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# A General Strategy for the Separation of Immiscible Organic Liquids by Manipulating the Surface Tensions of Nanofibrous Membranes

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**Abstract:** *Oil/water separation membranes with different wettability towards water are attractive for their economic efficiency and convenience. The key factor for the separation process is the roughness-enhanced wettability of membranes based on the intrinsic wetting threshold (IWT) of water, that is, the limitation of the wettability caused by hydrophobicity and hydrophilicity. However, the separation of organic liquids (OLs) remains a challenge. Herein, we manipulate the surface tensions of nanofibrous membranes to lie between the IWTs of the two OLs to be separated so that the nanofibrous membranes can be endowed with superlyophobicity and superlyophilicity for the two liquids, and thus lead to successful separation. Our investigations provide a general strategy to separate any immiscible liquids efficiently, and may lead to the development of membranes with a large capacity, high flux, and high selectivity for organic reactions or liquid extraction in chemical engineering.*

As energy-efficient and eco-friendly materials to resolve industrial wastewater or oil pollution,[1–4] membranes with different wettability (hydrophilicity and hydrophobicity) towards water are used in practical applications for the separation of oil/water mixtures. The hydrophilicity or hydrophobicity of membranes allows water to be released or blocked, respectively. The roughness-enhanced wettability[5,6] of the membranes is key to promote the separation process,[7–9] that is, roughness can make a surface superhydrophilic or superhydrophobic[10] when the water contact angle on the surface is smaller or larger than the intrinsic wetting threshold (IWT)—the limitation caused by the hydrophilicity and hydrophobicity.[11–14] The concept of roughness-enhanced hydrophilicity/hydrophobicity[5,6,10] has been used for the design of various membranes and devices, such as, metal-coated meshes,[1,3] inorganic fibrous membranes,[2] polymer textiles,[4,15] microneedle array collection,[7] nanoparticle networks,[8] and polymeric[9] or metal membranes,[17] for the separation of oil/water mixtures.[1–4,15–20] However, these hydrophilic/hydrophobic surfaces fail to separate organic liquids (OLs) because they show homogeneous wettability for the OLs.

To realize successful separation, it is essential for membranes to have high selectivity and permit the penetration or stagnation of the liquid. Theoretically, membranes that simultaneously show lyophilicity for one liquid and lyophobicity for another are prerequisite. Unfortunately, however, it is very difficult to obtain such materials, either naturally or artificially, with a different wettability for OLs. A large obstacle is the uncertainty about the IWTs of OLs; in contrast, the IWT for water has been studied comprehensively.[11–14] The low surface tensions and good solvent properties of OLs also impede the generation of materials that show lyophobicity and lyophilicity for different OLs. To date, the efficient separation of OLs remains a challenge.

Herein, we report the separation of immiscible OLs by manipulating the surface tensions of nanofibrous membranes by modifiying the surfaces with different silanes. When the surface tensions of the membranes lie between the IWTs of the two OLs to be separated, the nanofibrous membranes can be endowed with superlyophobicity and superlyophilicity for the two liquids, and thus lead to a successful separation.

A fibrous membrane that exhibits superlyophobicity for formamide (FA) and superlyophilicity for $CCl_4$ (tetrachloromethane) was fabricated (Figure 1a). The fabrication process includes electrospinning, calcination, and surface modification. Scanning electron microscopy (SEM) images reveal that uniform fibers of submicrometer scale twine into a membrane with multilayer networks and random pores (Figure 1b–d). The thickness of the membrane is adjusted by the electrospinning time (Figure 1e and Figure S1), and the pore size of the membranes can also be tuned by varying the concentrations of the solutions as well as the operating voltages in the electrospinning process (Figure S2). Each fiber of the membrane has a continuous nanoporous structure (Figure 1f,g). The roughness of the fibers and modification of the surface contribute to the different wettability of the membrane for FA and $CCl_4$. Such a distinct difference in wettability allows the membrane to block FA while allowing $CCl_4$ to penetrate (Figure 1h,i, and Figure S3). Similarly, the membrane can separate a mixture of EG (ethylene glycol) and $CCl_4$ successfully (Figure S4). The separation capacities of the membranes are approximately 688 $\mathrm{L\,m^{-2}\,h^{-1}}$ for the

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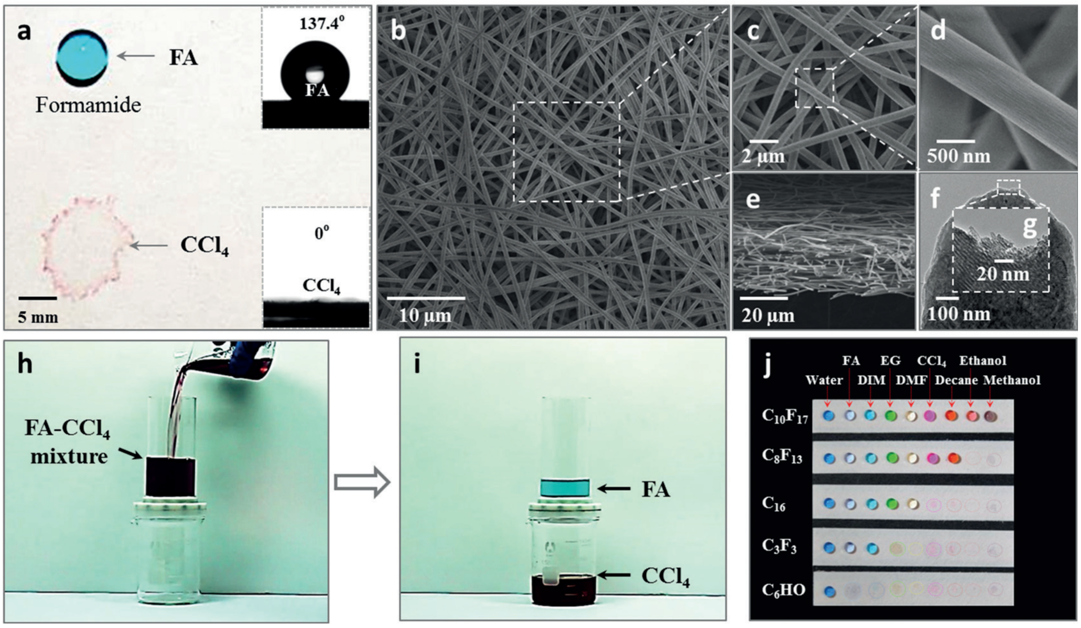

*Figure 1.* Membranes with a different wettability for separating organic liquids. a) A droplet of FA (formamide, blue, 5 µL) is deposited on the membrane modified by $C_{16}H_{33}SiCl_3$, while $CCl_4$ (tetrachloromethane, red, 5 µL) spreads out and wets the membrane. The insets show their contact angles on the membrane of 137.4° and ca. 0° respectively. b–d) SEM images of the membrane at different magnifications. b) Uniform fibers intertwine into the membrane and generate random pores of about 10 µm diameter (see Figure S14). The magnified SEM images show that the nanofibers of the membrane are $(618\pm36)$ nm in diameter (c,d and Figure S14). e) The cross-sectional SEM image shows the membrane is ca. 20 µm thick. f,g) The TEM images show a continuous nanoporous structure in the fiber. h,i) Separation of a FA/$CCl_4$ mixture by the as-prepared membrane. The membrane was fixed in an apparatus between a glass tube and a beaker. h) A mixture (wine red) of FA (blue, 30 mL) and $CCl_4$ (red, 60 mL) was poured into the upper glass tube. i) The $CCl_4$ penetrated through the membrane, while FA was blocked by the membrane and remained in the upper glass tube. j) Exemplary photographs of liquids on silanized membranes with different wettabilities. Each liquid was colored to allow them to be distinguished easily, including water ($\gamma = 71.6$ mN m$^{-1}$, dodger blue); FA ($\gamma = 58.4$ mN m$^{-1}$, light blue); DIM (diiodomethane, $\gamma = 50.8$ mN m$^{-1}$, cyan); EG ($\gamma = 48.8$ mN m$^{-1}$, green); DMF (dimethylformamide, $\gamma = 35.8$ mN m$^{-1}$, light yellow); $CCl_4$ ($\gamma = 25.9$ mN m$^{-1}$, magenta); decane ($\gamma = 23.8$ mN m$^{-1}$, red); ethanol ($\gamma = 22.9$ mN m$^{-1}$, salmon), and methanol ($\gamma = 23.5$ mN m$^{-1}$, mauve), respectively.

FA/$CCl_4$ mixture and 984 L m$^{-2}$ h$^{-1}$ for the EG/$CCl_4$ mixture (Movies S1 and S2).

Although a few oleophobic surfaces possess excellent liquid repellency,[21–23] they all show a homogeneous wettability for OLs. The different wettability (lyophobicity and lyophilicity) for OLs in our case is rare. It is known that the wettability of a liquid on a surface is mainly governed by surface tensions between the solid surface ($\gamma^{sv}$) and the liquid ($\gamma^{lv}$).[24] The surface tensions of several samples were modulated by modifying the surface with different silanes to separate mixtures of OLs. As shown in Figure 1 j, membranes with different surface tensions have a different wettability for different liquids. This result validates that it is feasible to control the wettability of membranes for OLs. As shown in Table 1, a series of liquids were examined on the membranes, which showed different lyophilic and lyophobic responses (herein membrane-m-$C_3NH$ means that the membrane was modified with (3-aminopropyl)trimethoxysilane, $(CH_3O)_3SiC_2H_6NH_2$. Unless specially described, other modified samples are similarly defined as membrane-m-$C_3NH$). The greater the silanization of the hydrocarbon chain, the more lyophobic the surfaces (Figures S6–S10). Diesel ($\gamma = 27.7$ mN m$^{-1}$) is lyophilic on membrane-m-$C_6$, but lyophobic on membrane-m-$C_8F_{13}$, which illustrates that replacing the hydrogen atoms by fluorine atoms enhances the lyophobicity. This trend can be enhanced with more replacements, as shown by comparing the lyophobicity of membrane-m-$C_8F_{13}$, membrane-m-$C_{10}F_{17}$, and membrane-m-$C_{12}F_{21}$. On the other hand, membrane-m-$C_3NH$, in which the hydrogen atoms are replaced by nitrogen atoms, leads to increased lyophilicity. Furthermore, we found that, for water, membrane-m-$C_3NH$ is hydrophilic, while membrane-m-$C_6HO$ is hydrophobic. Based on such a different wettability of these two membranes for water, we reconfirm that a wetting threshold of hydrophilicity and hydrophobicity indeed exists. Similarly, other liquids, such as, FA, EG, DMSO, also have their own thresholds of lyophobicity and lyophilicity. Moreover, the wetting thresholds for different liquids are not the same, as shown by the dotted lines in Table 1.

According to Young's model,[25] the hydrophobic state on a smooth surface is characterized by a contact angle $\theta > 90°$, whereas a hydrophilic surface has $\theta < 90°$; here 90° is considered as the mathematical wetting threshold that divides the surface into lyophobic and lyophilic categories. The latest studies reported $\theta = 65°$ to be an intrinsic wetting threshold between "hydrophobicity" and "hydrophilicity",[11,12] which was proposed on the basis of statistical experiments[13] and further proved by methods that modulated the surface tensions.[14] This conclusion was further supported by the emergence of superhydrophobic surfaces with water contact

***Table 1:*** Intrinsic wetting thresholds for organic liquids determined by manipulating surface tensions of membranes.[a]

| Surface tension | Liquids | Modified membranes $C_3NH$ | $C_6HO$ | $C_3F_3$ | $C_6$ | $C_{12}$ | $C_{16}$ | $C_{18}$ | $C_8F_{13}$ | $C_{10}F_{17}$ | $C_{12}F_{21}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| high | water | × | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| | formamide (FA) | × | × | √ | √ | √ | √ | √ | √ | √ | √ |
| | diiodomethane (DIM) | × | × | √ | √ | √ | √ | √ | √ | √ | √ |
| | ethylene glycol (EG) | × | × | × | √ | √ | √ | √ | √ | √ | √ |
| | dimethyl sufoxide (DMSO) | × | × | × | √ | √ | √ | √ | √ | √ | √ |
| | ethanolamine | × | × | × | √ | √ | √ | √ | √ | √ | √ |
| | nitromethane | × | × | × | √ | √ | √ | √ | √ | √ | √ |
| | acetophenone | × | × | × | √ | √ | √ | √ | √ | √ | √ |
| | dimethyl formamide (DMF) | × | × | × | √ | √ | √ | √ | √ | √ | √ |
| | dibutyl phthalate | × | × | × | × | × | × | × | √ | √ | √ |
| | ethylene dichloride | × | × | × | × | × | × | × | √ | √ | √ |
| | ethylene glycol monomethyl ether | × | × | × | × | × | × | × | √ | √ | √ |
| | diesel | × | × | × | × | × | × | × | √ | √ | √ |
| | tetrachloromethane ($CCl_4$) | × | × | × | × | × | × | × | × | √ | √ |
| | chloroform | × | × | × | × | × | × | × | × | √ | √ |
| | decane | × | × | × | × | × | × | × | × | √ | √ |
| | methanol | × | × | × | × | × | × | × | × | √ | √ |
| | ethanol | × | × | × | × | × | × | × | × | √ | √ |
| low | acetone | × | × | × | × | × | × | × | × | × | × |

[a] With surface tensions from high to low, liquids on the membranes modified with silanes change gradually from lyophilic to lyophobic. Importantly, most liquids have an intrinsic wetting threshold for going from lyophilicity to lyophobicity (depicted by the dotted line). Lyophobic: √, lyophilic: ×.

angles below 90° that were obtained from artificial and natural materials.[11,26–28] The combination of Young's Equation[25] and Berthelot's rule[24] leads to Equation (1),

$$\cos\theta_{\mathrm{IWT}} = -1 + 2\left(\gamma^{\mathrm{sv}}_{\mathrm{IWT}}/\gamma^{\mathrm{lv}}\right)^{1/2} \quad (1)$$

where $\theta_{\mathrm{IWT}}$ is the contact angle when a liquid on a smooth surface just reaches the wetting threshold state, $\gamma^{\mathrm{sv}}_{\mathrm{IWT}}$ is the surface tension of the surface corresponding to $\theta_{\mathrm{IWT}}$, and $\gamma^{\mathrm{lv}}$ is the surface tension of the liquid. In this Equation, $\theta_{\mathrm{IWT}}$ and $\gamma^{\mathrm{sv}}_{\mathrm{IWT}}$ are two parameters to denote the intrinsic wetting threshold (IWT). Unfortunately, the $\theta_{\mathrm{IWT}}$ values for OLs are so far unknown.

Herein, for the first time, we explore the $\theta_{\mathrm{IWT}}$ values for OLs by using the same method as we previously reported.[14,24] Several kinds of liquids were selected, such as, water, FA, and EG, which have surface tensions ranging from high to low (Figure 2 a,b, Figure S6–S10). The experimental results show that the $\theta_{\mathrm{IWT}}$ values for different liquids decrease as the $\gamma^{\mathrm{lv}}$ value decreases from high to low (Figure 2 c). The trend of the decrease in the $\theta_{\mathrm{IWT}}$ value as $\gamma^{\mathrm{lv}}$ decreases verified our speculation on the thresholds in Table 1, and explained why liquids with a low surface tension wet the surface easily.

According to Equation (1), $\theta_{\mathrm{IWT}}$ corresponds to $\gamma^{\mathrm{sv}}_{\mathrm{IWT}}$, thus we can separate immiscible OLs by simply manipulating the surface tensions of the membranes (Figure 2 d, Tables S3–S7). The surface tensions of the membranes ($\gamma^{\mathrm{sv}}$) can be manipulated by modification with different silanes: when the $\gamma^{\mathrm{sv}}$ value lies in between the IWTs of the two OLs (A and B) to be separated, that is, $\gamma^{\mathrm{sv(A)}}_{\mathrm{IWT}} > \gamma^{\mathrm{sv}} > \gamma^{\mathrm{sv(B)}}_{\mathrm{IWT}}$, the membrane is lyophobic for liquid A and lyophilic for liquid B. After introducing roughness, the nanofibrous membranes can be endowed with superlyophobicity and superlyophilicity for the two liquids to be separated, thus enabling liquids A and B to be separated successfully.

Based on this principle, not only can the different wettability of membranes be controlled to separate liquids, membranes with precise surface tensions can also be designed to separate a wide range of liquid mixtures (Table 1, and Tables S3–S6). Compared with oil/water separations reported in previous studies, which only depend on different wetting phenomena for oils and water on membranes, the separation principle given in our study is more beneficial for separating more kinds of liquid mixtures. For example, we can separate mixtures of FA/$CCl_4$ and EG/$CCl_4$ with membrane-m-$C_6$, membrane-m-$C_{16}$, or membrane-m-$C_8F_{13}$. Furthermore, many different liquid mixtures can be separated by one membrane (Figure 3, and Figure S11). As an example, FA and decane could be separated by using apparatus equipped with the membrane-m-$C_{18}$ (Figure 3 a). Mixtures of FA and five kinds of oils (Figure 3 b–d) were studied in detail to test the properties of the membrane. The robustness of the membranes is determined by the intrusion pressure, below which the membrane can work well (Figure 3 b and Figure S13). The experimental intrusion pressure can be obtained by Equation (2):

$$P_{\mathrm{exp}} = \rho g h_{\mathrm{max}} \quad (2)$$

Here, $\rho$ is the density of the liquid, $g$ is the acceleration of gravity, and $h_{\mathrm{max}}$ is the maximum height of liquid the membrane can support.[3,4] The intrusion pressures were calculated from five experimental values with a series of liquids.

For porous materials, the theoretical intrusion pressure can be calculated by Equation (3):

$$P_{\mathrm{theor}} = 2\gamma^{\mathrm{AB}}\cos\theta/d \quad (3)$$

Here, $\gamma^{\mathrm{AB}}$ is the interfacial tension between liquids A and B, $\theta$

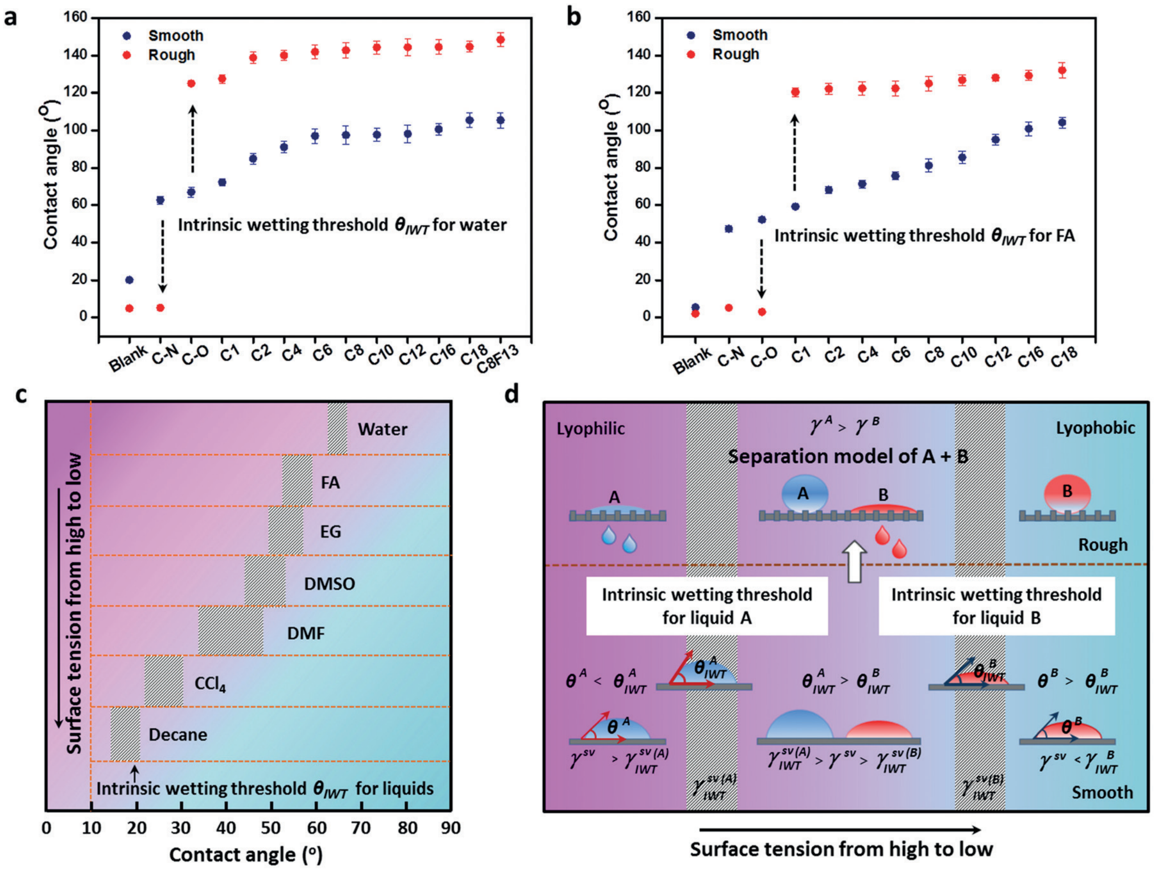

***Figure 2.*** Intrinsic wetting thresholds for liquids ($\theta_{IWT}$) on solid surfaces modified with silanes and mechanism of the liquid separation. a,b) $\theta_{IWT}$ values for water and FA on the modified solid surfaces. c) The $\theta_{IWT}$ value for different liquids decreases as their surface tensions decrease from high to low. d) Separation of the liquids by the membrane whose surface tensions ($\gamma^{sv}$) is precisely manipulated to lie between the IWTs of the two OLs to be separated (i.e. $\gamma^{sv(A)}_{IWT} > \gamma^{sv} > \gamma^{sv(B)}_{IWT}$), so that the membrane is lyophobic for liquid A and lyophilic for liquid B. After introducing roughness, the nanofibrous membranes can be endowed with superlyophobicity and superlyophilicity, respectively, for the two liquids to be separated, thus enabling liquid A and liquid B to be separated successfully. If $\gamma^{sv} > \gamma^{sv(A)}_{IWT}$, the membrane is lyophilic for the liquid (left, model of liquid A); whereas if $\gamma^{sv} < \gamma^{sv(B)}_{IWT}$, the membrane is lyophobic for the liquid (right, model of liquid B).

is the contact angle of liquid A on a smooth surface which was just immersed in liquid B ($\gamma^A > \gamma^B$), and $d$ is the average pore diameter, which is calculated from the SEM image of the fibrous membrane (Figure S14). The results show that the membranes show a good performance in terms of robustness.

The separation efficiencies of the membranes are determined from the oil content before and after separation by using an infrared spectrometer oil content analyzer. The separation efficiencies are calculated from the oil rejection coefficient ($R(\%)$) according to Equation (4):

$$R(\%) = (1 - C_v/C_o) \times 100 \tag{4}$$

Here $C_v$ and $C_o$ are the oil concentrations of the original mixture and collected non-oil liquid, respectively.[3,7] As shown in Figure 3c, the separation efficiencies of the membranes for various mixtures are above 99.0%, thus indicating that the membrane is a promising material for the separation of liquids that are in demand.

Stable performances are important for the practical application of separation membranes. Our membranes all show high and stable separation efficiencies over 10 cycles (Figure 3d), even after being stored for at least half a year (Figure S16), which indicates an outstanding antifouling and easy-cleaning performance. The membranes are also highly stable against heat and solvents. The heat resistance was tested by determining the wettability of the membrane after heat treatment. For example, the contact angles of water, FA, and acetone at 25 °C on the membrane-m-$C_{18}$ are $(144.7 \pm 2.9)°$, $(131.5 \pm 4.5)°$, and approximately 0°, respectively (Figure 3e). The contact angles remained constant even when the membrane was heated to 500 °C for 2 h. The modified silane decomposed completely after being heated at 700 °C for 10 h, while the fibrous networks of the membrane remained unchanged. Similar to the freshly prepared membrane, the recycled membrane can be used repeatedly. The solvent resistance of the membranes was determined by immersing the membrane in various OLs for 2 h in a vacuum. After removing the solvents, the membrane remained lyophobic for water and FA, but lyophilic for acetone (Figure 3f). This result verified the excellent stability of the membrane, which is a clear advantage over organic films.[1,3,4,9] Furthermore, the

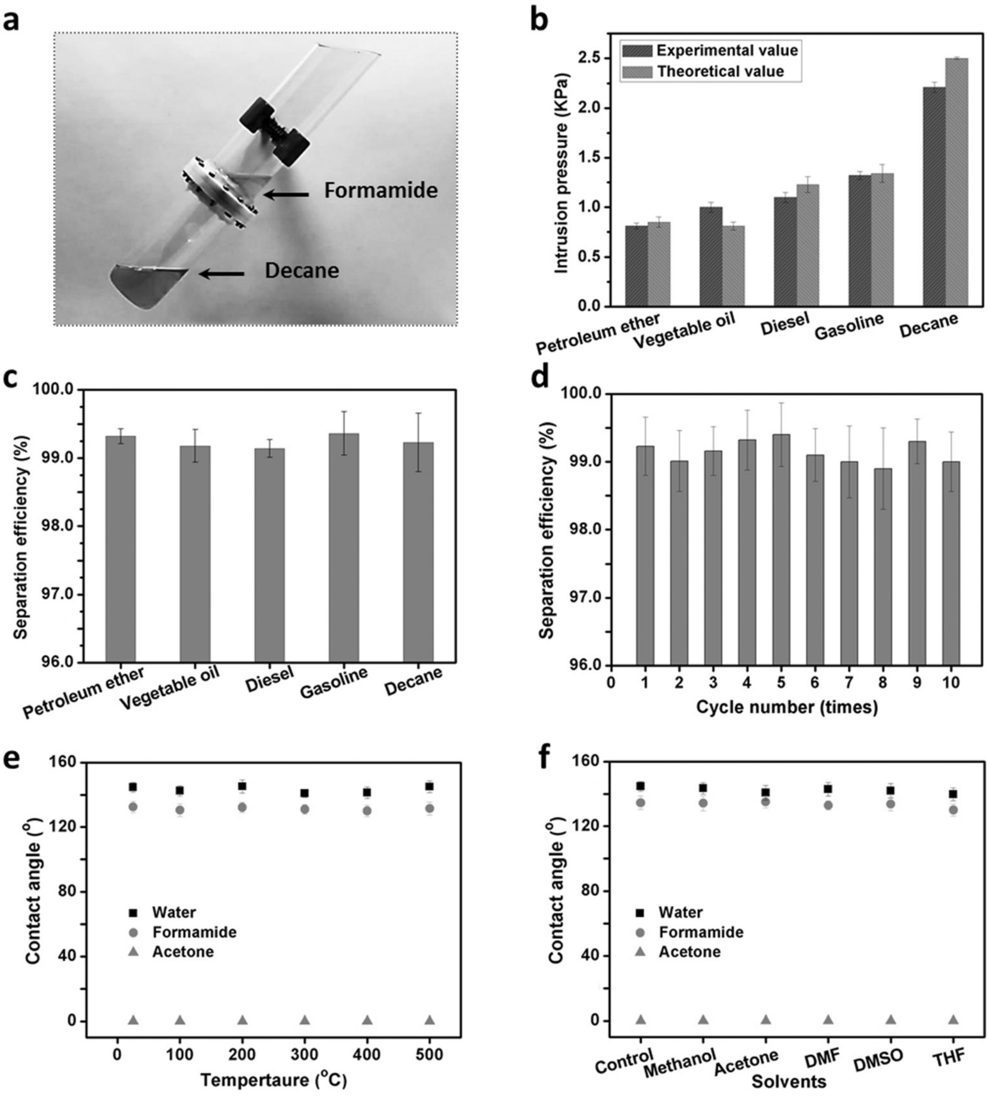

*Figure 3.* Separations of general organic liquid mixtures and studies of the membrane performances. a) Separated FA (formamide) in the upper glass tube and decane in the lower tube after passing the FA/decane mixture (15 mL of FA and 30 mL of hexane) through the membrane. The separation apparatus was tilted by an angle of ca. 45° for convenient contact of the decane with the membrane. b) The experimental and theoretical values of the intrusion pressures for mixtures of FA and various oils. c) The separation efficiency of the membranes is determined by the residual oil content in the upper liquids after permeation of the mixtures through the membranes. d–f) The stabilities of the membrane performance. d) The separation efficiency with cycle numbers for separating the FA/decane mixture (15 mL of FA and 30 mL of decane). The membrane was washed by passing 10 mL of ethanol through three times and then dried in air before each cycle. e) The heat resistance of the membranes. The contact angles of water, FA, and acetone on the membranes were measured after the membranes were heated for 2 h at different temperatures. f) The resistance of the membranes to the solvents. The contact angles of water, FA, and acetone were measured on the dry membranes after they had been soaked in various solvents for 2 h and then dried in air. The membranes used in these series were modified with octadecyltrichlorosilane ($C_{18}H_{37}SiCl_3$).

cost of materials for our membrane is about \$11.1 m$^{-2}$, and thus should be interesting for applications in commercial products.

In summary, no natural or artificial materials have, until now, been shown to possess controlled wettability for organic liquids, although a few lyophobic surfaces show repellency for water and oils.[21–23,31–35] Our fabricated membranes, whose surface tensions are precisely manipulated by surface modification, show different wettability for OLs. This controlled wettability of the membrane essentially arises from different IWTs for the OLs, and is reinforced by the roughness of its nanofibers. The different wettability of OLs on the membranes has allowed effective separations to be achieved. Compared with traditional separation techniques, this one shows greater promise and wider application.[24] This study may open up opportunities for designing materials with new functional properties, such as absorbability[2,8,36] and selectivity,[37] or allow the manipulation[32,38] of OLs in energy or chemical engineering.

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