

A Versatile Coating Approach to Fabricate Superwetting Membranes for Separation of Water-in-Oil Emulsions^{*}

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Abstract Separation of oil/water mixtures, especially for the emulsified oil/water mixtures, is important because of the frequent occurrence of oil spill accidents. Utilizing superwetting porous membrane has become a promising approach to separate either surfactant-free or surfactant-stabilized emulsions. Herein we report a facile and versatile strategy for preparing hydrophobic/under-oil superhydrophobic membranes by coating the skeletons of the membranes with the poly[(3,3,3-trifluoropropyl)methylsiloxane] (PTFPMS) nanoparticles. The obtained membranes could be used to separate various water-in-oil emulsions with high flux and separation efficiency. In addition, owing to the outstanding resistance of PTFPMS to the most organic solvents or oils, the modified membranes exhibited the excellent reusability and the antifouling properties that were critical in the practical applications. Many commercially available membranes can be modified by such a simple method.

Keywords: Emulsion; Membrane; Separation; Superwetting; Poly[(3,3,3-trifluoropropyl)methylsiloxane].

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INTRODUCTION

Oil/water separation, especially for the emulsified oil/water mixtures, has attracted considerable attention due to the frequently occurred oil spills^[1]. The materials with special wettability are believed to be one of the most promising solutions to separate oil/water mixture because of the less extra energy requirement. For example, the superwetting porous materials^[2], with a water contact angle > 150°, an oil contact angle < 5° and a water contact angle in oil > 150°, can allow the oil to pass through but retain the water, thus leading to the separation of oil/water mixtures.

Recently, porous materials with special wettability have been successfully used to separate the oil/water mixtures^[3, 4]. However, the porous materials cannot be used to separate emulsions because the size of emulsion droplets (less than 20 μm) is generally smaller than the pore size of these materials^[5, 6]. For the separation of emulsified oil/water mixtures, superwetting membranes with smaller pores have exhibited enormous potentials

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with high separation efficiency^[7–9]. Some of the modification methods, however, are complicated, time-consuming or only suitable for special membranes, and the corresponding materials cannot be used under harsh conditions^[10, 11]. Therefore, a simple, universal and scalable method to afford the robust membranes with good reusability and antifouling properties still remains a challenge.

We previously reported the separation of various oil/water mixtures based on the superwetting particles, fabrics and porous materials^[12–15]. Herein, we demonstrate a versatile coating strategy to modify various membranes for realizing the separation of water-in-oil emulsions. The dispersion of the poly[(3,3,3-trifluoropropyl) methylsiloxane] (PTFPMS) nanoparticles in acetone/water was prepared and used to modify the membranes by a simple coating process. The membranes showed superhydrophobicity with the PTFPMS nanoparticles covered on the skeletons. Because of the resistance of PTFPMS to the most of chemicals, the resultant superwetting membranes performed high efficiency, good reusability and antifouling properties in the separation of surfactant-free or surfactant-stabilized water-in-oil emulsions.

EXPERIMENTAL

Materials

Poly[(3,3,3-trifluoropropyl) methylsiloxane] (PTFPMS) ($M_w = 1.06 \times 10^5$, PDI = 1.4) was supplied by Chengdu Tuoli Co. Ltd., China. Acetone, ethanol, petroleum ether, chloroform, kerosene and xylene were purchased from Beijing Chemical Companies. Span-80 was obtained from Alfa Aesar. Commercially available nylon membrane, poly(vinylidene fluoride) membrane and polytetrafluoroethylene membrane were used as received. Deionized water was used for all the experiments and tests.

Preparation of PTFPMS Nanoparticles

Typically, 5 g of PTFPMS was dissolved in 100 mL of acetone, then 100 mL of water was added dropwise into the solution at room temperature under magnetic stirring. Then the obtained dispersion was centrifuged under 12000 r/min for 10 min. A translucent dispersion with blue opalescence containing the PTFPMS nanoparticles was obtained.

Preparation of Hydrophobic/Under-oil Superhydrophobic Membranes

The above mentioned membranes were washed with ethanol and distilled water before modification. The PTFPMS nanoparticles were coated on the membranes by using the membranes to filter certain amount of dispersions (800 μ L to 2500 μ L) under a vacuum pressure of 0.02 MPa. After drying, a robust layer of PTFPMS nanoparticles was coated on the skeletons of the membranes.

Characterization

Scanning electron microscope images were observed by a JSM-7500F (JEOL, Japan) field-emission scanning electron microscope at an accelerating voltage of 5 kV. Transmission electron microscope image was obtained on a JEM-2200FS (JEOL, Japan). The contact angles were measured using KRÜSS DSA 100 by a sessile drop method. Water droplet of 5 μ L was used for contact angle measurement, and the average value was obtained from three tests. An optical microscope (Olympus, Model IX71) was used to observe the water droplets in emulsions. Oil purity was measured by TY10916 Ti-Touch (Metrohm).

Preparation of Various Water-in-Oil Emulsions

The surfactant-free water-in-oil emulsions were prepared by mixing the oil and water with a volume ratio of 9:1, and then the mixture was sonicated for 2 h. The upper water-in-oil emulsion was used. The surfactant-stabilized water-in-oil emulsions were prepared by mixing the oil and water with a volume ratio of 100:1. Emulsifier Span-80 was added at a concentration of 2.5 mg/mL. The mixture was stirred by ULTRA-TURRAX at 15000 r/min and then sonicated for 2 h. Surfactant-free and surfactant-stabilized water-in-petroleum ether (W/P), water-in-xylene (W/X), water-in-chloroform (W/C) and water-in-kerosene (W/K) emulsions were prepared.

Separation of Water-in-Oil Emulsions

The separation process was carried out by a vacuum filtration device equipped with the modified membranes

(effective area $\sim 12.6 \text{ cm}^2$) under a vacuum pressure of 0.1 MPa. Water-in-oil emulsion of 10 mL was poured into the separation device. For the antifouling experiment, 5 mL of water-in-oil emulsion was separated each time, and then the membrane was washed by 3 mL ethanol. This process was repeated for 50 cycles. The flux was calculated according to the equation: $\text{Flux} = V/S \cdot t$, where V is the volume of the emulsion, S is the effective area of the membrane (12.6 cm^2), t is the performing time. The data of the flux is an average value of three different measurements.

RESULTS AND DISCUSSION

PTFPMS Nanoparticles

The solubility of PTFPMS decreased gradually with increasing the water amount to the solution, indicating that phase separation occurred^[16], and the micro-nano hierarchical aggregates of PTFPMS were formed. The resulting aggregates could not be used directly to modify the filtration membranes because the pores would be easily plugged by the large aggregates. The PTFPMS nanoparticles with much smaller size were obtained by centrifugation. The dispersion of PTFPMS nanoparticles exhibits blue opalescence due to the Rayleigh scattering (Fig. 1a). TEM image (Fig. 1b) indicates that the nanoparticles have irregular morphologies with the size of 30–40 nm. SEM image (Fig. 1c) shows a rough coating constructed with the PTFPMS nanoparticles by casting the dispersion, and a water contact angle of $(155 \pm 1)^\circ$ is observed due to the inherent low surface tension of PTFPMS and the roughness of the coating^[17–20].

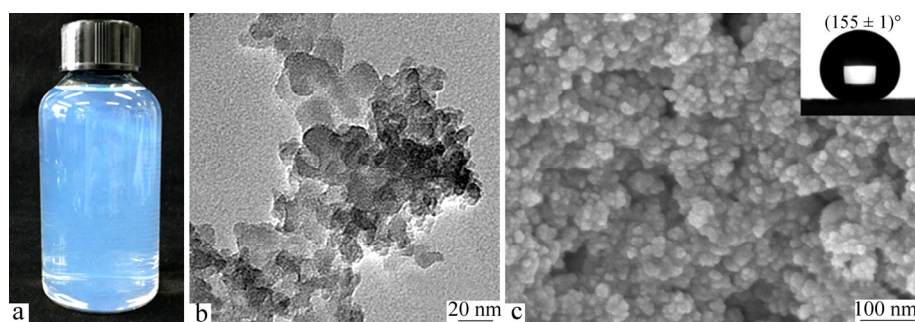


Fig. 1 (a) Digital photograph of the dispersion of the PTFPMS nanoparticles, (b) TEM image of the PTFPMS nanoparticles in (a), (c) SEM image of coating constructed by the PTFPMS nanoparticles (Insert is the water contact angle.)

PTFPMS Nanoparticles Coated Nylon Membrane

SEM images of the top and cross-section of the modified nylon membranes (pore size 450 nm) are shown in Figs. 2(b)–2(d) and 2(b')–2(d'), respectively. Compared to the pristine nylon membranes (Figs. 2a and 2a'), the PTFPMS nanoparticles were coated on the skeletons uniformly and the PTFPMS nanoparticles decorated on the membrane more densely with increasing the dispersion amount from 800 μL to 1000 μL . It can be seen that the pores of the membranes are not blocked (Figs. 2b–2c, 2b'–2c'). However, when the dispersion increased to 2500 μL , the effective pores either on the membrane surface or inner are blocked by the PTFPMS nanoparticles (Figs. 2d–2d'). In addition, the PTFPMS nanoparticles could also be coated on various membranes regardless of the shape and size of the pores, the wetting and the composition of membranes. Figures S1(b)–S1(c), S1(e)–S1(f) show the SEM images of the pristine hydrophilic polyvinylidene fluoride (pore size 220 nm) and hydrophobic polytetrafluoroethylene membranes (pore size 220 nm) coated with the PTFPMS nanoparticles. We observed that the PTFPMS nanoparticles also uniformly distributed on the skeletons of these membranes; while the original skeletons were relatively smooth (Figs. S1a–S1d), demonstrating the universal application of this strategy.

As shown in Figs. 3(a) and 3(b), there is no obvious distinction between the pristine and the PTFPMS nanoparticle modified nylon membranes in appearance. The hydrophilic nylon membrane turned to hydrophobic after the modification, with the water contact angle increased from 0 to 124° in air, and from 137° to 152° in oil,

respectively (Figs. 3c–3f). The results confirmed that the wettability of nylon membrane changed from the pristine hydrophilic/under-oil hydrophobic to the hydrophobic/under-oil superhydrophobic after modification.

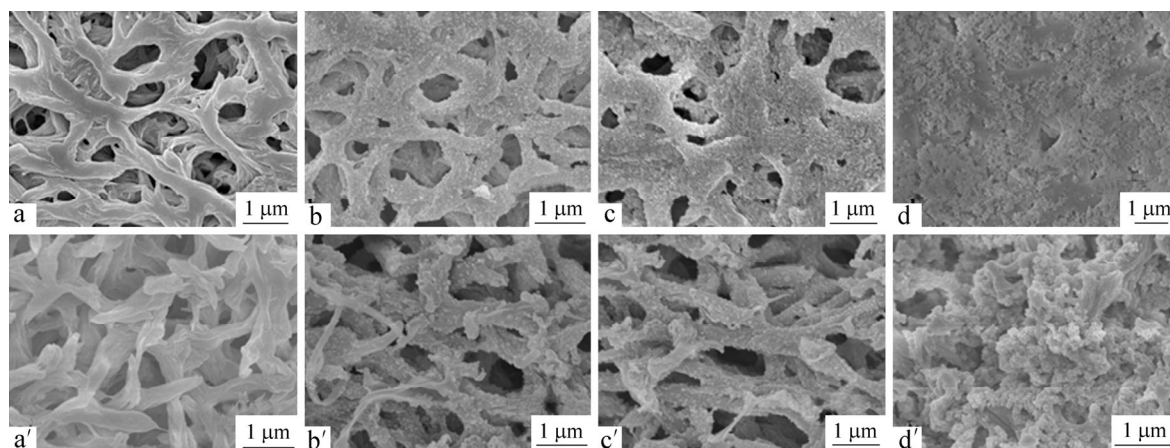


Fig. 2 SEM images of top and cross-section of (a, a') the pristine nylon membranes, the nylon membranes modified by the dispersion of PTFPMS nanoparticles, (b, b') 800 μL , (c, c') 1000 μL , (d, d') 2500 μL

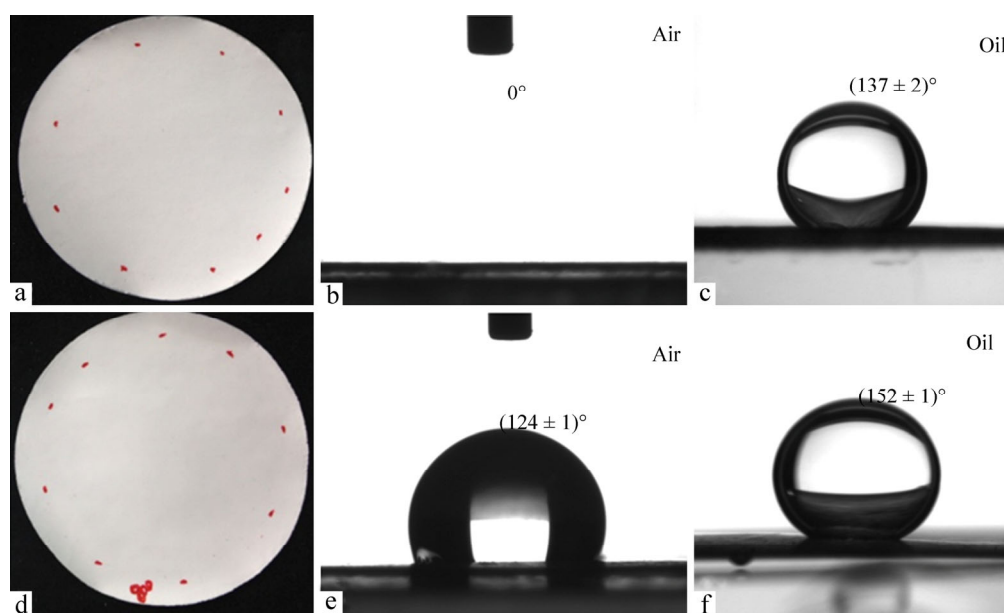


Fig. 3 Photo images of the pristine (a) and the modified (b) nylon membranes (800 μL dispersion); (c–d) water contact angles of the pristine (c) and the modified (d) nylon membranes in air; (e–f) water contact angles of the pristine (e) and the modified (f) nylon membranes in oil

Separation of Water-in-Oil Emulsions

The milky emulsion of 10 mL was poured into the device under constant transmembrane pressure of 0.1 MPa. All the following experiments were carried out on the membranes modified by 800 μL nanoparticles dispersion. The optical microscopy images (Figs. 4a–4b, 4e–4f) show that the dense water droplets at micro or sub-micro scale are observed clearly in the feeds, while no water droplets are found in the filtrate. Moreover, the original milky emulsion become clear after the separation (Figs. 4c–4d), suggesting the successful removal of the water droplets from the emulsions.

The modified nylon membrane can be used to separate various water-in-oil emulsions due to the inherent resistance of PTFPMS to the most solvents or oils (Fig. S3). The fluxes of these emulsions are shown in Fig. S2.

The factors including the surface tension, the viscosity and the density of the oil phase, the concentration of the emulsions and the dimension of the water phase will influence the flux. The fouling of the membrane is the key factor for the separation in the flux.

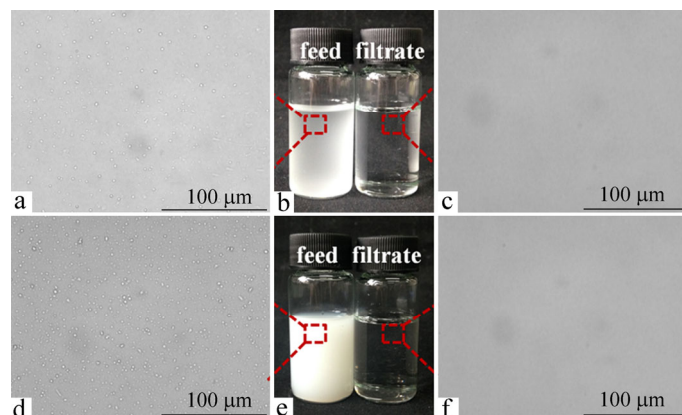


Fig. 4 The optical microscope images of the surfactant-free emulsion and the surfactant-stabilized emulsion (a–b) before and (c–f) after separation; (c) photographs of the surfactant-free water-in-kerosene emulsion and (d) the surfactant-stabilized water-in-kerosene emulsion before and after separation

The Antifouling Property and the Reusability

Although the membrane filtration is an efficient and simple technique for treating the emulsified oil/water mixture, the membrane fouling is an inevitable trouble during the separation. The fouling not only influences the reusability of membrane but also decrease the separation flux and efficiency. The antifouling property of the PTFPMS nanoparticle-coated membrane was examined by repeating the separation experiment. The purity of the filtrated oil kept almost 99.99% and the flux did not decrease with the repeating cycles (Fig. 5a), indicating the modified membrane processed a superior antifouling property^[3, 21–23]. Figures 5(b) and 5(c) show the SEM

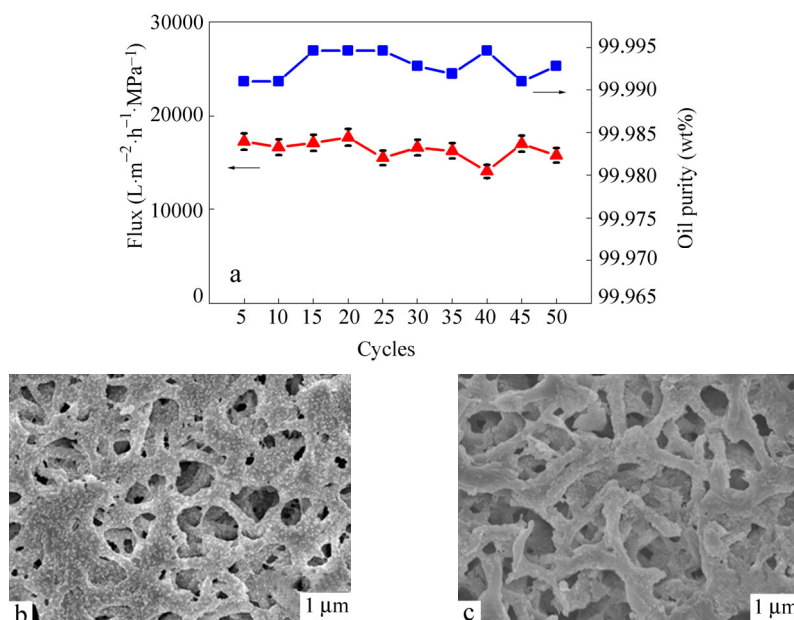


Fig. 5 (a) The change of flux and oil purity with the cycles when separating Span-80 stabilized water-in-kerosene emulsion; SEM images of the modified nylon membrane (b) before and (c) after separation for 50 cycles

images of the PTFPMS nanoparticle-coated membranes before and after 50 cycles of separation and washing. It can be seen that the PTFPMS nanoparticles still uniformly adhere on the skeletons of the membrane, and the amount of PTFPMS nanoparticles on the surface have no obvious decrease after the separation. Such good antifouling and reusability are ascribed to the low surface tension and adhesion of PTFPMS that hardly to be dissolved or washed away from the skeletons. It should be noted that operating under the vacuum for a long time may destroy the pores' structure of the membrane, which can hinder the separation efficiency.

CONCLUSIONS

In summary, the hydrophobic/under-oil superhydrophobic membranes were fabricated by a simple coating method using the dispersion of PTFPMS nanoparticles. A high flux rate and the separation efficiency of 99.99% were achieved. The modified membranes have the excellent reusability and antifouling properties, which hold the potential application for separating various surfactant-free or surfactant-stabilized water-in-oil emulsions. We believe the coating approach is a versatile strategy to prepare various superwetting membranes at the large-scale.

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