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Egg Shell Powders-Coated Membrane for Surfactant-Stabilized Crude Oil-in-Water Emulsions Efficient Separation

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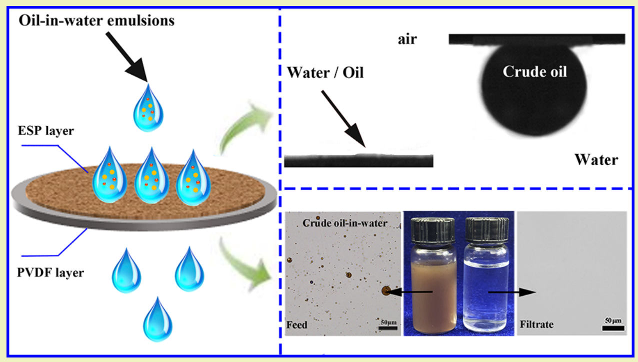
S Supporting Information

ABSTRACT: Low-cost, environmentally friendly superwetting materials are urgently desired in industrial oily wastewater situations. In our work, egg shell powders (ESP)-coated polyvinylidene fluoride (PVDF) membranes were fabricated by vacuum pumping ESP and sodium alginate suspensions onto a PDVF membrane. The ESP-coated PVDF membrane exhibited superamphilicity in air and showed superior underwater superoleophobicity with the contact angle above 156°. This membrane can efficiently separate low viscosity oil-in-water emulsions, which exhibit a high separation efficiency of more than 99.6%. What's more, it also successfully separated high viscosity crude oil-in-water emulsions. In addition, the ESP-coated PVDF membrane still demonstrated an efficient separation efficiency after 10 times. Hence, we believe that this environmentally friendly material combined with a simple and economical method will be a better choice for the Tween-80-stabilized crude oil-in-water emulsions separation.



KEYWORDS: *Egg shell powders, Underwater superoleophobicity, Crude oil-in-water emulsions separation, recyclable*

■ INTRODUCTION

Over the past few decades, water pollution has been a serious global issue, especially with regard to the increasing industrial crude oil wastewater and frequent crude oil leakage accidents,[1−4] which have caused serious negative impacts on the ecological environment and human health.[5] Therefore, an effective treatment of these pollution events is highly desired. Facing these tough challenges, some conventional methods have been proposed,[6−8] such as centrifugation, biological degradation,[9] and so on, while these methods are not only inefficient but also have high energy consumption. Consequently, it is necessary to develop highly energy efficient and low-cost methods to treat industrial oily wastewater. In recent years, with the progress of bionics and interface science, especially for the development of superwetting materials,[10] new methods have been provided to solve the problem of oily wastewater.[11−14] For example, Jiang et al. first prepared a novel coating mesh film with both superhydrophobicity and superoleophobicity by a simple and inexpensive spray-coating process,[1] and this film efficiently and quickly separated oil/water mixtures. Wang et al. prepared waste corn straw powder-coated fabric with dually prewetted underwater superoleophobic and under oil superhydrophobic by a facile, low-cost spraying method,[15] and this fabric can successfully separate a variety of light oil/water/heavy oil three-phase solution mixtures. Nevertheless, due to the oil contaminants in water, including various surface active substances, oil−water mixtures are easily converted into stable oil/water emulsions (oil droplet diameters < 10 μm). Therefore, the separation of oil/water emulsions is much more difficult than the separation of oil−water mixtures, which requires us to develop a suitable membrane to effectively separate various oil-in-water emulsions.

Generally speaking, for efficient preparation of oil/water emulsion separation membranes, the following basic conditions should be satisfied, the membrane interface should have good wettability, as well as rough structure, and suitable pore size.[16,17] Therefore, some porous materials with special wettability were prepared and applied in oil/water emulsions separation.[18−20] Feng and co-workers developed one-step coating method to simultaneously achieve oil/water mixtures and emulsions separation and Cu^{2+}/Dye adsorption.[21] Jin and co-workers reported a composite ultrathin film with underwater superoleophobicity for oil-in-water emulsions separation.[22] In recent years, PVDF membranes have also been widely used as the base of oil/water emulsions separation

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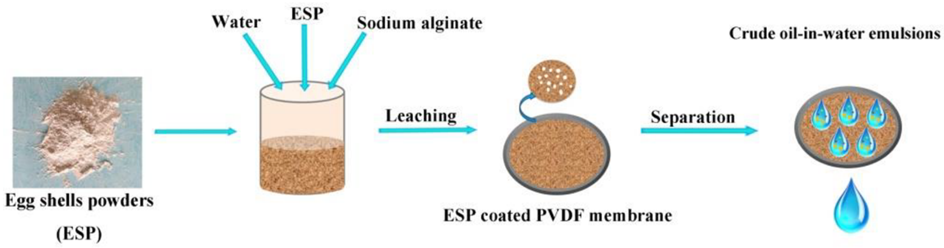

Figure 1. Illustration of the preparation processes of ESP-coated PVDF membrane and its application for emulsions separation.

owing to their small pore size. Meng et al. prepared a hydrogel-coated PVDF membrane with underwater superoleophobicity for the separation of oil/water emulsions.[23] Jin et al. reported a kind of ZNG-*g*-PVDF membrane with excellent antifouling performance for effective separation of oil-in-water emulsions.[24] On the one hand, multistep processes and the use of hazardous chemicals limit the practical applications of these materials. Environmentally friendly materials will be a better choice for oil/water emulsions separation in the future. On the other hand, these membrane materials only separate oil-in-water emulsions composed of organic solvents (hexane, petroleum ether, etc.) and low viscosity light oil (kerosene, diesel oil, etc.).[25−27] Generally, most industrial wastewater contains not only organic solvents and low viscosity light oil but also high viscosity crude oil. The crude oil tends to adhere to the filtration membrane, causing a decline of separation efficiency and water flux. To solve this issue, the membrane should first be hydrophilic, because the hydrophilic material tends to form more a stable water layer, preventing the membrane from directly contacting the oil droplets.[28,29] Then, the hydrophilic membrane with a micro/nanoscale roughness structure was further designed to improve the hydrophilicity of the membrane to superhydrophilicity.[30,31] Therefore, it is highly necessary to design an environmentally friendly and superhydrophilic filtration membrane to efficiently separate Tween-80-stabilized crude oil-in-water emulsions.

ESP is made of nature materials, which contains calcium carbonate and protein as well as microelements.[32,33] Owing to the presence of hydrophilic groups −OH and C═O, ESP has excellent capacity of holding water and oil. Herein, ESP-coated PVDF membrane was prepared by vacuum pumping ESP and sodium alginate suspensions. The ESP-coated PVDF membrane exhibited superamphilicity in air and underwater superoleophobicity. A series of Tween-80-stabilized oil-in-water emulsions were efficiently separated with the separation efficiency greater than 99.6%, including high-viscosity crude oil-in-water emulsions. More importantly, the membrane also showed a superior separation capability after 10 times, and the separation efficiency reached more than 99.5%. Therefore, low-cost, easily available, environmentally friendly ESP is considered to be a candidate new material for emulsions separation. When the membrane is used to separate crude oil-in-water emulsions, it has efficient separation efficiency and excellent cycle stability.

■ EXPERIMENTAL SECTION

Materials. Egg shells were collected from Lanzhou, China, and were composed of $CaCO_3$ (83−85%) and protein (15−17%). The PVDF membrane was obtained from Shanghai Xingya Co., Ltd. Oils (kerosene, diesel) and organic solvents (heptane, hexane, and petroleum ether) were supplied by Guangdong Guanghua Sci-Tech Co. Crude oil was provided by Gansu Yumen Oilfield Company. Tween-80 was supplied from Shanghai Zhongqin Chemical Reagent Co., Ltd. Sodium alginate was supplied from Sinopharm Chemical Reagent Co., Ltd.

Characterization. The morphology of the as-prepared membrane was characterized by field emission scanning electron microscopy (FE-SEM, Zeiss). The chemical composition was acquired by energy-dispersive spectrometry (EDS). Evaluation of the roughness of the samples was conducted using atomic force microscopy (AFM). The phase composition and structures of the egg shell powders was characterized by X-ray diffraction analysis (XRD, Rigaku Corp., Cu Ka, D/max-2400). FT-IR analysis (Bio-Rad FTS-165) of the ESP was carried out to monitor its functional group. The SL200 KB apparatus was used to measure the contact angles (CAs) and sliding angles (SAs). Optical images of the emulsion droplets were photographed by an Olympus U-RFL-T instrument. Droplet sizes of emulsions were obtained using DLS measurements (Malvern Zetasizer Nano ZS). The oil contents in the filtrates were measured by an infrared oil instrument (SN-OIL480).

Preparation of ESP. First, a large number of egg shells was washed with deionized water by multiple ultrasonic cleaning, and then the inner shells of the egg shells were stripped. Second, the shells were washed several times by deionized water and placed in a drying oven for 2 h at 80 °C. Finally, the shells were crushed with a high-speed multifunctional crusher and sieved through 240 meshes.

Preparation of ESP-Coated PVDF Membrane. First, 0.4 g of sodium alginate was dispersed in 40 mL of deionized water under continuous stirring. Second, 3 mL of sodium alginate solutions and 0.45 g of ESP were added to 36 mL of deionized water, and the mixture was magnetically stirred for 20 min. Then, the mixture was magnetically stirred at room temperature until uniform suspensions were obtained. Subsequently, 6 mL of ESP solution was leached onto a PVDF membrane under the pressure of 0.085 MPa by a vacuum pump. Finally, the ESP-coated PVDF membrane was dried at 50 °C for 30 min.

Preparation of Surfactant-Stabilized Oil-in-Water Emulsions. Tween-80-stabilized oil-in-water emulsions were prepared by mixing water and oil (kerosene, diesel, heptane, hexane, and petroleum ether, crude oil) in 1:50 (v/v) with adding 0.1 g of Tween-80, and the emulsions were stirred for 3 h. Six different oil-in-water emulsions were formed, namely, crude oil-in-water (C/W), kerosene-in-water (K/W), diesel-in-water (D/W), heptane-in-water (Hep/W), hexane-in-water (Hex/W), and petroleum ether-in-water (P/W).

■ RESULTS AND DISCUSSION

In our paper, ESP was chosen to prepare a superhydrophilic surface because of its strong water absorption and porous structure.[34] The preparation process and application of ESP-coated PVDF membrane is shown in Figure 1a. Simply speaking, driven by a vacuum filtration system, the sodium alginate and ESP suspensions were successfully coated onto a PVDF membrane. Here, the sodium alginate as a binder significantly improved the adhesive force between ESP and PVDF. Finally, the ESP-coated PVDF membrane with underwater superoleophobic property can separate various

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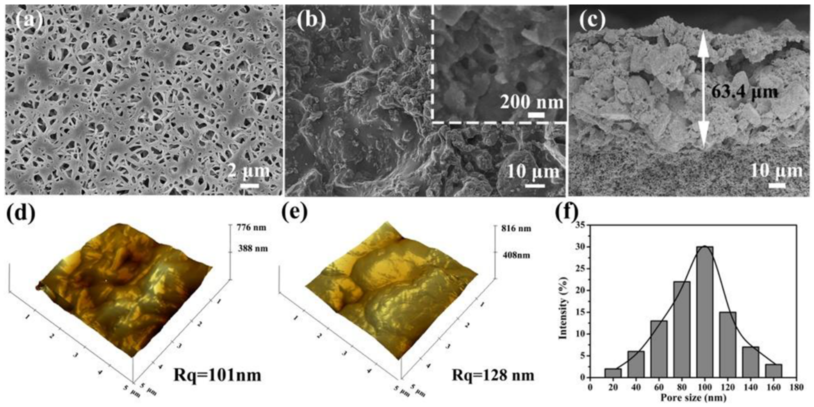

Figure 2. FE-SEM images of (a) the initial PVDF membrane and (b) the ESP-coated PVDF membrane, respectively. The insets are the (b) magnified image of the ESP-coated PVDF membrane and the (c) cross-section of images of the ESP-coated PVDF membrane surface. AFM image of the (d) initial PVDF membrane and the (e) ESP-coated PVDF membrane. (f) The pore size distribution of the as-prepared ESP-coated membrane.

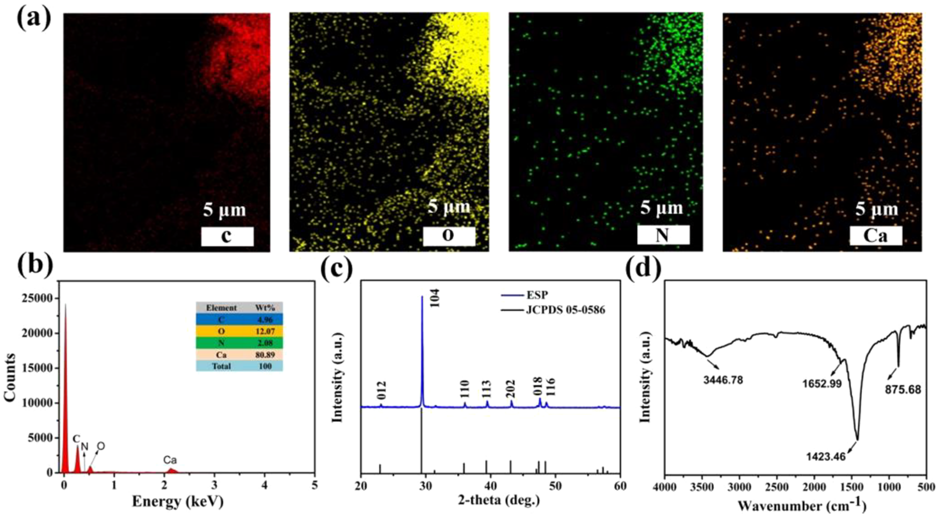

Figure 3. (a) EDS mapping image of ESP-coated PVDF membrane. EDS analysis of the (b) ESP-coated PVDF membrane. (c) XRD analysis of ESP. (d) FT-IR spectra of ESP.

Tween-80-stabilized oil-in-water emulsions, including high-viscosity crude oil-in-water emulsions.

The surface morphology of the initial PVDF membrane and the ESP-coated PVDF membrane was characterized by FE-SEM. The FE-SEM image of the original PVDF membrane exhibited that the PVDF membrane possessed a smooth surface with an average pore diameter of about 0.45 μm (Figure 2a). As shown in Figure 2b, compared with the initial PVDF membrane, a large number of ESP particles with different sizes and irregular shapes were randomly distributed on the surface of the ESP-coated PVDF membrane, resulting in a rough structure. Meanwhile, the FE-SEM image of the ESP was also researched and discussed (Figure S1); there are scattered holes on the surface of the rough structure. This unique porous structure is an important condition to produce micronanoscale roughness structure. The membrane thickness is controlled by adjusting the volume of ESP suspensions, and the increase of membrane thickness will cause the flux of emulsions separation to decrease; a too-thin membrane will affect the separation efficiency of the emulsions, so the volume of the ESP suspensions corresponding to one membrane was 6 mL. The cross-sectional image of the ESP-coated PVDF membrane and original PVDF membrane were also characterized. The thickness of the ESP layer was approximately 63 μm (Figure 2c), and the thickness of the original PVDF membrane was about 150 μm (Figure S2). Moreover, the ESP-coated PVDF membrane had an average pore size of about 98 nm, which was much less than the pore diameter of the PVDF (Figure 2f). Due to the addition of sodium alginate in the process of dispersing ESP, the ESP-coated PVDF membrane exhibited a certain degree of stability and flexibility, and it can still maintain its original appearance after bending for 100 times (Figure S3). Moreover, the AFM image of the initial PVDF membrane and the ESP-coated PVDF membrane is shown in Figure 2d and 2e, respectively. The ESP-coated PVDF membrane has a large number of gullies and protrusions. The root-mean-square roughness (R_q) of the ESP-coated PVDF membrane was about 128 nm, while the corresponding value of original PVDF membrane was about 101 nm. Obviously, ESP increased the roughness of the original PVDF membrane. Therefore, we determined that the structure of the ESP-coated PVDF membrane with micro/nanoscale roughness, which would play an important role in separating oil-in-water emulsions.

The surface chemical composition of ESP-coated PVDF membrane was confirmed by EDS. The EDS mapping image

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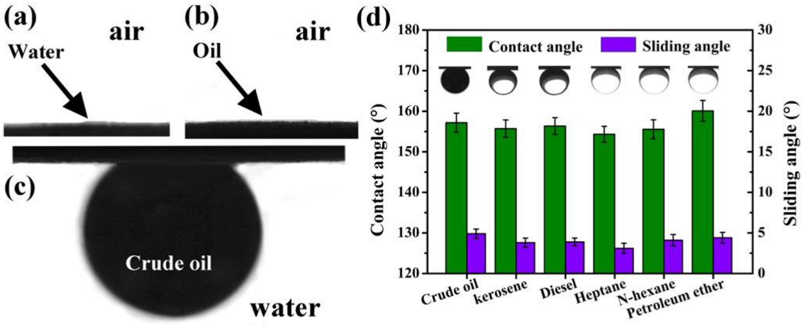

Figure 4. Wetting behaviors of the ESP-coated PVDF membrane toward (a) water in air, (b) crude oil in air, and (c) crude oil in water. (d) The CAs and SAs of various oil droplets underwater.

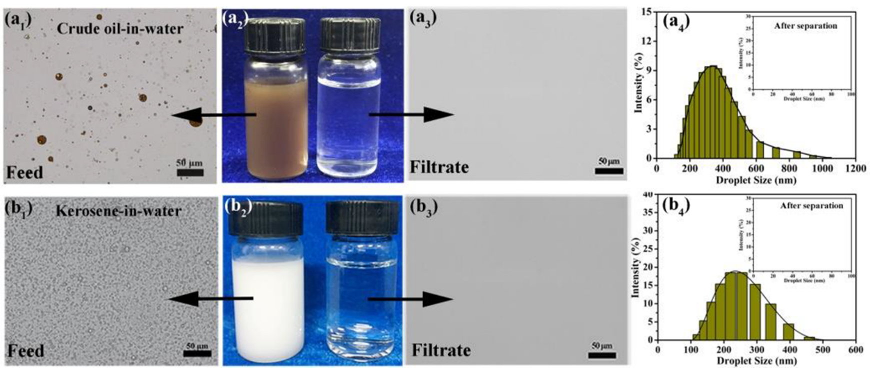

Figure 5. Image and particle size analysis of oil-in-water emulsions before and after separation: (a) C/W emulsions and (b) K/W emulsions.

was shown in Figure 3a. The results showed that the ESP-coated PVDF membrane contained carbon, oxygen, nitrogen, and calcium elements. EDS analysis of the ESP-coated PVDF membrane was shown in Figure 3b, the peaks of C, O, and Ca elements were observed, and the atomic percent of C, O, and Ca are 4.96%, 12.07%, and 80.89%, respectively. These results indicated that the surface of PVDF membrane has been successfully covered by ESP. XRD analysis of ESP was also investigated (Figure 3c). The results showed that there are a series of obvious peaks at 2θ = 29.41°, 39.40°, 43.15°, and 47.49°, corresponding to the reflections of (104), (113), (202), and (208) crystal planes of ESP, respectively, which indicate the formation of ESP. The peaks agreed well with standards of the crystalline $CaCO_3$ form (JCPDS no. 05-0586), which was consistent with the main component of the egg shells. Furthermore, the FT-IR spectra of the ESP are exhibited in Figure 3d. The infrared peak of ESP is about 3446.78 cm^{-1}, which matched the −OH stretching frequency. The characteristic absorption of calcium carbonate absorbs antisymmetrical stretching vibration of C═O, which is attributed to CO_3^{2-} near 1423.46 cm^{-1}, the surface of 875.68 cm^{-1} shows an outward curvature of the CO_3^{2-}, and the characteristic absorption of protein is around 1652.99 cm^{-1}.[35] The −OH and C═O functional groups in the egg shells endow the ESP-coated PVDF membrane excellent water absorption. In addition, the FT-IR spectra of the added binder sodium alginate are also characterized (Figure S4), and the results demonstrated that sodium alginate also contains a large number of amphiphilic functional groups. Based on the above discussion, it can be found that the ESP-coated PVDF membrane possesses micro/nanoscale roughness structures and amphiphilic groups, which will play a crucial role in oil-in-water emulsions separation.

It is well-known that the wettability of the material depends on its chemical compositions and surface roughness. Owing to the excellent water absorbing capacity of egg shells, i.e., that of $CaCO_3$,[35] the ESP-coated PVDF membrane demonstrated superamphiphilicity for water and oil in air. As shown in Figure 4a and 4b, when water and oil droplets come into contact with the as-prepared membrane, and all the obtained CAs were 0°. This is due to the synergistic effect of the membrane surface roughness and the hydroxyl groups present in the material (ESP and sodium alginate). The wettability of ESP-coated PVDF membrane to underwater−oil was studied, and the membrane showed an underwater−crude oil contact angle (OCA) of 156.4 ± 2.1° and underwater−oil sliding angle (OSA) of 5.3 ± 0.2°, demonstrating the underwater superoleophobic property. Moreover, Figure 4d indicated that the membrane exhibits underwater superoleophobicity for various oils and organic solvents; the underwater OCAs of the membrane were larger than 150°, and the underwater OSAs were all less than 7°. This is mainly due to the emulsions contacting the ESP-coated PVDF membrane, where water droplets can be trapped in the hydrophilic micronanopores to form an oil/water/solid three-phase system similar to Cassie state.[36] The trapped water layer significantly decreases the contact space between oil droplet and surface of the ESP-coated PVDF membrane and repels the oil.[37,38] As a consequence, the ESP-coated PVDF membrane exhibited underwater superoleophobicity by introducing a repelling liquid (i.e., water) into the porous interface in the oil/water/solid three-phase system. This characteristic of underwater superoleophobicity effectively prevents oil droplets from contaminating the ESP-coated PVDF membrane.

In order to ensure efficient membrane separation, the membrane aperture should be smaller than the size of the

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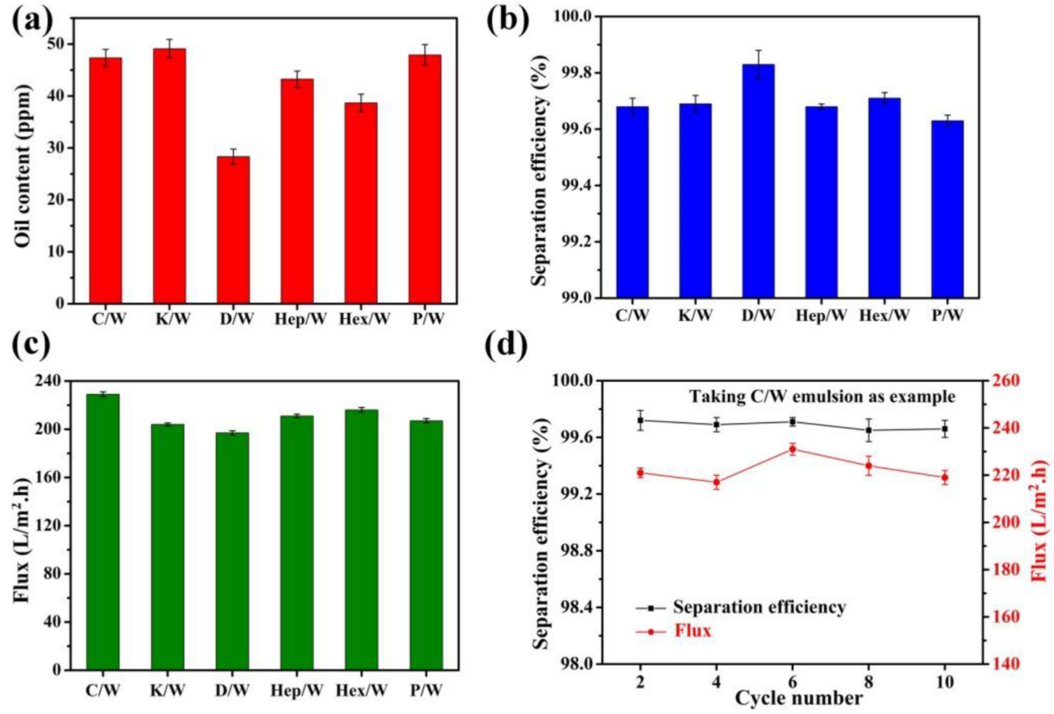

Figure 6. (a) Oil contents in filtrates. (b) Separation efficiency of the ESP-coated PVDF membrane. (c) Flux of Tween-80-stabilized oil-in-water emulsions. (d) Flux and separation efficiency of the C/W emulsions after 10 separation cycles.

emulsion droplets. Moreover, for the two components in the emulsions, the wettability of the membrane should be reversed. In other words, the membrane should be wetted by the continuous phase rather than being wetted by the dispersed phase. When separating oil-in-water emulsions, water can permeate the filter membrane but the oil is not allowed to permeate. Thence, the ESP-coated PVDF membrane combined micronanoscale roughness and the underwater superoleophobic property, and a series of Tween-80-stabilized oil-in-water emulsions were separated. The digital image of the ESP-coated PVDF membrane and the vacuum pumping system are shown in Figure S5. Herein, as shown in Figure 5, the oil-in-water emulsions, including crude oil, and kerosene-in-water emulsions were successfully separated. As seen from Figure 5a_2, the filtrates (right) obtained after separation were completely transparent compared with the dark brown emulsions (left). To further investigate the separation performance of the membrane, a C/W optical microscopy image before and after the separation was obtained. Obviously, scattered micro/nanoscale crude oil droplets were observed in the optical image of C/W emulsions (Figure 4a_1), while no crude oil droplets were tested in the filtrates (Figure 4a_3), which confirmed that the C/W emulsions was completely separated. In addition, the change in droplet size before and after the separation of crude oil-in-water emulsions was observed though DLS. As exhibited in Figure 5a_4, the crude oil particle size distribution in the C/W emulsions was mainly between 200 and 1000 nm, which were larger than the pore diameter of the coated membrane. After separation, the particle size distribution of filtrates was very small, which was beyond the range of the instrument and cannot be detected by the instrument (the inset of Figure 5a_4). The results showed that the ESP-coated PVDF membrane had excellent separation performance for C/W emulsions. Analogously, the separation results of K/W emulsions were also shown in Figure 5b. The original KW emulsions were milky, and the filtrate was clear and transparent (Figure 5b_2), there were no kerosene droplets in the whole view of optical microscopy image (Figure 5b_3). These results further prove that the ESP-coated PVDF membrane not only successfully separated oil-in-water emulsions containing low viscosity kerosene but also efficiently separated oil-in-water emulsions consisting of high viscosity crude oil. Furthermore, we also explored the separation ability of the ESP-coated PVDF membrane to other oil-in-water emulsions, including D/W emulsions, Hep/W emulsions, Hex/W emulsions, and P/W emulsions (Figure S6). Compared with the milky emulsions, the filtrate collected after separation was completely transparent, indicating that the membrane has excellent separation ability. As shown in all optical microscopy images, many oil droplets were observed in oil-in-water emulsions, and no obvious oil droplets were observed in the collected filtrate after separation. For comparison, the separation experiment of the original PVDF membrane was also conducted to examine the effect of substrate on separation efficiency (Figure S7). The results indicated that the original PVDF membrane cannot successfully separate crude oil-in-water emulsions. This phenomenon suggested that the ESP plays a vital role in the separation of surfactant-stabilized crude oil-in-water emulsions.

In order to more accurately study the separation efficiency of Tween-80-stabilized oil-in-water emulsions, the oil contents were quantitatively measured. As demonstrated in Figure 6a, the oil contents of all filtrates were less than 50 ppm, and the corresponding separation efficiency for the six emulsions were above 99.6% (Figure 6b). These results displayed that the ESP-coated PVDF membrane has superior separation ability for surfactant-stabilized oil-in-water emulsions. The following (eq 1) is used to calculate the separation efficiency (R_1):

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$$R_1 = \left(1 - \frac{C_p}{C_o}\right) \times 100\% \quad (1)$$

where C_p is the oil contents of the collected filtrates and C_o is the oil contents of the oil-in-water emulsions. In addition to separation efficiency, flux is another key parameter for characterizing ESP-coated membrane separation performance. The values of flux (F) were calculated as follows:

$$F = \frac{V}{St} \quad (2)$$

where V (L) is the volume of filtrate that passes through the membrane in 1 min and S (m^2) is the area of the ESP-coated area. As shown in Figure 6c, the fluxes of C/W emulsions, K/W emulsions, D/W emulsions, Hep/W emulsions, Hex/W emulsions, and P/W emulsions were around 229, 204, 197, 211, 216, and 207 L m^{-2} h^{-1}, respectively. Moreover, the separation efficiency and flux versus the recycle times were also investigated by taking the C/W emulsions as an example. As illustrated in Figure 6d, the separation efficiency of the ESP-coated PVDF membrane remained at 99.5% after 10 cycles; simultaneously, the flow slightly decreased, but the overall change was not significant, indicating that the membrane can be recycled multiple times.

In order to understand the separation mechanism of Tween-80-stabilized oil-in-water emulsions through the ESP-coated PVDF membrane, hypothetical schematic illustrations are shown in Figure 7. The membrane was fixed in the suction filtration device. After the emulsions touch the surface of the membrane, the emulsion droplets (black arrow in Figure 7) sink to the bottom of the membrane due to gravity being greater than buoyancy. Due to the preferential affinity of water to the membrane, the water rapidly spread and permeated into the membrane, forming a stable water/solid composite interface,[39,40] while oil droplets are completely repelled prevented from penetrating through. Therefore, the oil droplets were efficiently intercepted by the micro/nanoscale rough structure when θ_a > 90° and ΔP > 0 (intrusion pressure).[41] The intrusion pressure ΔP can be calculated as[42−44]

$$\Delta P = -\frac{2\gamma \cos\theta}{d} \quad (3)$$

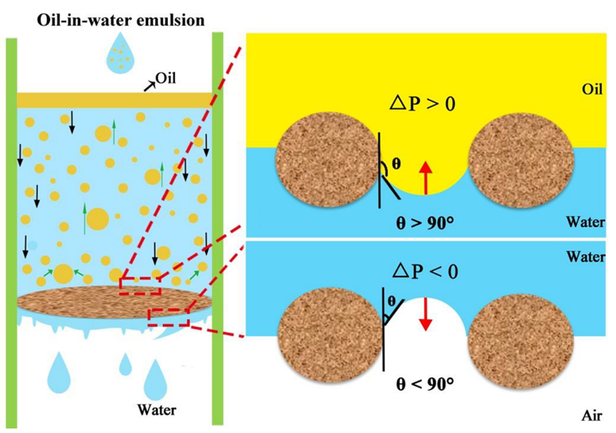

Figure 7. Schematic diagram illustrating the mechanism behind the separation of Tween-80-stabilized oil-in-water emulsions system.

where d is the radius of the meniscus, γ is the oil/water surface tension, and θ is advancing CA. Moreover, owing to the fact that OSAs were less than 7° and due to the low adhesion force, nanosized oil droplets could easily roll on the surface of the ESP-coated PVDF membrane and gradually coalesced into larger oil droplets.[45,46] The Stokes' law of resistance states that due to their larger radius the coalesced oil droplets completely leave the surface of the membrane and floated to the surface (green arrow in Figure 7), forming a free oil layer.[47] At the same time, the water continuously permeated the membrane under the action of external pressure and capillary force (ΔP < 0). Therefore, the synergistic effect of the above two factors enable the Tween-80-stabilized oil-in-water emulsions to be successfully separated.

CONCLUSION

In summary, an ESP-coated PVDF membrane with an underwater superoleophobic property has been successfully fabricated by a facile and low-cost method. Combining the wettability with surface micro/nanoscale roughness, the prepared membrane could be used for separating a series of Tween-80-stabilized oil-in-water emulsions and even high viscosity crude oil-in-water emulsions, and the separation efficiencies were all greater than 99.6%. In addition, the prepared membrane still showed a superior separation efficiency after 10 cycles of crude oil-in-water emulsions. On the basis of the above results, this research provides a novel, cost-effective, environmentally friendly material for efficient separation of Tween-80-stabilized oil-in-water emulsions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b01756.

(Figure S1) FE-SEM images of ESP at low and high magnifications; (Figure S2) cross-sectional image of the original PVDF membrane; (Figure S3) optical images of ESP-coated membranes before and after it was bent over 100 times; (Figure S4) FT-IR spectra of sodium alginate; (Figure S5) photograph of the as-prepared ESP-coated PVDF membrane and photograph of a complete separation system; (Figure S6) optical microscope images, photographs, and droplet size measurements of different stabilized emulsions; and (Figure S7) C/W emulsion separation result of the original PVDF membrane and the ESP-coated membrane (PDF)

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Notes

The authors declare no competing financial interest.

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