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Design strategy of poly(vinylidene fluoride) membranes for water treatment



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ABSTRACT

The development of facile, benign and energy-efficient water treatment technologies to produce clean water presents a major societal challenge. Membrane-based separation technologies stand out as an ideal solution for water treatment. PVDF-based polymer membranes are gaining popularity because of their desirable properties, such as high mechanical strength, thermal/chemical resistance, and favorable processing characteristics. This review comprehensively introduces the state-of-the-art strategies to modify and design high-performance PVDF membranes for water treatment. High-performance porous PVDF membranes introduced here focus on the pressure driven membrane process and membrane distillation. This review also covers the green fabrication of PVDF membranes, novel strategies to tailor the microstructure and surface properties, Janus and omniphobic PVDF membranes, emerging new materials-hybrid PVDF membranes containing novel 0D, 1D and 2D materials, and self-cleaning PVDF membranes for water treatment. Overall, this review aims to provide understanding of the fundamental science and engineering aspects underlying the use of PVDF and its copolymers for membrane fabrication as well as the challenges and opportunities to guide further advances towards the development of PVDF-based membrane technologies for a sustainable future.

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Abbreviations: APTES, 3-aminopropyltriethoxysilane; AC, alternating current; AM, additive manufacturing; BSA, bovine serum albumin; CA, cellulose acetate; COD, chemical oxygen demand; CNC, cellulose nanocrystal; DMP, dimethyl phthalate; DBM, dibutyl maleate; DSC, differential scanning calorimeter; DMF, N, N-dimethylformamide; DCMD, direct contact membrane distillation; EDA, ethylenediamine; FO, forward osmosis; FAS, 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane; FS, flat sheet; F, fluorine; GBL, y-butyrolactone; HA, humic acid; HF, hollow fiber; ILs, ionic liquids; LCST, lower critical solution temperature; MD, membrane distillation; MOF, metal organic framework; MBR, membrane bioreactor; MWNTs, multi-walled nanotubes; MWCNT, multi-walled carbon nanotube; NMP, N-methyl pyrrolidone; NPs, nanoparticles; NIPS, nonsolvent induced phase separation; PVDF, poly(vinylidene fluoride); PFSA, perfluorosulfonic acid; PC, propylene carbonate; PVA, poly(vinyl alcohol); PEG, polyethylene glycol; PFPE, perfluoropolyether; PVP, polyvinylpyrrolidone; PVC, polyvinyl chloride; PDA, polydiacetylene; PGAL, poly(gallic acid); PSF, polysulfone; PPG, poly(propylene glycol); PEI, polyethylenimine; PDMS, poly(dimethyl siloxane); PMMA, poly(methyl methacrylate); ATBC, acetyl tributyl citrate; AgNPs, silver nanoparticles; ATRP, atom-transfer radicalpolymerization; BC, butylene carbonate; CTA, cellulose triacetate; CNS, carbon nanostructure; CNT, carbon nanotube; DC, direct current; DEDAPS, N, N-d diethylethylenediamine; DMAc, N, N-dimethylacetamide; DMI, dimethyl isosorbide; DMAEMA, N,N-dimethylaminoethylmethacrylate; EC, ethylene carbonate; FTIR, Fourier transform infrared; FTCS, 1H, 1H, 2H, 2H-perfluorododecyltrichlorosilane; FRR, flux recovery ratio; GO, graphene oxide; GTA, glycerol triacetate; HSPs, Hansen solubility parameters; IP, interfacial polymerization; ICP, internal concentration polarization; LEP, liquid entry pressure; MF, microfiltration; MeOH, methanol; MWCO, molecular weight cut-off; MXene, Ti₃C₂T_x; NF, nanofiltration; NL, nanoimprinting lithography; O/W, oil-in-water; PEO, polyethylene oxide; PIM, phase inversion micromolding; PEMA, poly(ethylene-co methyl acrylate); PTFE, polytetrafluoroethylene; PP, polypyrrole; PA, polyamide; PHB, poly-3-hydroxybutyrate; PES, polythesulfone; PP, Polypropylene; PE, Polyethylene; PNIPAm, Poly(N-isopropylacrylamide); P(S-r-4VP), Poly(styrene-r-4-vinylpyridine); PAN, polyacrylonitrile; PTMD, photothermal membrane distillation; PEGMA, Poly(ethylene glycol) methyl ether methacrylate; PVDF-g-POEM, PVDF-g-poly(oxyethylene methacrylate);; PVDF-co-NMA, PVDF-g-N-methylolacrylamide; PVDF-co-CTFE, poly(vinylidene fluoride-co-chlorotrifluoroethylene); PVDF-co-TrFE, poly(vinylidene fluoride-co-trifluoroethylene); PVDF-co-TFE, Poly(vinylidene fluoride-co-tetrafluoroethylene); PVDF-g-PAA, PVDF-g-(poly(acrylic acid); PE-b-PEG, PVDF-polyethylene-block-poly (ethylene glycol); PVDF-co-HFP, Poly(vinylidene fluoride-co-hexafluoropropene); PVDF-g-PMABS, PVDF-g-4-methacrylamidobenzenesulfonic acid; PVDF-g-(PACMO-PAA-g-AG), PVDF-g-(polyacryloylmorpholine-(polyacrylic acid)-g-argatroban); PVDF-g-PAMCO, PVDF-gpolyacryloylmorpholine; PVDF-g-PEGMA, PVDF-graft-poly(ethylene glycol) methyl ether methacrylate; PFDTS, 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane; PE-b-PEG, polyethylene-block-poly (ethylene glycol); SDS, sodium dodecyl sulfate; TOC, total organic carbon; TA, tannic acid; TIPS, thermally-induced phase separation; UV, ultraviolet; VIPS, vapor induced phase separation; XPS, X-ray photoelectron spectroscopy; ZIF, zeolitic imidazolate framework; zP(S-r-4VP, zwitterionization of poly(styrene-r-4vinylpyridine); SS, stainless steel; TEP, triethyl phosphate; TGA, thermogravimetric analysis; UF, ultrafiltration; VMD, vacuum membrane distillation; W/O, Water-in-oil; XRD, X-ray diffraction.

1. Introduction

Membrane-based separation processes are significant separation technologies for water treatment [1]. Compared with ceramic materials, polymers and their blends have been widely used as membrane materials because of their low cost, diverse types, and facile fabrication processes. Among polymer membranes, poly(vinylidene fluoride) (PVDF) is one of the most widely used fluoropolymer materials for membrane fabrication due to their high mechanical strength, good thermal stability, and chemical resistance as well as aging resistance [2,3]. In addition, PVDFs can be easily fabricated into flat sheets, hollow fibers and tubular membranes that are suitable for diverse separation applications [4–6].

However, pure PVDF membranes are limited in a wide range of applications because they are neither very hydrophobic nor hydrophilic. For a pressure-driven membrane process, the pure PVDF membrane easily fouls with contaminants in waste-water treatment. For membrane distillation process, such membranes have poor long-term stability compared with polytetrafluoroethylene (PTFE) membranes since they are easily wetted by a feed solution containing foulants. Therefore, the development of PVDFbased membranes with enhanced properties is very important. Understanding and improvements of crystalline polymorphs, chemical/thermal stability, and hydrophobic/hydrophilic performance are needed to improve membrane performance. In addition, green fabrication of PVDF membranes is becoming important as well, since conventional solvents, such as N-methyl pyrrolidone (NMP), N,Ndimethylacetamide (DMAc), and N,N-dimethylformamide (DMF) have adverse effects on the environment and human health. Note that NMP has been banned since 2020 by the European Union due to toxicity concerns [7]. Green fabrication method by using nontoxic solvents and the solvent-free method are two important topics of interest in recent years.

It is worth mentioning that the number of annual publications related to PVDF approached 2000 in 2020, and nearly half of the publications are corresponded to produce PVDF membranes. Since 2010, two relevant reviews about the fabrication and application of PVDF membranes have been published in 2011 [8] and 2014 [9], respectively. As shown in Fig. 1a, the number of publications has stably grown since 2010. Since 2015, the annual publications of PVDF membrane reached above 500, and the number of publications in 2020 approached 1000. The specific percentages of PVDF, polythesulfone (PES) and polysulfone (PSF) membranes among all (PVDF+PES+PSF) publications are displayed in Fig. 1b as these are the top three polymer membranes. Notice that the percentage of PVDF membranes has increased from 53 to 60% in the last 10 years, indicating that the PVDF membranes are the most popular ones to study. Therefore, a timely review would identify current trends in research efforts and highlight various applications of PVDF membranes.

This review provides a comprehensive overview of recent strategies to design functional PVDFs for membrane applications. Recent advances and important trends on the design strategies for PVDF membranes are further discussed, including fabrication processing of PVDF membranes, novel materials-blended membranes, emerging 3D printed or patterned membrane surfaces and novel strategies for constructing functional membrane surfaces. Furthermore, self-cleaning PVDF membranes are introduced from the perspective of smart-responsive PVDF membranes, conductive PVDF membranes, photocatalytic PVDF membranes, superwetting PVDF membranes and β -phase based piezoelectric PVDF membranes. This review may provide insights into the future development of functional PVDF membranes.



Fig. 1. (a) Recent publications related to PVDF based polymers (via Web of Science based key words of (1) "PVDF" and "membrane" and (2) "PVDF" as of April 2021). (1) is used to search PVDF-based membranes and (2) is employed to search PVDF-based materials. From 2010 to 2014, the numbers of publications of PVDF and PVDF membranes were below 1000 and 500, respectively, while the number was above 1000 and 500, respectively, from 2015 to 2020, and (b) recent publication ratios among the top three polymer membranes (via Web of Science based key words of (A) "PVDF" and "membrane", (B) "PES" and "membrane" and (C) "PSF or PSU" and "membrane" as of April 2021).

2. Structure and properties of PVDF

PVDF is polymerized from vinylidene fluoride monomer via a free-radical polymerization, and therefore has various molecular weights due to the different degrees of polymerization. Compared with other fluoropolymers, PVDF is semi-crystalline with a low melting point of 170 °C and a density of 1.77 kg/m³. The glass transition temperature of PVDF is about -35 °C, and it is typically 50–60% crystalline [10]. Since this review is related to PVDF, its copolymers and their blends for high-performance membrane applications, developments of chemical/physical structures and properties of PVDF are briefly introduced in this section.

2.1. Solubility

Solubility represents the ability of polymers to dissolve in a solvent, which depends on their physical and chemical properties related to the temperature, pressure and presented chemicals or additives in the solution system. The solubility of PVDF in a solvent is based on the principle of "like-dissolves-like", where polarity plays a key role. PVDF is insoluble in alcohols, basic solutions, acid solutions, aliphatic compounds, aromatic compounds, and chlorine solution [11]. Usually, PVDFs are dissolved in conventional polar aprotic solvents, such as NMP, DMF and DMAc (see Table 2). No-

tice that the solubility of PVDF depends on its molar mass at the same condition, where lower molecule-weight PVDF displays better solubility. In the dissolution process, temperature plays an important role in the performance of PVDF membranes. Lin et al [12]. dissolved PVDF in DMF solvent with dissolution temperature ranging from 50 to 110 °C, and found the size of semicrystalline particles increased from 0.5 to 15 μ m. In fact, the surface properties and porosity were also affected by the differences in the degree of dissolution of polymer crystals and unfolding of polymer molecular chains prior to the solidification stage [13]. In addition to temperature, some other physical forms of energy input also affected the dissolution process and properties, such as ultrasonication [14]. In addition, an important problem that cannot be ignored is that these conventional solvents are always toxic and have strong adverse effects on human health and the environment. Therefore, it is urgent to find new non-toxic solvents to dissolve PVDFs, replacing conventional toxic solvents. Non-toxic solvent is harmless and environmentally friendly solvent that has no risks on both human health and the environment based on the principle of green chemistry [15]. The solubility of PVDF in non-toxic solvents will be discussed in Section 3.2 for sustainable PVDF membranes.

2.2. Alkali-resistance

The chemical and thermal stability of PVDF polymers is very important in polymer processing industries. It is meaningful to analyze the chemical properties of PVDFs as they are frequently exposed to harsh conditions, including acid/base environments and high temperatures. For example, NaOH solutions with high concentration were used to pretreat the PVDF surface based on the reported literature related to chemical modification of PVDF [16,17]. After being exposed to alkaline solution, the properties of PVDF were changed with an increase in treatment time. For example, a hot NaOH solution (60 °C, 7.5 M) was employed to pretreat the PVDF surface to enhance the hydrophilic properties [17,18]. The color of PVDF usually changed from white to brown and then to black. The formation of "-C=C-" double bonds was attributed to loss of "HF" units from long PVDF chains, in a dehydrofluorination reaction. After pretreatment with alkaline solution, "-OH" functional groups were detected on the PVDF surface by Fourier transform infrared (FTIR) spectroscopy [19]. Alkaline treatment of the PVDF easily deteriorated its mechanical strength. Therefore, the pretreatment time should be strictly controlled to balance the desired surface properties and mechanical strength.

Hence, PVDF barely maintains its chemical structure and its properties in basic environments for long duration. However, PVDF membranes are often employed for the treatment of alkaline wastewater or frequently washed by alkaline solutions to remove the contaminants in real and practical applications. Therefore, it is important to develop alkali resistant PVDFs for membranes. One important strategy is to wrap up the PVDFs with alkali-resistant materials. Sodium dodecyl sulfate (SDS) has excellent alkali-resistant properties. However, it is challenging to stabilize SDS around the PVDF surface. Wen et al [20]. attached the SDS on the PVDF surface and immobilized UV-curable polyester acrylate and tri(propylene glycol) diacrylate. The SDS employed in their work resisted alkali corrosion by NaOH solution. After immersing these membranes in NaOH solution (pH = 13) for 30 days, the F/C ratio of pristine PVDF decreased by \sim 20%, while that of SDS-modified PVDF decreased by \sim 2%. This demonstrated that SDS could effectively alleviate the dehydrofluorination that led to degradation of the PVDF membrane, improving the PVDF alkaline resistance. Ji et al [21]. prepared a homogenous aromatic polyamide (aramid) solution and coated it on the PVDF surface via phase inversion to improve the alkaline resistance. Then, a 1 M NaOH solution was used to test the alkali-resistant properties of aramid/PVDF polymers. After alkaline solution treatment for 24 h, the content of oxygen on the pristine PVDF increased to 19.3%, while that of the aramid/PVDF blends increased to only 3%. The final membrane was successfully used to concentrate alkaline solution with satisfactory long-term stability. In addition, a bioinspired accurate-deposition strategy was also used to improve the alkali resistant performance of PVDFs. Halloysite nanotubes/TiO₂ blends were prepared and fixed on the PVDF surface by a gallic acid (GA) and polyetherimine (PEI) assisted accurate-deposition method [22]. GA reacted with PEI to form tunicate-inspired coating, which could immobilize halloysite nanotubes/TiO₂ blends. This robust multifunctional surface provided PVDF membranes with extraordinary stability as the membranes were superoleophobic (underwater oil contact angles greater than 155°) and superhydrophilic (water contact angel of 0°) after immersing in 4 M NaOH and 4 M HCl solutions, respectively, for more than one week.

2.3. Thermal stability

In addition to the alkaline resistance, the thermal resistance of PVDF membranes should be noted as well. PVDF is a semicrystalline polymer with amorphous and crystalline phases. The decomposition temperature of PVDF is higher than 316 °C [11]. Of course, the highest temperature PVDF membranes can tolerate depends on many parameters, such as PVDF content and crystallinity.

Regarding the thermal properties of PVDF blends, the thermal stability varies with the addition of diverse polymers or inorganic particles. Thermogravimetric analysis (TGA) is an effective characterization method to determine the degradation temperature. Nthunya et al [23]. fabricated PVDF blends by adding SiO₂, silver nanoparticles (AgNPs) and carbon. The degradation temperatures of pristine PVDF and PVDF blends were 491 and 550 °C, respectively, showing enhanced thermal stability [24]. Such PVDF blends were employed to fabricate PVDF membranes for membrane distillation (MD). Notice that not all PVDF blends can enhance the thermal resistance. For example, the degradation temperature of both pristine PVDF and the zirconia titanate/PVDF film were 420 °C without any changes [25]. Santos et al [26]. designed a series of PVDF blends by incorporating TiO₂, Al₂O₃, Fe₃O₄ and SiO₂. The degradation temperatures of pure PVDF, PVDF/SiO₂, PVDF/Fe₃O₄, PVDF/TiO₂ and PVDF/Al₂O₃ were 439, 449, 409, 348, and 367 °C, respectively. Therefore, only PVDF/SiO₂ blend had improved thermal stability due to the interactions between SiO₂ and PVDF chains.

3. Fabrication of PVDF membranes

3.1. Membrane fabrication and characterization techniques

PVDF membranes can be fabricated in several ways such as phase inversion, melt extrusion, controlled stretching and tracking etching [27]. According to the literature, phase inversions are the most widely used methods [28,29]. There are three main phase inversion processes for the fabrication of PVDF membranes, including non-solvent-induced phase separation (NIPS), thermally induced phase separation (TIPS), vapor-induced phase separation (VIPS) and combinations of these such as N-TIPS, V-NIPS, and V-TIPS. Four steps were involved in the phase inversion process [30]. (1) A homogenous polymer solution was formed by mixing polymers and solvents at room temperatures or elevated temperatures. (2) The homogenous solution was then prepared into a desired shape, such as a flat sheet or hollow fiber. (3) These nascent membranes were immersed in a non-solvent coagulation bath (such as air, water, or other non-solvents) to induce phase separation that formed solid PVDF membranes. (4) Solvents and additives in the PVDF matrix were removed by extraction to form a porous structure.



Fig. 2. Scheme of important phase inversion processes. (a) NIPS, (b) TIPS, (c) VIPS, and (d) combination of NIPS and TIPS (N-TIPS).

The schematic of NIPS, TIPS, VIPS and N-TIPS (as a presentative of combination) is shown in Fig. 2. Accordingly, the structures and properties of three most used phase inversions and important parameters are listed and compared in **Table 1**. In general, the NIPS method usually provides an asymmetric PVDF membrane with a skin layer of smaller pore size, as is often used for PVDF UF or NF membranes. TIPS-prepared PVDF membranes obtain a larger pore size and are employed for MF membranes in membrane distillation applications. Compared with NIPS and TIPS methods [31], VIPS-prepared membranes can be applied in MF, UF and MD processes after finely tuning the parameters in Table 1.

Recently, the combinations of NIPS, TIPS and VIPS are becoming important methods to finely tune the membrane microstructure for desirable separation performance. For example, Jung et al [32]. used PolarClean, a water-soluble solvent, to fabricate PVDF membranes. PVDF powders were first dissolved in PolarClean at 140 °C to form a homogenous solution, and the cast nascent membranes were immersed in cold water to induce phase separation. Note that PolarClean exchanged with water so that the TIPS and NIPS effect existed simultaneously to tailor the microstructure of PVDF membranes.

A novel phase inversion process by combining VIPS and TIPS (V-TIPS) [33] was proposed for PVDF membranes. It was demonstrated that the pore structure and permeance could be finely regulated by controlling the vapor exposure temperature and exposure time. The resulting membranes exhibited an ultrahigh water

Table 1

Structure and properties of P	/DF membranes using	different phase inversion	methods.

Fabrication method	NIPS	TIPS	VIPS
Main influencing parameters	 Evaporation time prior to immersion Polymer concentration Non-solvent type Additives Temperature 	 Solvent type Polymer concentration Additives Cooling rate 	 Solvent and additives Exposure time Relative humidity Dissolution temperature Vapor temperature
Typical membrane structure	• $$ Finger-like structure $$ Sponge-like structure	\checkmark Cellular structure \checkmark Spherulitic structure	 ✓ Cellular structure ✓ Nodular structure ✓ Bi-continuous structure
Properties	 Smaller pore size Scalable and convenient 	 Process simplicity High reproducibility Low tendency to form defects High porosity Narrower pore size distribution 	• Better controlling the desired membrane morphologies compared with TIPS and NIPS

permeance of 3028 $Lm^{-2}h^{-1}bar^{-1}$ in the separation process of oil-in-water (O/W) emulsions at an ultralow trans-membrane pressure of 20 kPa.

Currently, PVDF membranes prepared from NIPS and TIPS have been commercialized by many industrial manufacturers [9,34], such as Asahi Kasei Group (Japan), Memstar (Singapore) and Toray Membrane (Japan), Beijing Scinor Membrane Technology Co. Ltd. (China), Nanjing Jiuying Membrane Technology Co. Ltd. (China), and Pure Envitech (Korea). It is expected that the PVDF membrane by the combinations of inversion processes can be industrialized in the future as the pore structures and other performance can easily be regulated compared with single phase inversion process.

In addition to the phase inversion methods, electrospinning is another important method to fabricate polymer membranes with high porosity, pore interconnectivity and surface area [35,36]. A typical electrospinning apparatus is usually composed of a polymer solution feed system, a high voltage supplier, and several collectors. When the electric potential is higher than the surface tension of the polymer solution, the solution can be ejected from the nozzle to the collector. During the flight from the nozzle to the collector, solvents will evaporate, making the nanofibers stack together to form electrospun membranes [27]. A one-step electrospinning strategy was developed [37] to fabricate PVDF/graphene membranes with a superoleophilic and under oil superhydrophobic surface, avoiding multistep-reactions and pre-treatments.

In addition to the fabrication techniques, characterization of some basic parameters, such as water permeance and pore size of the PVDF membranes are briefly introduced here.

First, the pore size and its distribution are responsible for the separation accuracy of PVDF membranes. Currently, the PVDF and its blend membranes are mainly composed of microfiltration (MF) (pore size > 50 nm), ultrafiltration (UF) (2–50 nm) and nanofiltration (NF) (1-2 nm) based on the pore size classification. For the MF and UF membranes with large pore size (usually ranging from 10 to 50 nm), a conventional bubble point method that employs the displacement of air with an original liquid available in the membranes is used to determine its pore size and pore size distribution. However, this method is not applicable for the membranes with reduced pore sizes, such as the pore size of 2-10 nm in UF membrane or NF membranes. In these cases, a molecular weight cut-off (MWCO) method is often used to characterize their pore size. Dextran and polyethylene glycol (PEG) solutions are widely employed to determine MWCO, where the former is used for UF membrane and the latter is beneficial for NF membranes.

Second, a crossflow or dead-end filtration device is often used to measure the water permeance under a certain trans-membrane pressure. Notice that the unit of water flux is $Lm^{-2}h^{-1}$ and that of water permeance is $Lm^{-2}h^{-1}bar^{-1}$.

3.2. Fabrication of green PVDF membranes

Green PVDF membranes are the membranes that use no toxic solvents in the whole PVDF membrane fabrication process. In this review, the PVDF membrane by using non-toxic solvents or without using any solvents in the membrane fabrication are reviewed.

3.2.1. Non-toxic solvents for PVDF membranes

As mentioned in Section 2.1, it is important to explore nontoxic solvents to replace conventional toxic solvents for PVDF polymers. Up to now, many non-toxic solvents have emerged, such as PolarClean, ionic liquids, organic carbonates, Cyrene, triethyl phosphate, acetyl tributyl citrate, and tributyl citrate. However, the solubility of PVDFs in non-toxic solvents is the main obstacle to widening their application. The detailed Hansen solubility parameters (HSPs) of non-toxic solvents to dissolve PVDF are provided in Table 2. In our previous work [38], PolarClean was proposed as a non-toxic solvent to fabricate PVDF membranes for the first time. Although PVDF could not be dissolved in PolarClean at room temperature, it was fully dissolved above 140 °C and formed a homogenous PolarClean/PVDF solution. Therefore, increasing the solvent temperature enabled the fabrication of PolarClean/PVDF membranes. Russo et al [39]. employed dimethyl isosorbide (DMI) as a non-toxic solvent to fabricate PVDF membranes. They also found a similar phenomenon that the PVDF was not dissolved in DMI at room temperature but formed a homogenous solution with DMI at 120 °C (See Fig. 3a). The final membranes were fabricated by a combination of NIPS and TIPS methods Figs. 3b-3c. represent HSPs of PVDF materials with the most commonly used non-toxic solvents and conventional solvents. HSPs strongly suggested that PVDF often showed poor solubility in non-toxic solvents compared with traditional solvents Table 3. lists recent advances in nontoxic solvents for the fabrication of PVDF membranes from 2017 to 2020. The structures of these non-toxic solvents are provided in Table 4.

Overall, the usage of non-toxic solvents is a key to promote the sustainable development of PVDF-based polymer membranes [40]. The poor solubility of PVDF in some non-toxic solvents can be addressed by considering the elevated temperature and the combinations of diverse phase inversion methods. Developing greener PVDF membranes has been an important worldwide issue.

3.2.2. Solvent-free processes

In contrast to non-toxic solvent/PVDF membrane systems, the solvent-free method involves no solvents in the whole membrane preparation process. Currently, the melt-spinning method is considered as a typical solvent-free method for polymer membranes that first melt polymers and then solidify to a desired shape. In a typical melt-spinning process, a melt polymer is spun, and the membrane pores are formed based on the stretching force acting on microcrystalline lamellae membrane. Since there are no solvents employed in this work, limited processing parameters need to be controlled, and the process is relatively simpler than PVDF/solvent systems [67]. However, this method is usually considered for polymers with high crystallinity, i.e., polypropylene (PP) and polyethylene (PE) membranes [68]. The crystallinity of the membranes depends on the melt-draw ratio and annealing temperatures. Since PVDF is a semi-crystalline material, it is difficult to use the melt-spinning method for PVDF membranes because of the low porosity and water permeance.

To overcome this problem, Ji et al [69-71]. fabricated a series of PVDF hollow fiber membranes by melt-spinning. These were composed of PVDF. PTFE and polv(ethylene oxide) (PEO) as the matrix phase, dispersed phase, and pore inducing agent, respectively (Fig. 3d). Air was used to solidify the nascent membranes. There was a considerable temperature gradient on the inner and outer surface, and thus PEO could not be distributed very well. When the nascent membranes were immersed in water, the PEO was exchanged with water to induce the pores on the membrane surface. Differential scanning calorimeter (DSC) curves of the PVDF, PTFE and PEO indicated that such a system had a poor compatibility but was beneficial for pore formation. However, the water permeance of PVDF membranes using PTFE as a dispersant phase was relatively lower. This was because the final water permeance was related to the surface pore size and porosity. The dispersant phase influenced the surface pores, so the dispersant materials should be further optimized. Based on this analysis, PSF was used as a dispersant agent, and PVDF and PEO as the matrix and pore inducer, respectively. They found that the shape of the PSF seemed unchangeable during the stretching process due to the higher glass transition temperature, which was beneficial for increasing the membrane pore size. The pore structure could be finely tuned by changing the stretching ratios.

Table 2

Hansen solubility parameters (MPa ^{1/2}) and polymer-solvent dista	nce between	PVDF ar	nd solvents	(NMP,	DMF	and D	MA .	are	considered	as
conventional solvents, and the others are considered as non-toxic) ¹ .									

	$\delta_{\rm h}~({\rm MPa})^{1/2}$	$\delta_{\rm d}~({\rm MPa})^{1/2}$	$\delta_{\rm p}~({\rm MPa})^{1/2}$	$\delta_{(\text{solvent-PVDF})} \text{ (MPa)}^{1/2}$
NMP	7.2	18.4	12.3	2.2
DMF	11.3	17.4	13.7	2.43
DMA	11.8	17.8	14.1	1.47
PolarClean	15.8	10.7	9.2	3.3
TEP	9.2	16.8	11.5	1.08
ATBC	6.2	15.4	4.1	9.1
DMI	17.6	7.1	7.5	5.7
DBM	16.5	6.1	7.2	6.8
GBL	7.4	19.0	16.6	4.8
Cyrene	18.8	10.6	6.9	4.3
PVDF	9.2	17.2	12.5	-

¹ Tributyl O-acetyl citrate: ATBC; Triethyl phosphate: TEP; γ-Butyrolactone: GBL; Dibutyl maleate: DBM; Dimethyl isosorbide: DMI.



Fig. 3. (a) A typical case to use non-toxic solvents for membrane formation [39], Copyright 2019. Reproduced with permission from American Chemical Society. (b) The three-dimensional Hansen solubility parameter to distinguish a bad solvent and good solvent. (c) Solubility property of non-toxic solvents and conventional solvents towards PVDF [72], Copyright 2019. Reproduced with permission from American Chemical Society. (d) Solvent-free method for the fabrication of PVDF membranes [69], Copyright 2020. Reproduced with permission from Elsevier Science Ltd.

3.3. Common design strategies for the fabrication of PVDF membranes

Microstructure and properties are important in constructing high-performance PVDF membranes for target separation systems. Hydrophobic-hydrophilic performance, surface charge, roughness, and pore size distribution have been considered as important variables affecting the membrane fouling behavior [73,74]. Basically, a smooth membrane surface can effectively prevent the deposition of contaminants on the membrane surface. A narrow pore size distribution can prevent pollutants from blocking the pores to enhance the anti-fouling performance of the membrane. A charged surface provides electrostatic repulsion to the pollutants bearing the same charge. A hydrophilic surface can form a hydration layer that alleviates the membrane fouling [75]. To construct high-performance PVDF membranes for potential water treatment, the following aspects need to be considered to regulate the properties of the polymers.

3.3.1. Blending and copolymerization

Blending PVDF with other polymers can effectively tailor the hydrophilic-hydrophobic properties (depending on the intrinsic properties of additional polymers), surface charges and mechanical strength. PVDF can also be copolymerized with other poly-

Table 3

Recent	advances of	f non-toxic so	lvents for the	fabrication	of PVDF-	based polym	er membranes	(from 2017	to 2020).	•
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Solvent	Materials	Fabrication method	Shape ¹	Potential application	Year	Ref.
Organic carbonate	PVDF	NIPS	FS	MF	2021	Ismail et al [27].
ILs ⁷	PVDF	TIPS	FS	MF	2020	Wang et al [41].,
PolarClean	PVDF/PSF	N-TIPS	FS	MF	2021	Jung et al [42].
TEP	PVDF	NIPS	FS	MF	2019	Nasrul et al [43].
TEP	PVDF	Others	FS	UF	2019	Maryam et al [44].
TEP	PVDF	N-TIPS	HF	MF	2019	Zhao et al [45, 46].
TEP	PVDF	N-TIPS	HF	MD	2019	Li et al [47].
TEP	PVDF-GO ²	V-NIPS	FS	Others	2020	Sabri et al [48].
TEP	PVDF-co-CTFE ³	NIPS	HF	N/A	2018	Hamed et al [49].
TEP	PVDF	NIPS	FS	MF	2017	Marino et al [50].
TEP	PVDF/Carbon nanotube	NIPS	FS	N/A	2017	Edgar et al [51].
TEP	PVDF	Others	HF	UF	2017	Chen et al [52].
TEP	PVDF	Others	HF	MD	2017	Chang et al [53].
TEP	PVDF	NIPS	FS	MD	2017	Chang et al [54].
TEP	PVDF	V-NIPS	FS	MF	2018	Tiziana et al [55].
TEP	PVDF	NIPS	HF	MD	2019	Yao et al [56].
GBL	PVDF	TIPS	HF	MD	2018	Wang et al [57].
ATBC	PVDF	TIPS	FS	MF	2020	Fan et al [58].
ATBC	PVDF	TIPS	HF	MF	2018	Fang et al [59].
ATBC	PVDF	TIPS	FS	MF	2019	Zhang et al [60].
Cyrene	PES/PVP ⁴	NIPS	FS	MF	2019	Roxana et al [61].
Cyrene	PVC ⁵ /PVDF	Others	FS	UF	2020	Clayton et al [62].
Cyrene	PVDF	TIPS	FS	MF	2019	Marino et al [63].
DMI	PVDF/PES	NIPS/N-VIPS	FS	MF/UF	2020	Russo et al [39].
DBM	PVDF	TIPS	FS	MF	2018	Cui et al [64].
TamiSolve®	P(VDF-	NIPS	FS	MD	2017	Marino et al [65].
NxG	HFP) ⁶		FS	MD	2021	Safa et al [66].

¹ Flat sheet: FS; Hollow fiber: HF.

² Graphene oxide: GO.

³ Poly(vinylidene fluoride-co-chlorotrifluoroethylene): PVDF-co-CTFE.

⁴ Polyvinylpyrrolidone: PVP.

⁵ Polyvinyl chloride: PVC.

⁶ PVDF-HFP. ILs: Ionic liquids.

Table 4

Structures of non-toxic solvents employed to dissolve PVDF polymers.



mers to obtain more hydrophobic copolymers, such as P(VDF-co-HFP) [76,77], P(VDF-co-CTFE) [78], P(VDF-co-TrFE), and P(VDF-co-TFE) [27]. Detailed molecular structures of these copolymers and full names are summarized in Fig. 4. These copolymers enhanced the hydrophobic nature of the PVDF. In contrast to the addition of hydrophobic polymers, the introduction of hydrophilic polymers, such as PVP or PEG and its derivatives suffered from poor affinity with a hydrophobic PVDF matrix, leading to a non-uniform pore structure [9,79]. Therefore, amphiphilic copolymers have been widely employed to improve the affinity between the PVDF matrix and hydrophilic polymers, such as PVDF-g-POEM, PVDFg-PMABS, PVDF-g-PEG, PVDF-g-PEGMA, PVDF-g-PACMO, PVDF-g-(PACMO-PAA), PVDF-g-PAA, and PVDF-g-NMA [80,81]. Molecular structures and full names of these copolymers can be found in Fig. 4. The amphiphilic copolymers contain both hydrophobic chains and hydrophilic chains. The hydrophobic chains of the



Fig. 4. Chemical structures of hydrophobic PVDF copolymers, hydrophilic PVDF copolymers and important hydrophobic polymers for coatings on PVDF membrane surface. Poly(vinylidene fluoride-co-hexafluoropropene): PVDF-co-HFP; Poly(vinylidene fluoride-co-tetrafluoroethylene): PVDF-co-TFE; Poly(vinylidene fluoride-co-trifluoroethylene): PVDF-co-TFE Poly(vinylidene fluoride-co-chlorotrifluoroethylene): PVDF-co-TFE. PVDF-g-N-methylolacrylamide: PVDF-co-NMA; PVDF-g-(poly(acrylic acid): PVDF-g-PAA; PVDF-g-poly(oxyethylene methacrylate): PVDF-g-POEM; PVDF-g-4-methacrylamidobenzenesulfonic acid: PVDF-g-PMABS; PVDF-g-(polyacryloylmorpholine-(polyacrylic acid)g-argatroban): PVDF-g-(PACMO-PAA-g-AG); PVDF-g-polyacryloylmorpholine: PVDF-g-PAMCO; PVDF-graft-poly(ethylene glycol) methyl ether methacrylate: PVDF-g-PEGMA; Poly(dimethyl siloxane): PDMS.

copolymer have Van der Waals interactions with the PVDF matrix, while hydrophilic chains can decorate the membrane pores and thus enhance the water transport.

Usually, PVDF or other PVDF copolymers should form a homogenous and compatible solution before membrane preparation. What will happen if other polymers are not compatible with a PVDF solution in solvents? Our previous work [42] showed that PolarClean dissolved PVDF and polysulfone (PSF) at 140 °C. Note that these polymers were not dissolved in PolarClean at room temperature. Also, PSF and PVDF were immiscible in PolarClean. The PVDF/PSF/PolarClean solution was spun into hollow fiber membranes that exhibited unexpected PSF fibers aligned in PVDF spherulitic structures by controlling the shear rate and reducing the capillary number. The mechanical strength of the resulting membrane increased and surpassed that of pure PVDF membrane. This work suggested a strategy to construct new PVDF-based membranes using immiscible polymers in non-toxic solvents.

3.3.2. Blending with inorganic nanoparticles

Inorganic nanomaterials with different dimensional properties can be incorporated to form PVDF blends. 0D materials include TiO₂, Al₂O₃, Fe₃O₄, ZnO, AgNPs, SnO₂, BiOCl, and SiO₂. 1D materials can be carbon nanotubes, ZnO nanotubes, and TiO₂ nanotubes. 2D materials employed include graphene oxide (GO) nanosheets, metal organic framework (MOF), zeolitic imidazolate framework (ZIF), Ti₃C₂T_x (MXene), Fe₃O₄ nanosheets, and WS₂ nanosheets. Blending these materials can tune the surface hydrophilic properties and mechanical strengths of the blends [82].

The formation of a stable interface between the inorganic nanoparticles (NPs) and PVDF is a main issue in the application process. To analyze the stability of the interface, X-ray photoelectron spectroscopy (XPS) is commonly used to characterize the surface components, and these are compared with the actual membrane performance of the blends and pure PVDF membranes. Take PVDF/TiO₂ blends for example, the bonding strength between the TiO₂ nanofibers and PVDF matrix was analyzed using XPS. The chemical binding energy of fluorine (F) in PVDF/TiO₂ membranes showed an increase compared with that in pure PVDF [83]. The shift was mainly caused by the changes in the chemical environment of F and Ti, indicative of the coordination bond between Ti and F. Similar results were also reported in the photocatalysts [84]. The C-F bonds were relatively stable in PVDF, and interactions between F and Ti should be coordination bonds like C-F-Ti. H-bonding was another mechanism to improve the stability between the inorganic particles and polymer matrix [85].

3.3.3. Surface modification

Surface modification of PVDF involves physical and chemical methods. Physical modification is often conducted by coating chemically active monomers or polymer solutions on the PVDF surface followed by crosslinking or anchoring treatments for solidification [86,87]. In this case, PVDFs always need to be pretreated by chemical reactions (such as alkaline solution) or with high-energy radiation, and then grafted with hydrophobic or hydrophilic modifiers to tailor the PVDF surface properties. Compared with physical modification, the chemical modification can provide stable performance for a long time due to the covalent bonding between the PVDF surface and modifiers.

For pressure-driven membrane processes (which will be discussed in Section 4), the PVDF always needs to be modified to obtain enhanced hydrophilic properties to decrease the water transport resistance. The surface coating or deposition of a hydrophilic layer is a facile and important method. Commercial polymers, like poly(vinyl alcohol) (PVA), PEG, and chitosan can be selected for this purpose. Furthermore, functional artificial modifiers can also be synthesized to modify the PVDF surface, like sulfonated N, N-diethylethylenediamine (DEDAPS) [88], and zwitterionization of poly(styrene-r-4-vinylpyridine) (zP(S-r-4VP)) [89]. For example,

Tang et al [89]. synthesized a copolymer with zwitterionization of P(S-r-4VP) as confirmed by ¹H NMR analysis. After immersing PVDF membranes in this copolymer solution, the hydrophobic interactions anchored the copolymer on the PVDF surface, and the hydrophilic segments modified the surface properties, showing a potential towards bovine serum albumin (BSA) systems. The resultant membranes were also immersed in 1 M NaOH and HCl solution for one week each, and copolymer remained on the PVDF surface, indicating strong chemical interactions between copolymer and PVDF in harsh base/acid environments. In addition, the surface treatments activated by alkaline solutions, plasma treatment, defluorination-sulfonation and others were also used as chemically hydrophilic modification methods for PVDF membranes [17,90].

For hydrophobic modification of PVDF, the mechanism is similar to a hydrophilic modification method. Other hydrophobic polymers, such as, poly(dimethyl siloxane) (PDMS) [91], Teflon [92], Hyflon [93], and perfluoropolyether (PFPE) [94] can be used where the their structures are shown in Fig. 4. In addition, fluorinated modifiers can be used to lower the surface energy of the membrane. They were often dissolved in suitable solvents to form homogenous dope solutions and to be coated on the PVDF surface followed by suitable thermal treatment The application of PVDF hydrophobic modifications will be discussed in Section 5 for membrane distillation.

Although various modifications have been reported to enhance the properties of PVDF membranes, the stability of the modified membrane needs to be emphasized when considering practical relevance. For example, is the membrane modified with water-soluble additives stably operating during water treatment? In addition, fluorinated modifiers are often employed to enhance the hydrophobic properties of PVDF membranes for MD. The stability of hydrophobic membrane properties is an important indicator to evaluate the stability of the modified membrane. Therefore, it is recommended that researchers simultaneously focus on enhancing membrane performance and stability in future work.

3.4. Novel design strategies of PVDF membranes

3.4.1. Patterned membrane surfaces

Surface porosity and regularity in the membrane determine the separation capability of a membrane. The patterning strategy has been employed to prepare the membranes with regular surface pores. Until now, there are two patterning strategies to construct desired membrane surface microstructures. (1) The nanoimprinting lithography (NL) method is used to imprint the sub-micron morphologies into commercial membranes through porosity-enhanced plastic deformation [95]. (2) The phase inversion micromolding (PIM) method is used to pattern the membrane surface using a phase inversion approach (mainly including NIPS and VIPS process) on a patterned template [96]. PIM technology is widely used to pattern PVDF membrane surfaces with features of high pattern fidelity, easily demolding, and high separation performance. However, a phase inversion process in a liquid coagulation bath can easily result in a dense membrane layer with closed pore structures. To solve this problem, Ilyas et al [97,98]. developed a spray-modified non-solvent induced phase separation method to fabricate a patterned PVDF membrane surface without decreasing the pore size. The pure water permeance of the patterned membrane increased about 40% compared with non-patterned membranes. Furthermore, patterned membranes also showed lower bovine serum albumin (BSA) adsorption performance in the filtration process. Kharraz and An [19] designed two-layer patterned superhydrophobic PVDF membranes by a combination of NIPS and VIPS, followed by a surface modification process to lower the surface energy (see Fig. 5a). In this process, a facile imprinting approach was employed to induce a uniform patterned surface, increasing 18% water permeance compared with non-patterned PVDF membranes.

Recently, a combination of NL and PIM was also developed for patterning PVDF membrane surfaces [58]. The results showed that a lower polymer concentration (\sim 20 wt%) and coagulation temperature of 25 °C resulted in a high-fidelity pattern replication. The effect of polymer concentration on the membrane surface was displayed in Fig. 5b. Compared with a non-patterned surface, mechanical characteristics and crystallinity were similar, but the patterned membrane showed a higher active surface area and water permeance.

3.4.2. 3D printing technology

3D printing is a kind of additive manufacturing (AM) technique that promotes the developments of advanced materials and systems for diverse applications of membranes from academia to industry [99]. PDMS was the first 3D printed membrane that emerged in 2015 [100]. Among the recent developments of AM techniques, an extrusion-based process was the most versatile because of the low-cost fabrication technique and simple printing mechanism, where materials for this technology included a wide selection from polymers, ceramics, and metal alloys. 3D printing of polymer membranes has been widely studied due to the easy fabrication and desired membrane morphologies with enhanced water permeance and precise separation performance [101].

There have been advances in PVDF membranes using a 3D printing method. For example, Liang et al [102]. fabricated a PVDF membrane with an ordered geometric pore structure based on 3D printing technology (Fig. 5c). The PVDF solution was first prepared and then electrospun into a series of membranes with diverse geometric pore structures, such as rectangle, hexagon, triangle, and cylindrical pores. The resulting membranes showed an improved water permeance of 1020.7 Lm⁻²h⁻¹bar⁻¹ and simultaneously showed great potential to separate solid-liquid systems. In addition, a PVDF layer coupled with 3D printing technology can also enhance the MD performance. Polyamide (PA) membranes were 3D printed with a larger pore size. Then, a PVDF layer was prepared on a PA membrane using phase inversion to decrease the pore size. A 3D-printed PVDF/PA membrane obtained a higher contact angle of 130° than pristine PVDF membranes (70°) fabricated by a single phase inversion process [103].

In general, the patterning or 3D printing methods provide desired membrane surface structures that further enhances the separation performance in water treatment, such as high water permeance and anti-fouling performance. In the future, it is expected that 3D printed PVDF membranes with controlled pore size and shape can further be designed to separate chemical products with super-high separation efficiency.

4. Pressure-driven membranes

As mentioned above, pressure-driven membranes usually need satisfactory hydrophilic properties that promote the water transport from a feed solution to the permeation side under a transmembrane pressure as a driving force. PVDF membranes are mainly divided into MF, UF and NF membranes according to the mean pore size. Furthermore, the research focus of pressure-driven PVDF membranes is concentrated on the optimization of water permeance, selectivity, anti-fouling performance, mechanical strength, pore size distribution and fabrication cost.

It is important to mention that PVDF membranes are advantageous over other polymer membranes in pressure-driven processes. PVDF is considered as a pure polymer because of their low level of extractable that makes it become suitable candidates in many pressure-driven separation systems, such as biochemical and



Fig. 5. (a) Diamond spacer used to imprint a pattern on the membrane surface [19]., Copyright 2020. Reproduced with permission from Elsevier Science Ltd. (b) PVDF contents on the patterned PVDF membrane microstructures [58], Copyright 2020. Reproduced with permission from John Wiley & Sons Inc. (c) 3D printing technology for different membrane structures [102]., Copyright 2021. Reproduced with permission from Elsevier Science Ltd.

bio-separation areas [8]. In addition, PVDF shows excellent thermodynamic compatibility with other polymers over a wide range of blend compositions between them, which can effectively tune the pore size, hydrophilicity and water permeance of PVDF membrane towards diverse separation systems. The following section discusses the state-of-the-art advances to design high-performance PVDF-based membranes for pressure-driven membrane processes based on the overall design strategies proposed in Section 3. The recent progress of PVDF membranes employed for pressure-driven membrane process is listed in Table 5.

4.1. Microfiltration membranes

PVDF MF membranes with pore sizes ranging from 50 nm to 10 μ m are often used for separating emulsion and solid-liquid systems. The common strategies to fabricate PVDF membranes involve the following two aspects. (1) Optimization of membrane processing parameters and fabrication methods. Note that phase inversion methods and electrospinning methods are widely used for [104–106]. (2) Construction of hydrophilic PVDF membranes focusing on the blending inorganic particles, hydrophilic polymers, and hydrophilic surface modification is a widely used way to improve the water permeance and anti-fouling performance.

Solid-liquid suspensions and emulsions are often used to characterize the separation performance of PVDF MF membranes, such as oil-in-water (O/W), water-in-oil (W/O) systems, and polystyrene systems. Pure PVDF membranes suffer from the fouling phenomenon as the oil droplets (or particles) are easily deposited on the membrane surface, resulting in pore blockage. Constructing a hydrophilic PVDF membrane surface is helpful to alleviate membrane fouling. As the hydration layer on the PVDF membrane surface was formed, it provided repulsion to contaminants such as oils droplets or solid particles in the wastewater, greatly enhancing the water permeance and flux recovery ratio (FRR) of the membrane. For example, Xu et al [107], grafted a hyperbranched phenolamine resin block polyether demulsifier on a styrene-co-maleic anhydride blended PVDF membrane surface. The contact angle of the resulting PVDF membrane surface was 0° (a super hydrophilic membrane surface) which was suitable for all kinds of emulsions, such as dichloroethane-in-water, kerosene-in-water, toluenein-water, and petroleum ether-in-water emulsions (Fig. 6a). Li et al [108]. designed a novel way for the treatment of solid-liquid systems by electrospinning PVA blended PVDF polymer membranes with superhigh water permeance $(40,000 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1})$ and a very low irreversible fouling ratio (below 5.9%) (Fig. 6b). This was because nanofiber membranes derived from PVDF and PVA with the ridge-and-valley structures enhanced the hydrophilic and wettability performance.

PVDF-based MF membranes are also becoming popular in biomass separation, but suffer from "biofouling" when employed in living systems because of the strong non-specific adsorption of microorganisms. This biofouling phenomenon, on one hand, could directly block the membrane pores and decrease water permeance. On the other hand, these living microorganisms could convert soluble nutrients into insoluble ones, leading to fouling. Therefore, the construction of anti-biofouling PVDF-based MF membranes has received much attention. The main strategies on migrating biofouling are to incorporate biocidal agents on the PVDF membrane surface, such as Cu and Ag, that can kill the bacteria and inhibit their growth. Zheng et al [109]. designed bi-layer Cu-MOF coated PVDF membranes. The results displayed that the Cu-MOF layer enhanced the hydrophilicity and anti-bacterial efficiency. Furthermore, Cu-MOF materials sustainably released Cu^{2+} to suppress E. coli for one week. These features were in favor of enhanced anti-

Table 5

Some progresses of PVDF membranes for pressure-driven membranes.

	Pure water	Application		Flux recovery	Contact	
Compositions of PVDF solution	$(Lm^{-2}h^{-1}bar^{-1})$	system	Rejection (%)	(%)	angle (°)	Year/Ref.
PVDF-g-PGAL ¹ : 9 wt%	N/A	MF	Oil: 97.39	94.59	50.92	2021, [130]
DMF:91 wt% PVDF: 20 wt%	3420	MF	O/W: 100	N/A	N/A	2021, [131]
PC:72 wt%						
PVP: 8 wt% PVP: 3 wt%	1527.78	MF	0/W: 91.3	N/A	95	2021. [132]
PVDF: 15 wt%	1021110		0,			2021, [102]
LiCl: 0.1 wt%						
MWCNT ² : 0.01 wt\%	2137	MF	BSA: 98	92.7	N/A	2020, [133]
PVDF: 16 wt%					,	
PVP: 0.03 wt%						
GO: 0.5 wt%	800	MF	N/A	74	N/A	2018, [134]
CNC ³ : 1.4 wt%						
PVDF: 12.1 wt% PVP: 2 wt%						
DMF ⁴ : 84 wt%						
Fe_3O_4 @TiO ₂ : 0.5 wt%	1752	MF	TOC ⁸ : 67.17	91.1	10	2020, [135]
PVDF-g-PEGMA: 3.5 Wt% PVDF: 18 wt%						
DMF: 78 wt%						
PTFE: 1 wt%	869	MF	N/A	N/A	76	2021, [136]
PVDF: 30 wt%						
DMP: 63 wt%						
CNT ⁵ : 0.02 wt%	N/A	MF	Methylene blue: 60	N/A	95	2018, [137]
PVDF: 8 wt%						
NMP: 89.98 wt%	10		DGA 01	27/4	70.0	
Fe ₃ O ₄ : 2.8 wt% PVDF: 14 wt%	48	UF	BSA: 91	N/A	/8.8	2018, [138]
DMF: 83.2 wt%						
GO: 0.2 wt%	253	UF	Naphthol blue	90.9	83	2021, [139]
NMP: 78 wt%			DIACK. 90			
PVP: 6.7 wt%	65	UF	BSA: 70	N/A	N/A	2020, [97]
PVDF: 20 wt%						
PVDF-g-PEGMA: 15 wt%	928.62	UF	Sodium alginate:	80	71.6	2020, [140]
DMAc: 85 wt%	1069	UE	82.9	70.9	4.4	2019 [141]
PVDF-g-PEGMA: 15 Wt% PVDF: 9 wt%	1068	UF	IN/A	70.8	44	2018, [141]
DMF: 76 wt%						
PE-b-PEG ⁷ : 30 wt%	420	UF	N/A	86.4	102.26	2021, [142]
DMAc: 55 wt%						
CA ⁶ : 7.41 wt%	1600	UF	γ -globulin: 89	N/A	56	2018, [143]
PVDF: 7.41 wt% Octane: 25.93 wt%						
DMF: 59.26						
MWCNT: 0.1 wt%	2.5	NF	BSA: 99	N/A	85.2	2014, [144]
PEG: 3 wt%						
DMAc:76.9 wt%						
PVDF: 20 wt%	2.961	NF	Methylene blue:	N/A	65.5	2019, [145]
DMAc: 79 wt%			52.61			
Clinoptilolite: 2.5 wt%	7	NF	Dye: 98.5	96	63.7	2020, [146]
PVDF: 18 wt% DMAc: 79.5 wt%						
SnO ₂ : 1 wt%	251	NF	Heavy metals:	N/A	69.4	2020, [147]
PVDF: 12 wt%			64~94			
PEG: 1.5 wt%						

Table 5 (continued)



Fig. 6. Strategies to design PVDF MF membranes for different applications. (a) O/W emulsion separation system [107]., Copyright 2020. Reproduced with permission from Elsevier Science Ltd. (b) Solid-liquid separation system [108]., Copyright 2019. Reproduced with permission from John Wiley & Sons Inc. (c) Biomass separation system [109], Copyright 2021. Reproduced with permission from Elsevier Science Ltd.

biofouling performance in the treatment of bio-mass separation (Fig. 6c). Ionic liquids (ILs) were also considered as an effective additive to improve the anti-fouling performance of PVDF. They finely tuned the surface hydrophilicity and charge of a PVDF membrane that lowered the adhesion capability of bacteria and inhibited their growth, acting as a sustainable agent in the PVDF matrix [110].

4.2. Ultrafiltration membranes

PVDF UF membranes with pore sizes ranging from 2 to 50 nm can separate and purify BSA solutions, humic acid (HA) solutions, dye wastewater, natural organic materials, and others [80,111]. The strategies to construct PVDF-based UF membranes include 1) phase inversion methods or a coating method that deposits another layer on the PVDF substrate (mostly MF membranes) and 2) modification of the PVDF membrane surface to obtain the desired pore structures for enhanced UF separation performance [112–115].

PVDF blending with functional NPs or polymers are most widely used for PVDF UF membranes due to the facile and effective decoration of pore structures and intrinsic properties. Tong et al [80]. synthesized PVDF-g-N-methylolacrylamide (NMA) copolymer and then fabricated PVDF-g-NMA membranes via NIPS. The water permeance and BSA rejection performance of the resulting membranes were 272 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ and 88.5%, respectively. Liu et al [111]. first synthesized perfluorosulfonic acid-g-graphene oxide (PFSA-g-GO). Such blends could be dispersed in PVDF/DMAc solution and then fabricated into PVDF/PFSA-g-GO UF membranes via NIPS (Fig. 7a). The pore size, hydrophilicity, and membrane roughness could be varied by the PFSA-g-GO content.

Surface modification by depositing a continuous layer or by depositing non-continuous particles on the PVDF membrane can also regulate the pore structure and surface properties [116]. Regarding the selection of PVDF substrate for UF membranes, PVDF hollow fiber membranes with high mechanical strength and porosity were a good choice as membrane substrates. MOF nanoparticles could be prepared into a homogenous coating solution and then be coated on PVDF MF hollow fiber membranes [117]. The resulting PVDF-based UF membranes had satisfactory rejection performance for BSA molecules (98.1%) and Cr (VI) ions (95.6%). Sakarkar et al [118]. prepared a polymer solution with the addition of TiO₂



Fig. 7. Strategies to construct PVDF UF membranes. (a) Inorganic particle blended PVDF for UF membranes via phase inversion method [111], Copyright 2020. Reproduced with permission from Elsevier Science Ltd. (b) Direct coating method using a continuous separation layer [118], Copyright 2020. Reproduced with permission from Elsevier Science Ltd. (c) Modification of pore structure by anchoring non-continuous NPs [119], Copyright 2020. Reproduced with permission from Elsevier Science Ltd. (e) Novel magnetic field assisted method [121], Copyright 2020. Reproduced with permission from Elsevier Science Ltd.

and PVA, and then coated it on PVDF MF membranes (Fig. 7b). Notice that a continuous layer was formed on the PVDF membrane surface, and the resulting membranes were used in UF systems that effectively rejected the dyes. Non-continuous particle deposition on the PVDF surface was also effectively to tailor the pore sizes of PVDF membranes. For example, β -FeOOH particles were employed to deposit on the PVDF membranes [119]. It was demonstrated that these NPs could decorate MF to UF pore sizes and improve hydrophilic surface properties (Fig. 7c).

Some unique approaches had also been developed for the fabrication of PVDF UF membranes. For example, PVDF membranes blended with polyacrylonitrile (PAN) was prepared via a hot-pressed method [120] without any chemical treatments (Fig. 7d). The hot-press temperature was mainly investigated for the UF separation performance with a higher water permeance of 50 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ and 100% rejection of polystyrene particles (~20 nm) In addition, a magnetic field assisted preparation of magnetic Ni–ZnO particles were incorporated in the PVDF solution and were magnetically attracted to the membrane surface using a magnet. Such PVDF UF membrane with a molecule weight cutoff (MWCO) of 100,000 Da showed ultra-high anti-fouling performance towards BSA and humic acid (HA) solutions.

4.3. Nanofiltration membranes

PVDF NF membrane with pore sizes of 1-2 nm showed a high separation efficiency towards many separation systems, such as small-molecule dyes and salts. PVDF NF membranes were mainly fabricated from two approaches. The first strategy was to construct PVDF blends that decreased the membrane pore size using phase inversion methods [122,123] or by only adjusting parameters to fabricate pure PVDF NF membranes in an additivefree phase inversion method [124]. Mertens et al [124]. fabricated additive-free PVDF NF membranes for the first time by accurately tuning parameters, such as polymer concentration, evaporation time and co-solvent concentration (Fig. 8a). The resulting membranes obtained a PEG (327 Da) rejection of 80% and a water permeance of 1.8 Lm⁻²h⁻¹bar⁻¹. Although the permeance or rejection was not high, this study provided a possible method to fabricate pure PVDF NF membranes without incorporating other additives.

The second strategy was to build a thin layer on the PVDF membrane surface by interfacial polymerization (IP) [125], cross-linking [126], chemical grafting [127], or a solvothermal method [128]. IP is an important way to fabricate PVDF-based NF membranes. IP refers to a polycondensation reaction that takes place



Fig. 8. The fabrication process of PVDF NF membranes. (a) Phase inversion method by assing nanoparticles [124]. Copyright 2018. Reproduced with permission from Elsevier Science Ltd. (b) IP process [125]., Copyright 2021. Reproduced with permission from Elsevier Science Ltd. (c) Cross-linking method using GO [129]., Copyright 2020. Reproduced with permission from American Chemical Society. (d) Solvothermal method by *in-situ* synthesizing NH₂-MIL-53 layer on PVDF membranes [128]., Copyright 2021. Reproduced with permission from Elsevier Science Ltd.

at the interface between two incompatible solutions containing two monomers dissolved separately. Wang et al [125]. first fabricated PVDF membranes via NIPS and then used the IP process to form a PA layer on the outside surface of the PVDF hollow fiber membranes (Fig. 8b). Such PVDF-based NF membranes exhibited a mediocre water permeance of 10.2 Lm⁻²h⁻¹bar⁻¹, 100% Congo Red rejection performance, and low NaCl rejection of below 6.2%, indicating the potential to separate dyes and salts in industrial dye waste-water containing high salt content. A similar cross-linking method using 2D GO nanosheets was also reported (Fig. 8c) [129]. Ethylenediamine (EDA) was used as a binder to enhance the adhesive ability between the GO layer and PVDF membranes, and the PVDF/GO NF membranes showed a 100% rejection for brilliant blue dyes.

The solvothermal method has emerged as an effective way for *in-situ* synthesizing a separation layer on the PVDF membrane surface (Fig. 8d). Solvothermal method dissolved one or several precursors in a non-aqueous solvent to form target nanoparticles (NPs) under supercritical conditions, and thus tuned the microstructure of PVDF membrane surface. Reaction temperature, time and concentration were controlled to optimize the separation performance of PVDF-based NF membranes. The resulting NH₂-MIL-53/PVDF NF membranes exhibited high dye rejection and ultra-high water permeance of 50 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ [128]. In addition, the resulting PVDF NF membranes using a solvothermal method exhibited excellent chemical stability and reusability for dye solutions with a molecular weight above 300 Da.

Currently, compared with PVDF-based UF or MF membranes, the publication records related to PVDF-based NF membranes are quite rare. Pure PVDF membranes are difficult to meet the standard for NF pore size ranges. The only report by Mertens et al [124]. required a strict control of the fabrication parameters, which was not beneficial for industrial practice. It is envisaged that the future PVDF membranes developments should be focused on the following two aspects. (1) The *in-situ* formation of functional NPs or other polymer layer on PVDF membranes to effectively tailor the pore size in NF range. (2) The construction of artificial molecular channels in porous PVDF membranes by introducing novel nanoparticles.

4.4. Forward osmosis membranes

Forward osmosis (FO) has been considered as a promising approach for water treatment to overcome the drawbacks of reverse osmosis (RO) processes [149,150]. In general, FO is a natural osmosis that needs low or no trans-membrane pressures. The difference in osmotic pressure in two solution sides allows the retraction of pure water, and thus the FO is considered as an energy-efficient and economical approach compared with the RO process. The first commercialized FO membrane was cellulose triacetate (CTA) [151]; however, such a membrane showed poor water permeance and low salt rejection rates.

Currently, many polymers have been employed as separation layers supported by PVDF membranes for FO, such as PA [152], cellulose acetate (CA) [153], CTA [154], and Nylon 6, 6 [155]. Among them, the PA layer has been the most frequently used as the separation layer for FO process [151,152,156,157]. Shat et al [152]. first fabricated a PVDF/bentonite nanofiber support and then deposited a PA layer via an IP process for PVDF FO membranes that exhibited ultra-high FO water flux (41 $\text{Lm}^{-2}\text{h}^{-1}$) without a considerable increase in reverse solute flux (Fig. 9a). The hydrophobicity of PVDF substrate hampered the formation of defect-free PA selective layers. Thus, hydrophilic perfluorosulfonic acid (PFSA) [156] was in-



Fig. 9. Recent strategies to construct PVDF membranes for FO process. (a) The fabrication process of PVDF/bentonite nanofiber-based PA membranes [152]., Copyright 2020. Reproduced with permission from Elsevier Science Ltd. (b) PFSA modified PVDF nanofiber substrate [156]., Copyright 2017. Reproduced with permission from Elsevier Science Ltd. (c) Thermal-responsive PVDF polymer support [158]., Copyright 2021. Reproduced with permission from Elsevier Science Ltd. (d) PVDF/CA polymer membrane support [151]., Copyright 2018. Reproduced with permission from Elsevier Science Ltd.

corporated in the PVDF matrix to enhance the hydrophilic performance of the PVDF membrane that formed a uniform PA layer on the PVDF nanofiber membrane surface during the IP process, thereby enhancing the water flux and selectivity (Fig. 9b). PVA, another kind of hydrophilic polymer material was also used to modify the PVDF substrate. The hydrophilic modification of the PVDF matrix improved the affinity between the PVDF and PA layer, guaranteeing the formation of a complete layer.

In addition, internal concentration polarization (ICP) of the membrane is the main obstacle to greatly affect the water permeance. There are several parameters that have important effects on the ICP phenomenon, such as the microstructure and hydrophilic properties of the membrane. Therefore, it is necessary to design and control the structure of the support layers.

Thermo-responsive microgels were incorporated in the PVDF dope solution, and then smart PVDF FO membranes were constructed [158]. These membranes showed high porosity (~85%) at higher temperatures that alleviated the ICP phenomenon. The resulting membranes exhibited an excellent water flux of above 40 $\rm Lm^{-2}h^{-1}bar^{-1}$ and a reduced salt flux of about 10 gm⁻²h⁻¹ (Fig. 9c). Blends of PVDF and CA [151] were fabricated into nanofiber membrane supports with high porosity, mechanical stability, and hydrophilicity, leading to a low ICP phenomenon in FO (Fig. 9d). Zhang et al [159]. incorporated SiO₂@MWNTs (multiwalled nanotubes) in the PVDF matrix and prepared a PA layer that decreased the ICP during the FO process due to the enhanced hydrophilicity of PVDF membranes.

Basically, to construct PVDF-based FO membranes, highperformance PVDF supports are very important. It is expected that further efforts should focus on the improvement of mechanical strength and the satisfactory hydrophilic properties of PVDF supports for future FO process. For example, non-woven fabrics can be incorporated in the PVDF matrix to produce super-robust PVDF supports with an ideal pore structure and water permeance for FO process.

5. Membrane distillation

Membrane distillation (MD) is a thermally driven membrane process in which the temperature difference between the hot feed and the cold permeate is the driving force to transport water through the hydrophobic membrane [160]. MD offers the ability to treat saline water including seawater, industrial waste-water, brine water and oil-gas field produced water [161]. It is worth mentioning that the PVDF membrane is particularly suitable for membrane distillation compared with other polymer membranes such as PES and PSF membranes. Although PVDF membranes are advantageous over PES and PSF membranes in membrane distillation due to the hydrophobic "-CF2" chains in the chemical structure, the water contact angle of the PVDF membrane usually ranges from 90 ° to 100°, which is lower than desired for MD application. In addition to intrinsic properties of materials, membrane roughness contributed to the hydrophobicity of the resulting membrane. Therefore, regulating membrane roughness or coating/grafting with other more hydrophobic materials on membrane surfaces is very useful to enhance the hydrophobicity of the conventional PVDF membrane. For PVDF MD membranes, the membrane surface should be hydrophobic with a high liquid entry pressure (LEP), low thermal conductivity, high permeate flux, low fouling rate, long-term stability, and high mechanical strength. Recent progress on PVDF-based MD membranes have focused on the hydrophobic modification of the PVDF membrane surface, construction of an anti-fouling surface and novel photothermal MD process. The following sections introduce recent advances on how to construct and enhance the hydrophobicity of PVDF for membrane distillation application.

5.1. Constructing hydrophobic membrane surface

Hydrophobic modification involves blending more hydrophobic materials in the PVDF matrix, the deposition of a hydrophobic layer on the PVDF surface and the hydrophobic modification by physical or chemical methods as mentioned in Section 3. Usually, hydrophobic layer often contains two different coating layers - a porous layer and a dense layer. Dense coating layers are always used for pervaporation [162], while a porous layer is used for membrane contactors.

Hyflon has been widely used as a hydrophobic layer that was deposited on the PVDF membrane surface [86,163]. The effects of Hyflon concentration, coating time and heat-treatment needed to be investigated. In Tong's work [86], the contact angle of PVDF/Hyflon membrane increased from 95 to 140°, whereas its LEP increased from 0.26 MPa to 0.7 MPa. In the treatment of a NaCl solution in a vacuum membrane distillation (VMD) process, the water permeance and NaCl rejection of the membranes were 10 kgm⁻²h⁻² and 99.9%, respectively, exhibiting stable performance for 30 h.

Elvaloy4170 [164] was recently employed to develop hydrophobic layer that was coated on the commercial PVDF membrane surface for MD process. Elavaloy4170 is an alkyl ester containing epoxide at one terminal end (see Fig. 4 for molecular structure) [165]. The coating layer fabricated from 1.5 wt% Elvaloy4170 in a dope solution exhibited a ordinary vapor flux of $\sim 2 \text{ kgm}^{-2}\text{h}^{-1}$ and a desalination performance above 99.7%. In addition, such a membrane also showed an enhanced anti-fouling performance with a FRR of 87%.

The PVDF membrane surface can also be treated with a fluorosilane agent to decrease the surface energy. The PVDF membrane surface was first treated with inorganic particles on the membrane surface or underwent chemical treatment to produce active groups. TiO₂ is a common inorganic particle that is often anchored on the PVDF membrane surface [166] followed by modification with a low surface energy material. PVDF/TiO₂ blends produced "-OH" groups on the membrane surface that reacted with 1H, 1H, 2H, 2H-perfluorododecyltrichlorosilane (FTCS) to construct hydrophobic membrane surfaces. Different from the TiO₂ anchoring method, Kharraz and An [19] used a NaOH solution to pretreat the membrane surface to produce "-OH" groups without using inorganic particles, followed by 3-aminopropyltriethoxysilane (APTES) and 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (FAS) treatments to obtain a super-hydrophobic membrane surface for MD processes.

5.2. Tuning membrane roughness

In addition to the intrinsic chemical properties of the PVDF, the membrane roughness is also key to the final hydrophobic properties. Finely-tuning PVDF membrane roughness during the fabrication process or coating a rough layer on the existing membrane enhanced the final hydrophobic properties. For example, Li and Zhu [167] fabricated a novel PVDF membrane by introducing flower-like Bi₂WO₆ as additives that worked as crystallization nuclei for PVDF precipitation, effectively improving the membrane roughness and hydrophobic performance. Compared with the neat PVDF membranes exhibiting water permeance and rejection of 9 Lm⁻²h⁻¹ and 95%, respectively, modified PVDF membrane with a flowerlike surface displayed better desalination performance (water permeance and rejection of 13 $Lm^{-2}h^{-1}$ and 99.99%, respectively) in the MD process due to the enhanced hydrophobic properties. Wang et al [90]. used a one-step method to prepare a hydrophobic layer on the PVDF hollow fiber membrane surface with superhydrophobic papillae-like surfaces and a contact angle of above 150° (Fig. 10a). In the separation of a mixed solution, containing NaCl, MgCl₂ and CaCl₂, these inorganic salts were prone to deposit on the pristine PVDF membranes, with the liquid suspending on the micro/nano-papillae structures of the modified membranes. However, an important problem they ignored was that the PVDF coating solution was a mixture of DMAc, propylene glycol and PVDF powders. When immersing the pristine PVDF membrane in the dope solution, such membranes were prone to dissolve and then induced phase separation that formed a relatively dense interface. Therefore, the dissolution process of pristine PVDF membranes on the final performance also needed to be considered.

The membrane roughness can also be adjusted by the rolling embossing method [168], solvent-thermal treatment [169,170], and template method [171]. A micromolding roller was used to roll on the PVDF membrane surface to construct micron-nano structures that greatly enhanced hydrophobic properties with a contact angle of 150° (Fig. 10b). The embossing membranes exhibited a high permeate flux of 25 $Lm^{-2}h^{-1}$ and a salt rejection of 99.9% while the un-embossed membranes showed a low permeate flux of 12 $Lm^{-2}h^{-1}$ and a salt rejection of 99.85% [168]. Qin et al [169,170]. developed a solvent-thermal treatment process to improve the surface roughness (Fig. 10c). They confirmed that the treatment of PVDF membrane with different alkyl chain-length alcohols improved the membrane roughness by creating nanofin structures on a PVDF membrane surface. The surface chemistry was finely-tuned by regulating the fraction of crystal phases, including the non-polar α -phase and polar β -phase using different alcohols. Such PVDF membranes resulted in an anti-wetting ability for MD. Furthermore, template methods [171] consisting of fabric substrates and a non-woven substrate were used for constructing a rough membrane surface (Fig. 10d). The results demonstrated that the templated membrane surface had a contact angle above 150°, while that of the pristine membrane was just below 90°. Such a hierarchical 3D membrane structure showed a high permeate flux of 24 $kgm^{-2}h^{-1}$ and a salt rejection of 99.9%.

5.3. Designing anti-fouling membrane surface

Although the PVDF-based MD process shows numerous advantages toward different feed systems, membrane fouling of the hydrophobic membranes is a challenging issue. The amphiphilic pollutants in the feed solution, i.e., organic matter and surfactants in wastewater can be easily adsorbed on the PVDF membrane surface by hydrophobic-hydrophobic interactions (van der Waals forces) or typical electrostatic attraction mechanisms. These pollutants had two adverse effects on the MD processes. (1) The wettability and life cycle of membranes were greatly decreased. (2) The pollutants covered the pore structure that dramatically restrained water vapor transport, sacrificing water permeance. Therefore, development of a PVDF MD membrane with hydrophobic and anti-fouling properties is very important. At present, PVDF-based omniphobic and Janus membranes have a great potential to simultaneously provide anti-fouling capability and stable separation performance.

5.3.1. Omniphobic surfaces

Omniphobic PVDF membranes with strong repellency towards both water and low-surface-tension liquids have been considered as an effective way to prevent fouling in the MD process [172]. To construct an omniphobic PVDF membrane surface for MD operation, three common steps are usually used in the preparation process. They are (1) treatment of the PVDF surface to produce "-OH" functional groups, (2) construction of a rough PVDF surface with a hierarchical reentrant microscopic structure using NPs and (3) chemical modification of PVDF surface to decrease the free energy Fig. 11.a showed a typical fabrication process for the omniphobic PVDF surface. Usually, the most common design strategy is to deposit inorganic particles to produce reentrant structures [173], such as SiO₂, CuO-TiO₂, and ZnO. For example, the PVDF surface



Fig. 10. Four strategies to construct a rough PVDF membrane surface for MD. (a) Coating a rough layer by optimizing the dope compositions [90]., Copyright 2017. Reproduced with permission from Elsevier Science Ltd. (b) Micro-molding rolling method [168]., Copyright 2020. Reproduced with permission from Elsevier Science Ltd. (c) Solvent-thermal treatment [169]., Copyright 2019. Reproduced with permission from Elsevier Science Ltd. (d) Template-based method [171]., Copyright 2020. Reproduced with permission from Elsevier Science Ltd.

was first pretreated [17,18] in basic environments, and SiO₂ particles were deposited on the PVDF membrane surface and then fluorinated with 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFDTS) to obtain a membrane with both anti-water and anti-oil characteristics. After that, polydopamine (PDA) was employed to deposit the TiO₂ particles on the membrane surface (Fig. 11a), that enhanced the stability of the final omniphobic membranes, resulting in high salt rejection of ~99.99% and water flux of 34 $\text{Lm}^{-2}\text{h}^{-1}$ in the MD operation.

However, some published works pointed out that these strategies were based on the construction of reentrant structure from external additives that may sacrifice the porosity and permeance of the PVDF membrane [174,175]. Furthermore, the long-term stability of these membranes also suffered from leakage or detachment of these inorganic particles. Therefore, strategies without coating NPs have emerged, such as polymerization of long chain fluorododecyltrichlorosilane [174], layer-by-layer assembly followed by fluorination treatment [175] and CF₄ plasma treat-

ments [176]. For example, Wang et al [177]. presented a particlefree method that resulted in ultra-fast fabrication (< 90 min) of omniphobic PVDF membranes for MD. PVDF membranes were first immersed in the etching solution and then washed completely. After modification via vapor-phase silanization at 90 °C using PFDTS, modified membranes showed excellent separation performance with water flux of 29 $\text{Lm}^{-2}\text{h}^{-1}$ and rejection of ~100% in a direct contact MD (DCMD) process to separate a hypersaline solution with surfactants (Fig. 11b). Qin et al [170]. also constructed a hierarchical reentrant microscopic structure without NPs (Fig. 11c). They developed a novel solvent-thermal induced roughening method to increase the roughness of PVDF membranes. Furthermore, their method employed PDA solution to construct "-OH" groups on the polymer surface without an etchant solution treatment, followed by fluorination. These omniphobic PVDF membranes displayed super repellence to diverse liquids and tolerated a 0.4 mM SDS solution and 480 ppm mineral oil in the DCMD process.



Fig. 11. Three strategies to construct an omniphobic PVDF surface: (a) TiO₂ particles used to enhance the PVDF surface [18], Copyright 2020. Reproduced with permission from Elsevier Science Ltd. (b) Particle-free method [177], Copyright 2019. This is an open-access article. (c) Solvent-thermal method [170], Copyright 2020. Reproduced with permission from Elsevier Science Ltd.

5.3.2. Janus membranes

PVDF-based Janus membranes with asymmetric surface wettability have been receiving more and more attention to be considered as MD membranes for water treatment [178-180]. The fabrication process of PVDF Janus membranes involves engineering super-hydrophilic surfaces by hydrophilic polymers or inorganic particles on PVDF membranes that are used as a liquid barrier. When such Janus membrane surfaces come in contact with wastewater, a hydration layer is formed on the membrane surface, resulting in a strong repulsive force on the contaminants, effectively decreasing fouling. Zhao et al [181]. fabricated a superhydrophilic catechol/chitosan-polyethylenimine (PEI) layer on the PVDF membrane surface. They demonstrated that the e two lavers (catechol/chitosan laver and PEI laver) showed satisfactory chemical stability in a wide pH range of 2-12 due to the synergistic effects of covalent bonding, non-covalent interactions and electrostatic interactions. Compared with the pristine PVDF membranes, the PVDF-based Janus membrane showed super-stable water vapor flux (nearly no flux decline) and low conductivity of 48.1 μ S cm⁻¹ in the permeate during long-term operation of O/W emulsions in a MD test (Fig. 12a). Li et al [180], employed a two-step process to construct a PVDF Janus membrane by first constructing an omniphobic surface and then adding a zwitterionic layer via surface-initiated atom-transfer radical-polymerization (ATRP) (Fig. 12b). PVDF Janus membrane displayed superior wetting and fouling resistances, with a ${\sim}100\%$ salt rejection.

In addition to the polymer coating technique, *in-situ* formed metal particles is also an effective approach to construct high-performance PVDF-based MD Janus membranes. For example, Chew et al [182]. designed novel PVDF Janus membranes with hierarchical structures followed by an oxidant-induced dopamine polymerization and immobilization of AgNPs on PVDF membranes (Fig. 12c). The introduction of PDA enhanced the hydrophilicity of the membrane surface, while the AgNPs effectively healed the defects and showed an anti-bacterial property. The resulting Janus membrane showed highly stable separation performance in the treatment of low-surface-tension saline water during 72 h running time.

PVDF Janus membranes with pore sizes below 500 nm are often employed for MD applications. What will happen if a PVDF membrane with a pore size below 1 nm is employed for MD? A recent work answered this question. Chen et al [183]. coated a PEI/PDA/carbon quantum dot NF layer on a PVDF MF membrane (Fig. 12d). Note that the pore sizes of the PVDF MF and NF membranes were 175 nm and 0.58 nm, respectively. However, the vapor flux of the NF membrane decreased a little from 27 to 23 $\text{Lm}^{-2}\text{h}^{-2}$. In addition, the wetting and fouling resistance decreased simultaneously due to a robust hydration layer on the membrane surface.



Fig. 12. Important strategies to construct a PVDF Janus surface for MD: (a) Coating a hydrophilic polymer layer [181], Copyright 2021. Reproduced with permission from Elsevier Science Ltd. (b) Chemically modified by zwitterionic polymer [180], Copyright 2019. Reproduced with permission from American Chemical Society. (c) Combination of polymers and inorganic particles [182], Copyright 2019. Reproduced with permission from American Chemical Society. (d) PVDF based NF Janus membrane for MD desalination [183], Copyright 2021. Reproduced with permission from American Chemical Society.

This study provided important insights and strategies for nextgeneration anti-fouling MD PVDF membranes in UF or NF ranges.

5.4. Photothermal polymers and processes for membrane distillation

Photothermal membrane distillation (PTMD) is a nextgeneration MD-based water treatment process by utilizing the lights as heat source without consuming high-grade power. Photothermal PVDF blend are prepared by mixing PVDF with photothermal particles, such as AgNPs [184], MXene [185], carbon black NPs [186], carbon nanotubes [187,188], antimony doped tin oxide [189], Fe₃O₄ [190] and TiN [191] Fig. 13.a displays a schematic of the PTMD process, involving three significant procedures. (1) The photothermal effects that convert light to heat are controlled by photothermal nanomaterials. (2) The thermal efficiency of the produced heat for vaporization is associated with the vaporization process that transforms water to the gas phase. (3) The condenser changes vapor into distillate. Therefore, in the PVDF-based PTMD process, the photothermal performance and structure design are the two important factors that contribute to the final MD performance Fig. 13.b compares the temperature polarization between the PTMD process and conventional MD process. Notice that the temperature of the membrane interface is lower than the bulk feed in a conventional MD process $(T_f > T_{fs1})$ because of the heat loss. However, it is very different from the PTMD process. The temperature of the PVDF membrane interface

is higher than the bulk feed temperature ($T_f < T_{fs2}$) due to the thermal effect of photothermal NPs that increases the localized heating process, enhancing the thermal efficiency in the PTMD process.

Politano et al [192]. prepared PVDF/AgNPs membranes and applied them in PTMD by employing a vacuum membrane distillation (VMD) configuration for the first time, achieving an 11-fold higher water permeance than pristine PVDF membranes using ultraviolet (UV) irradiation. The PVDF/AgNPs membranes were relatively stable even after six months (Fig. 13c). The MD water permeance towards saline water and actual sea water were similar $({\sim}25~Lm^{-2}h^{-1})$ (Fig. 13d). However, the VMD process created a high absolute trans-membrane pressure such that the membrane employed in this process requires high mechanical strength and long-term interfacial stability between the photothermal materials and PVDF matrix [193]. Tan et al [185]. reported a bi-layer PVDF/MXene membrane with both photothermal and anti-fouling performance for the DCMD process. Infrared thermal imaging of the MXene/PVDF membranes in Fig. 13e demonstrated the thermal effect of novel 2D MXene materials in the PTMD process. The feed solution with a mixture of BSA and NaCl solution was fed through pristine PVDF membranes and PVDF/MXene membranes. The heater energy input per unit volume distillate showed a 12% reduction in PVDF/MXene systems.

In the next-generation PTMD process, novel and high activation photochemical materials are expected to combine with the PVDF



Fig. 13. (a) Schematic of mechanism of the PTMD process and (b) effect of temperature polarization compared with a conventional MD process [193], Copyright 2021. Reproduced with permission from John Wiley & Sons Inc. (c) Stable performance of AgNPs/PVDF membranes and (d) PTMD performance [192], Copyright 2017. Reproduced with permission from John Wiley & Sons Inc. (e) Infrared thermal imaging of three kinds of PVDF membranes [185], Copyright 2018. Reproduced with permission from Elsevier Science Ltd.

membranes for high water permeance. In addition, solar radiation as a free heat source can be further utilized for cost-effective PVDF-based PTMD process.

6. Self-cleaning PVDF membranes

Although there are many reports on enhancing the anti-fouling properties of PVDF membranes, these modified membranes are inevitably fouled by contaminants during operation and can require many cleaning cycles. Recently, many strategies have been reported to produce better "self-cleaning" anti-fouling PVDF membranes that could *in-situ* remove or degrade contaminants on the surface, which greatly increased the permeance and decreased fouling. There are five main strategies suggested to construct self-cleaning PVDF membranes. Recent developments and remaining issues of the strategies are discussed below.

6.1. Piezoelectric membranes

Piezoelectric membranes are one of two important self-cleaning membrane materials for water treatment; the other is ceramic membranes. These membranes can *in-situ* vibrate upon application of electrical current to remove existing containments and avoid further deposition of new containments on the membrane surface. High-performance of a piezoelectric PVDF membrane depends on formation of PVDF with high β -phase content. This section will discuss the strategies of high β -phase PVDF polymers and their applications in self-cleaning PVDF membranes.

6.1.1. Crystalline polymorphism

PVDF is usually composed of five multi-crystalline phases, α , β , γ , δ , and ε phases, which are determined by their thermal mechanical history [27]. PVDF with α -, β -, and γ -phases are mostly used. The α -phase PVDF is a kinetically favorable non-polar crystalline form, while the β form is the most thermodynamically stable polar form. FTIR and X-ray diffraction (XRD) characterizations can be employed to distinguish α - and β -forms. Polymorphism is important as it can greatly affect intrinsic properties, such as dielectric constant, ferroelectric properties, and polarity. β phase PVDF has the best piezoelectric properties compared with other crystalline phases that has attracted great interests in terms of transformation from another crystalline phase to the β -phase. There are two ways to increase the β -phase content in PVDF [194].

The first one focuses on the fabrication process. A PVDF solution is cast on a glass plate followed by evaporating the solvents to form films. The crystalline form in PVDF using this method is mainly α -phase with a little β and γ . To increase the β -content, researchers can use special fabrication techniques, such as electrospinning [195], dehydrofluorination [196], nanoconfinement [197], and orientation [198]. External force or electrical fields can be used to induce orientation or polarization, and thus increase the β -phase content, leading to enhanced piezoelectric performance.

Another option is to include additives in the PVDF matrix to produce chemical polarization to increase the β -phase content and dielectric constant. These additives are composed of small molecules, polymers, or various NPs [199–201]. These additives function as a nucleating agent to promote the formation of the β -phase, such as poly(methyl methacrylate) (PMMA), PVP, and poly-3-hydroxybutyrate (PHB) are widely used.

Recently, a series of novel methods such as the precipitationprinting method [202], double-step molding [203], anti-solvent crystallization process [201], 3D printing technology [204], using polar non-toxic solvents (i.e., organic carbonates [205], PolarClean [206], and ionic liquids [60]) have been introduced to enhance β phase PVDF. Precipitation printing is a novel additive manufacturing technique based on rapid precipitation of a polymer from solution when exposed to a non-solvent. The method uses a robotic gantry system with polymer solution dispensed into a non-solvent reservoir to create 3D structures [207]. The precipitation-printing process and the conventional solvent-cast method was compared. The precipitation-printing process showed high β -phase content characterized from FTIR, unlocking a novel strategy to obtain high β -phase PVDF. In addition, molecular modeling is an effective approach to understand the microstructure of polymers that provides important information on the structure-property relationships. For example, phase transformation from the α - to β -phase in PVDF could be studied by molecular simulations [208]. These theoretical approaches provided an understanding of the changes at the molecular level that could be confirmed by experimental results, such as FTIR, XRD, etc [206].. For example, Ismail et al [205]. investigated the formation of β -phase polymorphs in the fabrication process using experimental and theoretical studies. In their work, three kinds of non-toxic solvents were employed, including ethylene carbonate (EC), propylene carbonate (PC), and butylene carbonate (BC). The modeling results of the β -phase formation displayed that the β -phase depended on the extent of hydrogen bonding at the interface of polymer-solvent. To confirm the rationality of this molecular dynamics simulation, experimental results (XRD and FTIR characterizations) were used to characterize the phase polymorphs. PVDF polymers prepared using EC or PC could form β -phase products, whereas that fabricated using BC formed a mixture of α - and β -phases consistent with the simulations. Other non-toxic solvent systems together with molecular dynamic simulations could also be found in PolarClean/PVDF systems [206].

6.1.2. Recent advances of piezoelectric membranes

Coster et al [209]. prepared a PVDF piezoelectric membrane successfully in 2011 for the first time. Fig. 14a–c showed the current self-cleaning mechanism, poling process, and separation devices of the piezoelectric membrane process, respectively. The feature of the piezoelectric membranes was to *in-situ* vibrate under a certain electrical voltage that could effectively remove the existing contaminants and further prevent the new pollutants from depositing on the membrane surface (Fig. 14a). After applying a high voltage direct current (DC) to the two sides of the PVDF membrane, the direction of the electric dipole was arranged and parallel to the polarization electric field, thereby giving PVDF membranes piezoelectricity (Fig. 14b). Subsequently, applying an alternating current (AC) at two sides of the polarized PVDF membrane excited the PVDF membranes to generate vibrations perpendicular to the membrane surface. There were two flat sheet electrodes on

the two sides of the membrane that was submerged into feed solution. Both electrodes were wired to a waveform generator that provided AV signals and amplitudes (Fig. 14c). When the voltage and AC frequency were 17 V and 5 Hz, respectively, the vibration displacement of the PVDF membrane reached about 2 nm.

The influence of electrical polarization on the microstructure and separation performance of PVDF membranes was also investigated by Darestani et al [210–213]. The microstructure of the unpolarized PVDF membrane was relatively uniform, while the membrane pores in the PVDF membrane were connected with each other. After polarization, obvious delamination was observed in the PVDF membranes dividing into three layers in the direction perpendicular to the polarization electric field. The pore size of the unpolarized PVDF membrane was 220 nm without obvious rejection of sodium alginate. Meanwhile, the rejection of sodium alginate in the polarized PVDF membrane increased to above 50%. In addition to the different internal crystalline structures, the surface roughness of the PVDF membrane after polarization also decreased by \sim 27% compared with that of the unpolarized membrane surface.

Therefore, β -phase PVDF membranes are a key to fabricating piezoelectric membranes. High-voltage polarization can promote the formation of the β -phase, and the content is mainly influenced by the polarization voltage. Chen and Pomalaza-Raez [214] used an electric field to pole the PVDF membrane and tested its self-cleaning performance using a kaolin suspension. The results demonstrated that the vibration of PVDF membrane under AC excitation removed the contaminants on the membrane surface. When the applied voltage was 24 V, the frequency was 1601 Hz, and the amplitude was 6.5 nm, the poled PVDF membrane flux increased by 87.3% compared with conventional unpoled PVDF membrane (Fig. 14d). Since there were many voids in the PVDF membranes, the polarization effect could be limited because of the discharge and breakdown phenomenon when a high DC electric field was applied.

In addition to the high electrical poling, there are many other strategies related to the transformation from other phases to the β -phase mentioned in Section 6.1.1. Herein, recent case studies were performed to construct self-cleaning piezoelectric PVDF membranes. Cao et al [215]. proposed that the different solvent/PVDF systems had a great impact on the final phase compositions of PVDF membranes. They used ILs to dissolve PVDF powders and promoted the formation of β -phase crystals due to the strong electrostatic interactions between the PVDF chains and -CF₂ chains in the ILs. Such piezoelectric PVDF membranes were employed in complex membrane bioreactor (MBR) systems and exhibited highly stable performance during 30-days operations with a chemical oxygen demand (COD) removal rate over 90% (Fig. 14e). Similar results were also discovered in Zhang's work [60]. They fabricated two kinds of membranes using TEP and TEP/ILs systems and concluded that the ILs promoted the formation of the β -phase. In addition, an electrospinning technology to fabricate PVDF membranes with piezoelectric properties and high β -phase content was developed [195]. The advantage of this method was to form the β -phase during the electrospinning membrane fabrication process instead of poling after membrane formation. Therefore, such a method decreased the fabrication cost and improved the efficiency simultaneously. Electrospinning parameters, such as solvent ratio, spinning distance, flow rate and voltage were optimized to fabricate a PVDF membrane with a β -phase content of 90.9%. The flux of the pristine PVDF membrane decreased from 21 Lm⁻²h⁻¹bar⁻¹ to 16 Lm⁻²h⁻¹bar⁻¹, while the piezoelectric PVDF membrane flux did not decrease under the excitation of AC with a voltage of 10 V and a frequency of 1 kHz, showing satisfactory self-cleaning performance in the treatment of a feed solution containing sodium alginate and calcium chloride.



Fig. 14. (a) Schematic diagram piezoelectric PVDF membranes for self-cleaning performance, (b) electrical poling process, and (c) resonant frequency response testing equipment [214]., Copyright 2019. Reproduced with permission from Elsevier Science Ltd. (d) The effect of the frequencies on the self-cleaning performance and (e) performance of piezoelectric PVDF membranes in a MBR system [215]., Copyright 2020. Reproduced with permission from Elsevier Science Ltd.

Recent interesting reports focused on the effect of crosssectional structure of PVDF membranes on the dielectric and piezoelectric properties [216]. Three membrane structures were fabricated from different solvents, such as TEP, DMF, and NMP The results displayed that the finger-like structure from NMP/PVDF system exhibited higher piezoelectric performance than membranes with other cross-sectional structures. In the treatment of a colloidal silica solution, the piezoelectric PVDF membrane with a finger-like structure removed pollutants from the membrane surface and thus obtained a 46% increase in critical flux.

In general, the pore sizes of piezoelectric PVDF membranes were classified into UF and MF ranges to separate solid/liquid mixtures from emulsions. Piezoelectric PVDF UF membranes with smaller pore sizes or piezoelectric PVDF NF membranes are needed to improve the separation accuracy in UF and NF. For example, addition of 2D-GO nanosheets in the PVDF doping solution using ILs as non-toxic solvent is expected to tune the pore sizes and improve the electrical conductivity of PVDF membranes. On the other hand, the ILs promote β -phase formation of NPs and non-toxic solvents is suggested to prepare piezoelectric PVDF membranes in future work.

6.2. Photocatalytic PVDF membranes

Photocatalytic processes together with membrane separation system have been proposed as sustainable water separation technologies. Photo-induced self-cleaning membranes can effectively degrade the organic matter adsorbed on the membrane surface under visible or UV light irradiation, converting them to small and even non-toxic molecules [217,218]. Photocatalytic PVDF membranes are prepared by incorporating photocatalytic NPs in the PVDF matrix or coating photocatalytic NPs on the PVDF membrane surface. The most interesting self-cleaning PVDF blend is PVDF/TiO₂ because TiO₂ is inexpensive and easy to obtain. However, such membranes are usually activated by UV light as single TiO₂ has a limited efficiency. Considering this fact, the development of photocatalytic PVDF membranes with visible-lightbased activation properties will have a huge potential to enhance the separation performance of next-generation PVDF-based selfcleaning membranes. Luo et al [219]. prepared PVDF/TiO₂ membranes to degrade BSA in a MBR system, and the results showed that the PVDF/TiO₂ membranes exhibited a FRR of ~95% under UV radiation. Zhang at al [220]. found that the N-doped TiO₂ materials showed self-cleaning performance just under visible light because a new band inserted into the original bandgap of TiO₂ decreased the bandgap energy and enhanced its light harvesting ability.

Other PVDF blends such as ZnO/PVDF, SnO₂/PVDF and g- C_3N_4 /PVDF were reported for photocatalytic membranes. For example, Xie et al [221]. assembled tannic acid (TA) - Fe (III) on the PVDF membrane surface, and then in-situ mineralization of β -FeOOH was conducted to engineer PVDF/TA/ β -FeOOH membranes (Fig. 15a). Note that the PVDF membranes incorporating β -FeOOH NPs showed a decreased membrane roughness, alleviating the fouling deposition on the membrane surface. The membrane showed very fast (<600 s) and super-high water flux ratios (>98%) in the treatment of O/W emulsions because of the photocatalytic features of β -FeOOH. Referring to photocatalytic mechanism in Fig. 15b, β -FeOOH was excited to produce photo-generated electrons (e⁻) and holes (h⁺) using visible light irradiation. Then, electrons (e⁻) transferred to the surface of β -FeOOH NPs and reacted with H₂O₂ to produce "OH" hydroxy radicals. In addition, the h⁺ in the valence band of β -FeOOH reacted with "OH^{-"} (hydroxide ion) to form "·OH" (hydroxyl radical). Finally, "·OH" decomposed the organic matter into CO₂ and H₂O. Such membranes displayed a high TOC rejection rate of 99.1% and a water permeance of $\sim 2100 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$.



Fig. 15. (a) Fabrication process of PVDF/TA/β-FeOOH membrane and (b) mechanism of decomposition of oil droplets [221], Copyright 2019. Reproduced with permission from the Royal Society of Chemistry. (c) Catalytic performance of PVDF/binary catalyst polymer membranes [222], Copyright 2016. Reproduced with permission from Elsevier Science Ltd.

Many researchers discovered that PVDF photocatalytic membranes using a single catalyst had limited photocatalytic performance. Therefore, they began to embed multi-component catalysts into the PVDF to enhance the degradation performance of organic contaminants. For example, GO-TiO2/PVDF [222], GO-ZnS/PVDF [223], GO-SnO₂/PVDF [224], GO-C₃N₄/PVDF [225], Ti-MOFs/PVDF [226], LiCl-TiO₂/PVDF [227], and Bi₂MoO₆-C₃N₄/PVDF [228] selfcleaning PVDF membranes have been reported by incorporating binary catalysts with the enhanced self-cleaning performance. Xu et al [222]. investigated the combination of catalysts on the performance of PVDF membranes, such as single TiO₂, single GO and TiO_2 -GO. Notice that the membrane with TiO_2 or GO showed a larger porosity and lower membrane roughness because of the presence of inorganic nanomaterials within the concavities of the hybrid membrane surface. They demonstrated that the membranes with binary catalysts showed a higher self-cleaning performance than that using single photocatalyst (Fig. 15c). Besides, the membranes showed a higher water permeance of \sim 500 Lm⁻²h⁻¹bar⁻¹, which was two times higher than that of the original PVDF membranes

Although the photo-catalytic performance of PVDF membranes is very interesting, there is also an important issue that needs to be considered. As the membranes are exposed to the UV radiation and oxidative environment, whether these PVDF blends can maintain their stability is still an issue. The formed incident photons react with polymer chains that are able to trigger the degradation. Therefore, stable performance should be considered, and the separation performance should not be compromised even under harsh conditions. China et al [229]. investigated the stable performance of a series of polymer membranes under UV irradiation, and the results demonstrated that the PVDF, PTFE and PAN membrane materials were stable even after one-month of UV irradiation. After that, they also found that doping NPs affected the stable performance, and the oxidative compounds accelerated the degradation rate. In general, PVDF and PTFE membranes showed a relatively stable performance [230]. Lee et al [231]. systematically investigated the stable performance of PVDF/TiO₂ membrane under the UV irradiation for 250 h. The results demonstrated that there were some defects on the membrane surface when the exposure time was about 120 h. As the exposure time to UV irradiation further increased, the polymer structure collapsed, and the tensile strength greatly decreased with an increase in water flux from 10.89 to 21.89 Lm⁻²h⁻¹bar⁻¹. They pointed out that the stability of the separation performance should be considered in detail in the photocatalytic process.



Fig. 16. (a) The mechanism of electrochemical oxidation process [238]., Copyright 2014. Reproduced with permission from Elsevier Science Ltd. (b) Three methods for constructing self-cleaning electrochemical membrane process [245]., Copyright 2021. Reproduced with permission from American Chemical Society. (c) Two membrane types for electrochemical processes, including flat sheet membranes and hollow fiber (or tubular) membrane [245]., Copyright 2021. Reproduced with permission from American Chemical Society.

6.3. Conductive membranes for electrochemical processes

Electrochemical technique is an important strategy in designing self-cleaning PVDF membrane processes that can reduce membrane fouling via electro-assistance, and this method has been investigated for over 50 years [232,233]. Contaminants in wastewater, such as organic colloids, solid particles, and proteins, are always negatively charged, and electrostatic repulsion can be induced with negatively charged membranes [234]. Besides, these pollutants can move towards an oppositely charged surface by electrophoresis, and thereby detach from the membrane surface. The use of a direct current electric field to remove membrane fouling is effective. The conductive PVDF membranes can both electrooxidize those organic contaminants into carbon dioxide and water (Fig. 16a), and show electronic repulsion against the pollutants.

Two major strategies have been reported to design a PVDFbased electrochemical membrane process [235]: incorporation of a metal mesh to construct a conductive system (Fig. 16b) or adding conductive materials into the PVDF matrix (Fig. 16c). In the first strategy, the cathode material was platinum mesh, and the anode was usually made of titanium because of its economics, versatility and corrosion resistance. The main factor that had limited its further application was the insulation properties of the PVDF material such that the external high electric field should be used to overcome the resistance (above several hundred volts) [236]. Li et al [237]. fabricated a novel PVDF/stainless steel (SS)/polypyrrole (PPy) cathode membrane via in-situ electro-polymerization, and such a membrane exhibited excellent electrocatalytic performance. Thus, a battery system with a PVDF/SS/PPy membrane cathode and Fe sacrificial anode was combined to produce hydroxy radical "·OH". The pH value and area ratio of Fe anodes to PVDF/SS/PPy were optimized, and the resulting membranes increased the rejection from 54.7 to 79.3%, indicating an enhanced self-cleaning performance.

To construct conductive membranes, PVDF was blended with conductive materials [238] in the PVDF matrix, such as CNTs [239, 240], carbon fiber [241], carbon nanostructures [234], reduced GO [242] and stainless steel mesh [243] (Fig. 16b). Such conductive PVDF membranes can be directly used as negative electrodes. A highly conductive PVDF/CNT membrane was fabricated by a phase inversion method [240]. Compared with pristine PVDF membranes, such conductive membranes had a high electrical conductivity and super-higher water permeance with higher porosity and rougher membrane surface. The membrane acted as a cathode and display super self-cleaning performance in the presence of external electric fields. The results demonstrated that the self-cleaning performance was enhanced using a 0 V/2V-pulse mode compared with that with a 2V-constant mode. Anis et al [244]. fabricated zeolite/carbon nanostructures (CNS)/PVDF conductive membranes and then used such membranes for the separation of a sodium alginate solution to test their self-cleaning performance. Such membrane combined with electrolysis showed a higher FRR (above 70%) than that of the conventional membrane process (\sim 20%), and the membrane surface was not covered with contaminants if electrolysis was used (Fig. 16c) Fig. 16.d exhibited three membrane modules in electrochemical processes, including flat sheet, hollow fiber, and tubular membranes. In the water treatment, PVDF conductive membranes generally acted as one electrode, while the other electrode could be placed on the feed or permeate side [245].

Although PVDF conductive membranes are potentially interesting for self-cleaning application in combination with an electrical field, it is necessary to innovate the conductive materials to advance the low-cost and sustainable PVDF conductive membranes. For example, CNTs have been the most common conductive material in PVDF, but CNTs have suffered from many obvious drawbacks, such as high cost and harsh synthesis conditions. Future efforts need to focus on cost-effective and environmentally friendly



Fig. 17. Smart-responsive PVDF polymers for membranes: (a) Thermo-responsive mechanism [246], Copyright 2016. Reproduced with permission from Royal Society of Chemistry. (b) Reversible thermo-responsive phase transitions of SiO_2 -PNIPAm [249], Copyright 2020. Reproduced with permission from Elsevier Science Ltd. (c) pH-responsive mechanism [246], Copyright 2016. Reproduced with permission from Royal Society of Chemistry.

PVDF conductive membranes with high porosity, conductivity and stability for long-term membrane operation.

6.4. Smart-responsive PVDF membranes

Inspired by biological cell membranes with stimuli-responsive pore channels for self-tuned surface microstructure and properties in response to the environmental signals, smart responsive PVDF self-cleaning membranes were prepared. Once the environmental conditions such as temperature and pH change, these smart membranes can automatically tune the pore size and surface properties, and thus manipulate the self-cleaning performance [246].

Thermo-responsive polymers. such as poly(Nisopropylacrylamide) (PNIPAm), have been widely used for smart surfaces with reversible dynamic adsorption and desorption performance (see Fig. 17a) [158]. PNIPAM was first synthesized in 1956 and demonstrated excellent thermo-responsive performance due to its lower critical solution temperature (LCST) of \sim 32 °C in aqueous media [247]. Therefore, it is very meaningful to combine such smart polymers with membrane materials to obtain excellent separation properties. Usually, these thermo-responsive materials were embedded in the PVDF matrix during the fabrication process [248]. Zhao et al [249]. reported a novel thermo-responsive self-cleaning membrane by synthesizing PNIPAm-grafted silica NPs (SiO₂-PNIPAm) and incorporating them into the PVDF UF membranes via a blending method. SiO₂-PNIPAm effectively improved the hydrophilicity and water permeance of PVDF membranes. Super-high thermo-responsible flux variation and stable performance were obtained when the temperatures were controlled between 25 and 37 °C. The resulting SiO₂-PNIPAm blended PVDF membranes exhibited high FRR and a low irreversible fouling ratio, showing exceptional self-cleaning performance due to the continuous increase of BSA adsorption-desorption ratio (Fig. 17b).

Vanangamudi et al [250,251]. conducted a series of works related to fabricating thermal-responsive self-cleaning PVDF/PNIPAm materials. They demonstrated that PVDF/nylon/PANIPAm membranes showed high hydrophilic performance and thermalswitchability below the LCST. The BSA rejection rate of the selfcleaning membranes improved from 4 to 96%. After a two-cycle UF separation process of a BSA solution, a super-high recovery ratio (> 97%) was obtained by varying temperatures, while the FRR of commercial PVDF membranes was only maintained at 56%.

Recently, Yuan et al [252]. synthesized the copolymer of poly(ethylene glycol) methyl ether methacrylate (PEGMA) and N-isopropylacrylamide (NIPAM)) (poly(PEGMA-co-NIPAM) (via reversible addition fragmentation chain-transfer (RAFT) polymerization with PEGMA and NIPAM. Such a copolymer was then grafted on the PVDF surface using PDA via a Michael addition reaction, forming covalent bonds between the PVDF and copolymers. The copolymer resulted in a membrane surface with tailored hydrophobic and hydrophilic properties by changing temperatures from 4 to 37 °C, achieving variable water fluid transport efficiency. Reversible wettability controlled by poly(PEGMA-co-NIPAM) enabled PVDF membranes with adjustable and self-cleaning properties in the treatment of bacteria solutions.

Besides thermo-responsive self-cleaning PVDF membranes, pHresponsive self-cleaning PVDF membranes (Fig. 17c) also have been reported. Poly(acrylic acid) (PAA) is a typical pH-responsive polymer. When the molar mass of PAA was below 16.5 kDa, it did not show a pH-responsive change, but above this molar mass, a pHdependent conformational change was observed for PAA [253]. A smart PVDF grafted with PAA (PVDF-g-PAA) was reported as PAA showed pH-responsivity (pKa of PAA = 4.5–4.9) [127,254]. PVDF-g-PAA was prepared via a homogenous solution polymerization, and a one-step electrospinning process was adopted to fabricate the electrospun membranes [255]. The electrospun PVDF-g-PAA membranes changed their wettability by realizing deprotonation at pH \sim 6.5 and protonation at pH \sim 2, leading to smart switchable surface wettability in aqueous media. The resulting membranes exhibited excellent rejection and high flux in the separation of O/W emulsions. N,N-dimethylaminoethylmethacrylate (DMAEMA) is another significant pH-responsive material that can be incorporated in PVDF by a combination of *in-situ* polymerization and a phase separation process (*pKa* of PDMAEMA is ~7.0) [256]. The results showed that when the feed pH was controlled at 7.4, the deprotonated PDMAEMA was no longer immobilized, and the oils easily penetrated into the permeate side. However, once the pH was controlled at 2, the PDMAEMA became protonated, and a hydrophilic layer was formed on the PVDF membrane, blocking the oil droplets. The resulting pH-responsive self-cleaning PVDF membrane showed a high FRR of 97% in the treatment of a BSA solution.

In the future, smart 2D nano-sheets with artificial nanochannels are expected to be used as smart-responsive polymer membranes responding to various environments. A combination of PVDF membrane and these smart nano-sheets can effectively enhance the separation accuracy and water permeance while obtaining self-cleaning performance in a wide range of separation systems.

6.5. Superwetting surface for potential self-cleaning membranes

As discussed in Section 3, one goal in developing PVDF-based membranes is to enhance the hydrophilic properties and thus obtain an anti-fouling surface. Usually, membranes with a contact angle below 5° are defined as superwetting membranes. Notice that not all superwetting membranes have self-cleaning performance as it requires a balance between the specified application and microstructure/chemical properties of the PVDF membrane surface.

Constructing a superwetting PVDF membrane surface is a key to treating O/W emulsions. Oil foulants are excluded from the hydration layer on a superwetting surface or resisted from the air layer on the super-omniphobic membrane surface [257]. Liao et al [258]. prepared a PVDF nanofibrous layer on the non-woven supports by electrospinning process. Then a thin nano/micro-beaded rough layer was produced by electrospinning a PVDF dope with well-dispersed hydrophobic-modified Si NPs. Such membrane was continued to be modified to obtain in-air superamphiphilic, underwater superoleophobic and under-oil superhydrophobic properties that exhibited self-cleaning performance to treat O/W emulsions in a 50 h continuous cross-flow separation process. Jia et al [259]. developed superwetting PVDF-based self-cleaning membranes by forming micro-structured gel layers using a facile immersion method based on the PVDF membrane. The gel structures on the membrane surface were tailored from nanoparticle patterns to nanoparticle-string interconnected networks by optimizing the precursor concentration, exhibiting stable superwetting performance toward many O/W emulsion systems, such as soybean-inwater, hexane-in-water, and chloroform-in-water. When the membranes were removed from the oil emulsion, oil droplets were automatically detached from the membrane surfaces without any residuals. In contrast, the pristine PVDF membranes had obvious oil fouling when lifting from the emulsion.

7. Conclusion and future recommendations

In this review, the state-of-the-art advances of PVDF and its modification technologies for membranes have been comprehensively reviewed. First of all, the development of chemical and physical properties of PVDF and its blends, such as solubility, alkaliresistance, and thermal stability were analyzed.

Recent developments in phase separation processes for membrane fabrication were briefly discussed based on the latest advances in NIPS, TIPS, VIPS, and their combinations. After that, fabrication strategies for PVDF membranes were reviewed from the perspective of non-toxic solvents and solvent-free methods. In addition, the main designing strategies together with some emerging approaches were reviewed and introduced to enhance the performance of PVDF membranes. Finally, these strategies were employed to design porous PVDF membranes for different watertreatment applications, such as pressure-driven membranes and MD process. Self-cleaning PVDF membranes and processes were also highlighted in this review.

Although there have been more efforts to develop PVDF and its blends for membranes, the growth potential is still high, and more efforts need to be made as summarized in the following:

- (1) PVDF often suffers from poor alkali-resistance due to the dehydrofluorination reaction that limits their applications in basic environments and long-term stability. The development of alkali-resistant PVDF for wide applications in harsh conditions is an important future task.
- (2) Modification and fabrication processes of PVDFs need to be emphasized. First, Chemical modification of PVDF surface needs to be deliberately conducted to obtain a more hydrophilic or hydrophobic surface that often needs pretreatments and requires more laborious and sophisticated procedures. These complex pretreatments will produce more wastewater, and more studies are required to simplify the surface treatments of PVDF polymer. In addition, green fabrication of PVDF membranes towards greener processes are urgently required. More efforts should be put into using non-toxic solvents or solvent-free strategies to fabricate PVDF membranes. Chemists and membrane scientists should find more non-toxic solvents with tunable microstructures and performance to support the future developments of PVDF-based polymer membranes.
- (3) Stable performance of PVDF blends by introducing NPs is a major issue that limited their developments and industrial applications to some extent. For example, in the PVDF-based photocatalytic membrane process, the addition of NPs can accelerate the degradation of polymer chains in UV radiation and an oxidative environment. However, the reaction mechanism needs to be further clarified. Preventing polymer degradation can increase the life cycles of the PVDF membrane. In addition, in the separation of food solutions using these PVDF blend membranes, the leakage of NPs in these solutions has great adverse effects on human health.
- (4) PVDF-based NF membranes have been rapidly developed in recent years. They usually require deposition of another layer by an IP process or cross-linking on a PVDF substrate to obtain a low molecule weight cut-off. Furthermore, current PVDF NF membranes are usually flat sheets. A one-step extrusion of hollow fiber PVDF NF membranes by designing spinnerets and dope solution is more cost-effective and advantageous.
- (5) Single self-cleaning PVDF membrane processes have always limited water treatment capacity. Combination of diverse selfcleaning processes can be used to treat wastewater containing complex contaminants using membranes with more antifouling performance and higher water permeance. For example, GO nanosheets, on one hand, can be employed to construct conductive membranes in the electrochemical PVDF selfcleaning membrane process. On the other hand, it also can be used in the photocatalytic membrane process. The combination of the two self-cleaning systems will be advantageous.

Declaration of Competing Interest

No conflict of interest exists in the submission of this manuscript, and the manuscript is approved by all the authors for publication. All the authors listed have approved the manuscript that is enclosed.

CRediT authorship contribution statement

Dong Zou: Investigation, Writing – original draft, Writing – review & editing. **Young Moo Lee:** Conceptualization, Supervision, Writing – review & editing, Funding acquisition.

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