

REVIEW

Recent progress in developing advanced membranes for emulsified oil/water separation

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The separation of oily wastewater, especially emulsified oil/water mixtures, is a worldwide challenge because of the large amount of oily wastewater produced in many industrial processes and daily life. For the treatment of oily wastewater, membrane technology is considered the most efficient method because of its high separation efficiency and relatively simple operational process. In this short review, the recent development of advanced filtration membranes for emulsified oil/water mixture separation is presented. We provide an overview on both traditional filtration membranes, including polymer-dominated and ceramic-based filtration membranes, and recently developed nanomaterial-based functional filtration membranes, especially one-dimensional nanomaterials, for effectively treating emulsified oil/water mixtures. The liquid flux and antifouling property, which are the most important factors for membrane performance evaluation, are described for different types of membranes. Conclusions and perspectives concerning the future development of filtration membranes are also provided.

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INTRODUCTION

During industrial processing, such as petrochemical, daily chemical, textile, leather and steel processing and metal finishing, a large amount of oily wastewater is produced every day.¹ These oil/water mixtures must be appropriately handled owing to environmental and health requirements. The effect of this wastewater on the ecosystem is long term and lethal, which can be observed by the consequences of the oil spill accidents that occurred recently.^{2,3} In addition, with rapid population growth and steadily worsening of the climate, freshwater scarcity has become a severe problem in the world, especially in certain underdeveloped regions.^{4–6} Recycling oily wastewater could improve the efficiency of freshwater use.^{7,8}

To date, various technologies, such as air flotation, gravity separation, oil-absorbing materials, coagulation and flocculation have been used to separate oil/water mixtures.^{9–12} However, these methods are either ineffective in treating emulsified oil/water mixtures, especially emulsions with oil droplet sizes smaller than 20 μm ,^{9,13} or demulsify the emulsions upon applying an electric field or adding chemicals, which usually involves energy consumption and secondary pollution.^{14–16} An efficient and broadly applicable approach for the effective separation of various emulsions, especially surfactant-stabilized emulsions, remain highly desired. Filtration membranes have been acknowledged as an advanced technology for the separation of various emulsions, especially surfactant-stabilized emulsions, with

acceptable discharge quality and a relatively simple process from an operational viewpoint.^{17,18} Despite these advantages, the widespread application of filtration membranes in various industrial fields for treating oily wastewater remains limited. The major problem is membrane fouling because of surfactant adsorption and/or pore plugging by oil droplets, which would cause a severe decline of the flux and rejection rate.^{19–21}

In this short review, we introduce the recent developments in advanced membrane filtration technology for emulsified oil/water separation. Because of their low cost, superior chemical and mechanical stability, and highly integrated operation, polymer-dominated membranes are discussed in the first section. Then, ceramic filtration membranes for oily wastewater treatment are introduced. In the third section, nanomaterial-based ultrathin filtration membranes are discussed. Finally, we provide conclusions and perspectives concerning the future development of filtration membranes for oily wastewater treatment.

POLYMER-DOMINATED FILTRATION MEMBRANES

Polymers such as polyvinylidene fluoride (PVDF) and polysulfone have been widely used for preparing microfiltration and ultrafiltration membranes for treating various types of wastewater including emulsified oil/water mixtures.^{22–27} The popularly used membrane-preparation process involves so-called liquid–liquid phase inversion,

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where the exchange of the solvent in the homogeneous polymer solution with its nonsolvent from the coagulation bath results in a porous polymer film.²⁸ Owing to the intrinsic property of most polymers, polymeric membranes tend to be oleophilic, which causes the aforementioned fouling issue and decline of flux, especially for treating oily wastewater.^{20,29} To improve the hydrophilicity and antifouling performance of polymeric membranes, many approaches involving either blending with hydrophilic components^{30–32} or surface modification^{33–35} are used.

Blending

Blending a polymer matrix with hydrophilic components during the phase inversion process is an effective method and can be easily achieved, and this process has been well investigated. In this process, hydrophilic polymers, amphiphilic copolymers and inorganic nanoparticles as the three main types of additives have been extensively employed to modify the porous filtration membrane.³⁶ Although the effects of different additives on the membrane performance differ, the main objective of blending is to enhance the membrane permeability and antifouling property. Especially for the application of purification of oily wastewater, polymer-dominated membranes must be more hydrophilic to prevent the adhesion of oil droplets on the membrane surfaces. Many studies have demonstrated the effectiveness of blending of these hydrophilic components into polymeric membranes in improving membrane performance.^{37–40} However, because of the water-favoring property of these additives and the weak interaction between the additives and the polymer matrix, the additives tend to release from the membranes during long-term use. Therefore, the stability of the blending membranes remains an issue that needs to be addressed.

Blending poly(methyl methacrylate) (PMMA) with a PVDF ultrafiltration membrane was preliminarily reported by Nunes and Peinemann.⁴¹ Marchese and co-authors⁴² later investigated in detail the effect of PMMA in different blending amounts on the degree of hydrophilicity of the resulting PVDF membranes. It was concluded that upon increasing the amount of PMMA, there was a corresponding increase in the hydrophilicity of the PVDF membranes, and simultaneously, the porous structure of the membrane was also observed to change with the addition of PMMA. In addition to neutral hydrophilic components, charged hydrophilic polymers, such as sulfonated polycarbonate⁴³ and sulfonated poly(ether ether ketone),⁴⁴ were also blended with PVDF and polyetherimide-based ultrafiltration membranes. In general, the addition of hydrophilic polymers could indeed improve the membrane permeability and fouling resistance to some extent. However, in some cases, the introduction of these hydrophilic polymers may affect the membrane structure, especially the generation of microvoids as defects in the membranes, which sometimes cause negative effects on membrane fluxes and even causes the collapse of membranes under transmembrane pressure.⁴²

Amphiphilic copolymers that are composed of both hydrophilic and hydrophobic segments are also used as additives to blend with host polymers. On the one hand, the hydrophilic segments are useful for improving the membrane hydrophilicity, and on the other hand, the hydrophobic segments are useful for improving their compatibility with host polymers.^{45–47} Mayes and co-workers⁴⁸ first used a comb-like copolymer P(MMA-*r*-POEM) (poly(methyl methacrylate) (PMMA) back bone and poly(ethylene oxide) (PEO) side chain) as an additive. Their results demonstrated that the antifouling property of the membrane was improved greatly, whereas the membrane structure

was little affected. Since then, many amphiphilic copolymers, such as tri-block,⁴⁹ comb-like⁵⁰ and branched copolymers,⁵¹ have been used as additives to blend with host polymers to produce composite membranes with enhanced antifouling properties. Among these copolymers, ternary copolymers containing a hydrophobic ‘anchoring’ segment, hydrophilic fouling resistance segment or non-polar hydrophobic segment with low surface free energy have received much attention because of their excellent complicated structure.^{52–54} During the phase inversion process, dragged by the hydrophilic segments, the non-polar hydrophobic segment tends to migrate to the membrane surface to form micro-domains. These micro-domains are advantageous to antifouling performance because of their low surface free energy. Therefore, in ternary copolymers, both the hydrophilic segments and non-polar hydrophobic segments contribute to antifouling. Thus, the flux decline of the membrane could be greatly reduced during the separation of the oil-in-water emulsion. For example, Jiang and co-workers⁵² investigated blending ternary copolymers with PVDF to construct a tunable antifouling membrane surface (Figure 1). This blending led to a PVDF membrane with tunable amphiphilic or hydrophilic antifouling surfaces because the microphase separation and surface segregation behavior of the ternary copolymers during the phase inversion could be well manipulated. Thus, the membrane with amphiphilic surfaces exhibited a much smaller flux decline during oil-in-water emulsion separation.

In addition to various polymers, inorganic nanoparticles, such as Al₂O₃, TiO₂ and SiO₂,^{13,23,25,26,55–58} have also been used to blend with host polymers. It is well known that nanoparticles have large surface areas and abundant surface-active groups. The addition of inorganic nanoparticles has been demonstrated to be helpful to membrane permeability and fouling resistance by either changing the pore structure or increasing the hydrophilicity of the membranes. A simple and commonly used approach is to directly blend pre-prepared nanoparticles with polymers in solution. Li and co-workers⁵⁵ blended Al₂O₃ nanoparticles with PVDF ultrafiltration membranes. It was observed that the addition of a certain amount of Al₂O₃ nanoparticles could increase slightly the hydrophilicity of the PVDF membrane but had no effect on the effective pore size and porosity of the membrane. Consequently, the permeation flux and flux recovery of the membrane were both improved compared with the membrane without Al₂O₃ blending. Zhang and co-workers²⁶ used TiO₂ nanoparticles to blend with a polysulfone ultrafiltration membrane. The membrane was successfully used for separating kerosene-emulsified wastewater with improved antifouling property. However, because of the poor dispersibility of nanomaterials, the nanoparticles easily formed aggregates in polymer membranes and thus caused limited improvement in the membrane permeability and antifouling performance or even defects in the membranes. In addition, direct blending may suffer from the release of the nanoparticles from the membranes because there is no established interaction with host polymers. Instead of directly blending nanoparticles with polymers, Jiang and co-workers⁵⁷ blended tetraethyl orthosilicate, which is used as precursor for SiO₂ nanoparticles, with cellulose acetate polymer. The SiO₂ nanoparticles were then generated *in situ* in acid or alkali conditions during the subsequent phase inversion. This process ensured that the SiO₂ nanoparticles would be dispersed in the polymer membrane as well as possible and avoided aggregation to the maximum extent. It appears that these nanoparticles could act as both hydrophilic additives and pore-forming agents to improve the membrane performance.

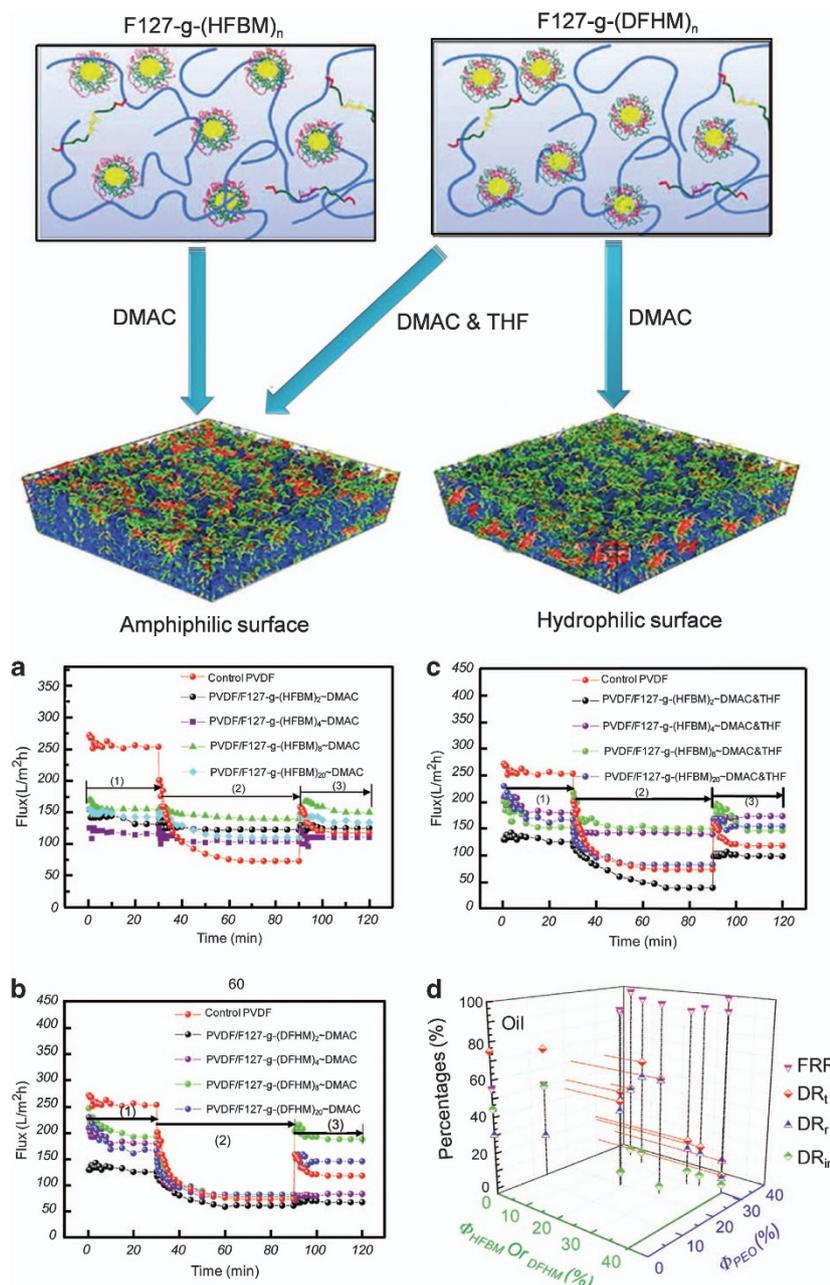


Figure 1 Amphiphilic or hydrophilic surface prepared by surface segregation during the commonly utilized wet phase inversion membrane formation process and the time dependent water permeation flux during oil/water emulsion filtration of (a) PVDF/F127-g-(HFBM)_n-DMAC, (b) PVDF/F127-g-(DFHM)_n-DMAC, and (c) PVDF/F127-g-(DFHM)_n-DMAC and THF membranes and (d) a summary of the corresponding DR_t, DR_r, DR_{ir}, and FRR values as functions of ϕ_{HFBM} (ϕ_{DFHM}) and ϕ_{PEO} values. The operation process includes three steps: pure water filtration (1), oil/water emulsion filtration (2), 20 min of water washing (not shown) and the second-round pure water filtration (3). (Reproduced from Chen *et al.*⁵² with permission from the American Chemical Society.)

Surface modification

Surface modification by either chemical reaction or physical absorption is another efficient approach to overcome surface fouling. Surface grafting is a method in which hydrophilic polymer chains are immobilized onto the membrane surface to provide a stable fouling resistance layer. For this purpose, reactive groups need to be first introduced on the membrane surface by either introducing initiator sites^{59,60} or exposing the membrane to low-temperature plasma,^{61,62} ultraviolet,⁶³ γ -ray⁶⁴ or electron beam radiation.⁶⁵ The surface-grafted polymer can be grown by either 'grafting to' or 'grafting from' approaches.²² Both approaches can generate a dense brush layer on

the membrane surface. Surface coating is a relatively simple process that improves the hydrophilicity of various filtration membranes and can be applied for industrial membrane manufacturing.³⁶ In this process, various hydrophilic layers are constructed by dipping or spraying steps or by directly adsorbing water-soluble polymers or amphiphiles onto membrane surfaces. The main disadvantage of these approaches is the instability of the coated layers, which may result in release from the membranes.³⁶

Surface modification through chemical reactions could firmly introduce hydrophilic polymers such as poly(ethylene glycol) methyl ether methacrylate,⁶⁶ poly(2-hydroxy-ethyl methacrylate),⁶⁷

poly(acrylic acid)⁶⁷ or zwitterionic polyelectrolyte⁶⁸ or small molecules⁶⁹ onto membrane surfaces via the formation of covalent bonds. The introduced hydrophilic materials form compact hydrated layers to prevent the fouling of oil droplets on membrane surfaces and allow the fouled oils to be easily removed during the following cleaning process. Jiang and co-workers conducted an extensive study on the surface grafting of filtration membranes. These authors recently grafted a low surface free energy molecule pentadecafluorooctanoic acid onto the surface of an aminated polyacrylonitrile ultrafiltration membrane via an acrylated reaction.⁶⁹ The modified membrane exhibited excellent antifouling property. Very recently, our group reported a zwitterionic polyelectrolyte-grated membrane for the separation of water-rich oil/water mixtures and emulsions.⁶⁸ In the work, a novel zwitterionic polyelectrolyte brush poly(3-(*N*-2-methacryloxyethyl-*N,N*-dimethyl) ammonatopropanesultone), was grafted onto a PVDF membrane via a surface-initiated atom transfer radical polymerization process. The modified membrane exhibited a superhydrophilic and underwater superoleophobic property with an 11° water contact angle and >150° underwater oil contact angle with ultralow oil adhesion. This special surface wettability endowed the membrane with superior hydrophilic and antifouling performance.

In addition to chemical reactions, directly depositing hydrophilic materials such as polydopamine,⁷⁰ poly(ethylene glycol),⁷¹ polyvinyl alcohol⁷² and chitosan⁷³ onto membrane surfaces via physical adsorption is another approach by which to modify membranes. Freeman and co-workers successfully deposited dopamine onto a polyamide reverse osmosis membrane.⁷⁰ It is well known that dopamine has a strong adaptability to cover any type of surface

through the formation of an adhesive polydopamine layer via self-polymerization, which can tremendously alter surface properties such as wettability and biocompatibility.^{74–77} In this work, the reverse osmosis membrane coated by the polydopamine layer exhibited a higher flux for oil/water emulsion separation than the one without modification, although there was no obvious change in the membrane hydrophilicity.

As an alternative to traditional polymer filtration membranes, Chu and co-workers^{78–81} reported the surface modification of the hydrophilic layer on nanofibrous ultrafiltration membranes to achieve high flux for oil-in-water emulsion separation. As illustrated in Figure 2, a nanofibrous polyacrylonitrile weave as a scaffold was first placed onto a non-woven poly(ethylene terephthalate) micro-filter substrate, and then, chitosan, as the hydrophilic layer, was spin-casted onto the polyacrylonitrile weave to form a three-tier nanofibrous membrane. Because of the high porosity and thin and smooth barrier layer of the membrane, the membrane exhibited outstanding performance including high flux and antifouling property. During the long crossflow filtration experiment using an oil-in-water emulsion as the feed, the water flux maintained a much higher value than the commercial ultrafiltration membrane, and no obvious loss of oil rejection was observed. A similar strategy was also investigated by Freeman and co-workers,^{72,82} who used a porous membrane prepared by phase inversion to prepare an asymmetric hydrophilic ultrafiltration membrane.

The main purpose of surface modification is to increase the hydrophilicity of membrane surfaces and thus improve membrane performance. However, the forms of emulsified oil/water are diverse, including both water-rich oil/water mixtures, such as oil-in-water emulsions, and oil-rich oil/water mixtures, such as water-in-oil emulsions. Hydrophilic membranes are applicable for the separation of water-rich oil/water mixtures but do not work for the separation of oil-rich oil/water mixtures. A breakthrough was recently achieved by Tuteja and co-workers,⁸³ who prepared a mixture of fluorodecyl polyhedral oligomeric silsesquioxane (f-POSS) and cross-linked poly(ethylene glycol) diacrylate (x-PEGDA)-modified hygro-responsive mesh membrane that was both superhydrophilic and superoleophobic in air and under water, as illustrated in Figure 3. The membrane is valuable for the separation of both water-rich and oil-rich oil/water mixtures and various emulsions driven only by gravity (as shown in Figure 3b). The authors ascribed the hygro-responsive wettability of their membrane to the migration and reconfiguration of f-POSS and x-PEGDA, respectively, on the membrane surface in air and under water. The oleophobic property in air is essential for separating water-rich oil/water mixtures and water-in-oil emulsions. The only weakness of this membrane is its low breakthrough pressure (the maximum height of liquid that the membrane can support), which causes some limitations in practical operation when treating a large quantity of oil/water mixture.

To date, many studies have been performed to design advanced functional membranes for oil/water separation. Much effort has been focused on the methods of blending and surface modification with the aim of enhancing the membrane permeability and antifouling properties. For oily wastewater separation, the most important issue to be addressed is to decrease the adsorption of oil droplets on the membrane surface, which has been extensively investigated. In addition to oil droplets, membrane fouling caused by the adsorption of other organic molecules, such as surfactants, remains a problem but is often overlooked. More attention must be paid to this issue.

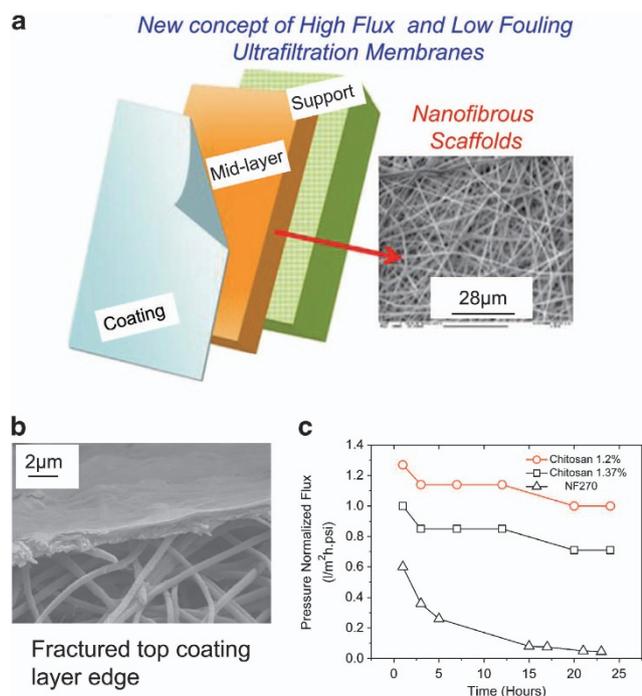


Figure 2 The typical structure of three-tier nanofibrous ultrafiltration membranes and their performance. (a) The three-tier approach to fabricate high-flux and low-fouling ultrafiltration membranes. (b) Typical top structure of a fractured composite membrane. (c) Antifouling property in a long-term separation experiment using oily wastewater as the feed. (Reproduced from Yoon *et al.*⁷³ with permission from Elsevier.)

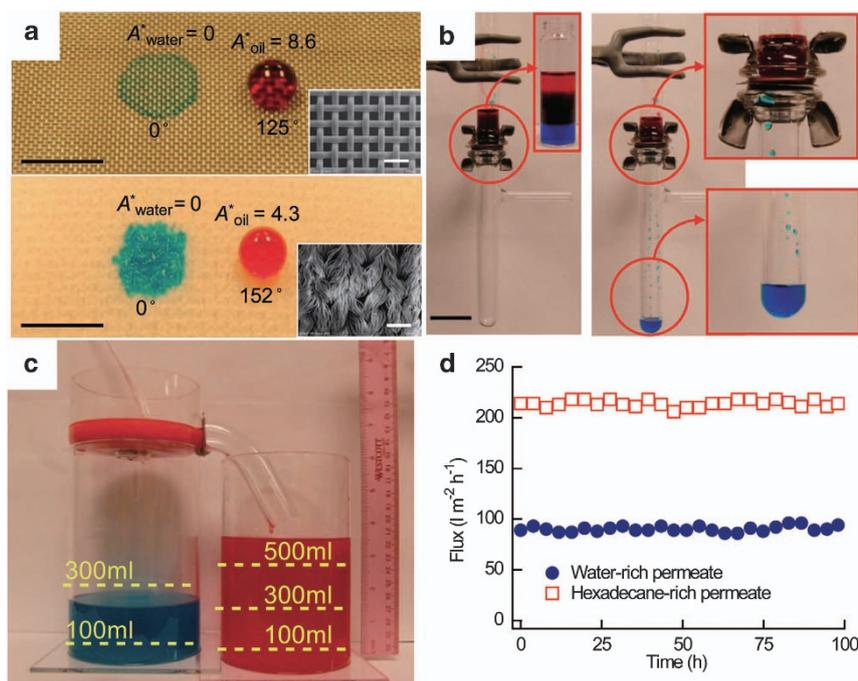


Figure 3 Hygro-responsive membranes prepared by dip-coating with fluorodecyl polyhedral oligomeric silsesquioxane (f-POSS) and cross-linked poly(ethylene glycol) diacrylate (x-PEGDA): (a) droplets of water (dyed blue) and rapeseed oil (dyed red) on stainless steel mesh 100 and polyester fabric; (b) separation of four-component mixtures: water, hexadecane, a 30:70 (v:v) water-in-hexadecane emulsion and a 50:50 (v:v) hexadecane-in-water emulsion; (c, d) continuous separation of water-in-oil emulsions, which demonstrates that the membrane possesses superior antifouling properties in the presence of the oil. (Reproduced from Kota *et al.*⁸³ with the permission from Nature Publishing Group.)

Membranes with superwetting surfaces

Because of the different interfacial tension of oil and water, utilizing the superwetting behavior (that is to say, superhydrophobic-superoleophilic or superhydrophilic-superoleophobic) of solid surfaces to design oil/water separation processes has been considered an efficient and facile approach.⁸⁴ The wettability of a solid surface is governed by its surface free energy and surface geometrical structure.⁸⁵ To achieve the superwetting property, rough surfaces with hierarchical macro-/nanostructures have been created using various technologies. Many superwetting materials have been fabricated by designing in combination with surface chemistry and roughness and have been applied to oil/water separation.^{84,86–90} Unfortunately, most of these materials are fabricated through coating water-avoiding or water-favoring materials on mesh-like substrates. Owing to the micrometer scale pores of the substrates, the substrates can only be applied for the separation of immiscible oil/water mixtures but are not suitable for emulsions because emulsions usually have much smaller droplet sizes. If superwetting surfaces are combined with traditional filtration membranes, self-powered or low-pressure-driven emulsified oil/water separation with excellent selectivity and high flux could be achieved.^{91,92}

Recently, our group made a breakthrough in preparing polymer filtration membranes with a superwetting property, where a superhydrophobic and superoleophilic PVDF membrane was successfully fabricated using a modified phase inversion process.⁹³ Unlike the common phase inversion process, a small amount of ammonia water was added to the PVDF solution in our work. The added ammonia tended to induce localized microphase separation and caused the formation of ‘incipient precipitation’ in the form of PVDF clusters in the solution. These PVDF clusters functioned as a growing point that gradually grew into spherical particles in the subsequent phase-

inversion process. A superhydrophobic and superoleophilic PVDF membrane was thus produced (as shown in Figure 4). The membrane could effectively separate both micrometer- and nanometer-size surfactant-free and surfactant-stabilized water-in-oil emulsions solely driven by gravity with high separation efficiency (an oil purity in the filtrate after separation above 99.95 wt%, with some purities as high as 99.999%). Most importantly, the membrane exhibited a high flux, which was several times higher than that of commercial filtration membranes driven by external pressure and reported materials with similar permeation properties, and was easily recyclable.

Traditional ultrafiltration and microfiltration membranes applied for separating oily wastewater mainly take advantage of the ‘size-sieving’ effect driven by applied pressure, in which oil droplets with certain sizes are not allowed to pass through the ‘pores’ of the membrane. In general, a high transmembrane pressure up to several bars is needed, which is relatively energy consuming. Filtration membranes with superwetting surfaces not only offer superior antifouling performance but also could break out of their dependence on high transmembrane pressure. This achievement opens a new direction for designing advanced filtration membranes with improved performance. There remains a broad research space in this direction, and in-depth and extensive studies should be performed.

CERAMIC FILTRATION MEMBRANES

In the family of filtration membranes, ceramic-based membranes occupy an important position because of their high chemical, thermal and mechanical stabilities, which make them suitable for use in harsh conditions such as corrosive and high temperature environments.^{94–96} Employing ceramic filtration membranes for oily wastewater treatment is also studied and reported by some researchers.^{96–109}

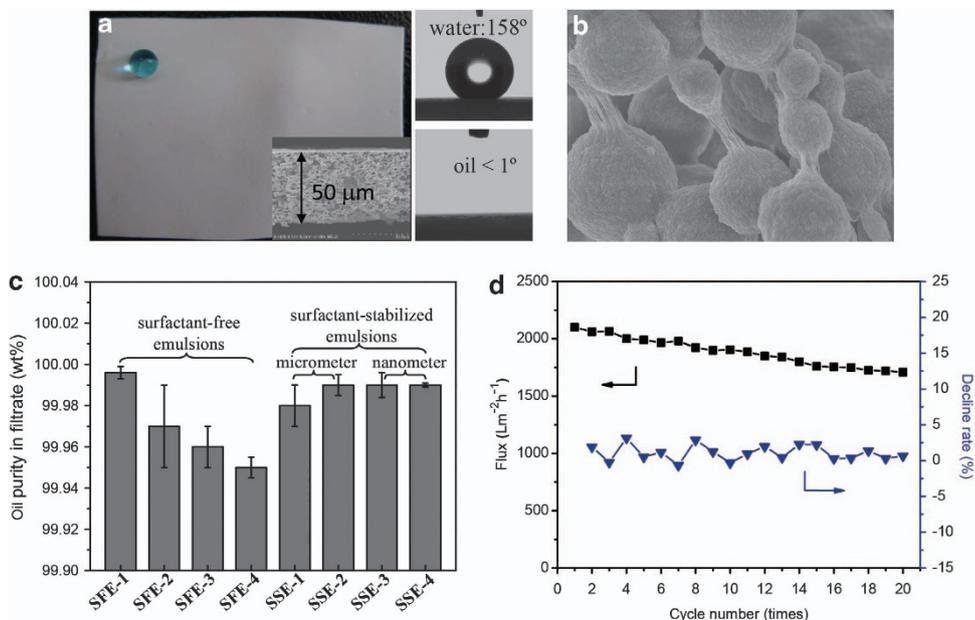


Figure 4 The superhydrophobic and superoleophilic polyvinylidene fluoride (PVDF) membrane for efficient emulsified oil/water mixture separation: (a) a photograph of the as-prepared PVDF membrane, where the water contact angle on the membrane is 158° and the oil contact angle is nearly zero contact angle; (b) a magnified image of the PVDF surface, where the scale bar is $1\ \mu\text{m}$; (c) oil purity in the filtrate after permeating through the PVDF membrane; (d) change of the flux and decline rate with increasing cycle number. The decline rate was obtained by dividing the flux difference of two adjacent cycles by the former flux. (Reproduced from Zhang *et al.*⁹³ from WILEY-VCH.)

Because of the limitation of their pore sizes, directly employing ceramic membranes for the separation of emulsified oil/water mixtures would cause severe fouling problem and low fluxes.^{99,104,108} Among the various ceramic filtration membranes, zirconia ceramic membranes exhibit better performance than others for oily wastewater treatment. Xu and co-workers prepared a zirconia-composite microfiltration membrane on a symmetric α -alumina support and an asymmetric α -alumina support with sub-micrometer pore sizes.¹⁰⁰ Compared with commercial tubular zirconia membranes, these zirconia composite microfiltration membranes exhibited much higher water permeability and a much smaller decrease of flux during continuously permeating oil-in-water emulsion. Recently, Chang and co-workers also prepared a nanosized zirconia-particle-modified Al_2O_3 microfiltration membrane using ZrCl_4 as a precursor.¹⁰³ Similarly, the modified membrane exhibited an improved and stable flux for oil/water emulsion separation compared with the Al_2O_3 microfiltration membrane without modification because of the high hydrophilicity of ZrO_2 . In addition to the zirconia-based filtration membrane, zeolite- and polymer-modified ceramic membranes were also investigated with regard to oil-in-water emulsion separation.^{95,96,101}

For ceramic filtration membranes, the general synthesis routes involve a sol-gel process followed by sintering of the initial ceramic into ceramic microcrystals. These processes usually cause the resulting membranes to exhibit relatively rough surfaces. It is acknowledged that surface roughness is an important factor that affects membrane performance.²⁷ Because of the increase of surface roughness, the surface area will increase correspondingly, which causes a more serious fouling problem than smoother surfaces.^{110,111} Therefore, investigations on the effect of surface roughness of ceramic membranes on membrane performance and on the methods to control the surface roughness of ceramic membranes have also been conducted. Xing and co-workers¹⁰⁹ prepared a series of ceramic

membranes with controllable surface roughness using PMMA particles as the template with different diameters. In the process of oil/water emulsion separation, the membrane with higher surface roughness exhibited a more severe flux decline. In this study, the researchers also observed that the size of the oil droplet had the reverse effect. The results were identical to those reported by Elimelech and co-workers.¹¹¹

Although the potential of ceramic-based membranes for separating emulsified wastewater has been demonstrated, the low separation efficiency and oil-fouling remain large obstacles that are even more serious than polymer-dominated filtration membranes. The poor antifouling performance of ceramic-based membranes usually causes an unfavorable oil rejection rate. The performance of ceramic-based membranes for oily wastewater treatment must be continually improved. In this process, more preparation methods and surface modification technologies toward making ceramic-based membranes with negligible pore defects and good antifouling properties should be developed, and sustained efforts should be made.

NANOMATERIAL-BASED ADVANCED MEMBRANES

Pressure-driven traditional filtration membranes have been widely used in treating wastewater. However, these membranes usually contain a thick active separation layer typically in the range of sub-micrometer to several micrometer scales to withstand the high transmembrane pressure, which largely restricts the increase of the membrane flux. Permeation theory predicts that the filtration rate is directly proportional to the square of the effective pore size of the membrane and inversely proportional to the thickness of the membrane.^{112,113} The rational design of membranes for emulsified oil/water separation requires the optimization of these two important physical characteristics. An ideal membrane is expected to have an active separation layer that is as thin as possible and does not sacrifice its effective pore size.^{113,114} However, such a structure is difficult to

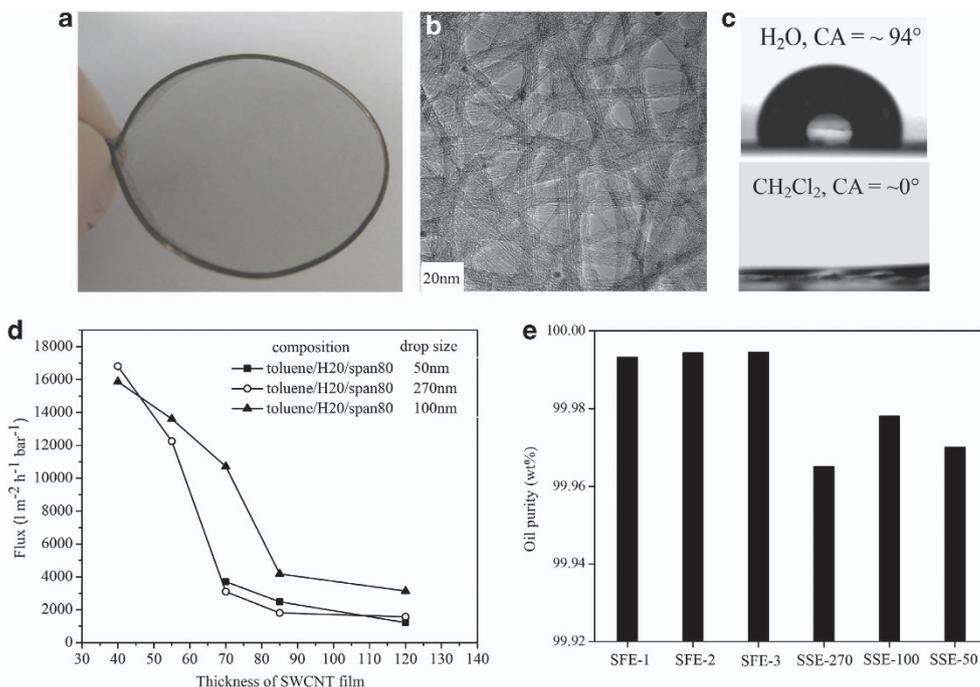


Figure 5 Ultrathin free-standing single-walled carbon nanotube (SWCNT) network films for ultrafast separation of emulsified oil water mixtures: (a) the ultrathin SWCNT network films suspended by a steel hoop; (b) transmission electron microscope image of an ~ 70 -nm thick SWCNT film exhibiting a porous network structure, in which carbon nanotubes are interlaced with each other; (c) photographs of a water droplet and an oil (dichloromethane) droplet on the SWCNT film with CAs of $\sim 94^\circ$ and nearly 0° , respectively; (d) plots of the fluxes of surfactant-stabilized emulsions as a function of the thickness of SWCNT film; (e) oil purity of filtrates after separating various emulsions (SFE: surfactant-free emulsion; SSE: surfactant-stabilized emulsion). (Reproduced from Shi *et al.*¹¹⁶ with permission from WILEY-VCH.)

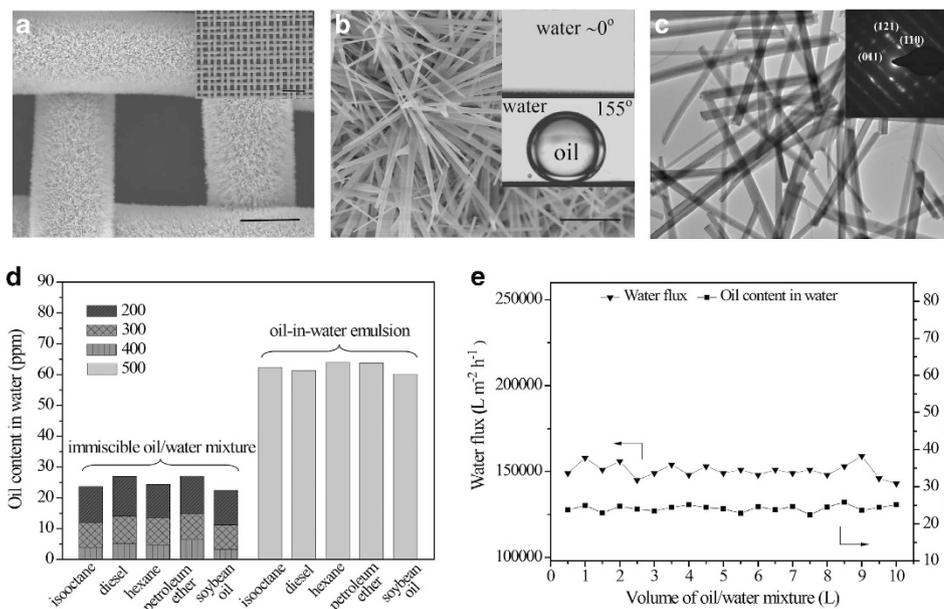


Figure 6 Nanowire-haired inorganic membranes with superhydrophilicity and underwater ultralow adhesive superoleophobicity for high-efficiency oil/water separation. (a–c) Structure characterization of nanowire-haired membrane and the water contact angle and oil contact angle underwater on the surface of this membrane. (d) Oil content in the filtrate after permeating a series of immiscible oil/water mixtures and oil-in-water emulsions through the membranes with different mesh numbers. (e) Real-time monitoring of the variation of flux and oil content in the filtrate as a function of the permeated volume of the oil/water mixture up to 10 L. (Reproduced from Zhang *et al.*¹²⁴ with permission from WILEY-VCH.)

achieve in the system of traditional polymeric or ceramic-based membranes. Recent progress in fabricating ultrathin filtration membranes with innovative structures composed of nanomaterials

and advanced nanotechnologies provides a new future to revolutionarily improve the membrane performance, especially the flux.^{113–117} One-dimensional nanomaterials, such as carbon

nanotubes, nanowires and nanofibers, are most attractive for constructing fibrous films.^{115,116,118–122} Because of their small diameter, a membrane composed of these structures can possess both an adjustable effective pore size and an ultrathin active separation layer on the nanometer scale.^{113,114}

Recently, our group produced ultrathin free-standing single-walled carbon nanotube (SWCNT) network films for the ultrafast separation of an emulsified oil/water mixture (Figure 5).¹¹⁶ The thickness of the SWCNT films could be tuned from 30 to 120 nm, and the effective pore size of the SWCNT films could be tuned from 20 to 200 nm. The SWCNT film with surface wettability of superoleophilicity and hydrophobicity could effectively separate both micrometer- and nanometer-sized surfactant-free and surfactant-stabilized water-in-oil emulsions. Because of the nanoscale thickness and uniform pore size, the films exhibited fluxes as high as $100\,000\text{ l m}^{-2}\text{ h}^{-1}\text{ bar}^{-1}$, which is 2–3 orders of magnitude higher than commercial filtration membranes with similar separation performance, and a high separation efficiency (> 99.95 wt% in terms of oil purity in the filtrate). The good chemical stability of these SWCNT films demonstrates their potential application in the chemical industry. Although the area of current SWCNT films is limited because of laboratory filtration instruments, the fabrication of SWCNT films in the form of meter-scale rolls is indeed commercially available. Our work provides a new route for designing a new type of nanomaterial-based membrane for effective emulsified oil/water separation. Instead of SWCNTs, Wang and co-workers¹²³ reported the use of MnO_2 nanowires as building blocks to fabricate nanofibrous membranes via suction filtration. The membranes have hydrophilic surfaces because of the numerous oxygen atoms exposed on the surfaces of the nanowires. These oxygen atoms could serve as hydrogen bond acceptors (with water molecules as the donors) to bind water molecules. The water molecules therefore could be trapped in the pores of the nanofibrous membranes. Consequently, water could permeate through the membranes, and oil droplets resisted above the membranes.

The aforementioned SWCNT and MnO_2 ultrathin nanofibrous films are both prepared via vacuum filtration. This technique requires a well-dispersed solution of SWCNTs or MnO_2 nanowires to prepare membranes with well-distributed pore sizes. As an alternative to this strategy, we recently designed a $\text{Cu}(\text{OH})_2$ nanowire-haired copper mesh membrane by *in-situ* oxidizing copper mesh in alkaline conditions (Figure 6).¹²⁴ The membrane with superhydrophilicity and underwater ultralow adhesive superoleophobicity could effectively separate both immiscible oil/water mixtures and oil-in-water emulsions, solely driven by gravity, with an extremely high separation efficiency. The residual oil in the filtrate after only one separation was lower than 30 p.p.m., which meets the stringent standards for wastewater discharge. Most importantly, the membrane exhibited a high separation capacity, being able to separate 10 l of an oil/water mixture continuously without a decrease in flux, and excellent antifouling properties. The excellent capability for oil/water separation and the low cost and easily scaled-up preparation process of the membrane indicate its great potential for practical application.

Nanomaterials as a hot topic have drawn significant attention in recent years. Constructing nanomaterial-based or nanomaterial-modified advanced nanofiltration, microfiltration and reverse osmosis membranes has great potential from the viewpoint of both experimental results and theoretical predictions.^{125–129} Because of their high surface area and special surface properties, nanomaterial-dominated membranes exhibit some advantages in the area of high flux and high

rejection rate compared with traditional filtration membranes. However, despite these pioneering advances, research toward designing broad nanomaterial-dominated membranes remains far less developed, and a thorough study is highly desired.

CONCLUSIONS AND OUTLOOK

Membrane technology as a simple, low-cost and efficient method has been extensively used in many separation processes, such as water purification, desalination and oily wastewater treatment. In this review, we concentrated on the recent development of advanced filtration membranes including polymer-dominated membranes, ceramic membranes and nanomaterial-based advanced membranes for oily wastewater treatment, especially the separation of an emulsified oil/water mixture. For these applications, the antifouling property of the membranes is of importance because oils are highly susceptible to adsorption onto the membranes, which leads to blocking of the pores, causing the rapid decline of the flux and separation efficiency. Increasing the membrane flux is another important target for advanced membranes. To date, most research focuses on the design and preparation of various membranes. Less attention is paid to in-depth investigations of the oil/water separation process and understanding how the oil droplets demulsified and coalesced together at membrane surfaces, which is often neglected but very important. Clarifying this point could provide a theoretical direction for designing high-performance membranes. Nanomaterial-based membranes undoubtedly present a new opportunity for achieving high performance. The rational design of the structure of the separation layer at the nanoscale and of the surface chemical and adhesive properties of these membranes is becoming more prominent.

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