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# The poly(vinyl alcohol-co-ethylene) nanofiber/silica coated composite membranes for oil/water and oil-in-water emulsion separation

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ABSTRACT

In this study, the superhydrophilic and under water oleophobic nanofiber/$SiO_2$ (N/S) coated composite membranes with two kinds substrates of polyamide mesh (PM) and poly(vinyl alcohol-co-ethylene) nanofiber membrane (NM) were prepared for the oil/water mixture and oil-in-water emulsion separation. The addition of nanofibers could enhance the film forming ability of $SiO_2$ nanoparticles and the mechanical property of $SiO_2$ coatings. Besides, the preparing processes of nanofibers, N/S coatings and composite membranes possessed advantages of high throughput, lower cost, and environmental friendness. The morphology, structure, wettability of the composite membranes were characterized. The composite N/S-PM membranes were used to separate the oil/water mixtures by gravity, while the N/S-NM membranes were used to separate the oil/water emulsions by pressure driven. The separation efficiency, flux, and reusability were analyzed. The results demonstrate the good oil/water separation performance of N/S coated composites membranes, and the great potential application of which in the industrial oil/water separation.

## 1. Introduction

With the increasing damage of oily wastewater to health, environment and ecological balance, there are intense demands for the efficient oil/water separation technology [1,2]. The most common used methods for oil/water separation include adsorption, gravity or pressure-driven separation, coalescence and so on [3,4]. Among those methods, the gravity or pressure-driven separation based on superwetting membranes has become the most promising technology due to its high separation efficiency and relatively simple operational process, which can effectively separate the immiscible oil/water mixtures and oil/water emulsions [5,6].

To enhance the oil/water separation efficiency, many different superwetting membranes were prepared, such as the robust superhydrophobic-superoleophilic polytetrafluoroethylene (PTFE) nanofibrous membrane, modified $Mg(OH)_2$ powders coated stainless steel mesh, poly(vinylidene fluoride) (PVDF)/graphene composite membrane and so on [7–9]. Compared with the superhydrophobic/superoleophilic membranes, the superhydrophilic/superoleophobic membranes exhibite advantages of antifouling and reusable properties because they can effectively avoid or reduce external oily fouling by the formation of water barrier between the membranes and oil phase [10,11].

Moreover, as a base material, nanofiber membranes get more and more attention gradually due to their higher porosity, permeability, and versatility. In recent years, plenty of nanofibers and composite nanofiber membranes have been designed to separate the immiscible oil/water mixtures and oil/water emulsions [12,13]. However, nearly all the nanofiber membranes are prepared by the electrospinning technology, which is difficult to realize mass produce due to the limitation of low production and high cost. Besides, the high skill requirements, high cost, environment unfriendliness and secondary pollution caused by various modification process also limit the industrial application of functional nanofiber membranes.

In this study, the poly(vinyl alcohol-co-ethylene) (PVA-co-PE) nanofiber were prepared by an high throughput, environmental friendly method invented in our group [14,15]. Based on this method, the superhydrophilic and under water oleophobic nanofiber/$SiO_2$ (N/S) coated composite membranes with two kinds substrates of polyamide meshes (PM) and PVA-co-PE nanofiber membranes (NM) were prepared for the oil/water and oil-in-water emulsion separation. The morphology, structure, wettability, oil/water separation efficiency, flux,

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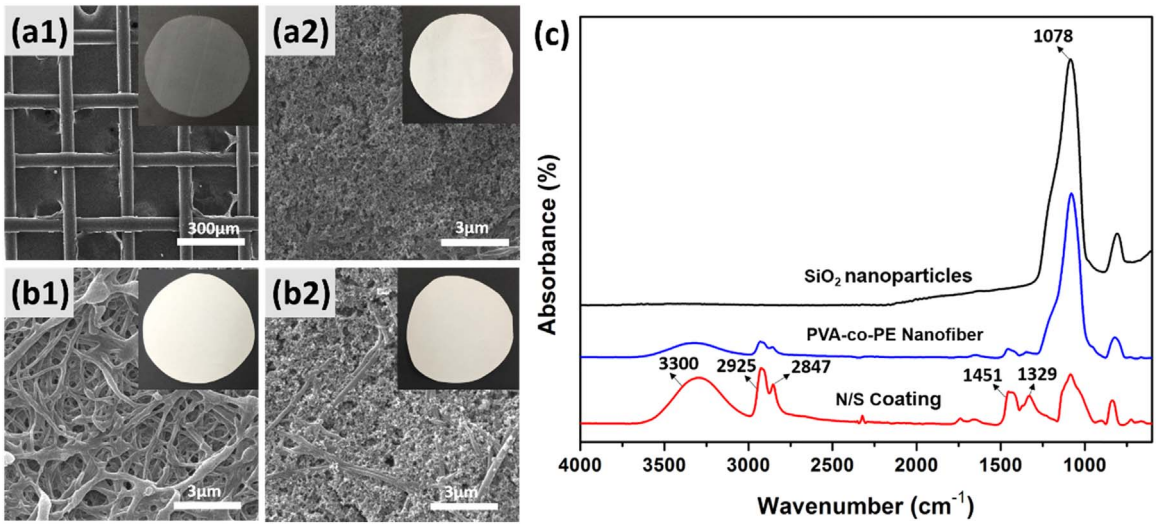


**Fig. 1.** SEM images and photographs of the (a1) PM, (a2) N/S-PM membrane, (b1) NM and (b2) N/S-NM membrane, (c) FTIR spectra of $SiO_2$ nanoparticles, NM and N/S coating.

and reusability were analyzed. The results demonstrate the good oil/water separation performance of N/S coated composites membranes, and the great potential application of which in the industrial oil/water separation.

## 2. Materials and Methods

### 2.1. Materials

Poly(vinyl alcohol-co-ethylene) (PVA-co-PE; 44% ethylene) was obtained from Sigma-Aldrich (Milwaukee, WI, USA). Cellulose acetate butyrate (CAB) was obtained from Eastman Chemical Company. The hydrophilic nano-fumed silica ($SiO_2$, 99.8%, 7–40 nm, the specific surface area is 150 $m^2/g$) was obtained from Aladdin Industrial Co., Ltd. Acetone, alcohol, polyethylene glycol 4000 (PEG 4000) were obtained from Sinopharm Chemical Reagent Co., Ltd. The polyamide (PA) mesh (mesh number 150) was obtained from Hangzhou Daheng Filter Cloth Co., Ltd.

### 2.2. Preparation of the PVA-co-PE nanofiber/$SiO_2$ coated composite membranes

The PVA-co-PE nanofibers and nanofiber membranes were prepared by our previously invented method [14,15]. The stable PVA-co-PE nanofiber/$SiO_2$ (N/S) suspension was obtained by dispersing 1.1 g PVA-co-PE nanofibers, 0.9 g $SiO_2$ and 0.4 g PEG in 200 ml water based solution with a high speed shear mixer. Two kinds of N/S coated composite membranes were prepared by spraying the N/S suspension onto the PA mesh (PM) and PVA-co-PE nanofiber membrane (NM), which were defined as N/S-PM and N/S-NM respectively.

### 2.3. Characterization

#### 2.3.1. Morphology and structure

The morphologies of PA mesh, PVA-co-PE nanofiber membrane and corresponding N/S-PM, N/S-NM were analyzed by the scanning electron microscopy (SEM, JEOL JSM-5510LV, Japan). The structures were tested by the FTIR-ATR (FTIR, Vertex70, Bruker). The wettability of the N/S coated composite membranes were evaluated by the contact angle goniometry (KRUSS DSA30S, KRUSS Co., Germany). The droplet size distribution of oil-in-water emulsion was analyzed by the laser particle size analyzer (Malvern Zetasizer Nano-ZS). The solutions before and after the separation were observed by the COIC Biological Microscope H6000i (Chongqing COIC Industrial CO., Ltd). The concentration of oil was measured using a total organic carbon analyzer (Element vario TOC select).

#### 2.3.2. Oil/water separation by gravity

A series of surfactant-free oil/water mixtures were prepared to perform the oil/water separation test by gravity. The oils were dyed in red color using Sudan III. The water was dyed in blue color using methylene blue. The dyed oils and water (v:v = 1:1) were mixed in a mixture to form the oil/water mixtures before testing. The N/S-PM membrane (effective area is 11.94 $cm^2$) was fixed between two glass containers. The separation efficiency (S) was calculated according to the Eq. (1) [16].

$$S = (m_1/m_0) * 100 \quad (1)$$

where $m_0$ and $m_1$ are the mass of oil before and after the separation process, respectively.

#### 2.3.3. Oil-in-water emulsion separation by pressure driven

The surfactant-stabilized and surfactant-free oil-in-water emulsions were prepared to perform the oil/water emulsion separation test. The surfactant-stabilized emulsions were obtained by mixing 1 g of non-ionic surfactant tween 80, 2.5 mL of oil and 497.5 mL of deionized water under intensively stirring for 3 h. While, the surfactant-free emulsions were prepared by directly mixing the oil and water together to avoid the effect of surfactant on the separation efficiency analysis. The separation efficiency (S) was calculated according to the Eq. (2).

$$S = (1 - C_p/C_0) * 100 \quad (2)$$

where $C_p$ and $C_0$ are the oil concentration of collected water and original oil-in-water emulsions, respectively.

## 3. Results and discussion

### 3.1. Morphology and structure

To modify the wettability, the PVA-co-PE nanofiber/$SiO_2$ (N/S, 50/50) suspension was prepared as the coating material. Then, the N/S suspension was sprayed onto the substrates of PA mesh (PM) and PVA-co-PE nanofiber membrane (NF) to prepare the N/S-PM and N/S-NM composite membranes. Fig. 1 shows the morphologies of substrates and composite membranes. As shown in Fig. 1(a1), the mesh number of PM is 150. The network structure of PM ensures the formation of N/S coating on it. The nanofibers and $SiO_2$ nanoparticles could be observed on the surface of N/S-PM membrane, as shown in Fig. 1(a2). Due to the