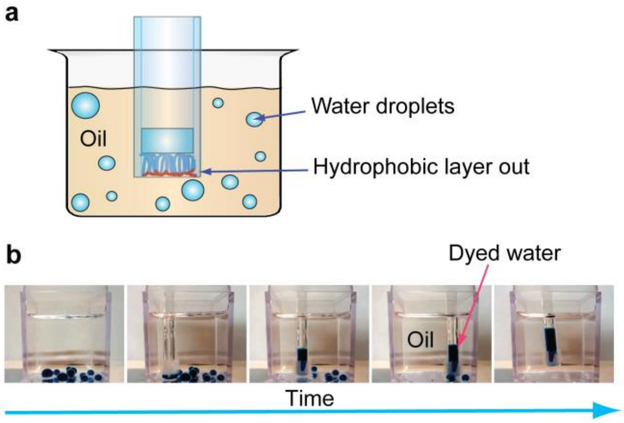

Figure 8: Liquid purification using Janus membrane. (a) Scheme showing the construction of "Janus trapper" for water droplet collection from oil. (b) Sequential snapshots showing collection of water droplets from oil by the Janus trapper.

The directional liquid permeability of the Janus membrane with integrated selectivity in oil-water systems inspired us to construct "Janus trapper" for water droplet collection from oil (Figure 8a). As a water droplet can penetrate freely through the Janus membrane from hydrophobic side to hydrophilic one, water spills in oil reservoir should be able to penetrate into the Janus trapper and trapped there. The Janus trapper was indeed able to scavenges effectively water spills deposited at the bottom of an oil reservoir (Fig8b).

The directional and selective liquid gating behaviors of the Janus membranes can bring about unique applications involving liquid transport and manipulation in air-liquid and liquid-liquid environments, including fluid diodes, advanced separation, biomedical materials, and smart textiles.

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