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Hierarchical Al_2O_3/SiO_2 fiber membrane with reversible wettability for on-demand oil/water separation

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Abstract−This work presents an effective method of fabricating hierarchical Al_2O_3/SiO_2 fiber membrane with reversible wettability for on-demand oil/water separation. In this strategy, the superhydrophilic/underwater superoleophobic surfaces are fabricated by in-situ growing hierarchical Al_2O_3 nanosheets on the SiO_2 fiber surfaces that can be used as water-removing materials for oil/water separation. Then, the superhydrophobic/oleophilic surfaces are obtained by surface chemical modification with sodium laurate, which can be used as oil-removing materials for oil/water separation. Interestingly, the reversible wettability transformation of Al_2O_3/SiO_2 fiber membrane can be controlled by the annealing and modification treatment alternately. The as-prepared Al_2O_3/SiO_2 fiber membrane, combining the advantages and overcoming disadvantages of two modes, achieves reversible wettability transitions and on-demand oil/water separation. In addition, the Al_2O_3/SiO_2 fiber membrane shows a significant chemical stability and super-wettability even after five annealing and surface modification cycles, indicating its excellent durability. The separation efficiency in both oil-removing mode and water-removing mode is over 95% for various oil/water mixtures through multiple recycle separation processes. This work not only provides a simple and cost-effective method to fabricate separation membrane with reversible wettability, but also shows great potential in remediation of large-scale oil spillage or organic solvents discharge at different environmental conditions.

Keywords: Al_2O_3 Nanosheets Coating, Fiber Membrane, Reversible Wettability, Oil/Water Separation, Recyclability

INTRODUCTION

With the advance of industrialization, oil pollution arising from oil spillage and organic chemical leakage has led to severe environmental and ecological problems, since oily wastewater may threaten human health, the natural environment and the safety of transportation [1,2]. Thus, the removal of oil from oily wastewater is quite desirous for environmental protection and oil transportation safety [3]. Due to diverse oil/water mixtures and different separation process, from the point of view of preparation process, separation efficiency, operational complexity, cost-effective and the needs of industrialization, it is of great economic and social significance to seek an oil separation technology with simple operational process and high performance [4]. To date, several conventional techniques have been reported for free oil/water mixtures separation, such as gravity, centrifugation, adsorption, flotation, and chemical methods [5,6]. However, compared with these conventional separation methods, membrane separation technology has the advantages of high single stage separation efficiency and flexible and simple process without phase change [7]. Previous works demonstrated that the separation efficiency of membranes was determined by surface wetting properties in separating oily wastewater, since wetting processes play a critical role in the transport of solute molecules in and out of membranes [8]. Therefore, it is necessary to choose an appropriate membrane material based on special surface wettability for oil/water mixture separation and solving practical pollution problems.

Usually, oil-water separation membrane can be divided into two categories of oil-removing mode and water-removing mode according to different superwetting surface. In this regard, oil-removing mode membranes with hydrophobic/oleophilic properties have been developed for oily wastewater separation because they selectively absorb oil or organic solvents while repelling water [9]. However, oil-removing membranes are easily fouled or even the membrane apertures are blocked up by oils with high viscosity, which seriously affects the separation efficiency. Thus, it is important to develop novel membrane materials for oil-water separation with antifouling properties, high separation capacity and easy recyclability. In this context, water-removing mode membranes with hydrophilic/oleophobic properties have also attracted considerable attention within the scientific community and potential applications in the area of oil/water separation due to their high separation efficiency and resistance to oil fouling [10], such as TiO_2-coated mesh [11], zeolite-coated mesh membranes [12] and mineral-coated polymer membranes [13]. Nevertheless, membranes of water-removing mode are not able to be applied in the separation of heavy oil and water-in-oil emulsions. Therefore, the design and fabrication of functional membranes with double characters of water-removing mode and oil-removing mode are necessary in the terms of

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practical applications, such as the various types of oil/water mixtures and the complexity of the operational process. The functional membrane, respectively, combines the advantages and overcomes disadvantages of both modes, achieving on-demand oil/water separation based on surface special wettability transition.

Generally, the types of membranes with double super-wettability consist of Janus membranes [14], stimuli-responsive membranes [15] and reversible wettability membranes according to inherent nature of the material (such as superamphiphilic TiO_2 coated mesh [16]) or chemical treatments alternately [17]. Gu et al. [18] reported polymer/carbon nanotube asymmetric hybrid Janus membranes for oil/water separation by grafting hydrophobic poly(styrene) (PS) and hydrophilic poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA), respectively, on different sides of CNT membranes. However, the permeation flux of the Janus membranes is comparatively lower than conventional monohedral membranes with superhydrophilicity or superhydrophobicity solely due to the increased transmembrane resistance [19]. As for stimuli-responsive membranes, integrating surface chemistry and polymer science, membrane surfaces wettability for both oil and water are switchable due to surrounding stimulation such as pH [20], light [21], temperature [22], humidity [23] and electricity [24], which is possible to realize on the basis of stimuli-responsive polymer systems [25]. Polymers and organic macromolecular play an important role in fabrication and application of stimuli-responsive membranes as well Janus membranes. Nevertheless, high cost, poor corrosion resistance and underdeveloped preparation process limit their industrial transition. Fiber membranes are an ideal substrate membrane material due to mechanical strength, tensile properties and corrosion resistance, such as SiO_2 fiber membrane [26] and carbon fiber membrane [27,28]. Therefore, a reversible wettability membrane based on fiber materials is necessary to fabricate and use for on demand oil/water separation, which has great potential in fundamental research and practical applications.

Herein, we present a facile and efficient approach to fabricate hierarchical nanosheets Al_2O_3/SiO_2 fiber membrane with reversible wettability for on-demand oil/water separation. First, hierarchical nanosheet Al_2O_3/SiO_2 fiber membrane with superhydrophilicity/underwater superoleophobicity was fabricated by in-situ growing nanosheets on the SiO_2 fiber surfaces, which can be used as water-removing mode for oil/water separation. Then, superhydrophobic surfaces of hierarchical Al_2O_3/SiO_2 fiber membrane were obtained by chemical modification with sodium laurate, which is more low-cost and environmentally friendly than macromolecular modifier such as fluorosilane. The modified Al_2O_3/SiO_2 fiber membrane can be used as oil-removing mode for oil/water separation. Besides, the prepared Al_2O_3/SiO_2 fiber membrane can achieve reversible wettability transition between superhydrophilicity and superhydrophobicity via annealing and modification treatment alternately, which can resolve the problem of membrane pollution and improve flux and separation efficiency. Therefore, this work provides an effective method to fabricate separation membrane with reversible wettability that can be applied to on-demand oil/water separation.

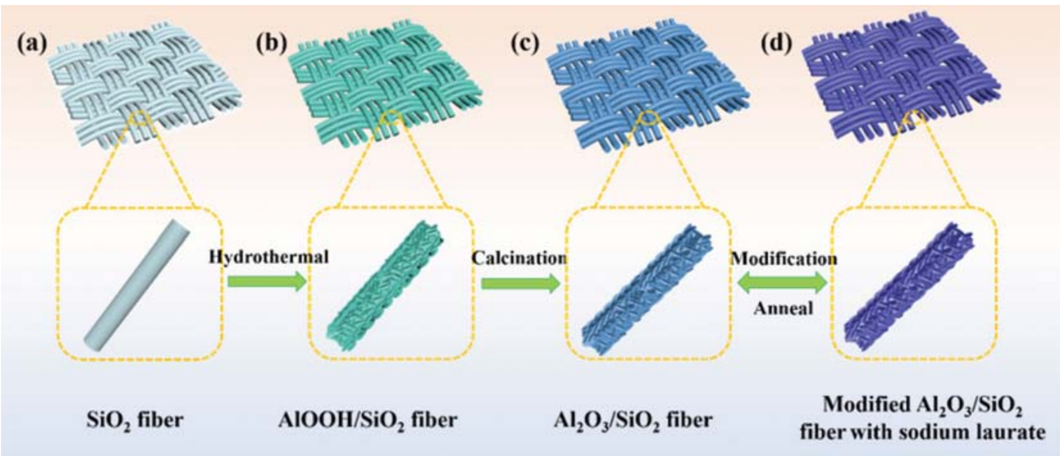
EXPERIMENTAL SECTION

1. Materials

SiO_2 fiber membranes were purchased from Toray Industries Co., Ltd. (Shanghai, China). After being washed several times with deionized water, they were immersed in a bath of sodium hydroxide aqueous solution (about 2 M) at 50 °C for 5 h, and then washed with deionized water to obtain pretreated SiO_2 fiber membrane. Other chemical reagents were of analytical grade and used as received without further purification. Sodium hydroxide (NaOH), sodium aluminate ($NaAlO_2$), urea (NH_2CONH_2) and sodium laurate ($C_{12}H_{23}NaO_2$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the chemical reagents used in this work were commercially available and deionized water was used in all experiments.

2. Preparation of Hierarchical Al_2O_3/SiO_2 Fiber Membrane

The $AlOOH/SiO_2$ fiber membrane was prepared by hydrothermal growth of AlOOH nanosheets on the surfaces of SiO_2 fiber. In a typical procedure, 1 mmol of sodium aluminate and 4 mmol of urea were dissolved in 60 mL of deionized water, a homogeneous solution. Then, the pretreated SiO_2 fiber membrane (2 cm×2 cm) was immersed in the above mixed solution and transferred into a



Scheme 1. The schematic diagram of fabrication process of hierarchical Al_2O_3/SiO_2 fiber membrane with reversible wettability.

stainless-steel autoclave, and the autoclave was placed in a drying oven and heated at 160 °C for 12 h. After cooling to room temperature, the resulting fiber membrane was taken out and washed by deionized water several times and dried in a vacuum oven at 60 °C for 12 h to obtain precursor $AlOOH/SiO_2$ fiber membrane.

The hierarchical Al_2O_3/SiO_2 fiber membrane was obtained by thermal annealing of the precursor $AlOOH/SiO_2$ fiber membrane. In detail, the above precursor $AlOOH/SiO_2$ fiber membrane was placed in a tube furnace and calcimined at 600 °C for 4 h in air to obtain the hierarchical Al_2O_3/SiO_2 fiber membrane. The fabrication process of Al_2O_3/SiO_2 fiber membrane is shown in Scheme 1.

3. Reversible Wettability

The reversible wettability treatment process of the hierarchical Al_2O_3/SiO_2 fiber membrane is described as follows: First, the as-obtained hierarchical Al_2O_3/SiO_2 fiber membrane was immersed in 0.05 M aqueous solution of sodium laurate and heated at 50 °C for 7 h, and then rinsed with ethanol and dried in a vacuum oven at 50 °C for 12 h to achieve superhydrophobicity. Secondly, the superhydrophobic Al_2O_3/SiO_2 fiber membrane was annealed at 300 °C for 2 h to disintegrate the grafted sodium laurate and then converted into superhydrophilic surfaces again. Moreover, to achieve reversible wettability of membrane surface, the surface modification and annealing treatments can be conducted for several times alternately and the wettability transition process is shown in Scheme 1.

4. Characterization

The micromorphology of the as-prepared hierarchical Al_2O_3/SiO_2 fiber membrane was accomplished with a scanning electron microscope (SEM, S-4800, Hitachi, Tokyo, Japan). The crystal structures and phase compositions were characterized by X-ray diffraction (XRD, mode HZG41 B-PC) in the 2θ range from 7° to 90° with a scanning rate of 4° min^{-1}. Fourier-transform infrared (FT-IR) spectra were measured in the range of 400-4,000 cm^{-1} using an FT-IR spectrophotometer (Thermo Nicolet, NEXUS, TM) to identify the surface functional groups. Water contact angles in air and underwater oil contact angles measurements were gauged by a contact angle goniometer (KSV CAM 101) at ambient temperature. The volume of the individual water and oil droplets was 5 μL, and the contact angle values were the average of four measurements at different positions on each sample surface in all measurements.

5. Separation Performance

The oil/water separation efficiency of hierarchical Al_2O_3/SiO_2 fiber membrane with reversible wettability was measured by filtration device with available area of 4 cm^2. In separation experiments, oil and organic reagent were dyed by Sudan III and the volume ratio of oil/water mixtures is 1 : 1. Besides, the separation process was achieved by only the force of gravity. For water-removing mode, the hierarchical Al_2O_3/SiO_2 fiber membrane was tested to separate different kinds of light-oil/water mixtures (toluene/water, cyclohexane/water, and gasoline/water). The membrane needed to be completely prewetted by water before installing it into the filtration device, and the light-oil/water mixtures were poured onto the membrane slowly achieving separation process. For oil-removing mode, the modified hierarchical Al_2O_3/SiO_2 fiber membrane was tested to separate different kinds of heavy-oil/water mixtures (chlorobenzene/water, chloroform/water and tetrachloromethane/water). The membrane was installed into the filtration device, which needs not be prewetted, and then the heavy-oil/water mixtures were poured onto the membrane slowly achieving separation process. The masses of initial oil and remaining oil were measured by electronic balance. In all measurements, each separation process of oil/water mixtures was repeated three times and the results were averaged. The oil/water mixture separation efficiency of the as-prepared membranes was calculated as follows:

$$\eta\% = \frac{M_t}{M_i} \times 100 \tag{1}$$

where M_i and M_t are the mass of the initial oil before separation and the remaining oil after separation, respectively.

6. Recycling Test

The toluene/water mixture and the chloroform/water mixture were, respectively, used to test separation efficiency based on water-removing mode and oil-removing mode membrane. The process of recycling test was as follows: after each separation process, the membrane was removed from the filtration device and rinsed with alcohol to remove the absorbed solvent, and then dried in vacuum oven at 60 °C for 6 h to achieve cleaned membrane again that could be used for next separation operation. This separation process was repeated 20 times. After each cycle, the separation efficiency was measured.

RESULTS AND DISCUSSION

1. Morphology Characterization

Super-wettability greatly depends on surface morphology structure and chemical composition. The surface morphology of the original SiO_2 fiber substrate membrane and the Al_2O_3/SiO_2 fiber mem-

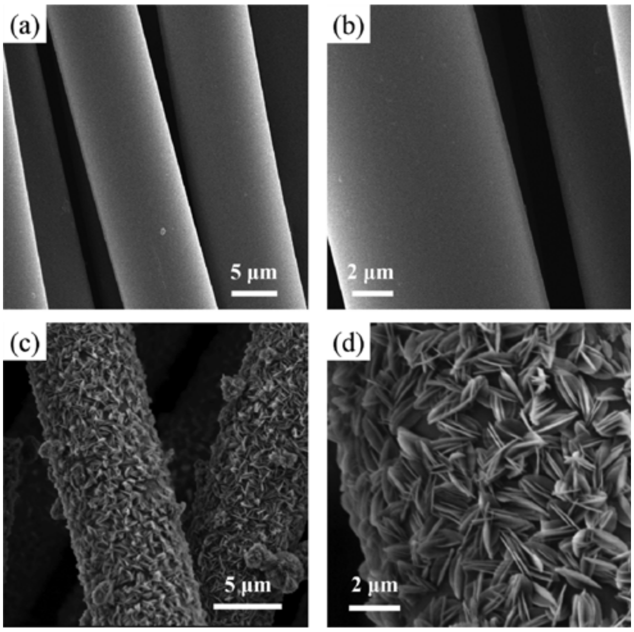


Fig. 1. Low- (a) and high- (b) magnification SEM images of SiO_2 fibers. Low- (c) and high- (d) magnification SEM images of and as-obtained Al_2O_3/SiO_2 fibers.

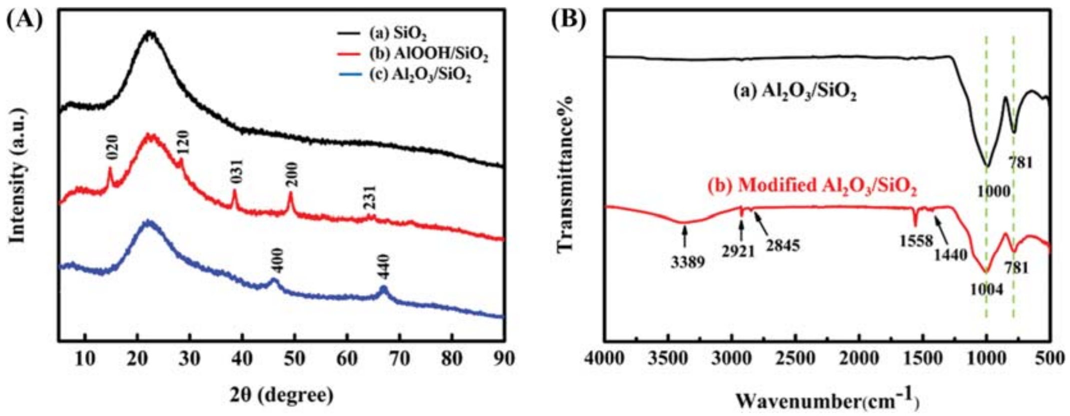


Fig. 2. (A) XRD patterns of (a) SiO_2 fiber membrane, (b) hierarchical AlOOH/SiO_2 fiber membrane and (c) hierarchical Al_2O_3/SiO_2 fiber membrane. (B) FT-IR spectra of hierarchical Al_2O_3/SiO_2 fiber membrane((a) unmodified, (b) modified with sodium laurate).

brane is displayed in Fig. 1. As shown in Fig. 1(a) and (b), the original SiO_2 fibers show uniform cylindrical morphology with about 10 μm diameters and have a smooth surface, which could provide enough surface to use for fabricating hierarchical Al_2O_3 nanosheets coating. The surface morphology of obtained Al_2O_3/SiO_2 fiber membrane is shown in Fig. 1(c)-(d). In Fig. 1(c) the original fiber has been completely covered by densely distributed Al_2O_3 nanosheets at micro/nanoscale. The magnified view of Fig. 1(d) reveals Al_2O_3 nanosheets with about several hundred nanometers length and stacked up with each other to form sunflower seed-like hierarchical structure. This hierarchical rough micro/nanostructure is immense necessity for the super-wettability of Al_2O_3/SiO_2 fiber membrane because it can provide the structural foundation for both superhydrophobicity and superhydrophilicity. The Al_2O_3/SiO_2 fiber membrane was obtained from calcining the precursor AlOOH/SiO_2 fiber membrane. As shown in Fig. S1(a), the micro/nanostructure of the precursor AlOOH/SiO_2 fiber membrane is slightly different from Al_2O_3/SiO_2 fiber membrane, such as AlOOH nanosheets vertically coat on SiO_2 fiber surface without assembling each other, and the size of AlOOH nanosheets is a little larger than Al_2O_3 nanosheets. The micro/nanoscale rough structure and inherent hydrophilicity of Al_2O_3 nanosheets play an important role in the superhydrophilicity in air and underwater superoleophobicity of Al_2O_3/SiO_2 fiber membrane for water-removing mode separation.

To obtain a surface with superhydrophobicity, generally, surface chemical modification is a common method by grafting low surface energy molecules on material surface. SEM image of modified Al_2O_3/SiO_2 fiber membrane with sodium laurate is shown Fig. S1(b). It indicates the presence of the sheet-like agminated protrusions on the surface of Al_2O_3 nanosheets, which could be regarded as grafted sodium laurate so that the fiber membrane possessed superhydrophobicity by increasing the roughness and decreasing surface energy of the Al_2O_3/SiO_2 fiber membrane surface. As shown in Fig. S1(c), the sheet-like agminated protrusions disappeared after annealing treatment of modified Al_2O_3/SiO_2 fiber membrane. However, as shown in Fig. S1(d), the smaller sheet-like agminated protrusions appeared again after re-modification with sodium laurate of annealed modified Al_2O_3/SiO_2 fiber membrane, and the surface micro-nanostructure of Al_2O_3 nanosheets coating had no obvious change or damage. These results indicate that the surface structures of Al_2O_3/SiO_2 fiber membrane have no change after annealing and modification treatments alternately, and the sheet-like protrusions more likely could be grafted sodium laurate; nevertheless, this possibility needs to be proved further.

X-ray diffraction (XRD) analysis was used to identify the components and crystallography of our samples. The XRD pattern of SiO_2 fiber membrane is shown in Fig. 2(A)(a), in which a relatively broad diffraction peak at around 22° is the diffraction peak of amorphous SiO_2. As shown in Fig. 2(A)(b), five typical peaks at 2θ=14.8°, 28.3°, 38.5°, 49.3°, and 64.5° can represent the (020), (120), (031), (200), and (231) reflections of γ-AlOOH (orthorhombic Boehmite) according to JCPDS card no. 83-2384, respectively, while a broad peak at around 22° which was obtained in all curves is the characteristic diffraction peak of amorphous SiO_2 fiber substrate membrane. It is further demonstrated that hierarchical AlOOH/SiO_2 fiber membrane was fabricated successfully. Fig. 2(A)(c) reports the XRD pattern of hierarchical Al_2O_3/SiO_2 fiber membrane that was obtained by calcining AlOOH/SiO_2 fiber membrane. The diffraction peaks at 2θ=46.1° and 67.1°, which are attributed to (400) and (440) crystalline phases of γ-Al_2O_3. The phase transition from γ-AlOOH to γ-Al_2O_3 is confirmed after being calcined at 600 °C for 4 h. Fig. S2(a) shows the XRD pattern of modified hierarchical Al_2O_3/SiO_2 fiber membrane, which could indicate the crystal planes of γ-Al_2O_3 have no obvious transformation, except an additional diffraction peak is indicated with asterisk which could be regarded as an unknown impurity cause. The XRD pattern of annealed modified hierarchical Al_2O_3/SiO_2 fiber membrane is reported in Fig. S2(b), which is very close to the pattern of Al_2O_3/SiO_2 fiber membrane in Fig. 2(A)(c). It could suggest that the lower temperature of annealing treatment (300 °C) is hard to affect the crystal structure of Al_2O_3 nanosheets.

Whether the surface modification of hierarchical Al_2O_3/SiO_2 fiber membrane with sodium laurate is successful could be further verified by FT-IR spectra. Fig. 2(B)(a)-(b) show the characteristic FT-IR spectra of hierarchical Al_2O_3/SiO_2 fiber membrane and surface modified Al_2O_3/SiO_2 fiber membrane, respectively. It is found that the strong characteristic absorption peaks nearby at 780 cm^{-1} and 1,000 cm^{-1} in the two curves of (a) and (b) could be

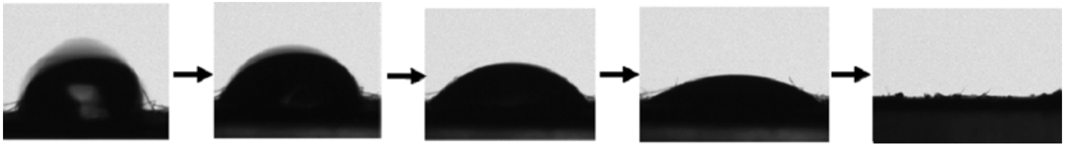


Fig. 3. A series of continuous snapshots of water droplet penetrated the hierarchical Al_2O_3/SiO_2 fiber membrane.

assigned to bending vibrations peak and asymmetrical stretching vibration peak of Si-O-Si bond; nevertheless, the characteristic absorption peaks of the Al-O bond are not found probably because the content of Al_2O_3 coating is so less compared to SiO_2 substrate membrane that the absorption peaks of the Al-O bond could be undetected by infrared spectrometer or covered up the absorption peak of Si-O-Si bond in the wave number range of 400-1,000 cm^{-1}. Besides, by comparing the curve of (a) with the curve of (b), the spectra of modified hierarchical Al_2O_3/SiO_2 fiber membrane have obvious changes in the wave number range of 1,000-4,000 cm^{-1}, while the spectra of hierarchical Al_2O_3/SiO_2 fiber do not show significant absorption peaks. In Fig. 2(B)(b), some new characteristic absorption peaks of the modified hierarchical Al_2O_3/SiO_2 fiber membrane with sodium laurate appear nearby at 1,440 cm^{-1}, 1,558 cm^{-1}, 2,845 cm^{-1}, 2,921 cm^{-1} and 3,389 cm^{-1}. The wide absorption band of 3,389 cm^{-1} could be attributed to O-H bond, which may be due to the sample adsorbing water. The sharp absorption peak at 1,558 cm^{-1} could be deemed to be the characteristic absorption peak of $-COO^-$ bond. The characteristic absorption peaks at 1,440 cm^{-1}, 2,845 cm^{-1} and 2,921 cm^{-1} correspond to deformation vibration peak, symmetrical stretching vibration peak and asymmetrical stretching vibration peak of C-H in methylene, respectively. The characteristic absorption peaks in the wave number range of 1,000-4,000 cm^{-1} of the Al_2O_3/SiO_2 fiber membrane correspond to the absorption peaks of pure sodium laurate powder shown in Fig. S3(A). These results demonstrate the successful modification of Al_2O_3/SiO_2 fiber membrane with sodium laurate. In addition, the success of reversible wettability transition between Al_2O_3/SiO_2 and modified Al_2O_3/SiO_2 fiber membranes could be proved by FI-TR spectra in Fig. S3(B) further.

2. Surface Wettability

Wettability of hierarchical Al_2O_3/SiO_2 fiber membrane to liquids is one of the most important considerations since wetting properties determine the transport processes of liquid in and out of membranes. According to a series of verification methods above, hierarchical Al_2O_3/SiO_2 fiber membrane with reversible wettability was successfully fabricated by combined hydrothermal method, calcination and modification treatments. Fig. 3 shows that the water droplet spread and penetrated rapidly the hierarchical Al_2O_3/SiO_2 fiber membrane in 0.6 s via capillary force, and the WCA was nearly 0°. These indicate that the hierarchical Al_2O_3/SiO_2 fiber membrane is extremely superhydrophilic. In addition, as shown in Fig. 4(a), red oil droplet dyed with Sudan III presented a spherical shape on hierarchical Al_2O_3/SiO_2 fiber membrane placed in water. The water contact angle (WCA) in air and the underwater oil contact angle (OCA) were measured for nearly 0° (shown in Fig. 4(b)) and 155.1° (shown in Fig. 4(c)), respectively. Thus, the hierarchical Al_2O_3 nanosheets coating possesses characteristics of superhydrophilicity and underwater superoleophobicity, which provide a theoretical basis for the hierarchical Al_2O_3/SiO_2 fiber membrane used for light-oil/water separation (water-removing mode). Fig. 4(d) shows that water droplets exhibit spherical shape upon the modified hierarchical Al_2O_3/SiO_2 fiber membrane without penetration. Furthermore, the OCA and WCA in air were measured to be 0° (shown in Fig. 4(e)) and 158.6° (shown in Fig. 4(f)), respectively. These results reveal that the surface modified Al_2O_3/SiO_2 fiber membrane had excellent superhydrophobic property, which also provides a theoretical basis for heavy-oil/water separation (oil-removing mode).

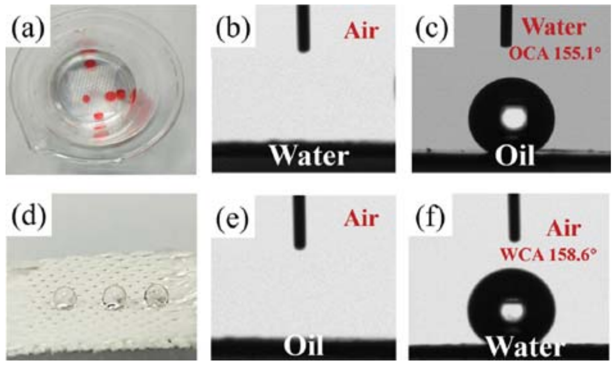


Fig. 4. Special wettability of obtained samples. Photograph of underwater superoleophobicity (a), WCA in air (b) and OCA in water (c) of hierarchical Al_2O_3/SiO_2 fiber membrane. Photograph of superhydrophobicity (d), OCA in air (e) and WCA in air (f) of modified hierarchical Al_2O_3/SiO_2 fiber membrane.

3. The Reversible Transition of Surface Wettability

The WCAs were tested to demonstrate the wettability transfor-

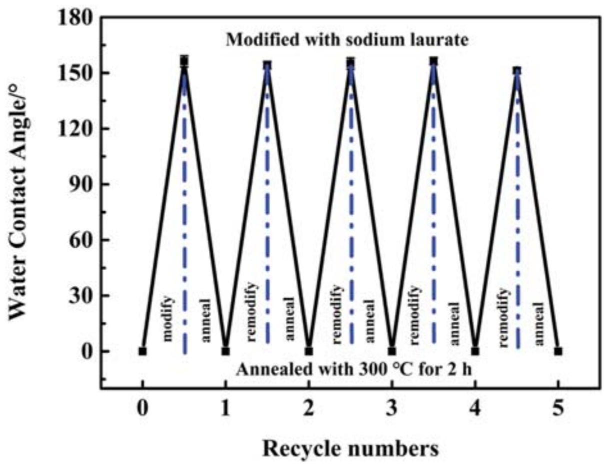


Fig. 5. WCA variation with recycle numbers of modification and annealing treatments.

mations between superhydrophilicity/underwater superoleophobicity and superhydrophobicity by annealing and modification (or re-modification) treatments, respectively. Fig. 5 shows the WCA variation with recycle numbers of modification and annealing treatments. As mentioned, the SEM and XRD analyses indicated that there was no obvious change in the surface structure of Al_2O_3 nanosheets coating that could influence the wetting behavior. As shown in Fig. 5, the values of WCA of modified Al_2O_3/SiO_2 fiber membrane are above 150° and show a slight decrease after several modification treatments, so the superhydrophobicity of the surface has no apparent change. In addition, WCAs of Al_2O_3/SiO_2 fiber membrane after several annealing treatments were nearly 0° and had no obvious change, implying the excellent reversible wettability of material surface.

4. The Durability Measurement

Chemical stability of membrane materials is a very important indicator and consideration in practical applications with harsh environmental circumstance. Herein, a set of measurement experiments of underwater OCA and WCA in air of modified Al_2O_3/SiO_2 fiber membrane in different environment were done to test the durability of samples. Fig. 6(a) shows that the underwater OCAs of the Al_2O_3/SiO_2 fiber membranes are larger than 150° and the variation of values is not apparent, when the membranes are placed in a broad pH range of water solutions to measure the underwater wettability. And all WCAs in air are 0° and have no change when water droplets with different pH are dropped onto the membrane surface. These results indicate that the Al_2O_3 nanosheets coating possesses acid and alkali stability. As shown in Fig. 6(b), the WCA and OCA of modified Al_2O_3/SiO_2 fiber membrane was measured by water droplets and oil droplets with different pH dropping into the membrane surface, respectively. The majority of WCAs exceed 150° and the values reach the maximum at pH 8, and the OCAs in air are all 0°. The results demonstrate that the modified Al_2O_3/SiO_2 fiber membrane is still an excellent high-hydrophobic property, and sodium laurate modifier has certain acid and alkali resistance.

To further verify the durability of the prepared Al_2O_3/SiO_2 fiber membranes, the contact angles of Al_2O_3/SiO_2 fiber membrane were tested by storing at ambient temperature and using 1 M NaCl solution. As shown in Fig. S4(a) and (b), the contact angles of Al_2O_3/SiO_2 and modified Al_2O_3/SiO_2 fiber membranes placed in indoors are all more than 150° and have no obvious change with storage time increasing, which suggests the Al_2O_3/SiO_2 fiber membrane and modified Al_2O_3/SiO_2 fiber membrane are resistant to moisture, oxygen and carbon dioxide gas. Besides, the Al_2O_3/SiO_2 fiber membrane was immersed into 1 M NaCl solution and tested underwater oil contact angles in different corrosion time, while the WCA of modified Al_2O_3/SiO_2 fiber membrane was measured by droplets of NaCl solution dropping into the membrane surface. As shown in Fig. S4(c) and (d), the contact angles of Al_2O_3/SiO_2 and modified Al_2O_3/SiO_2 fiber membranes are still as high as 150° although decreasing slightly with the extension of corrosion time; nevertheless, the overall changes are not obvious. These indicate the obtained fiber membranes have admirable anticorrosive ability.

In summary, all the results show that Al_2O_3/SiO_2 fiber membrane and modified Al_2O_3/SiO_2 fiber membrane possess certain chemical stability and durability in hard environment conditions such as temperature, humidity, acid, alkali and salt, which presents a great potential in practical applications of industry.

5. The Oil/Water Separation Performance

The obtained Al_2O_3/SiO_2 fiber membrane exhibits excellent surface super-wettability and achieves reversible wettability transitions between superhydrophilicity/underwater superoleophobicity and superhydrophobicity by annealing and modification treatments, which make it extremely promising for efficient separation for various oil/water mixtures. A series of certification studies were done to verify the separation efficiency for various oil/water mixtures achieving on-demand separation. As shown in Fig. 7(a) and (b), the Al_2O_3/SiO_2 fiber membrane with superhydrophilicity/underwater superoleophobicity and the modified Al_2O_3/SiO_2 fiber membrane with superhydrophobicity were fixed in the filter device to achieve separation process and used for water-removing mode and oil-removing mode, respectively. For water-removing mode separation, the calculated flux of water pre-wetting Al_2O_3/SiO_2 fiber membrane was about 7.2 mL/s, when it was used for separating toluene/water mixtures as the model of light-oil/water mixtures (Video S1). For oil-removing mode separation, by contrast, separation procedures were similar to that of water-removing mode, except that pre-wetting treatment was not required and the type of oil belongs to heavy oil such as chloroform as the model, the cal-

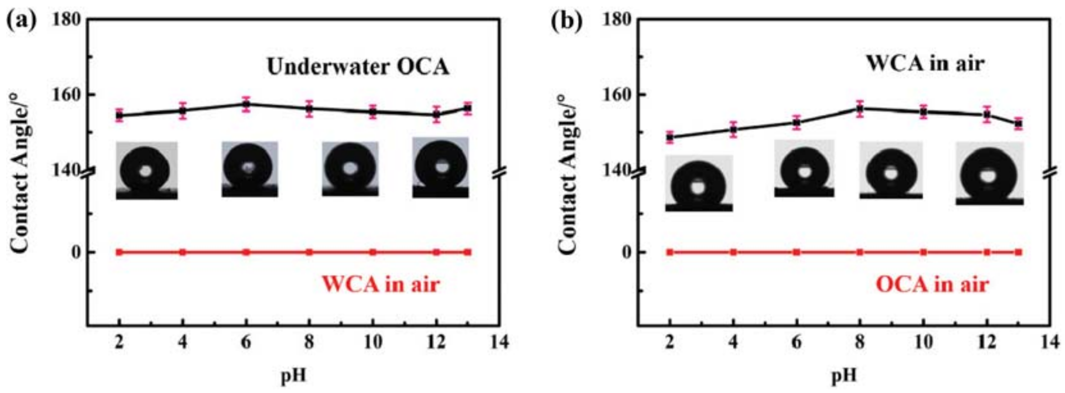


Fig. 6. Variation of underwater OCA of Al_2O_3/SiO_2 fiber membrane (a) and WCA in air of modified Al_2O_3/SiO_2 fiber membrane (b) in different measurement conditions of pH value.

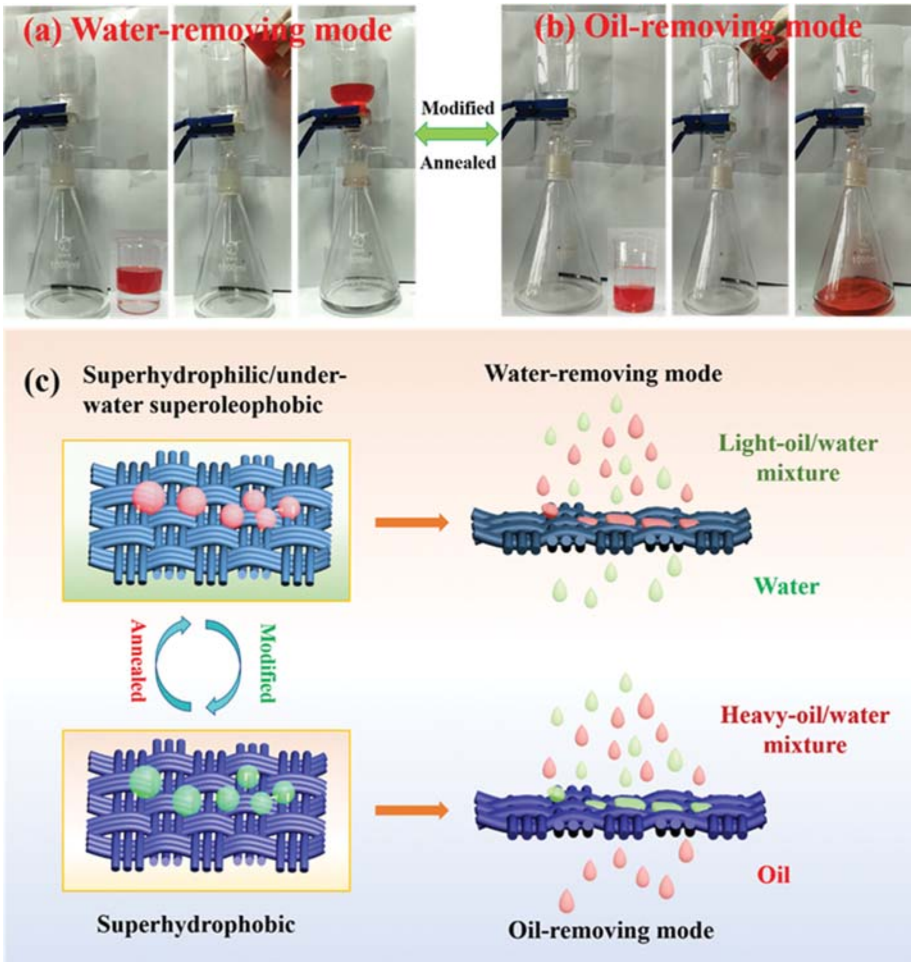


Fig. 7. Reversible oil/water separation process. (a) Snapshot of water-removing mode separation (Toluene was dyed with Sudan III). (b) Snapshot of oil-removing mode separation (Chloroform was dyed with Sudan III). (c) Schematic diagram of water-removing and oil-removing modes in different oil-water separations.

culated flux of modified Al_2O_3/SiO_2 fiber membrane was about 4.1 mL/s (Video S2). The two separation modes could be transformed into each other by being annealed and modified treatments alternately. Moreover, the schematic diagram of both water-removing mode and oil-removing mode shows vividly the separation process and the conversion process of the prepared membranes with super-wettability (Fig. 7(c)).

Various light-oil and heavy-oil (toluene, cyclohexane, gasoline,

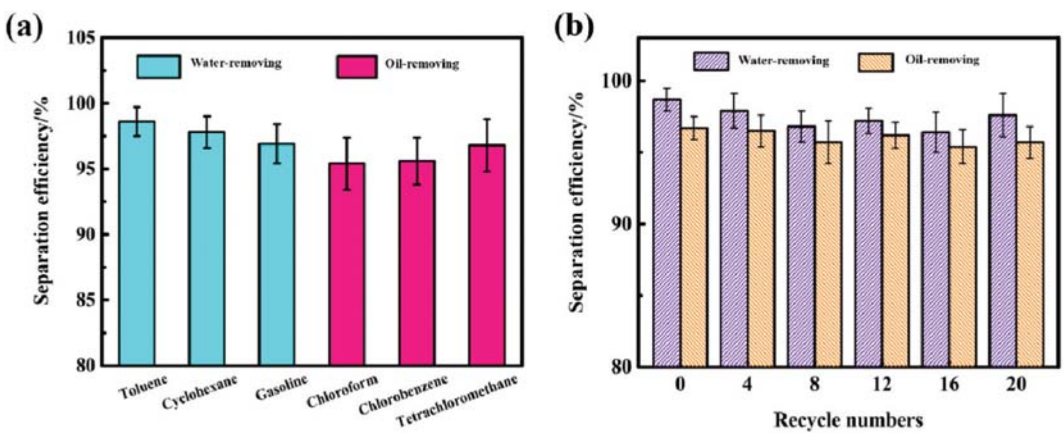


Fig. 8. (a) Separation efficiency of Al_2O_3/SiO_2 fiber membrane with both water-removing model and oil-removing model for various oil/water mixtures. (b) Separation efficiency in two models versus the recycle numbers of separation operation.

chlorobenzene, chloroform and tetrachloromethane)/water mixtures (50% v/v) were separated by both water-removing and oil-removing techniques. The separation efficiencies of water-removing mode and oil-removing mode were calculated according to Formula (1) and the results shown in Fig. 8(a) indicate both light-oil/water mixtures and heavy-oil/water mixture are successfully separated and the all separation efficiencies are over 95%. Fig. 8(b) shows the variation of separation efficiency of both modes with recycle numbers. For water-removing mode, the separation efficiency has no obvious fluctuation, which further proves that Al_2O_3 nanosheet coating is durable. Moreover, the separation efficiency of heavy-oil/water separation in oil-removing mode also has no apparent change, which indicates that the modified Al_2O_3/SiO_2 fiber membrane with sodium laurate is firm and the chemical stability of sodium laurate is admirable once more. However, the separation efficiencies of heavy-oil/water are slightly lower than light-oil/water separation. It might be due to absorption of membrane itself resulting in a small amount of oil being stored in the modified Al_2O_3/SiO_2 fiber membrane, resulting in the decrease of separation efficiency. On the contrary, in the water-removing mode, the Al_2O_3/SiO_2 fiber membrane was prewetted by water before separation, so there was no oil stored in the membrane.

CONCLUSIONS

Hierarchical Al_2O_3/SiO_2 fiber membrane with reversible wettability for on-demand oil/water mixtures separation was successfully fabricated by in situ growing hierarchical Al_2O_3 nanosheets on SiO_2 fiber surfaces. The reversible wettability transition between superhydrophilicity/underwater superoleophobicity and superhydrophobicity can be achieved by annealing and surface modification alternately. In this system, the hierarchical Al_2O_3/SiO_2 fiber membrane has superhydrophilicity/underwater superoleophobicity, which can be used for water-removing mode to separate light-oil/water mixtures. The superhydrophobic modified Al_2O_3/SiO_2 fiber membrane with low-cost sodium laurate can be used for oil-removing mode to separate heavy oil/water mixtures separation. The superwettability of two modes had no obvious change after five cycles of reversible wettability transition, showing admirable stability and practical value. The prepared hierarchical Al_2O_3/SiO_2 fiber membranes displayed excellent chemical stability and durability in different hard separation conditions, such as acid, alkali and salt solutions. Besides, the separation efficiency for various oily wastewaters was all up to 95%. This work provides a potential simple route to preparing oil/water separation membrane with reversible wettability. The as-prepared fiber membrane also has more significant potential in industrial transition than many membranes with reversible wettability, such as Janus membrane and stimuli-responsive membranes in terms of cost, preparation process and stability. Thus, this work has great significance and potential not only in fundamental research but also practical applications.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Hierarchical Al_2O_3/SiO_2 fiber membrane with reversible wettability for on-demand oil/water separation

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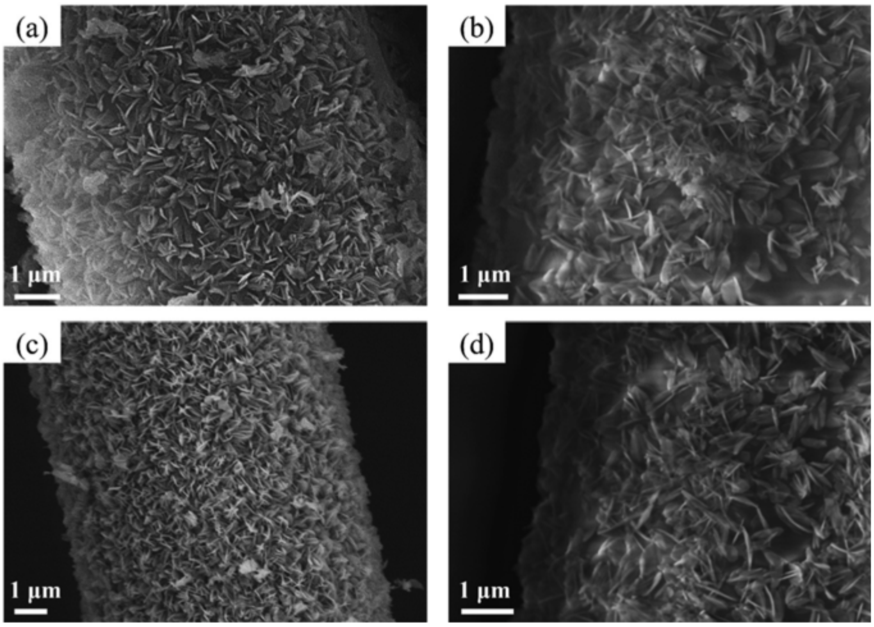

Fig. S1. SEM images of (a) $AlOOH/SiO_2$ fiber, (b) modified Al_2O_3/SiO_2 fiber, (c) annealed modified Al_2O_3/SiO_2 fiber and (d) re-modified annealed Al_2O_3/SiO_2 fiber.

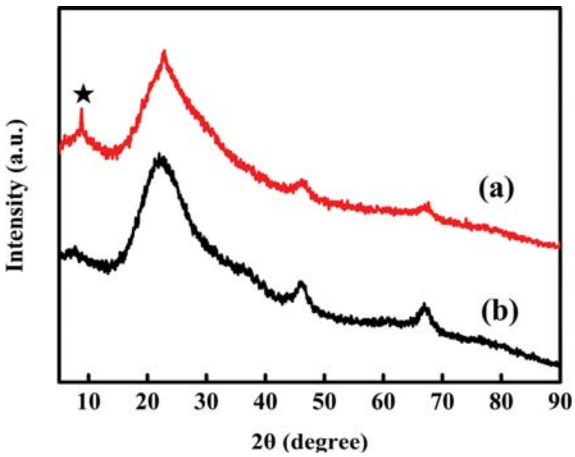

Fig. S2. XRD patterns of (a) hierarchical modified Al_2O_3/SiO_2 fiber membrane and (b) hierarchical modified Al_2O_3/SiO_2 fiber membrane via annealed treatment.

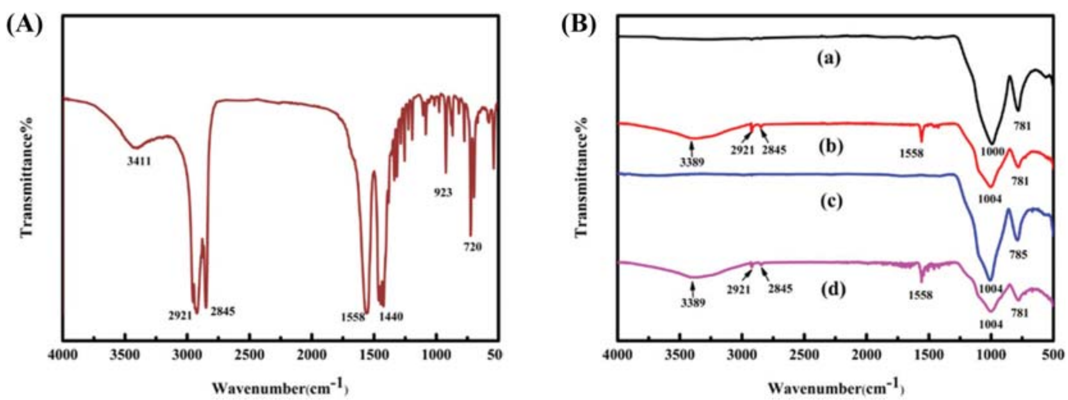

Fig. S3. FT-IR spectra of (A) pure sodium laurate powder and (B) hierarchical Al_2O_3/SiO_2 fiber membrane ((a) Al_2O_3/SiO_2, (b) modified Al_2O_3/SiO_2, (c) Al_2O_3/SiO_2 via annealed treatment and (d) re-modified annealed Al_2O_3/SiO_2).

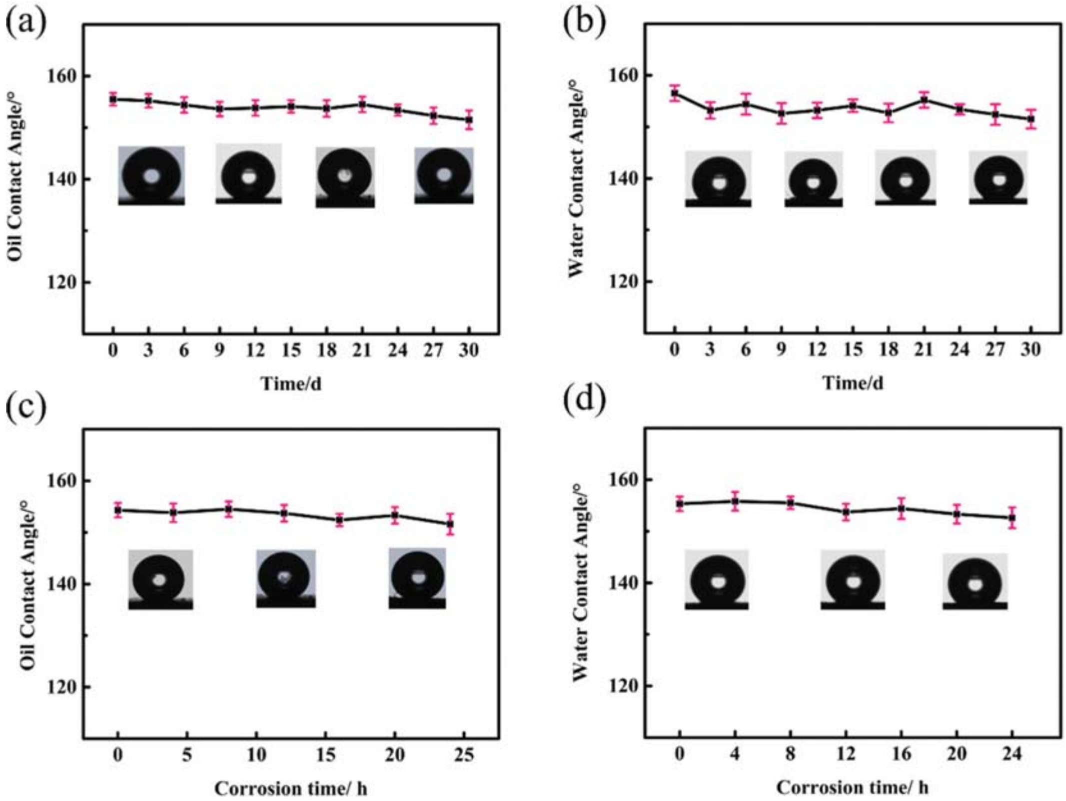

Fig. S4. Variation of underwater OCA of Al_2O_3/SiO_2 fiber membrane and WCA in air of modified Al_2O_3/SiO_2 fiber membrane in different measurement conditions. ((a) and (b) storage time, (c) and (d) corrosion time of 1M NaCl solution).