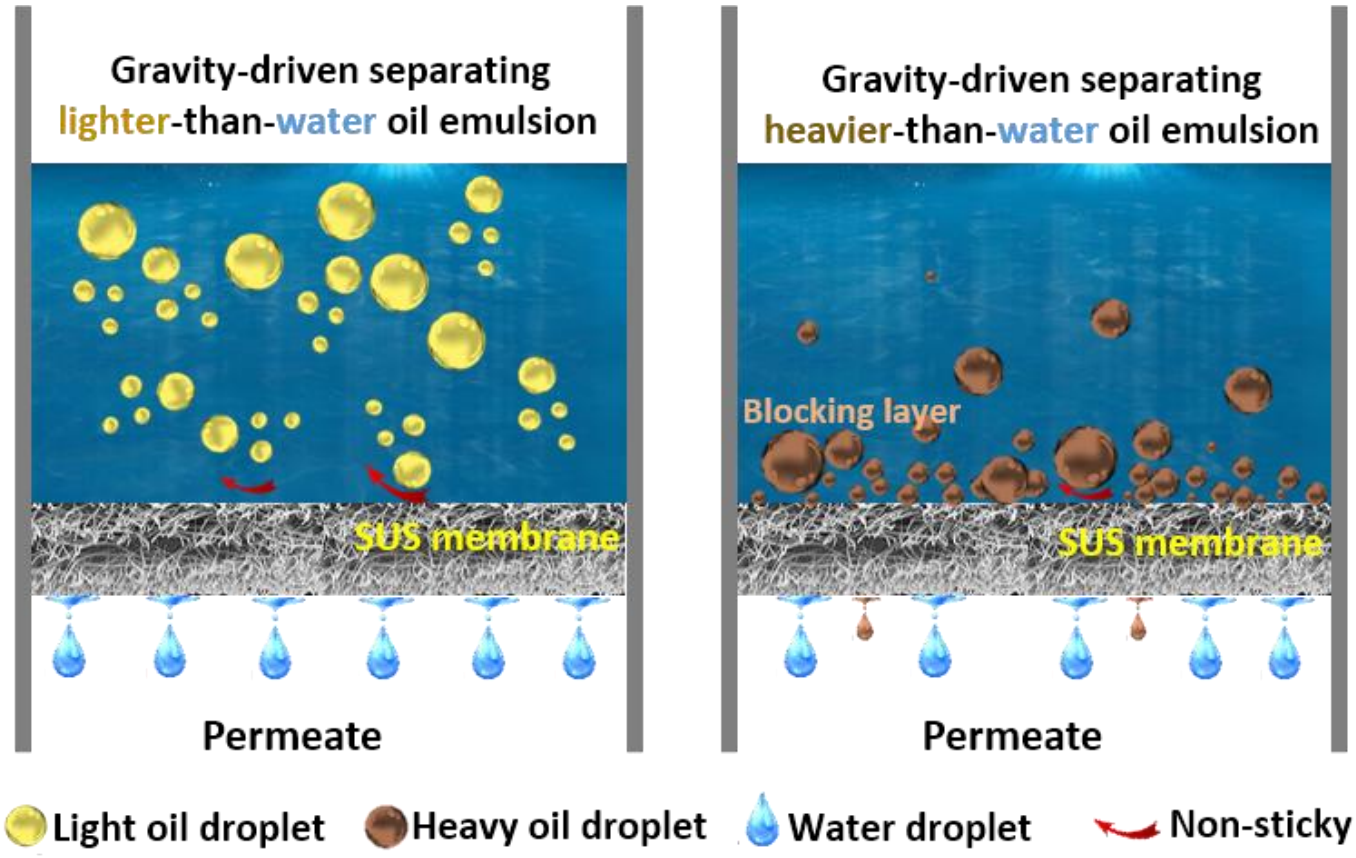
Graphical Abstract



In Situ Silica Growth for Superhydrophilic-Underwater Superoleophobic Silica/PVA Nanofibrous Membrane for Gravity-driven Oil-in-water Emulsion Separation

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Abstract: Superhydrophilic-underwater superoleophobic (SUS) membranes have been demonstrated to be promising materials for oily wastewater treatment. However, development of facile, low cost and robust SUS membrane with high flux and less membrane fouling is still challenging. In this study, we reported a simple electrospinning/in-situ growth strategy to prepare SUS SiO_2@PVA nanofibrous membrane for gravity-driven separation of oil/water mixture. In specific, a highly porous PVA nanofibrous membrane was first fabricated by electrospinning technique, followed by an in-situ growth of silica nanoparticles on the pristine PVA nanofibers through a modified Stöber reaction. The abundant hydroxyl groups on PVA nanofibers enabled uniform and stable deposition of silica nanoparticles, thus simultaneously realizing high surface energy surface (hydrophilic nature of PVA and silica) and multi-scale roughness. As expected, the resultant membrane exhibited excellent in-air "water-loving" (instantaneous in-air water wetting) and underwater "oil-hating" properties (underwater oil contact angle of 161.8° and sliding angle of 6.2°). The SUS SiO_2@PVA membranes exhibited efficient separation of both free oil/water mixture and a variety of surfactant-stabilized oil-in-water emulsions in a gravity-driven filtration process. In addition, oil density played an important role during the separation process, due to superior separation performance was achieved for lighter-than-water oil when compared to heavier-than-water oils. Moreover, the membrane showed robust

reusability that it maintained stable oil rejection and permeate flux in cyclic experiments.

Key words: Oil/water separation, emulsion separation, superhydrophilic membrane, under-water superoleophobic membrane, silica nanoparticle

1. Introduction

In recent decades, increasing amount of oily wastewater has been generated from frequent oil spill accidents [1, 2] or various industrial processes, such as leather, food, textile, and metal finishing [3, 4]. Therefore, it has become indispensable to purify oil-contaminated wastewater to protect human health and ecological environment. In most cases, oily wastewater exists in the form of oil-in-water emulsion with oil droplets of less than 20 μm. The micro-sized droplet size and good stability of the emulsion, especially those stabilized by surfactants, present huge challenges for efficient oil/water separation. Conventionally, oily wastewater can be separated by gravity or centrifugal settling, chemical or electrostatic demulsification, or biological treatment [5]. However, gravity or centrifugal settling are ineffective for treating emulsified mixtures due to the stabilization of emulsion by surfactants in the mixture, and chemical or electrostatic demulsification methods usually involves high energy consumption and secondary pollution [6]. Therefore, development of an efficient and broadly applicable technique for oily wastewater treatment, especially surfactant-stabilized emulsions, is highly desirable.

Membrane technology exhibits various attractive merits such as low energy cost, small footprint, easy operation and high efficiency [7]. Recently, inspired by lotus leaf's superhydrophobic property, fabrication of porous membrane of special wettability for oil/water separation has gained increasing attention [8]. Wettability is an intrinsic feature of an solid surface which governs the wetting behavior when a liquid contacting with it [9]. If a material displays opposite wetting behavior between oil and

water (e.g., superhydrophobic/superoleophilic, or superhydrophilic/superoleophobic), it can realize selective oil/water separation. Up to date, superhydrophobic/superoleophilic membranes for oil removal have been extensively reported for oil-rich oil/water mixture separation [8]. However, this type of "oil-removing" membrane may not work for oily wastewater (e.g., oil-in-water emulsion) separation. For typical oils with lower density than water, water often forms a barrier layer over the membrane surface, preventing oils penetration [10].

In this regard, preparation of superhydrophilic-underwater superoleophobic (SUS) membranes as "water-removing" materials have been proposed for oily wastewater treatment [11]. The water droplets can instantaneously wet and penetrate the SUS membrane, and the trapped water in the membrane acts as a superoleophobic barrier to effectively reject oil droplets [12]. Constructing SUS surface generally requires synergy of high surface energy with multi-scale surface roughness [13]. In specific, high surface energy is often realized by using intrinsic hydrophilic materials (e.g., polyvinyl alcohol [14], polyacrylonitrile [15], cellulose [16]) or hydrophilic modification of hydrophobic materials (e.g., polyvinylidene difluoride [17], polytetrafluoroethylene [18]), and multi-scale surface roughness can be constructed by either "top-down" or "bottom-up" strategies [19]. Up to date, a variety of methods (based on grafting [20] or surface coating of polymeric membranes [21], non-solvent phase separation [22], in-situ mineralization of polymeric membranes [23]) have been reported to fabricate SUS membranes for the separation of oil-in-water emulsion. Unfortunately, a major challenge of low permeation flux remains due to low porosities of the SUS membranes in most of the studies.

Electrospinning is a promising technique that offers unparalleled advantages to fabricate membranes with high porosity, controllable pore size and thickness. In recent years, increasing efforts have been devoted to fabricate SUS nanofibrous membranes by electrospinning technique for high

efficient oil/water separation. The as-prepared nanofibrous membrane offers such a high porosity that often the oil/water separation can be realized solely under gravity. The pristine nanofibrous membranes mostly does not have superhydrophilicity (thus insufficient water affinity to trap water to form the oil repulsive layer [24]), and a second surface roughness enhancement by coating of hydrophilic polymers or inorganic nanoparticles is usually followed to further amplify the "water-loving" property of the membrane for efficient water trapping [13]. These toppings can be coated either by physical deposition (e.g., spraying [25], dip-coating [26], filtration [27]) or chemical modification (e.g., grafting [20], surface polymerization [28], polydopamine binding [29]). Nevertheless, coating by physical deposition often suffers from poor reusability due to the weak noncovalent coating-substrate interactions [30]. To make it worse, severe nanoparticles aggregation often occur due to the high surface energy [31], resulting in poor particle distribution and nanostructure uniformity. Alternatively, though coating by chemical modification offer better reusability, most of existing chemical methods often involves multiple steps (such as surface pre-activation [24], binding layer deposition [14], coating agent pre-synthesis [30, 32]) and expensive raw materials usage. Apparently, development of facile, low cost and robust SUS nanofibrous membrane remains a continuing challenge for efficient oily wastewater treatment.

In the present study, we report an eco-friendly SiO_2@PVA SUS nanofibrous membrane fabricated by a facile electrospinning/In-situ growth strategy for gravity-driven separation of oil-in-water emulsion. PVA is well recognized as a low cost, non-toxic, biocompatible polymer with excellent hydrophilicity, and the abundant hydroxyl groups in PVA molecules readily serve as intrinsic activate sites to facilitate the surface modification [33]. Up to date, PVA-based SUS nanofibrous membrane has yet not been reported for oil/water separation. In specific, a hydrophilic PVA nanofibrous membrane was first fabricated by electrospinning, followed by an in-situ growth of

97 silica nanoparticles on the pristine PVA nanofibers through a modified Stöber reaction. The resultant
98 SiO_2@PVA nanofibrous membrane was systematically characterized to reveal its morphology and
99 chemical component variations when compared to the pristine PVA nanofibrous membrane. Through
100 a variety of wettability measurements, we show that the hybrid SiO_2@PVA nanofibrous membrane
101 exhibit excellent in-air "water loving" and underwater "oil hating" properties. Gravity-driven
102 separation of oil/water mixture were carried out to evaluate the membrane separation performance.
103 Finally, reusability of the SUS membrane was also investigated by conducing cyclic emulsion
104 separation experiments.
105
106 **2. Methodology**
107 **2.1. Materials:**
108 PVA powder (98-99% hydrolyzed, Mw of ~88,000-97,000) was obtained from Alfa Aesar.
109 Tetraethyl orthosilicate (TEOS), ammonia hydroxide (33 wt. % NH_3 in H_2O), glutaraldehyde, ethanol,
110 hydrochloric acid (HCl, 37 wt.%), acetone were all purchased from VWR Chemicals Ltd. Kerosene,
111 n-heptane, toluene, chloroform, Tween 80 were all analytical grade and purchased from Dieckmann
112 chemical industry company limited. All the chemicals were used as received. Milli-Q water with
113 resistivity over 18 MΩ.cm (Millipore, MA) was used in all the experiments.
114 **2.2. SUS SiO_2@PVA nanofibrous membrane fabrication**

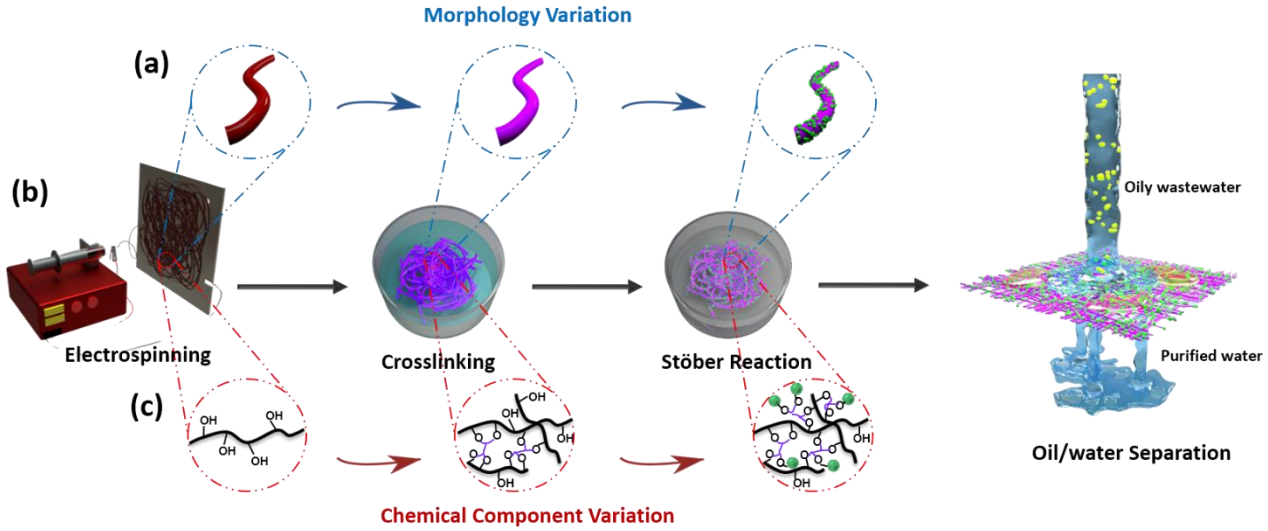

Figure 1. Schematic illustration of the (a) morphology variations during the preparation process, (b) preparation procedure of the SUS SiO_2@PVA membrane, and (c) Chemical component variation during the preparation process.

2.2.1. Hydrophilic PVA nanofibrous membrane fabrication

The fabrication process of SUS SiO_2@PVA nanofibrous membrane is illustrated in **Figure 1b**. First, a 10 wt.% PVA solution was first prepared by dissolving the polymer in water and stirring the mixture at 90 ^oC overnight. Afterwards, a PVA nanofibrous membrane was prepared by electrospinning technique with the following conditions: collector/spinneret distance of 15 cm, flow rate of 0.37 mL/h, and applied voltage of 18 kV, drum diameter of 10 cm, drum rotation speed of 80 rpm, and total electrospun PVA solution of 15 mL. Finally, the membrane was cross-linked by immersion the membrane in cross-linking agent containing acetic acid and glutaraldehyde (96/4 v/v) for 0.5 hour, before being dried in the electric oven at 60 ^oC overnight.

2.2.2. SiO_2 in-situ growth on the PVA nanofibers

Based on the hydrophilic PVA nanofibers, a secondary roughness was created by in-situ growth of SiO_2 nanoparticles on the pristine PVA nanofibers using a modified Stöber reaction. First, a small piece of PVA nanofibrous membrane (4×4 cm) was soaked in a flask containing 300 mL ethanol and 30 mL ammonium hydroxide (33 wt.%). The flask was then immersed in an oil bath at 60 ^oC. Under

magnetic stirring, 15 mL TEOS was added into the solution dropwise to start the reaction. After 24 hours, the resultant SUS SiO_2@PVA membrane was carefully picked out and rinsed with ethanol and water three times to remove any residual chemicals. Finally, the SUS membrane was dried completely in oven at 60 ^oC overnight before further use.

2.3. Membrane characterizations

Membrane morphologies were investigated by scanning electron microscopy (SEM) images (LEO1530 FEG SEM). Energy dispersive X-ray (EDX) mapping was also carried out during the SEM measurement to determine the elements distribution on the nanofibers. In addition, mean diameter distribution of membranes was obtained by SEM image analysis using software of Nano Measure System. For chemical component analysis, FTIR-ATR and XPS spectra of the membranes were obtained by Nicolet 8700 (Thermo-Electron, wavenumber range of 4000-500 cm^{-1}) and ESCALAB 250 (Thermo Scientific, X-ray source of monochromic Al Kα 150 W), respectively. To evaluate the wettability of the membranes, the in air water contact angle, underwater oil contact angle, in air water contacting behavior, and underwater oil contacting behavior were all measured by Attention Theta (Biolin Scientific, Sweden). Note that chloroform was chosen as a model oil for all oil wettability measurements due to its larger density than water. For contact angle measurements, a small droplet (~6 μL) was deposited on the membrane surface, and allowed for 10 s of stabilization. Average contact angles were calculated from six measurements at different spots of the sample surface. Underwater oil sliding angles were also measured by a goniometer (HWHR Instruments, China). Average membrane thicknesses were also determined by six measurements using a digital caliper. The pore size distribution of the membranes were measured by a capillary porometer (PoroLux™ 1000, German) using the gas-liquid displacement porometry method [34]. To reflect the membrane porosity, isopropyl alcohol (IPA) uptakes were measured by gravimetric method [35], where the

weights of the dry membrane and wet membrane (pre-soaked with IPA solution for over 8 hours) were measured and calculated by the following equation:

$$\delta(\%) = \frac{m_w - m_d}{m_d} \times 100 \qquad (1)$$

where δ is the IPA uptake ($g \cdot g^{-1}$), and m_w and m_d are the weight of the dry and wet membranes, respectively.

2.4.Oil/water emulsion preparation

Four kinds of surfactant-stabilized oil-in-water emulsion were prepared, including kerosene-in-water (k/w), n-heptane-in-water (h/w), toluene-in-water (t/w), and chloroform-in-water (c/w) emulsions. In specific, 4 mL oils, 0.4 g surfactant (Tween 80), and 200 mL water were vigorously stirred under room temperature for over 8 hours. The resultant milky emulsions were stable with no observation of demixing for at least 24 hours. In addition, free kerosene/water mixture was also prepared with volume ratio of 1:1 to evaluate the free oil/water mixture separation performance.

2.5. Gravity-driven oil/water separation tests

Separation of oil/water mixture were performed in a customized dead-end filtration module. In brief, two cylindrical glass tubes were vertically fixed, with a membrane sealed in the middle (effective membrane area of 11 cm^2). To start the separation process, the membrane was first pre-wetted with small amount of water, and then the oil/water free mixture or emulsions were pour into the upper tube. The water spontaneously permeated the membrane and was collected at a bottom beaker. The entire process was driven by gravity without any other external pressure (with a height difference of 6.4 cm, equivalent to a driving pressure of ~0.006 bar). Separation time was recorded

to determine the membrane permeate flux, and the oil content in the oil/water mixture and permeate were measured by a total organic carbon (TOC) analyzer (TOC-V CPH, Shimadzu). The oil rejection of the membranes can be calculated using the following equation:

$$\eta(\%) = \frac{C_0 - C_p}{C_0} \times 100 \qquad (2)$$

where η is the oil rejection rate, and C_0 and C_p are the oil content in the oil/water emulsion and permeate, respectively.

3. Results and Discussion

3.1. Membrane surface morphology

The morphologies of the membranes were revealed by SEM, and the results are shown in **Figure 2**. The pristine PVA membrane exhibited a typical morphology of electrospun material, in which nanofibers with mean diameter of 460 nm were interconnected with each other to form a three-dimensional porous structure. However, the surfaces of the PVA nanofibers were very smooth (**Figure 2a**). After the membrane was treated with a modified Stöber reaction, monodisperse spherical nanoparticles with diameter of ~120 nm were evenly deposited on the pristine PVA nanofibers (**Figure 2b and Figure S1**). Further EDX mapping of single nanofiber revealed that silicon elements were uniformly distributed along the nanofiber (**Figure 2c**), revealing successful deposition of silica nanoparticles by the reaction (further evidences are discussed in the following section). The silica nanoparticles created secondary nanostructures (finer texture) on pristine nanofibrous surface (coarser texture), which, together with their intrinsic hydrophilicity, were expected to amplify the wettability of the membrane from hydrophilicity to superhydrophlicity. Though the mean diameter of the treated nanofibers increased from 460 to 770 nm, and mean pore size slightly decreased from

decreased from 532±3 to 433±5 nm due to the nanoparticles coating, the membrane thickness remained almost unchanged after the treatment (as shown in **Table 1**), which is desirable for a high efficient oil/water separation. In addition, the slight difference of IPA uptakes (**Table 1**) between the treated and pristine membrane implied that the silica coating caused negligible changes to the porosity of pristine membrane.

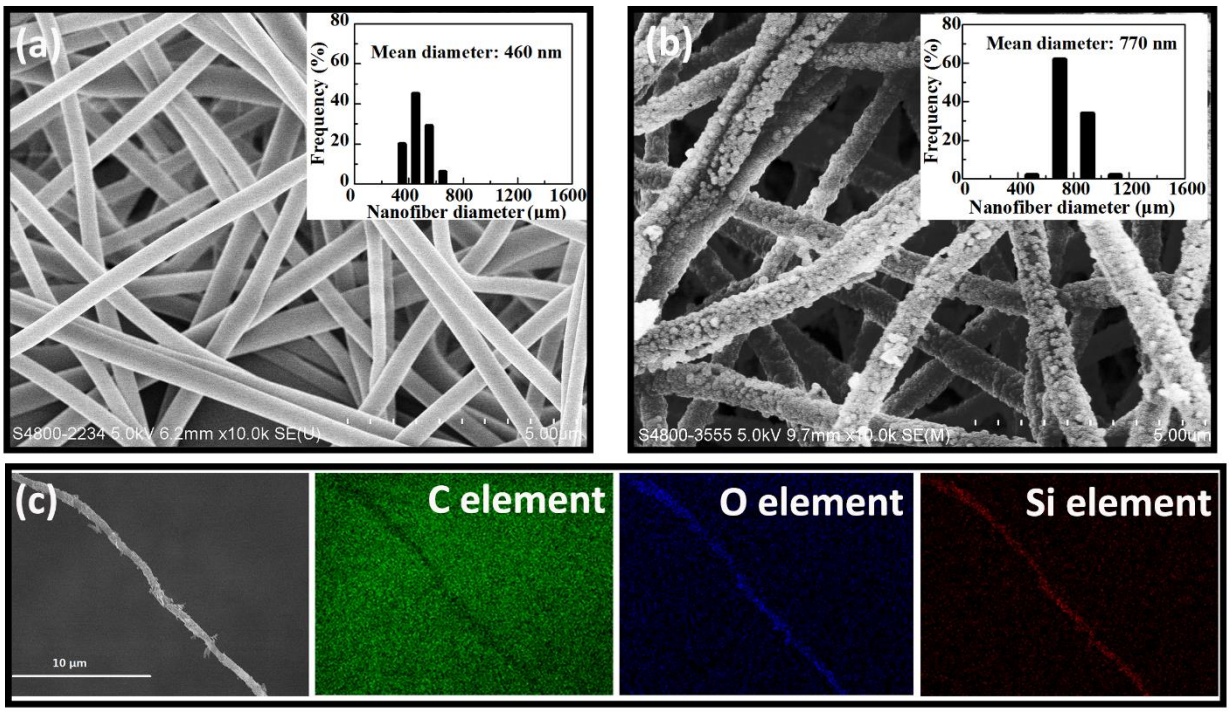

Figure 2. SEM images and corresponding nanofiber diameter distribution of pristine (a) and silica-coated (b) PVA nanofibrous membranes. (c), EDX mapping images of the SiO_2@PVA nanofibrous membrane

Table 1. Characteristics of the pristine PVA and hybrid SiO_2@PVA nanofibrous membranes

	Mean fiber diameter (nm)	IPA uptake ($g \cdot g^{-1}$)	Thickness (mm)	Mean pore size (nm)
Pristine PVA membrane	460±70	4.95±0.02	0.40±0.02	532±3
Hybrid SiO_2@PVA membrane	770±90	4.62±0.27	0.39±0.03	433±5

3.2. Chemical analysis

The surface chemistry variation before and after the Stöber reaction were characterized by FTIR and XPS, respectively. In **Figure 3a**, the absorption peak at 3370 cm^{-1} in both spectra were assigned

to O-H stretching [36], and the peaks at 2922 and 2857 cm^{-1} were due to the stretching of -CH from alkyl groups [37]. These absorption peaks verified the presence of PVA. In comparison, new peaks at 1095 and 950 cm^{-1} appeared in the spectra of treated nanofiber, which could be assigned to Si-O-Si asymmetric stretching [38] and Si-OH stretching [39], respectively. This observation demonstrated the successful deposition of silica nanoparticles in the treated nanofibrous membrane. In addition, the abundant hydroxyl groups on the pristine PVA nanofiber surface can form strong hydrogen bonds with the silanol (Si-OH) group (as illustrated in **Figure 1c**) [40, 41], thus enhanced silica nanoparticles stability on the nanofibers was expected. Moreover, XPS spectra of both membranes were presented in **Figure 3b**. Only carbon and oxygen elements were detected in the pristine PVA membrane, whereas, Si(2s) and Si(2p) signals were detected in the treated membrane, further confirming the deposition of silica on the PVA nanofibers.

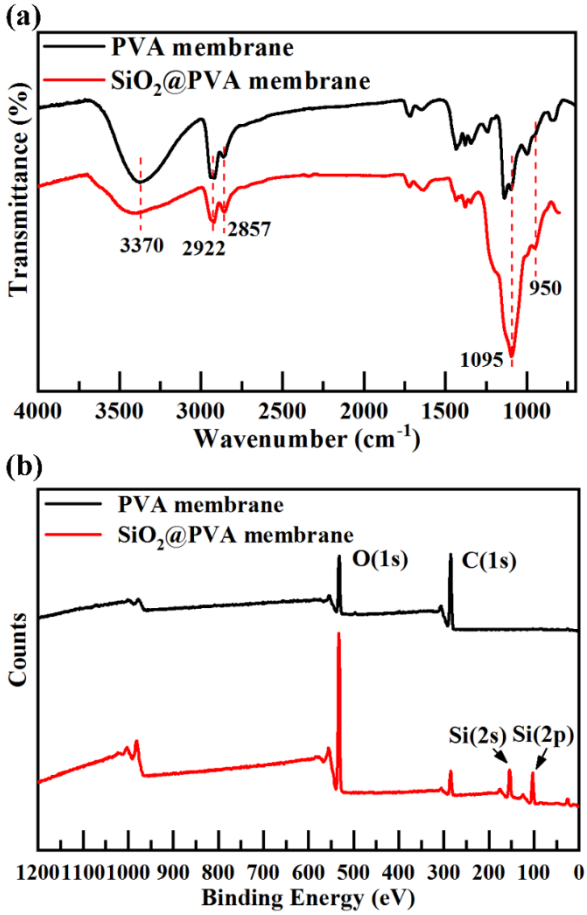

Figure 3. Chemical components characterizations: (a), FTIR analysis and (b) XPS analysis of the pristine PVA

membrane and SiO_2@PVA membrane

3.3. Membrane wettability

The wettability were investigated through in-air contact angle, underwater oil contact angle, as well as dynamic wetting behavior of water or oil droplets on the membranes. In air, the pristine and the treated membranes both had water and oil contact angles of 0°, showing in-air amphiphilicity. When immersed in water, the pristine PVA membrane showed underwater oleophobicity with underwater oil contact angle of 120.6° (**Figure 4a**), however, the oil droplets were sticky on the pristine membrane surface with underwater oil sliding angle of 180°. Remarkably, the SiO_2@PVA membrane exhibited underwater oil contact angle of 161.8° (**Figure 4b**), and underwater oil sliding angle of merely 6.2°, indicating that underwater superoleophobicity was achieved after the silica deposition on the pristine PVA nanofibrous membrane.

The dynamic wetting behavior of water or oil droplets on the membranes were recorded using a high-speed camera. For in-air water wetting process, both the pristine PVA membrane and treated SiO_2@PVA membrane can "capture" the water droplet when the latter touched the membrane surfaces. However, it took almost 7.02 s for the water droplet to completely spread into the pristine membrane (**Figure 4c**), whereas, only 0.53 s was required for the same process on the SiO2@PVA membrane (**Figure 4d**). More than one order of magnitude improvement in wetting speed was displayed after the silica coating, showing a superior in-air "water-loving" property of the silica decorated PVA membrane. This enhanced water affinity has been demonstrated to one of the key for better oil/water separation performance, because it enable instantaneous water layer formation on the membrane surface to completely reject oil droplets [42].

As for the underwater oil wetting process, one oil droplet was slowly lifted into contact with the

membrane surfaces with an obvious deformation, and then lifted away. Remarkably, the oil droplet was dramatically elongated when being lifted up, and eventually deposited on the pristine PVA membrane (**Figure 4e**), indicating a strong underwater adhesion of the oil droplet with the pristine PVA membrane. In contrast, during the same process on the SiO_2@PVA membrane surface (**Figure 4f**), the oil droplet easily slipped aside due to uneven pressure, and was lifted away from the membrane surface without observable droplet deformation. These observations confirmed a very weak underwater adhesion of the oil droplet (i.e., excellent "oil-hating" property) with the SiO_2@PVA membrane surface, which is highly desirable to reduce membrane fouling [8]: Various previous studies [25, 29, 43] have observed rapid flux drop for using hydrophilic membranes in oil/water separation due to surface pores blockage by strong underwater adhesion of the oil droplet with the membrane surface, whereas superhydrophilic membrane was able to maintain stable separation flux because of the underwater non-sticky property of the membrane towards oil droplet, which will be further confirmed in the following sections. In addition, the enhanced underwater superoleophobicity of the SiO_2@PVA membrane can be attributed to the multiscale roughness created by deposition silica nanoparticles (finer texture) on the pristine nanofibrous surface (coarser texture) [11]. According to Cassie–Baxter theory, when micro/nanostructures are induced on the surface, water can be easily trapped into the hierarchical textures, leading to a composite water-solid interface. In this way, the water trapped in the hierarchically rough structures serves as a repulsive liquid phase to prevent the penetration of the oil droplets, yielding enhanced underwater superoleophobic and low-adhesive properties [8].

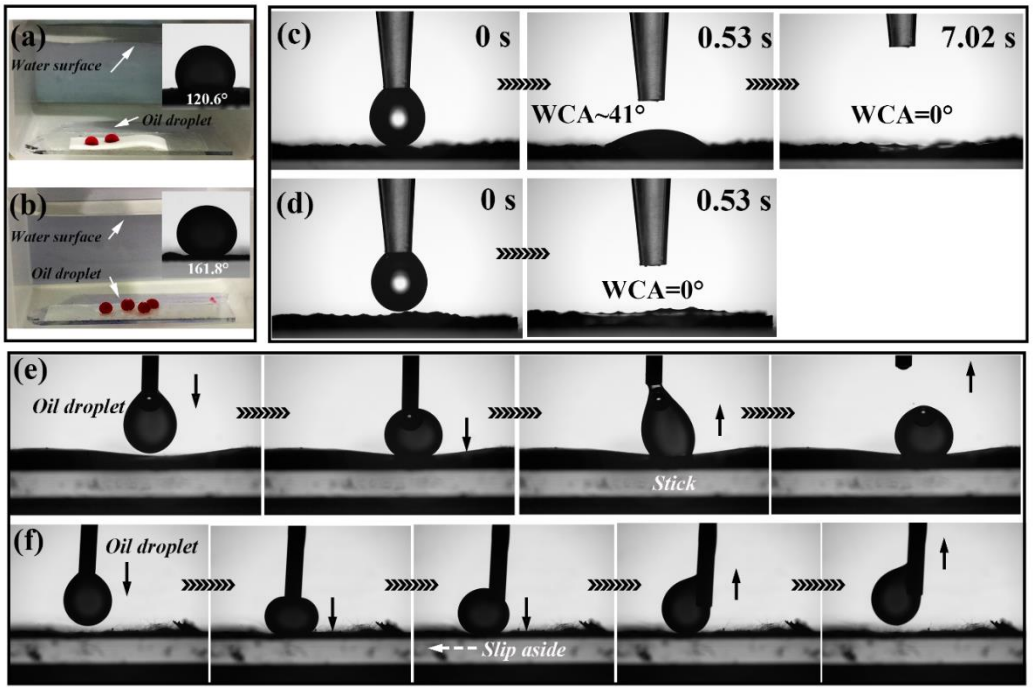

Figure 4. Wettability characterization of the membranes: Under-water oil droplet contact angle on the (a) pristine PVA membrane and (b) SiO_2@PVA membrane, respectively. Snap shots of water droplets spreading on (c) PVA and (d) SiO_2/PVA membrane surfaces. Dynamic underwater contacting behavior of oil droplet with the (e) pristine PVA membrane and (f) SiO_2@PVA membrane.

3.4.Oil/water separation experiments

As evidenced above, the SiO_2@PVA membrane displayed intriguing selective wettability (superhydrophilicity-underwater superoleophobicity) with highly porous membrane structure, which made it an attractive material for oil/water separation application. Therefore, a series of experiments were carried out to evaluate its oil/water separation performances.

First as a proof of concept, free kerosene/water mixture and surfactant-stabilized kerosene-in-water emulsion were separated using the SiO_2@PVA membrane. As shown in **Figure 5a,b**, one prewetted membrane was sealed in the middle of a dead-end model filtration module, and the oil/water mixtures were directly poured into the upper tube. Driven solely by gravity, the water instantaneously wetted the membrane and penetrated into the bottom tube, whereas the oil remained in the upper tube. For both experiments, the penetrates in the bottom tubes were very clear when

compared to the initial mixtures, indicating high separation ability. Furthermore, the optical microscopic images of the kerosene-in-water emulsion showed that the initial emulsion was milky with numerous oil droplets dispersed in the water bulk (mean diameter of 1.36 μm), whereas no visible oil droplets were observed in the permeate, further confirming the oil in the surfactant-stabilized emulsion can be efficiently removed by the SiO_2@PVA membrane (**Figure 5c**). The same SiO_2@PVA membrane was used in recycle kerosene-in-water emulsion separation experiments during which the membrane was simply rinsed with ethanol and water after each cycle. As shown in **Figure 5d**, both the oil rejection and permeate flux remained stable in five cycles of repeated experiments, showing outstanding reusability of the membrane. It can be attributed to the stable silica coating on the PVA fibers (as shown the SEM image of the used membrane in **Figure S2**), which enable the sustained superhydrophilic-underwater superoleophobic properties.

In practical processes, oils of different densities can be generated to form emulsified oily wastewater. Herein, the effect of oil density on the oil/water emulsion separation performances was investigated. The model oils were n-heptane, kerosene, toluene, and chloroform with density of 0.684, 0.8, 0.867, and 1.49 $g \cdot cm^{-3}$, respectively. As shown in **Figure 5e**, for n-heptane, kerosene, and toluene which have lower densities than water, the oil rejections were all over 95% with permeate flux as high as ~ 1500 $L \cdot m^{-2} \cdot h^{-1}$ under gravity driven of ~0.006 bar (This separation performance was much superior than that of conventional micro/ultra filtration membranes [44, 45], and was comparable to recently reported SUS nanofibrous membranes, as shown in **Table 2**). As for chloroform whose density is higher than water, in contrast, both the oil rejection and flux were reduced to 81% and 1159 $L \cdot m^{-2} \cdot h^{-1}$, respectively. Clearly, the oil density played an important role during the emulsion separation process, which can be hypothetically illustrated in **Figure 6**. When the light oil whose density was smaller than water approaches the membrane surface during the separation process, it

can easily detach back to the bulk feed due to the non-sticky property of the SUS membrane. In contrast, though also non-sticky, the heavy oil droplets were more likely to rest on the membrane surface due to heavier density, which gradually builds an unfavorable oil accumulation near the membrane surface leading to a reduced permeate flux. To make it worse, the oil droplets whose diameters were smaller than the membrane pore size would have greater chances to permeate the membrane pore, and thus compromised the oil rejection rate.

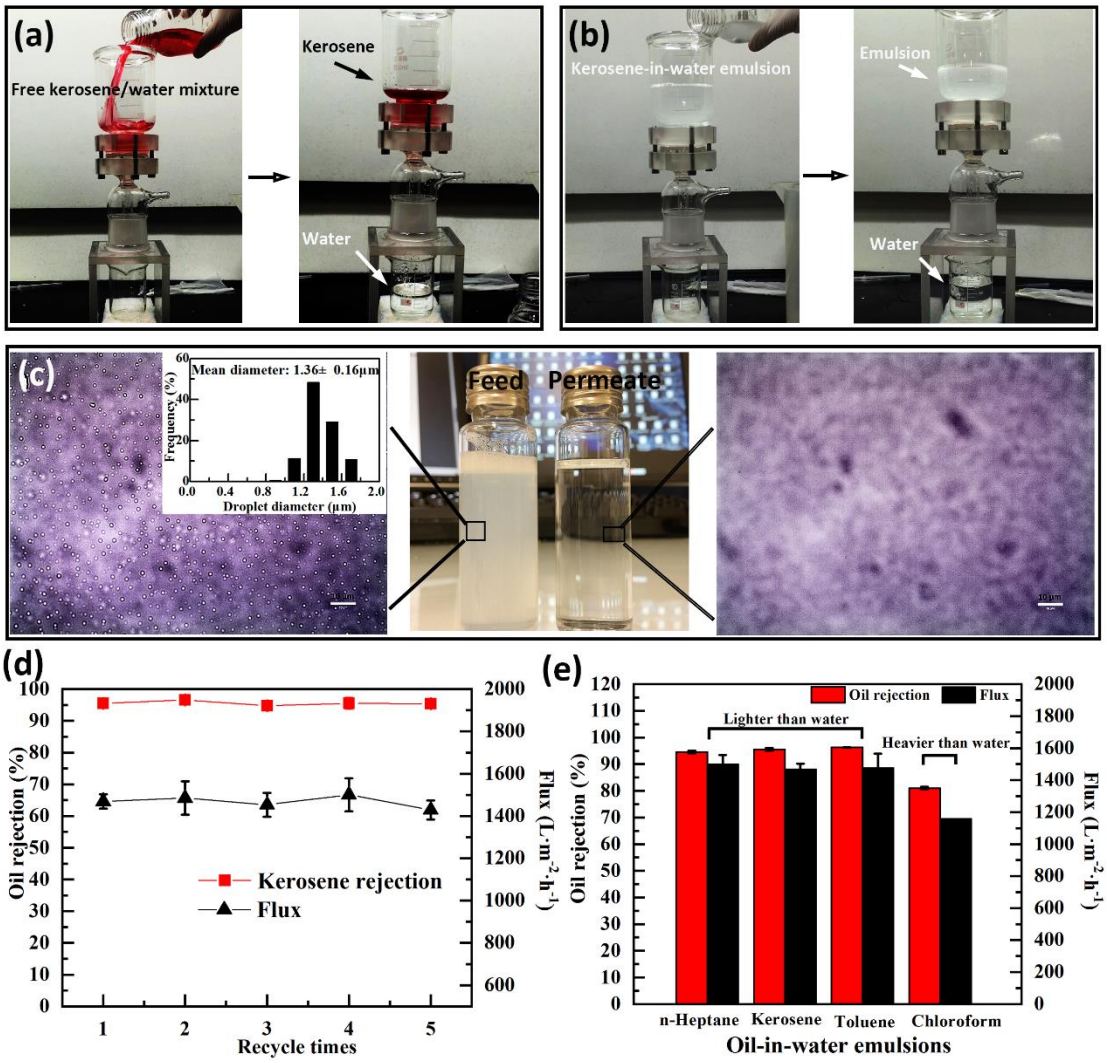

Figure 5. Oil/water separation performances: (a), photos showing free kerosene/water mixture separation process; (b), photo showing kerosene/water emulsion separation process; (c), optical photos of the kerosene/water emulsion and the permeate after separation, the figure inserted at the upper left showed the droplet distribution; (d), oil rejection and separation flux stabilities of kerosene/water emulsion separation using the same SiO_2@PVA membrane; (e), oil rejection and separation flux for different oil-in-water emulsion separation processes.

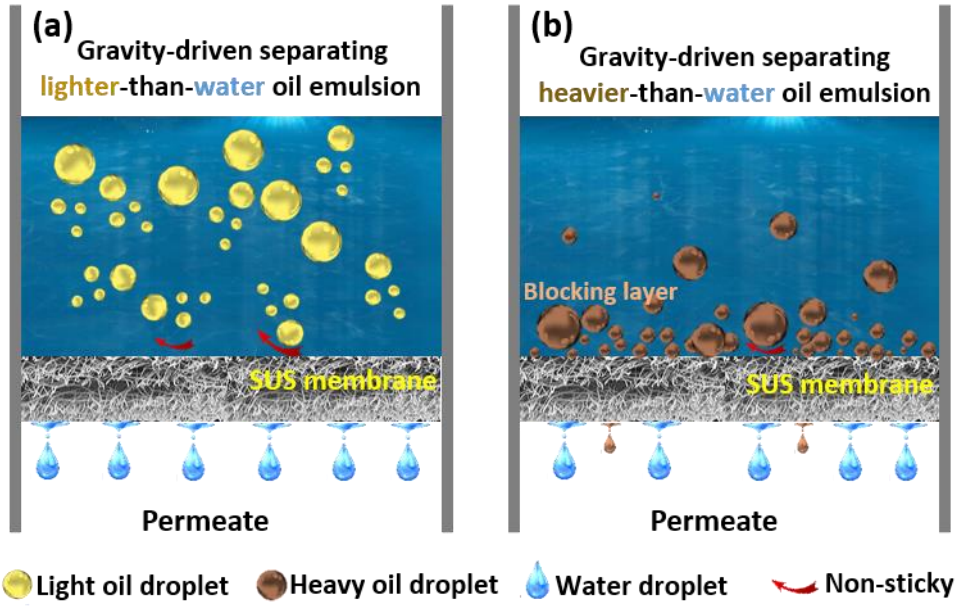

Figure 6. Schematic illustration of different oil/water separation behaviors of (a) lighter-than-water and (b) heavier-than-water oil droplets.

Table 2. Comparison of oil-in-water emulsion separation performances using different nanofibrous membranes

Membrane material	Type	Oil-in-water emulsion	Pressure (bar)	Flux ($L \cdot m^{-2} \cdot h^{-1}$)	Rejection (%)	Publication year and Ref.
P(NIPAAm-co-NMA)/Chitin	Nanofibrous	Edible oil/water	0.3	~1300	99.1	2017, [30]
Composite PAN	Nanofibrous	SDS/n-hexane/water	0.01	692	N.A.	2018, [25]
SiO_2/PAN/PAN composite	Nanofibrous	SDS/diesel/water	0.01	267	> 96.5	2018, [43]
Clay/PVA	Nanofibrous	DC193 fluid/soybean oil/water	2~6	20~60	> 90	2017, [46]
ZNG-g-PVDF	Nanofibrous	Crude oil/water	N.A.	> 600	> 98.7	2019, [47]
CNT/PAN	Nanofibrous	Tween 20/Canola oil/water	0.2	~60	95	2020, [48]
SiO_2@PVA	Nanofibrous	Tween 80/toluene/water, Tween 80/heptane/water, Tween 80/kerosene/water	0.006	~1500	> 95	This work

4. Conclusions

In summary, we have reported a simple, low cost electrospinning/In-situ growth strategy to prepare robust superhydrophilic-underwater superoleophobic SiO_2@PVA nanofibrous membranes for efficient oil/water separation. The pristine PVA nanofibrous membranes are abundant with hydroxyl groups which facilitated in-situ growth of silica nanoparticles on the nanofibers. The stable silica deposition created secondary roughness to the pristine membrane, amplifying its wettability

from hydrophilicity to superhydrophlicity. Wettability characterizations revealed that the SiO_2@PVA nanofibrous membrane exhibited outstanding "water-loving" and "oil-hating" properties, with in-air instantaneous water adsorption (0.53s) and underwater oil contact / sliding angle of 161.8° / 6.2°, respectively. The as-prepared SUS membrane showed efficient separation performances for both free oil/water mixture and a variety of surfactant-stabilized oil-in-water emulsions. In addition, light oils were more efficiently rejected by the SUS membrane when compared to heavy oils, which underscored the important role of the oil density during the oil/water separation process. Finally, the SUS membrane showed robust reusability that it maintained stable oil rejection and permeate flux in cyclic experiments.

Acknowledgements

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