Facile hydrophilic modification of PVDF membrane with Ag/EGCG decorated micro/nanostructural surface for efficient oil-in-water emulsion separation

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HIGHLIGHTS

- PVDF membrane was facilely modified via coating of EGCG and Ag^+.
- High membrane hydrophilicity and underwater superoleophobicity were achieved.
- The membrane exhibited desired performance while treating oily emulsions.
- The membrane possessed satisfactory antifouling property and stability.

GRAPHICAL ABSTRACT
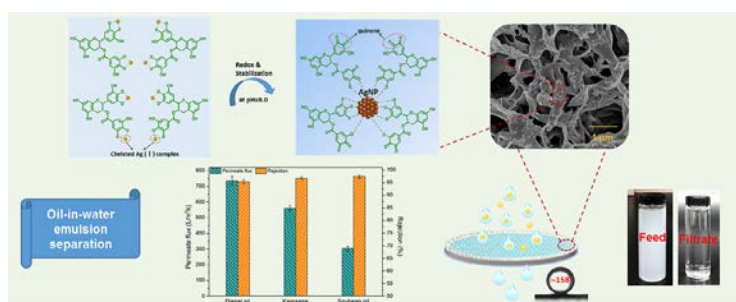
ABSTRACT

Wettability of porous materials is crucial for the separation of emulsified oil/water mixtures. Herein, high hydrophobicity of polyvinylidene fluoride (PVDF) membrane has been facilely transformed to high hydrophilicity and underwater superoleophobicity via single-step coating of plant-derived epigallocatechin gallate (EGCG) and silver ion (Ag^+) in aqueous solution. EGCG can chelate with Ag^+ and in-situ reduced it into Ag nanoparticle, meanwhile Ag/EGCG composite was adhered on membrane surface due to the high surface binding affinity of EGCG. The hydrophilic EGCG and formed micro/nanostructure together improved membrane hydrophilicity and oleophobicity. The optimally Ag/EGCG modified PVDF membrane possesses high permeate flux (e.g. 735 L/(m^2h) for diesel-in-water emulsion, while it is zero for pristine PVDF membrane) under a low operation pressure of 0.5 bar and high oil rejections in the treatment of surfactant-stabilized oil-in-water emulsions consisting of micro/nano scale droplets. In addition, the membrane exhibits excellent antifouling property with a flux recovery ratio of 98.1% and satisfactory reusability in a 5-cycle test. Moreover, the membrane possessed desired stability during long-term rinsing test and Ag leaching test. This work would offer new insights into surface hydrophilic manipulation of porous membrane towards practical oil emulsion purification.

1. Introduction

Oily wastewater, especially the emulsified one, has become a serious environmental concern, as huge amounts of oil-contaminated water is being discharged from industries such as petrochemical, food processing, smelting, and mineral industry as well as oil spill accidents [1–3]. Before being released into the ecosystem, oily wastewater must be well tackled. As known, conventional methods such as skimming,

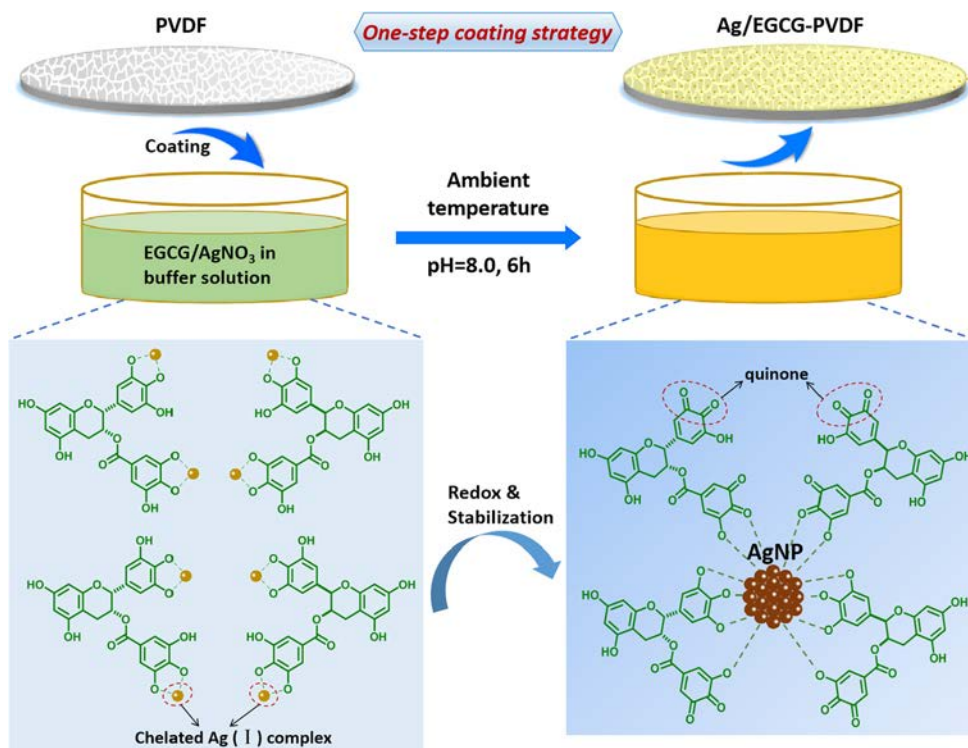**Scheme 1.** Schematic diagram of the preparation of hydrophilic and underwater superoleophobic Ag/EGCG-PVDF membrane via one-step coating and the formation mechanism of Ag/EGCG composite.

adsorption, centrifugation, chemical coagulation and air flotation are suitable to handle immiscible oil/water mixtures rather than emulsions stabilized by surfactants, which are difficult to separate due to their small droplet size and good stability [4–6]. To address this issue, filtration membrane has been noted as an efficient medium to isolate emulsified mixtures due to its high separation efficiency, low energy consumption, and easy operation process [3,7]. Compared to other emerged porous materials like mesh [8], sponge [9], foam [10] and textile [11], membrane possesses more proper pore sizes smaller than the oil droplets (diameter less than 20 μm [12]) and higher throughput, making them valid for oil-in-water emulsion separation. Nonetheless, membrane fouling during oil/water emulsion separation is still a serious hindrance to membrane efficiency and longevity, ascribed to the hydrophobic inherence of polymeric membranes coupled with the strong adhesion property of oil droplets. In this regard, many researchers are devoted to developing new strategies or applying novel materials to confer membrane with superhydrophilic and underwater superoleophobic properties.

Coating as a feasible and effective method is widely used for surface modification purposes. Polydopamine and plant polyphenol derived coatings have been proved to be spontaneously formed ascribed to the oxidative oligomerization of precursors and firmly adhered on various substrates via multiple anchoring interactions under mild conditions [13,14]. Considering that plant polyphenols are less costly, more structurally and chemically diverse than dopamine, and the corresponding coatings are colorless or light in color [15], we focused on surface modification on the basis of plant polyphenol inspired coatings. Especially, since the first report of one-step assembly of natural polyphenols and Fe (III) ions by Ejima et al. in 2013, metal-polyphenol coordination networks have emerged as promising candidates in surface engineering of films and particles [16,17]. In the past several years, the potential of membrane modification based on the coordination of natural phenolic compound tannic acid (TA) and transition mental ions was demonstrated by researchers. Typically, Jong-Chan Lee et al. found that the formation of TA-Fe (III) complex on ultrafiltration membrane

surface could endow membrane with excellent fouling resistance, antimicrobial properties as well as enhanced heavy metal ions removal efficiency [18]. Wu and coworkers enhanced the performance of polyamide thin film nanocomposite membrane with the assistance of TA-Fe (III) functionalized mutiwalled carbon nanotubes [19]. TA-metal ion coordination network also found its place in membrane hydrophilic modification for oily wastewater treatment. Song et al. reported a twopot coating method for fabricating TA-Fe (III) complex on membrane surface to transform membrane hydrophobicity to superhydrophilicity and underwater superoleophobicity [20]. For the same purpose, Zhao and coworkers introduced TA-Ti^{4+} coordination networks into PVDF membrane matrix via non-solvent induced phase inversion [21]. Recently, Wu's group modified PVDF membrane via assembly of TA and polyvinylpyrrolidone followed by complexation and immobilization of Fe (III) to improve membrane fouling resistance in oily wastewater remediation [22]. Despite of these explorative and inspiring studies, the utilization of other plant polyphenols for membrane surface engineering is relatively limited. There're great opportunities to expand both the polyphenol and transition metal ion systems to construct membrane surface architecture, which might enable membrane to exhibit decent performance.

Herein, special attention has been paid to another category of inexpensive and eco-friendly plant polyphenol, epigallocatechin gallate (EGCG), which is the most abundant catechin extracted from green tea. The abundant gallol groups endow EGCG with good hydrophilicity and feasibility of chemical modification. EGCG can not only undergo oxidative covalent crosslinking with nucleophilic reagents under alkaline conditions according to our previous work [15], but also take part in coordination chemistry with metal ions due to its strong metal chelation ability similar to TA [23]. Besides, it has been found that EGCG can serve as reducing agent as a result of the electron-donating *ortho*-phenolic hydroxyls to effectively prepare and stabilize metal nanoparticles [24,25]. These facts suggest that EGCG could be potentially utilized to yield a hydrophilic composite surface with micro/nanostructure on porous membrane via coordination chemistry and redox reaction. The

micro/nano structure is supposed to further benefit the simultaneous improvement of hydrophilicity and oleophobicity, ultimately favoring effective oil-in-water emulsion separation.

In this work, we focus on the surface hydrophilic modification of PVDF membrane by means of EGCG involved metal/polyphenol network based on its metal chelation ability, reduction ability and surface binding affinity. To avoid tedious modification steps and enhance coating binding strength with substrate, a novel one-step approach was explored to facilely fabricate metal/EGCG composite on PVDF membrane, in which AgNO$_3$ was employed as it could be easily reduced into silver nanoparticles (AgNPs), as illustrated in Scheme 1. The whole coating process was conducted in an aqueous buffer solution at room temperature, in the absence of organic solvents and toxic chemicals. The surface chemistry of membrane combined with the property of soaking solutions was characterized to investigate the formation mechanism of Ag/EGCG composite on PVDF membrane. The effects of different metal ions, coating time as well as Ag/EGCG molar ratio on membrane wettability and separation performance were systematically studied. Furthermore, experiments were conducted to evaluate the separation performance, antifouling performance, reusability and stability of the optimally modified membrane. The strategy proposed in this work may provide more opportunities for the construction of superwettable surface.

2. Experimental section

2.1. Materials

PVDF membranes with a pore size of 0.1 μm and diameter of 100 mm were purchased from Zhongli Filtration Co., Ltd. (Haining, China). Epigallocatechin gallate (EGCG) and 3-(N-morpholino) propanesulfonic acid (MOPS) were obtained from Dalian Meilun Biotechnology Co., Ltd. (China). AgNO$_3$ was provided by Aladdin (China). CuSO$_4$·5H$_2$O, FeCl$_3$·6H$_2$O, sodium dodecylsulfate (SDS) and 1, 2-dichloroethane were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. (China). The water used in all experiments was deionized water. All chemicals were used as received.

2.2. Characterizations

Surface morphology and elemental mapping of pristine and modified PVDF membranes were characterized by a field-emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan) coupled with an energy-dispersive spectroscopy (EDS). Surface roughness analysis was conducted on an atomic force microscopy (AFM, Bruker, Dimension icon, Germany) in a tapping mode with a scanning area of 5 μm × 5 μm. Membrane surface chemistry was characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Bruker, TENSOR II, Germany) and X-ray photoelectron spectroscopy (XPS, Thermo, USA). The ultraviolet–visible (UV–vis) absorption spectra of the soaking solutions (which were diluted eight times) were measured by a UV–vis spectrophotometer (UV-4802S, Unico, USA). Water contact angle (WCA) in air and underwater oil (using 1,2-dichloroethane) contact angle (UOCA) were measured by a JC 2000 goniometer (Powereach, China) with a droplet size of 2 μL and 3 μL, respectively. At least five different positions of each sample were measured to obtain an average value. Droplet size distribution of the oil-in-water emulsion was analyzed by a dynamic light scattering (DLS) particle size distribution analyzer (Nano ZS, Malvern, UK).

2.3. Hydrophilic modification of PVDF membrane

Hydrophilic coating on PVDF membrane was constructed via a facile strategy. Prior to surface modification, PVDF membranes were soaked in ethanol for 4 h and washed with deionized water to prewet membrane samples and remove impurities. Subsequently, soaking

solution was prepared by mixing AgNO$_3$ (or CuSO$_4$·5H$_2$O or FeCl$_3$·6H$_2$O) aqueous solution with EGCG solution in MOPS buffer (pH = 8.0). The concentration of EGCG is fixed at 0.8 mg/mL. The molar ratios of metal ion and EGCG were chosen at 1:5, 1:2, 1:1 and 5:1, respectively. Afterward, PVDF membranes were immersed in the freshly prepared solution for certain time. As a control, PVDF membranes modified with EGCG in the absence of metal ion under the same conditions were also fabricated. After thoroughly washed with deionized water, the modified membranes (denoted as Ag/EGCG-PVDF, Cu/EGCG-PVDF, Fe/EGCG-PVDF and EGCG-PVDF, respectively) were dried at 40 °C for 6 h before characterizations and tests.

2.4. Permeation and oil/water separation evaluation

Permeation test was performed in a dead-end stirred cell (MSC 300, China) with effective membrane area of 33.18 cm^2. The flux was measured at 0.05 MPa and calculated by the following equation:

$$Flux = \frac{V}{A\Delta t} \tag{1}$$

where V (L) is the permeate volume, A (m^2) is the effective membrane area and Δt (h) is the time interval.

Oil-in-water emulsions were prepared by adding 1 g oil (including diesel oil, kerosene and soybean oil) and 0.1 g SDS into 1 L deionized water. Consequently, the mixture was dispersed with a homogenizer (FLUKO FA25, German) at 10000 rpm for 30 min to obtain stabilized off-white emulsions.

Separation experiments of oil-in-water emulsions were carried out in the aforementioned filtration cell at a relatively low operating pressure of 0.05 MPa. For each experiment, the membrane sample was pre-wetted with deionized water and 300 mL as-prepared emulsions were poured into the filtration cell. Considering the flux decline caused by the gradually formed oil cake, the filtrate was collected within the first 4 min. The permeate flux was calculated by Eq. (1) and the rejection ratio (R) of oil-in-water emulsion was determined by Equation (2):

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{2}$$

where C_p and C_f are the oil concentrations in the permeate and feed, respectively, which were determined by a total organic carbon analyzer (TOC, SHIMADZU, Japan).

2.5. Antifouling performance, reusability and stability of membrane

In the antifouling test, pure water flux of membrane was measured before and after diesel-in-water emulsion filtration. The flux recover ratio (FRR) was calculated by the following equation:

$$FRR = \frac{J_w}{J_{w0}} \times 100\% \tag{2}$$

where J_{w0} is the initial pure water flux, and J_w is the pure water flux after emulsion filtration.

To further investigate membrane antifouling property and reusability, the real-time permeate flux of diesel-in-water emulsion was recorded every 1 min for 10 min. The oil rejection was also measured. The operation pressure was kept at 0.05 MPa and the volume of the emulsion in the feed was 300 mL for each cycle test. Before next measurement, the membrane sample was simply rinsed by deionized water to remove the absorbed oil on membrane. The process was repeated five times.

The stability of membrane hydrophilicity and underwater superoleophobicity was tested by long-term rinsing experiments. Specifically, pure water and 1 g/L SDS-stabilized diesel-in-water emulsions were employed to rinse the membrane samples in petri dishes on a platform

shaking incubator (TQZ-312, Jinghong, China) at 100 rpm for 12 days. During the rinsing process, UOCAs and initial WCAs of membrane samples (which were thoroughly washed with pure water and then dried) were measured every 4 days. Besides rinsing tests, quantified analysis of Ag leaching was also performed to test the stability of AgNPs immobilized on membrane surface. In Ag leaching test, deionized water was filtered through the membrane at 0.05 MPa. The filtrate was collected and acidified by 1% HNO$_3$. And the dissolved Ag concentration was measured using an inductively coupled plasma mass spectrometry (ICP-MS, Thermo Scientific, iCAP Q) instrument.

3. Results and discussion

3.1. Effect of metal ions on modified PVDF membrane

To construct metal/polyphenol coordination network on PVDF membrane, EGCG was chosen as the organic ligand and metal ions with different valence (Ag$^+$, Cu^{2+} and Fe^{3+}) were chosen as the inorganic cross-linkers. The molar ratio and coating time of metal ion with EGCG were kept at 1:2 and 6 h, respectively.

Surface morphologies of the membranes were characterized by SEM. As presented in Fig. 1A, the original PVDF membrane has smooth surface with clear porous structure. And there's no obvious change in surface morphologies of Cu/EGCG and Fe/EGCG coated membranes compared to that of the original PVDF membrane. However, it's

interesting to find that Ag/EGCG-PVDF is uniformly decorated with numerous nanoparticles. It is postulated that EGCG with strong reducibility can chelate silver ions and reduce them into nanosphere silver particles in situ [26,27]. Nonetheless, the coating seldom affects membrane pore structure. The presence of metal element in EDX mapping (Supporting Information, Fig. S1) coupled with the improvement of hydrophilicity and oleophobicity (Fig. 1B and Fig. 1C, respectively) of the modified membranes demonstrate the successful formation of metal/polyphenol complexes. Of note, Ag/EGCG-PVDF possesses best hydrophilicity with initial WCA of 41° and UOCA of 156°, which might be contributed to the hydrophilic groups originating from EGCG on membrane surface associated with the special micro/nanostructure [28,29]. As illustrated in Fig. 1D, the hierarchical micro/nano surface could magnify membrane wettability, transforming the underwater oleophobicity to underwater superoleophobicity.

The as-prepared membranes were employed in oily emulsion separation. Fig. 2A depicts the dead end filtration cell used for separation experiments. Fig. 2B displays the droplet size distribution of surfactant-stabilized diesel-in-water emulsion, which agrees well with the optical microscopy image. It's noteworthy that the prepared emulsion can remain stable without demulsification for a long time (at least three months) as indicated in Fig. S2. It's an effective strategy to separate emulsions by superwetting porous materials whose pore size is much smaller than the oil droplets [1]. Separation performance of the membranes towards diesel oil emulsion is shown in Fig. 2C. Due to the
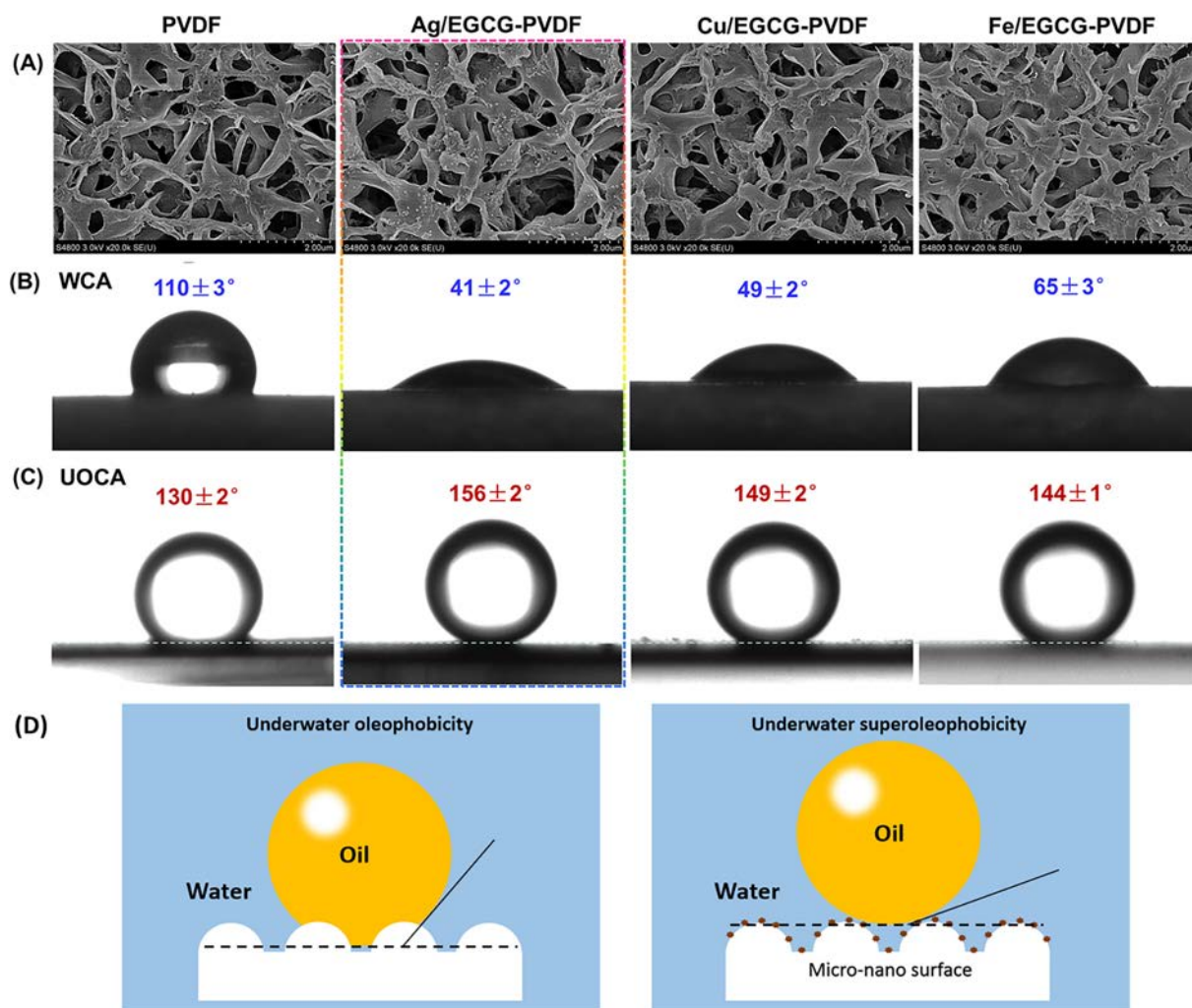

Fig. 1. (A) Surface SEM images, (B) water contact angles, and (C) underwater oil contact angles of the original PVDF and modified PVDF membranes with metal/EGCG coordination networks; (D) schematic illustration of an underwater oil droplet on PVDF, Cu/EGCG-PVDF, Fe/EGCG-PVDF (left) and Ag/EGCG-PVDF (right), respectively. The molar ratio and coating time of metal ion with EGCG were kept at 1:2 and 6 h, respectively.
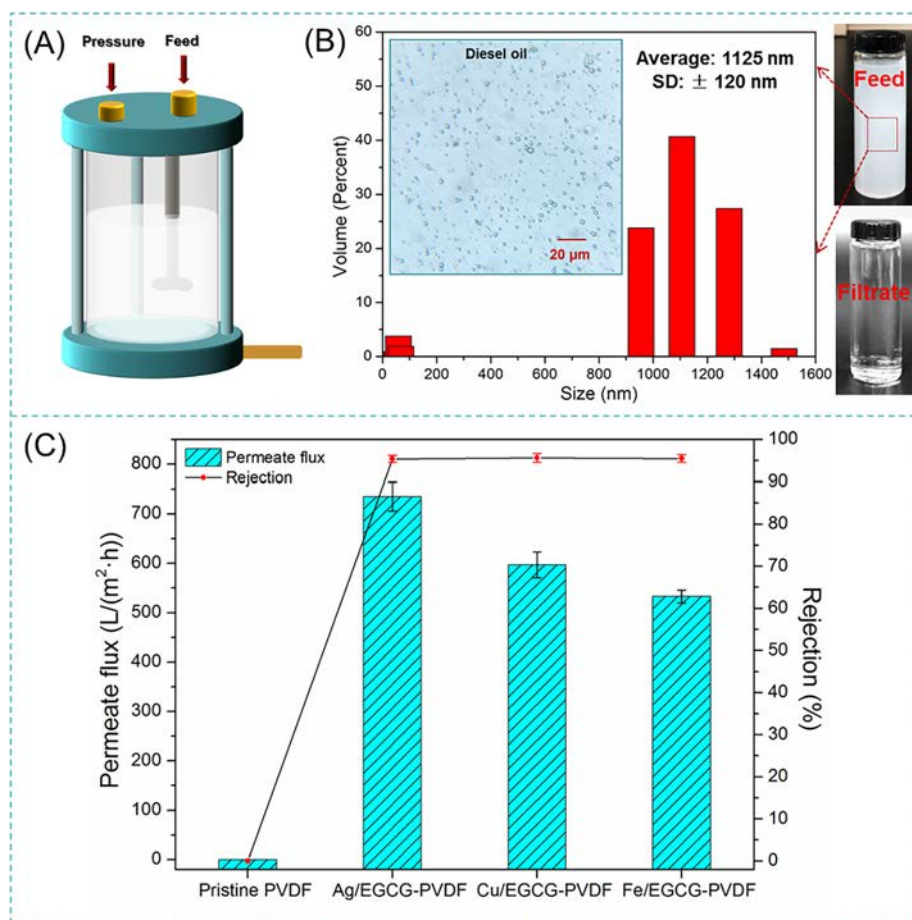
Fig. 2. (A) The apparatus used for oil-in-water emulsion separation; (B) size distribution of diesel oil droplets (The inset is captured on a microscope) and (C) separation performance of the membranes towards surfactant-stabilized diesel-in-water emulsion at 0.05 MPa.

strong hydrophobicity, permeate flux of pristine PVDF membrane is zero under the driving pressure of 0.05 MPa. Thus, its filtration performance was no longer compared and discussed in the following section. Apparently, Ag/EGCG-PVDF possessed the highest permeate flux (735 L/(m^{2}h)), owing to its best hydrophilicity and underwater oleophobicity as shown in Fig. 1. However, oil rejections of the three types of metal/EGCG composite membranes are nearly the same, about 95.5%, possibly because the membrane pore sizes are all smaller than oil droplet (~1.125 μm). Considering that higher permeate flux generally means higher output in practical use, Ag/EGCG-PVDF was further investigated in the following sections.

3.2. Surface chemistry of Ag/EGCG-PVDF

To better investigate surface chemistry of Ag/EGCG-PVDF, EGCG-PVDF was also prepared and characterized as a control (at EGCG concentration of 0.8 mg/mL in soaking solution and coating time of 6 h). First, ATR-FTIR analysis was performed to observe chemical structure of the membranes. As shown in Fig. S3, the new peak at 1605 cm^{-1} on the spectra of EGCG-PVDF and Ag/EGCG-PVDF was assigned to C = C stretching vibration of aromatic ring, which confirmed the existence of EGCG on membrane surface [22,30]. To further investigate the surface chemistry of the modified membranes, XPS analysis was carried out. As shown in Fig. 3, the presence of O 1 s peak and Ag 3d peak on the spectrum of Ag/EGCG-PVDF demonstrated the successful construction of Ag/EGCG composite on PVDF membrane. The elemental compositions of the membranes are shown in Table S1. Moreover, the O 1 s XPS spectra of EGCG-PVDF and Ag/EGCG-PVDF both presented two peaks. One at 532.9 eV was assigned to C-OH, the other at 531.4 eV was

attributed to C=O [24,25]. The enhanced O 1 s signal at 531.4 eV in the spectrum of Ag/EGCG-PVDF could be attributed to the accelerated oxidation of phenolic hydroxyls by means of redox reaction between Ag$^+$ and EGCG. In addition, the UV–vis absorption spectra of the soaking solutions after 6 h corresponding to EGCG-PVDF and Ag/EGCG-PVDF are exhibited in Fig. S4. A shoulder peak appeared at ~325 nm on the spectrum of sole EGCG soaking solution, corresponding to the phenolate form of EGCG in basic solution [31]. However, when Ag$^+$ was added in the solution, the concomitant shoulder disappeared and a new peak at ~420 nm emerged instead, which was attributed to the formed Ag nanoparticle (AgNP) via redox reaction [32].

On the basis of the above analysis, the underlying mechanism of the formation of Ag/EGCG composite on PVDF membrane is illustrated in Scheme 1. On the one hand, EGCG as a typical plant polyphenol consists of multiple pyrogallols, which could serve as bidentate ligands to bind with silver ions. The bonded silver ions tend to be reduced into silver atoms due to its strong redox potential, meanwhile a fraction of phenolic hydroxyls of EGCG are oxidized into quinones. Both the quinones and hydroxyls in EGCG contribute to the stabilization of the formed AgNP due to their affinity with AgNP [33]. In addition, the rigid aromatic rings of EGCG could also prevent AgNP from aggregation as a result of the steric hindrance. On the other hand, EGCG could spontaneously deposit on membrane surface together with AgNPs under basic conditions, thanks to its inherent affinity towards surface [27].

3.3. Effects of coating time and molar ratio of Ag$^+$ and EGCG on membrane performance

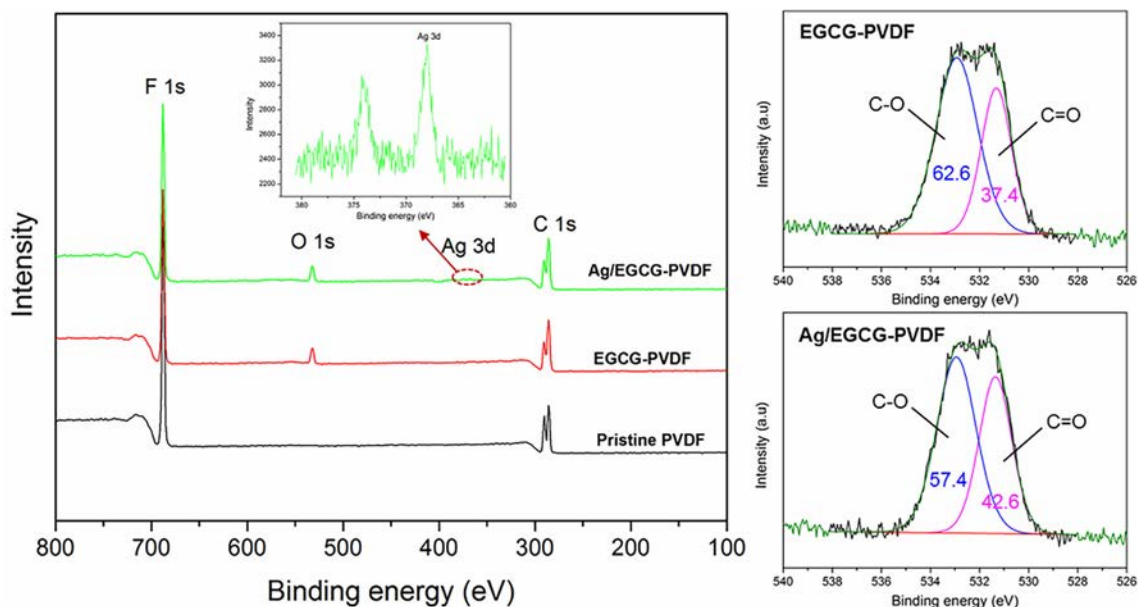Efforts have been devoted to optimizing the coating time of PVDF

Fig. 3. XPS survey spectra of pristine PVDF, EGCG-PVDF and Ag/EGCG-PVDF (The inset is Ag 3d core-level spectrum of Ag/EGCG-PVDF) and O1s core-levels XPS spectra for EGCG-PVDF and Ag/EGCG-PVDF.
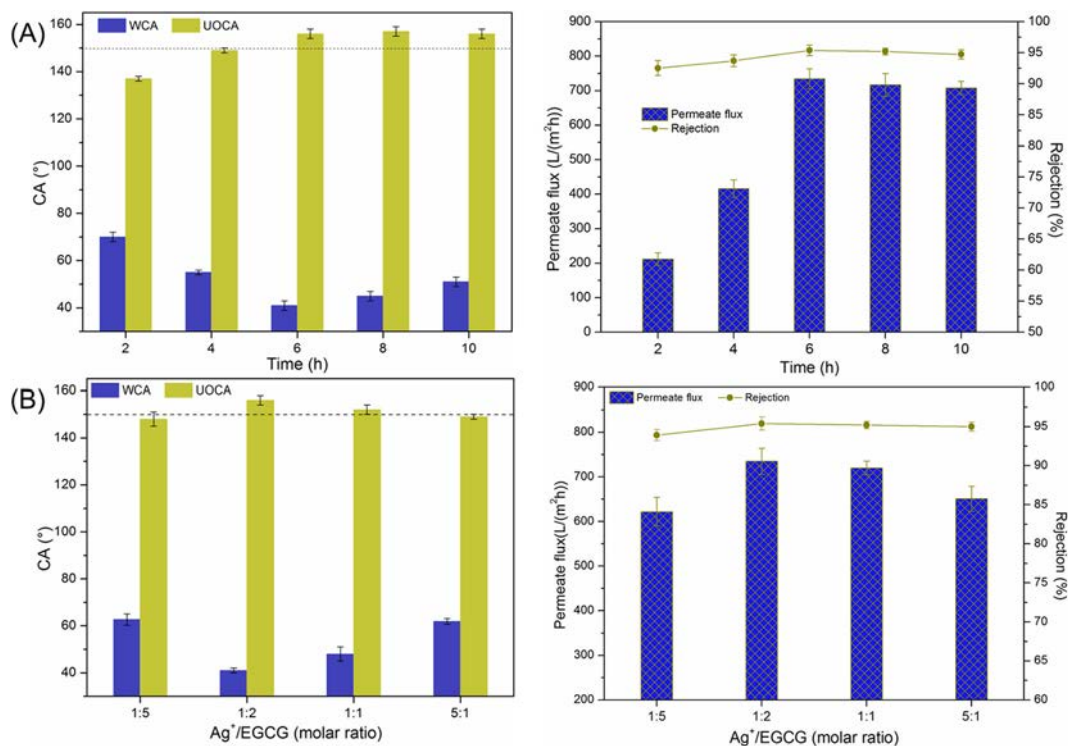

Fig. 4. (A) Wettability and separation efficiency of PVDF membranes treated by soaking solutions containing AgNO$_3$ and EGCG at a molar ratio of 1:2 for 2 h, 4 h, 6 h, 8 h and 10 h, respectively; (B) wettability and separation efficiency of PVDF membranes treated by soaking solutions containing AgNO$_3$ and EGCG for 6 h at molar ratio of 1:5, 1:2, 1:1 and 5:1, respectively.

membrane treated by AgNO$_3$ and EGCG involved solution and the molar ratio of Ag$^+$ and EGCG in the solution. Fig. 4A shows the influence of coating time on membrane wettability and separation efficiency. Clearly, when the coating time increased form 2 h to 6 h, both the hydrophilicity and oleophobicity of the fabricated membrane improved dramatically, with the initial WCA decreased from 70° to 41° and UOCA increased from 137° to 156°, respectively. Consequently, the separation efficiency of the resultant membranes improved significantly. Combined with the UV–vis spectra of corresponding soaking

solutions (Fig. S5), it can be deduced that the redox between AgNO$_3$ and EGCG is a mild and stepwise process. When the coating time further prolonged, the redox reaction strengthened to some extent, leading to a reduced amount of hydrophilic hydroxyl groups on membrane surface, which might account for the gradually increased WCA. And the permeate flux and oil rejection could not be further enhanced and declined slightly instead. Therefore, 6 h is the most appropriate coating time under the current conditions.

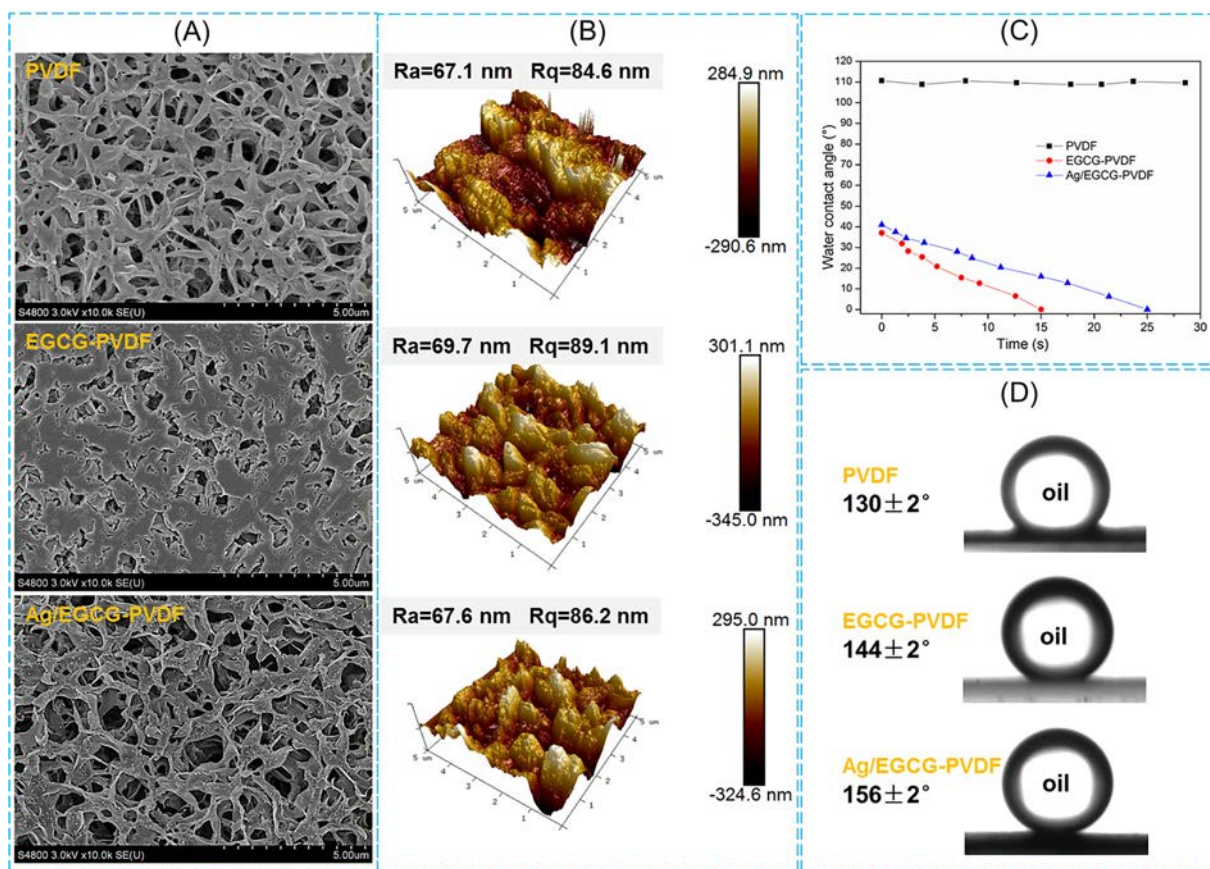Similarly, it can be seen from Fig. 4B that with the fixed

Fig. 5. (A) SEM images; (B) AFM images; (C) dynamic water contact angles and (D) underwater oil contact angles of PVDF, EGCG-PVDF and Ag/EGCG-PVDF membranes.

Table 1
Comparison in separation performance and antifouling property of EGCG-PVDF and Ag/EGCG-PVDF.

Membrane	PWF (L/m²h)	Permeate flux (L/m²h)	Rejection (%)	FRR (%)
EGCG-PVDF	1437 ± 54	664 ± 33	94.3 ± 1.5	95.2 ± 1.8
Ag/EGCG-PVDF	1392 ± 18	735 ± 29	95.4 ± 1.7	98.1 ± 0.7

concentration of EGCG in soaking solution (0.8 mg/mL), certain concentration of Ag^+ is conducive to the enhancement of membrane wettability and separation efficiency. It was found that 1:2 is the most suitable molar ratio. At smaller molar ratio, less Ag^+ was reduced into AgNPs, leading to a lower underwater oleophobicity and hydrophilicity due to the undeveloped micro/nanostructure. Consequently, membrane separation efficacy is low. However, at higher molar ratio, more EGCG participated in redox reaction with Ag^+ thus less hydroxyl groups remained [34], resulting in the gradually decreased membrane wettability. Hence, at the molar ratio of 1:2, the modified membrane exhibited most attractive separation performance as well as best hydrophilicity and underwater oleophobicity, which would be favorable for membrane fouling resistance.

3.4. Separation performance evaluation

To systematically investigate the separation performance of the optimally Ag/EGCG modified PVDF membrane, the surface morphologies and wettability of PVDF, EGCG-PVDF and Ag/EGCG-PVDF membranes were compared first. It is noted from Fig. 5A that the surface morphology of PVDF membrane with individual EGCG coating changed

greater than Ag/EGCG decorated membrane. Aggregates formed in EGCG coating due to the covalent bindings among aryl rings along with π-π stacking and hydrogen bonding interactions, and deposited on membrane surface, similar to the behavior of PDA coating [35–37]. While in Ag^+-EGCG coating, small Ag^+-EGCG complexes formed immediately after AgNO₃ and EGCG were mixed in the solution and subsequently bond to the surface in addition to the adsorption of free EGCG, which was similar to Fe^{3+}-TA assembly [16,17]. Ultimately, the bonded silver ions were in-situ reduced to AgNPs. Accordingly, the roughness of EGCG-PVDF was higher than that of Ag/EGCG-PVDF. Both the improved roughness and abundant hydroxyl groups of EGCG-PVDF accounted for its better hydrophilicity and higher PWF as shown in Fig. 5B, Fig. 5C and Table 1 [38]. However, Ag/EGCG-PVDF exhibited best oleophobicity (see Fig. 5D) resulting from its micro/nanostructural advantage. Consequently, Ag/EGCG-PVDF exhibited more attractive separation performance in terms of higher permeate flux and oil rejection as well as better antifouling property than EGCG-PVDF, as shown in Table 1. The FRR of Ag/EGCG-PVDF could reach up to 98.1% after fouled by diesel oil emulsion.

Besides diesel oil, kerosene and soybean oil were also employed to prepare surfactant-stabilized emulsions. These oily emulsions are quite common in real-life scenarios, thus it's of great guiding significance to use them to evaluate membrane efficiency in oily wastewater reclamation. The optical microscopy images, droplet size distributions associated with photographs of kerosene and soybean oil emulsions are shown in Fig. 6A. It's worth noting that there's a small fraction of oil droplets falling in the range of 1–100 nm.

It can be seen from Fig. 6B that the permeate flux of oil emulsion follows the sequence of diesel oil (735 L/(m²h)) > kerosene (561 L/(m²h)) > soybean oil (304 L/(m²h)), while the corresponding rejection exhibits an opposite trend with values of 95.4%, 96.8% and 97.5%,
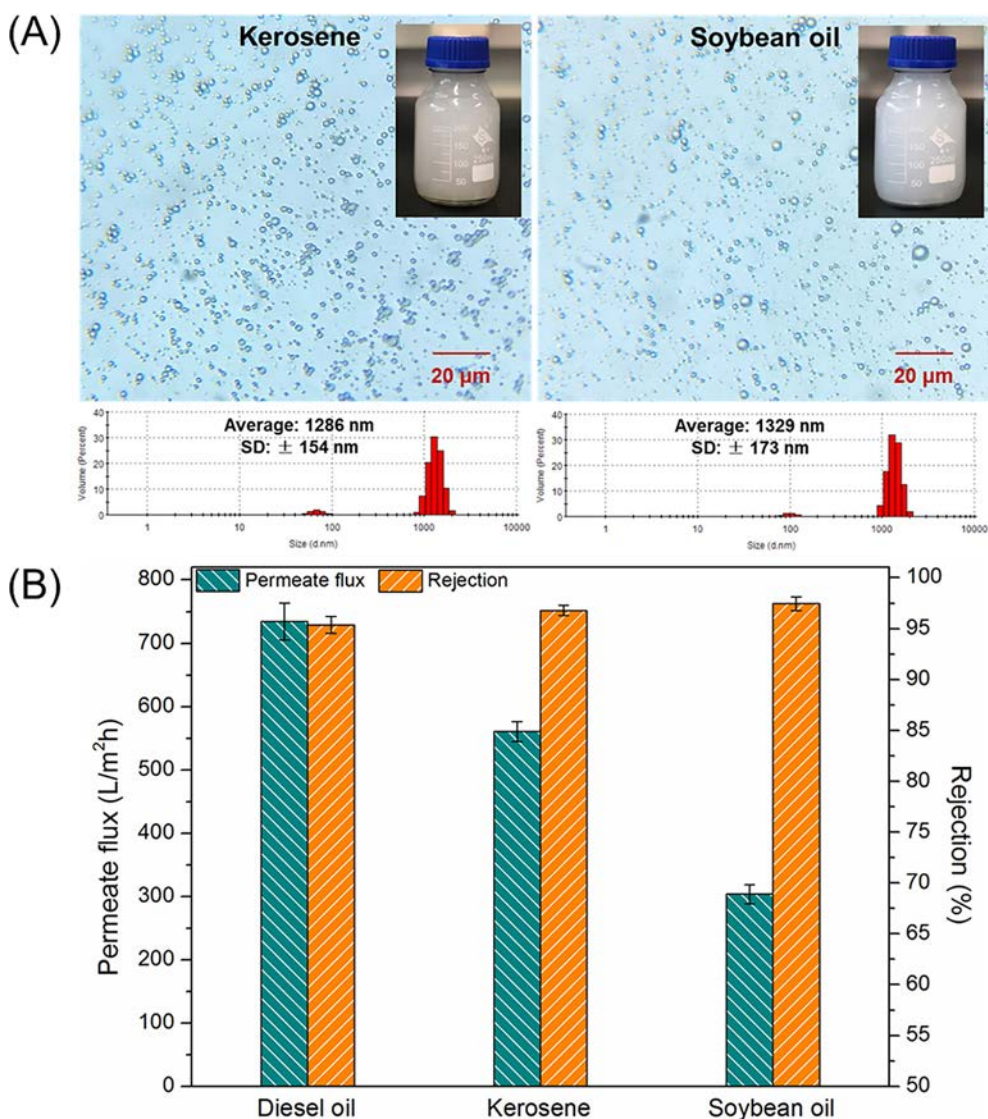
Fig. 6. (A) Droplet distributions of kerosene and soybean oil emulsions, (B) separation efficiency of optimal Ag/EGCG-PVDF membrane (the operating pressure is 0.05 MPa) for three types of SDS-stabilized oil-in-water emulsions.
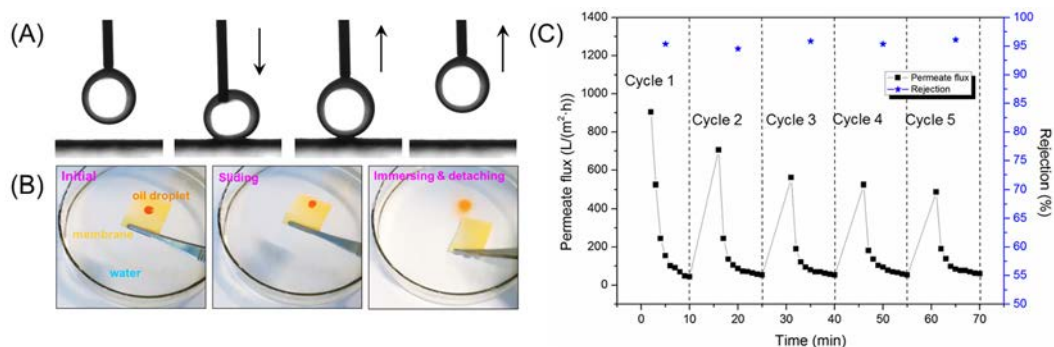

Fig. 7. (A) Dynamic images of oil adhesion on the optimal Ag/EGCG-PVDF membrane; (B) Dynamic images record the excellent antifouling performance of the optimal Ag/EGCG-PVDF membrane; (C) Permeate flux and rejection of the optimal Ag/EGCG-PVDF membrane during five cycles of SDS-stabilized diesel-in-water emulsion separation.

respectively. The flux variation for different emulsions might be due to the difference in viscosity and oil droplets concentrations of the emulsions derived from oils with different properties (see Table S2, Supporting Information) [38–40]. The rejection variation should be attributed to the droplet size difference, as oil/water separation using filtration membrane is mainly dominated by size-sieving effect. Due to the intrinsic pore size of PVDF membranes and the size distribution of the oil droplets, the obtained oil rejections are not very high. To further improve oil removal efficiency, home-made PVDF UF membranes with mean pore radius of ~ 20 nm were fabricated via immersion
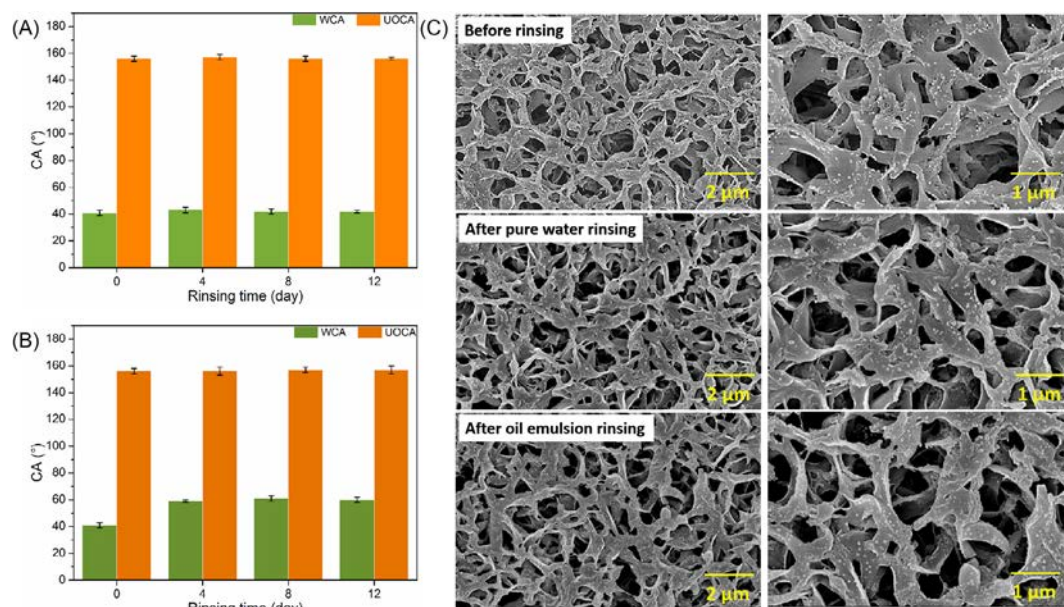
Fig. 8. UOCAs and initial WCAs of Ag/EGCG-PVDF membranes after being rinsed with (A) pure water and (B) 1 g/L SDS-stabilized diesel-in-water emulsion for different days; (C) SEM images of Ag/EGCG-PVDF membranes after being rinsed by pure water and 1 g/L SDS-stabilized diesel-in-water emulsion (the second row exhibits the magnified images corresponding to the first row).

precipitation method according to our previous work [41] and used as substrates. As exhibited in Fig. S6, the Ag/EGCG modified home-made PVDF UF membranes exhibited excellent oil rejections, which were all above 99.0% for diesel oil, kerosene, and soybean oil emulsions. The results demonstrated that oil rejections could be further improved by modifying membranes with smaller pore size, indicating the potential of Ag/EGCG composite membranes for full-scale applications.

3.5. Antifouling property and reusability

Antifouling property is another key criterion for filtration membrane in the treatment of oil-containing wastewater, as oil adhesion severely shortens membrane service life. The anti-oil fouling of the optimal Ag/EGCG decorated PVDF membrane was characterized by the oil adhesion experiments. As shown in Fig. 7A, the oil droplet barely adhesive to membrane even though forced to adequately contact the membrane surface. More details can be seen in Video S1. In addition, Fig. 7B depicts that an oil droplet attaches on membrane surface, and then it slides when the membrane is inclined. The oil droplet is easily separated from membrane surface when immersed into deionized water, implying that the membrane possesses excellent oil resistance. More details can be seen in Video S2.

To deeply assess the antifouling performance and reusability of the optimal Ag/EGCG-PVDF membrane, we recorded the variations in permeate flux and oil rejection in a five-cycle SDS-stabilized diesel-in-water emulsion separation. As shown in Fig. 7C, the permeate flux decreased rapidly at the beginning of each cycle due to formation of a filter cake on membrane surface induced by high flux, which seriously block the surface pores and reduced the effective filtration area of the membrane [42–44]. Even though the initial flux (within the first two minutes) decreased gradually in the first three cycles, it remained stable after the 3rd cycle. The result reveals that oil fouling cannot be completely avoided in the separation of oily emulsions. Nonetheless, the membrane still exhibits favorable antifouling performance. Moreover, the oil rejections are all above 95% in the cycle tests, indicating that the separation efficiency is not sacrificed after several separation times.

3.6. Stability

The stability of high hydrophilicity and underwater super-oleophobicity presents the quality of the coating layer decorated on membrane surface, which is also essential for the membrane to separate oil-in-water emulsions with high efficiency in long-term operations. As presented in Fig. 8A and B, the initial WCA of the membrane did not change (about 42°) after being rinsed by pure water for 12 days. But it increased from 41° to 59° after 4-day rinsing by oil emulsion, and then kept stable from 4 days to 12 days. Furthermore, Ag/EGCG-PVDF membrane showed UOCAs all above 156° during 12-day rinsing tests both by pure water and diesel-in-water emulsion. Additionally, it can be observed from SEM images (shown in Fig. 8C) that the micro/nanostructural surface could be well reserved after long-time rinsing tests. These facts suggest that the fabricated Ag/EGCG composite membranes possess high stability, implying their good reliability in practical oily emulsion treatment.

The stability of AgNPs immobilized on membrane was quantitatively analyzed by Ag leaching test. As shown in Fig. S7, silver concentration was less than 6 µg/L in the initial 0.02 L permeate and further decreased to 1.2 µg/L after 1.5 L water permeating through the membrane. Of note, the concentration of Ag in the permeate was much lower than the maximum contaminant limit of Ag in drinking water (100 µg/L) mandated by the World Health Organization and the U.S. Environmental Protection Agency [45]. Therefore, Ag/EGCG modified PVDF membrane would be stable enough for water treatment application with no health concern caused by Ag leaching.

4. Conclusions

This study integrates the adhesive deposition of hydrophilic plant polyphenol-involved coating and the introduction of nanoparticle through coordination and redox reactions. The single-step strategy transformed PVDF membrane from intrinsic high hydrophobicity to good hydrophilicity and underwater superoleophobicity with micro/nanostructural surface via soaking pristine membranes in an aqueous buffer solution containing EGCG and $AgNO_3$. The optimized soaking conditions were at Ag/EGCG coating time of 6 h and Ag^+/EGCG molar ratio of 1:2. Three kinds of real oils were employed to prepare

surfactant-stabilized oil-in-water emulsions with micro/nano dispersed droplets, which were close to those in real-life scenarios. The optimal Ag/EGCG-PVDF exhibited the permeate flux of oil emulsions in the sequence of diesel oil (735 L/(m^2h)) > kerosene (561 L/(m^2h)) > soybean oil (304 L/(m^2h)) with rejections of 95.4%, 96.8% and 97.5% at 0.5 bar, respectively. The surface of optimal Ag/EGCG composite membrane showed high oil-resistance property, enhancing membrane antifouling performance and reusability. Moreover, the Ag/EGCG composite possessed benign stability, which would benefit the practical application of oily emulsion purification.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2020.126200.

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