

# A facile approach in fabricating superhydrophobic and superoleophilic poly (vinylidene fluoride) membranes for efficient water–oil separation

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**ABSTRACT:** New preparation strategies for films that exhibit separation of emulsified oil/water mixtures through a simple, practical, and cost-effective method are highly desirable. Herein a poly (vinylidene fluoride) membrane with superhydrophobic and superoleophilic surface had been successfully fabricated via a facile dip-coating process. As-prepared membrane exhibits good stability of wettability and can be applied for oil and water mixture separation. After cycles, the membranes still keep a relatively high flux, which indicates their great potential for practical applications. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42077.

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## INTRODUCTION

Separation of water and oil mixture is a worldwide challenge because of the increasing industrial oily wastewater as well as the frequent oil spill accidents such as the Deepwater Horizon oil spill in the Gulf of Mexico.<sup>1,2</sup> Several conventional techniques<sup>3–6</sup> have been reported that can separate the free oil/water mixtures; such as gravity separation, flotation, and skimming flotation, but are not applicable to water/oil emulsions. Thus, there is need to develop facile energy and cost-effective processes for effective separation of water/ oil emulsion.<sup>7</sup>

In the last year, superhydrophobic materials have attracted great attention for potential applications in filtration or absorption of oil from water selectively and effectively.<sup>8–12</sup> And since Jiang and co-workers first reported a superoleophilic and superhydrophobic coated mesh film for effective oil and water separation.<sup>13</sup> A number of superwetting materials have been fabricated to separate the oil/water mixtures.<sup>14–19</sup> Various methods, including electrospinning,<sup>20</sup> sol-gel process,<sup>21</sup> dip-coating,<sup>22</sup> and phase separation<sup>23</sup> have been reported for constructing superhydrophobic membrane to separate oil/water mixtures. Compared to metallic membranes, PVDF is one of the most used materials for forming microfiltration and ultrafiltration membranes because of its unique properties, such as good processability, low cost, thermal stability, chemical resistance, and high mechanical strength. Various methods to fabricate polymer superoleophobic surfaces have emerged. Jin *et al.*<sup>16</sup> fabricated a superhydrophobic–superoleophilic poly (vinylidene fluoride) (PVDF) membrane via an inert solvent-induced phase-inversion

process (NIPS). NIPS is one good method because of its high efficiency and simplicity. In our article, we have attempted to prepare highly hydrophobic surfaces using organic/inorganic hybrid materials by dip-coating method, which is also a facile approach to prepare the superhydrophobic membrane. The inorganic materials first modified with low surface energy compounds and then coated on the substrates are a versatile technique to construct the roughness and low surface energy surface.

We first fabricated SiO<sub>2</sub> nanoparticles modified with hexamethyldisilazane (SiO<sub>2</sub>-TMS).<sup>24</sup> However, the coatings should have strong adhesion with substrates in order to attain excellent superoleophobic durability. PVDF is one of the most commonly used adhesive. So the superhydrophobic surface was prepared by using PVDF and SiO<sub>2</sub>-TMS solution on the PVDF microfiltration membrane by dip-coating, to form a superhydrophobic and superoleophilic surface. As a consequence, the membrane can separate surfactant-free water/oil emulsions with high separation efficiency as well as high flux. Most interestingly, the membrane exhibits an excellent antifouling property. The outstanding performance of the membrane for the separation of water/oil and its industrially processable preparation process indicate its great potential for practical applications.

## EXPERIMENTAL

### Materials

PVDF microfiltration membranes (average pore size, 0.45 μm) were purchased from Beijing Sheng He. Silica nanoparticles

(14 nm) and PVDF powders ( $M_n = 238,000$ ) were obtained from Sigma-Aldrich. *N,N*-Dimethylformamide (DMF, 99.7%) and Hexamethyldisilazane (HDMS, 99.8%, Sinopharm Chemical Reagent) were used as received.

### Modification of Silica Nanoparticles

First, 3 g silica nanoparticles and 50 mL methyl-isobutyl-ketone were mixed with vigorous stirring for 30 min at 50°C. After 100 mL of HDMS was added into the above solution, it was stirred for 24 h under  $N_2$  inert atmosphere protection and the temperature was maintained at 50°C. Finally, the nanoparticles were separated by centrifugation with absolute ethanol for three times and dried at 70°C under vacuum. The modified silica nanoparticles were recorded as  $SiO_2$ -TMS.<sup>24</sup>

### Preparation of PVDF Superhydrophobic Surface

The PVDF microfiltration membrane was immersed in the  $SiO_2$ -TMS/DMF or  $SiO_2$ -TMS/PVDF/DMF mixture solution for 1 min. Then the membranes coated with  $SiO_2$ -TMS or  $SiO_2$ -TMS/PVDF mixture were dried at 80°C for 2 h.

### Superhydrophilicity and its Durability Study

The superhydrophobic and its durability of membrane surface were tested by ultrasonic bath processing. Then the variation of the water contact angle (CA) of the membrane with different ultrasonic time was measured at ambient temperature. The average CA values (with 5  $\mu$ L water droplets) were obtained by measuring the same sample at five different positions.

The pH stability of the membranes superhydrophilicity was evaluated by different pH values aqueous solution. The dried membranes were immersed in different pH values aqueous solution for 1 h at room temperature. Then the membranes were dried at 80°C for 6 h. The average CA values (with 5  $\mu$ L water droplets) were also obtained by measuring the same sample at five different positions.

### Absorption Capacity Measurement

The dried membranes were put into the various organic solvents or oils keeping for 1 h at room temperature, including chloroform, petroleum ether, gasoline, coil oil, and soybean oil. The absorption capacity of membrane was calculated by the following relationship:

$$Q(\%) = \frac{W_{\text{absorbed}}}{W_{\text{dry}}} \times 100$$

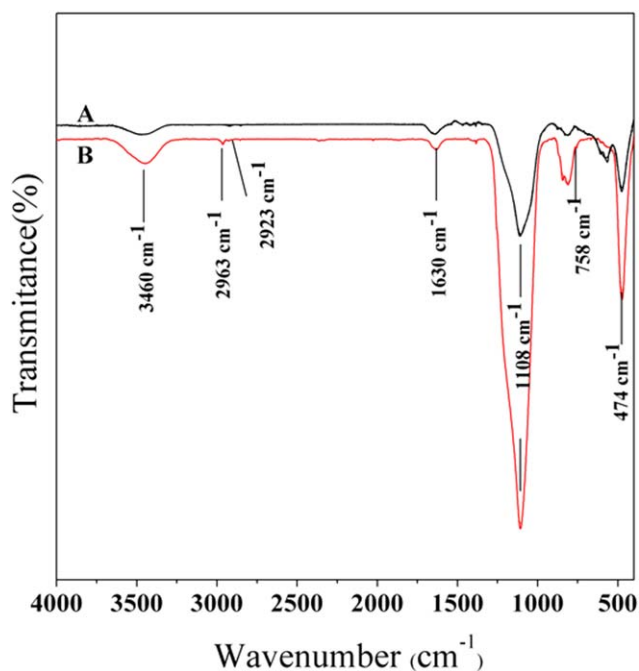
where  $Q$  is the absorption content of membrane,  $W_{\text{dry}}$  is the dry sample weight (g);  $W_{\text{absorbed}}$  is the wet sample weight (g).

### Emulsion Separation Experiments

Water/oil emulsions were prepared by mixing water and toluene in 1 : 9 (v : v) and sonicated under a power of 2 kW for 2 h to obtain a milky solution.<sup>16</sup> The PVDF membrane was placed between one vertical glass tube with a diameter of 40 mm and one conical flask. Separation experiments were carried out under the pressure difference of 0.08 MPa. The flux was calculated on the permeated volume of emulsion through the membranes with in 5 min.

### Characterization

The Fourier Transform Infrared (FTIR) spectroscopy was measured by Bruker IFS 66v/s IR spectrophotometer (Bruker optics,



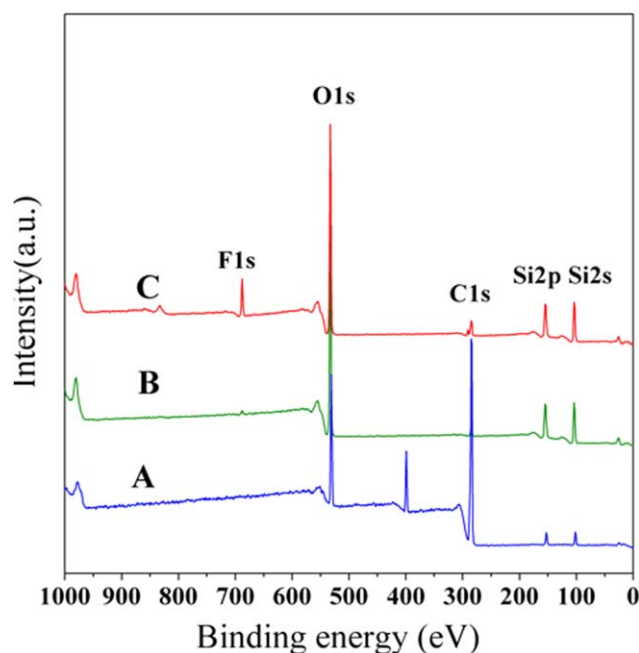
**Figure 1.** FTIR spectra: (a) raw  $SiO_2$  nanoparticles; (b)  $SiO_2$ -TMS nanoparticles. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Germany). X-ray photoelectron spectroscopy (XPS) was conducted on a PHI-5702 electron spectrometer (Perkin-Elmer, USA) using an AlK $\alpha$  line excitation source with the reference of C1s at 284.80 eV. FE-SEM images were obtained with a field emission scanning electron microscope (JSM-6701F). Water CA of film surface was measured at ambient temperature on a DSA100 machine (Krüss, Germany). Optical microscopy images were obtained with MM6C-AF-2 (OlympusJapan) by dropping emulsion solution in a dish.

## RESULTS AND DISCUSSION

The successful conjugation of the trimethylsiloxane (TMS) to the surface of the silica nanoparticles was confirmed using FTIR spectra. The FTIR spectra of raw  $SiO_2$  and  $SiO_2$ -TMS nanoparticles are shown in Figure 1. The pristine  $SiO_2$  exhibits typical bands around 1108 and 474  $cm^{-1}$ , which are ascribed to symmetric stretching modes and bending vibrations of Si-O-Si. The broad band at 3464  $cm^{-1}$  and the medium band near 1630  $cm^{-1}$  can be assigned to the stretching and bending vibrations of Si-OH. After the reaction with TMS, new bands at 2963 and 2904  $cm^{-1}$  appear, which are attributed to the asymmetric and symmetric C-H stretching, respectively. The very weak absorption band at 758.54  $cm^{-1}$  can be ascertained from vibration of  $Si(CH_3)_3$ .<sup>24</sup>

The PVDF microfiltration membrane with superhydrophobic property was covered with the hybrid PVDF/ $SiO_2$ -TMS or  $SiO_2$ -TMS thin film by dip-coating. The chemical composition of the superhydrophobic surface was confirmed by XPS measurement. As shown in Figure 2, compared to the original membrane [Figure 2(a)], the new characteristic Si peak of  $SiO_2$ -TMS [Figure 2(b)] is observed at 99.5 (Si 2s) eV, which originated from the



**Figure 2.** XPS spectra of (a) untreated membrane, (b) membrane surface deposited with  $\text{SiO}_2$ -TMS solution, and (c) membrane surface deposited with PVDF/ $\text{SiO}_2$ -TMS solution. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

peaks of  $\text{SiO}_2$ -TMS. Figure 2(c) shows that XPS spectra are obtained from the PVDF membrane surface deposited with PVDF/ $\text{SiO}_2$ -TMS solution. Obviously, the Si2s and F1s peaks in the surface should originate from the characteristic element peaks of the PVDF and  $\text{SiO}_2$ -TMS.

### Structure and Morphology of Membrane

The morphology change of origin and modified PVDF membranes covered with the hybrid PVDF/ $\text{SiO}_2$ -TMS or  $\text{SiO}_2$ -TMS thin film by dip-coating are shown in Figure 3. The surface of the origin PVDF film is rather flat and smooth without adding  $\text{SiO}_2$ -TMS particles. It can be seen that modified membrane surfaces [Figure 3(b, c)] are covered by a layer with a relatively uniform distribution of aggregates of silica particles. Such surface structure is beneficial to the surface hydrophobicity because of air may be trapped in micro/nano hierarchical rough area. However, we all know that most of the pores can be blocked

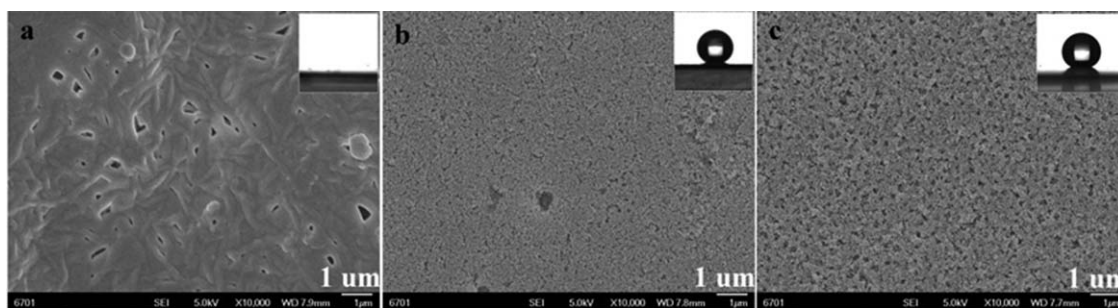
as shown in Figure 3, which corresponds to a sharp decrease of the flux, but this is inevitable.

The surface wettability of the membrane was tested by the water CA measurements. As shown in Figure 4, the pure PVDF membranes show superhydrophilicity with a water CA of  $0^\circ$  and superoleophilicity with an oil CA of  $0^\circ$ . All the modified membrane show superoleophilic properties with an oil CA of  $0^\circ$  and superhydrophobic properties with a water CA of greater than  $150^\circ$ . So it is considered that such modified membrane could be used for the effective separation of oil and water.

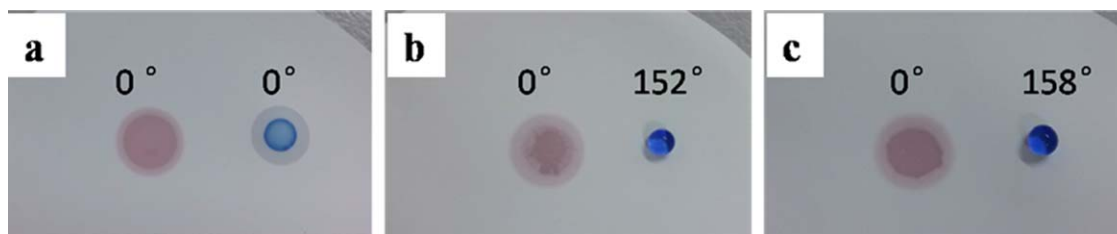
### Superhydrophobic and Its Durability Study

The superhydrophobicity and durability of membrane are still significant challenges to meet practical applications. Therefore, the membranes coated with  $\text{SiO}_2$ -TMS or  $\text{SiO}_2$ -TMS/PVDF mixture, which the PVDF was used as adhesive layer to test its effect on superhydrophobic and its durability study of the membrane. The superhydrophobic and its durability of film surface were tested by ultrasonic bath processing. Figure 5 shows time-dependent variations of static water CA of the membrane surface deposited with  $\text{SiO}_2$ -TMS and PVDF/ $\text{SiO}_2$ -TMS. The water CA of the membrane surface deposited with  $\text{SiO}_2$ -TMS [Figure 5(a)] decreases from  $166.2^\circ$  to  $82^\circ$  as the ultrasonic bath processing time increases from 0 to 60 min. However, the water CA of the membrane surface deposited with  $\text{SiO}_2$ -TMS/PVDF [Figure 5(b)] is little changed after ultrasonic bath processing. The results indicate that the PVDF used as the adhesive layer plays complementary roles on the design of superhydrophobic surfaces in air. So the membrane surface deposited with PVDF/ $\text{SiO}_2$ -TMS shows stable superhydrophobic and superoleophilic properties and can be used to separate water/oil emulsion.

Although the membrane can separate successfully oil/water mixtures, for practical applications, particularly, in corrosive liquids, including the acidic or basic solutions, the stable wettability membrane surface should be studied to test the stability of the membrane to expand the scope of application. So the stable wettability was studied through water CAs as shown in Figure 6 to provide the correlation between the CAs and the pH values. As shown in Figure 6, the membranes maintain ultrahigh hydrophobicity behavior of water for a range of pH. The wettability behavior of a surface is mainly governed by its chemical composition and roughness, which indicates that  $\text{SiO}_2$ -TMS nanoparticles bring about a greater roughness and possess its



**Figure 3.** SEM images of (a) untreated membrane, (b) membrane surface deposited with  $\text{SiO}_2$ -TMS solution, and (c) membrane surface deposited with PVDF/ $\text{SiO}_2$ -TMS solution.



**Figure 4.** The images of droplets of oil (dyed red) and water (dyed blue) on the (a) untreated membrane, (b) membrane surface deposited with  $\text{SiO}_2$ -TMS solution, and (c) membrane surface deposited with PVDF/ $\text{SiO}_2$ -TMS solution, respectively. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

excellent stability against extreme pH condition to meet practical applications.

### Absorption Capacity Measurement

PVDF composite material makes it a potential candidate for separating or absorbing insoluble from water. When there is a little oil in the water, the membrane with the superhydrophobic and superoleophilic properties can absorb immediately insoluble from water, and do not need a filtration system. As seen in Figure 7(a), when brought into contact with a layer of oil on water surface, the PVDF membrane can absorb the oils or organic solvents from water. Figure 7(b) shows uptake capacities for a collection of organic solvents and oils, such as chloroform, petroleum ether, soybean oil, coal oil, and gasoline. The oil-absorbing ability and high selectivity are assigned to the superoleophilic and superhydrophobic and porous structures features of the PVDF membrane.

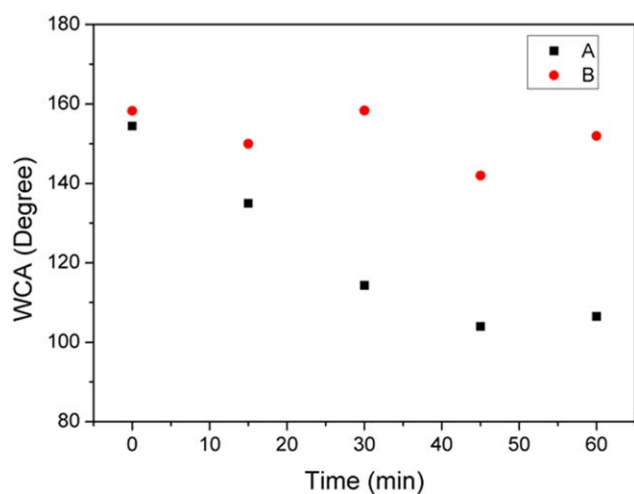
To test and evaluate the practical usage performance, the recyclability of absorbent for the removal of organics or oils from water in 10 cycles was performed as displayed in Figure 7(c). After each absorbent of the oil, the membrane was simply washed with ethanol to recover the oil-absorbing ability. It can be seen that the absorbing ability maintain little change gradu-

ally with increasing cycle times and no sharp decline is observed. It indicates an outstanding absorption capacity performance of the membrane, which is an important parameter for practical application.

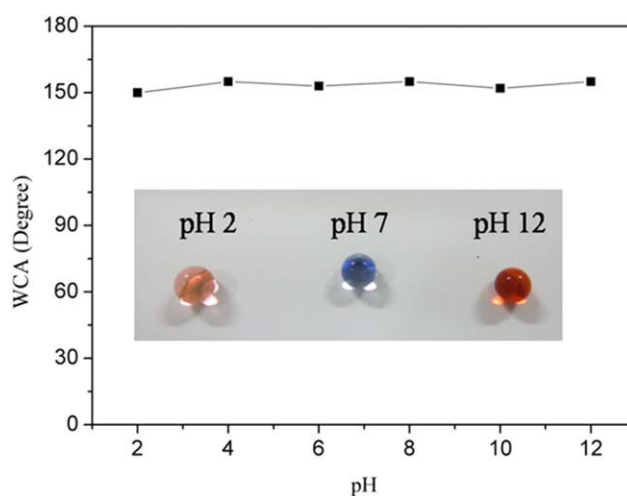
### Separation of Water-in-Oil Emulsions

A repeating separation experiment was comprehensively investigated on the membranes to test their separation capability and recyclability. As shown in Figure 8(a), the as-prepared emulsions were poured onto PVDF membrane. Within minutes, the oil passed through the membrane while the water was retained above the membrane because of the superhydrophobicity and low water-adhesion of the membranes. Moreover, the membranes exhibit a promising flux, which is significantly higher than that of commercial filtration membranes (usually with a flux of less than  $300 \text{ L m}^{-2} \text{ h}^{-1}$ ). After 10 cycles, the membrane still keeps a relative high flux. It indicates that the membrane can maintain its superhydrophobicity and is easily washed using ethanol to recover the flux, which is an important parameter for practical application.

Then optical microscopy [Figure 8(b)] was used to clearly see an effective separation. And there is a significant difference in phase composition between the feed and the corresponding filtrate, indicating the effectiveness of the PVDF membranes for separating various water-in-oil emulsions.

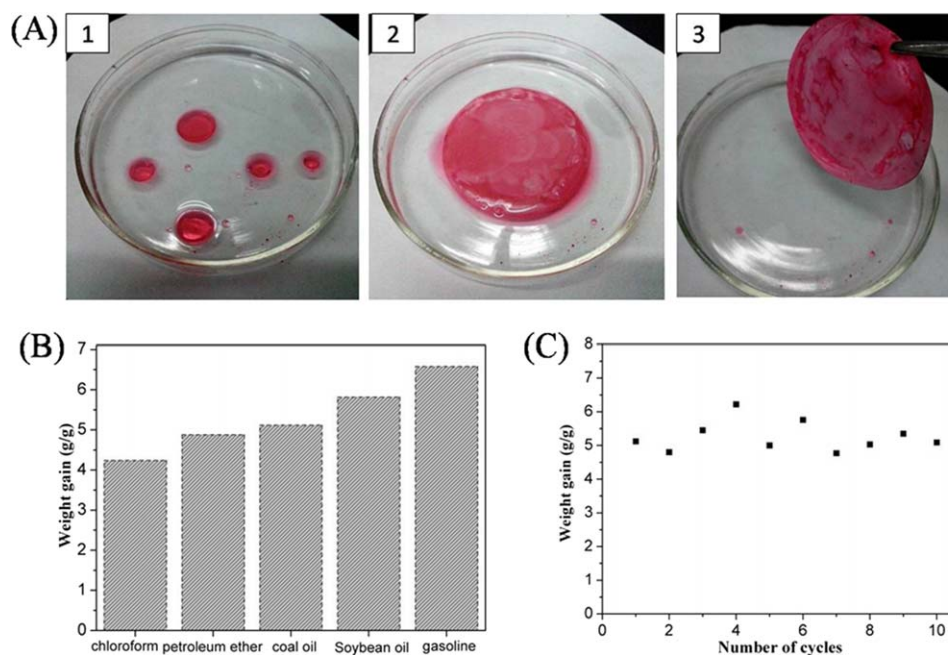


**Figure 5.** Variation of the water CA of the membrane with ultrasonic time: (a) membrane surface deposited with  $\text{SiO}_2$ -TMS solution and (b) membrane surface deposited with PVDF/ $\text{SiO}_2$ -TMS solution. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

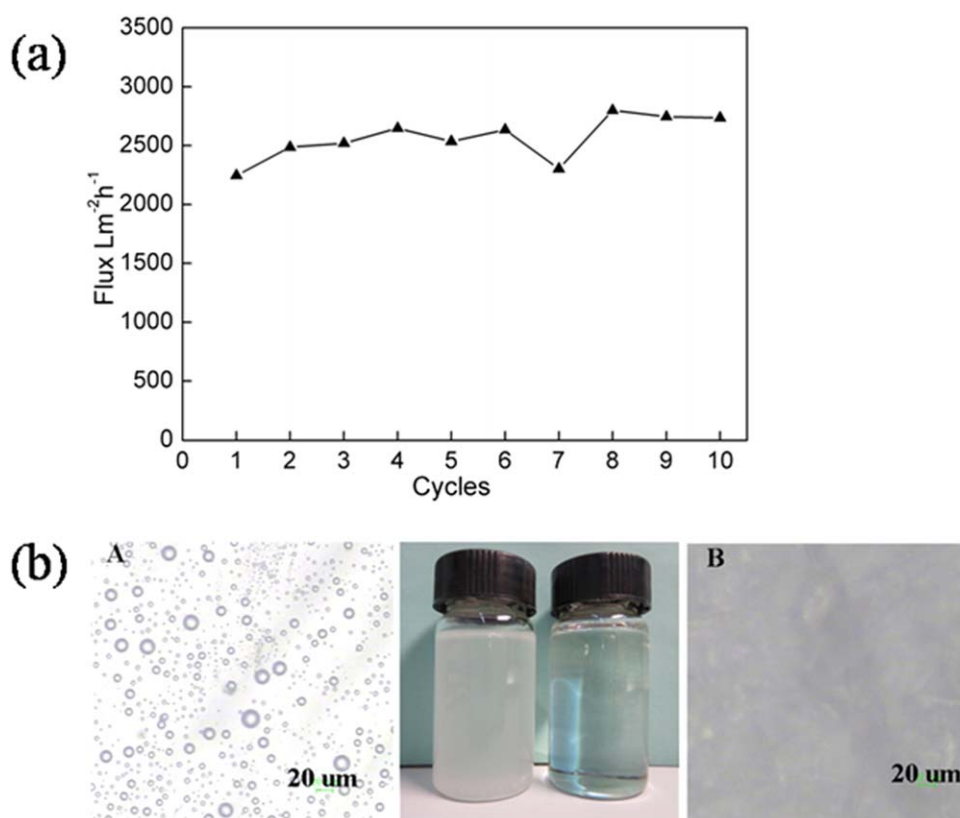


**Figure 6.** The water CA of membrane (deposited with PVDF/ $\text{SiO}_2$ -TMS solution) when exposed to aqueous solutions with different pHs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 7.** Oil absorption studies of superhydrophobic and superoleophilic PVDF films. (a) Snapshots showing the absorption of a colored (dye with Oil Red O) distributed on a water bath by a piece of PVDF oil absorption film. (b) The absorption capacity (weight gain) of PVDF membrane for different organic solvents and oils. (c) The recyclability test for absorbing coal oil showing stable performance of PVDF oil absorption films. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8.** (a) Change in the flux with increasing cycle number using membrane surface deposited with PVDF/  $\text{SiO}_2$ -TMS solution and (b) photographs and optical micrographs of the water-oil emulsion before and after separation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

## CONCLUSION

In summary, the superhydrophobic and superoleophilic PVDF membranes have been successfully achieved via a facile solution-immersion process. The resultant membranes exhibited self-cleaning and water/oil separation properties. The solution-immersion method was simple, time-saving, and inexpensive and therefore exhibited great potential application.

## ACKNOWLEDGMENTS

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