



Design of superhydrophilic and underwater superoleophobic polyketone-based porous membrane for high performance oil/water separation

张, 雷

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Doctoral Dissertation

Design of superhydrophilic and underwater
superoleophobic polyketone-based porous membrane for
high performance oil/water separation

高性能な油水分離のためのポリケトンを基材とした超親水性で水中
超疎油性な多孔質膜の作成

July 2020

Graduate School of Engineering

Kobe University

ZHANG LEI

张雷

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ZHANG LEI

Graduate School of Engineering

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Chapter 1

General introduction

1.1. Introduction of oily wastewater

1.1.1 Oily wastewater: sources, compositions and classification

Recently years, oily wastewater has become an extremely common pollutant and global environment issue due to the rapid increase of discharge from our daily life and industrial activities, such as oil and gas extraction, manufacturing of petrochemicals, food, steel, and so forth. For example, the global amount of produced water in oil/gas extraction process is about 250 million barrels every day to obtain around 80 million barrels oil obtained [1]. In addition, crude oil leakages and oil spill accidents during oil transportation and extraction are also huge source of oily wastewater, which severely threaten the ecosystem and people's health. Taking the Exxon Valdez oil spill accident as example, the leaked oil caused fatal damage to about 300 000 species in the marine ecosystem, and the long-term impact sill lasts to now [2]. The compositions of oily wastewater are complex because of its different "birthplace". For the produced water, except for oils, it still contains other hydrocarbons, aromatic hydrocarbons, metals and additive chemicals [3]. The oily wastewater from foods, drinks and milk may consist of proteins, microorganism and food additives.

In general, the oily wastewater can be divided into three types based on the situation of oil in water: floating oil; just mixed oil with water (unstable dispersion with the oil droplet size between 20 μm to 150 μm); emulsified oil stabilized by surfactants (oil-in-water emulsion with the size less than 20 μm) [3]. The just mixed oils are thermodynamically unstable, and the oil will spontaneously separate from water after a while. However, the surfactant stabilized oil-in-

water emulsions are extremely stable due to the existence of a strong oil/water interface [4], resulting in it is difficult to separate.

1.1.2 Discharge standard of oily wastewater

If the oily wastewater directly discharges into environment without treatment, it would cause seriously harm to the ecosystem and human's health. Therefore, most countries make a strict discharge standard of oily wastewater. For example, the Oslo in North Sea region regulates that the oil content should be not more than 30 mg/L for discharge [5]. Besides, based on the Paris treaty, the upper discharge limit of oil content is 40 mg/L for the offshore area and 5 mg/L for on land area [6]. In America, the Environmental Protection Agency gives a maximum oil content of 72 mg/L for any 24 h and 45 mg/L during the last 30 days [7]. In China, the oil concentration to discharge is under 10 mg/L [8]. These strict policies and regulations encourage researches to develop efficient technologies for oily wastewater treatment to reach the discharge standard. The commonly used technologies for oily wastewater treatment in industry are summarized in the next part.

1.1.3 Treatment technologies for oily wastewater

1.1.3.1 Traditional methods for oily wastewater treatment

Traditional oil/water separation technologies include air flotation [9], coagulation [10], adsorption [11], and biological methods [12]. Air flotation is a promoted gravitational separation technology that small air bubbles are injected into the oily wastewater, and then dispersed oil droplet in water will be adsorbed on the bubble surface as shown in Fig. 1.1. Finally, the oil droplets will float to the top with the assistant of air bubbles due to its lower density than water [9]. The oil removal efficiency can reach to more than 90% as reported by AL-Shamrani's group [13]. Coagulation technology is widely used for drink water and oily wastewater treatment because of its better destabilizing and aggregating ability. A.L. Ahmad et al. reported that the coagulant of chitosan was used to coagulate the residue oil and suspended solid from palm oil effluent, and removal efficiency could reach to more than 95% [10]. Qian

et al. reported a novel superhydrophobic poly(dimethylsiloxane) coated polyurethane sponge to adsorb oil from water as shown in Fig. 1.2, which showing a high adsorption ability of 16.7 g/g for the pump oil, diesel oil and silicone oil [11]. This kind of material is also suitable for treatment of marine oil spill accidents. Biological technology for oily wastewater treatment is using the microbial metabolism to change the dissolved colloidal organic pollutants into harmless substances [12]. However, these traditional methods have many disadvantages, such as low separation efficiency (especially for the surfactant stabilized emulsions with small oil droplet), high cost, complex operation procedure, and secondary pollution, which greatly impedes their application.

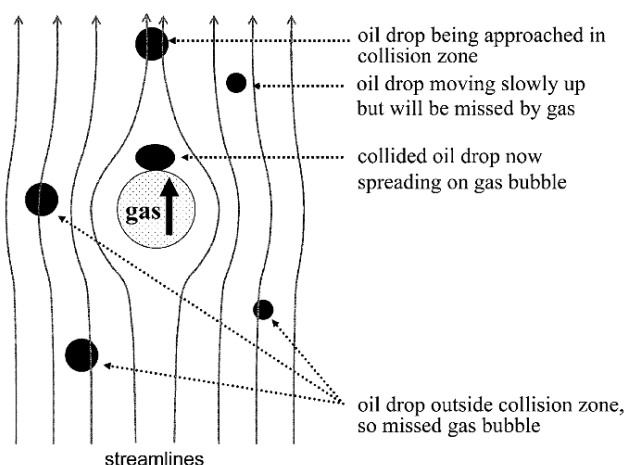


Fig.1.1. Air flotation of oil droplets.[9].

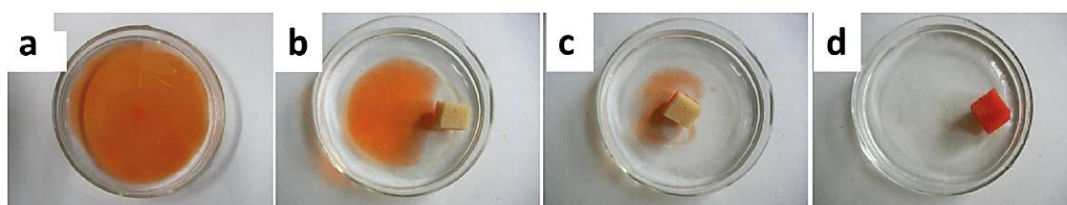


Fig.1.2. Photos of oil adsorption by a piece of poly(dimethylsiloxane) coated polyurethane sponge. The floating oil (colored to orange) will be adsorbed by the superhydrophobic sponge due to the strong interaction between the oil and sponge[11].

1.1.3.2 Membrane technology for oily wastewater treatment

Membrane as a separation barrier possesses special selective permeability. It is widely used in wastewater treatment, sea water desalination, gas separation, concentration or purification in food and medical industries. Based on the pore size distribution, membrane can be divided into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) as shown in Fig. 1.3 [14]. For the MF membrane with pore size from 100 nm to microns, it can effectively remove suspended colloid, particles, viruses and bacteria. For the UF membrane with the pore size from 20 nm to 100 nm, it can effectively reject dissolved macromolecules in solution, such as protein. The NF membrane can reject multivalent salts and small molecule solutes with the molecule weight from 200 Da to 1000 Da via electrostatic repulsion and size sieving. For the RO membrane, it only allows water to pass through. The size of oil droplets in oily wastewater is usually from nanometers to microns, therefore the MF and UF membranes are more suitable as substrate for oil/water separation due to their high filtration efficiency and low operation pressure.

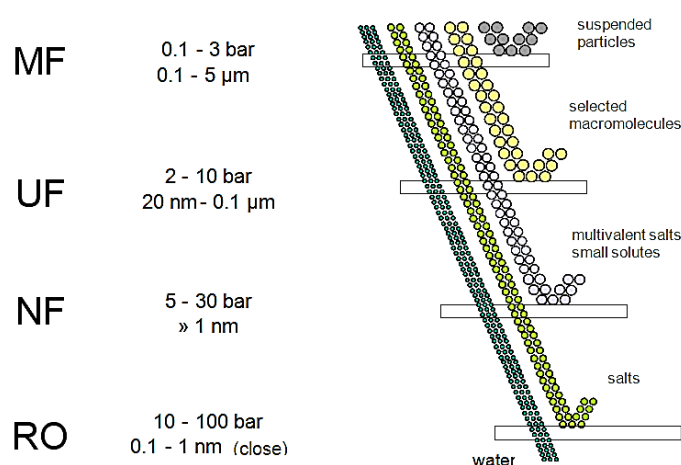


Fig.1.3. Membrane classification based on the pore size distribution.

Recently, membrane separation technologies are considered as a more promising method to treat oily wastewater due to its high separation efficiency, simple operation process, no need for extraneous chemical additives and therefore without second pollution, and lower energy cost [15, 16]. The traditional membrane separations are mainly based on the size-sieving to remove the dispersed oil droplet under pressure driven [17]. However, rapid flux reduction,

short lifetime and low recyclability caused by membrane fouling greatly impedes the practical application of current membranes for oily wastewater treatment. It was reported that the membranes produced by hydrophobic materials (such as polyvinylidene fluoride (PVDF), polyethersulfone (PES), polypropylene (PP)) were easily fouled by oily wastewater due to the formation of oil layer on membrane surface or adsorption of oil droplets in the inner pore [18, 19]. Therefore, how to improve the antifouling performance is a critical issue to expand its application for oily wastewater treatment.

1.1.3.3 Superwetting porous materials for oily wastewater treatment

Recently, design of superwetting porous materials for oil/water separation via adsorption or filtration process also attracts many attentions due to its high separation efficiency. Wettability is an inherent property of a solid surface, which is strongly determined by the surface chemical composition and surface morphology. It can be divided into four situations in the vapor-liquid-solid system for oil and water on any surface as shown in Fig.1.4: superhydrophilicity and superoleophilicity, superhydrophobicity and superoleophilicity, superhydrophobicity and superoleophobicity, and superhydrophilicity and superoleophobicity. It should be noted that in most case the superhydrophilicity surface shows underwater superoleophobicity. Therefore, oil droplet in the oily wastewater could be rejected by the superhydrophilic-superoleophilic or superhydrophilic-superoleophobic porous materials by filtration methods. In contrast, the water could be removed by superhydrophobic-superoleophilic materials via filtration. Besides, the oil could also be adsorbed by superhydrophobic-superoleophilic powder or 3D network. It was reported by Yang et al. that a novelty fluororous metal organic framework (FMOF) was constructed by Ag and 3,5-bis(trifluoromethyl)-1,2,4-triazolate, and showed high affinity towards C₆-C₈ hydrocarbons but no affinity for water molecules [20].

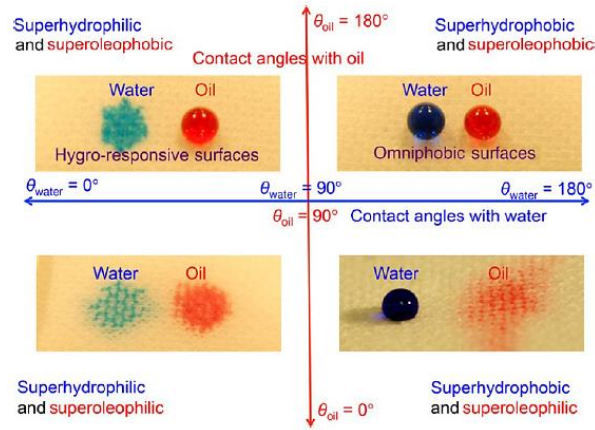


Fig.1.4. The wettability of oil and water on the substrate in a vapor-liquid-solid system[4].

For filtration methods, Jiang's group makes a groundbreaking work for oil/water separation by design superwetting mesh as shown in Figs. 1.5 and 1.6. It can be seen from Fig.1.5 the polytetrafluoroethylene (PTFE)-coated mesh shows hierarchical micro-/nano-composite structure, leading to a robust superhydrophobicity and superoleophilicity with high remove efficiency for water [21]. However, this kind of superhydrophobic material easily fouls due to the high reaction between oil and the hydrophobic mesh, which leading to rapidly flux reduction. In contrast, as shown in Fig. 1.6, a novel superhydrophilic and underwater superoleophobic polyacrylamide (PAM) coated mesh was developed and demonstrates a high oil removal efficiency and better anti-oil fouling performance due to its strong hydration ability [22]. The detailed discussions of superwetting oil/water separation material will be illustrated in Sections 1.3 and 1.4.

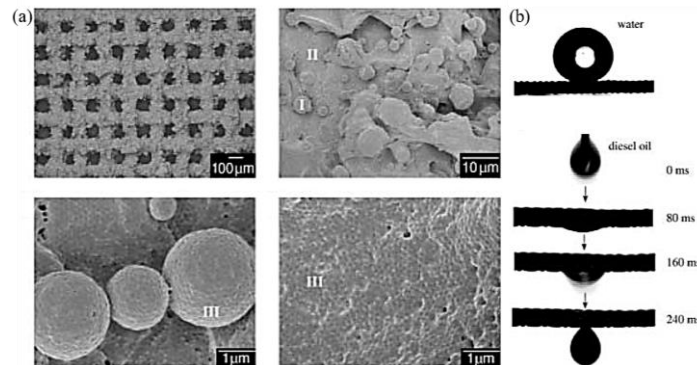


Fig.1.5. SEM images of the polytetrafluoroethylene (PTFE)-coated stainless-steel mesh (a) and the wettability for water and diesel oil (b)[21].

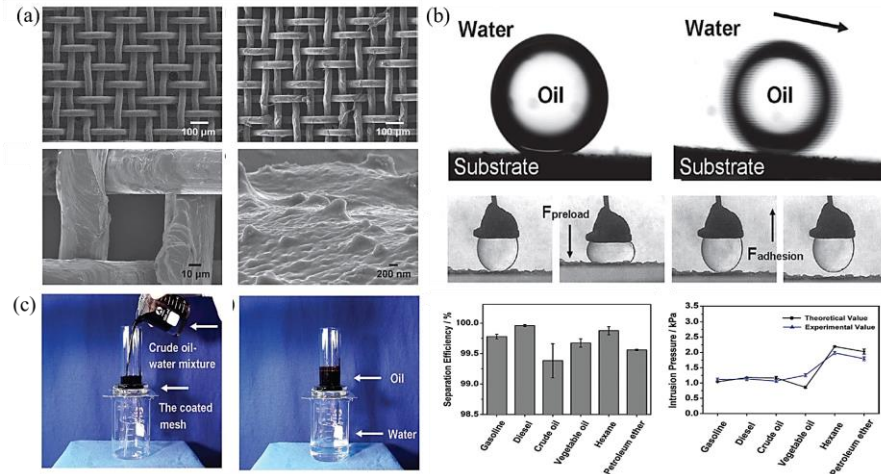


Fig.1.6. SEM images of the polyacrylamide (PAM)-coated mesh (a); underwater 1,2-dichloroethane (DCE) oil contact angle and sliding angle (b); crude oil/water separation (c) [22].

Recently, a reliable separation technology based on demulsification was also developed to treat the surfactant stabilized emulsions. The emulsified droplet can be capture, coalesced, and detached from the surface of superwetting material surface [23]. This novel separation material possesses excellent continuity and high production in practical application.

1.2. Fundamental theories of wettability

1.2.1 Liquid wettability on a solid surface in vapor-liquid-solid system

Wettability is an intrinsic property of solid surface, which is determined by the surface chemical composition and can be enhanced by the surface microstructure. This phenomenon is widely existed in nature, for example, water droplet can be easily sliding on the upper surface of lotus leaves. It is generally acknowledged that the solid surfaces with water contact angle (CA) $\theta < 90^\circ$ is hydrophilicity while the surface with CA $> 90^\circ$ is hydrophobic. The critical value of 90° to distinguish hydrophilic and hydrophobic materials is originated from the Young's equation, Eq. (1-1)

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (1-1)$$

Where γ_{SV} is the surface energy of solid surface, γ_{SL} represents the interface energy between liquid and solid, γ_{LV} represents the surface tension of liquid [24]. However, it should be noted

that the θ value is regarded as intrinsic contact angle on an ideal smooth surface in the vapor as shown in Fig. 1.7 (a). Furthermore, the surface energy or surface tension is usually contributed by two parts: dispersive and non-dispersive parts [25]. Therefore, the total interfacial energy at the solid-liquid interface can be given by Eq. (1-2):

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2\sqrt{\gamma_{SV}^d \gamma_{LV}^d} - 2\sqrt{\gamma_{SV}^h \gamma_{LV}^h} \quad (1-2)$$

where the superscript d indicates the contribution of surface tension or surface energy due to the dispersion force interactions and the superscript h represents the contribution of the dipole-dipole interactions and hydrogen bonding. It should be noted that $\gamma_{SV} = (\gamma_{SV}^d + \gamma_{SV}^h)$ and $\gamma_{LV} = (\gamma_{LV}^d + \gamma_{LV}^h)$. From Eqs. (1-1) and (1-2), $\cos\theta$ is given by Eq (1-3):

$$\cos\theta = \frac{2\sqrt{\gamma_{SV}^d \gamma_{LV}^d} + 2\sqrt{\gamma_{SV}^h \gamma_{LV}^h}}{\gamma_{LV}} - 1 \quad (1-3)$$

Therefore, it can be concluded that the liquid wettability on a solid surface in vapor can be determined by the surface tension of liquid and the surface energy of solid surface.

However, Young's equation is established on an ideal smooth surface, which is not available for the most practical solid surface with rough micro-/nano-structure. It should be noted that the real contact area between liquid and rough solid surface is bigger than a smooth surface as shown in Fig. 1.7 (b). Therefore, Wenzel modified Young's equation by introducing a roughness factor r as defined by Eq. (1-4):

$$\cos\theta^* = r \cos\theta \quad (1-4)$$

where θ^* is the real contact angle, θ is the intrinsic contact angle on a smooth solid surface, r represents the ratio between real area on the rough surface and the geometric projected area [26]. Because the r is always larger than 1, the surface wettability can be greatly enhanced by increasing surface roughness degree. That is to say, if the surface is hydrophilic, it will become to superhydrophilic by increasing roughness degree. On the other hand, if the surface is hydrophobic, it will become to superhydrophobic by increasing roughness degree.

Wenzel's equation gives a great contribution to understand the wettability in a more real situation, but it should be noted that the liquid can't completely contact with a roughness surface because the air is easily captured in the valley on the surface as shown in Fig. 1.7 (d). That is

to say, some parts of liquid contact with the material while other parts contact with the air pocket. Based on this reality, Cassie and Baxter [27] proposed another equation, Eq. (1-5):

$$\cos \theta^* = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (1-5)$$

where f_1 and f_2 represent the contact area ratio of surface 1 and surface 2, respectively ($f_1 + f_2 = 1$), θ_1 and θ_2 are the intrinsic contact angles of the liquid on surface 1 and surface 2, respectively. Usually, the liquid droplet contact angle on an air layer is assumed as 180° , thus the θ^* on an air-solid composite surface can be expressed by Eq. (1-6):

$$\cos \theta^* = f \cos \theta + (1 - f) \cos 180^\circ = f \cos \theta + f - 1 \quad (1-6)$$

where θ is the intrinsic contact angle of the solid surface, and f is the fraction of the surface contacted with liquid. Therefore, the surface wettability can be finely tuned by adjusting the surface energy (control of θ) and designing micro-/nano-composite structure (control of f).

Besides, there is still a transition wettability state between Wenzel state and Cassie state as shown in Fig. 1.7 (c). In this case, the liquid will partly permeate into the surface but still show a big apparent contact angle, and a strong adhesion property similar with Wenzel state.

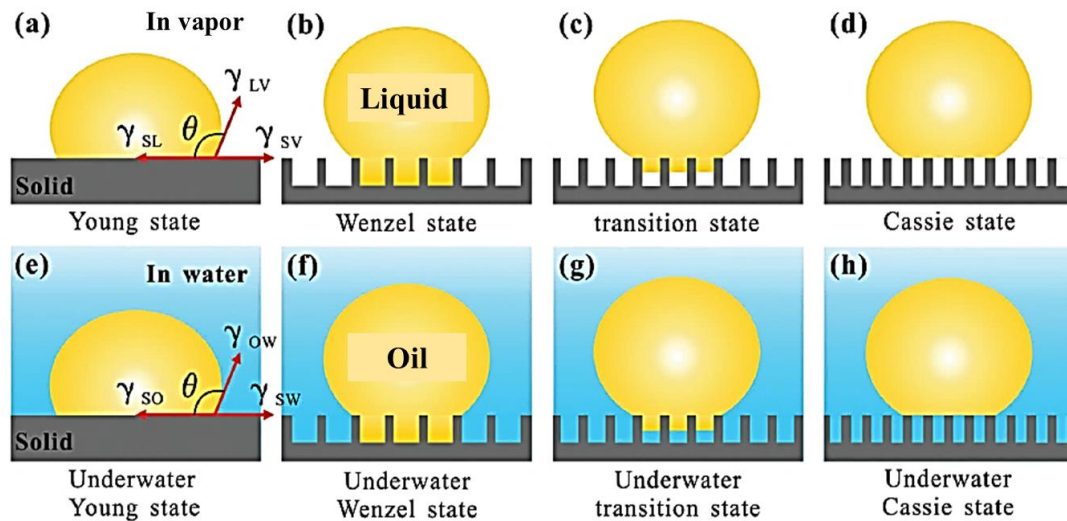


Fig.1.7. Liquid wettability on a solid surface in vapor-liquid-solid system (a)-(d); oil wettability on a solid surface in water-oil-solid system (e)-(h) [28].

1.2.2 Oil wettability on a solid surface in water-oil-solid system

The above discussed four wetting state of liquid in vapor are also available for an oil droplet on smooth or rough solid surface in water as shown in Fig. 1.7 (e)-(h). In this situation,

the oil corresponds to the liquid in the vapor-liquid-solid system, and the water corresponds to the vapor. Thus, from Eq. (1-1), the oil droplet contact angle on a smooth solid surface underwater can be given by Eq. (1-7)

$$\cos \theta_{OW} = \frac{\gamma_{SW} - \gamma_{SO}}{\gamma_{OW}} \quad (1-7)$$

where γ_{OW} , γ_{SO} , γ_{SW} , are the interfacial tensions of oil/water, solid/oil, and solid/water, respectively [29]. The intrinsic contact angles of water (θ_w) or oil droplet (θ_o) in vapor on such a smooth solid surface can be expressed by Young's equation as follow:

$$\cos \theta_w = \frac{\gamma_{SV} - \gamma_{SW}}{\gamma_{wV}} \quad (1-8)$$

$$\cos \theta_o = \frac{\gamma_{SV} - \gamma_{SO}}{\gamma_{OV}} \quad (1-9)$$

where γ_{SV} , γ_{wV} , γ_{OV} , are the interfacial tensions of solid/vapor, water/vapor, oil/vapor, respectively.

Therefore, from Eqs, (1-7), (1-8), and (1-9), Eq. (1-7) can be re-written by Eq. (1-10)

$$\cos \theta_{OW} = \frac{\gamma_{OV} \cos \theta_o - \gamma_{wV} \cos \theta_w}{\gamma_{OW}} \quad (1-10)$$

For a hydrophilic surface in vapor, it also most shows an oleophilicity in vapor because oils have lower surface tension than water with the contact angle order: $\theta_o < \theta_w < 90^\circ$. Therefore, the $\cos \theta_o$ and $\cos \theta_w$ are always positive. Because the γ_{OV} is always less than γ_{wV} due to the lower surface tension of oil or organic solvent than water (72.1 Mn m^{-1}), leading to the $\gamma_{OV} \cos \theta_o - \gamma_{wV} \cos \theta_w$ is commonly negative. Therefore, it can be concluded from Eq. (1-10) that most hydrophilic surface is underwater oleophobicity.

In the Wenzel state as shown in Fig.1.7 (f), the underwater oil droplet contact angle can be given by Eq. (1-11):

$$\cos \theta_{OW}^* = r \cos \theta_{OW} \quad (1-11)$$

where r is the roughness factor, which is the area ratio of real area to the projected area; $\cos \theta_{OW}^*$ and $\cos \theta_{OW}$ are the underwater oil contact angles on rough and smooth surface, respectively.

In the transition state between Wenzel state and Cassie state as shown in Fig. 1.7 (g), a part of oil permeates into the surface, which showing a high adhesion interaction force between the surface and oil.

In the Cassie state as shown in Fig.1.7 (h), the micro-structure is filled with water. In fact, the oil droplet sited on the water-solid composite interface. The captured water layer will show robust oil-repellence and result in a high underwater oil contact angle and low slide angle. The underwater oil contact angle in Cassie state can be given by Eq. (1-12):

$$\cos \theta_{OW}^* = f^* \cos \theta_{OW} + f^* - 1 \quad (1-12)$$

where f^* is the fraction of the surface contact with the oil, θ_{OW} is the underwater oil contact angle on a smooth surface[28].

1.3. Superwetting materials for oil/water separation

For the stratified oil/water mixture with oil droplet size more than 20 μm , superwetting material with bigger pore size, such as mesh, can be used to separate the oil/water mixture. For the oil/water emulsion with smaller droplet size less than 20 μm , on the one hand, the superwetting materials with smaller pore size, such as membrane, can be used to remove the oil or water droplets. Meanwhile, the new developed demulsification technology with the process of “capture-coalesced-detached” can be also used to separate oil/water emulsion. Based on the wettable characterizations, the superhydrophobic and superoleophilic surface can reject water, thus it is referred as “water blocking” type. In contrast, the superhydrophilic/underwater superoleophobic or superhydrophilic/in air superoleophobic surfaces can reject oil, thus it is referred as “oil blocking” type [4]. The combinations between pore size and removing type are summarized in Fig. 1.8.

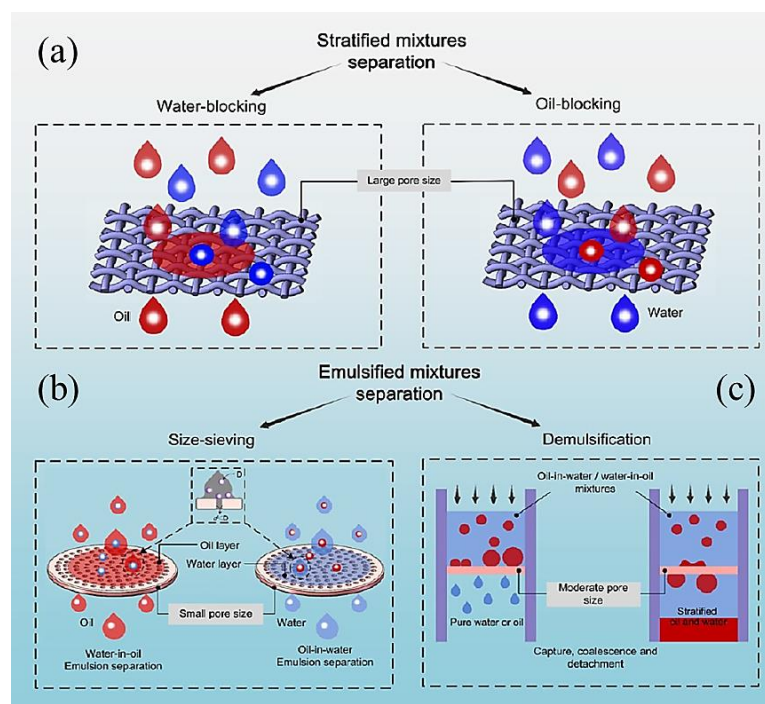


Fig.1.8. Super-wettable materials for oil/water separation:(a) stratified oil/water mixture separation by mesh with big pore size; (b) oil/water emulsion separation by membrane with small pore size; (c) oil/water emulsion separation by demulsification [4].

1.3.1 Separation of oil/water mixture by filtration

1.3.1.1 “water blocking” type oil/water mixture separation

The materials with superhydrophobicity and superoleophilicity can effectively reject water while allow oil adsorb and permeate, thus achieving oil/water separation. There are two main methods to fabricate this type of super-wetting materials: the first method is that decoration of low surface energy chemicals on roughly porous materials; the second one is that construction of micro-/nano-composite structure using low surface energy material. For example, the superhydrophobic and superoleophilic porous material for oil/water mixture separation was first prepared by Jiang’s group via coating PTFE with low surface energy on stainless steel mesh as shown in Fig. 1.5. The PTFE-coated mesh showed a high water contact angle of 156° for water and low contact angle of 0° for diesel oil, and the oil droplet can quickly adsorbed and permeated mesh only in 240 ms [21]. Besides, the results also demonstrated that the pore size of mesh had a big influence on the superhydrophobicity. This newly developed

mesh showed great potential for oil/water mixture separation in the “water blocking” type. According to this idea, many superhydrophobic and superoleophilic porous materials are developed by different material and method as summarized in Table 1.1.

Table 1.1. Superhydrophobic and superoleophilic materials for oil/water mixture separation

Materials	Method	Separation efficiency	references
PTFE	Self-assemble	98%	[30]
Lauric acid	Electrodeposition	93	[31]
PDMS/Mesh	Electroless deposition/UV irradiation	96.8%	[32]
DTMS/PDA	Dip coating	95%	[33]
PTFE film	Laser ablate	~	[34]
SiO ₂ @PDMS	3D print	~99.6%	[35]

PDMS: poly(dimethylsiloxane), DTMS: dodecyltrimethoxysilane, PDA: polydopamine, SiO₂@PDMS: SiO₂ mixed with PDMS.

It is well acknowledged that fluoropolymers, such as PVDF, PTFE, fluorinated alkyl silane, 1H,1H,2H,2H-perfluorododecanethiol, are the outstanding candidate as a hydrophobic modifier due to its low surface tension. For instance, Chen et al. reported a novel method to prepare PTFE nanofibrous coated metal mesh by electrostatic interaction driving self-assemble approach. The resulted metal mesh showed superior superhydrophobic and superoleophilic properties, as well as high oil/water mixture separation performance [30].

However, fluoropolymers are expensive and poison to the environment and people's health. Thus, hydrophobic modifier without fluorine is also attractive. As shown in Fig. 1.9, Wang et al. reported a bioinspired one-step dip coating method to preparation of superhydrophobic surface on various commercial porous materials. The resulted surfaces show high water contact angles due to the rough structure and hydrophobicity of DTMS. Besides, the coated stainless steel mesh shows high oil/water mixture separation efficiency and superior recyclability [33].

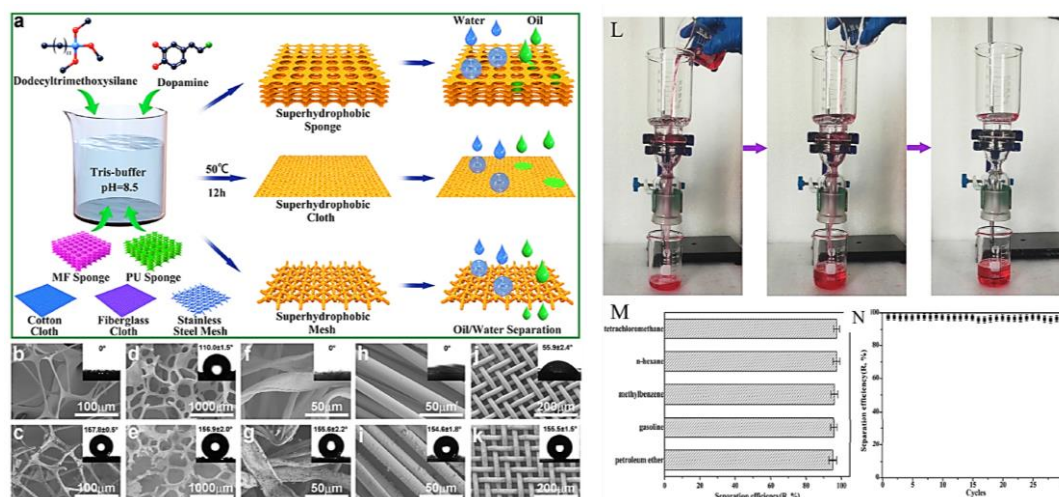


Fig.1.9. Bioinspired one-step preparation of superhydrophobic surface for oil/water separation: (a) schematic illustration of preparation route; (b)-(k) surface morphologies and water contact angles; (L) oil/water separation process; (M) separation efficiency for different oil/water mixture; (N) recyclable ability [33].

In addition to the mentioned superhydrophobic/superoleophilic materials modified by hydrophobic modifier, some intrinsically hydrophobic materials are also employed for construction oil/water separation material. As reported by Yong's group, a durable superhydrophobic PTFE film with micro-holes was prepared via laser ablated technology on PTFE substrate for oil/water separation [34]. Furthermore, preparation of superhydrophobic porous material by 3D print technology using hydrophobic material was also attractive recently [35].

1.3.1.2 “oil blocking” type oil/water mixture separation

For the “oil blocking” type materials, it will let the water through the material and reject oil. Besides, it possesses better antifouling performance due to the formed water layer compared with “water blocking” type material, thus maintaining a continuous oil/water separation. There are two kinds of superwetting materials can be used for oil/water separation in “oil blocking” type: superhydrophilicity-superoleophobicity (in vapor) or superhydrophilic and underwater superoleophobic. Jiang's group firstly developed the novel superhydrophilic and underwater

superoleophobic material for oil/water separation with high anti-oil-fouling performance by coating PAM on stainless steel mesh as shown in Fig. 1.6 [22]. According to eq. 1-10, a hydrophilic surface in vapor is sometimes oleophobic underwater. By introducing micro-/nano-structure, the surface can be changed into superoleophobicity like “Cassie state”. Based on this concept, various of superhydrophilic and underwater superoleophobic porous materials were developed as summarized in Table 1.2. It can be seen that various hydrophilic materials including inorganic and organic are fixed on the surface of porous material via spray, heat treatment, dip coating and so on to construct hydrophilic chemistry and rough morphology at the same time.

Table 1.2. Superhydrophilic and underwater superoleophobic materials for oil/water mixture separation

Materials	Method	Separation efficiency	references
Palygorskite/mesh	Spray	99.6%	[36]
NiO/Ni/mesh	Heat treatment	99%	[37]
GO/mesh	Dip coating/heating	98%	[38]
PEI/SA/Ca ⁺ mesh	Dip coating/cross linking	99.4%	[39]
PVA/filler paper	coating	99.8%	[40]

NiO: nickel oxide, GO: graphene oxide, PEI: polyethyleneimine, SA: sodium alginate, PVA: polyvinyl alcohol.

For the superhydrophilic and superoleophobic in the vapor materials, it has many advantages compared with above mentioned super-wettable materials, such as anti-oil-fouling, self-cleaning ability and so on. It doesn't need a water pre-wetting process before oil/water separation process. However, it is very difficult to engineer a superhydrophilic and superoleophobic surface in the vapor, because it is hard to find a material with its surface energy lower than oil but higher than water at the same time. Pan's group developed a superhydrophilic and superoleophobic surface in the vapor based on the difference of polarity between oil (nonpolar) and water (polar) as shown in Fig. 1.10 [41]. That is to say, the surface should have strong interaction with polar liquids (water), but low interaction with nonpolar liquids (oil). By

coating the sodium perfluorooctanoate (S-PFO) molecule on the substrate, the fluorinated parts are exposed into air interface to reduce the overall surface energy, leading to an oil-repellent manner. However, the water molecule can be adsorbed into the porous substrate due to the strong polar group of sodium atoms as shown in Fig. 1.10 (g). The coated substrate showed a robust superhydrophilicity and superoleophobicity in the vapor as shown in Fig. 1.10 (a)-(f). Besides, the coated mesh also exhibited high oil/water mixture separation performance as shown in Fig. 1.10 (h).

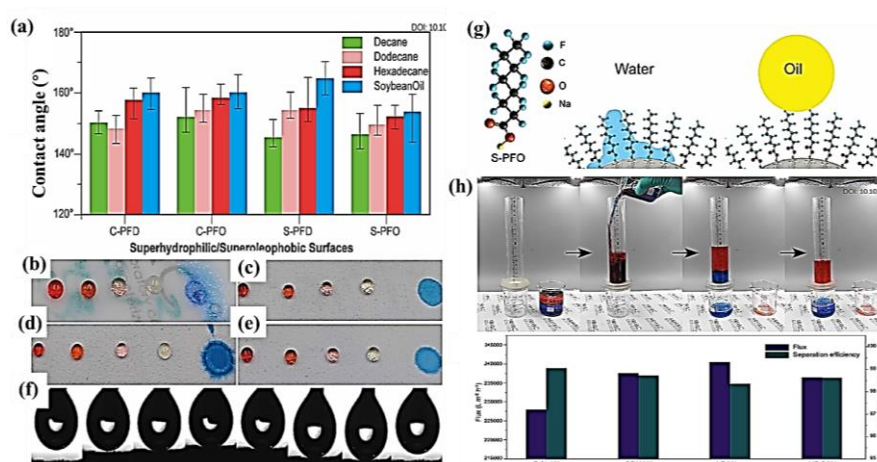


Fig.1.10. Design and characterization of the superhydrophilic and superoleophobic surfaces: (a) oil contact angles on the copper perfluorododecane (C-PFD), copper perfluorooctane (C-PFO), sodium perfluorododecane (S-PFD), sodium perfluorooctane (S-PFO) surfaces; (b)-(e) photos of decane, dodecane, hexadecane, soybean oil and water (order from left to right) on the C-PFE, C-PFO, S-PFD, S-PFO surfaces, respectively; (f) the dynamic adhesion process of soybean oil on S-PFO surface; (g) the illustration of water and oil wettability on the S-PFO surface; (h) oil/water separation by S-PFO coated steel mesh [41].

1.3.2 Separation of oil/water emulsion by filtration

In most practical situation, the mixture of oil and water exists as a stable emulsion state (oil-in-water or water-in-oil) with small dispersed droplets less than 20 μm . Therefore, the superwetting porous material with bigger pore size, such as mesh, sponge, fabrics and so on, shows low separation efficiency for the oil/water emulsion. For the oil/water emulsion

separation, superwetting materials with smaller pore size than water or oil droplet are more suitable.

1.3.2.1 “water droplet blocking” type water-in-oil emulsion separation

Superhydrophobic and superoleophilic materials with small pore size are suitable for water-in-oil emulsions separation to purify the oil. Jin’s group firstly prepared a superhydrophobic and superoleophilic PVDF membrane using a non-solvent induced phase separation (NIPS) process for water-in-oil emulsions separation as shown in Fig. 1.11 [42]. It can be seen from Fig. 1.11(b) that the PVDF membrane surface was rough and consisted of spherical microparticles. Besides, the membrane showed high water contact angle of 158° and oil contact angle of $\sim 0^\circ$ as shown in Fig. 1.11(c). Furthermore, it was found from Figs 1.11 (e) and (f) that the obtained membrane exhibited high separation efficiency more than 99.95% for the surfactant-free or surfactant-stabilized water-in-oil emulsions due to its robust hydrophobicity and small pore size. Based on this concept, many superhydrophobic and superoleophilic membranes were prepared for oil purification as summarized in Table 1.3. However, this kind of membrane is easily fouled because of its high interaction with oil, always leading to quick flux reduction.

Table 1.3. Superhydrophobic and superoleophilic membrane for oil/water emulsion separation

Materials	Method	Separation efficiency	references
Carbon nanotube	Vacuum-filtering	99.97%	[43]
SiO ₂ nanofiber	In-situ polymerized	~	[44]
SiO ₂ /ECTFE	TIPS	99.6%	[45]
PVDF	Electrospun/spary	99%	[46]
SiO ₂ /PVDF	NIPS	99.95%	[47]
ZIF-8/PDMS/NTU	In-situ growth	99.9%	[48]
PDA/PDMS	SI-ATRP	98.7	[49]
polybenzoxazine	Self-assembly	99.95%	[50]
PLA	Electrospun	~	[51]
Cellulose/SiO ₂	Phase inversion	99.99%	[52]

ECTFE: poly(ethylene chlorotrifluoroethylene), NTU: carbon nanotube, PLA: polylactic acid.

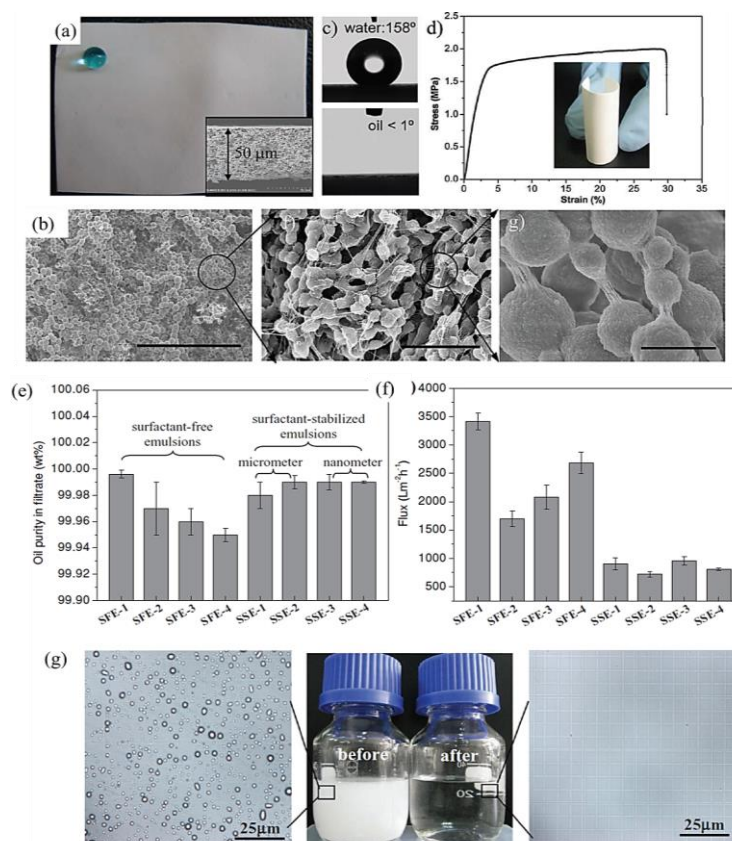


Fig.1.11. Design of superhydrophobic and superoleophilic PVDF membrane: (a) image of the PVDF membrane; (b) SEM images of the surface; (c) water and oil contact on membrane surface; (d) mechanical strength of PVDF membrane; (e) and (f) separation efficiency and flux of surfactant-free or surfactant-stabilized water-in-oil emulsion; (g) photos of the emulsion before and after separation [42].

1.3.2.2 “oil droplet blocking” type oil-in-water emulsion separation

The superhydrophilic and underwater superoleophobic membrane with suitable pore size is effective to remove oil droplet, while let the water pass through. Besides, it has many advantages compared with superhydrophobic and superoleophilic membrane, such as high antifouling performance, high flux and so on. In addition, the oily wastewater mainly exists in the state of oil-in-water emulsion manner. Therefore, recently many researches mainly focus on engineering superhydrophilic and underwater superoleophobic membrane for oil-in-water emulsion separation. The detailed discussion of materials, approaches, separation performance and fouling mechanism would be presented in Section 1.4.

1.3.3 Separation of oil/water emulsion by demulsification

Recently, oil/water emulsion separation via demulsification is also attractive. This process can be divided into three stages. First, the emulsified droplets approach the coalesce surface driven by external pressure, electric interaction or hydrodynamic force. Then, the droplets can be captured by the surface and coalesce with each other to form a big droplet. Finally, the coalesced droplets detach from the substrate [4]. Xu's group developed a Janus membrane with negatively or positively charged carbon nanotube (CNT) on hydrophobic microfiltration membrane for oil-in-water emulsion separation as shown in Fig. 1.12. The prepared membrane was effective to remove oil from oil-in-water emulsion through demulsification due to the charge-screening effect. That is to say, the dispersed oil droplets can be captured by the charged surface, and then aggregated into big oil droplet. Finally, the oil can permeate into the hydrophobic sublayer [53].

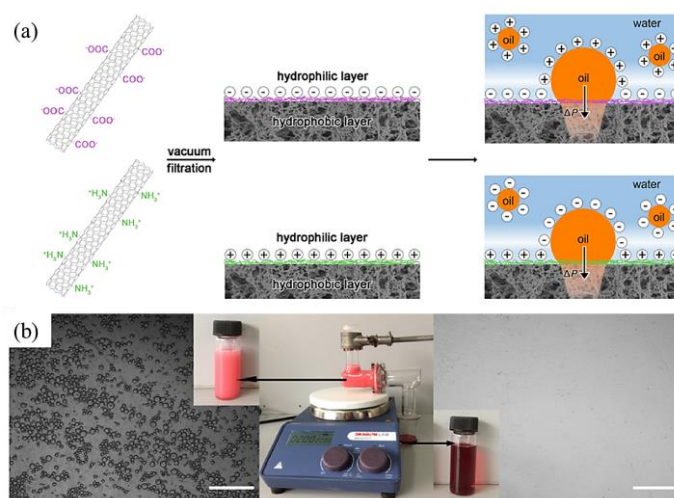


Fig.1.12. (a) Schematic illustration of the Janus membrane and the demulsification and separation of the oil-in-water emulsion; (b) optical microscope photos of the emulsion before and after separation. The scale bar is 500 μm [53].

1.4. Superhydrophilic and underwater superoleophobic membrane for oil-in-water emulsion separation

1.4.1 Introduction of superhydrophilic and underwater superoleophobic membrane

Construction of superwetting interface on MF or UF membranes, such as superhydrophilic and underwater superoleophobic membrane, can significantly improve the separation efficiency and anti-oil-fouling performance during oil/water separation process. For the superhydrophilic and underwater superoleophobic membrane with suitable pore size, it can effectively reject oil droplets, while let the water go through. It should be noted that the membrane should be wetted by water before oil/water separation. Once wetted by water, a water layer will be formed on the membrane surface via hydrogen bonding or electrostatic interaction between the hydrophilic group and water molecules. Therefore, the hydration layer will prevent oil from a contact with membrane surface. There are mainly two approaches to engineer a superhydrophilic and underwater superoleophobic membrane. On the one hand, a surface modification on rough membrane surface with hydrophilic materials or a construction of micro/nano-structure using hydrophilic material on smooth membrane surface is useful to prepare structure-dependent superhydrophilic and underwater superoleophobic membrane. On the other hand, a construction of a smooth molecule layer using superhydrophilic materials with strong hydration ability (such as polyelectrolyte material) is also favorable to fabricate structure-independent superhydrophilic and underwater superoleophobic membrane [54]. Both of the approaches are discussed in Section 1.4.2.

1.4.2 Materials and methods for the construction of superhydrophilic and underwater superoleophobic membrane

Due to the distinguished merits of superhydrophilic and underwater superoleophobic membrane for oil-in-water emulsion separation, there are lots of hydrophilic materials and methods employed to construction this kind of membrane. it will be discussed precisely in this section.

1.4.2.1 Mussel-inspired dopamine deposition

Dopamine (DA), known as a “bio-glue” inspired by mussel adhesion, can be easily coated on various substrate due to the catechol and amine structures via covalent and noncovalent interaction in an autoxidative polymerization process [55]. A hydrophilic polydopamine (PDA) layer can be formed on the substrate under the optimized condition of 2 mg mL⁻¹ dopamine in tris(hydroxymethyl) aminomethane hydrochloride (tris-HCl) solution (pH=8.5) under an ambient atmosphere for a certain period of time [56]. DA is also widely used to modify the porous membrane to improve the hydrophilicity and antifouling property due to the existence of catechol and amine groups for oil/water separation [57-61]. For instance, Wang et al. [62] reported that decoration of polydopamine nanocluster on electrospun nanofibrous membrane for oil/water separation. The membrane with hierarchical structure shows superhydrophilic and underwater superoleophobic property, as well as high oil/water separation performance. In addition, He et al. [63] constructed polydopamine (PDA) micro-/nano-sphere on polyacrylonitrile (PAN) nanofibrous membrane by filtration and secondary decoration for sustaining oil/water separation. The antifouling mechanism of PDA layered membrane was first theoretically elucidated based on hydration ability and adhesion free energy. Furthermore, DA as an adhesion material, it can also fix hydrophilic nano-particles (such as Fe₃O₄) on the membrane surface to improve the surface wettability and antifouling performance for oil/water separation [61]. More important, polydopamine also can act as an intermedia layer to react with other hydrophilic molecule via Michael addition reaction and Schiff’s base reaction [60].

1.4.2.2 Bio-inspired mineralization

Mineral materials, such as SiO₂, CaCO₃, TiO₂, Al₂O₃, are considered as the superior candidates to engineer oil/water separation material due to their inherent superhydrophilicity and high surface area, which can effectively enhance the surface energy and micro/nano-structure [64-67]. Therefore, how to cleverly combine the mineral nanomaterials with a suitable porous substrate is the core question [68]. Yang et al. [69] demonstrated an attractive strategy to prepare crude-oil-repellent PVDF membrane by oxide coating via atomic layer deposition

(ALD). The TiO_2 and SnO_2 coating surfaces showed robust anti-oil wettability and fouling ability because of its high water molecule densities near the surface and strong interactions with water. Furthermore, Xu et al. [70, 71] developed a bioinspired mineralization strategy to engineer mineral layer on the hydrophobic polymer membrane. According to this method, a hydrophilic poly(acrylic acid) or polyethylenimine media-layer was introduced to improve the stability of coating layer due to the weak interaction between the hydrophilic mineral layer and hydrophobic membrane matrix [72]. The prepared mineralization membrane showed high separation and anti-oil-fouling performance for oil-in-water emulsions.

1.4.2.3 Blending hydrophilic materials

Blending hydrophilic materials into the membrane matrix directly during the phase inversion process is a common method to improve hydrophilicity due to its simple operation process and easy scale up. The frequently used additives can be basically divided into three types: hydrophilic polymers (such as polyethylene glycol, zwitterionic), amphiphilic copolymers (such as Pluronic F127), and inorganic particles. For instance, Zhu et al. reported a superhydrophilic and underwater superoleophobic zwitterionic-poly(vinylidene fluoride) (PVDF) blending membrane for oil/water separation using a two-part process with an in situ crosslinking reaction during non-solvent induced phase separation and a subsequent sulfonation reaction. In this process, a novel copolymer of poly- (dimethylaminoethyl methacrylate-co-2-hydroxyethyl methacrylate) was synthesized as a hydrophilic additive [73].

1.4.2.4 Surface coating with hydrophilic materials

Surface coating with hydrophilic materials is another simple method to construct superhydrophilic and underwater superoleophobic membrane for oil/water separation. Usually the hydrophilic materials can be coated on membrane surface by dip coating, spin coating and casting. For example, Sun et al. developed a poly(tetrafluoroethylene-r-vinylpyrrolidone) (F-VP) modified PVDF membrane with comprehensive antifouling property for highly efficient oil/water separation via dip coating method. The hydrophilic and anti-oil-fouling performance

of the modified membrane obviously improved via forming a F-VP hydrophilic layer on PVDF membrane surface [74].

1.4.2.5 Construction of superhydrophilic membrane by vacuum filtration

Recently, lots of nanomaterials, such as carbon nanotube (CNT) [57], graphene oxide (GO) [75], metal organic frame (MOF) [76], cellulose nanocrystal [77], chitin nanofibrous [78], and so on are also employed to prepare oil/water separation membrane by vacuum filtration method. For example, Gao et al. developed a single-walled carbon nanotube-polydopamine-polyethyleneimine (SWCNT/PD/PEI) composite ultrathin film with robust superhydrophilicity and underwater superoleophobicity for ultrafast separation of surfactant stabilized oil-in-water nanoemulsions which contained the oil droplets size of tens nanometers in diameter. The composite film with effective pore size of ~ 10 nm and thickness of ~ 160 nm can effectively separate oil-in-water nanoemulsions in an ultrafast manner with permeance up to $\sim 6\,000\text{ L m}^{-2}\text{h}^{-1}\text{bar}^{-1}$, which is 10-fold higher than traditional ultrafiltration membranes with similar rejection property [57]. Besides, Zhang et al. reported a novel nanoporous cellulose membrane fabricated by filtration of the tunicate cellulose nanocrystals (TCNCs) suspensions. The obtained membrane showed a hierarchical structure, as well as superhydrophilicity and underwater superoleophobicity [77].

1.4.2.6 Construction of polyelectrolyte molecule layer via grafting

Even though the hydrophilic modification by blending or coating is simple, the hydrophilic components are easily leak from membrane during the operation process due to the weak interaction with membrane material. However, the hydrophilic molecules can be sturdily fixed on membrane surface via covalent bonding by grafting. It is well-known that zwitterionic materials, carrying zwitterions of carboxybetaine or sulfobetaine, have ultralow fouling potential to various foulants [79, 80], owing to their strong hydration ability, which arise from the electrostatic interactions between the zwitterions and water. For instance, Jin et al. reported the fabrication of a membrane comprising a zwitterionic sulfobetaine grafted onto a

poly(vinylidene fluoride) (PVDF) substrate that exhibited comprehensive antifouling properties in the filtration of oil-in-water emulsions containing bovine serum albumin (BSA), and humic acid (HA) foulants [81, 82]. It should be noted that this roughness-independent superhydrophilic and underwater superoleophobic membrane possesses distinguishing advantages than the roughness-dependent type. Because an overdependence on the surface structure greatly limits its applications. Once the micro/nano-structure is destroyed during the operation process, the wettability will change from “Cassie state” to “Wenzel state”, which leading to a reduced separation and antifouling property. Besides, it is also found that the roughness surface would be a hinder to self-cleaning because of the interlocking effect [83].

1.4.3 Challenges for oily wastewater treatment by superwetting membrane

1.4.3.1 Membrane fouling by oily wastewater

Membrane fouling is the main obstacle that hinders the widespread application of membrane technology for practical oily wastewater treatment. Once the membrane is fouled, the permeation will reduce quickly and not be easily recovered only by water washing. Membrane fouling is a complex phenomenon. Moreover, the fouling by oily wastewater further increases the complexity due to the unique characterization of oil droplets, such as coalescence, deformation, moving oil layer, viscous effects, effect by different surfactants and other pollutants. Many researchers used blocking filtration laws to explain the membrane fouling mechanism during the separation of oily wastewater [18]. That is to say, emulsified oil droplets accumulate on the membrane surface, which leads to cake layer formation or pore blocking.

In addition, Zhu et al. investigated the fouling of UF and NF membranes by surfactant-stabilized oil-in-water emulsion with three different charged surfactants of the negative sodium dodecylbenzenesulfonate (DDBS), positives cetyltrimethylammonium bromide (CTAB) and non-charged Triton X-100 (TX-100) [84]. By comparing the fouling behavior of surfactant stabilized emulsions and pure surfactant solutions, it was found that the emulsified oil, not the free surfactant molecules, was responsible for the membrane fouling. Besides, an electrostatic interaction between membrane surface and the emulsified oil droplet was important for the

fouling and rejection. The positively charged CTAB emulsion can easily adsorb on negative PSF membrane, and leads to quickly flux reduction and low rejection. Besides, it also concludes that cake layer formation is responsible for the observed linear increase in transmembrane pressure during oil/water filtration. Once the pressure drop across the cake layer reaches a critical value, oil droplets in the bottom of the cake layer can wet the membrane, which leads to an irreversible membrane fouling. In contrast, when the operation pressure below critical value, membrane flux can be recovered after hydraulic cleaning.

1.4.3.2 Suppression of membrane fouling

First, improving the hydrophilicity of membrane is a common method to enhance the anti-oil-fouling property. This is because that a water layer can be formed on membrane surface via hydrogen bonding or electrostatic interaction between hydrophilic groups and water molecules to prevent the contact between oil and membrane. The hydrophilicity of membrane can be improved by blending hydrophilic additives or modifying the membrane surface by grafting or coating as discussed in Section 1.4.2.

Besides, controlling mass transfer of oil to the membrane surface in membrane modules is also effective to inhibit membrane fouling. Hydrodynamics is one of the most important factors in the filtration system that can effectively control the membrane fouling. The flow condition in the membrane module can be quantified via Reynolds number (Re). It is generally acknowledged that the bigger Re , the higher shear rate near the membrane surfaces that can compress concentration polarization and remove deposited foulants. Promoting turbulence in membrane flow channels can be achieved by lots of methods, such as vibration, bubbling, and ultrasound [85].

1.5. Purpose and overview of this dissertation

Previous sections have generally introduced the source, composition, classification, discharged standard, treatment methods of oily wastewater. Besides, the research progress and challenges for oily wastewater treatment by superwetting porous materials are systematically

summarized. In this dissertation, the main purpose is to develop novel superhydrophilic and underwater superoleophobic polyketone-based porous membrane with high separation and anti-oil-fouling performance for oily wastewater treatment. The overview of each chapter is described as follows.

This dissertation included 6 chapters.

In **Chapter 1**, the background as well as the objectives of this dissertation were generally introduced.

In **Chapter 2**, starting with an aliphatic polyketone (PK) polymer with intrinsic intermediate hydrophilicity and good membrane formation ability, a robust PK composite membrane with the ideal abrasion-resistant, chemical-resistant, and super-anti-oil-fouling property was effortlessly prepared by a simple one-step non-solvent induced phase separation (NIPS) process. Besides, the polyvinyl alcohol (PVA) was introduced into PK substrate as pore former and hydrophilicity enhancer to perfect the underwater oil-repellency. Moreover, a nylon mesh was embedded in the PK-PVA blending membrane as a reinforcing support. Molecular dynamics (MD) simulations revealed that the intermolecular and intramolecular hydrogen bonds are responsible for the stable confinement of PVA within the PK matrix, leading to the all hydrophilic PK-PVA mixed surface chemistry. In addition, this membrane showed a high flux recovery of 93-96% in the cross-flow filtration with a high flux up to $420 \text{ L m}^{-2} \text{ h}^{-1}$ at 0.1 bar, even for the highly adhesive and highly fouling soybean oil emulsions (up to 100 000 ppm). The prepared membrane, with outstanding performance, high cost-effectiveness and simple preparation method, is very promising in practical application of O/W emulsions separation.

In **Chapter 3**, aiming at the realization of comprehensive fouling-resistant and fouling-release properties, an ultrathin silica (SiO_2) layer was conformally engineered onto a porous polyketone (PK) substrate via the electrostatic attraction force silicification process. This in situ silicification formed a superhydrophilic and underwater superoleophobic surface that allowed the realization of ultrahigh water permeance up to $7533 \text{ L m}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$, and an exceptionally high emulsion flux up to $6000 \text{ L m}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$, as well as a high rejection of >99.9% against various oily emulsions. The unique design of the superhydrophilic silicification layer grown on

the hydrophilic PK substrate also endowed the membrane with comprehensive antifouling properties for the oily emulsions containing various pollutants such as proteins, surfactants, and other natural organic materials (NOM). A nearly 100% recovery ratio of permeation flux could be obtained after several cycles of oily emulsion filtration. The use of highly chemically inert PK membrane with an inorganic SiO_2 modified layer (SiO_2 -d-PK membrane) enabled the application of membrane process under more challenging conditions, where great tolerance and long-term stability of membrane toward salty and strongly acidic/alkaline solutions and various organic solvents were further required. Overall, this study provides an insight into engineering of membrane with ultralow fouling propensity for treating challenging oily emulsions.

In **Chapter 4**, a novel polyketone (PK) membrane with hierarchic micro-/nano-structure modified with polydopamine (PDA-d-PK) was fabricated via in-situ dopamine self-assembly onto porous PK membrane. The morphology of PDA particle layer could be finely controlled by the deposition time and the composition of dopamine solution. Thanks to the finely tuned PDA layer with superhydrophilicity and hierarchical structure, the obtained PDA-d-PK membrane showed a robust superhydrophilicity and underwater superoleophobicity, as well as distinguished self-cleaning ability. In addition, the PDA-d-PK (9h) membrane also achieved a high pure water flux of $116 \text{ L m}^{-2}\text{h}^{-1}$ under 0.01 bar only driven by gravity of feed solution due to the porous structure and superhydrophilicity. It also showed an exceptional high emulsion flux of $106 \text{ L m}^{-2}\text{h}^{-1}$ under 0.01 bar for hexane-in-water emulsion, as well as high rejection of $>99.9\%$. Owing to the unique design of PDA-d-PK membrane with hydrophilic PDA layer on intrinsically hydrophilic PK substrate, a high antifouling performance could be achieved for the hexadecane-in-water emulsion. Furthermore, the PDA-d-PK membrane also exhibited a great tolerance and durability against acidic, salty, alkaline and organic solvents due to the cooperation of robust PDA layer and highly chemical inertness of PK substrate. This indicates the possibility to apply a membrane process for oil/water separation under harsh condition.

In **Chapter 5**, a new class of zwitterionic-polyelectrolyte-grafted aliphatic polyketone (PK) membrane (PK-g-PSBMA) was prepared by the highly controllable surface-initiated atom transfer radical polymerization (SI-ATRP) of N-(3-sulfopropyl)-

N-methacroyl-oxyethyl-N,N-dimethylammonium betaine (SBMA) on highly porous and hydroxylated PK membranes. The PK-g-PSBMA membrane prepared with 10-min grafting modification exhibited excellent solvent-resistant underoil superhydrophilicity as well as underwater superoleophobicity and ultralow protein adhesion. The low mass-transfer resistance of the porous hydroxylated PK substrate along with the low fouling zwitterionic SMBA layer endowed the PK-g-PSBMA membranes with high emulsion permeance of 1200-1800 Lm⁻² h⁻¹ bar⁻¹, low oil permeations at 6-33 ppm, and high flux recovery ratios of 82-98%, even for difficult micro- and nano-emulsions containing small oil droplets and complicated pollutants. Thus, PK-g-PSBMA membranes fabricated by simple process show comprehensive performances, and great potential for treatment of challenging oily wastewater.

In **Chapter 6**, the conclusions of this dissertation were summarized.

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Chapter 2

One-step fabrication of robust and anti-oil-fouling aliphatic polyketone composite membranes for sustainable and efficient filtration of oil-in-water emulsions

2.1. Introduction

Aquatic environment pollution caused by substantial industrial oily wastewater and frequent oil spill accidents (e.g., the catastrophic Deepwater Horizon oil spill in 2010) has stimulated the great efforts of scientists and engineers in developing scalable and cost-effective treatment strategies [1-5]. Traditional technologies, such as gravity separation and dissolved air flotation, are only effective in the treatment of separated oil and just mixed oil having a bigger droplet size [6-8]. For the surfactant stabilized oil with droplets size less than 20 μm , membrane filtration is considered as the most promising solution owing to its high separation efficiency, simple operation procedure, low cost, and eco-friendliness [9-12].

Knowing that the essence of the membrane separation of oil/water mixtures is an interfacial phenomenon, membrane materials with special wettability have been developed by mimicking natural surfaces with superwettability based on the synergetic effect of surface chemistry and surface morphology [3]. Superhydrophilic and underwater superoleophobic membranes have attracted the most attention for the low-fouling-propensity “water-removing” oil/water separation [13]. In contrast, the conventional membranes made of hydrophobic-oleophilic polymers, such as polyvinylidene fluoride (PVDF) and polysulfone (PSf), are prone to severe oil fouling [14]. Various modifications (e.g., coating, grafting, and blending) have been carried out to introduce hydrophilic chemistry and multi-scale roughness to these hydrophobic membranes to achieve a desired superhydrophilicity and underwater

superoleophobicity [15-18]. However, membrane fouling may still occur due to incomplete coverage of the intrinsically hydrophobic substrate by hydrophilic materials. On the other hand, over hydrophilization and over roughening by tedious modifications usually weaken the engineered superwetting membranes, leading to poor structural integrity, performance stability and production scalability [19]. It is no doubt that an ideal oil/water separation membrane should be robust, fouling-resistant and easy up-scaling for sustainable and high efficiency operation.

Keep the goal in mind, a robust polymeric composite membrane with an abrasion-resistant and chemical-resistant super-anti-oil-fouling performance was developed by an extremely simple, scalable and actually conventional one-step non-solvent induced phase separation (NIPS) process without any template-assistance and post-modification. Most notably, a semi-crystalline aliphatic polyketone (PK) polymer with intrinsic intermediate hydrophilicity and good membrane formation ability was chosen as the membrane matrix material, different from the commonly used hydrophobic polymers [20, 21]. Besides, polyvinyl alcohol (PVA), a pore-forming and hydrophilicity-enhancing additive, and nylon (or polyamide) mesh, a reinforcing skeleton embedded in membrane matrix, were employed together during the NIPS process to further improve surface hydrophilicity and mechanical strength. The effortlessly obtained PK composite membrane (named as PK/PVA-Nyl), can enable high efficiency and fouling-resistant separations of difficult oil-in-water emulsions under either the energy-saving gravity-driven dead-end mode or the more dynamic cross-flow mode.

It is worth noting that, the described synthesis strategy involving only available materials and techniques is not taken for granted but derived from our systematic innovations and investigations in the PK-based superwetting membrane. Our previous studies have shown that robust microporous PK membranes with tunable pore structure and permeability can be easily fabricated by the NIPS process [22]. The pure PK membrane exhibiting a bicontinuous fibril-like morphology was found to be superhydrophilic and underwater superoleophobic to common apolar oils (e.g. hexane). However, it can be wetted by polar oils (e.g. chloroform) in water [23]. This great but less-than-ideal underwater superoleophobicity is ascribed to the interplay between the fibril-like texture being inherently re-entrant and the intermediate hydrophilicity

of PK. In solid-oil-water systems, re-entrant structure can help establish a stable or metastable non-wetting composite state when $\theta > \psi$, even with $\theta < 90^\circ$. θ refers to the equilibrium contact angle of oil against water (θ_{ow}) or water against oil (θ_{wo}) on the smooth surface with the same chemistry of the textured surface, and ψ is the local geometrical angle of the texture. θ_{ow} and θ_{wo} are determined by the equilibrium contact angle of water in air (θ_w), and possible contact angle hysteresis, giving θ_{ow} , $\theta_{wo}^{-1} \propto \theta_w$. The re-entrant fibril-like texture (characterized by $\psi=73^\circ$) of the pure PK membrane facilitates underwater superoleophobicity, even though PK is only moderately hydrophilic (characterized by $\theta_w = 69^\circ$) [23]. This finding implies that improving PK's hydrophilicity slightly while keeping the re-entrant texture by certain means, the simpler the better, can finish the last mile for reaching the ultimate underwater oil-repellency. Herein, we report that by just blending “water-loving” PVA with PK during the one-step phase inversion, a small amount of PVA chains can be firmly retained within the PK membrane matrix as a hydrophilicity enhancer. Dosage is little but effect is great. The obtained all hydrophilic PK-PVA mixed surface chemistry gives rise to the desirable anti-oil-adhesion property for fouling-resistant filtration. Noting that, similar PVA addition in the preparation of common hydrophobic membranes, e.g. PVDF, cannot achieve such amazing underwater oil-repellency [24].

2.2. Experimental

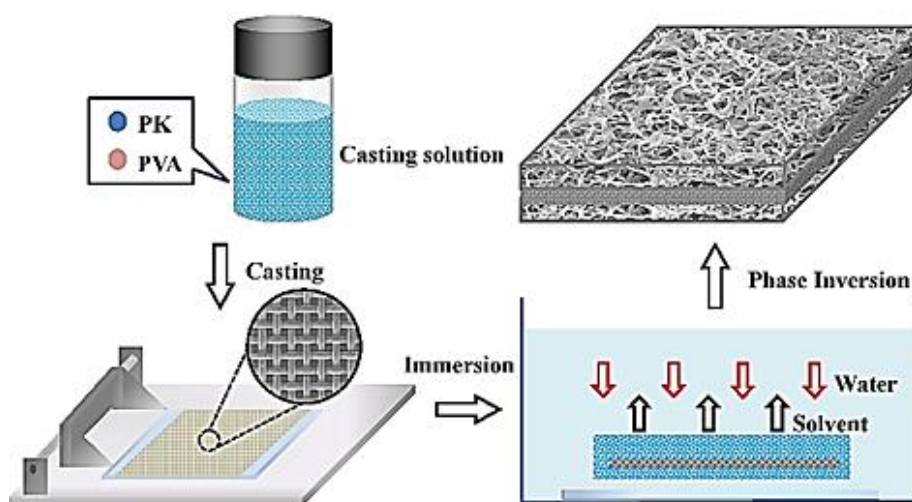
2.2.1. Materials

Aliphatic polyketone (PK; $M_w=200000 \text{ g mol}^{-1}$) was kindly supplied by Asahi Kasei Co. Ltd. (Japan). Polyvinyl alcohol (PVA) with a 90% hydrolysis degree and different polymerization degrees of 3500, 1500, and 500 (named as PVA3500, PVA1500 and PVA500), resorcinol, hexane, hexadecane, dichloroethane, chloroform, soybean oil, ethanol, acetone, N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), N-methyl pyrrolidone (NMP), and sodium dodecyl sulfate (SDS), were obtained from Wako Pure Chemical Industries Co. Ltd. (Japan). A nylon mesh fabric (100 mesh) was purchased from As One Co. Ltd. (Japan). Polystyrene nanoparticles with 100, 200 and 300 nm diameters were purchased from Thermo Scientific Inc. (USA). Polyethylene glycol (PEG, $M_w=35000$), polyvinyl pyrrolidone (PVP,

Mw=90000), and Pluronic F127 were obtained from Sigma-Aldrich Japan. Four kinds of commercial hydrophilic microporous membranes exhibiting underwater superoleophobicity were purchased, including MF-Millipore™ mixed cellulose ester (MCE, 0.22 μm), Durapore® PVDF (0.22 μm), and Omnipore™ PTFE (0.2 μm) membranes from Sigma-Aldrich Japan, and GVS Magna™ Nylon (0.22 μm) membrane from Thermo Fisher Scientific (USA). Milli-Q water (Milli-Q integral 3, Millipore SAS, France) was prepared in our lab.

2.2.2. Membrane preparation

The compositions of the casting solutions for membrane preparation with or without a nylon mesh are listed in Table. 2.1. A 10 wt% of PK powder or a mixture of PK and PVA powders (90:10 w/w) was dissolved in a resorcinol/water solvent (65:35 w/w) by stirring at 80 °C for 3 h to obtain a homogenous solution. After degassing, the solution was spread on a glass plate with or without a nylon mesh by a stainless steel casting knife with a 200 μm gap. Then, the casting film was immediately immersed into a methanol/water coagulation bath (35:65 w/w) at 25 °C. After solvent exchange and solidification, the membrane was fixed using metal frames and then washed by acetone and hexane in sequence with 20 min for each. Finally, the membrane was air-dried for further tests. Scheme. 2.1 shows the typical preparation process of a composite membrane formed by the PK/PVA1500 with nylon mesh embedded, named as PK/PVA1500-Nyl.



Scheme 2.1. Schematic illustration of the one-step NIPS process to prepared a composite membrane embedded with nylon mesh, name as PK/PVA1500-Nyl.

Table 2.1. Compositions of the dope solutions for PK membrane casting with and without PVA additives.

Membranes	PK (g)	PVA (g)	Resorcinol (g)	H ₂ O (g)
PK	5.0	0.0	29.75	15.75
PK/PVA500	4.5	0.5	29.75	15.75
PK/PVA1500	4.5	0.5	29.75	15.75
PK/PVA3500	4.5	0.5	29.75	15.75

2.2.3. Membrane characterization

The surface morphologies of the membranes were observed by a field-emission scanning electron microscopy (FE-SEM; JSF-7500F, JEOL, Japan). The surface chemical compositions were analyzed by Fourier-transform infrared spectroscopy with attenuated total reflectance (FTIR; ALPHA, Bruker, USA) and X-ray photoelectron spectroscopy (XPS; JPS-9010 MC, JEOL, Japan) with Al K α X-rays. The average pore sizes of the membranes were measured by a capillary flow porometer (CFP-1500AXLC, Porous Materials Inc., USA) with at least five times measurements to obtain an averaged value. The surface wettability was evaluated using a contact angle goniometer (Drop Master, Kyowa Interface Science Co., Japan). A droplet of water or oil with a 4–20 μ L volume was dispensed onto the membrane surface in air or in water. Each membrane was analyzed at least five times at different locations. The physical abrasion-resistance and chemical-resistance of the PK/PVA1500-Nyl composite membrane were conducted by monitoring the change of underwater hexadecane contact angle after the corresponding experiments. For the abrasion test, a membrane coupon attached onto a glass slide was pressed against an abrasive sandpaper (Grit No. 180) under a weight of about 100 g. The membrane was transversely and then longitudinally (10 cm in each direction) abraded by the sandpaper, as shown in Fig. 2.3, called one test cycle. To evaluate the effect of abrasion on the separation performance, filtrations of hexadecane-in-water emulsion (10000 ppm oil, 1 ppm SDS) and nanoparticles (100 nm and 200 nm) were conducted using the pristine and abraded membrane. For the chemical-resistance test, a piece of membrane was immersed in acidic, salty, alkaline aqueous solutions and five typical organic solvents, respectively, with 20 h for each. Then the underwater hexadecane contact angle was measured.

2.2.4. Preparation of oil-in-water emulsions and membrane filtration

In accordance with the literature [8], hexane-in-water and hexadecane-in-water emulsions were prepared by adding 1 mL oil into 99 mL water containing 0.1 mg SDS (i.e., 10000 ppm oil and 1 ppm SDS), followed by 12 h stirring at 1000 rpm min⁻¹. Soybean oil-in-water emulsions with different oil concentrations (10000-100000 ppm) were prepared by the same procedure. The oil droplet sizes and size distributions of the emulsions were analysed using a dynamic light scattering (DLS; ELSZ-1000ZA, Otsuka Electronics, Japan) apparatus and an optical microscope (BX50, Olympus, Japan). The oil contents in the permeants were measured by a total organic carbon analyser (TOC; TOC-VCSH, Shimadzu, Japan).

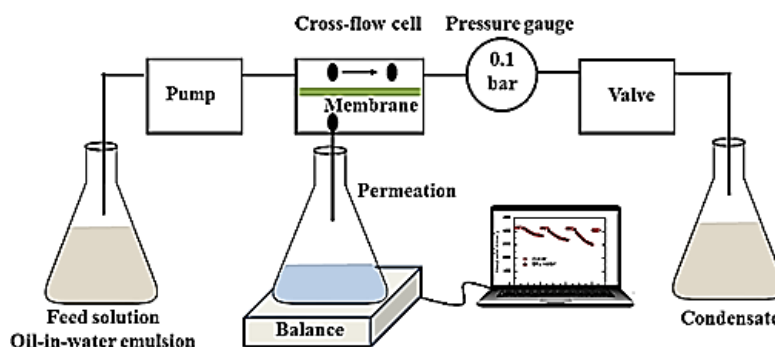
Membrane filtrations were conducted with the prepared PK/PVA1500-Nyl composite membrane in a cross-flow membrane cell with an effective area of 22 cm² under a pressure of 0.1 bar and a flow rate of 150 mL min⁻¹, as shown in Scheme. 2.2. Firstly, the pure water flux, J_1 , was measured and calculated according to Eq. (2-1):

$$J_1 = \frac{V}{A \times t} \quad (2-1)$$

where V is the permeate volume (L), A is the membrane area (m²) and t is the sampling time (h). Then, the feed solution was exchanged to oil-in-water emulsion. After a certain filtration volume, pure water was charged into the system to remove the rejected and accumulated oil layer on the membrane surface, and the recovered pure water flux was also recorded. The pure water flux measured at the end of filtration, J_2 , was used to evaluate the anti-oil-fouling property of the membrane by calculating the flux recovery ratio (FRR) using Eq. (2-2):

$$FRR = \frac{J_2}{J_1} \times 100\% \quad (2-2)$$

The PK/PVA blend membranes without nylon mesh (PK/PVA3500, PK/PVA1500, and PK/PVA500), and the other four commercial hydrophilic membranes were tested in dead-end membrane filtrations, to compare their anti-oil-fouling properties. A membrane filtration apparatus (KG25, ADVANTEC MFS, Inc., Japan) with an effective area of 2.1 cm² was used. Pure water or the prepared emulsion was poured directly onto the membrane surface to keep a 10 cm liquid column (about 0.01 bar) to initiate gravity-driven filtration for the PK-based membranes. The flux variation and water flux recovery were determined by the same method described above.



Scheme 2.2. Schematic illustration of the laboratory-scale cross-flow filtration system to conduct membrane filtration of oil-in-water emulsions.

2.2.5. Molecular dynamic (MD) simulation of PK/PVA blend system

Two model polymers, PK and PVA with the respective monomeric units of $\text{CH}_2\text{CH}_2\text{C}=\text{O}$ and $\text{CH}_2\text{CH}-\text{OH}$, were created following the MD simulation procedures using the BIOVIA Materials Studio commercial software, to analyse the intermolecular and intramolecular interactions in the PK/PVA blend system in water. Firstly, the PK/PVA blend system with a molar ratio of 10:1 and a total density of 1.3 g cm^{-3} (close to that value of crystalline PK) was constructed using an Amorphous Cell module [25, 26]. Geometry optimization was introduced to minimize the energy of the model structure, energy calculations and changes in the structures of 5000 iterations were carried out to establish the initial polymer structure. Thereafter, an MD duration with an NVT ensemble (fixed atom number, system volume, and temperature) was applied to obtain equilibrium molecular structures. Finally, the reasonable equilibrium structure was adopted for the next calculation. The PK/PVA blend system described above was set between two baths of water molecules. To understand the interaction between the polymers and water molecules, a simulation period of 4000 ps was used for the NVT ensemble [27-29]. In this simulation, the condensed-phase optimized molecular potential for atomistic simulation studies (COMPASS) force field was adopted to perform the energy minimization and MD calculation processes. Radial distribution function (RDF) analyses were employed to reveal the possible intramolecular hydrogen bonds within the polymers and the intermolecular hydrogen bonds between the polymers and water molecules.

2.3. Results and discussion

2.3.1. Characterization of the PK/PVA1500-Nyl composite membrane

Fig. 2.1(a)-(d) show the SEM images of the prepared composite membrane, PK/PVA1500-Nyl. A nylon mesh with regular cylindrical fibers (Fig. 2.1(c)) was skilfully embedded in the PK/PVA membrane matrix consisting of interconnected microfibrils throughout the cross-section (Fig. 2.1(a) and 2.1(b)) and the top surface (Fig. 2.1(d)) areas. FTIR spectrum in Fig. 2.1(e) confirms the strong characteristic carbonyl band ($\text{C}=\text{O}$) at 1687 cm^{-1} and the small but visible hydroxyl band ($-\text{OH}$) at 3300 cm^{-1} , ascribed to PK and PVA, respectively. XPS C1s core-level analysis shown in Fig. 2.1(f) indicates three curve-fitted peaks at 291.5 eV ($\text{C}-\text{C}$), 292.7 eV ($\text{C}-\text{O}$), and 294.2 eV ($\text{C}=\text{O}$) [21], then the relative ratio of hydroxyl to carbonyl groups within the membrane surface region can be estimated as 29%, corresponding to a PK-PVA mixed surface chemistry.

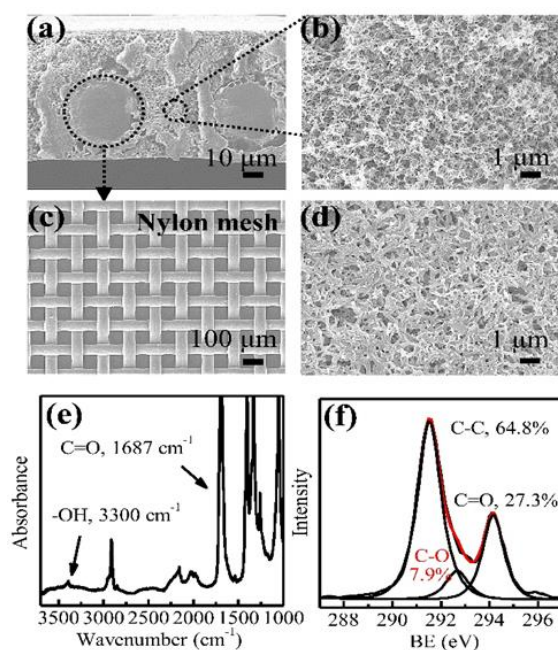


Fig.2.1. Surface morphology and surface chemistry of the prepared composite membrane, PK/PVA1500-Nyl. (a)-(d) SEM images of (a) the composite cross-section, (b) an enlarged part of the PK/PVA membrane cross-section, (c) the nylon mesh and (d) the top surface of the composite. (e) FTIR spectrum and (f) XPS spectrum of C1s core-level signal of the composite membrane.

Fig. 2.2 (a) presents the results of the underwater oil contact angles measurements on PK/PVA1500-Nyl. The observed very large apparent contact angles for hexane (164 °), hexadecane (164 °), soybean oil (166 °), dichloroethane (155 °), and chloroform (151 °), indicate the excellent underwater superoleophobicity toward typical apolar, polar and adhesive oils. Different from many underwater superoleophobic composite materials relying on a delicately engineered thin functional layer [9,12,13,30-33], the composite membrane formed by phase separation exhibits a uniform chemistry and structure across the whole matrix (see Fig. 2.1(b)-(d)), which provides the inherent abrasion-resistance desired for practical applications. Fig. 2.2 (b) shows that a membrane sample being abraded against a sandpaper under 100 g weight with 10-30 cycles (details shown in Fig. 2.3), similar to the previous study [34], can still maintain the high underwater hexadecane contact angle on its obviously distorted surface (Fig. 2.3 (b)). However, the membrane filtration efficiency (Fig. 2.3 (c)) and cut-off size (Fig. 2.3 (d)) are also kept the same. On the other hand, the composite membrane demonstrated excellent chemical-resistance as expected, due to the inherently solvent-inert nature of the employed materials, including PK, nylon, and PVA [20,34-36]. As shown in Fig. 2.2 (c), after 20 h immersion into 0.1 M HCl, 1 M NaCl, 0.1 M NaOH, ethanol, acetone, DMAc, DMSO, and NMP, no change in the underwater hexadecane contact angles can be observed. Moreover, the composite membrane can display an intriguing self-cleaning ability even when pre-wetted by oil in a dry state because of its strong underwater oil-repellence and water affinity. Fig. 2.2 (d) shows that the composite membrane wetted by the low-surface-intension soybean oil can be easily cleaned by just immersing in water. The adsorbed oil was quickly squeezed out and beaded up on the membrane surface, then left by gently shaking.

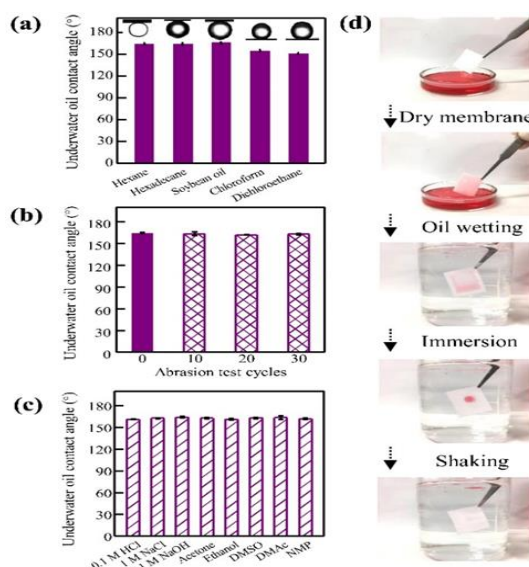


Fig.2.2. Surface wettability and its abrasion-resistance and chemical-resistance of PK/PVA1500-Nyl. (a) Underwater oil contact angles. (b) Underwater hexadecane contact angles after different abrasion cycles. (c) Underwater hexadecane contact angles after immersing the composite in different aqueous solutions and organic solvents for 20 h. (d) Self-cleaning ability of an oil pre-wetted membrane sample.

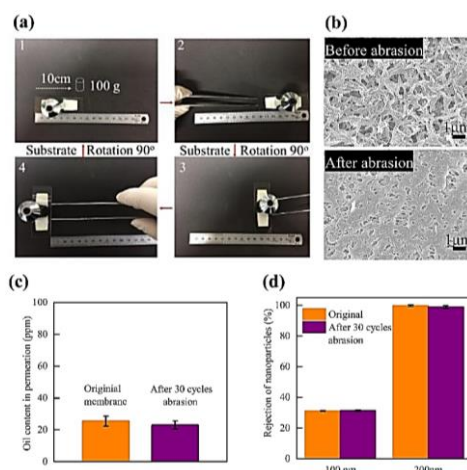


Fig.2.3. Effect of abrasion test on the performances of the PK/PVA1500-Nyl composite membrane: (a) Photographs of the sandpaper abrasion test procedures including four steps in one cycle; (b) SEM images of the composite membrane surface before and after the abrasion test; (c) Oil/water separation performances before and after abrasion for the filtration of hexadecane-in-water emulsion (10000 ppm oil and 1 ppm SDS); (d) Rejections of nanoparticles before and after abrasion.

Further, in the cross-flow membrane filtration using PK/PVA1500-Nyl, a high pure water flux at about $420 \text{ Lm}^{-2}\text{h}^{-1}$ under 0.1 bar, and a 99.7% rejection of the 200 nm nanoparticle and 31.2% rejection of the 100 nm nanoparticle were observed. The membrane cut-off size is thus estimated to be less than 200 nm, which is sufficient for many emulsions containing small oil droplets. Fig. 2.4. presents the results of cross-flow filtrations of four kinds of oil-in-water emulsions. As shown in Fig. 2.4 (a), a milky white feed emulsion containing 10000 ppm soybean oil and 1 ppm SDS with the droplet size mainly distributed around 200 nm, turned completely transparent with no visible oil droplets in the optical microscope observation and DLS measurement. Only the TOC analysis showed a very low oil content at 20.3 ± 1.1 ppm in the permeant, corresponding to the free passage of a few very small oil droplets (<200 nm). Such high separation efficiency was also achieved for the less difficult hexane-in-water and hexadecane-in-water emulsions, with the oil permeate at 23.2 ± 2.9 and 25.5 ± 3.2 ppm, respectively.

Fig. 2.4(b)-(e) show the real-time flux variations and water flux recoveries after water cleaning for the soybean oil-in-water and hexadecane-in-water emulsions. Overall, the flux decline during each filtration was very slow, and the composite membrane easily restored its water flux (about $420 \text{ Lm}^{-2}\text{h}^{-1}$) by water flushing, giving a very high flux recovery ratio (FRR) at 93-96%. With increasing the oil content of soybean oil emulsions from 10000 ppm (Fig. 2.4(b)) to 100000 ppm (Fig. 2.4(c)), the rate of flux decline was relatively faster as expected. For the high-salinity soybean oil emulsion containing 3.5 wt% sea salt (Fig. 2.4(d)), there is almost no difference between the emulsion flux and the pure water flux, indicating no membrane fouling. This excellent antifouling property can be attributed to the lower fouling propensity of the insufficiently emulsified feed solution in the presence of high salinity, and also to the salinity-tolerant underwater superoleophobicity of the prepared composite membrane. A similar non-fouling filtration was also achieved with the less fouling hexadecane-in-water emulsion containing 10000 ppm oil as shown in Fig. 2.4(e). In addition, the filtration test was conducted under the more difficult hydrodynamical conditions (Fig. 2.5), that is, lower water cleaning frequency or no cross-flow circulation of the feed solution (by blocking the outlet of the feed pipe). As expected, the emulsion flux dropped more rapidly, even to zero at

the approximated dead-end mode, but a high FRR of 92 % was still achieved after water flushing. This clearly testifies to the excellent super-anti-oil-fouling property of PK/PVA1500-Nyl even faced with challenging feed emulsions and filtration conditions, and also the advantages of cross-flow mode in enabling continuous and sustainable oil/water separation.

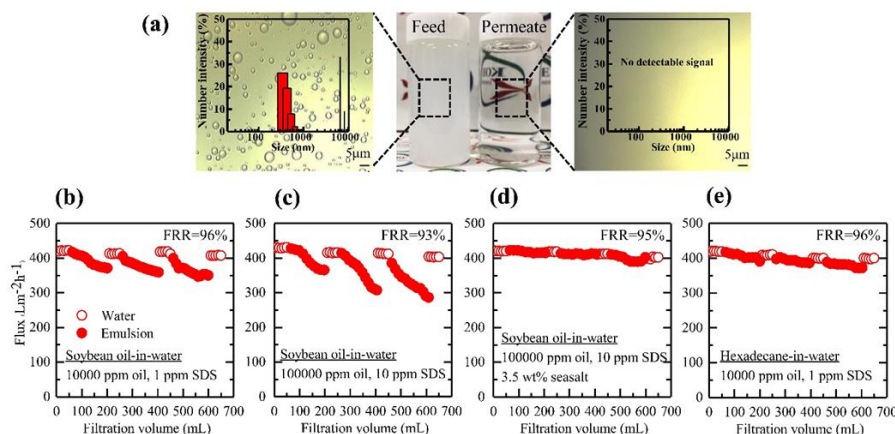


Fig.2.4. Cross-flow filtrations of oil-in-water emulsions by PK/PVA1500-Nyl under 0.1 bar: (a) Photographs and microscope images of a soybean oil-in-water emulsion containing 10000 ppm oil and 1 ppm SDS before and after filtration. The inset pictures show the corresponding oil droplets size and size distribution of the emulsions determined by DLS measurements; (b)-(e) Flux variations recorded during the cross-flow filtrations of different soybean oil-in-water emulsions, including (b) 10000 ppm soybean oil and 1 ppm SDS, (c) 100000 ppm soybean oil and 10 ppm SDS, and (d) 100000 ppm soybean oil, 10 ppm SDS, and 3.5 wt% sea salt, (e) 10000 ppm hexadecane and 1 ppm SDS.

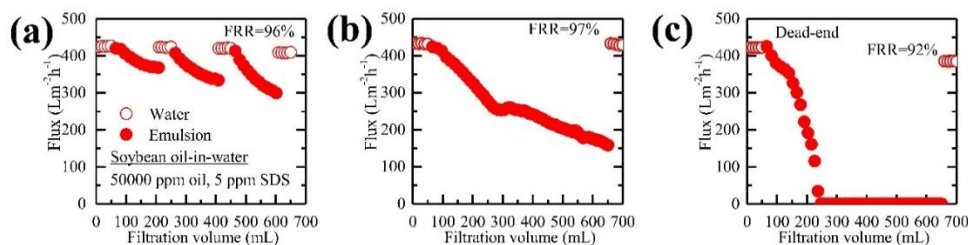


Fig.2.5. Flux variations and flux recoveries after water cleaning for the filtrations of a soybean oil-in-water emulsion containing 50000 ppm oil and 5 ppm SDS by PK/PVA1500-Nyl in the cross-flow cell with (a) three times regular water cleaning, (b) only once water cleaning and (c) no circulation, equivalent to the dead-end mode.

Table 2.2 compares the prepared PK/PVA1500-Nyl with a list of selected high-performance superwetting membranes for oil-in-water emulsion separation. The control membranes were prepared by different materials and methods, e.g., hydrogel coating [16], polydopamine (PDA) deposition [13,15], electrospinning [14], alkaline-induced phase separation [1] vacuum filtration [37], surface oxidation [38] and so on. From the membrane production scalability point of view, the simple one-step NIPS process with conventional conditions reported in this work is more advantageous [19]. Meanwhile, even for the highly fouling soybean oil emulsion (100000 ppm oil), PK/PVA1500-Nyl demonstrated the outperforming or at least comparable filtration flux ($420 \text{ Lm}^{-2}\text{h}^{-1}$ under 0.1 bar), flux recovery ($\sim 93\%$), and oil rejection (~ 20 ppm permeate). It is worth noting that the PK/PVA1500 membrane without the nylon mesh support can also demonstrate similar filtration performance with a slightly higher water flux at $480 \text{ Lm}^{-2}\text{h}^{-1}$ at 0.1 bar, due to its improved membrane porosity. By contrast, a previously reported inorganic nano-wired copper mesh-based membrane with estimated less than $1 \mu\text{m}$ pore size, delivered $500 \text{ Lm}^{-2}\text{h}^{-1}$ flux and about 60 ppm oil permeate under gravity-driven dead-end filtration [38]

The above characterizations clearly demonstrate the simplicity, robustness and high performance of the prepared composite membrane. Next, we clarified how PVA effects the PK membrane's surface chemistry and surface morphology as a pore-former and more importantly, a hydrophilicity-enhancer by its interplay with PK, and why PVA1500 is the optimal choice among other PVAs with different polymerization degrees. Noting that as a well-known membrane additive, PVA has been widely used in preparation of common hydrophobic polymeric membranes, e.g. PVDF and PSf. However, to the best of our knowledge, none of them can be granted a sufficient or satisfactory underwater oil-repellency, due to the difficulty in the full coverage of the hydrophobic membrane matrix and the poor low retention of incompatible PVA [24,39].

Table 2.2. Comparison of the selected high performance membranes for separation of oil-in-water emulsions

Material, Method	Underwater oil contact angle	Underwater oil sliding angle	Oil emulsion type, content (ppm)	Emulsion flux (Lm ⁻² h ⁻¹ bar ⁻¹), Flux recovery	Filtration mode, Pressure (bar)
PAN, Electrospinning & Electrospinning [14]	Hexane, 160 °	-	Hexane, 10000	693, 95%	Dead-end, 0.1
TCNCs suspension, Vacuum filtration [37]	Hexane, 157 °	-	Isooctane, 10000	1800, 95%	Dean-end, 0.5
Hydrogel on PVDF, Grafting [16]	Hexane, 153 °	-	n-Dodecane, 3600	900, 96%	Cross-flow, 0.2
PAN, Alkaline-induced NIPS [1]	Hexane, 156 °	-	Isooctane, 10000	2500, 85%	Cross-flow, 1.0
PDA on PVDF, Coating [15]	Chloroform, 155 °	-	Chloroform, 20000	1800, 91%	Dead-end, 0.9
PDA/TiO ₂ on PVDF, Coating [13]	Hexadecane, 150 °	-	Hexadecane, 10000	600, 94%	Dead-end, 0.9
Cu(OH) ₂ nanowire on copper mesh, Surface oxidation [38]	Soybean oil, 155 °	-	Soybean oil, 100000	500, -	Dead-end, gravity
PK/PVA1500-Nyl, NIPS (this work)	Hexane, 164 °	3 °	Hexadecane, 10000	4200, 96%	Cross-flow, 0.1
	Soybean oil, 166 °	5 °	Soybean oil, 100000	4000, 93%	

“-” means no report.

2.3.2. Characterization of PK/PVA blend membranes with different PVA additives

The PK/PVA blend membranes without nylon mesh were prepared to clearly characterize the effects of PVA additives on the membrane properties. Three different PVA polymers (namely, PVA3500, PVA1500, and PVA500) were used in the NIPS process with all the other fabrication conditions kept the same, giving the corresponding PK/PVA3500, PK/PVA1500,

and PK/PVA500 membranes. Fig. 2.6(a) compares the SEM images of the top surfaces of the blend membranes and a pure PK membrane. The addition of PVA resulted in the gradually increased surface porosity with $\text{PK} < \text{PVA3500} < \text{PVA1500} < \text{PVA500}$, and increased average pore size from 63 to 140 nm as measured by a capillary flow porometer, as shown in Fig. 2.6(b). This indicates that a shorter PVA chain with a better mobility and water solubility can easily leach out from the membrane matrix into the aqueous environment during phase inversion, leading to a stronger pore-forming effect. Fig. 2.6(b) also displays the calculated ratio of hydroxyl to carbonyl groups at the membrane surfaces according to the XPS C1s core-level analyses, giving $\text{PK} (0\%) < \text{PK/PVA500} (10.2\%) < \text{PK/PVA1500} (27.0\%) < \text{PK/PVA3500} (43.4\%)$. A larger PVA can be more easily retained in the PK substrate and lead to a higher surface hydroxyl content at the membrane surface. In addition, the large PVA polymer also caused more macrovoids in the membrane cross-section (shown in Fig. 2.7), possibly because its stronger interactions with PK (e.g., hydrogen-bonding and chain entanglement) result in the formation of PK-PVA complexes with decreased solubility as the poor phase in the dope solution. Then the nucleus will gradually grow by absorbing the solvent and non-solvent during the membrane formation process and finally form macrovoids [40].

The contact angles of water-in-air and oil-in-water shown in Fig. 2.6(c)-(f) clearly demonstrate that the higher surface hydroxyl content led to the stronger underwater oil-repellency of the PK/PVA blend membranes. Fig. 2.6(c) shows that all of the pure and blend membranes were easily wetted by water in air, with the initial contact angles slightly decreased from 52.5° (PK) to 41.1° (PK/PVA3500). Fig. 2.6(d)-(f) show that the underwater oil contact angles increased with surface hydroxyl content, from 0° to 157.3° for chloroform, 160.5° to 164.5° for hexadecane, and 166.0° to 170.2° for soybean oil. The PK membrane was completely wetted by chloroform in water due to its intermediate hydrophilicity, as discussed detailed in our previous study [23]. Fig. 2.6(f) shows the underwater soybean oil sliding angles. An oil droplet easily rolled off on the blend membranes at a tilt angle of $3\text{--}9^\circ$, but pinned on the PK membrane surface even at 9° . In addition, a dynamic “approach-compress-detach” contact angle test (Fig. 2.8) performed on the membranes further displayed the decreasing oil adhesion force with increasing surface hydroxyl content, corresponding to a larger soybean oil droplet

with the least volume to allow feasible releasing from the dispensing needle onto the membranes by the aid of larger buoyance.

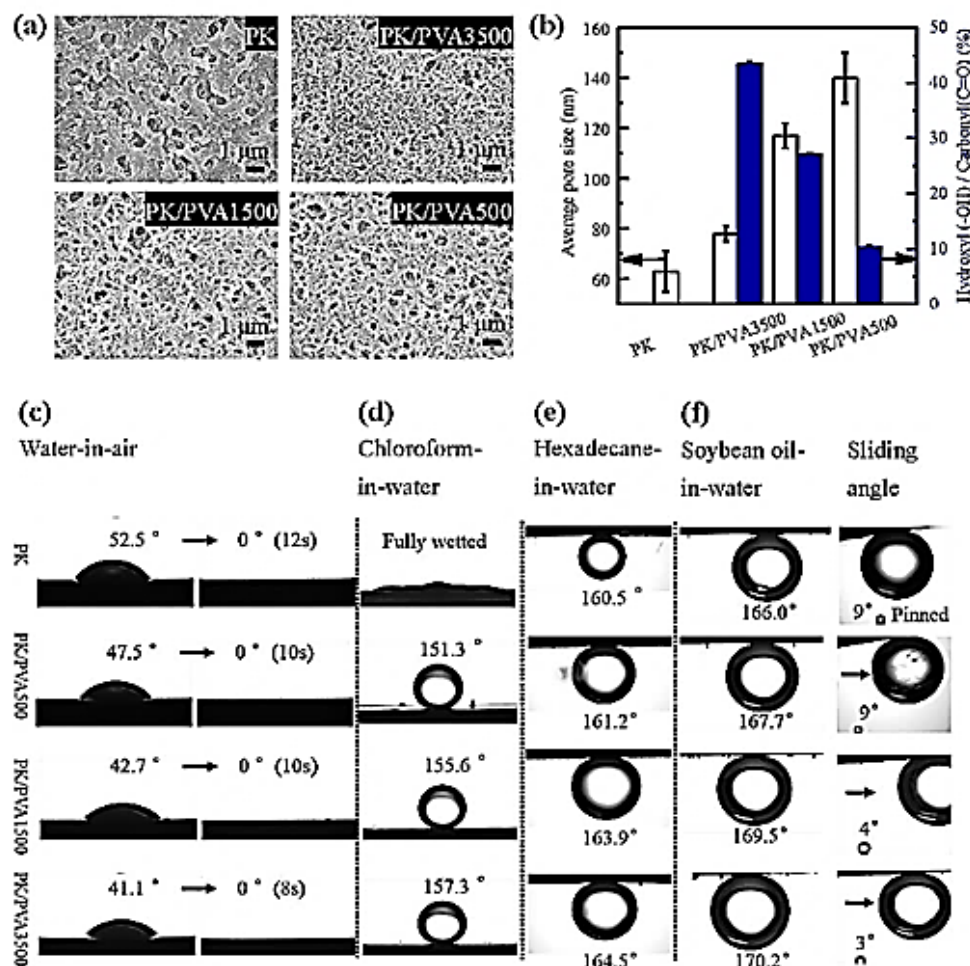


Fig.2.6. Effects of different PVA additives (PVA3500, PVA1500, and PVA500) on the surface morphology, pore size, and chemical composition of the corresponding PK/PVA blend membranes without nylon mesh: (a) Top surfaces of the pure PK membrane and the blend membranes; (b) Average pore sizes analyzed by capillary flow porometer and surface ratios of hydroxyl groups (from PVA) to carbonyl groups (from PK) calculated from the XPS C1s core-level signals; (c)-(f) Photographs of water-in-air and oil-in-water contact angle tests: (c) water-in-air, (d) chloroform-in-water, (e) hexadecane-in-water, and (f) soybean oil-in-water.

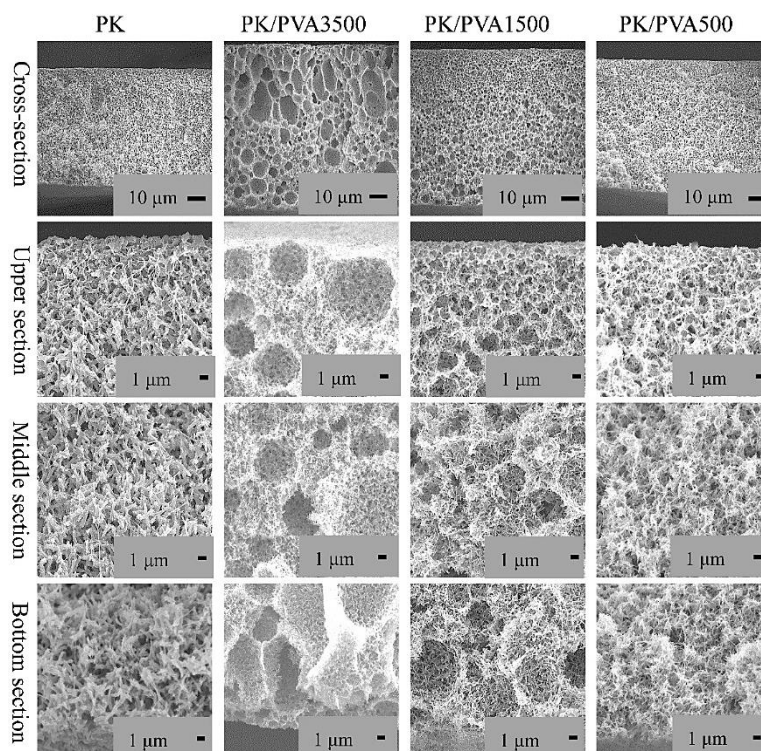


Fig.2.7. Cross-section morphologies of the pure PK membrane and PK/PVA blend membranes.

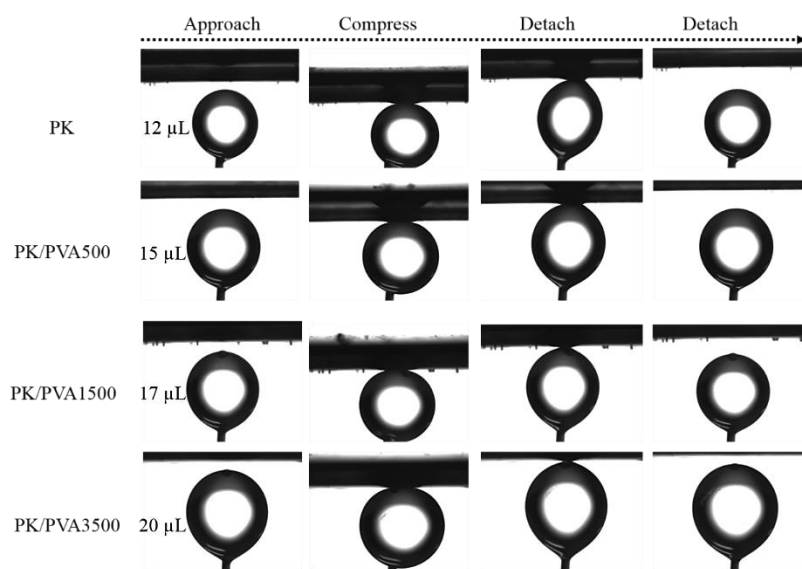


Fig.2.8. Dynamic underwater soybean oil-adhesion measurements on the pure PK membrane and the PK/PVA blend membranes, showing the critical oil droplet volume beyond which the oil droplet release from the dispensing needle can be achieved.

Then, dead-end filtration driven only by gravity (0.01 bar) was employed to test the anti-oil-fouling performances of the PK/PVA blend membranes. In this nearly static operation mode without high shearing flow, the surface property and pore structure of the membrane should be mainly responsible for the filtration performance. Fig. 2.9(a) demonstrates that the pure water fluxes and rejections of polystyrene nanoparticles (100, 200, and 300 nm diameters) are consistent with the enlarged membrane pore size due to the pore-forming effect of PVA. The tight PK membrane completely rejected the smallest 100 nm nanoparticle, while the loose PK/PVA1500 with about two times larger water flux ($168 \text{ Lm}^{-2}\text{h}^{-1}$) allowed its free passage, but completely rejected the 300 nm and 200 nm nanoparticles. The cut-off size of PK/PVA1500 is sufficient for the clearance of the emulsified oil droplets larger than 200 nm (see Fig. 2.9(a)).

The oil/water filtrations using hexadecane-in-water and soybean oil-in-water emulsions containing 10000 ppm oil and 1 ppm SDS were conducted by the membranes. As shown in Fig. 2. 10, no oil droplet can be observed in the permeant under the optical microscope observation. Fig. 2.9(b) shows the low oil content of 21-29 ppm detected in the permeant for each membrane, far less than the discharge standard set by the Environment Protection Agency of the US government (42 ppm) [7]. Fig. 2.9(c) and 2.9(d) compare the recorded flux variations and flux recoveries. A very small flux decline and a very high FRR at 94-98% were observed for each membrane during the filtrations of hexadecane emulsion. For the highly fouling soybean oil, all membranes displayed obvious and gradual flux declines. The FRR at the end of the filtration is in the order of PK (70%)< PK/PVA500 (82%)< PK/PVA1500 (90%)< PK/PVA3500 (94%), correlating very well with the trend of increasing surface hydroxyl contents and thus hydrophilicity and underwater oil-repellency. Based on the results above, PVA1500 was regarded as the optimal additive resulting in excellent anti-oil-fouling property and filtration efficiency (flux and rejection) of the PK blend membrane, thus was chosen to prepare the composite membrane with nylon mesh support for long-term operation in the more intensive cross-flow filtration.

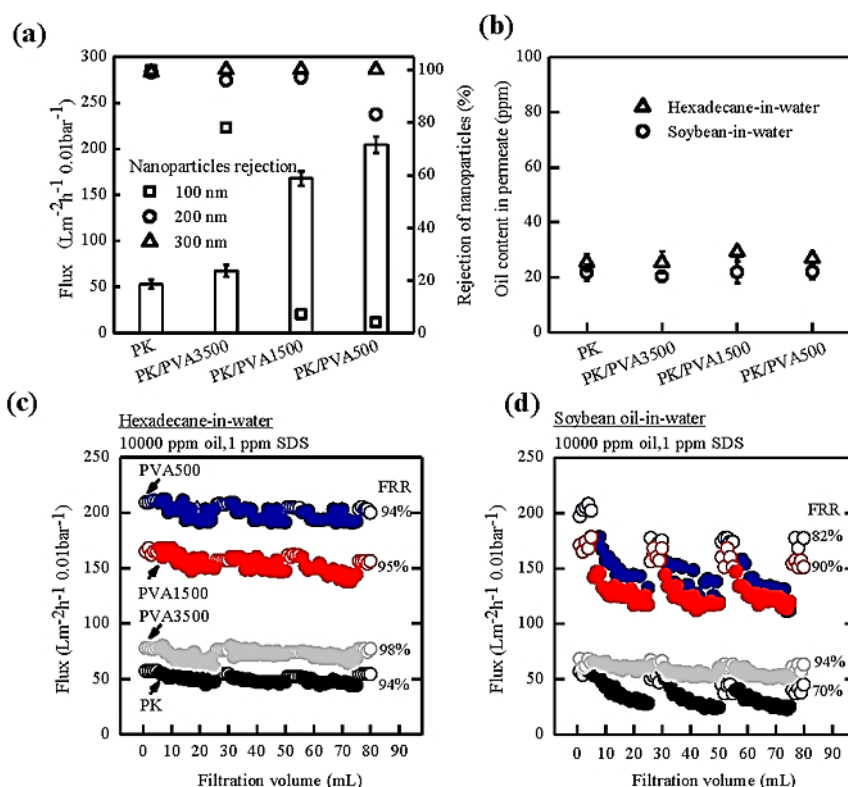


Fig.2.9. Effects of different PVA additives (PVA3500, PVA1500, and PVA500) on the gravity-driven filtration performances (10 cm liquid column height, ~ 0.01 bar) of the corresponding PK/PVA blend membranes without nylon mesh: (a) Pure water flux and rejection of polystyrene nanoparticles with 100 nm, 200 nm, and 300nm diameters; (b) Oil content in permeate for filtrations of hexadecane-in-water and soybean oil-in-water emulsions with 10000 ppm oil and 1 ppm SDS; (c)-(d) Flux variations recorded during the filtrations of (c) hexadecane-in-water and (d) soybean oil-in-water emulsions.

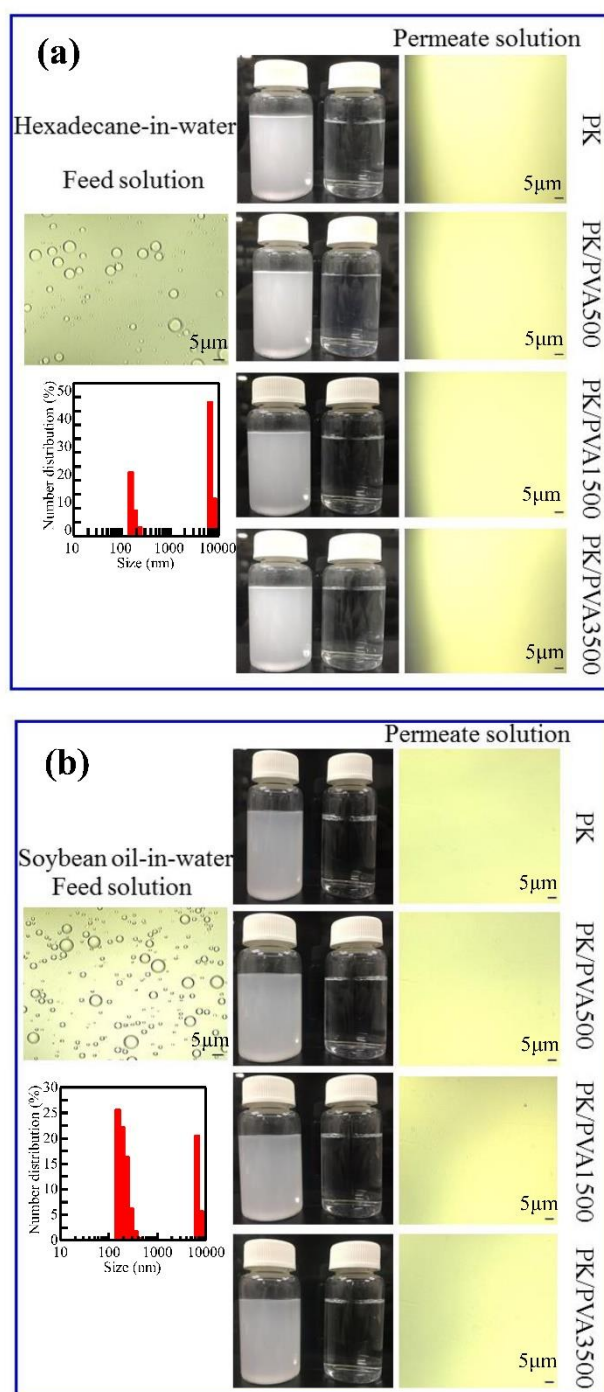


Fig.2.10. Optical microscope images and digital photos of the oil-in-water emulsions (10000 ppm oil and 1 ppm SDS) before and after filtration by the PK/PVA blend membranes under the dead-end mode: (a) hexadecane-in-water emulsion and (b) soybean oil-in-water emulsion.

In addition, four representative commercial membranes, including MCE, Nylon, PTFE, and PVDF with intrinsically or endowed hydrophilicity and underwater superoleophobicity [41], were also tested for comparison. It can be seen from Fig. 2.11, at the same initial flux of $170 \text{ Lm}^{-2}\text{h}^{-1}$, all of them suffered much severer flux declines and gave a lower FRR at 83%, 74%, 70% and 10%, respectively. Table 2.3 summarizes their unsatisfactory surface wettabilities and filtration performances as compared to PK/PVA1500. Another interesting finding is that other water-soluble additives widely used in the NIPS process for membrane hydrophilization, such as polyethylene glycol (PEG), polyvinyl pyrrolidone (PVP) and Pluronic F127, cannot deliver the same hydrophilicity improvement as PVA does. Fig. 2.12 shows that the PK blend membranes prepared using these three additives with the same dosage instead of PVA, can be easily wetted by chloroform in water, similar to the pure PK membrane without additives. Favourable molecular level interactions like hydrogen-bonding between PK and PVA shall be responsible for the stable entrapment of PVA in the PK matrix.

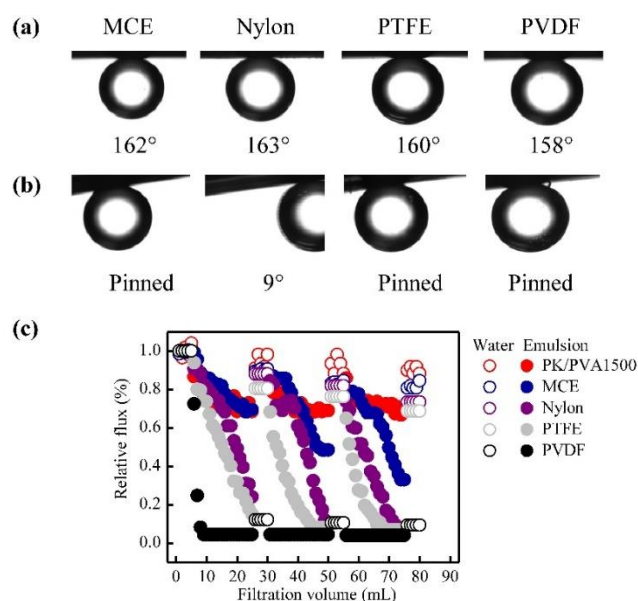


Fig.2.11. Comparison of the surface wettabilities and oil-in-water emulsion filtration performances of four commercial hydrophilic membranes and PK/PVA1500: (a) underwater soybean oil contact angles; (b) underwater soybean oil sliding angles; (c) Flux variations and recoveries recorded during the filtrations of soybean oil-in-water emulsion (10000 ppm oil and 1 ppm SDS) at the same initial flux of $\sim 170 \text{ Lm}^{-2}\text{h}^{-1}$.

Table 2.3. Summary of the performances of the commercial hydrophilic membranes and PK/PVA1500

Membranes	Water contact angle (°)	Underwater oil contact angle ^a (°)	Sliding angle ^a (°)	Emulsion flux ^b (Lm ⁻² h ⁻¹ 0.01 bar)	Oil rejection ^b (%)	Flux recovery ^b (%)
MCE	38	162	pinned	100	99.8	83
Nylon	43	163	9	51	99.5	74
PTFE	49	160	pinned	116	99.5	70
PVDF	62	158	pinned	21	99.6	10
PK/PVA1500	42	170	4	140	99.7	90

^aSoybean oil as the probe oil, ^bSoybean oil-in-water emulsion (10000 ppm oil and 1 ppm SDS) filtrated under gravity-driven dead-end mode under 0.01 bar.

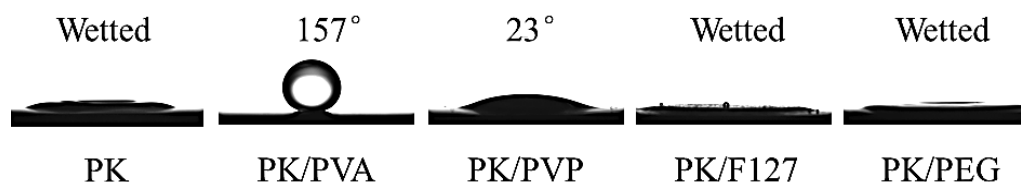


Fig.2.12. Underwater chloroform contact angles on the prepared PK, PK/PVA, PK/PVP, PK/F127, and PK/PEG membranes.

2.3.3. Molecular dynamics (MD) simulation on PK/PVA blend system

MD simulation was carried out to reveal how the underlying molecular-level interactions contribute to the retention of “water-loving” PVA within the moderately hydrophilic PK matrix, rather than leaching out completely. Fig. 2.13(a) shows a constructed PK/PVA blend film (10:1 ratio) set between two water tanks. It is found that the PVA chains were stably confined within the PK matrix in the water environment after reaching an equilibrium state. Radial distribution function (RDF) analyses of the bonds between the oxygen-oxygen of PVA (Fig. 2.13(b)) and between the oxygen of PK and oxygen of PVA (Fig. 2.13(c)) indicate that there are strong intramolecular hydrogen bonds (H-bonds) formed within PVA chains and intermolecular H-bonds formed between PVA and PK, by showing the first peak at about 0.28 nm (corresponding to direct H-bonds between the relevant atoms). In addition, both the PVA chains (albeit, in the minority) and PK chains near the solid-water interface can interact strongly with water by H-bonds (Fig. 2.13(d)) as expected. This emphasizes the complete hydrophilic surface chemistry

of the PK/PVA blend system without a hydrophobic domain, which is far superior than that of many reported functional membranes with mixed hydrophobic and hydrophilic chemistries.

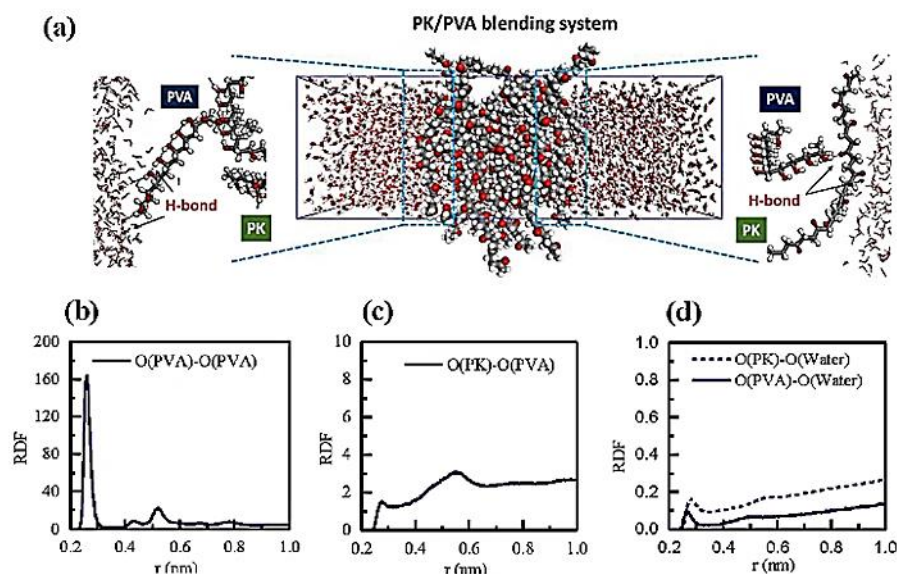


Fig.2.13. Molecular dynamics (MD) simulation analysis of the PK/PVA blend system: (a) A representative snapshot of the simulated PK/PVA blend (10:1 molar ratio) system in water, with the enlarged part on the left showing intermolecular H-bonds formed between PVA and water and intramolecular H-bonds within PVA, and the enlarged part on the right showing intermolecular H-bonds between PK and PVA and between PK and water. Atoms are color-coded as follows: C, gray; O, red; H, white; (b)-(d) RDF analyses in (b) between oxygen atoms of PVA, (c) between oxygen of PK and oxygen of PVA, and (d) between oxygen of PK or PVA and oxygen of water.

2.4. Conclusions

This study demonstrated an innovative PK composite membrane with super-anti-oil-fouling property, strong abrasion-resistance and chemical-resistance for sustainable and high efficiency filtration of oil-in-water emulsions in large-scale. Most notably, this membrane was effortlessly developed by the extremely simple and scalable phase separation approach using PK with intrinsic intermediate hydrophilicity as membrane matrix, hydrophilic PVA as membrane formation additive, and nylon mesh as mechanical support. Comprehensive

experimental and theoretical analyses revealed that a small amount of PVA additive trapped within the PK membrane matrix can help reach the desirable underwater superoleophobicity. The composite membrane can enable outperforming fouling-resistant cross-flow filtrations of highly fouling oil-in-water emulsions with very low or no fouling occurred, as compared to the state-of-the-art membranes reported. The fascinating membrane performance and the preparation cost-effectiveness highlight the high application potential of the newly developed membrane, especially for the substantial treatment of challenging emulsified oily wastewater.

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Chapter 3

Ultrathin in situ silicification layer developed by an electrostatic attraction forced strategy for ultrahigh performance oil/water emulsion separation

3.1. Introduction

While historical trends indicate the rapid expansion of manufacturing industries, there is an increasing interest in high-performance oil-in-water emulsions separation [1-3]. Generally, the pollutants in oily emulsions are immiscible mixtures, such as insoluble fatty glycerides, and other related oil/water mixtures composing of unstable oil droplets, free-floating oils, or stable emulsions [4, 5]. Handling the oily contaminated wastewater to meet the requirements of discharge standard for these emulsions is of distinct importance for augmenting water supply. Compared to the traditional purification technology against oily wastewater, such as chemical coagulation, electrocoagulation, physical adsorption, and centrifugation, membrane separation has been acknowledged as a more effective alternative, with the main advantages of low operational cost, high energy saving, high flexibility, and facile scalability [6-8].

Although the membranes used for the emulsified oil/water separation have been developed greatly, most of those are still suffering from severe membrane fouling issue that leads to a quick permeating flux attenuation due to the irreversible adsorption of oil droplets onto the surface, or the inner-pore structures of the membranes when used for oily emulsions purification [9-11]. To a large extent, the membrane fouling has resulted in a great impedance on the development of membrane technology for the practical oil/water emulsions separation [12, 13]. To resolve this issue, many efforts have been devoted to introducing the membranes with high wetting selectivity that can repel the attachment of oil phase while allowing the easy

penetration of water phase through several approaches [14-16]. By noting the essence that oil/water phase has different properties of interfacial tension and wettability on a solid surface, the tailoring of special surface chemistry and nanoarchitecture with special wetting selectivity, in respect of superhydrophilic and underwater superoleophobic propensity has been proved as an effective way to realize the highly-efficient oily wastewater treatment, because its strong hydrated ability to construct a kinetic barrier with ultralow oil-adhesion property on the membrane surface or inner pores of membrane [17, 18]. Along with this concept, various hydrophilic materials (such as hydrogel, zwitterionic polyelectrolyte, mineral particles) with inherent water affinity, or oil-repellent property have been anchored on the membrane surface for emulsified oil/water separation [19-23]. Nevertheless, most of the reported works were unable to spontaneously achieve the realization of surface hydrophilic modification with its original shape retention, which only offered surface hydrophilic decoration without arisen of any intrinsic resistance [24-26]. This is because that the most reported hydrophilic decoration was achieved onto the intermediate layer of polymer matrix with additional affinity sites, thus leading to a significant increase in permeating resistance with lower oily wastewater separation efficiency [26]. Many other surface modification strategies such as atomic layer deposition (ALD), biomimetic mineralization, and chemical grafting were also analysed, as follows: ALD is an effective method to improve the surface hydrophilicity with its shape retention by depositing an inorganic layer onto an organic substrate [27]. However, to realize the formation of the uniformly defect-free inorganic layer, this technique must conduct hundreds of complicated surface modification cycles of “pulse-exposure-purge” process, with extremely demanding operating conditions of high vacuum, and high temperature ($> 80\text{ }^{\circ}\text{C}$), severely limiting the effectiveness of practical scalability [28, 29]. Biomimetic mineralization is one of the most popular methods to modify the surface chemistry by immobilization mineral particles onto the polymeric substrate surface. The deposited mineral particles thus not only contribute to the membrane surface hydrophilicity, but also lead to the pore size decreasing, which results in the higher intrinsic resistance for oil/water molecules transporting [30]. Chemical grafting is a common method to implement the hydrophilic surface modification, however, most of the grafting materials (hydrogel, zwitterionic polyelectrolyte) suffer from relatively worse

chemical resistance toward acid, alkaline, salt, and organic solvents compared to the inorganic modification materials such as SiO_2 , indicating that the chemical grafting membranes cannot be survived in relatively harsh conditions for the comprehensive oily wastewater treatment [26].

In the present work, we engineered an ultrathin silica (SiO_2) layer in situ onto the porous polyketone (PK) substrate, via the electrostatic attraction forced silicification process, as shown in Fig. 3.1. Owing to the oppositely charged forces (the APTES functionalized PK substrate with positively charged and the mineral precursor of TEOS with negatively charged), an ultrathin silicification layer with superhydrophilic and underwater superoleophobic property could be generated conformally, achieving an ultrahigh water permeance up to $7533 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, an exceptional high emulsion flux up to $6000 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ (close to the pure water permanence), with a high rejection ratio of $> 99.9\%$ against various of oily emulsions (hexane-in-water, hexadecane-in-water, petroleum ether-in-water, soybean oil-in-water, and chloroform-in-water). Compared to the water permeance of nascent PK substrate ($7669 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$), nearly no deterioration on permeating flux was obtained after the in situ mineralization process, and the overall separation property toward oily emulsions outperformed most of the state-of-the-art membranes reported so far. Due to the highly robust property of the inorganic silicification layer and the highly chemical inert of PK substrate, the SiO_2 decorated PK membrane (SiO_2 -d-PK) further exhibits a great tolerance and durability against salty, strong acid/alkaline solutions, and organic solvents.

It should be noted that the proposed in situ silicification onto the PK substrate via the well-known materials and novelty method is not taken for granted but derived from our systematic investigations on PK based super-wetting membranes [31]. Our group reported that the nascent PK material with fibril-like microstructure was found to be intrinsically hydrophilic with underwater superoleophobic property to apolar oils [32], compared to other polymers (PVDF, PP) that were commonly used for membrane substrates [19, 23]. In such circumstance, we envisioned that a nanosilica-decorated layer created surface chemistry and nanostructure with an extremely low oil-adhesion propensity, while the underlying PK substrate was presumed to act as “interface-breaking barrier” for the intruded oil droplets. The resultant SiO_2 -d-PK membrane thus rendered a thoroughly oleophobic property throughout the entire membrane-

thick range uniformly, enabling the membrane an ultrahigh antifouling property with a nearly full (100%) recovery ratio of permeating flux over the long-term cyclic emulsified oily/water separation process, even displaying a distinguished antifouling property to comprehensive oily emulsions containing various of pollutants, such as proteins, surfactants, and other natural organic materials (NOM). To sum up, for the first time, we realized the full potentiality of oily wastewater treatment by developing an ultrathin silicification layer onto a hydrophilic PK substrate, via the electrostatic attraction forced in situ silicification process, where the resultant ultrathin modification enables the simultaneous achievements of superior antifouling property for oily emulsions separation, and the ultrahigh permeating flux without arisen of any intrinsic resistance.

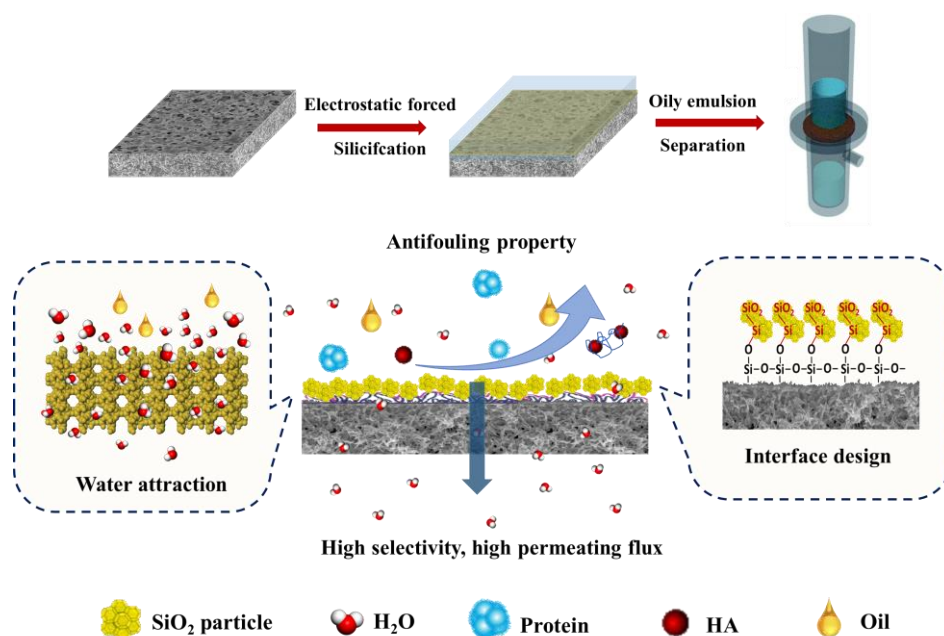


Fig.3.1. Schematic illustration of SiO₂-d-PK membrane and its application for highly-efficient oily emulsions separation.

3.2. Experimental section

3.2.1 Materials and reagents

Polyketone (PK) with the molecular weight of 200,000 g mol⁻¹ was kindly supplied by Asahi Kasei Co. Ltd. (Japan). Resorcinol, methanol, ethanol, acetone, (3-Aminopropyl)-triethoxysilane (APTES), tetraethoxysilane (TEOS), ammonia (25%) chloroform, hexane, hexadecane, petroleum ether, soybean oil, bovine serum albumin (BSA), sodium alginate (HA)

sodium dodecyl sulfate (SDS), and Tween 80 were bought from Wako Pure Chemical Industries Co. Ltd. (Japan). Polyethylene glycol (PEG, $M_w = 20000 \text{ g mol}^{-1}$), N,N-dimethylformamide (DMF) were bought from Sigma Co. Ltd (Japan). Polystyrene nanoparticle with a diameter of 100 nm was purchased from Thermo Scientific Inc. (USA). Durapore® PVDF membrane (0.22 μm) was purchased from Millipore Co. Ltd. (Japan).

3.2.2 Preparation of PK substrate, APTES-d-PK membrane, and SiO₂-d-PK membrane

The PK substrate was prepared via the non-solvent induced phase separation (NIPS) process [31]. The 10 wt% of PK and PEG powder (90:10 wt%) was dissolved into the 65 wt% of resorcinol aqueous solution, and stirred for 3h at 80 °C to obtain the homogeneous solution. After removing air bubbles, the prepared dope solution was cast on a glass plate under the gap between the casting knife and the plate of 200 μm , and then the nascent film was immediately immersed into the methanol/water coagulation bath (65:35 wt%, thermostated at 20 °C). After the desired solidification process, the resultant membrane was rinsed by hexane and acetone solution, and stored in air for further analysis. The newly-prepared membrane was designated as PK substrate.

APTES surface decoration was carried out by immersing the PK substrate into the APTES solution (2 wt.%) for desired periods, denoted as APTES-d-PK membrane. After the APTES surface decoration (24h), the positively charged APTES-d-PK membrane was subsequently immersed into a mineral precursor solution consisting of TEOS (3 ml, 5 ml, 7 ml), ammonia (4 ml), and ethanol (100 ml) to initiate the in situ silicification process, denoted as SiO₂-d-PK membrane. The SiO₂-d-PK membranes prepared under different silicification periods varied from 1 h to 9 h were also designated as from SiO₂-d-PK (1h) to SiO₂-d-PK (9h), respectively.

For comparison, the in situ silicification without APTES pretreatment was also carried out under the same process of the SiO₂-d-PK membrane to further investigate the role of APTES addition for the realization of ultrathin silicification layer, and the resultant membrane without APTES was denoted as SiO₂-PK. The SiO₂ decoration onto the commercial hydrophobic PVDF membrane was also carried out by using the same silicification process of the SiO₂-d-PK membrane, denoted as SiO₂-d-PVDF membrane.

3.2.3 Membrane characterizations

The membrane microstructures were investigated by field emission scanning electron microscopy (FESEM; JSF-7500F, JEOL Ltd, Japan), under the accelerator voltage of 7 kV and emission current of 10.0 mA. The cross-sectional microstructure, and chemical composition of the SiO₂-d-PK (6h) membrane was investigated by energy-dispersive X-ray (EDX) analysis, under the accelerator voltage of 10.0 kV and emission current of 20.0 mA. The surface porosity of the as-prepared membrane was evaluated by using the Image J software (National Institute of Health (NIH) Products) as previously reported [33, 34]. The thickness of SiO₂ layer on the prepared SiO₂-d-PK membrane was evaluated by field emission transmission electron microscopy (FE-TEM, JEM-2100F, JEOL) under 200 kV acceleration voltage, and the detailed operation process was referred to our previous work [35].

The chemical compositions of membranes were measured by using X-ray photoelectron spectroscopy (XPS, JPS-9010 MC, JEOL Ltd, Japan) and Fourier-transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR; ALPHA, Bruker, USA). The zeta potential of PK, APTES-d-PK, and SiO₂-d-PK (6h) membranes were measured under the condition of 75 ppm KCl electrolyte solution using an electro-kinetic analyzer (Anton Paar SurPASSTM 3, Austria). The membrane pore sizes were measured at least three times using a capillary flow porometer (CFP-1500AXLC, Porous Materials Inc., USA).

Contact angle (CA) measurements (water-in-oil, and oil-in-water) and dynamic oil drop sliding experiments were conducted to evaluate the surface hydrophilicity and underwater oleophobicity of the membranes. All samples were tested using a goniometer (Drop Master 300, Kyowa Interface Science Co., Japan). For the water-in-oil measurement, 6 μ L water droplet was dispensed onto the soybean oil pre-wetted membrane, then the CA values were measured at least five times. For the oil-in-water measurement (static contact angle and dynamic sliding angle), special J-shaped needles were employed to release oil drops in an upward direction. Larger oil drops (6~20 μ L) were forced to contact with membrane to measure the static contact angle and dynamic sliding angle. The sliding angles were defined as the minimum tilt angle to slid.

Dynamic oil adhesion tests were conducted to evaluate the oil-repellent property of the pristine PK substrate, APTES-d-PK, and SiO₂-d-PK membranes: a 6 μ L droplet of chloroform was compressed on the membrane surface to make the droplet deformation, then the droplet was gently detached from the membrane surface. The self-cleaning experiment was carried out to evaluate the fouling-resistant property: a dry membrane was immersed into soybean oil, then the oil-wetted membrane was immersed into water, followed by gently shaking to remove the oil droplets [36]. To evaluate the durability of underwater superoleophobicity, the mineralized SiO₂-d-PK membrane was immersed in water under slightly shaking; then the underwater chloroform contact angles were examined. To investigate the acid, salty, alkaline, and solvent resistance, the prepared SiO₂-d-PK membranes were immersed into the solution 24 h; then the Si content and underwater chloroform CAs were measured [18].

3.2.4 Molecule dynamic (MD) simulation

In order to analyze the molecular interactions between water and PK, APTES, SiO₂ at the atomic scale, a classic MD simulation was constructed by using BIOVIA Materials Studio[®] commercial software. Geometry optimization was introduced to adjust the energy of the model structure at the initial stage of MD simulation. An NVT ensemble (constant atom number, model volume, calculation temperature) was conducted to access the steady-state of simulation structures during the MD simulation duration. For discussion, radial distribution function (RDF) was employed to present the hydration behavior of PK, APTES, and SiO₂ [37].

3.2.5 Preparation of oil-in-water emulsions and membrane filtration

The various of oil-in-water emulsions (hexane-in-water, hexadecane-in-water, petroleum ether-in-water, and soybean oil-in-water) were prepared according to literature [38]. 5 ml of oil was diluted to 500 ml solution by Milli-Q water containing surfactant stabilizer of 0.5 mg of SDS, and was stirred for 12 h to obtain the homogeneous solution. For the chloroform-in-water emulsion, 5 ml chloroform was dissolved into 500 ml Milli-Q water containing 0.5 g Tween 80, and was stirred for 12 h [21]. The complex oily emulsions were prepared by mixing the BSA (0.5g), or HA (0.5g) with the previously-developed soybean oil-in-water emulsion. The

oil droplet size was measured by dynamic light scattering (DLS; ELSZ-1000ZA, Otsuka Electronics, Japan) and optical microscope (BX50, Olympus, Japan), and the oil contents were measured by total organic carbon (TOC) analyzer (TOC-VCSH, Shimadzu, Japan).

The oil/water separation experiments were carried out using a glass filtration apparatus with an effective area of 2.1 cm² (KG25, ADVANTEC MFS, Inc., Japan) only driven by self-gravity (10 cm liquid column, about 0.01 bar). Firstly, the pure water flux, J_1 , was calculated according to Eq. (3-1):

$$J_1 = \frac{V}{A \times t} \quad (3-1)$$

where V is the permeate volume (L), A is the membrane area (m²) and t is the filtration time (h). The polystyrene nanoparticles (100 nm) rejection of PK, APTES-d-PK, and SiO₂-d-PK membrane was measured using the same method as our previously reported [21]. The emulsion flux was evaluated by calculating the average value within 10 min filtration. For the antifouling experiment (containing six pure water stages and five emulsion stages), after 0.5h pure water filtration, the feed solution was changed as an oil-in-water emulsion. After 1h filtration of emulsions, the membrane was washed by water to remove the surface oil, and the recovered pure water flux was also recorded as J_2 . The fouling-resistant/fouling-releasing property of the membrane against oily emulsion was evaluated by calculating the flux recovery ratio (FRR), using Eq. (3-2):

$$FRR = \frac{J_2}{J_1} \times 100\% \quad (3-2)$$

To compare the fouling potential of the hydrophilic and hydrophobic substrate, the antifouling experiment was also conducted using SiO₂-d-PVDF membrane at the same operating condition.

3.3 Results and discussion

3.3.1 Physicochemical properties of nascent PK substrate, APTES-d-PK membrane, and SiO₂-d-PK membrane

For the emulsified oil/water separation, the ideal membranes can repel the oil phase completely, while allowing the water molecules to pass through or become readily adsorbed,

with large efficiency and selectivity. This work mainly focuses on controlling the surface chemistry while maintaining the intrinsic highly porous nature of PK substrate, thus realizing the improvement on the membrane surface wettability and underwater oil-repelling property for the highly-efficient oily emulsions separation. The ultrathin SiO_2 modification layer was in situ synthesized on the surface of APTES-d-PK substrate, as schematically presented in Fig. 3.2(a). The main interaction between pristine PK membrane and APTES layer should be mainly based on electrostatic attraction and hydrogen bonding, as the following reasons: Fig. 3.3 shows the surface charge of PK substrate of -13.6 mV at the pH value of 7, indicating that the positively charged APTES monomer was easily absorbed onto the PK substrate, due to the attractive electrostatic forces. Afterwards, the APTES layer was in situ formed on the PK substrate followed by the self-hydrolysis and condensation process, as schematically illustrated in Fig. 3.4 (a). Therefore, the bonding mechanism between APTES layer and pristine PK substrate could be ascribed to the electrostatic attraction incorporated with H-bond forces [23]. Then the APTES-d-PK membrane was immersed in the ethanol dispersed solution containing TEOS and ammonia, allowing the negatively charged TEOS monomer to be attached onto the positively charged APTES functionalized substrate, induced by the electrostatic attraction force in the first step. Afterward, the in situ silicification including the self-assembly hydroxylation, dehydration, and condensation process between the TEOS monomers occurred on the surface of APTES-d-PK substrate (as shown in Fig. 3.4 (b)), thus leading to the formation of ultrathin silicification layer [23, 30].

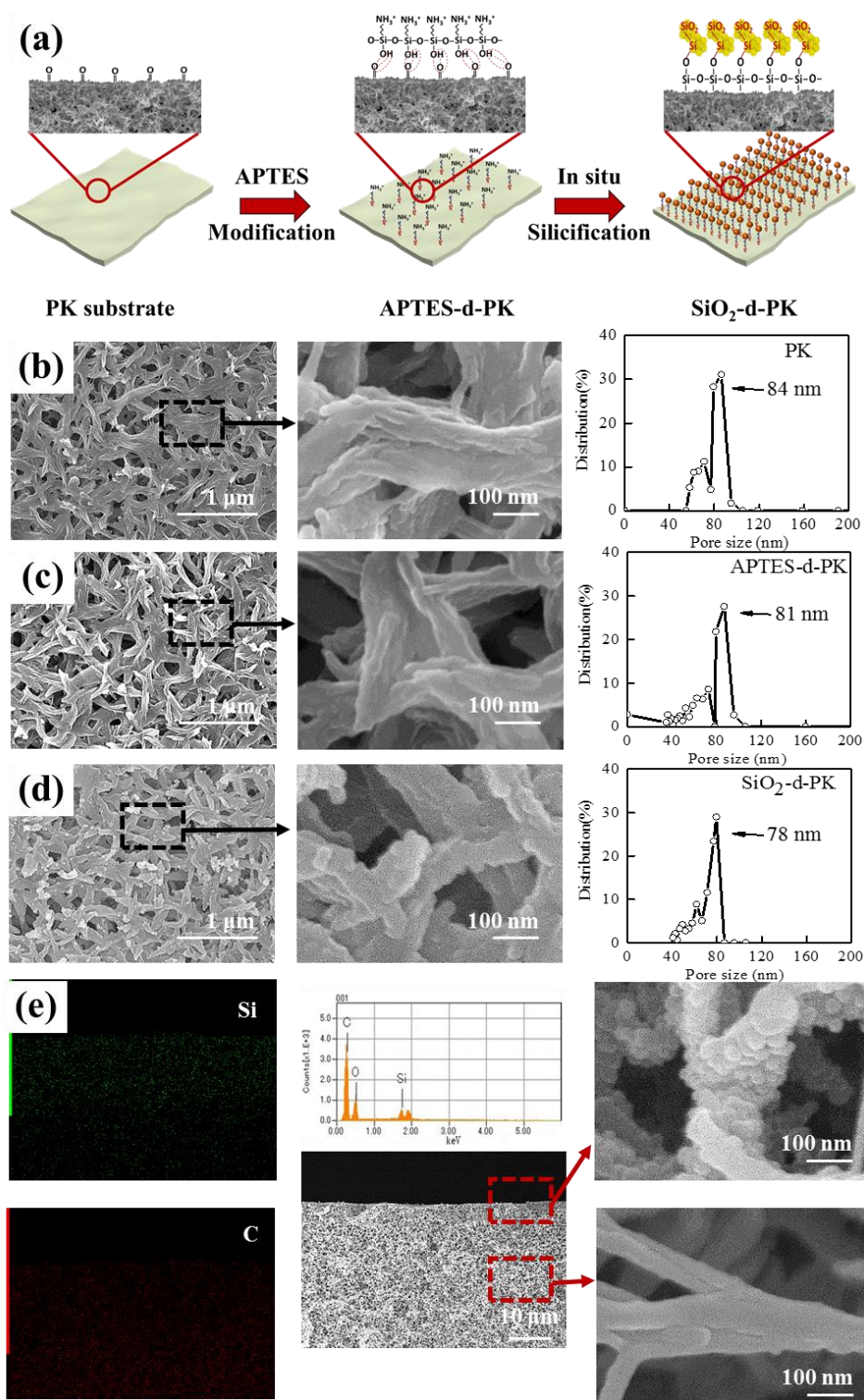


Fig.3.2. (a) Schematic illustration of in situ silicification process for the preparation of SiO_2 -d-PK membrane; FESEM images and pore size distributions of (b) nascent PK substrate; (c) APTES-d-PK membrane; (d) SiO_2 -d-PK (6h) membrane; and (e) cross-sectional image, EDS spectrum (plot in the upper middle of the figure), and EDS-mapping results of SiO_2 -d-PK (6h) membrane.

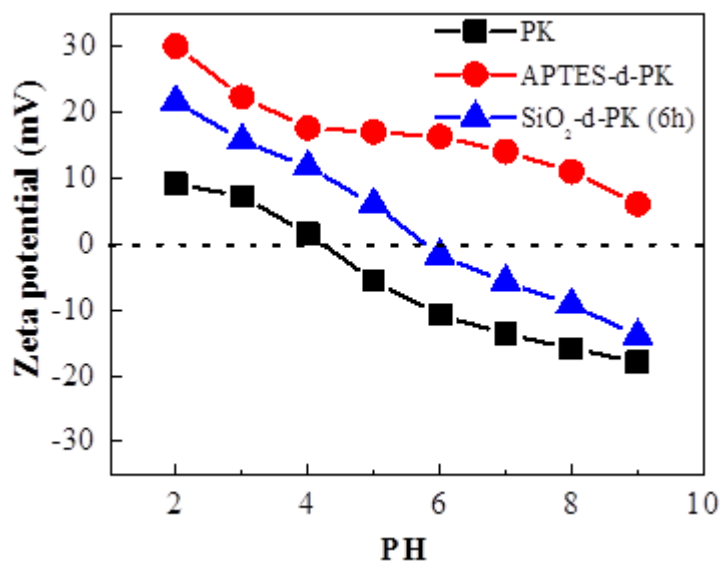


Fig.3.3. The surface zeta potential of nascent PK substrate, APTES-d-PK membrane, and SiO₂-d-PK membrane at the PH value of 2-9.

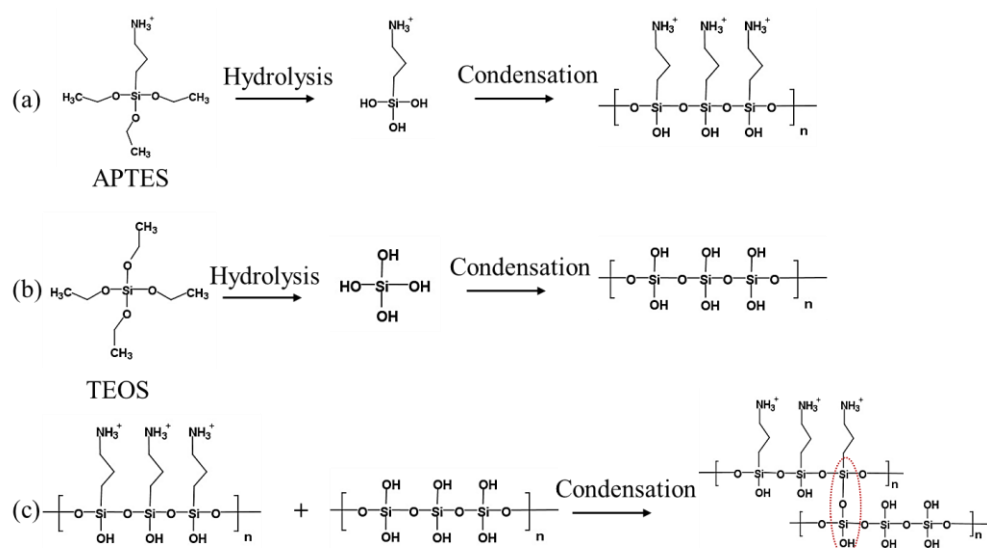


Fig.3.4. The mechanism of electrostatic attraction forced in-situ surface silicification for the preparation of SiO₂-d-PK membrane: (a) the hydrolysis and condensation process of APTES monomer; (b) the hydrolysis and condensation process of TEOS monomer; (c) the condensation process between the surface silicification layer with APTES layer.

Fig.3.2 (b), (c) and (d) exhibit the surface microstructures of pristine PK substrate, APTES-d-PK membrane, and SiO₂-d-PK membrane, respectively. According to these results, both APTES-d-PK membrane and the nascent PK substrate showed similar hierarchical concave topographic features, which implies that the APTES decoration had nearly no effect

on surface morphology. For the SiO₂-d-PK membrane (Fig. 3.2(d)), however, the uniform deposition of SiO₂ nanoparticles on the PK substrate surface could be observed, which suggests the successful in situ silicification. The enlarged SEM image of SiO₂-d-PK membrane also revealed the rougher surface microstructures compared to the pristine PK substrate, which could be explained as the formation of the coherent micro/nanosphere-like surface architecture. According to the TEM cross-sectional images of SiO₂-d-PK membrane (Fig. 3.5), an ultrathin SiO₂ modification layer with the thickness of ~9 nm could be observed, proving that the in situ synthesized silicification only contributed to the hydrophilic surface modification, but nearly without sacrificing the highly porous characteristic of PK substrate. Moreover, it should be noted that the SiO₂-d-PK membrane also exhibited a slight decrease in the pore size from 84 nm for pristine PK substrate, to 78 nm for SiO₂-d-PK membrane. We also compared the surface porosities of the newly developed SiO₂-d-PK, APTES-d-PK, and the pristine PK substrates. It could be found that the surface porosity slightly decreased from 44.3% for the pristine PK substrate to 41.0% for the SiO₂-d-PK membrane, and this could be attributed to the partial coverage by the silicification layer. In addition, it should be noted that the surface porosity nearly remained after the APTES decoration (with the porosity of 43.4% for the APTES-d-PK membrane), further demonstrating that the APTES decoration only contributed to the surface chemistry, but without sacrificing the intrinsically porous structure of PK substrate. In contrast, the pore size of SiO₂-PK membrane without APTES modification significantly decreased to 61 nm, due to the coverage of in situ generated SiO₂ nanoparticles with larger sizes, which may lead to the arisen of higher mass-transfer resistance for the oily emulsions filtration because of the undesirable pore blocking (Fig. 3.6). For the cross-sectional FESEM images of the SiO₂-d-PK membrane (Fig. 3.2(e)), no obvious SiO₂ coating could be observed, indicating the formation of an ultrathin layer that only directly contributes to the surface chemistry without sacrificing the intrinsic highly porous characteristic of PK substrate. According to the EDS results, however, the mineral SiO₂ particles were also distributed on the inner structure of the SiO₂-d-PK membrane. This could be attributed to the mineral precursors intrusion during the silicification process.

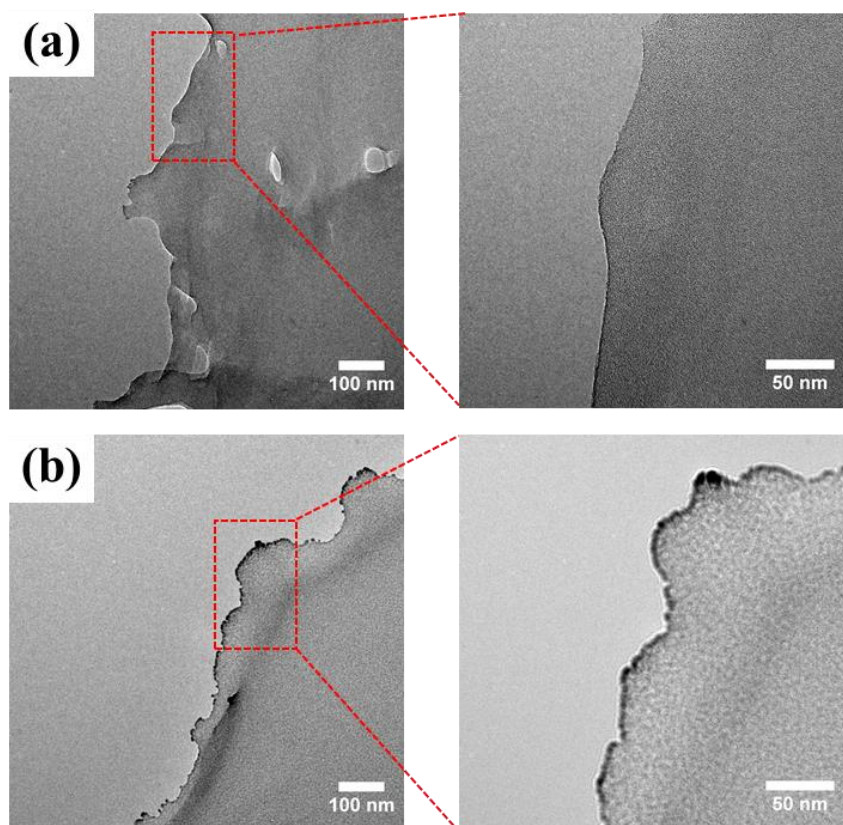


Fig.3.5. TEM cross-section images of the prepared membranes: (a) PK and (b)SiO₂-d-PK.

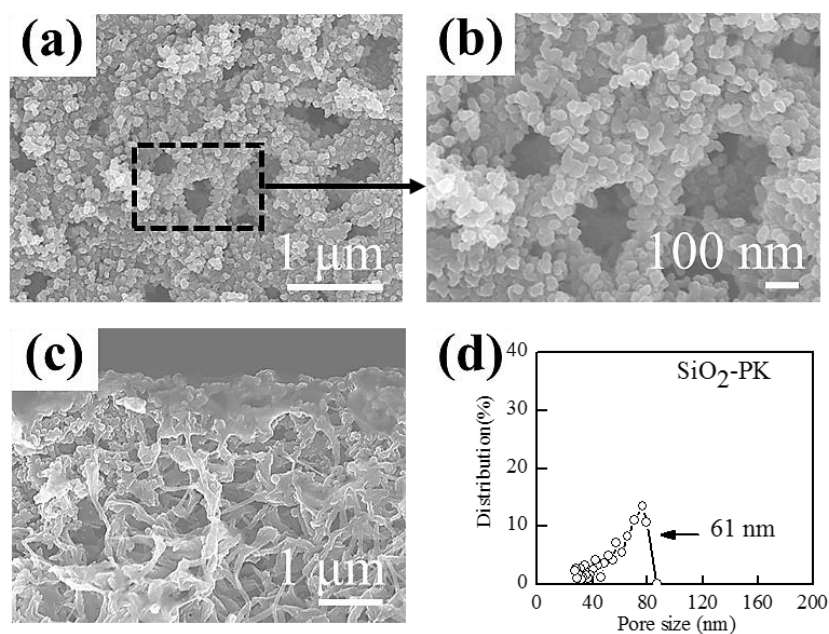


Fig.3.6. Morphologies and pore size of the SiO₂-PK membrane without APTES pretreatment:(a) surface morphology; (b) enlarged surface morphology; (c) cross-section morphology; (d) pore size distribution.

The formation of ultrathin interface layer (SiO_2 -d-PK membrane) could be ascribed to the electrostatic attraction forced silicification process, as follows: the negatively charged TEOS monomers could be absorbed by the strong positively charged APTES-d-PK membrane (+16.5 mV, at pH=6, Fig.3.3), thus the more nuclei would be in situ formed on the membrane surface. According to the conventional particle-growth theory [39], the nucleation is accomplished at a very early stage, and then the nuclei growth continued until the formation of stable colloidal particles [40]. By knowing the essence that the nucleus can continuously grow up to the isolated particles until the level of soluble silica reaches the solubility of amorphous silica, because after this point the chemical potential is no longer high enough to overcome the repulsive barriers between two primary particles with the same negative charge [41]. Along with this concept, the typical precipitates consisting of smaller silica particles were thought to be formed on the positively charged APTES-d-PK membrane surface, since the higher nuclei concentration may lead to the faster growth rate, this resulted in the rapid formation of individual primary particles with higher electrostatic repulsive forces that probably preclude the continuing particle growth. In contrast, for the SiO_2 -PK membrane without APTES pretreatment (as shown in Fig. 3.6), the negatively charged nascent PK substrate (-10.8 mV, at pH=6) tend to absorb fewer TEOS monomers due to the electrostatic repulsion force, where the lower nuclei concentration allowed the particles freely restructure themselves until the stable colloidal particles appear, thus bringing about the formation of larger sized silica particles.

To further clarify the mechanism of silicification, the process of SiO_2 layer formation over the prolonged silicification process was investigated, under the same TEOS concentration of 5 mL, as shown in Fig. 3.7. It could be observed that at the initial stage for silicification period of 1 h, the TEOS precursors, together with the APTES as bridging aid, were deposited onto the PK substrate, where the nuclei particles emerged. As the silicification processing (for silicification periods from 3 h to 6 h), the nuclei particles grew larger, and a continuous SiO_2 layer gradually formed over the APTES-d-PK substrate surface. By increasing the silicification period to 9 h, a more prominent interconnected cluster composing of SiO_2 particles could be observed, and the silicification layer partially covered the surface pores of the original APTES-d-PK membrane. This result indicated that the surface microstructures could be tuned by

controlling the silicification time, from which the longer silicification process may lead to the formation of denser and thicker silicification layer. We further investigated the SiO_2 nuclei growth process over the hydrolysis-condensation process, as shown in Fig. 3.8. It could be observed that the SiO_2 nuclei grew faster under the increased TEOS monomer concentrations from 3 mL to 7 mL, under the same hydrolysis-condensation period of 6 h. This result could be illustrated as follows: during the hydrolysis-condensation process, the added TEOS monomers would hydrolysis with water molecules to break the oxolation bond and thus peptized the precipitates, leading to the nucleation and particle growth. Since the growth of the SiO_2 nanoparticles is dynamically unstable, and the generated SiO_2 nuclei were continuously in random moving (the Brownian motion), so that the more nuclei may also grant the higher collision probability and more severe coagulation, thus leading to the formation of larger-sized SiO_2 nanoparticles [39]. Therefore, it concluded that by controlling the TEOS concentration could also realize the controlling of the silicification layer formation, because its microstructure is intrinsically subject to the agglomeration of SiO_2 nanoparticles.

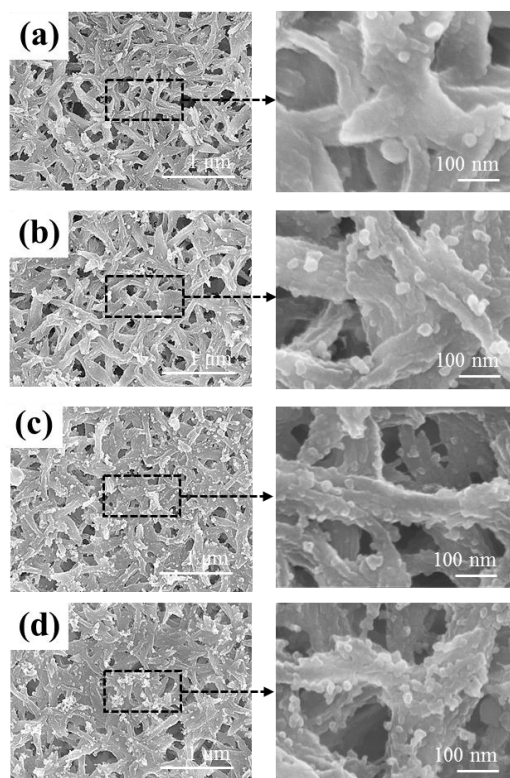


Fig.3.7. The surface morphologies of SiO_2 -d-PK membrane during the surface silicification process over the prolonged silicification process: (a) 1h; (b) 3h; (c) 6h; (d) 9h.

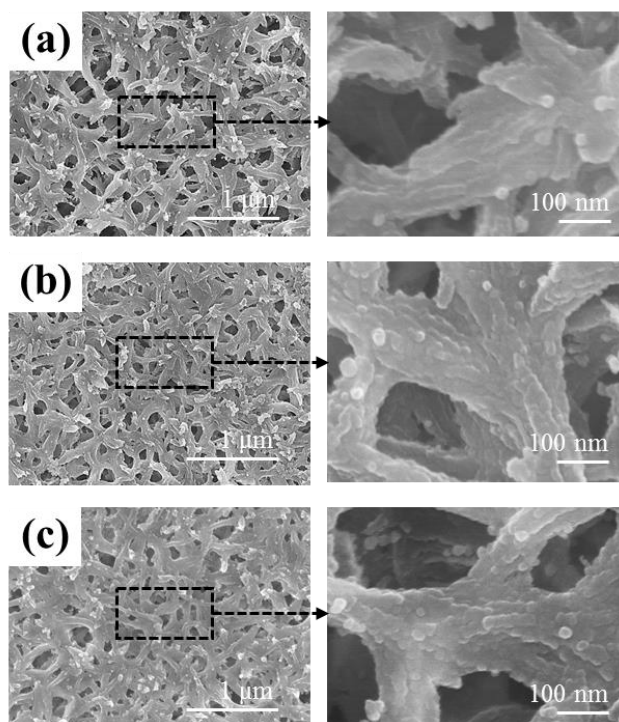


Fig.3.8. The surface morphologies of SiO₂-d-PK membrane with different TEOS concentration under the surface silicification period of 6 h: (a) 3 ml, (b) 5ml, and (c) 7 ml in 100 ml ethanol solutions.

The surface chemistry and chemical components of nascent PK substrate, APTES-d-PK membrane, and SiO₂-d-PK membranes were further investigated by FTIR, and XPS, as exhibited in Fig. 3.9. According to the FTIR result of Fig. 3.9 (a), the peaks at 1690, 1405, and 1055 cm⁻¹, corresponding to the C=O, -CH₂-, and C-C bonds that belong to the characteristic peaks of PK substrate [21]. The presence of new peaks at 1100 cm⁻¹ in the FTIR spectra of the APTES-d-PK membrane could be assigned to the Si-O-Si stretching vibration arisen from the APTES self-hydrolysis, and condensation onto the PK substrate, under the prolonged self-polymerization process (Fig. 3.10) [42]. For the SiO₂-d-PK membranes, the peak at 960 cm⁻¹, corresponding to the Si-OH stretching vibration, apparently increased over the prolonged silicification time from 1h to 6h, further signifying the successful in situ silicification onto the APTES-d-PK membrane surface [30].

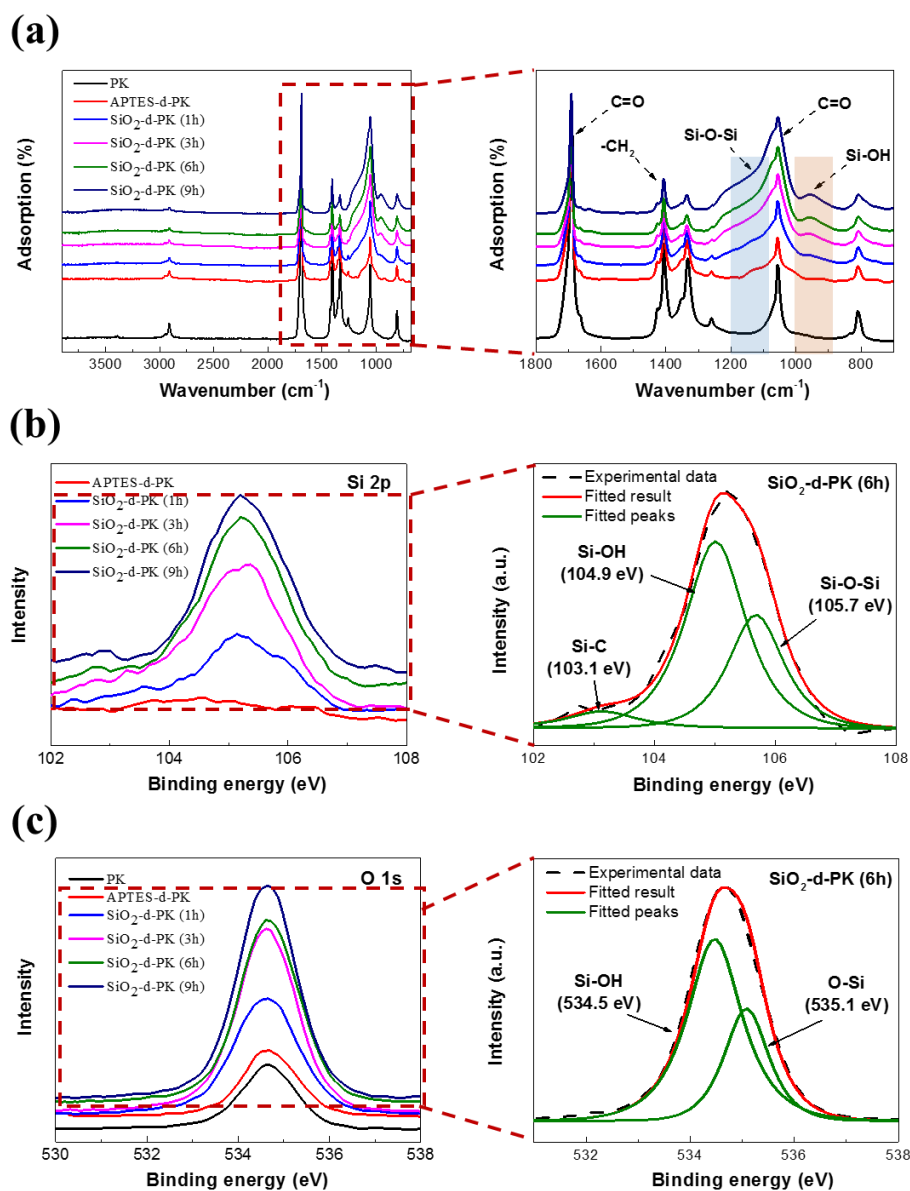


Fig.3.9. Physicochemical characterizations of (a) FTIR, and XPS spectra of (b) Si and (c) O element of PK substrate, APTES-d-PK membrane, and various of SiO₂-d-PK membranes prepared under different silicification periods.

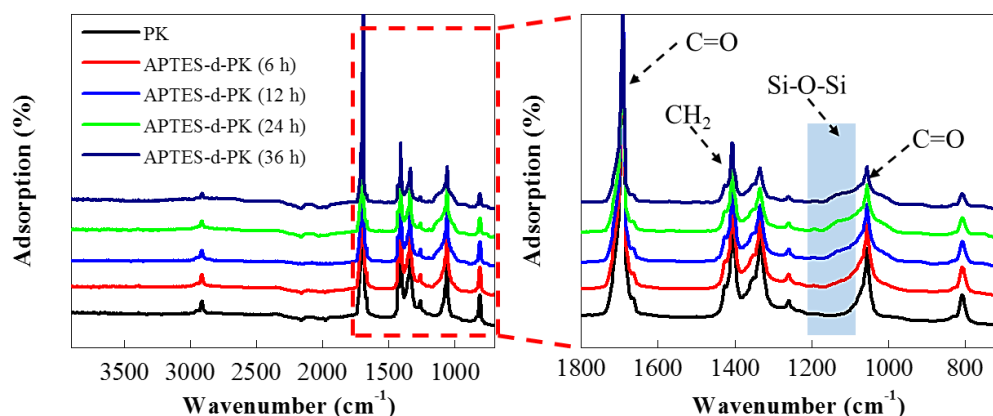


Fig.3.10. Characterization of the surface chemical composition of PK and APTES-d-PK with different deposition time.

Fig. 3.9 (b) and (c) exhibit the XPS spectra of Si and O elements of nascent PK substrate, APTES-d-PK membrane, SiO₂-d-PK membranes fabricated under the prolonged silicification process. The Si 1s peak exhibited that the Si-O-Si (105.7 eV), and Si-OH (105.1 eV) bonds were introduced, while its intensity was also increased after the prolonged silicification processes. For the bonding mechanism of SiO₂-d-PK membrane could be explained as follows: during the in situ silicification process, the TEOS monomer were exposed to water, and thus the hydrolysis occurred, followed by the generation of the -OH groups that act as binding sites to chemically bond with APTES layer, forming the covalent bonding via the condensation (formation of the Si-O-Si bond) process, as illustrated in Fig. 3.4 (c). The covalently bonding theoretically indicates a strong adhesion force between the SiO₂ layer and APTES-d-PK membrane [43]. Moreover, according to the result of O 1s peaks, the O-Si (535.1 eV), and the -OH (534.5 eV) peaks also presented the similar trend to that of the Si 1S peak, where the intensities ascended along with the increased periods of silicification processes, so that this could be attributed to the reason that a denser and thicker silicification layer could be formed onto the APTES-d-PK membrane surface under the protracted silicification process. For the SiO₂-d-PK membranes fabricated under the prolonged silicification process, it should be noted the elemental composition of Si and O firstly increased from 19.5% (with the silicification of 1h) to 31.2% (with the silicification of 6h), and 41.3% (with the silicification of 1h) to 55.1% (with the silicification of 6h), respectively, but afterward their chemical compositions were

nearly remained without apparent increase by continuing protracting the silicification period from 6h to 9h (Table 3.1 and Fig.3.11). This could be explained that the prolonged periods of silicification process brought in the higher Si/O elemental concentrations, since the formation of the more decent silicification layer. The 6h of silicification has almost achieved the complete coverage of SiO₂ modification coated onto the PK substrate, so that there is no need to protract the silicification longer than 6h to deposit denser and thicker silicification layer onto the membrane surface. Since we postulated that the controlling factor of surface hydrophilicity is the coverage of surface silicification, so that SiO₂-d-PK (6h) membrane was chosen for further study.

Table 3.1. The elemental compositions of the prepared membranes

Membrane	C (%)	O (%)	N (%)	Si (%)
PK	77.1	22.9	0	0
APTES-d-PK	67.3	20.1	3.2	9.4
SiO ₂ -d-PK (1h)	37.7	41.3	1.5	19.5
SiO ₂ -d-PK (3h)	19.5	50.5	0.5	29.5
SiO ₂ -d-PK (6h)	13.6	55.1	0.1	31.2
SiO ₂ -d-PK (9h)	11.6	55.7	0.1	32.6

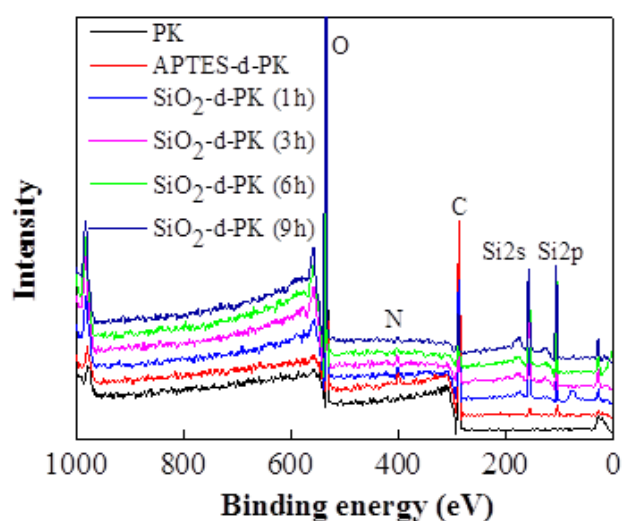


Fig.3.11. Characterization of the surface chemical composition of PK, APTES-d-PK and SiO₂-d-PK by XPS.

3.3.2. Wettability of the nascent PK substrate, APTES-d-PK membrane, and SiO₂-d-PK membrane

The surface wettability of the nascent PK substrate, APTES-d-PK membrane, and the SiO₂-d-PK membrane was primarily determined by their chemical composition and surface structure, where the underwater chloroform contact angles (CAs) on each surface were measured to investigate the interface decoration effects developed under different periods of electrostatic attraction forced in situ silicification processes. Fig. 3.12. shows the water CAs in soybean oil on the surfaces of nascent PK substrate, APTES-d-PK membrane, and SiO₂-d-PK membrane, where it could be observed that the water droplet remained a relatively higher CAs of 150 °(PK substrate), and 137 °(APTES-d-PK membrane) after contacted with the membrane for 5 min. For the SiO₂-d-PK (6h) membrane, in contrast, the water droplet quickly penetrated the membrane bulk and spread within the 30s, signifying a hydrophilic property compared to those of PK substrate and APTES-d-PK membrane.

The underwater wetting behaviors of chloroform droplets on the surfaces of the nascent PK substrate, APTES-d-PK membrane, and the SiO₂-d-PK (6h) membrane were shown in Fig. 3.12 (b) and (c). It could be observed that the SiO₂-d-PK membrane exhibited a much better underwater oleophobicity (underwater chloroform CA of ~158 °) than that of the pristine PK membrane (underwater chloroform CA of ~0 °), implying that the SiO₂-d-PK membrane possessed a better antifouling property, due to its ultralow adhesion forces toward dispersed oily droplets for the oily emulsions separation process, as shown in Fig. 3.12 (b) and (c) [44]. For the dynamic wetting behavior of the chloroform droplet on the membrane surface (Fig. 3.12 (c)), it could be observed that the chloroform droplets spread on the PK substrate, and tightly pinned on the APTES-d-PK membrane surfaces when they are placed at a tilt angle of 9 °. For the SiO₂-d-PK membrane, on the contrary, the chloroform droplet could easily roll off from the membrane surface, showing an extremely low dynamic sliding angle of ~2 °. The surface hydrophilicity of SiO₂-d-PK membrane was considerably superior to the APTES-d-PK membrane, and the pristine PK substrate, since the stronger orientation against water molecules stemmed from the hydroxyl groups of surface silica particles (the shortest atom distance, and the highest intramolecular interaction of O(SiO₂)-O(H₂O)), compared to the weaker orientation

between the PK/H₂O and APTES/H₂O (the longer atom distances, and the lower intramolecular interactions), owing to the impaired intermolecular interactions of the carbonyl and silanol groups against water molecules, as demonstrated by the MD simulation in Fig. 3.13.

The comprehensive underwater wetting behavior of SiO₂-d-PK (6h) membrane to various oils (hexane, hexadecane, petroleum ether, and soybean oil) was further investigated, as presented in Fig. 3.12(d). It could be observed that all the underwater oil CA of the SiO₂-d-PK (6h) membrane showed the high oil CAs (170 ° for hexane; 169 ° for hexadecane; 168 ° for soybean oil, and 167 ° for petroleum ether) and extremely small sliding angles (1 ° for hexane; 2 ° for hexadecane; 2 ° for petroleum ether and 4 ° for soybean oil), which all donates the SiO₂-d-PK (6h) membrane with an excellent underwater superoleophobicity property.

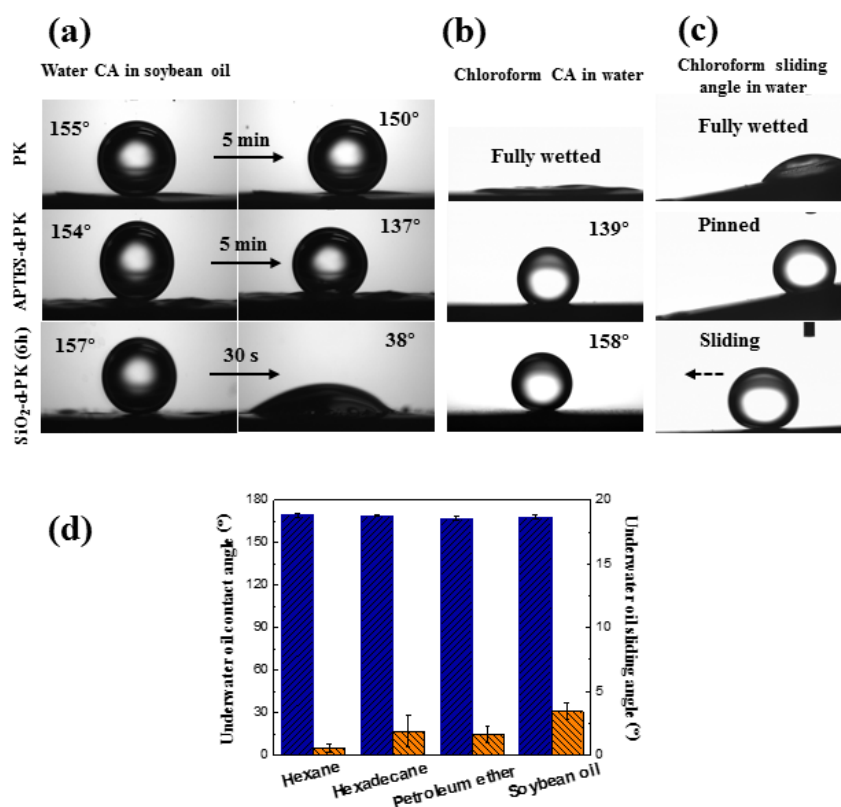


Fig.3.12. Wetting behaviors of the nascent PK substrate, APTES-d-PK membrane, and SiO₂-d-PK (6h) membrane under various conditions of (a) water CA under soybean oil, (b) underwater chloroform CA, (c) underwater chloroform sliding angles. (e) The underwater CAs of hexane, hexadecane, petroleum ether, and soybean oil, and their underwater sliding angles on SiO₂-d-PK (6h) membrane surface.

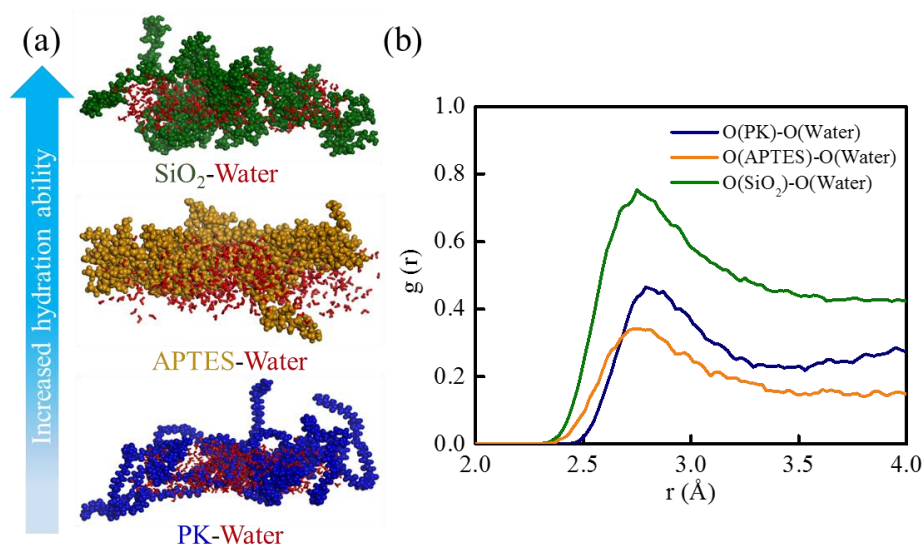


Fig.3.13. MD simulation result of (a) models between water molecules and PK, APTES, and SiO₂ within 3.5 Å, where the molecular chains are colored as follows: PK: blue; APTES: yellow; SiO₂: green; water: red; (b) RDF analysis between the oxygen atom of water and the oxygen atoms of PK, APTES, and SiO₂.

For the emulsified oil/water filtration process, the membrane fouling was mainly caused by the adhesion of the dispersed oil phase (oil droplets in the oily emulsion), where the dispersed oil droplets adhered on the membrane surface, so that lead to the deterioration of wetting selectivity, thus resulting in the membrane fouling and subsequent pores blocking [45]. Hence, the low adhesion property to dispersed droplets is supposed to be an important factor for the long-term oil-in-water emulsions separation with high efficiency and selectivity [46, 47]. The dynamic adhesion tests with a process of “approach-compress-detach” were conducted to evaluate the underwater oil adhesion forces against the APTES-d-PK membrane, and SiO₂-d-PK membranes, as shown in Fig. 3.14(a). It exhibits that all the oil droplets were compressed to deform from a spherical to ellipsoidal shape after contacting with membranes. However, the droplets can only be lifted from the SiO₂-d-PK (6h) membrane surface, and nearly no shape deformation of the droplet could be observed. Also, various SiO₂-d-PK membranes prepared under the different silicification periods were tested to compare the oil-repellent properties (Fig. 3.15). According to the result, for the SiO₂-d-PK membranes with relatively longer silicification of 6h and 9h, the oil droplets could be easily detached from the membrane surfaces without

obvious deformation. This indicated their ultralow oil-adhesion property, due to the complete coverage of superhydrophilic silicification layer onto the PK substrate. In principle, by protracting the silicification duration also brings in the denser and thicker modification layer (as demonstrated in Table 3.1), which may lead to the higher intrinsic resistance and thus resulted in the lower permeating flux for the oily emulsion separation [44]. Therefore, a balance between the surface silicification (hydrophilic modification) and permeating flux needs to be considered to achieve the high mass-transfer efficiency for oily emulsions separation. From this point, there is no need to further protract the silicification longer than 6h, since the solid surface with non-wetting “Cassie state” can be realized without sacrificing of its intrinsic highly porous characteristic of PK substrate after 6-h silicification (Fig. 3.2(d)) [48], so that the SiO₂-d-PK (6h) was chosen for the further study.

The self-cleaning property of the nascent PK substrate, APTES-d-PK membrane, and SiO₂-d-PK (6h) membrane was investigated, where all the membranes were pre-wetted by soybean oil (dyed with red color). The Fig. 3.14(b) showed that the oil droplets were easily squeezed out from the pre-wetted SiO₂-d-PK (6h) membrane when immersing into the water with gentle shaking. In contrast, the APTES-d-PK membrane, and the pristine PK substrate were nearly completely wetted by soybean oil without bounce off, leaving a pool of oily dye marks. This result indicated that the SiO₂-d-PK membrane possessed an ultralow adhesion property against oils, so that enabled the membrane in favor of preferentially antifouling property for the oily wastewater separation [36].

For the real oil-in-water emulsions separation, the durability and stability are critical factors in determining the practical application prospects of such materials [31, 49]. The SiO₂-d-PK membrane was thereby systematically evaluated by treated with various environments of water, acid, salt, alkaline, and organic solvents, as exhibited in Fig. 3.14. According to the result of Fig 3.14(c), the SiO₂-d-PK membrane showed a stable underwater chloroform CA up to 155 ° after shaking in water for 30 days, showing an excellent stably oleophobic property. Fig. 3.14(d) shows the underwater chloroform CAs of SiO₂-d-PK membranes after acid, alkaline, salty, and organic solvents (DMF and Hexane) treatments. It found that all the membranes exhibited the CAs of ~158 °, implying that the surface silicification layers remained intact without

compromising toward the operating conditions of acid, salt, alkaline and organic solvent. Moreover, Fig. 3.14(d) also showed that the Si content remained nearly the same before/after treated by various operating conditions (with slightly less than 3% decrease from the initial value of 31%), proving superior bonding stability between SiO₂ layer and APTES-d-PK membrane. This result could be ascribed to the strong adhesion force between surface silicification layer and APTES-d-PK membrane via the Si-O-Si bond that cannot be easily destroyed when treating challenging emulsions with complex objects. Since the inorganic silicification layer exhibited intrinsic robustness against various of challenging solutions [50], while the PK substrate used was also highly inert [21], the newly-developed SiO₂-d-PK membrane could be potentially applied in harsh applications involving organic solvent, as well as at wide pH range.

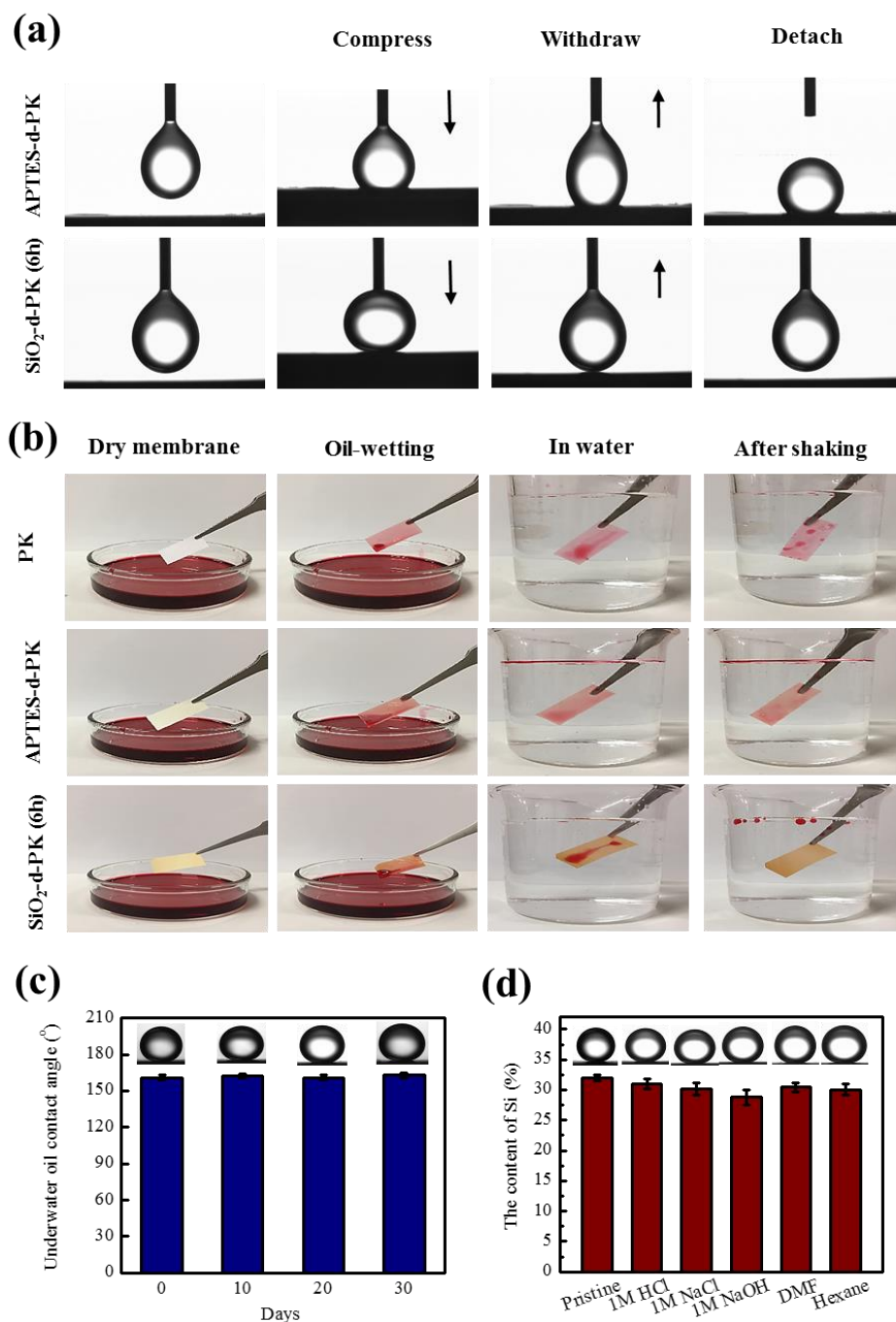


Fig.3.14. Surface dynamic adhesion tests of (a) underwater chloroform droplet “attach-compress-detach” experiment, and (b) self-cleaning test of pristine PK substrate, APTES-d-PK membrane, and SiO₂-d-PK (6h) membrane. Long-term durability test of (c) time-dependence underwater chloroform CA of SiO₂-d-PK (6h) membrane shaken in water for 30 days, and (d) the variation of underwater chloroform contact angles and Si content of SiO₂-d-PK membrane treated by acid (1M), salt (1M), alkaline (1M), and organic solutions for 24 h.

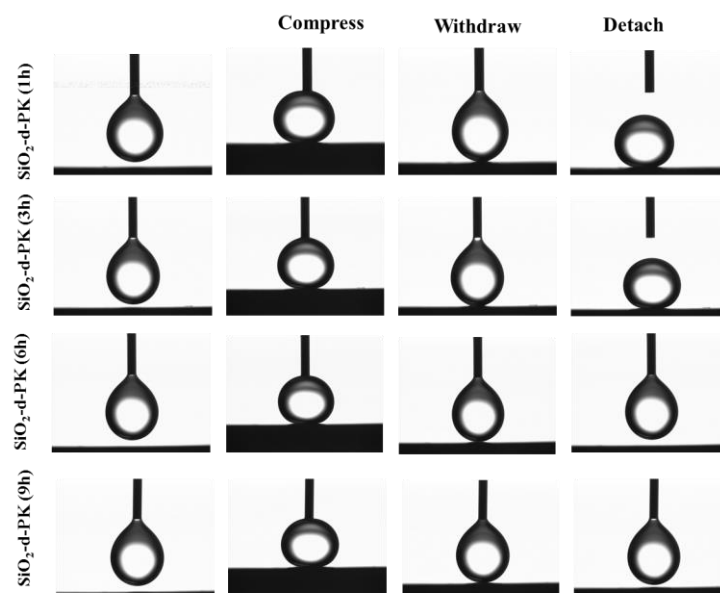


Fig.3.15. Underwater dynamic oil-adhesion tests on the SiO_2 -d-PK membranes surface prepared under different silicification periods, and the chloroform was used as the probe oil in this test.

3.3.3. Separation properties of the nascent PK substrate, APTES-d-PK membrane, and SiO_2 -d-PK membrane

The high wetting selectivity, namely underoil superhydrophilicity and underwater superoleophobicity, endowed the SiO_2 -d-PK membrane with great potential in respect of oily wastewater purification. Fig. 3.16 (a) shows the water permeations against the PS nanosphere (100 nm) rejections for the nascent PK, APTES-d-PK membrane, SiO_2 -d-PK membranes, and SiO_2 -PK membrane without APTES pretreatment. The nascent PK substrate exhibited a moderately high water permeance of $7669 \text{ Lm}^{-1}\text{h}^{-1}\text{bar}^{-1}$. However, the newly-prepared SiO_2 -d-PK membrane showed significantly higher water permeance up to $7533 \text{ Lm}^{-1}\text{h}^{-1}\text{bar}^{-1}$, by merely decreasing of 1.7% from the original value of nascent PK substrate. The ultrathin silicification layer developed in this study should contribute to the ultralow mass transfer resistance toward water permeance, while allowing the realization of a significant improvement on surface wetting selectivity of underoil superhydrophilicity and the underwater superoleophobicity [44]. More notably, the SiO_2 -PK membrane without APTES pretreatment showed lower water permeance of $5311 \text{ Lm}^{-1}\text{h}^{-1}\text{bar}^{-1}$, suffering from a more severe flux drop to 31% from the initial

value of nascent PK substrate. This was mainly attributed to the tighter microstructure of SiO₂-PK membrane, as a result of denser silicification layer composing of larger sized SiO₂ particles (Fig. 3.6). The rejection of 100-nm nanosphere of the membranes was also considerably high (100% rejection ratio), illustrating a 100 nm cut off pore size in the ultrafiltration range [51]. The incorporation of tightened pore structure in the SiO₂-d-PK (6h) membrane enabled its better-emulsified oil/water separation property, as shown in the oily emulsion separation results later on.

Fig. 3.16 (b) shows the filtration performance of SiO₂-d-PK (6h) membrane for five types of surfactant stabilized oil-in-water emulsions, comprising soybean oil-in-water, hexadecane-in-water, hexane-in-water, petroleum ether-in-water, and chloroform-in-water emulsions. It could be observed that the membrane showed very high fluxes at $\sim 6000 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ (close to the pure water flux of $7533 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) for the oily emulsions of hexane ($5329 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$), hexadecane ($6315 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) and petroleum ether ($6053 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$); and a relatively lower fluxes ($3718 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) for soybean oil and ($3570 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) for chloroform. The lower emulsions flux of soybean oil and chloroform could be ascribed to the deposited thicker filtration cakes with higher intrinsic resistances, due to their higher viscosity and density (higher than pure water) characteristics [52]. Filtration results for oily emulsions of hexane-in-water, hexadecane-in-water, petroleum ether-in-water, and soybean oil-in-water, chloroform-in-water were also investigated, as shown in Fig. 3.16(c), (d), (e), (f) and (g). The oil droplets size distribution in the emulsions is from tens of nanometers (the most frequent particle size of $\sim 80 \text{ nm}$, for hexane-in-oil emulsion) to thousands of nanometers, according to the result of DLS measurement (Fig. 3.16(c)). It could be observed that all the milky white-colored feed emulsions turned transparent with no visible oil droplet after the membrane separation, and all the collected filtrates displayed exceptional low oil contents of 5~11 ppm (Fig. 3.16(b)), reaching a considerably high rejection rate of 99.9%, outperforming other membranes used for oily emulsions separation (Table 3.2). Based on the previous result, we further investigated the chloroform-in-water emulsion separation, where it could be observed that the SiO₂-d-PK membrane showed a better-purified permeate with TOC value of 26 ppm, meanwhile the pristine PK membrane exhibiting permeate with much higher TOC value of 130 ppm (higher

than the discharged standard value of 42 ppm [26]), as shown in Fig. 3.16(g). This result indicates that the pristine PK membrane is not appropriate to be used for the chloroform based oily emulsions separation.

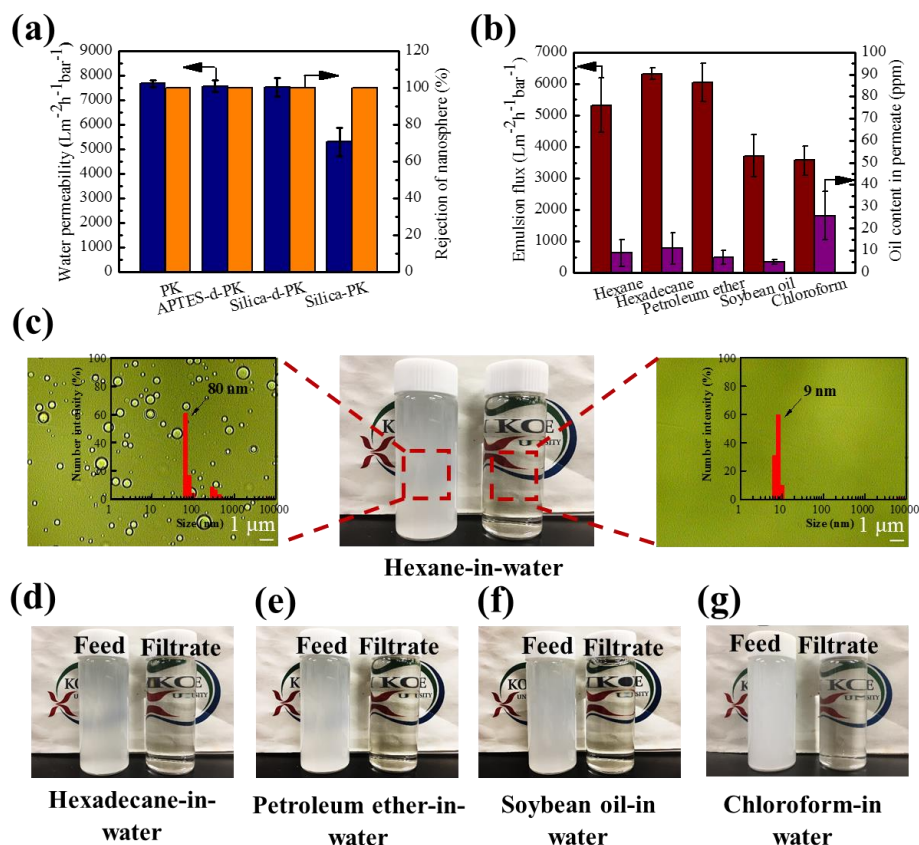


Fig.3.16. Membrane filtration results of (a) pure water permeance and rejection result of PS nanosphere (100 nm); (b) emulsion fluxes and oil contents in permeates filtrated by SiO₂-d-PK (6h) membrane; (c) particle sizes/particle size distributions of oil droplet of the hexane-in-water emulsion before/after filtrated by SiO₂-d-PK (6h) membrane (the scale bar was 1 μm), and other oily emulsions of (d) hexadecane-in-emulsion, (e) petroleum ether-in-water emulsion, (f) soybean oil-in-water emulsion, and (g) chloroform-in-water emulsion before before/after filtrated by SiO₂-d-PK (6h) membrane.

Fig. 3.17 shows the filtration-cleaning cycling process of the nascent PK substrate, and the newly-developed SiO₂-d-PK membrane for the separation of surfactant stabilized emulsions with/without other contaminants of BSA and HA, from which all the membranes were tested at the same initial flux of $\sim 7500 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ by controlling each of the transmembrane

pressure. For the relatively less challenging surfactant stabilized emulsion containing only soybean oil, as shown in Fig. 3.17(a), the SiO₂-d-PK (6h) membrane showed a much higher residual flux of ~ 50% of the initial flux, and a nearly 100% FRR over 5 cycles, indicating its superior antifouling property for oily emulsions separation due to the intrinsically hydrophilic silicification layer that captured a dense hydration layer with ultralow adhesion to the dispersed oil droplets, thus the generated filtration cake of foulants could be easily washed away from the membrane surface [46]. In contrast, the nascent PK membrane lost nearly 85% of its initial flux, from which the FRR of 80% could only be obtained after the hydraulic washing, indicating that the nascent PK substrate was more prone to fouling due to its less hydrophilic property, compared to the superhydrophilic silicification layer.

For more troublesome emulsions containing other comprehensive foulants of 1000 ppm BSA, and 1000 ppm HA (Fig. 3.17(b), and (c)), the SiO₂-d-PK membrane performed 80~% and 84% drops from the initial values over 5 filtration cycles. The more severe permeating flux attenuation compared to the surfactant stabilized soybean oil emulsion (Fig. 3.16(a)) could be ascribed to the BSA and HA aggregation that leads to the more severe pores blocking [53]. However, it is worth noting that the high FRRs of 97% for BSA/oil, and 96% for HA/oil could be obtained after rinsed by DI water, signifying that the SiO₂-d-PK membrane possessed an excellent recyclability and reusability, due to the exceptional fouling-resistant/fouling-releasing property not only against oils, but also against other comprehensive foulants (surfactant, proteins, and other NOM) that easily cause membrane fouling usually. In contrast, the nascent PK substrate exhibited an extremely lower residual permeating flux after the oily wastewater treatment, and all of which could only be recovered partially after hydraulic washing (FRRs of 65% for BSA/oil, and 77% for HA/oil), indicating a more severely irreversible fouling occurred due to the adsorption of comprehensive foulants on the PK substrate surface.

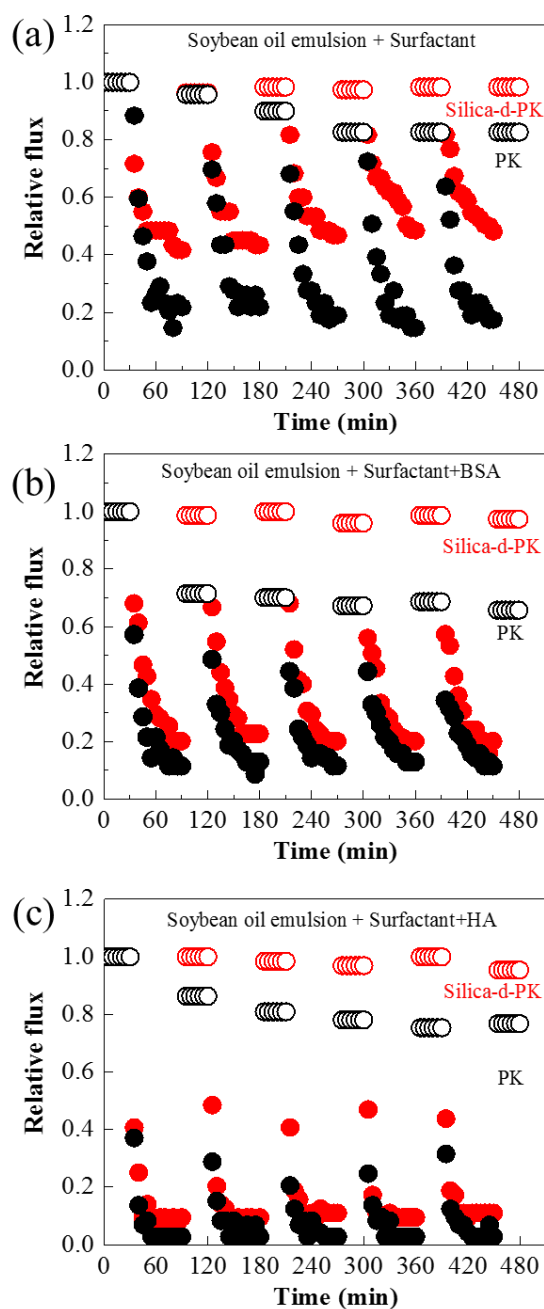


Fig.3.17. Fouling-resistant/fouling-releasing property of PK and SiO₂-d-PK (6h) membranes for SDS stabilized (a) soybean oil-in-water emulsion; (b) soybean oil-in-water emulsion with 1000 ppm BSA; and (c) soybean oil-in-water emulsion with 1000 ppm HA.

To further demonstrate the role of hydrophilic PK substrate assisting the thoroughly fouling-resistant and fouling-releasing property of SiO₂-d-PK membrane, the SiO₂-d-PVDF membrane was used as a control experiment for the filtration of the surfactant stabilized

soybean oil emulsions, as shown in Fig. 3.18. It could be observed that a more severe fouling propensity could be observed, where the permeating flux declined to ~20% from the initial value, and only 82% of which could be recovered after simple hydraulic washing over the 5 filtration cycles. This could be likely attributed to the irreversible adsorption of oil droplets on the PVDF substrate, due to the penetrated oily emulsions through the silicification layer during the filtration process. This result indicated that irreversible fouling could also be occurred on the inner structures of the substrate, due to the hydrophobicity of PVDF nature [19]. Overall, the superior separation performance of SiO₂-d-PK membrane in terms of high water permeation and high antifouling property should be mainly stemmed from the following reasons: 1). the construction of the ultrathin silicification layer with extremely low-mass-transfer resistance endowed the membrane with an exceptional permeating capability; 2). the unique architecture of superhydrophilic silicification layer deposited onto the hydrophilic PK substrate enabled the membrane thoroughly fouling-resistant and fouling-releasing property against various foulants, not only oil droplets but also other foulants such as proteins, surfactant, and any other NOM.

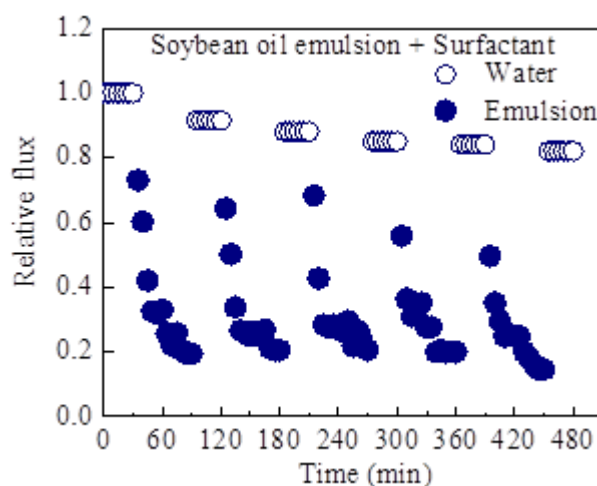


Fig.3.18. Antifouling property of SiO₂-d-PVDF membranes for soybean oil-in-water emulsion.

The oily emulsion separation property in terms of emulsion flux, oil rejection, and the antifouling property of the newly-developed SiO₂-d-PK membrane is compared with those reported membranes in the latest literature, as summarized in Table 3.2. The comparison result suggests that the performance of SiO₂-d-PK membrane is, to a large extent, superior to all of

the other membranes prepared by different materials and methods, including in situ mineralization (TiO_2 , SiO_2 , CaCO_3), copolymer (F127), zwitterionic (SBMA), hydrogel (alginate) and any other surface hydrophilic modification. The newly-developed SiO_2 -d-PK membrane exhibits several folds of increase in emulsion flux ($6300 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$), while maintaining a considerably high oil rejection (99.9%) even toward the relatively small oil droplets ($\sim 80 \text{ nm}$, for hexane), showing an ultralow-fouling-propensity with a nearly full flux recovery against highly fouling emulsions. To sum up, compared to the commonly used ALD, biomimetic mineralization, and chemical grafting methods, the proposed method of electrostatic attraction forced in situ silicification has been proven to be simple and low-cost. For the reason that the ultrathin silicification layer could be easily in situ synthesized after the self-hydrolysis and condensation process, replacing hundreds of complex cycles of “pulse-exposure-purge” process of ALD method. Moreover, the surface silicification layer could remain integrated without compromising under the harsh operating conditions toward acid, alkaline, salt, and organic solvents.

Table 3.2. Comparison of the filtration performance of various membranes used for surfactant-stabilized oily emulsions separation

Materials	Pore size (nm)	Oil feed content (ppm)	Oil droplet size in feed (mean, nm)	Emulsion flux ($\text{Lm}^{-2}\text{h}^{-1}$), Pressure	Oil content in permeate (ppm)	FRR (%)
CaCO_3 / polypropylene[54]	200	10000	140-5000	2000, 0.5 bar	<100	90
SiO_2 /PEI/polypropylene[23]	200	10000	100-8000	1228, 0.4 bar	<70	95
SiO_2 /PDA/PVDF[30]	<1000	20000	4000-14000	1800, 0.9 bar	-	97
SiO_2 /PDA/PVDF[55]	-	10000	-	600, 1 bar	25	99
SiO_2 /GO[56]	-	100000	1000-2000	4124, 1 bar	<100	98
TiO_2 /PVDF[57]	<220	10000	-	605, 0.9 bar	66	96
Nanocrystal/Palygorskite[58]	-	100	50-200	883, 0.5 bar	10	94
TiO_2 /PLA[59]	-	-	-	963, 1 bar	<100	95
Ceramic membrane[60]	50	5000–30000	175–280	40-80, 1-5 bar	200-750	-
SnO_2 /PVDF[22]	200	20000	-	800, 1 bar	82	92
SWCNT/PDA/PEI[61]	0	10000	54	1515, 0.5 bar	30	-
TiO_2 /PAN[62]	-	10000	10-100	1100, 0.01 bar	<100	98
F127/PES[63]	-	900	2100	80, 1 bar	0	94
SBMA/PVDF[20]	<220	10000	100-5000	1500, 1 bar	19	97
Alginate/PVDF[46]	60	10000	800-2000	1300, 1 bar	18	93
PEGDGE/PVDF[19]	<220	3600	1000	900, 1 bar	20	99
CS/PVDF[64]	<1000	10000	431	180, 1 bar	30	98
Cellulose[7]	<220	10000	-	3700, 1 bar	40	96
SiO_2 -d-PK membrane (this work)	78	10000	>80	6300, 1 bar	11	99

3.4. Conclusions

An ultrathin silica layer is in situ engineered onto the porous PK substrate, via the electrostatic attraction forced silicification process. The ultrathin silicification enabled the SiO_2 -d-PK membrane a comparable water permeance of $7533 \text{ Lm}^{-1}\text{h}^{-1}\text{bar}^{-1}$, and a superior emulsions separation property in respect of high oily emulsions fluxes for the oily emulsions

of hexane ($5329 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$), hexadecane ($6315 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$), petroleum ether ($6053 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$), and soybean oil ($3718 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$); and high rejection rates up to $\sim 99.9\%$ against various of oily emulsions. Owing to the unique architecture of superhydrophilic silicification layer deposited onto the hydrophilic PK substrate, a thoroughly antifouling property of the SiO_2 -d-PK membrane was developed, endowing the membrane with a nearly full recovery ratio of permeating flux after several cycles of filtration process by simple hydraulic washing. As the inorganic silicification incorporated with the PK substrate used were highly chemical inert, the as-proposed SiO_2 -d-PK membrane could be potentially applied in harsh conditions involving salty, strong acid/alkaline solutions, and various organic solvents. In summary, the newly-developed SiO_2 -d-PK membrane shows a promising prospects in challenging oil-in-water emulsions separation.

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Chapter 4

Finely tuned dopamine assembling on a polyketone substrate to engineer a robust underwater superoleophobic membrane for high performance oil/water separation

4.1. Introduction

Since the historical trends have indicated an extensive expansion of manufacturing industries, oil pollution stemming from the oil spills or discharged oily wastewater has become an ongoing worldwide threaten to the environment and ecosystem [1]. In comparison with the conventional separation methods like oil skimming, centrifugation, flocculation, and settling separation, membrane based separation technology has been acknowledged as a more promising prospect to remove oil from oily wastewater due to its high separation efficiency, low energy cost and easy scalability [2-4]. Over the past few decades, traditional membranes used in the oil/water separation always suffer from serious fouling issue that results in fast permeating flux decline due to the adsorption of oil droplets on the membrane surface or blocking the inner pore channels, thus leading to a severe impedance on the membrane development for highly efficient oily wastewater treatment [5-7]. Therefore, improving the fouling-resistant/fouling-releasing properties of membranes is of great importance for practically oily wastewater treatment.

It is well-known that introduction a hydration shell on membrane surface by utilization of the synergetic effect of hydrophilic chemistry and micro-/nano-composite structure is an effective strategy to engineer a fouling-resistant/fouling-releasing membrane due to the reduced contact area between pollutants and membrane [8]. Along with this concept, various of methods were reported to prepare superhydrophilic and underwater superoleophobic membranes for

oil/water separation, such as atomic layer deposition (ALD) [9], biomimetic mineralization [10, 11], electrospray [12], electrochemical deposition [13], salt-induced [14], coating [15], grafting [16] and so on, however, most of which were subjected to a complex, non-scalable, time-consuming modification procedure that seriously restricts the practical applications. For instance, Zhu et al. fabricated a zwitterionic nanosized hydrogel (~ 50 nm) grafted poly(vinylidene fluoride) (ZNG-g-PVDF) membrane with excellent fouling-tolerant property for comprehensive oil-in-water emulsions separation. Despite its superior advantages on oil-in-water emulsions separation, the grafted membrane still undergoes a complex and time-consuming modification process that lasts 42 hours [17]. Moreover, most of the modified methodologies were inability that only achieved surface hydrophilic decoration without generating extra permeating resistance due to the difficulty of ultrafine nano-sized surface modification. Yuan et al. fabricated a superhydrophilic and underwater superoleophobic hydrogel grafted PVDF membrane via an interfacial polymerization process, and the flux reduced from $5000 \text{ Lm}^{-2}\text{h}^{-1} \text{ bar}^{-1}$ to $2000 \text{ Lm}^{-2}\text{h}^{-1} \text{ bar}^{-1}$ after modification due to the increased permeation resistance [18]. Therefore, developing a simple method for the realization of an ultrathin surface modification with robustly fouling-releasing/fouling-resistant property is urgently needed for the practical oil/water separation.

In the present work, an ultrafine polydopamine (PDA) nanoparticles (NPs) assembling was in-situ engineered on polyketone (PK) substrate via the facilely ammonia initiated dopamine (DA) self-polymerization process, to meet the above mentioned challenges. Oxy-polymerization of DA could be immediately triggered by ammonia initiator to form a solidly adhered layer composed of stacked ultrafine PDA NPs with superhydrophilic and underwater superoleophobic property. An exceptional high water permeance up to $11600 \text{ Lm}^{-2}\text{h}^{-1} \text{ bar}^{-1}$, and an ultrahigh permeance up to $10600 \text{ Lm}^{-2}\text{h}^{-1} \text{ bar}^{-1}$ for hexane-in-water emulsion with high rejection ratio of 99.9% were obtained, outperforming most of the existing membranes used for oil/water separation reported so far. When comparing with the water permeance of the nascent PK substrate ($13600 \text{ Lm}^{-2}\text{h}^{-1} \text{ bar}^{-1}$), a slightly decrease by only 14% was obtained after the ultrafine PDA NPs in-situ assembling without arisen of extra permeance resistance, but only directly contributed to the surface chemistry and micro-structure. In addition, Due to the highly

chemically inert of PDA layer and PK substrate, the newly-developed PDA decorated PK membrane (PDA-d-PK) also showed a robust tolerance against the operating environments of salty, strong acid/alkali, and organic solutions, exhibiting a highly potential for practical oily wastewater treatment.

It should be noted that this proposal of ultrafine PDA NPs in-situ assembling on PK substrate by using the well-known material of PDA is not just following the previous research, but stemmed from our systematic studies in the PDA NPs in-situ assembling process and PK substrate [19]. For the mussel-inspired surface modification study, PDA layer exhibited a hydrophilic and underwater oleophobic property to common oils, where most researcher ascribed to its hierarchical structure consisting of PDA particles or nanoclusters, yet its nucleation and growth process in-situ was rarely reported [20-24]. Thus, for the first time, we unveiled the in-situ nucleation of PDA, and its subsequent self-assembling process on the PK substrate, realizing a simultaneously control of both surface chemistry (superhydrophilic/underwater superoleophobic to oils) and surface microstructure (ultrafine micro/nanospherical structures for amplified Cassie state) for the comprehensively oily emulsions separation containing various of pollutants such as surfactant, protein, and natural organic materials (NOMs). Overall, the ultrafine PDA NPs in-situ assembling not only endowed a significant improvement on the antifouling property, but also maintained its high porosity without obvious permeation sacrificing.

4.2. Experimental

4.2.1. Materials

Polyketone (PK) powder with molecule weight of $200\,000\text{ g mol}^{-1}$ was kindly provided by Asahi Kasei Co., Ltd., Japan. Resorcinol, methanol, acetone, hexane, petroleum ether, hexadecane, soybean oil, chloroform, sodium dodecyl sulfate (SDS), ethanol and ammonia solution (25%) were bought from Wako Pure Chemical Industries Co., Ltd., Japan. Dopamine (DA), polyethylene glycol (PEG) with molecule weight of 20000 g mol^{-1} , humic acidic salt, bovine serum albumin (BSA) were purchased from Sigma-Aldrich, Japan. Polystyrene (PS) nanoparticles with the diameter of 200 nm and Triton X-100 were bought from Thermo

Scientific Inc. (USA) and Alfa Aesar A Johnson Matthey Co. Ltd, respectively. Milli-Q water was produced by our lab.

4.2.2. Membrane preparation and modification

PK and PEG powders with the concentration of 10 wt% and the weight ratio of 80:20 were dissolved in a 65 wt% resorcinol aqueous solution with 3 h stirring at 80 °C to get a homogenous solution. After removing bubbles, the dope solution was casted onto a glass plate with the height of 200 µm using a casting knife. Then, the nascent film was kept into a methanol/water mixture solution (35:65, w/w) at about 25 °C for 20 min. After membrane formation, it was washed with acetone and hexane for 20 min for each, and finally dried in air. The obtained membrane was named as PK.

The PDA hydrophilic layer was in-situ assembled onto PK substrate as shown in Fig.4.1. The PK membrane with a diameter of 37 mm was immersed into ethanol (30 mL)/H₂O (70 mL) mixture solution containing 0.5g DA using ammonia solution (8 mL) as initiator for designed time under lightly shaking [25]. After designed deposition time, the membrane was washed by Milli-Q water, named as PDA-d-PK membrane. The deposition conditions with different ammonia content were also detailed studied. For comparison, the PK membrane was also decorated using the traditional condition [26], that is, 5 mg mL⁻¹ dopamine tris(hydroxymethyl) aminomethane hydrochloride (tris-HCl) solution (pH= 8.5) under an ambient atmosphere. The obtained membrane was named as PDA-PK.

4.2.3. Membrane characterization

Surface chemistry composition of PK and PDA-d-PK membranes were studied by Fourier-transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR; Alpha Bruker) and X-ray photoelectron spectroscopy (XPS; JPS-9010 MC, JEOL, Japan) with Al K α X-rays. The membrane morphologies were observed by field-emission scanning electron microscopy (SEM; JSF-7500F, JEOL, Japan). The wettability was measured using a contact angle goniometer (Drop Master, Kyowa Interface Science Co., Japan). A droplet of water or oil with a volume of 4-20 µL was dispensed on the membrane surface in air or water, then the contact

angle was recorded. Dynamic oil adhesion tests were also conducted to evaluate the anti-oil-adhesion property. A 4-6 μL droplet of chloroform was firstly compressed to the membrane surface and then drawn back slowly. To study the durability of PDA-d-PK membrane, it was immersed in water for designed time; then the underwater oil contact angle was measured. To investigate the chemistry-resistance, the PDA-d-PK membrane was immersed in acidic, salt, alkaline, ethanol and acetone for 12 h, then the underwater oil contact angle was recorded.

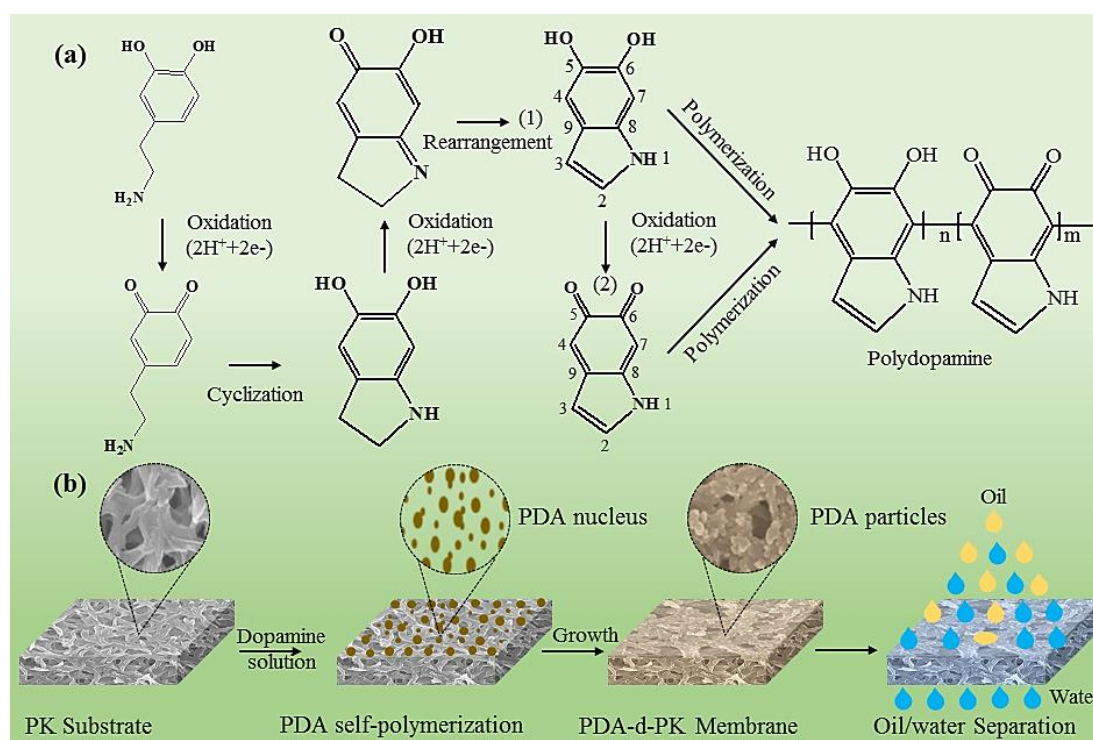


Fig.4.1. Schematic diagram of in-situ dopamine assembling on PK substrate for Oil/water separation.

4.2.4. Preparation of oil-in-water emulsions and membrane filtration

Surfactant stabilized oil-in-water emulsions, such as hexane-in-water, hexadecane-in-water, petroleum ether-in-water and soybean oil-in-water were prepared to evaluate the separation of PK and PDA-d-PK membranes. Exactly, the emulsions were prepared by adding 5 mL oil into 495 mL water containing 0.5 mg SDS and followed by 12 h stirring at 1000 rpm. The composite emulsions were prepared by adding BSA (0.5 g) or HA (0.5 g) with the previously prepared hexadecane-in-water emulsion. The droplet size and size distributions of

the emulsions were studied by dynamic light scattering (DLS; ELSZ-1000ZA, Otsuka Electronics, Japan) and optical microscope (BX50, Olympus, Japan).

Pure water fluxes (record as J_1) for each membrane were measured using a glass filtration device with an effective area of 2.1 cm² only driven by self-gravity (10 cm liquid column, ~0.01 bar), and was calculated according to Eq. (4-1) as follows:

$$J_1 = \frac{V}{A \times t} \quad (4-1)$$

where V is the permeate volume (L), A is the effective filtration area (m²), and t is the time (h). The rejection of polystyrene nanoparticle with the diameter of 200 nm for PK and PDA-d-PK membranes was measured using the same method as previously reported [11]. The emulsion flux was measured by calculating the average value within initial 10 min filtration and the oil content in permeate was measured using total organic carbon (TOC-VCSH, Shimadzu, Japan). To investigate the antifouling performances of PK and PDA-d-PK (9h) membranes, filtrations of pure water and oil-in-water emulsion were conducted at the similar initial water flux (containing three pure water stages and two emulsion stages). After 0.5 h of pure water filtration, the feed solution was changed to oil-in-water emulsion. After 1 h of emulsion filtration, the fouling membrane was washed using water to remove the adhesive oil droplet. The pure water flux after three recycles was recorded as J_2 , and the antifouling properties of the membranes was evaluated by calculating the flux recovery ratio (FRR), by using Eq. (4-2) as follows:

$$FRR = \frac{J_2}{J_1} \times 100\% \quad (4-2)$$

4.3. Results and discussion

4.3.1. Physicochemical properties of the nascent PK substrate and PDA-d-PK membranes

For the oil/water emulsion separation, the ideal membranes are supposed to perform well both in oil rejection and water permeation with large efficiency and selectivity. Therefore, this work mainly focuses on the tailored surface microstructure by regulating the ultrafine PDA NPs in-situ assembling onto the PK substrate without sacrificing its remarkable highly porous structure. As schematically in Fig. 4.1 (b), the dopamine monomers are firstly bond to the PK surfaces via hydrogen bonding followed by the PDA nucleation formation on PK substrate.

Next, the fast growth of PDA nucleus tends to be processed with its structural intersection, and subsequent the ultrafine PDA NPs in-situ assemble on PK substrate.

The SEM characterization was conducted to investigate the evolution of the ultrafine PDA NPs deposition on PK substrate as shown in Fig. 4.2. It was found from Fig. 4.2 (a) that the PK membrane was constructed with fibril-like structure throughout the surface and cross section, and nano-scale texture could be observed on the fiber surface from the enlarged SEM image. For the PDA-d-PK membranes as shown in Fig. 4.2(b)-(e), it was found that the surface was gradually covered with a thicker layer composed of micro/nanosphere-like PDA NPs under the prolonged self-polymerization from 3 h to 12 h, where clearly showed the growth process of dopamine nucleus on PK surface. For comparison, the PDA decorated PK membrane using the traditional method (5 mg/mL dopamine in 10 mM Tris solution with the pH about 8.5) was also conducted as shown in Fig. 4.3. Only several clustered PDA particles attached on the surface of the PK membrane after 9 h deposition. Besides, the particles were not homogenous and continuous.

The possible growth mechanism of dopamine particles on PK substrate was hypothesized like that: dopamine monomer was easily oxidized by dissolved oxygen to produce lots of radicals via oxidation, cyclization, and rearrangement, such as 5,6-dihydroxyindole (1) and 5,6-indolequinone (2) as shown in Fig. 4.1(a). These radicals were easily adsorbed on the PK surface via hydrogen bonding to produce dopamine nucleus, and the nucleus gradually grew with prolonged deposition time by stepwise polymerization reaction via 5,6-dihydroxyindole (1) and 5,6-indolequinone (2) at the position 2, 3, 4, and 7. Besides, the monomers, nanoaggregates and a relatively few small PDA particles coming from the solution were also capable of being incorporated into the deposited PDA layer by covalent bonding, stacking and other noncovalent interactions, which leading to an increased PDA layer with the prolonged deposition time as shown in Fig 4.2(c)-(e) [26, 27].

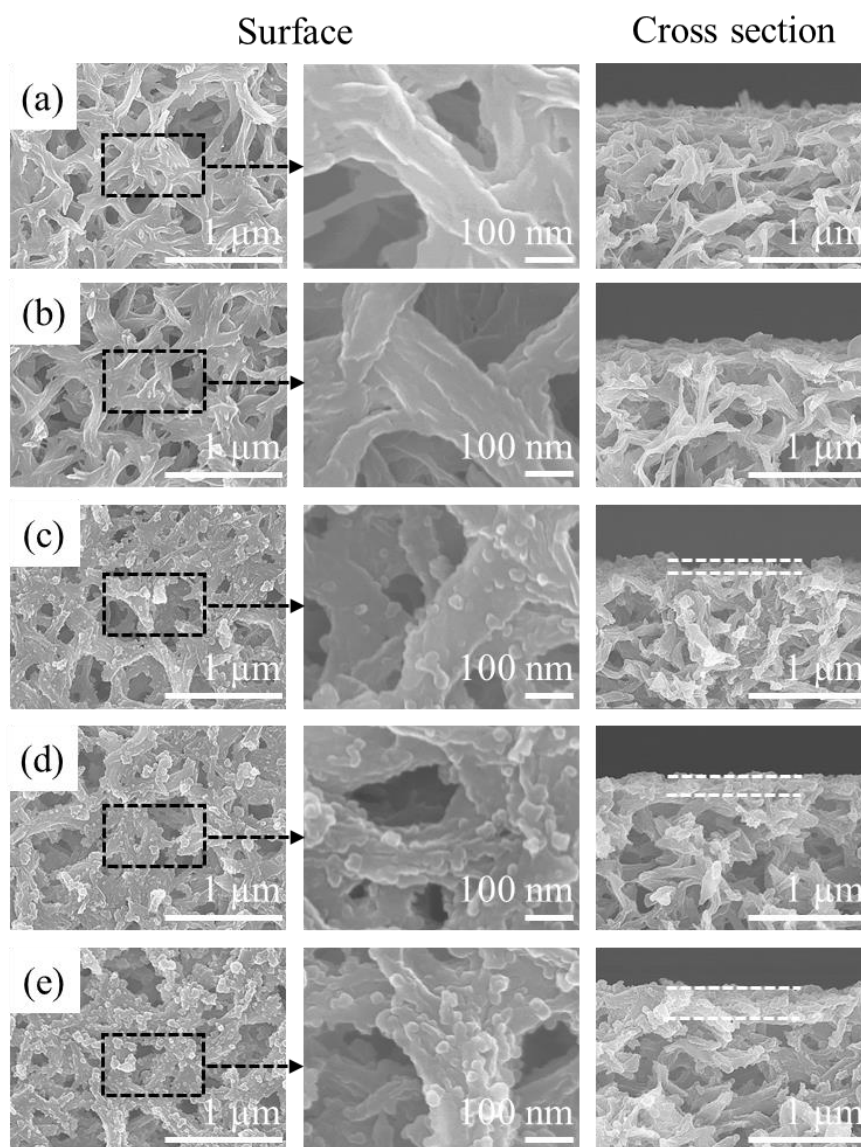


Fig.4.2. Surface and cross-section morphologies of (a) pristine PK membrane; PDA decorated PK membranes in 100 mL ethanol/water mixture (30:70) containing 8 mL ammonia solution with designed time (b) PDA-d-PK (3h), (c) PDA-d-PK (6h), (d) PDA-d-PK (9h), and (e) PDA-d-PK (12h).

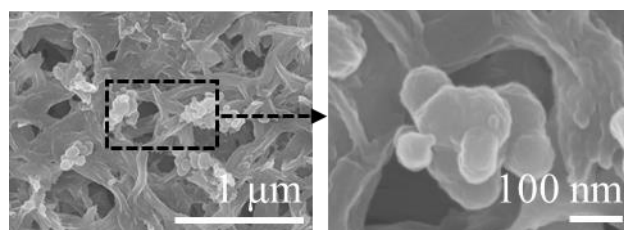


Fig.4.3. Surface morphologies of PDA-PK membranes under 9 h deposition using the traditional condition (5 mg/mL dopamine in 10 mM tris(hydroxymethyl) aminomethane solution with the pH of about 8.5).

To further unveil the mechanism of ultrafine PDA NPs in-situ deposition, the formation of PDA layer under the different ammonia initiator concentrations of 0 mL, 4 mL, 6 mL, 8 mL, and 10 mL (the same self-polymerization time of 9h) was investigated, as shown in Fig. 4.4. It could be seen from Fig. 4.4(a) that there were no PDA particles observed on PK substrate without ammonia initiator added. This was because that PDA polymerization was slow in a weakly acidic environment [21]. Besides, it was found that the larger-sized PDA clusters (~100 nm) linked randomly were in-situ generated when adding the lowest ammonia amount of 4 mL. By increasing the initiator concentration from 6 mL to 10 mL, a more prominent uniform layers composing of spherical NPs with smaller sizes (decreased from 51 nm by adding the initiator of 6 mL to 30 nm by adding the initiator of 10 mL) was obtained, suggesting that the surface microstructure could be precisely tuned by controlling the mass of ammonia initiator. This was because the existence of basic environment could facilitate the hydrogen atom abstraction from dopamine, and the subsequent ring closing progress and nucleus formation [21, 28]. As demonstrated by UV-visible spectra of dopamine in ethanol/water mixture solutions (Fig. 4.5), lots of PDA nucleus formed at the initial stage when addition 8 mL ammonia in the reactant solution (Fig. 4.5 (a)), however no changes were observed without ammonia initiator added (Fig. 4.5 (b)) [29]. By considering the balance between the free energy available for the driving force of nucleation-growth process and the energy consumed in forming the interfaces of each nucleus, the larger amount of small nucleus formed on the membrane surface with higher ammonia content tended to bring about the lower critical size within the involvement of external confinement factors for each individual cluster or embryonic nucleus growth, and leads to the ultrafine PDA NPs formation by accelerating the DA polymerization process [30-32].

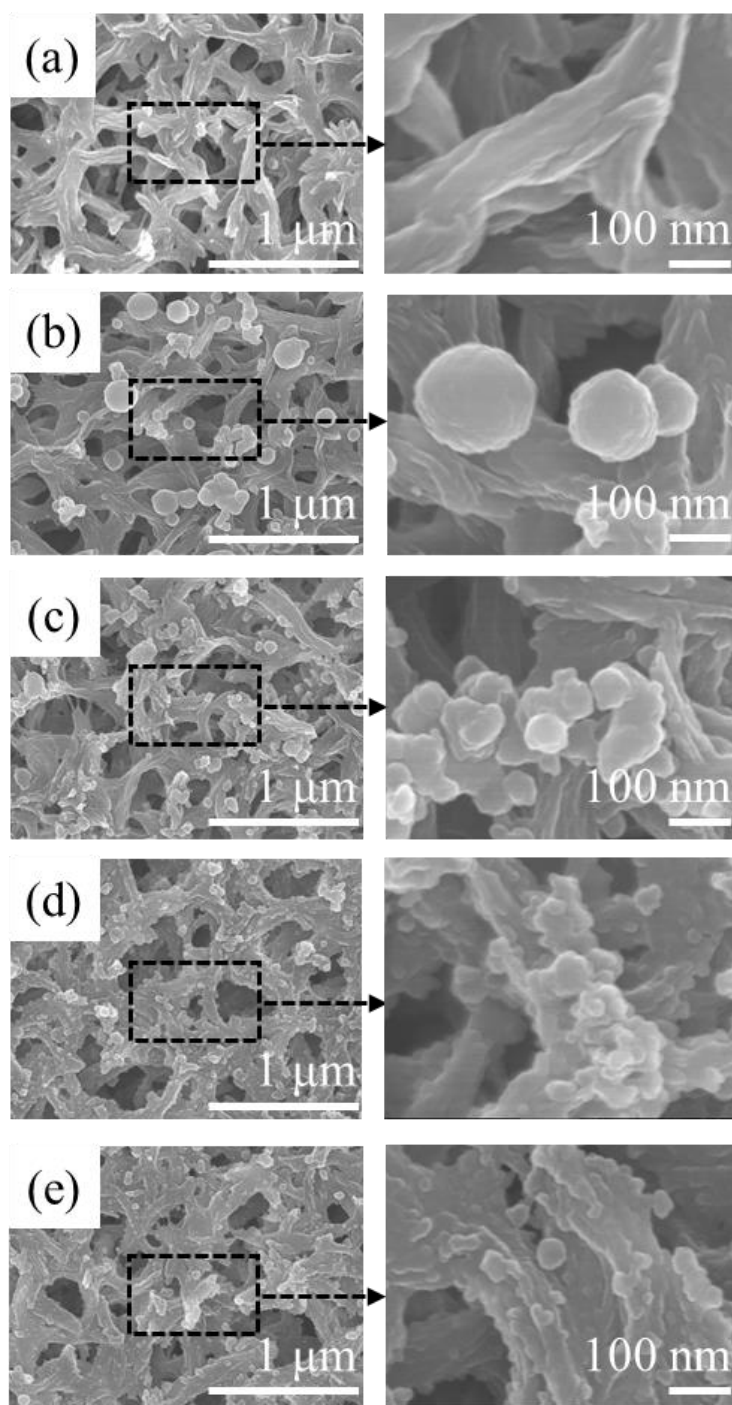


Fig.4.4. Surface morphologies of PDA-d-PK membranes under 9 h deposition in the ethanol/water mixture (30:70) with different ammonia content: (a) 0 mL, (b) 4 mL, (c) 6 mL, (d) 8 mL, and (e) 10 mL.

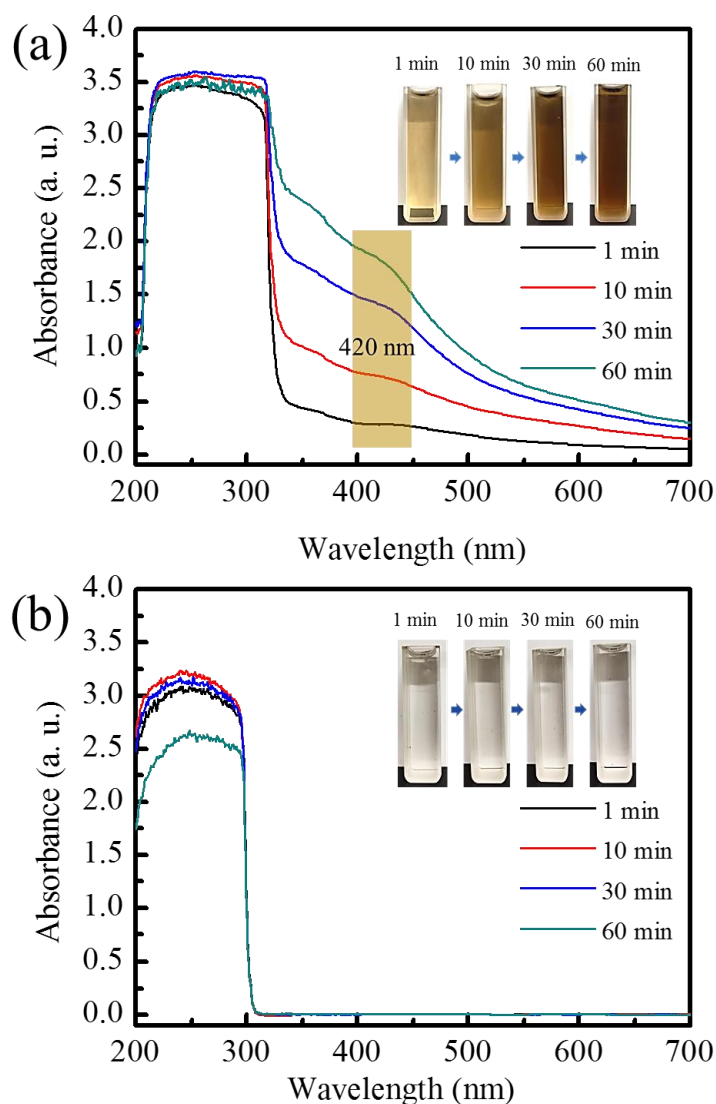


Fig.4.5. UV-visible spectra of dopamine in ethanol/water mixture solutions: (a) with 8 mL ammonia initiator and (b) without ammonia initiator.

The surface chemistry and chemical composition of the pristine PK substrate and PDA-d-PK membranes were studied by FTIR and XPS as shown in Fig. 4.6. It could be seen from Fig. 4.6(a) that the peaks at 1960, 1405, 1335, 1055 and 810 cm^{-1} were ascribed to the C=O, $-\text{CH}_2-$, $-\text{CH}_2-$, C-C characterization peaks and skeletal vibration of PK substrate [33]. Besides, the intensity of these peaks was weakened on the PDA-d-PK membranes due to the coverage of PDA layer. Four new peaks at 3300~3600, 1632, 1509, 769 cm^{-1} corresponding to the $-\text{OH}$, C=C, $-\text{NH}_2$, skeletal vibration originated from PDA layer were observed [20], and apparently increased trend with the prolonged deposition time from 3 h to 12 h, further indicating the

successful in-situ assembling of PDA layer on PK substrate. Besides, the effect of ammonia content on the surface chemistry of PDA-d-PK membrane was also shown in Fig. 4.7, and the peaks originated from PDA could be observed.

The surface chemistry compositions of PK and PDA-d-PK membranes were further characterized by XPS as shown in Fig. 4.6 (b)-(d). It could be seen from Fig. 4.6 (b) that there were only two peaks of O (29.53%) and C (70.47%) in the spectrum of PK substrate. After PDA deposition, new peak of N appeared for PDA-d-PK membranes, and the peak area gradually increased due to the increased N content from 2.86% to 5.70% as shown in Table 4.1 under the prolonged deposition time from 3 h to 12 h. These results were well corresponding to the observation of SEM images as shown in Fig.4.2. Furthermore, the detailed elements environment of C and O were analyzed as shown in Fig. 4.6 (c) and (d). Taking PDA-d-PK (9h) as example, the C element could be divided into four peaks at 287.5 eV, 285.6 eV, 285.1 eV and 284.9 eV ascribed to C=O, C-OH, C-N and C-C [34]. Similar, the O element could be divided into two peaks at 532.2 eV and 531.6 eV corresponding to the O=C and O-C [16]. Both of the analysis of C and O elements indicated that the PDA layer was successfully introduced onto the PK substrate by in-situ deposition.

Table 4.1. The surface elemental compositions of PK and PDA-d-PK membranes analyzed by XPS

Membranes	C	O	N
PK	70.47	29.53	0
PDA-d-PK-3h	72.57	24.57	2.86
PDA-d-PK-6h	72.35	23.21	4.44
PDA-d-PK-9h	74.28	20.55	5.17
PDA-d-PK-12h	75.13	19.17	5.70

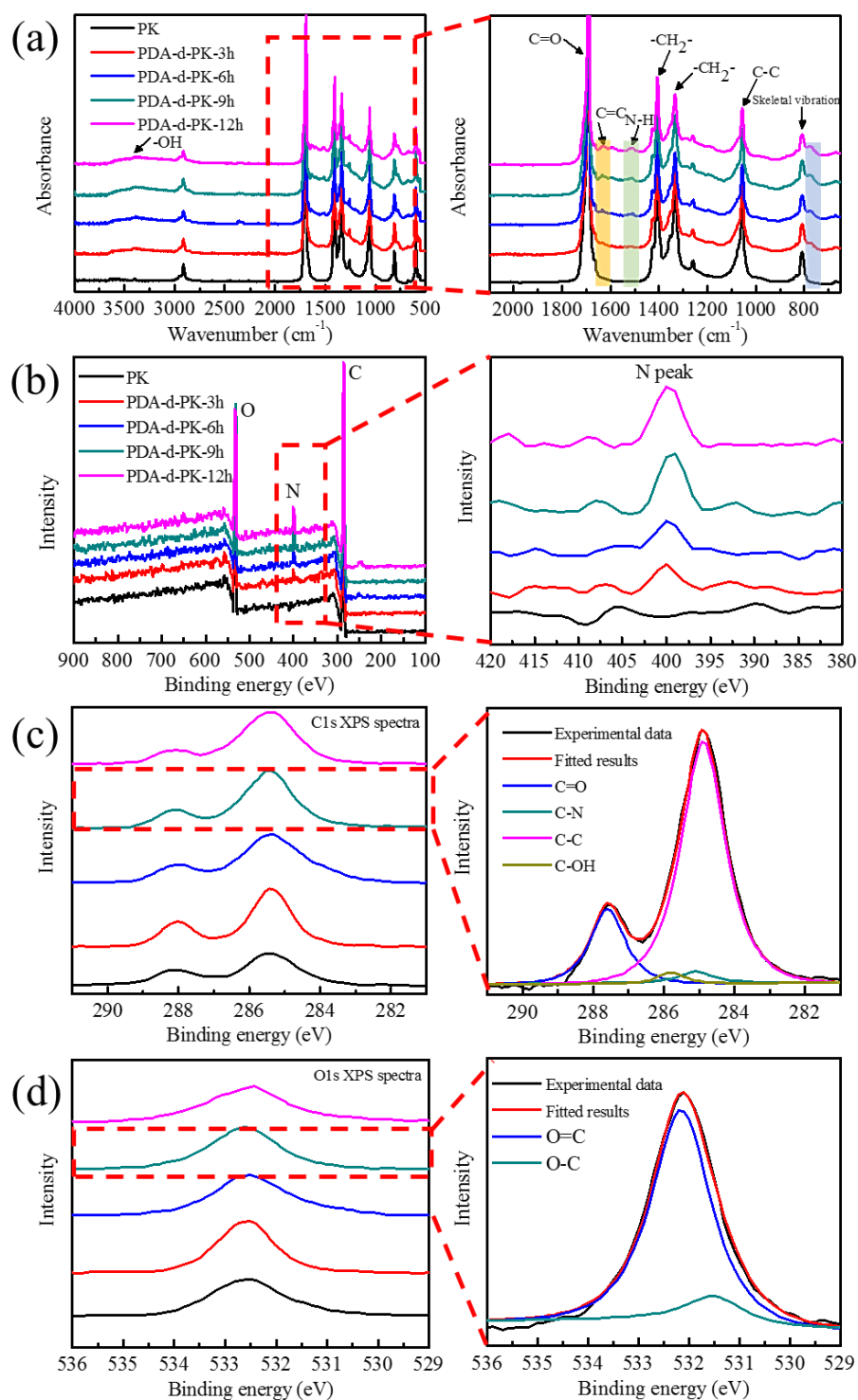


Fig.4.6. Chemical characterization of PK and PDA-d-PK membranes with different deposition time (a) FTIR, (b) XPS spectra, (c) C1s spectra and (d) O1s spectra.

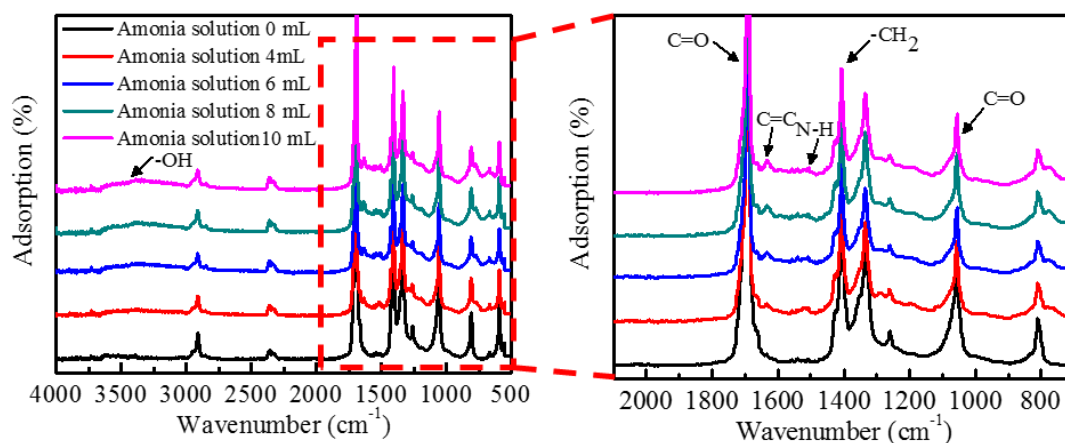


Fig.4.7. FTIR sepctrums of PDA-d-PK membranes udner 9 h deposition in the ethonal/water mixture (30:70) with different amonia content: (a) 0 mL, (b) 4 mL, (c) 6 mL, (d) 8 mL, and (e) 10 mL.

4.3.2. Wettability of the nascent PK substrate and PDA-d-PK membranes

The PDA layer constructed by hierarchical micro/nanosphere-like NPs and hydrophilic chemistry would promise the PDA-d-PK membranes with robust underwater superoleophobicity by forming a water layer through hydrogen bonding. Firstly, the underwater superoleophobicity of PK and PDA-d-PK membranes was characterized using chloroform as a probe oil as shown in Fig. 4.8 (a). It could be seen that the PK substrate was easily wetted by chloroform with an oil contact angle (CA) of about 7° due to its weak hydrophilicity. However, it should be noted that PK substrate showed better underwater superoleophobicity to apolar oil, such as hexane, hexadecane and soybean oil as reported in our previously paper [19], which was different from the commonly used membrane materials with natural oleophilicity, such as PVDF, PP. After 3 h deposition, the PDA-d-PK membrane shown a high underwater oil contact angle of 148° even though little PDA fixed on the membrane surface as demonstrated by SEM (Fig. 4.2(b)) and XPS (Fig. 4.6(b)) results. This phenomenon mainly ascribed to the distinguished hierarchical fibril-like structure of PK substrate, that was to say, the anti-oil-wettability could be greatly enhanced by the micro-/nano-composite structure and a little hydrophilic chemistry [35]. The underwater oil contact angles of PDA-d-PK membranes gradually reached a stable value of about 160° under the prolonged deposition time from 6h to

12 h due to the increased coverage of PDA layer on the PK substrate as demonstrated in Fig 4.2(d) and (e).

To further evaluate the anti-oil-adhesion property of PDA-d-PK membranes, the underwater oil adhesion test with the process of “compress-withdraw” was conducted as shown in Fig. 4.8 (b). It could be seen from PDA-d-PK (3h) membrane that part of the chloroform easily permeated into the PK substrate when the droplet was compressed on the membrane surface, which was mainly due to the weak chloroform-resistance of the PK substrate. For the PDA-d-PK membrane with 6 h deposition, the oil droplet was still hard to withdraw even though no obviously chloroform permeate into the membrane surface. This was due to the incompletely coverage of PDA layer on PK membrane as shown in Fig. 4.2 (c). For the PDA-d-PK membranes with 9 and 12 h deposition, the oil droplet was easily detached from the membrane surface even though after strongly compression to make the droplet deformation. The better anti-oil-adhesion of PDA-d-PK (9h) and PDA-d-PK (12h) membranes was ascribed to the sufficient decoration of PDA particle layer on the PK substrate to forming a thickness hydration layer, leading to the chloroform wettability changing from “Wenzel state” to “Cassie state” [36]. Based on the dynamic adhesion results, it demonstrated that an ultralow oil-adhesion surface could be reached after 9 h of ultrafine PDA NPs assembling. Therefore, the PDA-d-PK membrane with 9 h deposition was selected to further investigated the comprehensive underwater oleophobicity. As shown in Fig. 4.8 (c), the underwater oil contact angles were measured using another four kinds of oils. The PDA-d-PK (9h) membrane shown high underwater oil contact angles of 164°, 167°, 164°, 167° and 163° for the hexane, hexadecane, petroleum ether, soybean oil and chloroform, respectively. More importantly, the PDA-d-PK (9h) membrane shown low oil adhesion force for different oils as shown in Fig. 4.9, and the oil droplets were easily detached from membrane surface. The comprehensive underwater superoleophobicity and low oil adhesion force would guarantee the PDA-d-PK (9h) membrane with high separation efficiency for different oil-in-water emulsions.

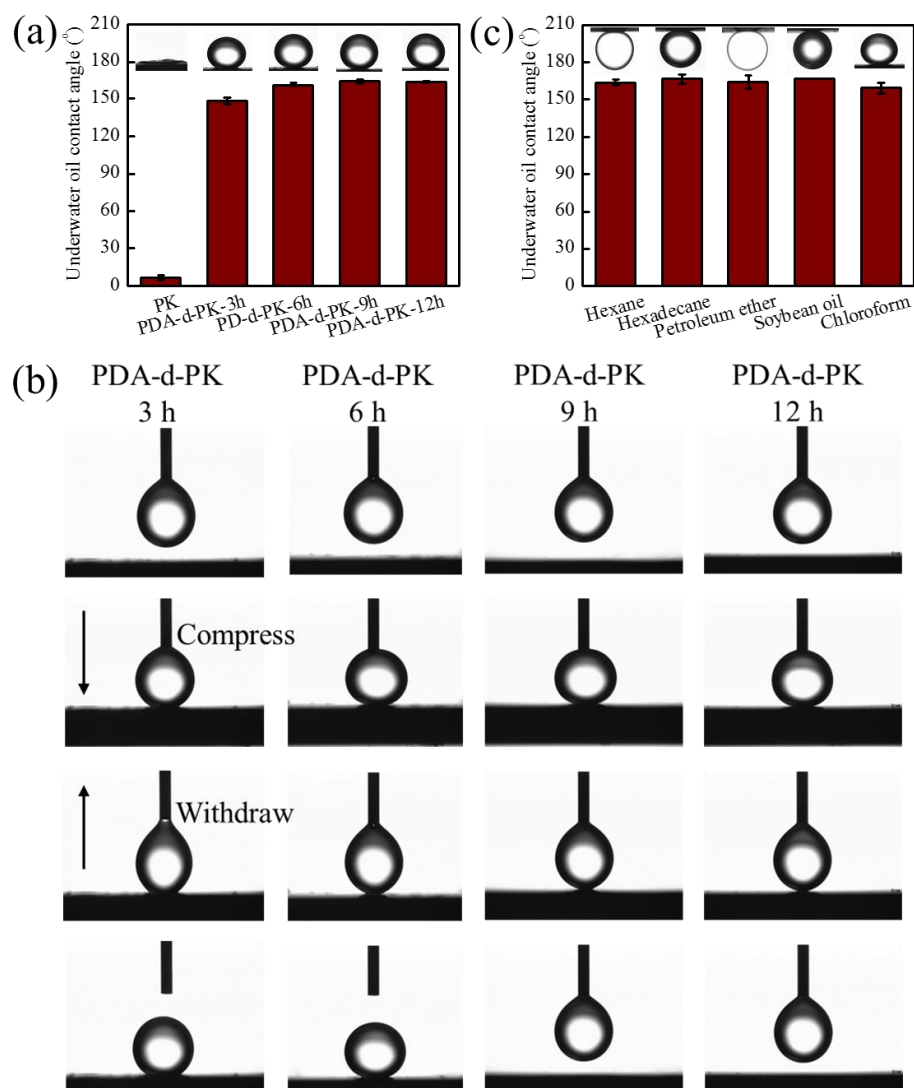


Fig.4.8. Surface wettability of PK and PDA-d-PK membranes with different deposition time: (a) underwater chloroform contact angles; (b) underwater oil dynamic adhesive property; (c) underwater oil contact angles of PDA-d-PK (9 h) membrane for hexane, hexadecane, petroleum ether and chloroform.

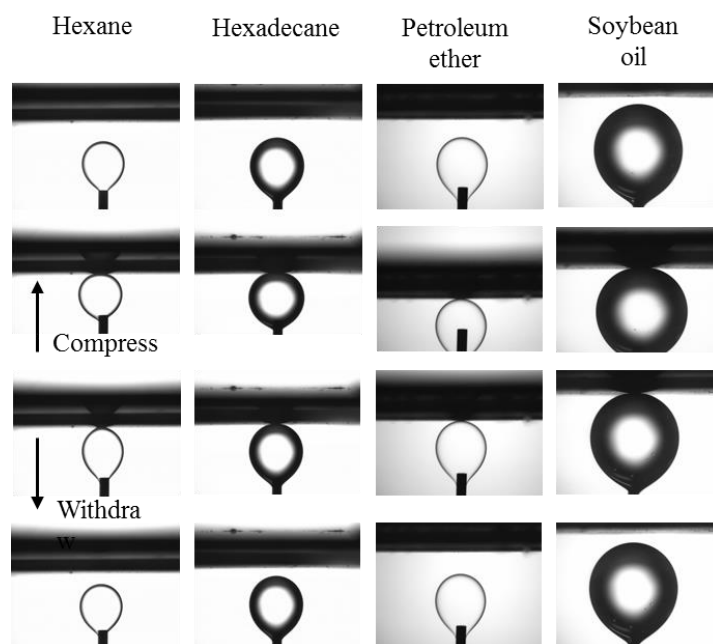


Fig.4.9. Underwater oil adhesion test of PDA-d-PK (9h) membrae using hexane, hexadecane, petroleum ether and soybean oil as probe oil. The oil droplet volume was changed from 4 mL ~20 mL due to its different density and viscosity.

The hydrophilicity and self-cleaning ability of PK and PDA-d-PK (9h) membranes were also investigated as shown in Fig. 4.10 (a) and (b). It could be seen from Fig. 4.10 (a) that the PK membrane shown a water contact angle (in air) of 43° at the initial time, and gradually reduced to 0° in 11s, showing a similar superhydrophilicity with the reported paper due to its hierarchical structure and inter-mediate hydrophilicity [37]. For the PDA-d-PK (9h) membrane, it shown a smaller initial contact angle of 17° than PK substrate and quickly disappeared in 4s. This was mainly because that the hydrophilic PDA layer would promote the adsorption and permeation of water into the membrane [23]. The self-cleaning ability of PK and PDA-d-PK membranes was tested with the process of “oil wetting-water washing”. It could be seen from Fig. 4.10 (b) that the dry membrane was easily wetted by colored oil due to the low surface tension of oil. When immersed the oil fouling PK membrane in water, the adsorbed oil was hardly to wash away even with strong shanking. In contrast, the oil rapidly aggregated to a big droplet on PDA-d-PK (9h) membrane surface when immersed into water, and detached from the membrane after shaking. The distinguished self-cleaning ability mainly ascribed to the strong water bonding ability of the PDA layer [38].

For the oil/water emulsions separation, membrane stability plays an important role in determining its practical application, the PDA-d-PK 9h membrane was thereby systematically treated by various environments such as water, acid, alkali, and organic solvents. The PDA-d-PK membrane showed stable underwater oil contact angles as shown in Fig. 4.10 (c) and low oil adhesion force as shown in Fig. 4. 11 even after 30 days. The good durability of PDA-d-PK membrane was ascribed to the strong adhesion force of PDA and the good compatibility between PDA and hydrophilic PK substrate [39]. Chemistry-resistance was also important for oil/water separation membrane to make it possible for working in harsh environment. It was reported that PDA coating layer was not stable in strong acidic and alkaline solution, as well as in polar organic solvents [29, 40]. However, it could be seen from Fig.4.10 (d) that all the PDA-d-PK (9h) membranes showed high underwater oil contact angles even after 12 h immersion in 0.01 M HCl, 1 M NaCl, 0.01 M NaOH, ethanol and acetone solutions. Besides, the appearance of PDA-d-PK (9h) membrane almost not changed after 12 h immersion as shown in Fig. 4.12, demonstrating a robust acid, salty, alkaline and organic solvent resistance.

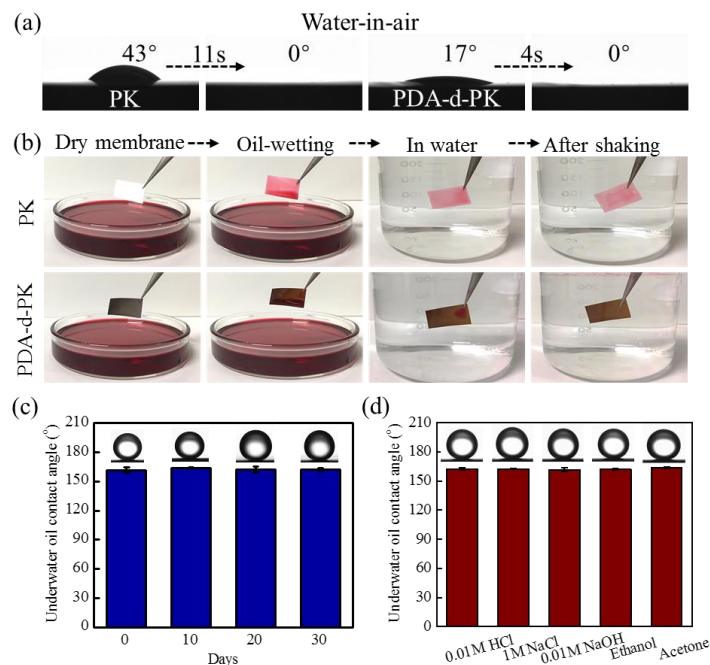


Fig.4.10. Self-cleaning ability and durability of PK and PDA-d-PK (9h) membranes:(a) water contact angle in air; (b) self-cleaning ability with the process of “oil wetting-water washing”; (c) underwater chloroform contact angles with different immersion time in water, (d) chemistry-resistance for acid, salty, alkaline, ethanol and acetone.

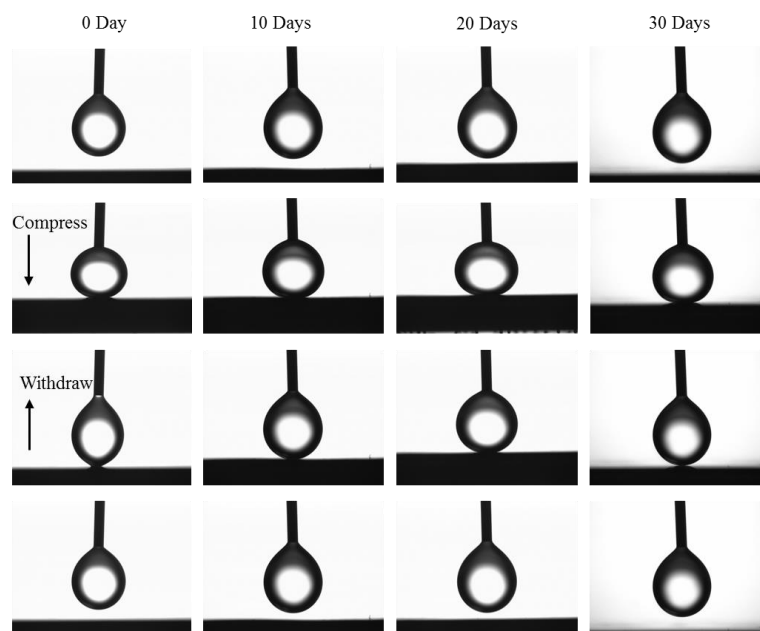


Fig.4.11. Underwater oil adhesion test of PDA-d-PK (9h) membranes using chloroform as probe oil with different immersion time in water.

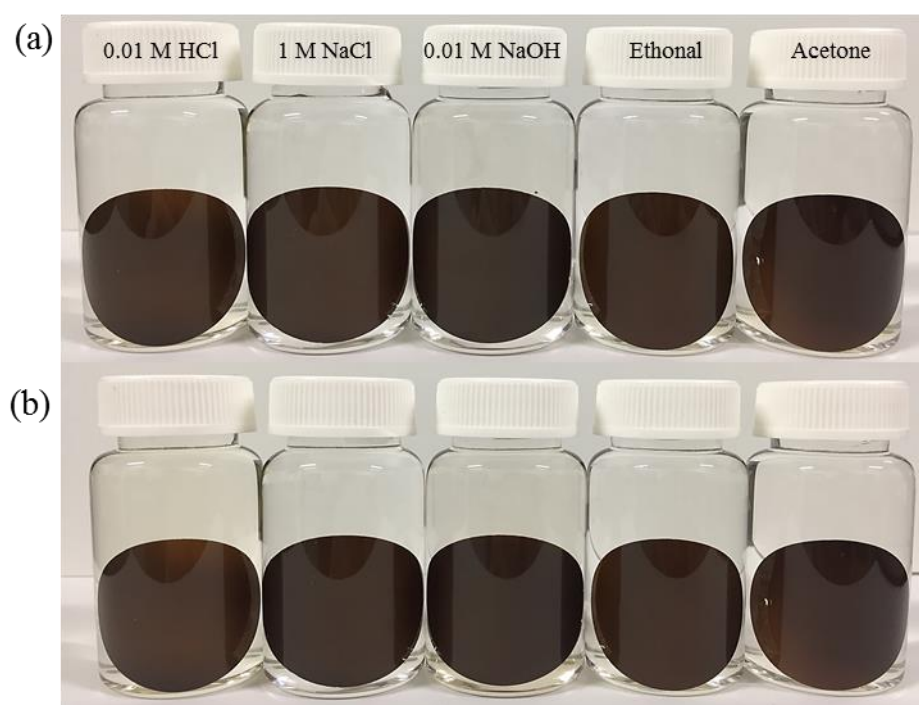


Fig.4.12. The appearance of the PDA-d-PK membrane immersion in 0.01 M HCl, 1 M NaCl, 0.01M NaOH, Ethonal and Acetone: (a) before and (b) after 12 h immersion.

4.3.3. Separation and antifouling performance of pristine PK substrate and PDA-d-PK membranes

The superior wetting selectivity (superhydrophilic and underwater superoleophobicity) featured the PDA-d-PK membrane with a great potential in oily emulsions separation with high efficiency. Fig. 4.13 (a) showed the water permeances against the PS nanosphere (200 nm) rejection ratios of the pristine PK and PDA-d-PK membranes. The pristine PK substrate showed a high water flux of $136 \text{ Lm}^{-2}\text{h}^{-1}$ due to its highly porosity structure and inter-mediate hydrophilicity, which the water was easily adsorbed and permeated into the membrane pores even under a low pressure of ~ 0.01 bar (10 cm liquid volume). For the PDA-d-PK membranes, the water fluxes gradually reduced from $132 \text{ Lm}^{-2}\text{h}^{-1}$ to $110 \text{ Lm}^{-2}\text{h}^{-1}$ with the prolonged deposition time from 3h to 12 h because of the coverage of PDA layer on the PK substrate as shown in Fig. 4.2, while remaining a full rejection ratio of 200 nm nanosphere. It should be noted that the flux reduction ratio of PDA-d-PK (9h) was only $\sim 14.7\%$ compared with the pristine PK substrate, which was lower than other modification method, such as surface grafting [16] or coating [15]. The lower flux reduction was mainly ascribed to the ultrafine in-situ PDA NPs assembling using ammonia as initiator. A balance between the surface hydrophilizing (namely, self-polymerization process of DA) and the permeating flux was needed to be considered to achieve the highly-efficient oil/water separation. Along with this concept, the 9h of self-polymerization process was chosen as the optimum condition due to the simultaneous realization of ultralow oil adhesion property (demonstrated in Fig. 4.8 and Fig. 4.9) and a relatively high water permeating flux of $116 \text{ Lm}^{-2}\text{h}^{-1}$.

The separation property for various surfactant stabilized oil-in-water emulsion was treated by PDA-d-PK 9h membrane, as shown in Fig. 4.13 (b). It was found that the PDA-d-PK (9h) membrane showed high emulsion fluxes of $106 \text{ Lm}^{-2}\text{h}^{-1}$, $99 \text{ Lm}^{-2}\text{h}^{-1}$, $98 \text{ Lm}^{-2}\text{h}^{-1}$, $83 \text{ Lm}^{-2}\text{h}^{-1}$ for hexane-in-water, hexadecane-in-water, petroleum ether-in-water and soybean oil-in-water emulsions, respectively. It should be noted that the lower emulsion flux of soybean oil-in-water were ascribed its higher density, viscosity and emulsification ability compared with other oils, easily leading to an oil layer formed on membrane surface during the filtration process [19]. Besides, the PDA-d-PK (9h) membrane also shown high emulsion separation efficiency for

hexane-in-water, hexadecane-in-water, petroleum ether-in-water and soybean oil-in-water with the oil content in permeation of 5 ppm, 7 ppm 5 ppm, 4 ppm, respectively, showing high rejections mere than 99.9%. In addition, it also could be observed from Fig. 4.13 (c) that the hexane-in-water emulsion was milk white due to lots of oil droplets existence with size from several hundred nanometers to microns demonstrated by dynamic light scatter (DLS). However, it become transparent and clear after separation without oil droplets could be observed by optical microscopy, which also demonstrating a high separation efficiency. The similar phenomenon could also be observed for the hexadecane-in-water, petroleum ether-in-water, soybean oil-in-water emulsion as shown in Fig. 4.13(d)-(f).

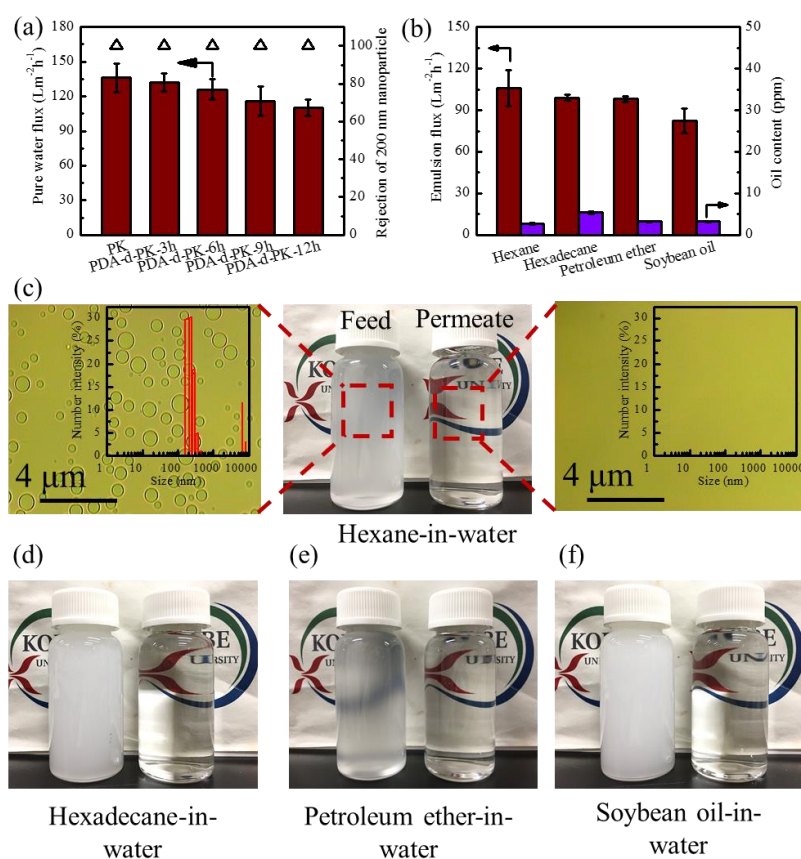


Fig. 4.13. Filtration performance of PK and PDA-d-PK membranes: (a) pure water flux and rejection of 200 nm polystyrene; (b) emulsion flux and oil content in permeate with filtration of PDA-d-PK (9h); (c) oil droplet size distribution and optical microscope images of hexane-in-water emulsion before and after filtration; (d) hexadecane-in-water; (e) petroleum ether-in-water; (f) soybean oil-in-water.

To systematically study the fouling-resistant/releasing property of the newly-developed PDA-d-PK 9h membrane, a lab-scale dead-end apparatus was used to monitor the variation of permeating flux over the 3 cycles of filtration-cleaning process, where all the membranes were tested at the similar initial flux of $\sim 116 \text{ Lm}^{-2}\text{h}^{-1}$ by controlling each of the exerted transmembrane pressure, as exhibited in Fig. 4.14. When treating the less troublesome emulsion containing only hexadecane and surfactant (SDS), a higher residual flux of 80% of the initial value and an extremely high flux recovery ratio (FRR) of $\sim 95\%$ were obtained for the PDA-d-PK 9h membrane after 3 filtration cycles, indicating a superior antifouling property when treating surfactant stabilized oil-in-water emulsions. For comparison, the pristine PK substrate showed an obviously decreased residual flux of around 50% of the initial value and lower FRR down to 86%. As for more challenging emulsions containing 1000 ppm proteins (Fig. 4.14(b)) and 1000 ppm humic acid (HA) (Fig. 4.14(c)), the newly-developed PDA-d-PK 9h membrane remained a relatively lower residual fluxes of 27%, and 10% of the initial values after 3 cycles of filtration process. The more dramatic decline in permeating flux should be ascribed to the aggregation of BSA and HA particles that caused the formation of “oil drop cake” and led to the severe pore blocking within the inner structure of membrane [16]. However, it was noteworthy that an insignificant decay in FRRs of 87% (for BSA/oil) and 92% (HA/oil) were obtained after simple hydraulic washing, showing a robustly fouling-resistant/fouling-releasing property. In contrast, the pristine PK substrate exhibited lower residual fluxes and limited FRRs 77% and 80% after 3 cycles of filtration-cleaning processes, indicating more severely irreversible fouling occurred due to the adsorption of comprehensive foulants.

The oil/water emulsion separation properties in terms of emulsion flux, oil rejection, and antifouling properties of the PDA-d-PK membrane were compared with the previously reported membranes, as summarized in Table 4.2. These results indicated that the performance of PDA-d-PK membrane was superior to most of the other membranes prepared using different materials and methods, including dopamine coating, mineralization, grafting, blending and vacuum filtration. The newly developed PDA-d-PK membrane showed a high emulsion flux, while maintaining a high oil rejection, and a low fouling propensity.

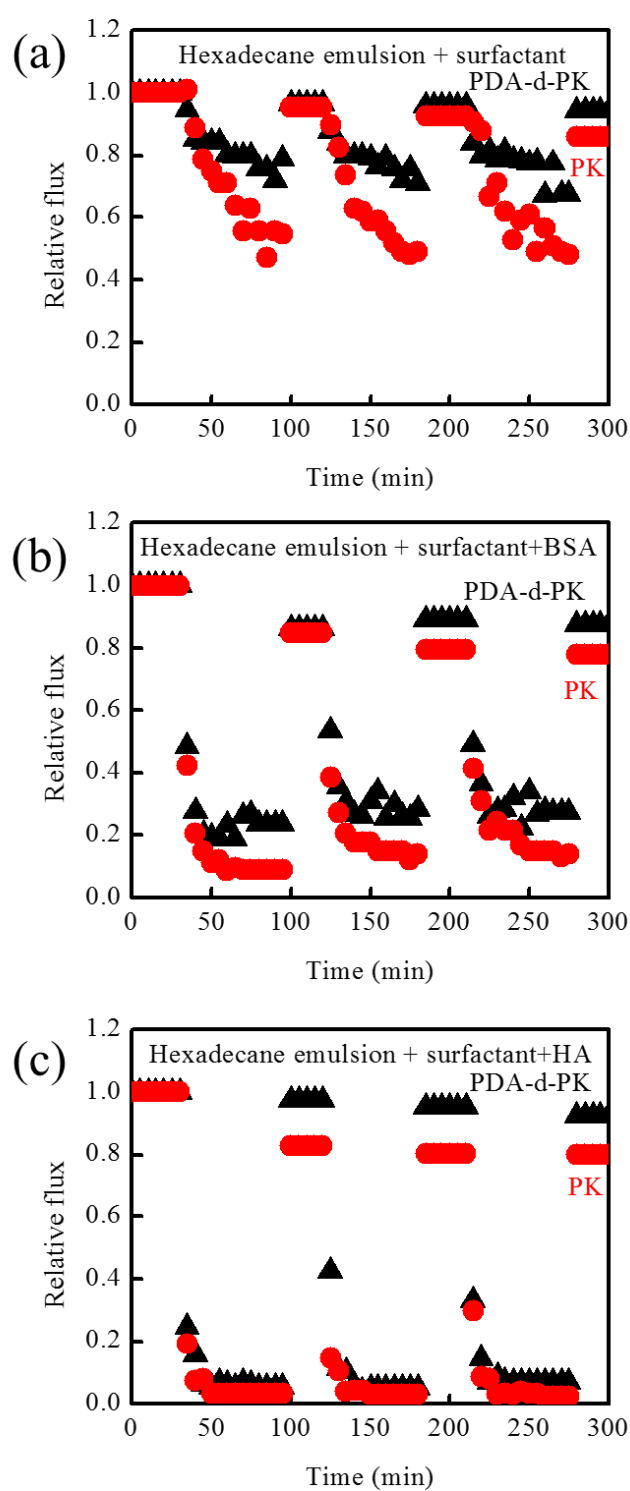


Fig.4.14. Fouling-resistance and fouling release performance of PK and PDA-d-PK (9h) membranes for surfactant-stabilized emulsion:(a) hexadecane-in-water emulsion; (b) hexadecane-in-water emulsion with 1000 ppm BSA; and hexadecane-in-water emulsion with 1000 ppm HA.

Table 4.2. Comparison of the filtration performance of various membranes used for surfactant-stabilized oily emulsions separation

Materials	Pore size (nm)	Oil feed content (ppm)	Oil droplet size in feed (mean, nm)	Emulsion flux ($\text{Lm}^{-2}\text{h}^{-1}$), Pressure	Oil content in permeate (ppm)	FR R (%)
PVDF/CS/PDA[41]	<1000	1000	431	201, 1 bar	<30	99.8
PAN/PDA [22]	<1000	10000	-	16000, 1 bar	<150	95
PVDF/PDA [20]	<450	10000	2000~32000	8649, 0.38 1 bar	<140	96
Cellulose/PDA/PEPA [42]	-	10000	180~200	10000, 1 bar	<20	-
CaCO ₃ /Polypropylene [43]	200	10000	140-5000	2000, 0.5 bar	<100	90
SiO ₂ /PEI/polypropylene [10]	200	10000	100-8000	1228, 0.4 bar	<70	95
Nanocrystal/Palygorskite [44]	-	100	50-200	883, 0.5 bar	10	94
TiO ₂ /PLA[45]	-	-	-	963, 1 bar	<100	95
Ceramic membrane[46]	50	5000-30000	175-280	40-80, 1-5 bar	200-750	-
SnO ₂ /PVDF[9]	200	20000	-	800, 1 bar	82	92
SWCNT/PDA/PEI[34]	~10	10000	50-70	3030, 1 bar	<35	96
F127/PES[47]	-	900	2100	80, 1 bar	0	94
Alginate/PVDF[48]	60	10000	800-2000	1300, 1 bar	18	93
PDA-d-PK membrane (this work)	<200	10000	500-6000	10600, 1 bar	5	95

4. 4. Conclusions

An ultrafine PDA NPs in-situ assembling was implemented on PK substrate via the facile self-polymerization process. The ultrafine PDA NPs surface modification endowed the membrane with an exceptional water permeance up to $11600 \text{ Lm}^{-2}\text{h}^{-1} \text{ bar}^{-1}$, and superior emulsions separation properties with high oily emulsions permeating fluxes of $10600 \text{ Lm}^{-2}\text{h}^{-1} \text{ bar}^{-1}$ for hexane-in-water, $9900 \text{ Lm}^{-2}\text{h}^{-1} \text{ bar}^{-1}$ for hexadecane-in-water, $9800 \text{ Lm}^{-2}\text{h}^{-1} \text{ bar}^{-1}$ for petrolether-in-water, and $8300 \text{ Lm}^{-2}\text{h}^{-1} \text{ bar}^{-1}$ for soybean oil-in-water that exhibit a negligible decrease when comparing to the pure water permeating flux; and a remarkable high rejection ratio of 99.9% for various of oily emulsions. Benefiting from the unique surface configuration

composed of micro/nanospherical PDA NPs, a robust “Cassie state” was accomplished that enabled the PDA-d-PK membrane a comprehensively fouling-resistant/fouling-releasing property against various of oil, protein and HA, where a nearly full recovery could be reached over 3-time filtration-cleaning cycles after simple hydraulic washing. Due to the chemically inert of PDA NPs, the newly-developed PDA-d-PK membrane could be potentially operated in challenging environments involve salty, various of organic solvents, and strong acid/alkali solutions. To sum up, considering the significantly enhanced superhydrophilicity and underwater superoleophobicity, the facile and cost-effective fabrication process of PDA NPs in-situ assembling shows a promising prospects in treating practical oily emulsions.

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Chapter 5

A comprehensively fouling- and solvent-resistant aliphatic polyketone membrane for high filtration of difficult oil-in-water micro- and nano-emulsions

5.1. Introduction

Rapid industrial development has led to increasing interest in highly efficient oil/water separation technologies for oily wastewater reclamation and purification [1]. In practical water environments, oily contaminants (e.g., insoluble hydrocarbons or fatty glycerides) are usually present in the form of free oils, unstable dispersions, stable emulsions, or even dissolved oil [2], along with other inorganic, organic, and biological pollutants in many different forms, such as bioorganisms, bacterial, and natural organic matter (NOM). Conventional oil/water separation technologies, such as electrochemical treatment, centrifugation, air floatation, and chemical coagulation suffer from high energy consumption and process complexity, and are useless for directly treatment of oil-in-water emulsions with micron ($<20\ \mu\text{m}$) or nano-scale ($<100\ \text{nm}$) oil droplets [3,4]. Membrane separation technology is recognized as one of the most efficient strategies for removing impurities from water due to its nanometer-to-micron size-based selectivity, energy and space efficiency, high operation flexibility, and scalability [5, 6]. To address the issue of serious flux decline (i.e., membrane fouling) associated with traditional hydrophobic-oleophilic membranes during oil/water separation [7-9], a new class of superhydrophilic and underwater superoleophobic membrane that can retain a surface hydration layer with ultralow, or nearly zero oil-adhesive force [10], has been developed by exploiting the synergistic effects of hydrophilic surface chemistry and rough surface geometry [11, 12]. Superwetting membranes prepared using various processing methods and different hydrophilic

materials have been demonstrated to exhibit efficient and anti-oil-fouling microfiltration (MF) and ultrafiltration (UF) capabilities for different model oil/water mixtures [13-16].

It has been suggested that “there are no membranes that are free from fouling under any circumstances” [17]. Of course, underwater super oil-repellency alone is not sufficient to keep a superwetting membrane free from fouling in harshly realistic scenarios. Various pollutants and aggressive chemicals (e.g., strong acids, alkaline and organic solvents) present in real-world oily wastewater can deteriorate and degrade the superhydrophilic membrane surfaces, after which more serious membrane fouling such as biofilm formation can occur [18]. It is well-known that zwitterionic materials, carrying zwitterions of carboxybetaine or sulfobetaine, have ultralow fouling potential to various foulants [19, 20], owing to their strong hydration ability, which arise from the electrostatic interactions between the zwitterions and water. Zwitterionic polyelectrolytes have already been used for surface modification to realize superhydrophilicity and underwater superoleophobicity for oil/water separation [21, 22]. For instance, Jin et al. first reported the fabrication of a membrane comprising a zwitterionic sulfobetaine nanohydrogel grafted onto a poly(vinylidene fluoride) (PVDF) substrate that exhibited comprehensive antifouling properties in the filtration of oil-in-water emulsions containing bovine serum albumin (BSA), and humic acid (HA) foulants [23]. The nanohydrogel was synthesized by an inverse microemulsion polymerization process and then coupled to a poly(acrylic acid) grafted PVDF substrate (PAA-g-PVDF) via a EDC/NHS catalyzed surface reaction. The grafted zwitterionic nanohydrogel layer prevented the adhesion and adsorption of foulants onto the hydrophobic PVDF matrix and the PAA brush. However, the complexity of this technical route may be partially attributed to the difficulty of introducing sufficient active sites onto the PVDF substrate for the subsequent high-density immobilization of the zwitterionic material.

Thus, seeking a class of comprehensively antifouling polymeric membranes that can handle oil-in-water micro/nanoemulsions in harsh environments is still a great challenge in this research area. The main obstacle here is the dominantly hydrophobic polymeric membranes usually adopted as the substrates for further decorating with ultralow-fouling materials (such as zwitterions), although they lacking of readily accessible reactive sites for stable covalent immobilization. If the surface coverage of the antifouling material is incomplete or insufficient,

the underlying hydrophobic substrate may still be exposed to fouling matters passing through the loose protective layer and thus suffer continuous foulant adhesion, especially for small foulants like biomacromolecules (e.g., BSA) [24, 25].

In the present study, to realize a robust and comprehensive fouling-resistant oil/water separation membranes, an alternative antifouling membrane that incorporates a non-fouling zwitterionic surface layer on a low-fouling and solvent-resistant hydroxylated aliphatic polyketone (PK) membrane substrate was developed. Starting from a hydrophilic PK substrate, a hydroxylated PK membrane (PK-OH) is obtained by a one-step reduction according to our previous study [26]. Then, surface-initiated atom transfer radical polymerization (SI-ATRP) is employed to graft the zwitterionic polyelectrolyte of N-(3-sulfopropyl)-N-methacryloxyethyl-N,N-dimethylammonium betaine (SBMA) in a controlled manner, as shown in Schematic 5.1. The prepared membrane is named as SBMA-g-PK. The surface reduction reaction generates many stable hydroxyl groups over the PK membrane surface as anchoring sites for the high-density SI-ATRP grafting of zwitterionic polyelectrolytes, which is completed within just 5-15 minutes. Even though the PK-OH membrane exhibits satisfactory antifouling properties in the separation of common oil/water emulsions, introduction of the zwitterionic surface layer imparts comprehensive fouling resistance against not only oils but also various other foulants, such as NOM. Compared to those of commercial and state-of-the-art oil/water separation membranes, the SBMA-g-PK membrane demonstrates superior sustainable emulsion flux and high oil rejection, even under harsh high-fouling and aggressive solvent conditions.

5.2. Experimental

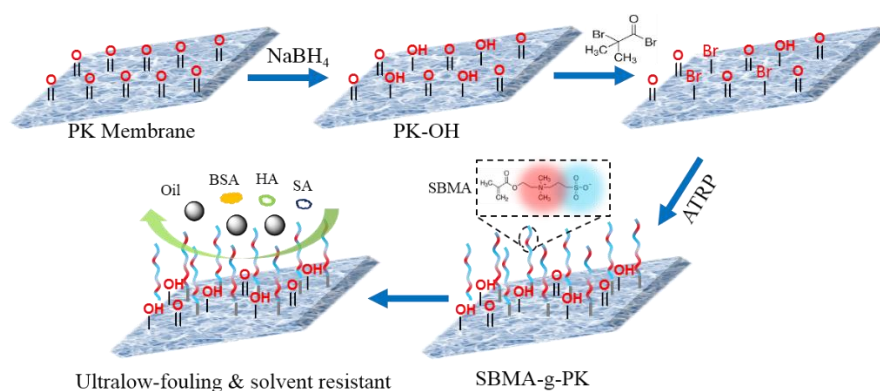
5.2.1. Materials

Aliphatic polyketone (PK; $M_w = 200\,000\text{ g mol}^{-1}$) was provided by Asahi Kasei Co., Ltd., Japan. Resorcinol, methanol, sodium borohydride (NaBH_4), acetone, hexane, hexadecane, soybean oil, chloroform, sodium dodecyl sulfate (SDS), BSA, lysozyme, sodium alginate (SA), and HA were purchased from Wako Pure Chemical Industries Co., Ltd., Japan. SBMA was purchased from EMD Millipore Co., Ltd. (Germany). α -Bromoisobutyryl bromide (BIBB), L-

ascorbic acid, copper (II) bromide (CuBr_2), tris(2-pyridylmethyl) amine (TPMA), and Tween-80 were obtained from Sigma-Aldrich, Japan. Polystyrene nanoparticles (50 nm diameter) were obtained from Thermo Scientific Inc. (USA). The Triton X-100 was purchased from Alfa Aesar A Johnson Matthey Co. Ltd. Milli-Q water (Milli-Q integral 3, Millipore SAS, France) was prepared in our lab.

5.2.2. Membrane fabrication

PK powder (10 wt%) was dissolved in a resorcinol/water solvent (65:35, w/w), and stirred for 3 h at 80 °C to obtain a homogenous solution. After degassing, the dope solution was spread onto a glass plate using a stainless steel casting knife with a 200 μm gap. Then, the casting film was immediately immersed into a methanol/water coagulation bath (35:65, w/w) at 25 °C. After solvent exchange and solidification, the membrane was washed with acetone and hexane solutions for 20 min for each, and finally air dried. The resultant membrane was named as PK.



Scheme 5.1. Schematic illustration of the SI-ATRP grafting of a sulfobetaine zwitterionic layer onto an aliphatic polyketone membrane.

The construction of the sulfobetaine zwitterionic surface layer on the PK membrane was performed using surface reduction and SI-ATRP reaction according to the procedures in our previous report [27]. As shown in Scheme 5.1, a pure PK membrane was firstly immersed in a 0.1 wt% NaBH_4 solution for 10 minutes to obtain a surface reduced membrane carrying many hydroxyl groups, named as PK-OH [26]. Then, the surface hydroxylated membrane was treated with a 3 wt% BIBB/hexane solution for 2 min to immobilize the initiator. The membrane was soaked in 156 mL of a water/methanol mixture (1:1, v/v) containing 15.56 g SBMA and 1.57

g L-ascorbic acid. After 10 min of nitrogen bubbling, 44 mL of water/methanol (1:1, v/v) containing 0.05 g CuBr₂ and 0.13 g TPMA was added to initiate the ATRP reaction. After a predetermined modification period of 5, 10, or 15 min, the zwitterionic polyelectrolyte grafted membranes were washed with water prior to further testing, and defined as SBMA-g-PK (5 min), SBMA-g-PK (10 min), and SBMA-g-PK (15 min), respectively.

5.2.3. Membrane characterization

The surface microstructures of the prepared membranes were observed using a field-emission scanning electron microscopy (SEM; JSF-7500F, JEOL, Japan). Surface chemical compositions were investigated by Fourier-transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR; Alpha Bruker) and X-ray photoelectron spectroscopy (XPS; JPS-9010 MC, JEOL, Japan) with Al K α X-rays. SEM image analysis was carried out by Nano MeasurerVersion1.2 software with one hundred points collected to obtain the surface average pore size and pore size distributions of the membranes. The average pore size was measured using a capillary flow porometer (CFP-15-AXLC, Porous Materials Inc., USA) at least three times to obtain an averaged value. The mechanical properties were measured using a tensile testing apparatus (AGS-J, Shimadzu Co., Japan). Initially, the thickness of the samples was measured using calipers. Then, the membrane samples (4*26 mm) were placed vertically between two pairs of pneumatic clamps, and a testing speed of 20 mm min⁻¹ to the upper clamp was applied until the sample broke [28]. The zeta potentials of the PK, PK-OH, and SBMA-g-PK (10 min) membranes in the pH range of 3-9 were measured using an electro kinetic analyzer (Anton Paar SurPASSTM 3, Austria) under a background electrolyte solution of 75 ppm KCl. The surface wettabilities of the membranes were evaluated by using a contact angle goniometer (Drop Master, Kyowa Interface Science Co., Japan). A droplet of water (or oil) with a volume of 4-20 μ L volume was dispensed on the membrane surface in air or (in water). Each membrane was analyzed at least five times at different locations. The oil-sliding angle was defined as the minimum membrane tilt angle required for an oil droplet to slide downwards. Dynamic oil adhesion tests were carried out to evaluate the anti-oil-adhesion property of the membranes [29]. A 6- μ L droplet of chloroform was firstly compressed against the membrane surface and then

pulled back slowly. Protein adsorption experiments using the fluorescence-labeled BSA and lysozyme were performed to assess the biofouling resistance of the pristine PK, PK-OH, and SBMA-g-PK membranes. Fluorescence intensity was detected using a confocal laser-scanning microscope (CLSM, FV1000D, Olympus, Tokyo, Japan) [30].

5.2.4. Preparation of oil-in-water emulsions and membrane filtration

Various surfactant-stabilized oil-in-water emulsions, namely hexane-in-water, hexadecane-in-water, soybean oil-in-water, petroleum ether-in-water, chloroform-in-water, and isooctane-in-water were prepared for membrane filtrations. To obtain the chloroform-in-water nano-emulsion, 2 mL chloroform was mixed with 500 mL water containing 0.21 g Tween-80 under 3 h stirring at 1000 rpm, according to the previously reported method [31]. The other micro-emulsions were prepared by adding 5 mL oil into 495 mL water containing 0.5 mg SDS and followed by 12 h stirring at 1,000 rpm. To investigate the comprehensive antifouling properties of the membranes, soybean oil-in-water emulsions containing an additional 1000 ppm BSA, or 20 ppm HA, or 20 ppm SA and isooctane-in-water emulsion containing 1000 ppm BSA were prepared using the same method. The droplet sizes and size distributions of the emulsions were obtained using a dynamic light scattering (DLS; ELSZ-1000ZA, Otsuka Electronics, Japan) apparatus and an optical microscope (BX50, Olympus, Japan).

Pure water flux (denoted as J_1) for each membrane was measured in a cross-flow membrane cell with an effective area of 22 cm², under a pressure of 0.1 bar and a flow rate of 150 mL min⁻¹, and was calculated according to Eq. (5-1) as follows:

$$J_1 = \frac{V}{A \times t} \quad (5-1)$$

where V is the permeate volume (L), A is the membrane area (m²), and t is the sampling time (h). Polystyrene nanoparticle rejection was measured using a polystyrene nanoparticle (50 nm diameter) dispersion solution as the feed solution, in which 1 g of polystyrene nanoparticle concentrate solution was dispersed in 300 mL Milli-Q water containing 1000 ppm Triton X-100. The contents of the feed solution and permeate were measured using UV-Vis spectrophotometry (U-2000, Hitachi Co., Japan) at wavelengths of 380 nm [26]. The emulsion

flux reported for each oil/water emulsion filtration was obtained by calculating the average value within 10 min filtration and the oil content in permeate after filtration was measured using a total organic carbon (TOC) analyzer (TOC-VCSH, Shimadzu, Japan). In addition, to compare the antifouling performances of the PK, PK-OH, and SBMA-g-PK membranes, filtrations of the highly fouling soybean oil-in-water emulsions containing BSA, HA, or SA were conducted at the same initial water flux of almost $1800 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ by adjusting the operating pressure. After filtration of 150 mL of the emulsion, the membrane was washed with water for 10 min to remove the rejected oil and other foulants. The pure water flux recovered after three cycles was recorded as J_2 , and the antifouling properties of the membranes was evaluated by calculating the flux recovery ratio (FRR), by using Eq. (5-2) as follows:

$$FRR = \frac{J_2}{J_1} \times 100\% \quad (5-2)$$

In order to assess the cycle stability and compare antifouling ability with the previously reported zwitterionic-nanohydrogel-grafted PVDF membrane, the fouling cycle experiment was also performed with six pure water stages (30 min per stage) and five emulsion stages (120 min per stage). After every emulsion filtration stage, the membrane was just washed with water for 10 min to remove the oil drop on membrane surface.

5.3. Results and discussion

5.3.1. Membrane characterization

First, the surface chemical compositions of the membranes were analyzed using FTIR spectroscopy, and the results are presented in Fig. 5.1(a). Three strong characteristic peaks at 1055, 1405, and 1690 cm^{-1} , attributed to carbon chain (C-C), methylene ($-\text{CH}_2-$), and carbonyl group ($\text{C}=\text{O}$) stretching vibrations, respectively, are observed in the spectrum of PK [32]. After NaBH_4 solution treatment, the new peak corresponding to the stretching vibration of hydroxyl groups ($-\text{OH}$) at 3400 cm^{-1} confirms the successful surface hydroxylation of the PK substrate [26]. In addition, three new peaks at 965, 1038, and 1726 cm^{-1} observed for all the SBMA-g-PK membranes are assigned to the amide (N-H), sulfonate ($\text{S}=\text{O}$), and ester group ($-\text{COO}$) stretching vibrations, respectively, arising from the surface grafted SBMA [21]. These

absorbances show increasing intensity with an increase in modification period from 5 to 15 min. In order to prevent interference from any physically adsorbed SBMA monomers and polymers, the grafted membranes were thoroughly washed in water before testing. There are no changes in the surface chemical compositions of the prepared membranes, even after storing in water for more than two months, as shown in Fig. 5.2. Thus, the chemically bonded SBMA layer was very stable.

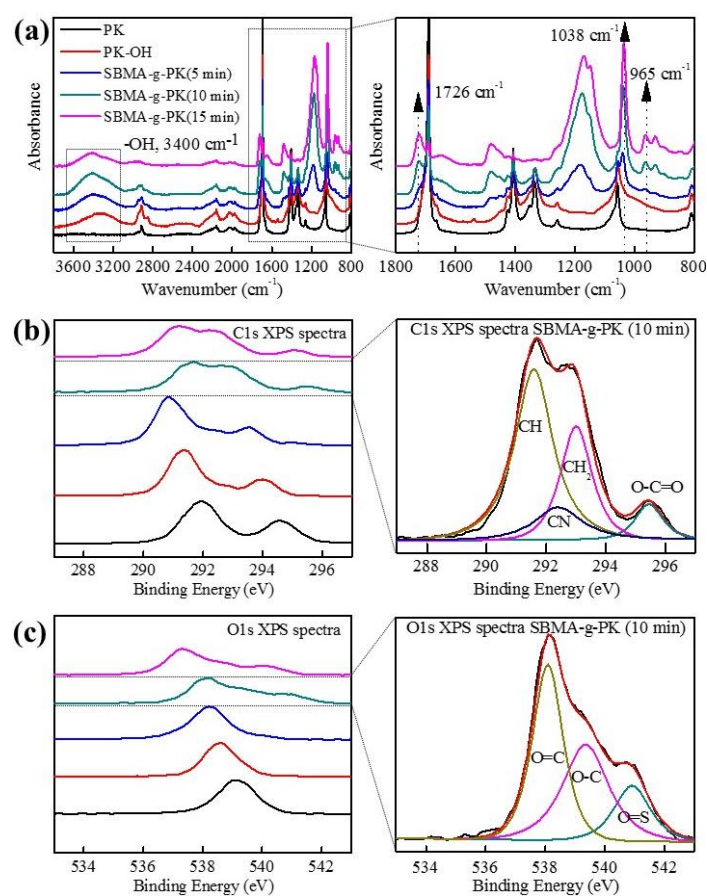


Fig.5.1. Surface chemistry of the pristine PK, PK-OH, and SBMA-g-PK membranes with different modification periods (a) FTIR spectra and (b) C 1s and (c) O 1s core-level signals of the XPS spectra.

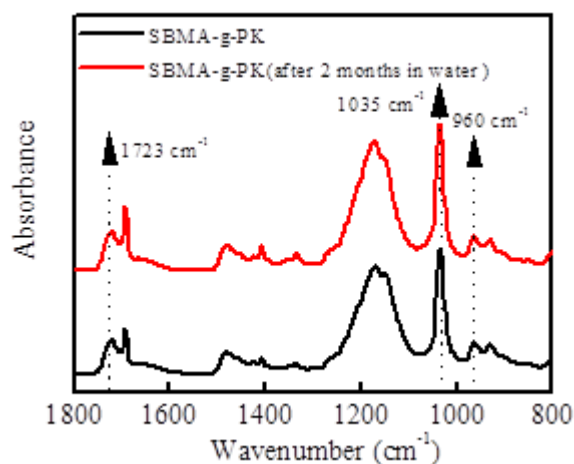


Fig.5.2. FTIR spectra of the SBMA-g-PK membrane before and after keeping in water for 2 months.

XPS was further used to analyze the surface chemical compositions as shown in Fig. 5.3 and Figs. 5.1 (b) and (c). The wide-scan XPS measurements (Fig. 5.3) show obvious peaks for N 1s, S 1s, and S 2p ascribed to the SBMA-g-PK membranes. The S and N atom percentages increase from 1.2% to 5.8%, and 1.0% to 5.7%, respectively, as the modification period increases from 5 to 15 min, as summarized in Table 5.1. Figs. 5.1 (b) and (c) further show the high-resolution core-level signals of C 1s and O 1s for each membrane prepared. The XPS curve shapes for the 0-min to 10-min grafted samples are clearly different, but there is little change after 10 min, implying that 10 min of grafting is sufficient for high coverage of the PK substrates by an SMBA layer. Typical curve-fitting analysis results for the SMBA-g-PK membrane (10 min) were also shown here. The C 1s signal comprises four peaks located at 291.6 (-CH), 292.4 (-CN), 293.1 (-CH₂), and 295.5 eV (-COO), and the O1s signal comprises three peaks located at 538.1 (O=C), 539.3 (O-C), and 540.9 eV (O=S) [23]. The area of the -CN, -COO, and O=S peaks increase over the prolonged modification period, indicating that an increasing amount of SBMA is grafted onto the membrane surfaces with time. This result is consistent with the denser and thicker SBMA surface layers observed in the SEM images as follow. Details of the chemical bonding between the SBMA grafting layer and the PK substrate are illustrated in Fig. 5.4.

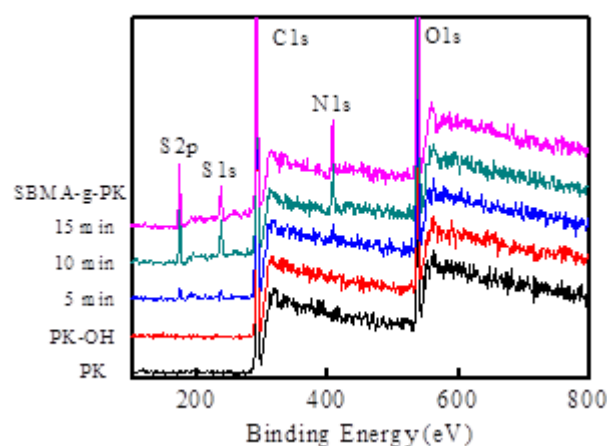


Fig.5.3. XPS spectra of the pristine PK, PK-OH, SBMA-g-PK membranes with different modification period.

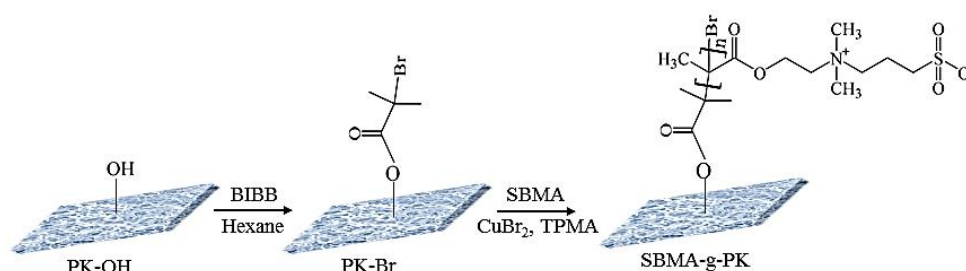


Fig.5.4. The corresponding chemical reaction formulas during modification process.

In addition, it is worthy of note that the BIBB-anchored PK membrane (before SI-ATRP) still maintained many hydroxyl and carbonyl groups at the membrane surface, thus showing similar superhydrophilicity and underwater superoleophobicity as the hydroxylated (PK-OH) membrane (Fig. 5.5). The amount of BIBB (3 wt% in hexane) used to convert the surface hydroxyl groups is a large excess. Therefore, the presence of surface hydroxyl groups after modification should be mainly attributed to the surface migration of internal hydroxyl groups within the membrane matrix when exposed to water, as indicated by our previous study [33]. This suggests that the obtained SBMA-g-PK membranes obtained after the SI-ATRP reactions can be simply regarded as the combination of a hydrophilic PK substrate and a zwitterionic grafting layer, which is different from previously reported zwitterionic composite membranes based on the hydrophobic PVDF substrates [16, 21, 23]. The all-hydrophilic surface chemistry of the SBMA-g-PK membranes provides a more robust and long-term fouling-resistance.

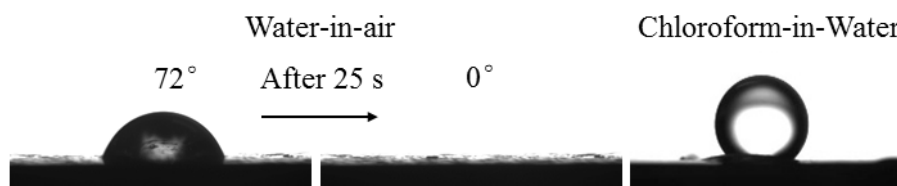


Fig.5.5. Contact angles of water-in-air and chloroform-in-water on the BIBB-modified PK membrane before the SI-ATRP reaction.

The SEM images in Figs. 5.6 (a)-(e) show the top-surface and cross-sectional morphologies of the pristine PK, PK-OH, and SBMA-g-PK (5, 10, and 15 min) membranes. The pristine PK substrate (Fig. 5.6 (a)) has a highly porous surface with an average surface pore size of 308 nm as estimated by image analysis. No obvious change or damage is observed for the microstructure of the membrane (Fig. 5.6(b)) after surface hydroxylation, which only generates many active anchoring sites for the SBMA polyelectrolytes. For the SBMA-g-PK membranes, Fig. 5.6(c)-(e) show that, with an increase in grafting time from 5 to 15 min, denser surface layers with a decrease in average pore sizes (200–300 nm), decreasing pore numbers, and increasing thicknesses (0.6–2.4 μm) are deposited onto the PK substrate. Similar changes can be observed throughout the whole cross-section of the grafted membranes (Fig. 5.7). Furthermore, the mechanical properties of the SBMA-g-PK membranes, especially for the breaking elongation, are obviously enhanced after grafting the SBMA layer, as shown in Fig 5.8. Thanks to the facile introduction of numerous hydroxyl groups to the PK membrane surface via a one-step in situ reduction, the subsequent surface grafting to construct a thick zwitterionic layer can be easily performed within a much shorter reaction time than that reported for a similar process in a previous study (24 h) [23].

Table 5.1. The elemental compositions of the prepared membranes as revealed by XPS

Membrane	C (%)	O (%)	N (%)	S (%)
PK	77.1	22.9	0	0
PK-OH	77.6	23.4	0	0
SBMA-g-PK (5 min)	74.9	22.9	1.0	1.2
SBMA-g-PK (10 min)	64.6	25.6	4.9	4.9
SBMA-g-PK (15 min)	63.2	25.3	5.7	5.8

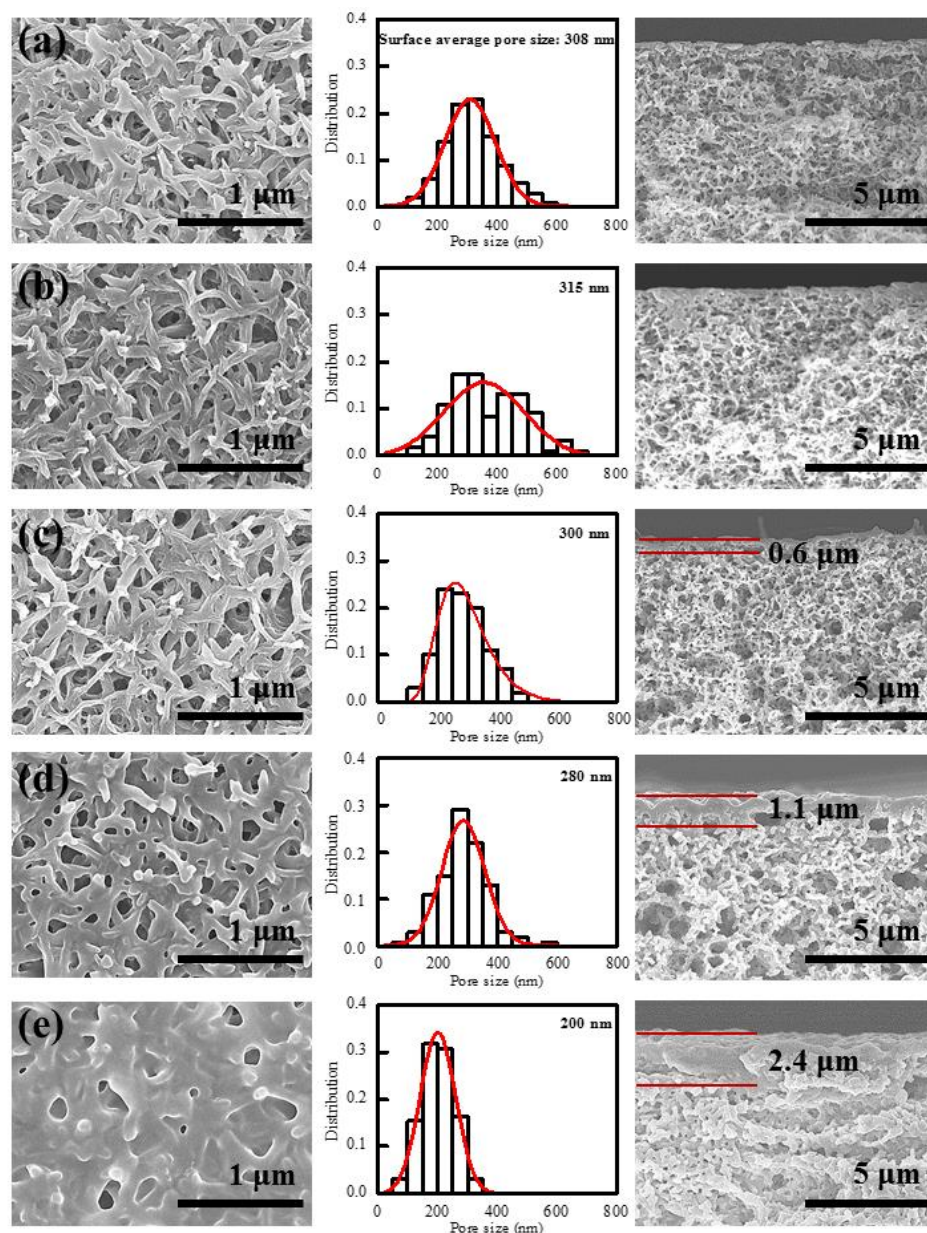


Fig.5.6. Top-surface (left column) and cross-sectional (right column) morphologies of (a) the pristine PK, (b) PK-OH, (c) SBMA-g-PK (5 min), (d) SBMA-g-PK (10 min) and (e) SBMA-g-PK (15 min) membranes as obtained by SEM observations. The inset figures (middle column) show the pore sizes and pore-size distributions of the corresponding top surfaces obtained by image analysis.

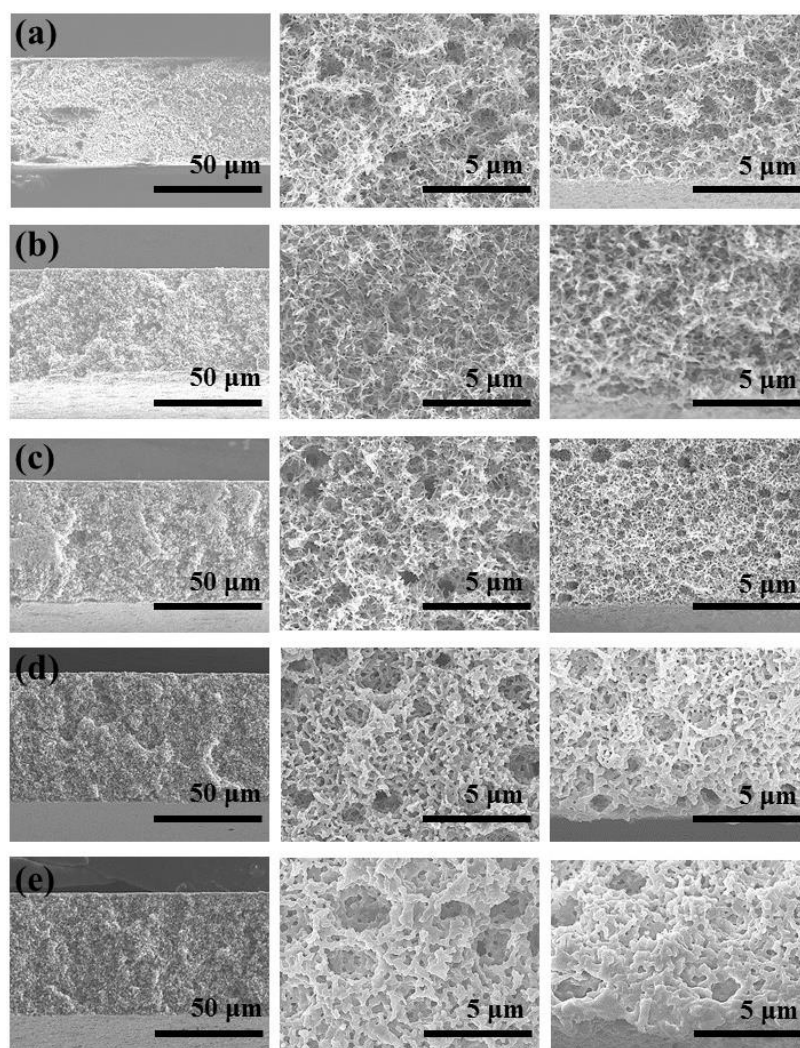


Fig.5.7. Cross-sectional morphologies of the (a) PK membrane, (b) PK-OH membrane, (c) SBMA-g-PK (5 min), (d) SBMA-g-PK (10 min), and (e) SBMA-g-PK (15 min), in terms of the whole cross-section and the enlarged middle and bottom parts.

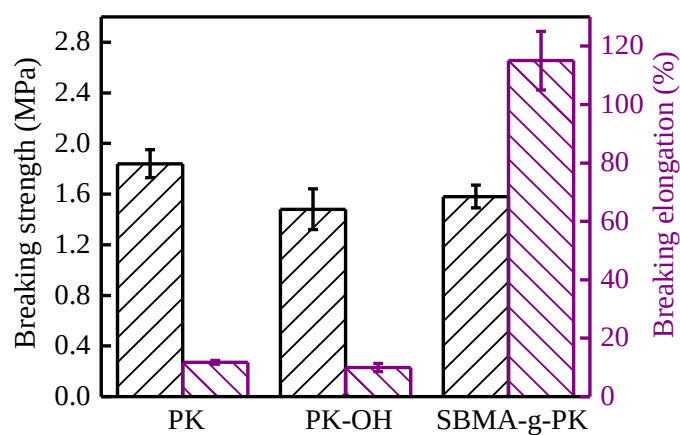


Fig.5.8. The mechanical properties of PK, PK-OH, and SBMA-g-PK (10min) membranes.

5.3.2. *Comprehensive and robust superwettability*

Fig. 5.9 compares the underwater oil-repellency of the membranes against chloroform. It should be noted that the unmodified PK membrane under water is easily wetted by polar oils like chloroform, but is not wetted by apolar oils like hexane owing to its critical hydrophilicity, as illustrated in our previous paper. Both the static oil contact angles (Fig. 5.9(a)) and sliding angles (Fig. 5.9(b)) in water improved after the grafting modifications. Although the oil droplet beads up on the PK-OH membrane with a very large contact angle (159°), indicating underwater superoleophobicity, it remains pinned to the membrane when tilted by 9° . In contrast, similar oil droplets roll on the SBMA-g-PK 5, 10, and 15 min membranes tilted at just 3° , 1° , and 1° , respectively. A dynamic “approach-compress-detach” contact angle tests were carried out to evaluate underwater oil adhesion force in which a $6\text{-}\mu\text{L}$ oil droplet is compressed against a membrane to cause a spherical-to-ellipsoidal shape deformation, as shown in Fig. 3c [29]. For the SBMA-g-PK 10 and 15 min membranes, it is easy to gently withdraw the oil droplets from the membrane surfaces without any deformation by the dispensing needle with a very weak drag force, as indicted by the two red arrows in the picture. However, for the PK-OH and the SBMA-g-PK (5 min) membranes, the receding oil droplet first distorts and is then pulled from the dispensing needle. This indicates the poorer underwater anti-oil-adhesion properties of the PK-OH and the SBMA-g-PK (5 min) membranes, probably due to the lack of or incomplete surface coverage by the SBMA layer.

In principle, surface wettability is determined by both surface chemistry and surface roughness, and a robust non-wetting ‘Cassie state’ is usually realized for surfaces with higher hydrophilicity and roughness [34]. Here, the SBMA grafted membranes prepared with prolonged modification times (10 and 15 min) are more hydrophilic and also less porous compared to the other two membranes (see Fig. 5.9). Therefore, the more robust underwater oil-repellency observed can be mainly attributed to the highly hydrophilic chemistry of the SBMA layer constructed. Comparing the surface morphologies and surface wettabilities of the membranes prepared with different modification times shows that SBMA layer coverage sufficient to give satisfactory surface wettability can be achieved with 10 min modification.

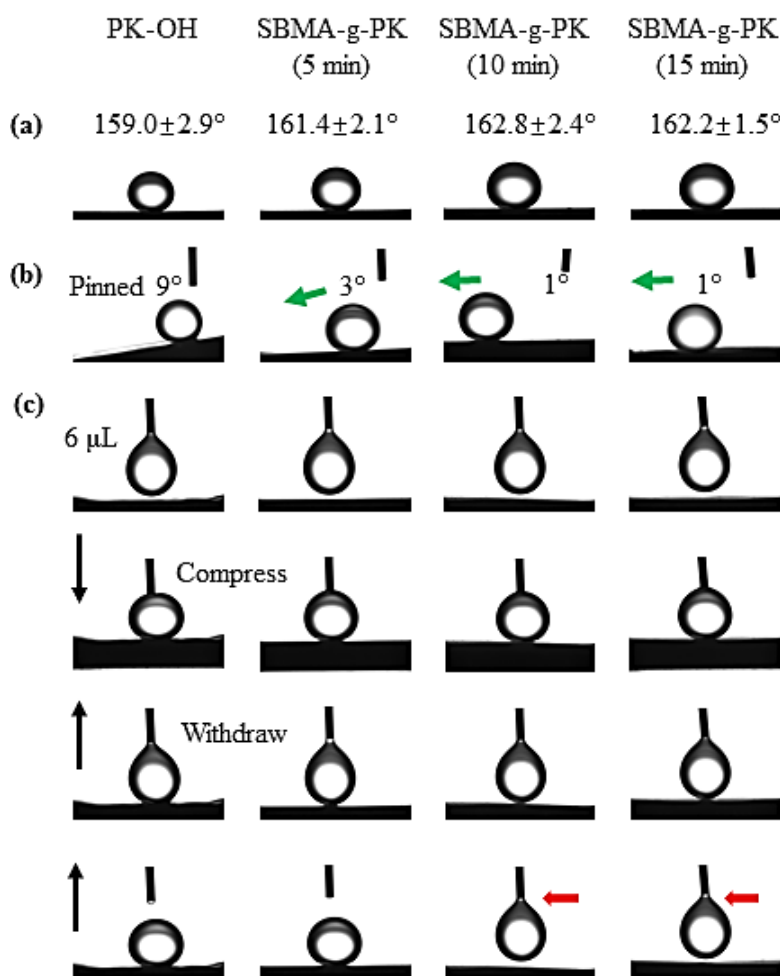


Fig.5.9. Underwater superoleophobicity of the prepared membranes with different surface chemistries. (a) underwater oil contact angles, (b) underwater oil sliding angles, and (c) dynamic oil-adhesion tests on the membrane surfaces in water. Chloroform was used as the probe oil in each test.

A more comprehensive surface wettability analysis was conducted on the SBMA-g-PK (10 min) membrane, as shown in Fig. 5.10. The membrane displays superhydrophilicity both in air (Fig. 5.10(a)) and in oil environment (Fig. 5.10(b)), indicating its strong water-affinity. The water droplet deposited on the membrane in hexane can quickly spread and penetrate into the membrane within 18 s with a low initial contact angle of 80° . Thanks to this underoil superhydrophilicity, robust self-cleaning is achieved, even for an oil-prewetted membrane (Fig. 5.10(d)). The soybean oil (dyed red) trapped within the membrane can be easily washed away by just immersing in water with gently shaking. In addition, various oils including hexane,

hexadecane, soybean oil, and petroleum ether were also tested to show the comprehensive and excellent underwater oil-repellency of the membrane (Fig. 5.10(c)). In all cases, very large contact angles of 158-160 ° and extremely small sliding angles of 2-3 ° are observed. More notably, the superwettability of the membrane is extremely organic solvent-tolerant and shows no appreciable change upon immersion in various solvents (Fig. 5.11), including strong organic solvents (methanol, ethanol, acetone, DMSO, NMP, and DMAc), acid (0.1 M HCl), base (0.1 M NaOH), and high salinity medium (1 M NaCl). Figure 5.10(e) shows that the SBMA-g-PK membrane (10 min) maintains its underwater superoleophobicity even after 24 h immersion in DMSO. This excellent solvent-tolerance can be attributed to the solvent-inert nature of the PK base material imparted by its the strong intra-molecular interactions [32], and the strong hydration ability of the zwitterionic layer [35], as well as the stable covalent linkages between the grafted layer and the PK substrate.

In addition to its excellent oil repellency, the SBMA-g-PK membrane also exhibits excellent anti-protein-adhesion owing to the non-fouling nature of zwitterionic materials. Fluorescence-labeled protein static adsorption tests (Fig. 5.12) revealed that less BSA and lysozyme adsorption occurs on the zwitterionic surface than on the pristine PK membrane. In summary, the comprehensive and robust surface properties of the SBMA-g-PK membrane in terms of anti-oil-adhesion, anti-protein-adhesion, solvent resistance, and self-cleaning demonstrate its great potential for oil/water separations under harsh environmental conditions.

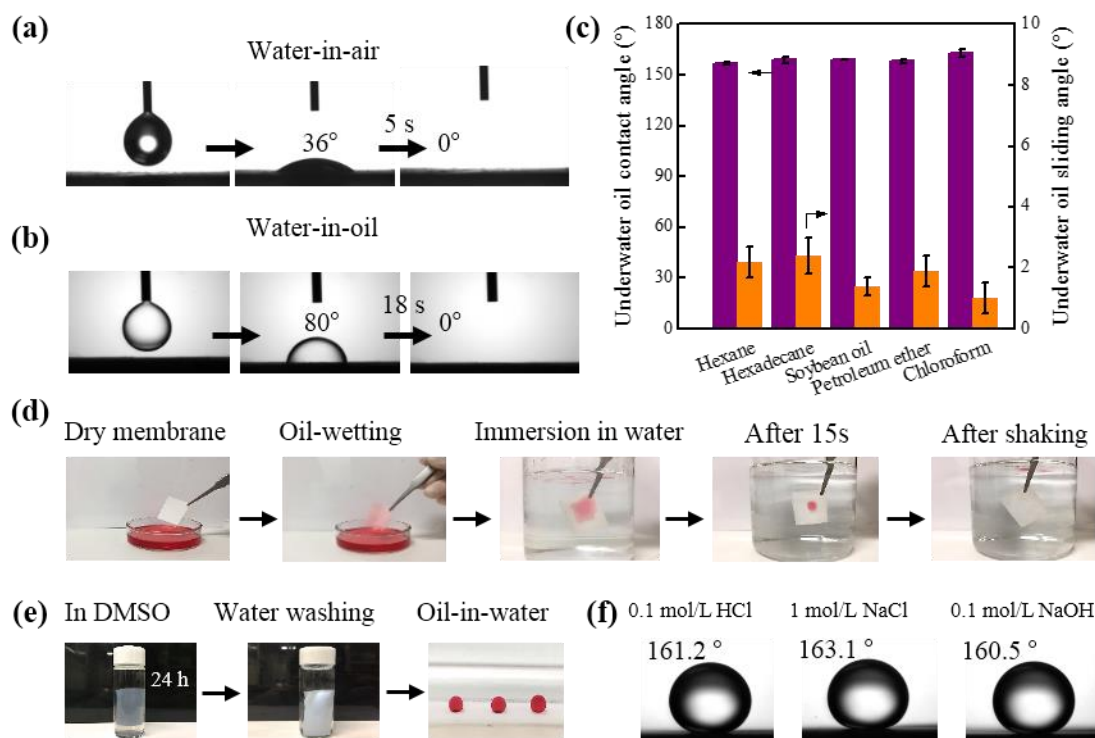


Fig.5.10. Comprehensive surface wettability characterizations of the SBMA-g-PK (10 min) membrane. Contact angles of (a) water-in-air and (b) water-in-oil. (c) underwater oil contact angles and sliding angles. (d) self-cleaning test of the oil-prewetted membrane by water washing. (e) organic solvent-tolerance test of the membrane by immersing in DMSO for 24 h. (f) contact angles of oil in 0.1 mol/L HCl, 1 mol/L NaCl, and 0.1 mol/L NaOH aqueous solutions.

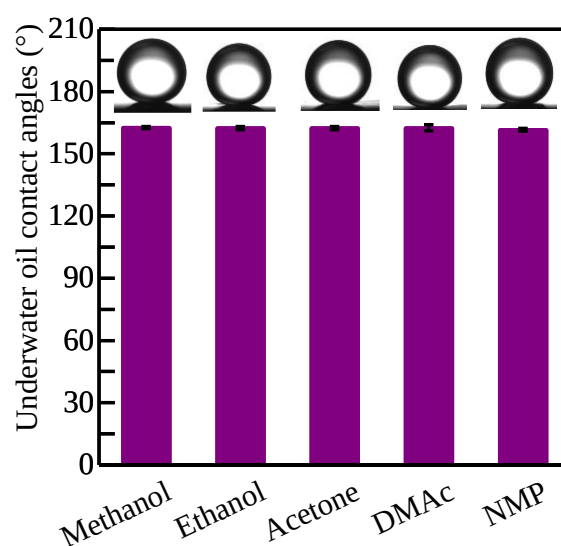


Fig.5.11. Underwater oil contact angles of the SBMA-g-PK membrane (10 min) after immersing in various solvents. Chloroform was used as the probe oil for contact angle tests.

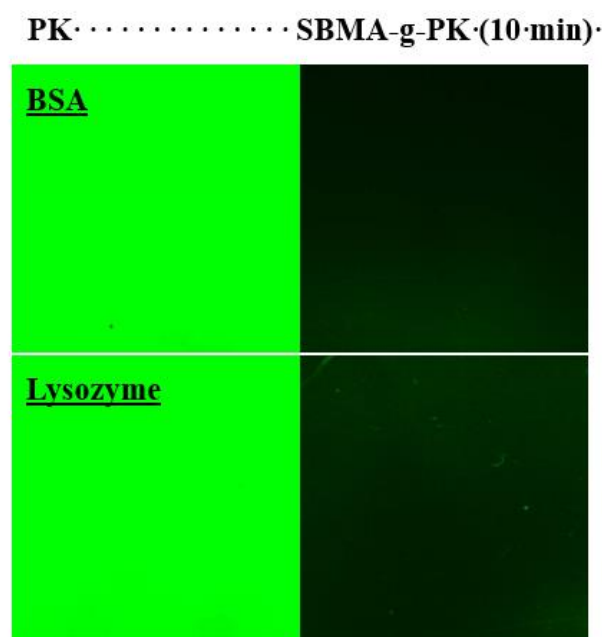


Fig.5.12. Representative fluorescence images of the pristine PK and SBMA-g-PK (10 min) membranes after FTIC-protein adsorption (a) Bovine Serum Albumin (BSA) and (b) lysozyme (LYS).

5.3.3. High efficiency filtration of difficult oil-in-water emulsions

Fig. 5.13(a) compares the pure water flux and the rejection of 50-nm nanoparticle for the membranes prepared. The PK and PK-OH membranes exhibit pure water fluxes of almost $2500 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and nanoparticle rejections of almost 70%, whereas the SBMA-g-PK membranes exhibit gradually decreasing pure water fluxes and increasing rejections with an increase in grafting period. This is explained by the increase in SBMA layer density and thickness as the modification period is extended. The resultant SBMA-g-PK (10 min) membrane exhibits an acceptable pure water flux of $1820 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and an improved nanoparticle rejection of 91%, indicating a 50-nm cut-off pore size, which is in the ultrafiltration range. In addition, the average membrane pore sizes were also measured using a capillary flow porometer, which operates based on a liquid-liquid displacement mechanism. The SBMA-g-PK (10 min) membrane has an average pore size of 41 nm, which is consistent with the nanoparticle rejection result.

Fig. 5.13(b) summarizes the filtration performances of the SBMA-g-PK (10 min) membrane for five types of surfactant-stabilized oil-in-water emulsions, including the hexane-

in-water, hexadecane-in-water, soybean oil-in-water, petroleum ether-in-water, and chloroform-in-water emulsions. Overall, all the emulsions become clear after filtration. Furthermore, all the collected permeates exhibit very low oil contents as determined by TOC analysis, showing 33 ppm (99.2% rejection) for the chloroform case, and 7-15 ppm ($\approx 99.9\%$ rejection) for the other cases. The resultant oil contents are much lower than the 42 ppm standard set by the Environment Protection Agent of the US government for Offshore Oil and Gas Activities in the Eastern Gulf of Mexico [16]. The slightly higher oil permeation observed for chloroform can be explained by the fact that the chloroform-in-water emulsion contained abundant nanoscale oil droplets with a DLS-determined mean droplet size of 67 nm (Figure 5.13 (c), left), whereas the other four emulsions had a mean droplet size of 1.33.6 μm (Fig. 5.14). The detected DLS signal of around 5.4 nm in the permeate for the chloroform case (Fig. 5.13 (c), right) can be attributed to the free passage of very few small droplets and Tween 80 surfactants. In addition to the very high oil rejections, the membrane also exhibits very high emulsion fluxes at a level of $\sim 1800 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ (very close to its pure water flux) for the hexane, hexadecane, soybean oil, and petroleum ether macro-emulsions containing large oil droplets, whereas a relatively lower flux of $\sim 1200 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ was obtained for the chloroform nano-emulsion due to a heavy oil layer of rejected chloroform presented on the membrane surface [7, 36]. Details of the real-time filtration processes for the five emulsions are given in Fig. 5.15.

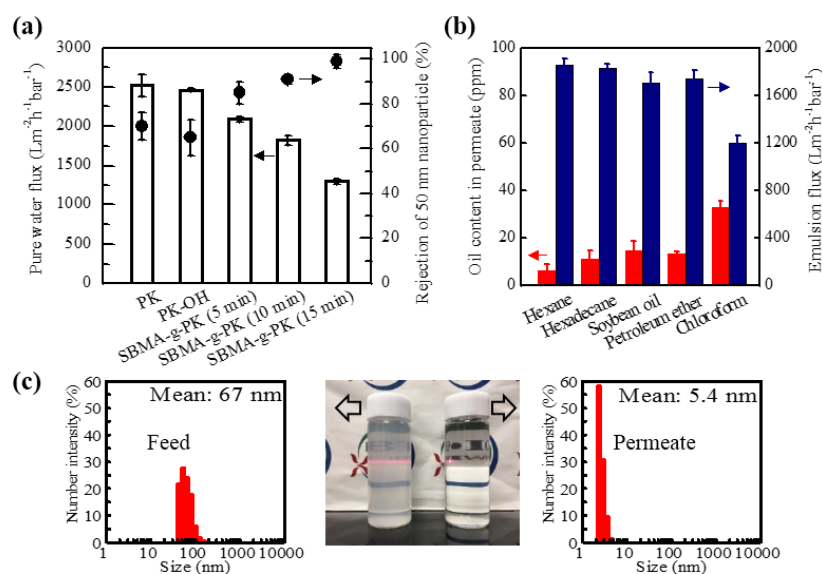


Fig.5.13. Membrane filtration performances (a) pure water flux and rejection of the 50 nm nanoparticle for the prepared membranes. (b) emulsion fluxes and oil content in permeate for the oil/water filtrations conducted by SBMA-g-PK (10 min), including hexane-in-water, hexadecane-in-water, soybean oil-in-water, petroleum ether-in-water, and chloroform-in-water emulsions. (c) droplet size distributions by DLS and a digital photo of the chloroform-in-water emulsion before (showing Tyndal effect) and after filtration using the SBMA-g-PK (10 min) membrane.

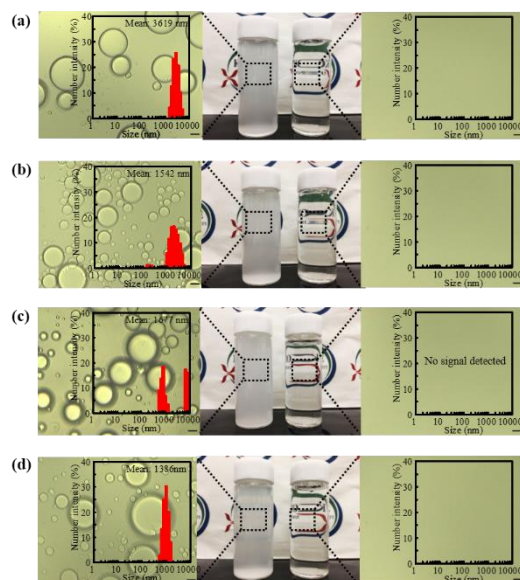


Fig.5.14. Optical microscope images incorporated with DLS characterizations of the oil-in-water emulsions before and after filtration by the SBMA-g-PK (10 min) membrane: (a) hexane-in-water, (b) hexadecane-in-water, (c) soybean oil-in-water, and (d) petroleum ether-in-water.

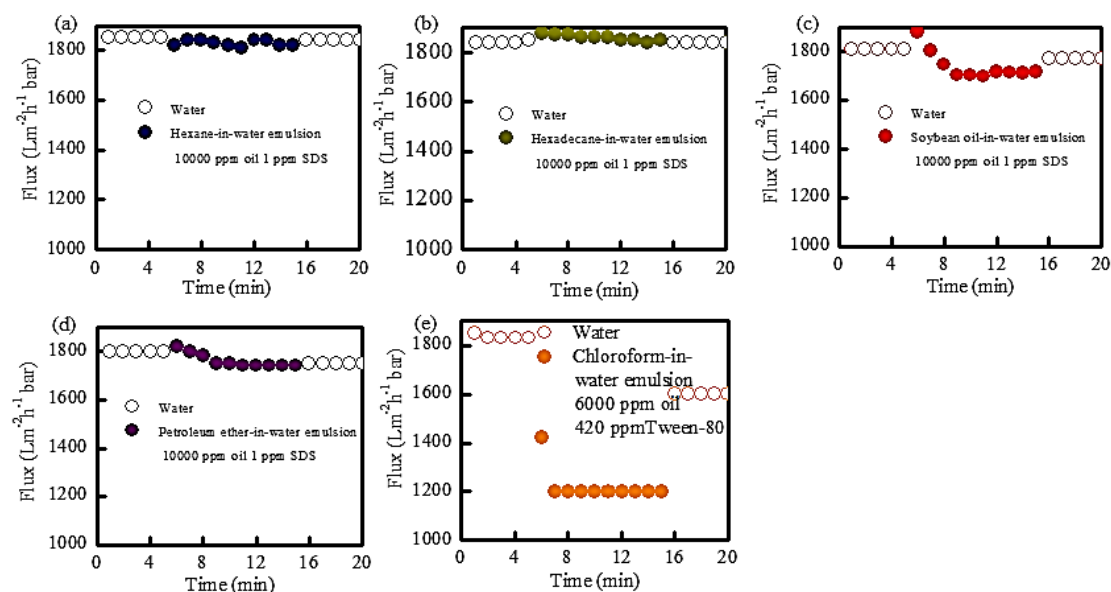


Fig.5.15. The real time filtration properties of SBMA-g-PK (10 min) membrane for (a) hexane-in-water, (b) hexadecane-in-water, (c) soybean oil-in-water, (d) petroleum ether-in-water micro-emulsions and (e) chloroform-in-water nano-emulsion.

Filtrations of even more challenging oil-in-water emulsions containing other pollutants such as proteins and NOM, which are commonly present in real-world oily wastewater, were also conducted. Three membranes with different surface chemistries and comparable membrane pore sizes, namely the pristine PK, PK-OH, and SBMA-g-PK (10 min) membranes, were compared at the same initial flux of $\sim 1800 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. Four highly fouling soybean oil-based emulsions with and without other foulants were used. For the relatively less trouble emulsion containing only soybean oil and surfactant (Fig. 5.16(a)), the PK-OH membrane and the SBMA-g-PK (10 min) membrane exhibit very slow decline of the emulsion flux by just 14% and 9% compared to their pure water fluxes, and very high flux recovery ratio (FRR) at 92% and 97% by simple hydraulic cleaning at the end of the three-cycle tests. The pristine PK membrane loses $\sim 40\%$ of its initial flux irreversibly after the first test cycle, indicating severe oil fouling. For the more fouling emulsions containing 1000 ppm BSA (Fig. 5.16(b)), 20 ppm HA (Fig. 5.16(c)) or 20 ppm SA (Fig. 5.16(d)), the SBMA-g-PK (10 min) membrane shows similarly high cyclic filtration stability with a high FRR at 98%, 86% and 82%, respectively, and higher emulsion fluxes than the other two membranes. This can be explained by the

zwitterionic surface chemistry possessing a comprehensive fouling-resistance to proteins, NOM and other foulants due to its denser and tighter hydration shell [32]. The zeta potential results shown in Fig. 5.17 indicate that the SBMA-g-PK membrane surface carries very weak negative charges from pH 3 to pH 9 due to favourable anions adsorption (OH^- , Cl^- , etc.) from the solution phase. This slightly negatively charge characteristic may also be advantageous to suppress oil and protein fouling by electrostatic repulsion [37]. The relatively weaker fouling-resistance and fouling-releasing for the cases of emulsions with HA and SA may be partially attributed to the formation of a dense cake layer or internal pore plugging caused by the rejected HA and SA components, which further promote the deposition and coalescence of emulsified oil on the surface [8, 38]. In contrast, the PK and PK-OH membrane surfaces exhibiting the less ideal fouling-resistance and also slightly larger pore sizes, resulting in more rapid flux drops and lower flux recoveries, as expected.

In order to further assess the cycle stability of the SBMA-g-PK (10 min) membrane and compare its antifouling properties with those of a previously reported SBMA-nanohydrogel-grafted PVDF membrane [23], another fouling cycle experiment was conducted using the same conditions as those used in the previous study. As shown in Fig. 5.18, the flux slowly decreases when using an isooctane-in-water emulsion as the feed solution, but the SBMA-g-PK membrane maintains a high flux (above 50% of the initial pure water flux), even after 2 h emulsion filtration. However, the flux for the SBMA-nanohydrogel-grafted PVDF membrane falls to <10% of its initial pure water flux. More importantly, the SBMA-g-PK membrane still shows a high FRR of 98% after five cycles, further demonstrating its high fouling resistance and fouling releasing properties.

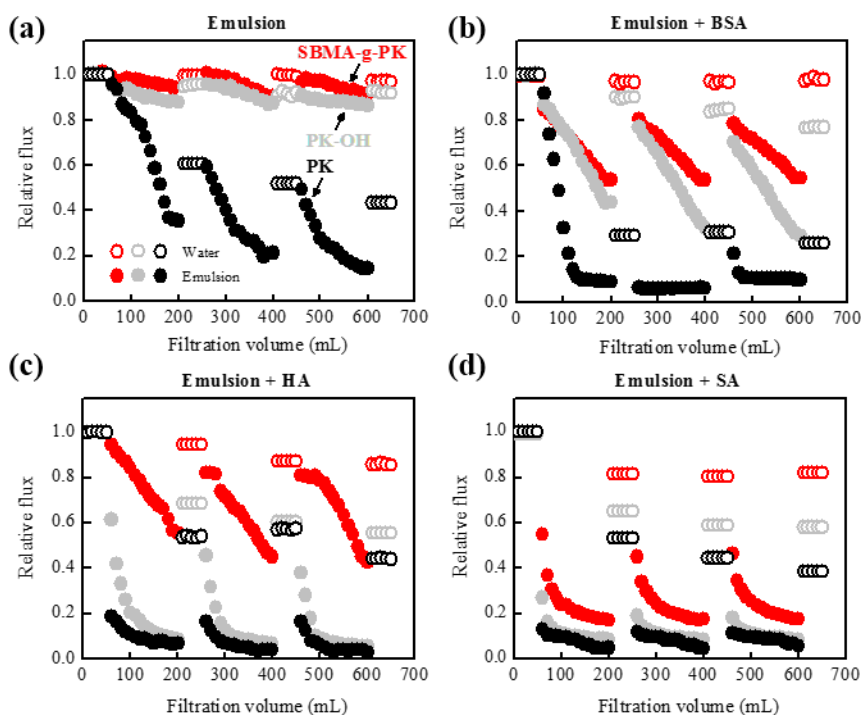


Fig.5.16. Membrane filtration tests of the pristine PK, PK-OH and SBMA-g-PK (10 min) membranes for various highly fouling soybean oil-in-water emulsions containing (a) 10000 ppm oil and 1 ppm SDS, and an additional (b) 1000 ppm BSA, or (c) 20 ppm HA, or (d) 20 ppm SA.

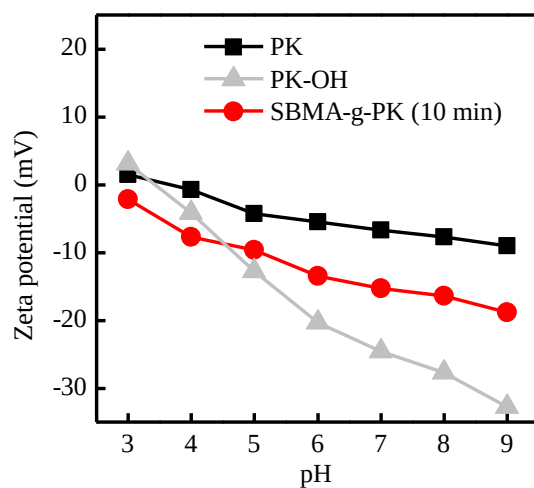


Fig.5.17. Zeta potentials of the PK, PK-OH, SBMA-g-PK (10 min) membranes at pH 3-9.

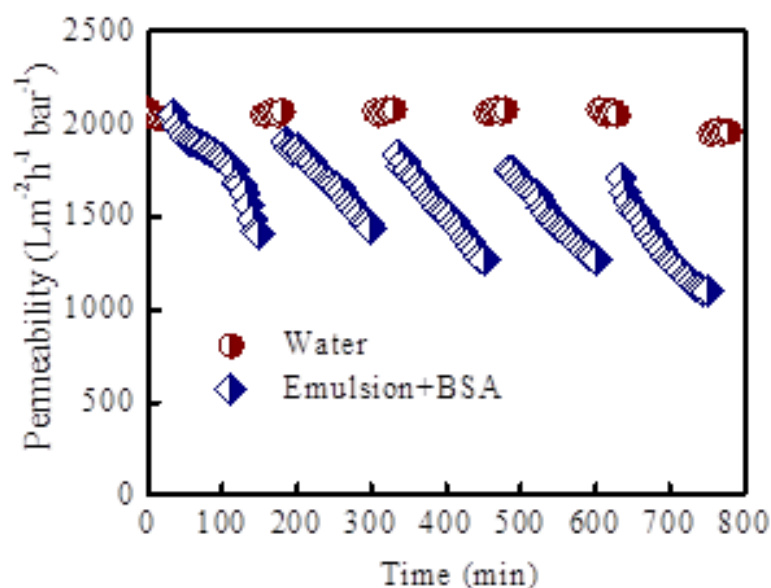


Fig.5.18. Cycle stability test of the SBMA-g-PK membrane (10 min) using isooctane-in-water emulsions containing 10000 ppm oil and 1000 ppm BSA.

Finally, comprehensive comparisons were made between the performances of the as-prepared SBMA-g-PK membrane, reduced PK (PK-OH) membranes, and various newly developed polymer/ceramic-based membranes, and unique nanomaterials that showing the state-of-the-art separation capabilities, as shown in Table 5.2. Furthermore, the data from Table 5.2 and the reported data for various commercial MF/UF polymeric membranes and the polydopamine (PDA) coated membranes [39, 40] are depicted together in Fig. 5.19, by plotting the reported emulsion fluxes (Fig. 5.19(a)) or oil contents in permeate (Fig. 5.19(b)) against the reported or estimated pore sizes of the membranes. The reported cut-off pore size or average pore size of the membranes reflects their size-sieving capabilities, approximating the size of the smallest oil droplets that the membrane can reject. However, both pore size and surface fouling propensity of the membranes play important roles in the obtainable emulsion flux, whereas the theoretically maximum pure water flux (i.e., before fouling) is determined only by pore size according to the Hagen-Poiseuille law [41]. Clearly, the performance of the membrane prepared in the current study is superior to those of previously reported materials in terms of both emulsion flux (1200-1800 L m⁻² h⁻¹ bar⁻¹, which is very similar to its pure water flux) and permeate oil content (6-33 ppm), especially for the difficult oil-in-water nanoemulsions

containing many sub-micron oil droplets. This is attributed to its non-fouling surface properties and highly porous membrane structure, which has a 50-nm cut-off that is sufficient for most practical oil/water emulsions. In addition, the dashed line in Fig. 5.19 (a) shows the estimated permeability–selectivity “trade-off” boundary for polymeric and ceramic MF/UF membranes, with pore size representing the membrane selectivity based on size exclusion. Clearly, the data points for the SBMA-g-PK membrane are located near the boundary line. Besides, its oil content in permeate is as low as those of the commercial UF membranes having a less than 10 nm pore size (shown in the lower-left corner in Fig. 5.19(b)).

Noting that, the data points located slightly above the “trade-off” line are ascribed to an ultrathin SWCNT/PDA/PEI composite (~160 nm thickness) [42], and cellulose nanosheet membrane (~100 nm thickness) prepared by vacuum filtration-assisted deposition on commercial cellulose acetate filters (see Table 5.2) [43]. Compared to the SBMA-g-PK membrane, they exhibited smaller pore sizes (~10 nm) but similarly high fluxes owing to their ultrathin selective layer. However, such nanostructured composite membranes are not self-supporting like the dominant polymeric membranes, and will suffer from poor structural integrity when operated in the common cross-flow filtration mode for continuous separation of difficult oil/water emulsions. In addition, the organic-solvent-sensitive cellulose acetate substrate used cannot endure harsh solvent conditions. As regards to the comprehensive antifouling property of the selected membranes, only the zwitterionic nanohydrogel grafted PVDF membrane and the SBMA-g-PK membrane have been qualified with similarly high emulsion flux and high flux recoveries even for highly fouling emulsions containing NOM foulants. Moreover, the SBMA-g-PK membrane exhibited a smaller cut-off pore size, i.e., higher size-sieving based selectivity, excellent solvent-resistance and self-cleaning ability.

Table 5.2. Comparison of various underwater superoleophobic membranes with sub-micron pore sizes for filtrations of surfactant-stabilized micro/nanoscale oil-in-water emulsions

Materials	Pore size (nm)	Oil feed content (ppm)	Oil droplet size in feed (mean, nm)	Emulsion flux ($\text{Lm}^{-2}\text{h}^{-1}$), Pressure	Oil content in permeate (ppm)
PAN electrospun nanofiber[2]	330	10000	100–500	738, 0.05 bar	72
GO/palygorskite[37]	<220	1000	210	1200, 0.5 bar	10
		1000	220	900, 0.5 bar	10
Cellulose nanocrystal[38]	48-70	10000	27	520, 0.5 bar	670
		10000	59	775, 0.5 bar	10
Cellulose nanocrystal/Palygorskite[39]	42-60	10000	5000–	70, 0.5 bar	13
		100	20000	883, 0.5 bar	10
			50-200		
Ceramic membrane[40]	50	5000–30000	175–280	40–80, 1–5 bar	200-750
Cellulose nanosheet [36]	10-12	10000	200–400	1272, 0.8 bar	350
SWCNT/PDA/PEI [35]	10	10000	54	1515, 0.5 bar	30
		10000	52	1695, 0.5 bar	33
PDA/PEI/SiO ₂ /PP membrane[41]	<200	10000	400–10000	900, 0.4 bar	10
Hydrogel/PVDF membrane[42]	<220	1500	1000–10000	900, 1 bar	18
Zwitterionic nanohydrogel grafted PVDF membrane[21]	<220	1000	100-5000	125, 0.1 bar	19
PDA/TiO ₂ /PVDF membrane[43]	220	10000	1000–20000	605, 0.9 bar	6.3
PSF-g-PEG membrane[44]	51	1150	1100	120, 1 bar	3.5
Alkaline-induced PAN membrane[7]	<50	10000	50	315, 1 bar	<20
		10000	4000	372, 1 bar	<20
Amphiphilic PES membrane[45]	8	900	/	110, 1 bar	4.5
PK-OH membranes[23]	100	10000	200-10000	200, 0.1 bar	20
	500	10000	200-10000	200, 0.02 bar	20
SBMA-g-PK membrane ^{this work}	50	10000	67	1200, 1 bar	33
		10000	1677	1710, 1 bar	15
		10000	1386	1740, 1 bar	13
		10000	1542	1830, 1 bar	11
		10000	3619	1860, 1 bar	6.5

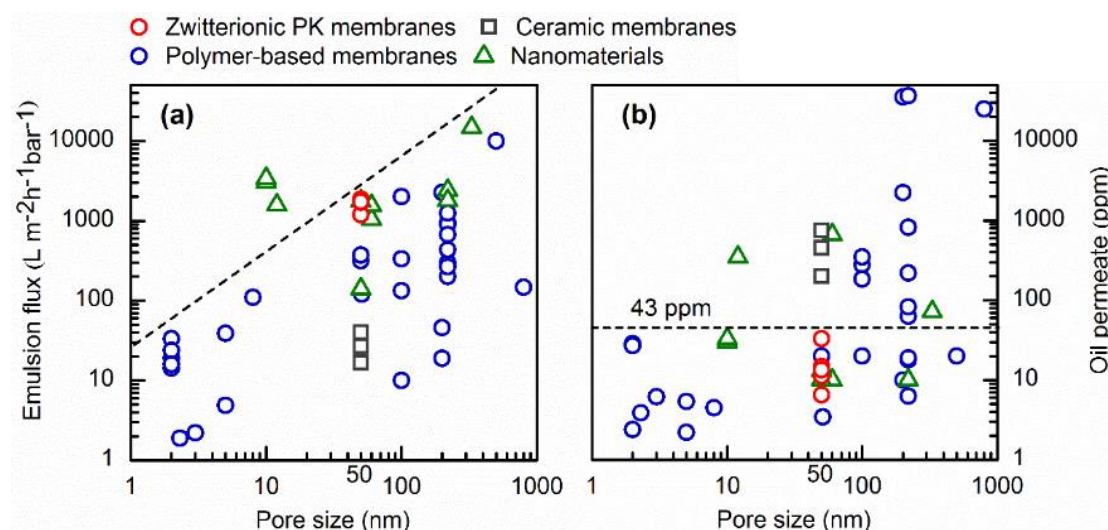


Fig.5.19. Experimentally measured (a) emulsion fluxes and (b) oil permeates as functions of pore sizes of the as-prepared SBMA-g-PK membrane and other polymer-based membranes, ceramic membranes and special nanomaterials that exhibiting underwater superoleophobicity and a cut-off or average pore sizes less than $1 \mu\text{m}$, for filtrations of micro/nano oil-in-water emulsions with mean droplet sizes between $0.02\text{--}20 \mu\text{m}$. The emulsion flux data are shown in the unit of $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ for easy comparison, the oil permeates after filtrations are either took from the literatures directly or calculated by the reported oil rejections multiplying the feed oil concentrations. The pore size data are the reported cut-off or average pore sizes, or estimations according to the pore sizes of the used membrane substrates before modifications or the reported MWCO data, or the sizes of the smallest solutes that were rejected.

5.4. Conclusions

A comprehensively fouling-resistant zwitterionic-polyelectrolyte-grafted PK membrane was designed and fabricated by simple surface hydroxylation and SI-ATRP for treating oil-in-water emulsions. The newly developed SBMA-g-PK membrane exhibits excellent solvent-tolerant superhydrophilicity and underoil superhydrophilicity with ultralow oil adhesion, as well as resistance to various fouling pollutants in nature. In comparison to those of commercial membranes and specific state-of-the-art membranes for oil-in-water emulsion separation, the SBMA-g-PK membrane exhibits superior separation efficiency in terms of both flux and rejection, even for highly fouling and aggressive oil-in-water micro/nanoemulsions. These excellent properties are realized by the combination of the porous, highly hydrophilic, solvent-

resistant, and easily modified PK substrate and the non-fouling zwitterionic surface layer. Thus, the excellent surface properties and separation capability of the as-proposed SBMA-g-PK membrane make it a promising candidate for the sustainable treatment of real-world oily wastewater that contains complicated pollutants.

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Chapter 6

Conclusions

In the past few decades, oil pollution stemming from the oil spills or discharged oily wastewater has become an ongoing worldwide threaten to the environment and eco-system. The conventional separation methods, such as air floatation, centrifugation, flocculation, and settling separation, can't high efficiency treatment of the surfactant-stabilized oil-in-water emulsion. Besides, it also suffers from complex operation process, high cost, second pollution. In contrast, membrane separation technology has been acknowledged as a more promising prospect to remove oil from oily wastewater due to its high separation efficiency, low energy cost and easy scalability. However, traditional membranes used in the oil/water separation always suffer from serious fouling issue that results in fast permeating flux decline due to the adsorption of oil droplets on the membrane surface or blocking the inner pore channels, thus leading to a severe impedance on the membrane development for highly efficient oily wastewater treatment. Therefore, improving the fouling-resistant/fouling-releasing properties of membranes is of great importance for practically oily wastewater treatment.

Therefore, the objective of this dissertation is to improve the separation and antifouling performance of PK-based membrane for oily wastewater treatment by blending with hydrophilic PVA, in-situ silicification, PDA assembling and surface grafting with zwitterionic polyelectrolyte. The modified membranes were characterized by ATR-FTIR, XPS, SEM, and AFM, water contact angle (CA) in air, underwater oil CA, zeta potential. Besides, the oil-in-water emulsion separation and antifouling performance were also tested. The detailed results exhibited in Chapters 2-5 are summarized as follow.

6.1. One-step fabrication of robust and anti-oil-fouling aliphatic polyketone composite membranes for sustainable and efficient filtration of oil-in-water emulsions

In this chapter, a novel aliphatic polyketone (PK) composite membrane with super-oil-repellency was prepared by a facile one-step NIPS method using highly hydrophilic poly (vinyl alcohol) (PVA) as an additive and nylon mesh as the reinforcing support, named as PK/PVA1500-Nyl. The all-hydrophilic chemical and near-symmetric porous fibril-like structure throughout the membrane cross-section resulted in an ultralow oil-adhesion underwater superoleophobicity. Besides, the composite membrane also indicated high flux ($\sim 420 \text{ Lm}^{-2}\text{h}^{-1} \text{ } 0.1 \text{ bar}^{-1}$) and anti-oil-fouling (93-97 % flux recovery after water cleaning) filtrations of oil-in-water emulsions in the cross-flow mode, even with highly adhesive, viscous, and concentrated (up to 100000 ppm) soybean oil emulsions. Molecular dynamic (MD) simulation of a constructed PK/PVA blend system indicated that the strong intramolecular hydrogen bonds (H-bonds) within PVA and intermolecular H-bonds between PVA and PK were responsible for the stable confinement of PVA within the PK matrix. In summary, the high oil-fouling-resistance and -releasing properties and the simple one-step membrane preparation approach makes this new composite membrane very promising for large-scale applications in the treatment of oily wastewater.

6.2. Ultrathin in situ silicification layer developed by an electrostatic attraction force strategy for ultrahigh-performance oil-water emulsion separation

In this chapter, aiming at the realization of comprehensive fouling-resistant/fouling-releasing properties, an ultrathin silica (SiO_2) layer is conformally engineered onto a porous polyketone (PK) substrate via an electrostatic attraction forced silicification process. This in situ silicification forms an ultrathin and superhydrophilic/underwater superoleophobic interface structure that allows the realization of ultrahigh water permeance up to $7533 \text{ Lm}^{-1}\text{h}^{-1}\text{bar}^{-1}$, an exceptional high emulsion fluxes up to $6000 \text{ Lm}^{-1}\text{h}^{-1}\text{bar}^{-1}$, as well as high rejections of $> 99.9\%$ against various of oily emulsions (hexane-in-water, hexadecane-in-water, petroleum ether-in-water, soybean oil-in-water).

Furthermore, the antifouling mechanism of the unique architecture design of the SiO₂-d-PK membrane would be intrinsically different from the most reported membranes used for oily emulsions separation. In this work, we envisioned that the silicification layer created a surface with extremely low oil-adhesion propensity, while the underlying PK substrate was expected to act as an “interface-breaking barrier” for the intruded oil droplets. The resultant SiO₂-d-PK membrane thus exhibited a thoroughly oleophobic property throughout the entire membrane-thick range uniformly. Therefore, the membrane showed an ultrahigh antifouling property with a nearly full flux recovery ratio (100%) after the long-term cyclic emulsion filtration. More important, the membrane displayed a distinguished antifouling property to comprehensive oily emulsions containing various of pollutants, such as proteins, surfactants, and other natural organic materials (NOM). In addition, the inorganic SiO₂ layer incorporated with highly chemical inert PK substrate (SiO₂-d-PK membrane) enabled the application of SiO₂-d-PK membrane under more challenging conditions, such as salty, strong acid/alkaline solutions, and various organic solvents.

6.3. Finely tuned dopamine assembling on the polyketone substrate to engineer a robust underwater superoleophobic membrane for high performance oil/water separation

In this chapter, an ultrafine PDA NPs in-situ assembling was implemented on PK substrate via the facile self-polymerization process. The ultrafine PDA NPs surface modification endowed the membrane with an exceptional water permeance up to 11600 Lm⁻²h⁻¹ bar⁻¹, and superior emulsions separation properties with high oily emulsions permeating fluxes of 10600 Lm⁻²h⁻¹ bar⁻¹ for hexane-in-water, 9900 Lm⁻²h⁻¹ bar⁻¹ for hexadecane-in-water, 9800 Lm⁻²h⁻¹ bar⁻¹ for petrol ether-in-water, and 8300 Lm⁻²h⁻¹ bar⁻¹ for soybean oil-in-water that exhibit a negligible decrease when comparing to the pure water permeating flux; and a remarkable high rejection ratio of 99.9% for various of oily emulsions. Benefiting from the unique surface configuration composed of micro/nanospherical PDA NPs, a robust “Cassie state” was accomplished that enabled the PDA-d-PK membrane a comprehensively fouling-resistant/fouling-releasing property against various of oil, protein and HA, where a nearly full recovery could be reached over 3-time filtration-cleaning cycles after simple hydraulic washing.

Due to the chemically inert of PDA NPs, the newly-developed PDA-d-PK membrane could be potentially operated in challenging environments involve salty, various of organic solvents, and strong acid/alkali solutions. To sum up, considering the significantly enhanced superhydrophilicity and underwater superoleophobicity, the facile and cost-effective fabrication process of PDA NPs in-situ assembling shows a promising prospects in treating practical oily emulsions.

6.4. A comprehensively fouling- and solvent-resistant aliphatic polyketone membrane for high flux filtration of difficult oil-in-water micro- and nanoemulsions

In this chapter, a superhydrophilic SBMA zwitterionic layer with strong hydration ability was grafted on the hydroxylated aliphatic polyketone (PK) membrane via a controllable and fast SI-ATRP reaction. The newly developed SBMA-g-PK membrane exhibits excellent solvent-tolerant superhydrophilicity and underoil superhydrophilicity with ultralow oil adhesion. Besides, the SBMA-g-PK membrane showed a sustainably comprehensive fouling-resistance to various oils, surfactants, BSA, SA and HA. Furthermore, the membrane also showed high emulsion flux of 1200-1800 L m⁻² h⁻¹ bar⁻¹ and high size-sieving based selectivity to any oil droplets larger than 50 nm in size. The excellent performance of the prepared SBMA-d-PK membrane makes it a promise candidate for the oil/water separation.

Publication list

Chapter 2:

Lei Zhang, Liang Cheng*, Haochen Wu, Tomohisa Yoshioka and Hideto Matsuyama*, One-step fabrication of robust and anti-oil-fouling aliphatic polyketone composite membranes for sustainable and efficient filtration of oil-in-water emulsions, Journal of Materials Chemistry A, 2018, 6, 24641-24650.

Chapter 3:

Lei Zhang, Yuqing Lin*, Haochen Wu, Liang Cheng, Yuchen Sun, Tomoki Yasui, Zhe Yang, Shengyao Wang, Tomohisa Yoshioka and Hideto Matsuyama*, An ultrathin in situ silicification layer developed by an electrostatic attraction force strategy for ultrahigh-performance oil-water emulsion separation, Journal of Materials Chemistry A, 2019, 7, 24569-24582.

Chapter 4:

Lei Zhang, Yuqing Lin, Shengyao Wang, Liang Cheng, Hideto Matsuyama*, Finely tuned dopamine assembling on polyketone substrate to engineer a robust underwater superoleophobic membrane for high performance oil/water separation, to be submitted.

Chapter 5:

Lei Zhang, Yuqing Lin, Liang Cheng*, Zhe Yang, Hideto Matsuyama*, A comprehensively fouling- and solvent-resistant aliphatic polyketone membrane for high-flux filtration of difficult oil-in-water micro- and nanoemulsions, Journal of Membrane Science, 582 (2019) 48-58.

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