Superwettable Nanofibrous Skins

Biomimetic and Superwettable Nanofibrous Skins for Highly Efficient Separation of Oil-in-Water Emulsions

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Developing a feasible and efficient separation membrane for the purification of highly emulsified oily wastewater is of significance but challenging due to the critical limitations of low flux and serious membrane fouling. Herein, a biomimetic and superwettable nanofibrous skin on an electrospun fibrous membrane via a facile strategy of synchronous electrospraying and electrospinning is created. The obtained nanofibrous skin possesses a lotus-leaf-like micro/nanostructured surface with intriguing superhydrophilicity and underwater superoleophobicity, which are due to the synergistic effect of the hierarchical roughness and hydrophilic polymeric matrix. The ultrathin, high porosity, sub-micrometer porous skin layer results in the composite nanofibrous membranes exhibiting superior performances for separating both highly emulsified surfactant-free and surfactant-stabilized oil-in-water emulsions. An ultrahigh permeation flux of up to 5152 L m⁻² h^{-1} with a separation efficiency of >99.93% is obtained solely under the driving of gravity (≈1 kPa), which was one order of magnitude higher than that of conventional filtration membranes with similar separation properties, showing significant applicability for energy-saving filtration. Moreover, with the advantage of an excellent antioil fouling property, the membrane exhibits robust reusability for long-term separation, which is promising for large-scale oily wastewater remediation.

1. Introduction

Over the past few decades, numerous oil pollutions have occurred with catastrophic consequences for water environment and ecology, which are mainly caused by the frequent oil

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spills, industrial chemical leaks, and the discharge of oily sewage.^[1,2] Therefore, effective oil/water separation processes are of great significance for oily wastewater purification. Generally, the oil contaminants in water are insoluble hydrocarbons or fatty glycerides,^[3] and the related oil-inwater mixtures mainly exist as three types, free floating oil, unstable free oil droplets. and stable emulsions (oil droplet diameters <20 µm), depending on the forming conditions.^[4] Conventional oil/water separation technologies, such as skimming, adsorption, air flotation, centrifugation, and chemical coagulation, suffer from the disadvantages of low separation efficiency, high energy cost, complex operation process, and secondary contamination, and they are seldom capable of separating highly emulsified oily wastewater.^[5,6] Alternatively, newly developed membrane separation technologies based on microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) have been studied for oily wastewater separations because of their advantages, such as high separation efficiency, relatively low cost, and

simple operation.^[3,7,8] However, critical limitations still remain, including a low permeation flux and high driving pressure of several bars, which result in the poor antifouling property against oils, low porosity, and undersized pores in conventional membranes.^[9,10] Therefore, more efforts are needed to develop a feasible and specialized membrane for the effective separation of various oil-in-water emulsions.

Currently, impressive progress has been made on the design and development of superwetting surfaces inspired by living organisms in nature,^[11–15] e.g., the lotus leaf, pitcher plant, and fish scales, which have been widely employed to further improve the antifouling performance of separation membranes. Generally, two criteria are necessary for the design of a superwettable surface:^[16,17] (i) creating a micro/nanostructured roughness surface, (ii) regulating the matrix surface free energy at an appropriate threshold value. Based on these principles, a few explorative works have been performed and representative membranes with superhydrophilicity and superoleophobicity have been invented for the treatment of oily wastewater. However, bottlenecks still remain because of the initial defects in the substrates used, i.e., the relatively low porosity of the phase inversion membranes^[9] and the larger pore size of various steel meshes.^[18] Therefore, further improving the permeation





flux based on a high separation efficiency and a low driving pressure is still an imperative challenge.^[2] Recently, a few pioneers membranes based on nanofibrous materials, e.g., carbon nanotubes (CNTs), have attracted increasing attention in the area of high-efficiency liquid filtration owing to their advantages of a small pore size and ultrathin thickness, which are critical factors that influence the permeation flux, according to the Hagen–Poiseuille equation $(J = \frac{\epsilon \pi r_p^2 \Delta p}{8 \mu L})$, where J is the permeation flux of the liquid, ε is the porosity, $r_{\rm p}$ is the effective pore radius, Δp is the applied pressure, μ is the viscosity of the liquid, and L is the thickness of the membrane).^[19–21] Obviously, apart from selective wettability, an ideal membrane for emulsion separation should also possess a high porosity and a thin separation layer with an effective pore size for the rejection of oil droplets without an excessive decline in the permeation flux. However, further improving the porosity of the CNT-based films was difficult due to their highly compact structures and functional additives, which were crucial for their mechanical strength and selective wettability.^[19]

Most recently, more attention has been paid to the research on electrospun fibrous separation membranes because of their high porosity, high surface area, and easily tunable structures, which make them exceptional candidates for oil/water separation with high permeation fluxes under lower driving pressures.^[22,23] Till now, a few works have been performed via directly regulating the surface wettability of as-spun fibrous membranes, but most of the obtained superwettable membranes are solely effective in separating immiscible oil/water mixtures (free oil) or emulsions with larger droplets and are incapable of treating the highly emulsified oil/water emulsions due to their relatively large pore size.^[24-29] To further improve the separation efficiency, a series of polymeric solid films were constructed on the surface of conventional electrospun membranes, but they resulted in a rapid decline in the permeation fluxes due to the low porosity of the obtained composite membranes.^[30-33] Therefore, balancing the permeation flux and separation efficiency of the electrospun fibrous oil/water separation membranes in an affordable and feasible way is still a principal issue that has yet to be solved.

Herein, inspired by the micro/nanostructures of the lotus leaf surface, we successfully constructed a hierarchically structured, sub-micrometer, porous skin layer on the surface of a common electrospun fibrous membrane by elaborately tuning the transient state of the electrospraying and electrospinning. The synergistic effect of the biomimetic micro/nanostructures and the superior hydrophilicity of the hydrated polymeric matrix resulted in the obtained nanofibrous skin layer exhibiting specific superhydrophilicity and underwater superoleophobicity with a nearly zero oil adhesion force. Most importantly, the conjunctive networks of the nanofilament formed an ultrathin and highly porous barrier with a sub-micrometer pore size in the skin layer, which effectively intercepted tiny oil droplets and allowed water permeation with a high flux. To the best of our knowledge, there is no similar membrane for emulsion separation reported before. Consequently, the related membrane equipped with the superwettable, nanofibrous skin was able to separate both highly emulsified surfactant-free and surfactant-stabilized emulsions, and ultrahigh separation fluxes were obtained at low driving pressures along with the desired antifouling and reusability, indicating promising utility for the next generation of energy-saving water treatment systems.

2. Results and Discussion

2.1. Preparation and Microstructure Characterizations

We designed the structures of the separation membranes based on three criteria: (i) the surface morphology should be a hierarchical structure to ensure the superwettability, (ii) the surface layer must be sub-micrometer porous with high porosity to effectively hold back the tiny oil droplets and ensure the water permeation flux, and (iii) the membrane must be mechanically robust enough to withstand the driving pressure. Consequently, as schematically shown in Figure 1a, a nanofibrous skin laver with a lotus leaf-like surface was in situ constructed by employing a specific transient state between electrospraying and electrospinning. During the fabrication process, a common electrospun polyacrylonitrile (PAN) nanofibrous membrane with randomly oriented nonwoven structures and sufficient mechanical strength was first prepared and used as the substrate (see the details in Figure S1 and the Supplementary Discussion section in the Supporting Information). Subsequently, a series of dilute PAN solutions with different concentrations were directly sprayed on the surface of the substrate for a constant time (6 h). After that, a composite nanofibrous membrane with a uniform, ultrathin skin layer (≈5 µm) was successfully constructed (Figure 1b). Interestingly, the obtained nanofibrous skin layer exhibited remarkable lotus leaf-like hierarchical structures^[13] with numerous randomly distributed microsized humps and a nanoscale rough surface that formed via conjunctive nanofilaments with bead-on-string structures (Figure 1c,d), which may be beneficial for the superwettability according to the Cassie model.^[34] Exactly, the obtained composite nanofibrous membranes after a partial hydrolysis exhibited superhydrophilicity in air with a water contact angle (WCA) of $\approx 0^{\circ}$ and superoleophobicity with an underwater oil contact angle (UWOCA) of ≈162° (Figure 1e,f), which are crucial for oil-inwater emulsion separation. In addition, the obtained composite membrane with proper skin layer was easily scalable and exhibited satisfactory mechanical properties, which is of great importance for practical applications (see details in Figure 1g and Figure S2 in the Supporting Information).

The influence of the polymer concentration on the pore structures and the surface morphologies of the skin layers was investigated. **Figure 2a**–d depict the SEM images of the as-spun composite nanofibrous membranes with skin layers derived from precursor solutions with PAN concentrations of 1, 3, 5, and 7 wt%, namely, CNFM-1, CNFM-3, CNFM-5, and CNFM-7, respectively. The surface morphologies of the obtained membranes were quite different from each other. With a low PAN concentration of 1 wt%, only a few microspheres were sparsely decorated on the surface of the single fibers, which mainly came from the electrospraying effect due to the low viscosity of the precursor solution (Table S1, Supporting Information).^[35] Interestingly, when the content of the polymer increased to 3 wt%, more microspheres connected with a few nanofilaments



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Figure 1. a) Schematic illustrating the formation process of the nanofibrous skin layers. b,c) Cross-section SEM images of the representative membrane (the inset in panel (c) is a high-magnification SEM of the skin layer). d) The digital photo of a lotus leaf and the corresponding SEM image of its surface. e,f) Photographs of the water droplet in air and the oil droplet under water on the nanofibrous skin layer. g) The tensile stress–strain curve of the composite membrane (the inset is a digital photograph of the as-prepared large-sized membrane: 50 cm \times 40 cm). The skin layer here was derived from 5 wt% PAN solutions and after 30 min hydrolysis.

were obtained, and the microspheres with diameters of $\approx 0.9 \,\mu m$ were uniformly stacked on the surface of the substrate form an intact skin layer. Further increasing the polymer concentration up to 5 wt% resulted in a large number of networks formed by conjunctive nanofilaments with diameters of ≈58 nm, and a few bottom embedded microspheres were obtained (Figure S3, Supporting Information), which indicated a transition from electrospraying to electrospinning. This was attributed to the enhanced polymer chain interactions at a higher polymer concentration.^[36,37] The conjunctive structures between fibers and microspheres were ascribed to the residual solvent, which is beneficial for the mechanical stability of the membrane.^[27,35] Numerous randomly distributed nanofibers with an average diameter of ≈75 nm were obtained from the precursor solution at a polymer concentration of 7 wt%, which was a typical electrospinning product. As demonstrated in Figure 2e, the average pore diameters of the obtained membranes were 2.59, 1.90, 0.49, and 0.48 µm, indicating an obvious decrease in the pore size as the polymer concentration increased, which was attributed to the construction of nanofibrous skin layers.^[38] In addition, the surface porosity of the skin layer decreased obviously, which could be well recognized from the SEM images. Despite that, the porosity of the CNFMs was >90%, which was contributed by the 3D nonwoven structures of the nanofibers and the cavities deriving from the supporting of microspheres.

The surface rough microstructures on the skin layer were further investigated. Figure 2f demonstrates the corresponding R_a values of the membranes detected via a noncontact optical profilometry analysis method. The CNFM-1 exhibited the lowest R_a value of 1.58 µm indicative of a relatively flat surface, which was due to the lower loading amount of the microspheres. As expected, the corresponding R_a value significantly increased to 8.6 µm when the PAN content was raised to 3 wt%, which was mainly contributed by the formed layer consisting numerous microspheres.^[13,35] However, the roughness gradually decreased and became more uniform with the further





Figure 2. a–d) SEM images of the obtained membranes with skin layers derived from dilute PAN solutions with concentration of 1, 3, 5, and 7 wt%, respectively. e) Pore size distribution plots of the membranes. f) The R_a values of the membranes (the insets are the corresponding optical profilometry images).

increase in the concentration of the polymer, which was resulted from the decrease in the number of individual microspheres and the formation of continuous fibers (Figure 2c). Thus, CNFM-5 and CNFM-7 exhibited R_a values of 6.1 and 2.4 μ m, respectively, which were consist with the results from the SEM characterizations.

2.2. Regulation of the Selective Wettability

A high selective wettability for oil and water is another crucial factor for oil/water separation materials.^[4,7] Thus, the wettability of the as-spun CNFMs was examined. As shown in Figure S4a,b (Supporting Information), the obtained membranes exhibited superhydrophilicity in air and underwater oleophobicity. Moreover, the UWOCAs were correlated positively with the surface roughness of the membranes. This phenomenon was attributed to the established rough surface layer and the relative hydrophilic property of the used PAN,^[39] which contained amide groups and nitrile groups (Figure S5, Supporting Information). Although the as-spun nanofibrous membrane (e.g., CNFM-5) was underwater superoleophobic (UWOCA = $\approx 153^{\circ}$), it could not resist the adhesion of oil. As shown in Figure S4c and Movie S1 (Supporting Information), when an oil droplet (3 μ L, 1,2-dichloroethane) came into contact with the surface of the membrane, it was pinned onto the surface and could not be removed, which indicated the poor antioil-fouling property of the membrane. Considering that the adhered oil droplets would seriously block the surface pores and decrease the wetting selectivity of the membrane,^[10,40] thus a facile and effective approach to further improve the antifouling ability of the skin layer was desired, and two criteria must be fulfilled: (i) the treatment for the membrane must be uniform; (ii) the pore structures must not be damaged after the hydrophilic treatment. Comprehensively considering the pore structures (pore size and surface porosity) and surface roughness, the CNFM-5 was selected for subsequent treatment with a 1 M NaOH solution to hydrolyze the amide groups and partial nitrile groups into carboxyl groups (Figure S5, Supporting Information),^[28,29] and the influence of the hydrolysis degree on the antioil wettability of the membranes was studied. Figure 3a demonstrates the corresponding advancing and receding UWOCAs of the membranes with different hydrolysis times. With the increase in hydrolysis time, both the advancing and receding UWOCAs obviously increased, and equilibrium was obtained after 30 min with advancing and receding UWOCAs of ≈163° and ≈161°, respectively. Meanwhile, the corresponding UWOCA hysteresis significantly decreased from 10° to 2°, indicative of a typical superoleophobic performance. However, the maximum advancing UWOCA of the corresponding flat film was only $\approx 133^{\circ}$, which further confirmed the effect of the surface roughness on the enhanced oleophobicity of the nanofibrous skin layer.^[41] Figure 3b demonstrates the static UWOCAs of the hydrolyzed nanofibrous membranes, which were similar to the advancing and receding UWOCAs, and an equilibrium was obtained at 30 min. The calculated adhesion force was near zero (see details in the Supplementary Discussion section in the Supporting Information),^[42] which indicated an ultralow adhesion between the oil and the membrane. The insets in Figure 3b and Movie S2 (Supporting Information) demonstrate a dynamic oil-repelling test to vividly show the underwater oil resistance property of the membrane. As depicted, an oil droplet was forced onto the skin layer of the membrane until an obvious deformation appeared. After that, the oil droplet







Figure 3. a) Advancing and receding UWOCAs of the hydrolyzed nanofibrous membranes. The maximum UWOCA on the hydrolyzed flat PAN films is also shown. b) Static UWOCAs and calculated adhesion forces of the corresponding membranes (the insets are photographs of the dynamic measurement of oil adhesion on the membrane). c) Plots of $\cos \theta^*$ with $\cos \theta$ for the UWOCAs of the nanofibrous membranes (θ^*) and the corresponding flat films (θ). d) Schematic diagram of the underwater superoleophobicity of the nanofibrous skin layer.

was slowly lifted up, and there was no significant deformation when the oil droplet completely detached from the membrane. Similarly, the sliding contact angles of the membranes with different hydrolysis sharply decreased to $\approx 3^{\circ}$ (Figure S6, Supporting Information), which is beneficial for the remove and coalescence of oil droplets on the surface of the corresponding membranes.

To find out the proper mechanism for the underwater superoleophobicity of the nanofibrous skin, the UWOCAs on the skin layer and the corresponded PAN flat films with different hydrolysis times (Figure S7, Supporting Information) were combined to construct a typical wetting diagram.^[41] As shown in Figure 3c, θ^* is the UWOCA of the nanofibrous skin and θ is the corresponding UWOCA of the flat film. The whole plot was established based on the relation of $\cos \theta^*$ versus $\cos \theta$. Generally, considering that the θ for the flat film without hydrolysis was $\approx 80^\circ$, the corresponding θ^* of the nanofibrous skins should be $<\theta < 90^{\circ}$ according to the Wenzel theory: $\cos \theta^* = r \cos \theta$, where *r* is the surface roughness, which was mentioned in section I (r > 1 for nanofibrous skins). Surprisingly, the nanofibrous skin before hydrolysis exhibited a higher apparent $\theta^* >$ 145°, which is located in section IV (red points). This unusual phenomenon may be attributed to the effect of the Cassie state $(\cos \theta^* = -1 + f_s(1 + \cos \theta))$, where f_s is the fraction of the solid in contact with the liquid), but according to the previous studies, there may also exist a transformation from the initial Cassie state to Wenzel state to some degree, causing the coexistence of the abovementioned high contact angle and the poor antioil adhesion property,^[41,43,44] which could also be confirmed by

the unstable UWOCA of the membrane with nanofibrous skin before hydrolysis (Figure S8a, Supporting Information) as well as the high sliding angles (Figure S6, Supporting Information). As expected, after the hydrolysis treatment, both the θ and corresponding θ^* were >90°, and all the points were located in section III, which is indicative of being in a more stable Cassie state, thus the corresponded UWOCA was quite stable (Figure S8b, Supporting Information). Additionally, it can be seen that the data points in sections III and IV exhibited a linear relationship. This result conformed to the Cassie equation and the calculated f_c was ≈ 0.12 . Figure 3d demonstrates a schematic illustration of the underwater superoleophobicity of our nanofibrous skin. Three aspects may contribute to this result: (i) the formed carboxy groups or carboxylate radical on the surface of the polymer matrix construct a stable hydrated sheath to prevent the directly contact with oil; (ii) the conjunctive nanofilaments with beadson-string structures form a hierarchically structured barrier network to further reduce the contact area of the oil with the surface skin; (iii) the microspheres under the nanofibrous barrier networks form numerous cavities and provide more space to seal water, which acts as a cushion to prevent the intrusion of oil into the surface layer.^[44]

Figure 4a demonstrates the dynamic wetting behavior of water and oil on the skin of the selected membrane (CNFM-5 after 30 min of hydrolysis). When a droplet of water (3 μ L) contacted the surface of the membrane in air, it quickly spread and permeated into the membrane within 1.2 \pm 0.1 s with a near-zero contact angle, which was indicative of superhydrophilicity. However, when a droplet of oil (vegetable oil) with the

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Figure 4. a) Dynamic photographs showing the fast water spreading and the long-term antioil property of the membrane. b) The UWOCAs of different oils and the corresponding maximum intrusion pressures. c,d) Real-time images recording the superior antioil-fouling performance of the membrane. The membrane used for characterization was the CNFM-5 after 30 min hydrolysis and the oil used in panels (a), (c), and (d) is vegetable oil.

same volume was placed on the skin layer underwater, it stayed without any spreading for a long time (>24 h), indicating a stable antioil performance.^[45] Moreover, the UWOCAs and corresponding critical intrusion pressures of different oils for the membrane were further evaluated (Movie S4, Supporting Information). As shown in Figure 4b and Figure S9 (Supporting Information), the UWOCAs of various oils on the membrane were >160°, and the corresponding critical intrusion pressures were beyond 22 kPa, indicating a superior oil rejection property.^[19,20] The ultrafast water permeation and high antioil intrusion pressures can be explained by the selective capillary effect of the membrane according to the Laplace theory (see details in the Supplementary Discussion section in the Supporting Information).^[6,46] To further demonstrate the antioil property of the membrane, as shown in Figure 4c and Movie S3 (Supporting Information), the viscous vegetable oil (labeled with oil red) was quickly ejected onto the membrane underwater, and the oil jet immediately bounced up from the surface without any adhesion. Moreover, when the oil-fouled prewetted membrane in air was immersed into water, the spread oil layer completely detached from the surface in an extremely short time (Figure 4d; Movie S5, Supporting Information), indicating a robust self-cleaning performance of the membrane. This result was contributed by the good water absorption capacity of the membrane (\approx 34 g g⁻¹), in which the absorbed water could act as the cushion to prevent the direct contact of oil with the membrane even in the air (see details in Figure S10 and the Supplementary Discussion section in the Supporting Information).^[44]

2.3. Evaluation of the Emulsion Separation Performance

The intriguing selective wettability, high porosity (>90%), and small pore size (Figure S11; Table S2, Supporting Information) of the obtained membrane (CNFM-5 after 30 min of hydrolysis) endow it with a promising capability for separating various oil-in-water emulsions. Therefore, a series of proof-of-concept studies were performed to evaluate the emulsion separation performance. Surfactant-free emulsions (SFE) and surfactantstabilized emulsions (SSE) derived from various oils (Table S3, Supporting Information) were used as the model emulsions (Figures S12 and S13, Supporting Information). As shown in Figure 6a and Movie S6–S8 (Supporting Information), during the separation, the prewetted membrane was fixed between two





Figure 5. a) Permeation flux and the corresponding TOC contents in filtrates for different SFEs under the driving of gravity. b) Permeation flux and the corresponding TOC contents of the filtrates from the surfactant-stabilized emulsions under the driving of different pressures. c) Optical microscopy images and photographs of the surfactant-free/stabilized emulsions before and after separation. d) Schematic showing the assumed separation process for the SFEs and SSEs.

glass tubes in a dead-end model filtration device, and emulsions were directly poured onto the top surface of the membrane with a fixed liquid level of ≈ 10 cm. Figure 5a demonstrates the separation performance of the membrane for various SFEs. As expected, all the emulsions were successfully separated in one step, and the total organic carbon (TOC) contents in the filtrates of the various emulsions were all <20 mg L⁻¹, especially for the filtrates from petroleum ether and n-hexane-based SFE, the corresponding TOC values were $<3 \text{ mg L}^{-1}$ and the calculated separation efficient were >99.93%. The corresponding separation fluxes of the SFEs derived from petroleum ether, *n*-hexane, diesel, and vegetable oil were 3712, 5152, 2877, and 1984 Lm⁻²h⁻¹, respectively. The change in the permeation fluxes may be attributed to the different viscosity and oil droplets concentrations of the emulsions derived from oils with different properties (Table S3, Supporting Information).^[9,19] Herein, it should be mentioned that all the separations were solely gravity driven (Figure 6a; Movie S6, Supporting Information), which was equal to a driving pressure of ≈ 1 kPa. Despite that, the obtained separation fluxes were one order of magnitude higher than that of commercial MF and UF filtration membranes and were superior to those of previous reported membranes with similar rejection properties under the driving of external pressures.^[9,19,20] And there was also some room for the improvement of the permeation flux under external driving pressures (Movie S7, Supporting Information), For example, the permeation flux of petroleum ether based SFE was 6400 L m⁻² h^{-1} under the external driving pressure of 5 kPa, and there was no obvious change in the separation efficiency (TOC content in the filtrate was <4 mg L^{-1}).

Emulsions stabilized by surfactants are difficult to separate due to their small droplet size and good stability.^[47] Herein, the separation performance of the as-prepared composite membrane for various oil-in-water emulsions stabilized by a surfactant (sodium dodecyl sulfate, SDS) was evaluated. As shown in Figure 5b, the permeation flux obviously increased from 711 to 2264 L m⁻² h^{-1} when an external driving pressure of 5 kPa was loaded (Movie S8, Supporting Information). Meanwhile, the TOC content (including the remaining SDS) in the filtrates slightly increased from 26 to 28 mg L⁻¹, indicative of a stable separation efficiency. However, further increasing of the driving pressure resulted in a decrease in the permeation flux and a higher TOC content in the filtrates, i.e., lower separation efficiencies. This phenomenon was ascribed to the fact that a few tiny droplets were forced to penetrate into the membranes and blocked the channels inside the membrane under excessive driving pressures.^[48] The digital photographs and optical microscopic images of the petroleum ether based SFE and SSE before and after separation are shown in Figure 5c. Both the initial SFE and SSE were milky with numerous micrometer and sub-micrometer oil droplets, and the solutions became transparent after separation. No droplets could be observed in the corresponding optical microscopic images after the separation, which further confirmed the high separation efficiency of the membrane. To provide insight into the mechanism of the oil-in-water emulsion separation, hypothetical schematic illustrations were provided in Figure 5d to describe the separating process of the membrane for the SFEs and SSEs. With respect to the separation of the SFEs, the oil droplets were first intercepted by the sub-micrometer porous skin layer. Then, the

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Figure 6. a) Digital photos showing the process of emulsion separation under the driving of gravity and external pressure. b) Permeation flux and the corresponding TOC content of the filtrates for various SSEs under the driving of gravity and external pressure of 5 kPa. c) The relative separation flux and driving pressure of representative separation materials. d) The cycling separation performance of the membrane for corresponding SSE.

droplets freely rolled on the fluctuant surface under the driving force of the hydraulic power and coalesced due to the excellent antioil performance of the membrane. After that, the coalesced oil droplets with larger diameter completely detached from the membrane surface without fouling and demulsified to form free oil according to the Stokes law.^[49] This speculate mechanism could well explain the high separation flux of the obtained membranes. However, when the surfactant was present, the oil droplets hardly aggregated because of the surrounding surfactant, and a filter cake formed on the surface of the separation membrane, which would enhance the separation efficiency to some extent, thus the membrane could separate the emulsions with even smaller oil droplets than the pore size. However, the cake would also seriously block the surface pores and reduced the effective filtration area of the membranes, which resulted in a rapid decrease in the permeation flux.^[50]

To further evaluate the separation performance of the membrane for different emulsions, the obtained SDS-stabilized emulsions, namely, SDS/*n*-hexane/H₂O, SDS/diesel/H₂O, and SDS/vegetable oil/H₂O, were directly poured onto the membrane and the separation processes were carried out under the driving force of gravity or with an external driving pressure of 5 kPa, respectively. As shown in Figure 6b, permeation fluxes of 692, 312, and 410 L m⁻² h⁻¹ for SDS/*n*-hexane/H₂O, SDS/diesel/ H₂O, and SDS/vegetable oil/H₂O, respectively, were obtained under the driving of gravity, and the corresponding TOC contents in the collected filtrates were 23, 31, and 45 mg L⁻¹,

respectively. For external pressure driven separations, the corresponding permeation fluxes increased to 1399, 463, and $738\ L\ m^{-2}\ h^{-1}$ with TOC contents in the filtrates of 45, 50, and 72 mg L⁻¹, respectively. Herein, it should be mentioned that all the obtained TOC values contained a large amount of surfactant, according to the previous studies,^[9,19,51] which indicated that the real oil content in the filtrates was much lower than the tested values. As a result, the separation performance of the obtained membrane for surfactant-stabilized oil-in-water emulsions was comparable to that of the conventional MF and UF filtration membranes and a series of pioneer membranes reported before,^[9,19,32,52] as shown in Figure 6c. In addition, the reusability of the membrane was further evaluated via a cycling separation for the SDS/n-hexane/H2O emulsion by using the same dead-end model filtration device. As shown in Figure 6d, the initial and final permeation fluxes were recorded, and after each test cycle (10 min) the membrane was simply rinsed with pure water several times, and then it was directly used for the next cycling test, the whole test process lasted for 50 min. The result demonstrates that the permeation flux decrease with the increasing of time, which was ascribed to the formation of filtration cake on the surface of membrane (Figure 5d). Fortunately, after simply washing with water, the permeation flux was completely recovered, and there was no significant change in the separation efficiency during the cycling test, indicating a robust reusability of the membrane due to the excellent antifouling property of the nanofibrous skin layer.

3. Conclusion

In summary, we successfully created a superhydrophilic and underwater superoleophobic nanofibrous membrane with a biomimetic and sub-micrometer porous skin layer via a facile method of synchronous electrospraying and electrospinning. With the synergistic effect of the lotus leaf like hierarchical structures and hydrophilicity of the hydrated polymer matrix, the obtained nanofibrous skin layer of the membrane exhibited excellent selective wettability for water and oil. In addition, a plausible mechanism for the underwater antioil-fouling property of the nanofibrous membrane was further proposed. With the aid of the sub-micrometer, porous, ultrathin skin layer, which consists of numerous conjunctive nanofilaments, the as-prepared superwettable nanofibrous membranes exhibited a robust separation performance for both highly emulsified surfactant-free emulsions and surfactant-stabilized oil-in-water emulsions. An ultrahigh permeation flux of 5152 L m⁻² h⁻¹ with a high separation efficiency of >99.93% was obtained solely under the driving force of gravity (~1 kPa), which was one order of magnitude higher than that of conventional filtration membranes with similar separation properties. Moreover, the excellent antioil-fouling property of the skin layer endowed the membrane with intriguing reusability for the long-term separations and indicated a promising practical application for oily wastewater remediation.

4. Experimental Section

Materials: The partially hydrolyzed polyacrylonitrile ($M_w = 90\ 000$) used in this work was commercially obtained from Kunshan Hongyu Plastics Co., Ltd., China. Sodium dodecyl sulfate, sodium hydroxide (NaOH), hydrochloric acid (HCl), oil red (sudan III), and organic solvents (petroleum ether, *n*-hexane, dimethylformamide (DMF), and 1,2-dichloroethane) were purchased from Aladdin Chemistry Co. Ltd., China. Diesel oil (National IV Standard) was provided by the China National Petroleum Corporation. Vegetable oil (blend) was obtained from the local supermarket. Pure water was obtained using a Heal-Force system. All chemicals were of analytical grade and used as received without further purification.

Fabrication of the Nanofibrous Substrate: The precursor solution was prepared by dissolving the sufficiently dried PAN powder in DMF at a concentration of 14 wt% and stirring for 8 h at room temperature. Then, an electrospinning machine (DXES-3, SOF Nanotechnology Co., China) was employed to fabricate the membranes. During electrospinning, the precursor solution was loaded into a group of syringes (5 of side by side) capped with 6-G metal that were pumped at a fixed rate of 1.0 mL h^{-1} . The syringes periodically scanned in the horizontal direction with a width of 50 cm. The voltage applied to each needle tip was 25 kV to provide a stable and sufficient electric field intensity. The generated fibers were collected by polypropylene nonwoven fabrics coated on a grounded, metallic rotating roller with a rotation rate of 50 rpm. The distance from the needle tips to the surface of the collector was 20 cm. The relative humidity and temperature during the electrospinning were 45 \pm 5% and 25 \pm 5 °C, respectively. The electrospinning process was maintained for 3 h, and then directly used as the substrate for the next step without any treatment.

Construction of the Superwettable, Biomimetic Nanofibrous Skin Layer. First, dilute PAN solutions with different concentrations (1, 3, 5, and 7 wt%) were prepared. Then, the as-prepared precursor solutions were loaded onto the same electrospinning machine (DXES-3, SOF Nanotechnology Co., China), and the feed rate of the solutions was $0.2 \text{ mL} \text{ h}^{-1}$. A voltage of 25 kV was applied to the needle tips to conduct



the atomization of the solutions. The relative humidity was controlled at $22\pm 3\%$, and the temperature was maintained at 25 ± 2 °C. The as-prepared common electrospun fibrous membranes were coated on the grounded, metallic rotating roller and directly used as the collector. The distance from the needle tips to the surface of the substrate membranes was fixed at 25 cm. The whole coating process was performed for 6 h without breaks. After that, the selected composite nanofibrous membranes were further treated in 1 m NaOH solutions (C₂H₅OH:H₂O = 1:1 (w:w)) at 60 °C for different times. The obtained membranes were then rinsed with pure water until they reached pH = 7, and then they were treated with 1 m HCl for 1 h. Finally, the membranes were again rinsed with pure water to reach pH = 7 and dried at 60 °C in a hot air circulating oven.

Preparation of the Emulsions: The surfactant-free oil-in-water emulsions were prepared by mixing oils and water in a volume ratio of 1:9, and the mixtures were under ultrasonic treatment for 2 h at 25–30 °C to obtain the emulsified, milky solutions. The as-prepared surfactantfree oil-in-water emulsions could be stable for \approx 4 h. To prepare the surfactant-stabilized oil-in-water emulsions, the SDS was first dissolved in water as the emulsifier, then the related oil was added to water, and the volume ratio of the oil and water was fixed to 1:99. Then, the mixtures were under ultrasonic treatment for 1 h at 25–30 °C to produce a milky emulsion. The as-prepared surfactant-stabilized oil-in-water emulsions could be stable for at least 24 h.

Oil-in-Water Emulsion Separation Experiments: The evaluation of the emulsion separation performance of the membranes was conducted using a dead-end filtration apparatus equipped with a vacuum pump. The membranes were fixed between two vertical glass tubes with an inner diameter of ~16 mm. Before conducting the emulsions separation, the membranes were prewetted with water. Then, emulsions were directly poured onto the membrane, and the water spontaneously permeated. During separation the solutions were maintained at a relatively stable liquid level of ~10 cm. The separation was driven by the gravity of the solutions and external pressure via a vacuum pump. The permeation flux was calculated with the volume of the collected filtrates during a fixed time (1 min) according to the previous studies.^[20,25] The average total organic carbon contents of the feed solutions and the corresponding filtrates were measured to evaluate the separation efficiency.

Characterizations: The microstructures of the membranes were characterized using scanning electron microscopy (Hitachi S-4800, Japan). FT-IR spectroscopic analysis was conducted on Nicolet 8700 Spectrometer (Thermo Fisher, USA). The topographic roughness parameters (R_a) were detected by a noncontact optical profilometry using an interferometer profiler (Wyko/Veeco, NT9100, USA). The porous structures of the membranes were analyzed using a capillary flow porometer (Porous Materials Inc. CFP-1100AI, USA). The water contact angle, underwater oil contact angle, and sliding contact angle (SA) were tested using a contact angle goniometer (Kino SL200B, USA) equipped with a tilting base. During the test of WCA and UWOCA, a droplet of 3 μ L liquid was used, and for the testing of SAs, a droplet of 10 μ L 1,2-dichloroethane was used. The whole testing process was recorded by a digital camera. The underwater oil advancing and receding contact angles were measured based on the increment and decrement method, and the maximum volume of oil used was 10 µL (1,2-dichloroethane). For each value, at least three measurements were carried out and the average value was obtained. The tensile mechanical property of the membrane was studied using a tensile tester (XQ-1C, China). The property oil-in-water emulsions were characterized by optical microscopy (Olympus VHS3000, Japan) and dynamic light scattering (Brookhaven BI-200SM, USA). The average TOC content in the feed solutions and the corresponding filtrates were measured using a total organic carbon analyzer (Shimadzu TOC-L, Japan).

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

biomimetic skin, nanofibrous membranes, oil-in-water emulsion separation, superhydrophilic, underwater superoleophobic

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