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Review

Organic solvent nanofiltration polymeric membranes: Recent progress, applications, challenges, and perspectives

Qianwen Su, Xiuming Zhang, Daohui Zhao, Ming Li *

School of New Energy and Electrical, Hubei Key Laboratory of Polymer Materials, Collaborative Innovation Center for Advanced Organic Chemical Materials Co-constructed by the Province and Ministry, Hubei University, Wuhan 430062, China

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ABSTRACT

Organic solvent nanofiltration (OSN) is an efficient, low-energy and environmentally friendly phase-free separation process. Obviously, the core of OSN lies in the fabrication of solvent-resistant nanofiltration membranes. Although membrane materials reported in the literature such as 2D membranes, porous organic cages, *etc.* have the potential for ultra-high performance, polymeric membranes provide key advantages in mass production and processability. Therefore, this review focuses on polymeric materials for OSN. This review summarizes the recent progress of polymeric materials, including emerging and traditional polymeric membranes. Then, a summary of recent progress about strategies developed for perm-selective nanofilms are presented, followed by a brief overview of commercial membrane technology for OSN. Finally, major challenges of OSN and future research directions are presented. Close interaction between the academic research and practical application would help improve greener and more sustainable manufacturing processes.

1. Introduction

Separation technology plays a vital role in the chemical industry [1]. Usually, three basic functions are included such as concentration, fraction and purification. Currently, the most commonly used separation techniques typically involve energy-intensive processes driven by fossil fuel combustion, such as evaporation and distillation, and which account of 10% to 15% of the world's energy consumption [2]. To achieve the long-term goal of carbon neutrality, it is urgent to transform the industry away from existing technology with carbon footprints.

Pressure-driven membrane separation is considered to be an efficient, low-energy and environmentally friendly separation process due to its no-need of phase change [3,4]. Organic solvent nanofiltration (OSN) is a good example of membrane application, which allows solute rejection based on size-exclusion between 200 and 1000 $g \cdot mol^{-1}$ [5,6]. The concept of OSN was first proposed by Sourirajan in 1964, when cellulose acetate membranes were used to separate liquid hydrocarbon mixtures [7]. However, membrane technology was not sufficiently developed at that time, which blocked the further development of OSN. Obviously, the core of OSN lies in the fabrication of solvent-resistant nanofiltration membranes. Therefore, there is an urgent need to develop membranes with better performance (permeability and selectivity) and membrane robustness for real-world application. Over the past few decades, many materials such as ceramic [8], carbon molecular sieve membranes (CMS) [9], mixed-matrix membranes (MMM) [10], two-dimensional lamellar materials (GO, MXene, TMD, *etc.*) [11,12] and metal oxide nanofilms [13] have been developed. As shown in Fig. 1, the number of publications per year has shown an increasing trend since 2000, which shows the importance of OSN field. Ceramics are stable without swelling in organic solvents owing to their chemical inertness and structural rigidity. However, their brittleness, expensive cost and difficult scalability make them uncompetitive. CMS membranes with rigid and uniform pore structures are idea for high-temperature and high-pressure separations [14]. But their gradual performance degradation due to the collapse of micropores has been the main bottleneck to reach commercialization [15]. Combining processable polymers with more permeable and selective fillers, mixed matrix membranes (MMMs) have the potential for molecular separation. But it is difficult to control their interfacial compatibility, especially under high packing loads [16]. With one-atom-thick thickness and precise control of the interlayer nanochannel, 2D lamellar membranes have the possibility to break the trade-off effect between permeability

* Corresponding author.
E-mail address: liming@hubu.edu.cn (M. Li).

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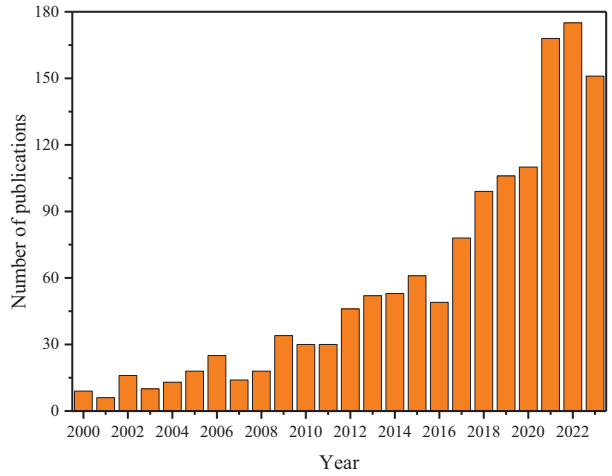

Fig. 1. Number of publications per year, including search details below in Scopus: search in the title/abstract/key words: "organic solvent nanofiltration" or "solvent resistant nanofiltration" and "membranes".

and selectivity. To achieve practical utilization, the problem of facile scale-up technology and their robustness should be addressed. Other materials that have been reported for OSN, such as metal-organic framework (MOF) [17], and porous organic cages [18], are explored on a laboratory scale as basic research topics. Although above materials have the potential for ultra-high performance, polymeric membranes provide key advantages in mass production and processability.

Different from several reviews about in OSN, which include a broad spectrum of OSN materials or molecular separation [4,19–25], this review focuses on state-of-the-art polymeric materials for OSN. The practical application of polymeric membranes for OSN faces the following challenges: (a) poor solvent resistance and performance degradation under extreme conditions [26,27], (b) the trade-off effect between permeability and selectivity [28], (c) complicated mass transfer mechanism. This reviews aims to provide a summary of recent significant advances [29–32]. The following sections are dedicated to summarize the recent progress of polymeric materials including emerging porous organic polymer membrane and commercial polymers, etc. (Section 2). Then, a summary of recent progress about strategies developed for permselective nanofilms are presented (Section 3), followed by a brief overview of commercial membrane technology for OSN (Section 4). Finally, major challenges of OSN and future research directions are presented (Section 5).

2. Recent Progress on Solvent-Resistant Polymeric Membranes

OSN can be directly defined as membranes in which the solvent flux with continuous fluids across the membrane boundary *via* transmembrane pressure gradients. Polymeric membranes for OSN can generally be divided into two types: (i) emerging porous organic polymer (POP) membranes, including crystalline and amorphous porous materials. (ii) Traditional polymer membranes, including polyimide (PI), polybenzimidazole (PBI), polyacrylonitrile (PAN), polyaniline (PANI), *etc.*

2.1. Porous organic polymer membranes

Typically, POPs have covalent bonded backbones with different geometries and topologies, showing high porosity, large specific surface areas and physicochemical stability. These porous materials with excellent stability exhibited potential for applications in several fields, especially for OSN [33]. Usually, POPs can be divided into two categories according to their degree of long-range order, including crystalline such as covalent organic framework (COF) and amorphous such as polymers of intrinsic microporosity (PIM), conjugated microporous polymers (CMP), hyper crosslinked polymers (HCP), porous aromatic framework (PAF), *etc.*

2.1.1. Crystalline porous materials

Covalent organic frameworks (COFs) are a new class of crystalline porous polymers with highly adjustable structures and functionalities. During recent years, researchers have pay attention to the rational design of COF-based membranes to achieve accurate and rapid membrane separation [34]. To date, many strategies have been developed to construct thin COF film, including in situ growth [35,36], vacuum-assisted filtration [37,38], electro polymerization [39], *etc.* All of them have the difficulty in obtaining large-scale membranes. Interfacial polymerization (IP) is a method suitable for large-scale synthesis of polymer films like polyamides and polyesters. At the water-dichloromethane (DCM) interface, Banerjee *et al.* [40] initially prepared a series of crystalline β-ketoenamine-linked COFs membranes with different thicknesses (50–200 nm) by IP. These nanostructured thin COF films demonstrated an ultrafast acetonitrile permeance of 339 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ (Fig. 2(a)). Chung *et al.* [41] developed an effective and simple method to construct flexible and free-standing COF membranes at room temperature and atmospheric pressure *via* IP. TAPA-TFP membrane had a methanol permeance of 241.9 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$, which was about four times that of existing polyamide nanofiltration membranes. The separation performance of high solute (>13 Å) was mainly based on the size-exclusion and shape selection (Fig. 2(b)). Despite these initial research advancements, it is still challengeable to achieve fine tuning of pore size. Ma *et al.* [42] reported a simple and scalable approach for growing large-area, flexible, independent COF membranes via IP (Fig. 2(c)). By changing the stacking mode of COF layers, the pore sizes of the membranes could be adjusted from >1 nm to sub-nm scale, which greatly improved the selectivity of COF membranes. However, with large pore size and limited pore connectivity, 2D COF membranes showed an inefficient selectivity for OSN. Wang *et al.* [43] proposed a 3D COF membrane, which enabled the construction of sub-nanoscale anti-swelling channels with high selectivity (Fig. 2(d)). In particular, it maintained a high and stable methanol permeability after operation for over 1000 h, showing its great utility for practical applications. In addition, they reported the synthesis of 3D-OH-COF on mesoporous CPI supports by solvothermal method. The membrane showed high crystallinity and narrowed pore sizes, enhancing selectivity for small molecules [44]. Especially, the 3D-OH-COF membranes had excellent chemical stability at extreme conditions. However, how to well coordinate processing-high crystallinity -high selectivity is still a major challenge. Jiang *et al.* [45] proposed a concept of heterocrystalline membranes comprised of high-crystalline regions and low-crystalline regions (Fig. 2(e)). Therefore, the COF membrane exhibited precise molecular sieving properties. Besides, the organic solvent permeance was up to 44-times that of the state-of-the-art membranes. Overall, the COF membranes demonstrate ultrafast separation performance, with many of them breaking the performance records in the literature. However, limited by the poor processibility in large-scale, high brittleness, and unsatisfied crystallinity, the development of COF membranes is still in its early stage [46].

2.1.2. Amorphous porous organic polymers

PIMs are special polymers, which relies on their own rigidity and nonplanar distorted structure of molecules to obtain high free

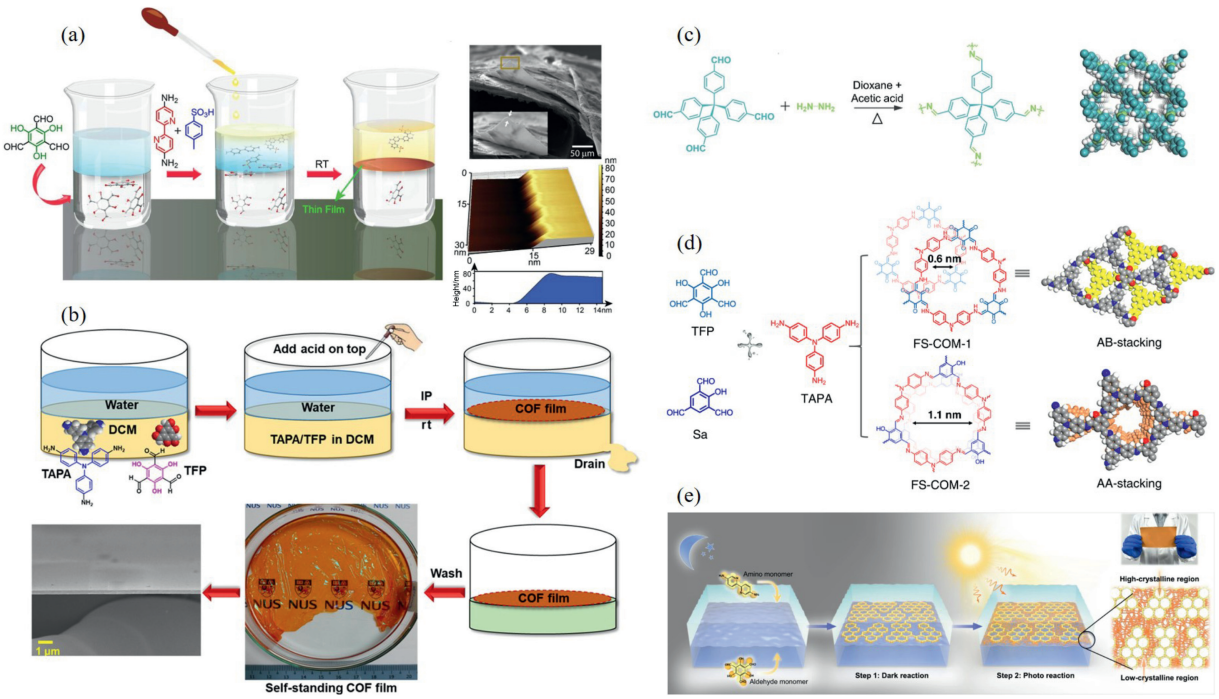

Fig. 2. (a) Synthesis scheme of Tp-Bpy thin films. Reproduced with permission [40]. (b) Fabrication process of the self-standing COF membranes. Reproduced with permission [41]. (c) Fabrication process of two free-standing COF membranes. Reproduced with permission [42]. (d) Synthesis and characterization of TFPM-HZ. (e) Fabrication of the hetero-crystalline COF membranes. Reproduced with permission [43].

volume and microporosity [47–50]. Compared to conventional polymer membranes, PIM membranes exhibit high permeance with a molecular weight cut-off of 190–650 $g \cdot mol^{-1}$. However, these inner polymers are subjected to swelling in small organic molecules, causing the decrease of separation performance. Usually, cross-linking is a common method to ensure membrane stability in a wide range of organic solvents. For instance, Choi *et al.* [51] reported a PIMs-based TFC hollow fiber membrane by intermolecular cross-linking and improved its stability in organic solvents (Fig. 3(a)). The membrane exhibited pure ethanol permeance of 10.9 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ with MWCO of 952 $g \cdot mol^{-1}$. Even after 7 days of immersion in ethanol, acetone, and toluene, the membrane showed stable rejection performance (>95%). However, despite the improvement of membrane stability, membrane crosslinking also affects the permeability due to the dense pore structure. McKeown *et al.* [52] found that introducing contorted monomer can effectively frustrate chain packing and rigidify ladder-type polymer structures. Inspired by this, Szekely *et al.* [53] reported three solution-processable iPEEKs using three different contorted monomers and 4,4′-difluorobenzophenone (Fig. 3(b)). The MWCO of the membranes was adjusted in the range of 450–845 $g \cdot mol^{-1}$, showing higher permeance (3.57–11.09 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$). Similarly, Thompson *et al.* [54] selected a spirodifluorene dibromo compound to react with a series of aromatic amines (Fig. 3(c)). The total retention rate of the SBAD-1 membrane was more than 60%, and it can effectively reject hydrocarbons with >12 carbon numbers in crude oil (boiling points higher than 200 °C). In addition, the swelling resistance of PIM membranes could be improved by thermal treatment and carbonization [55,56]. Szekely *et al.* [57] prepared ISA-CMS membranes using intrinsically microporous 6FDA-DMN pyrolyzed at different temperatures (Fig. 3(d)). The membrane based on the CMS showed excellent stability without swelling in organic, acidic, or basic media. In general, the physical aging, solvent resistance and swelling for PIM-based OSN need to be studied in detail.

Conjugated microporous polymers (CMP) are a unique class of porous organic materials with π-conjugation structures and intrinsic micropores. Most CMPs are insoluble in common solvents like DMF, DMSO, THF, acetone and so on. On the one hand, this property is conductive to solvent resistance, and on the other hand, it is difficult to fabricate CMP membranes by most common solution-based processes [58]. Since the discovery of the first CMP in 2007, various synthesis routes have been developed [59]. Liang *et al.* [60] used the surface-initiated polymerization strategy to prepare CMP membranes (Fig. 4(a)). Composed of only chemically inert C–C and C–H bonds, the all-rigid porous CMPs membranes exhibited high performance in OSN with a MWCO of 560 $g \cdot mol^{-1}$. Zhou *et al.* [61] reported an electro polymerization process to prepare a CMP membrane, in which rigid carbazole monomer was inside a robust carbon nanotube scaffold (Fig. 4(b)). The difference between MWRO and MWCO was only 240 Da. Especially, in 2022 our group developed a solution-processable strategy to fabricate C–C bonded CMP membranes by two-stage polymerization (Fig. 4(c)) [62]. When used in OSN, these CCMP membranes had high permeance for polar organic solvents and good rejection for molecules between 300 and 500 $g \cdot mol^{-1}$ (>85%). The strategy opened up the possibility of CMP membrane in large scale. Under mild conditions, Li *et al.* [63] reported a 31 nm-thick CMPnanofilms supported on porous substrates *via* IP (Fig. 4(d)). The water permeance of DHA-MPD membranes was up to 240.0 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ and a retention of 98.3% for brilliant blue R. The rigid CMP structures gives the membrane unique pore architecture and excellent solvent stability, but at the expense of the flexibility and mechanical strength of the membranes [58]. Overall, the development of CMP membrane still remains in its fancy.

Hypercrosslinked polymers (HCPs) and porous aromatic frameworks (PAFs) with their exceptional stability and structural flexibility are suitable for a wide range of separations. However, kinetically irreversible coupling reactions for HCPs or PAFs

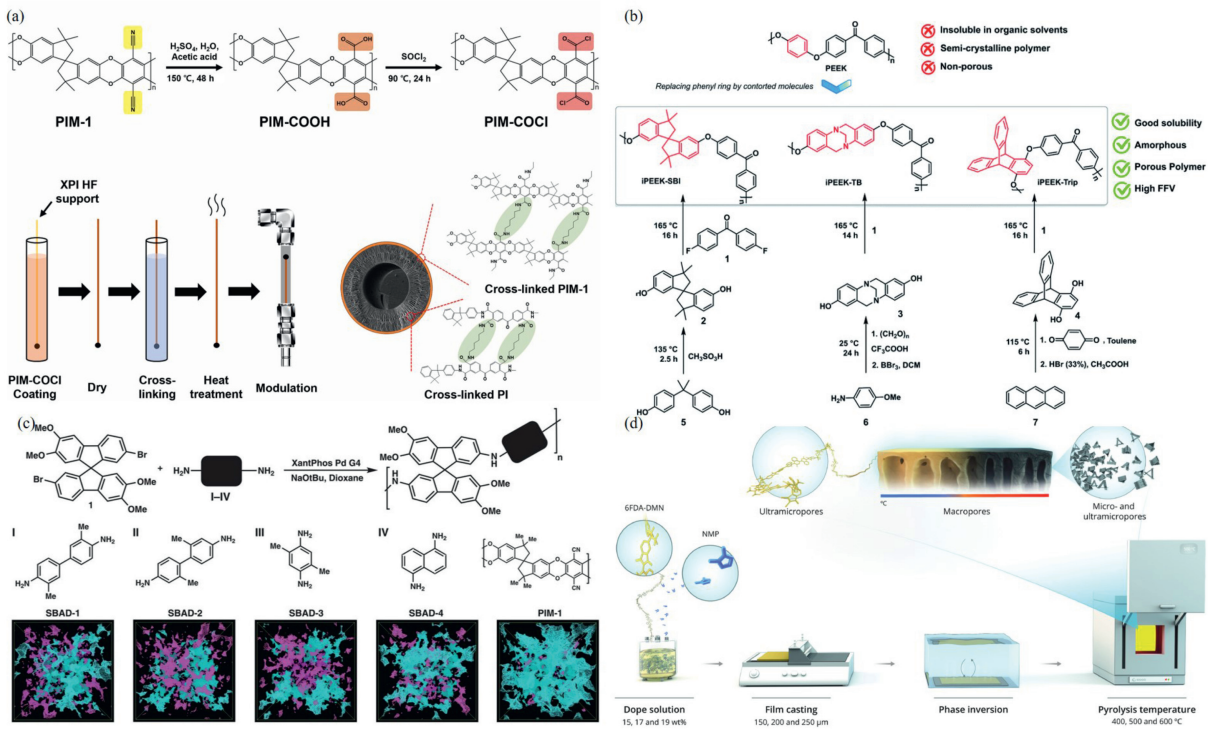

Fig. 3. (a) Schematic illustrations of XPIM TFC HF membrane preparation. Reproduced with permission [51]. (b) Synthetic route for iPEEKs. Reproduced with permission [53]. (c) Synthetic route for SBAD-1 to SBAD-4. Reproduced with permission [54]. (d) Schematic of ISA-CMS membranes. Reproduced with permission [57].

synthesis has resulted in the unpredictable connection of building units [64]. Currently, the majority of HCP-based or PAF-based membranes are constructed with powder and polymeric matrices [65]. To our knowledge, there are few reports to apply them for molecular separation in the liquid phase [67].

2.2. Traditional polymer membranes

Generally, the traditional membranes for OSN applications can be divided into two categories: (i) integrally skinned asymmetric (ISA) membranes, composed of a skin layer on the sublayer with the same composition. The top skin layer is formed at the same time as the underlaying support layer. The thin skin layer affects the final membrane performance [20]. (ii) Thin film composite (TFC) membranes, consisting of an ultra-thin selective layer deposited on the support with different chemical composition. Therefore, the ultra-thin dense barrier layer and the porous support layer can be individually designed and assembled to optimize the performance of the membranes [67].

2.2.1. Polymers for ISA membranes

The polymer materials for preparing ISA OSN membrane include polyimide (PI) [68], polybenzimidazole (PBI) [69], polyacrylonitrile (PAN) [70], polyaniline (PANI) [71], *etc.* These traditional polymers

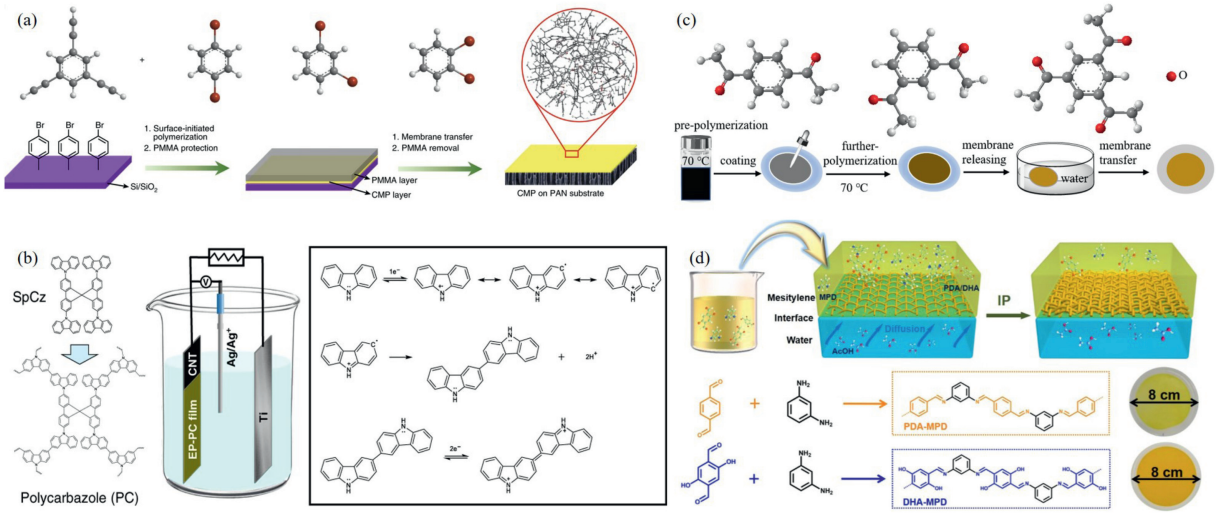

Fig. 4. (a) Surface-initiated polymerization of the CMP membrane. Reproduced with permission [60]. (b) The electro polymerization process of CMP membrane. Reproduced with permission [61]. (c) Two-stage polymerization towards CCMP membranes. Reproduced with permission [62]. (d) Fabrication of the CMP membranes via IP. Reproduced with permission. Reproduced with permission [63].

are widely used in OSN due to their solution processability and mechanical properties. However, there are still key challenges for polymer membranes including physical aging, membrane swelling and compaction [3]. In order to improve the stability of ISA membranes in harsh solvent environments, many crosslinking modification methods have been proposed. Chung *et al.* [72] developed a green crosslinking method to fabricate high-flux ISA PBI membranes for OSN (Fig. 5(a)). The X-PBI membrane shows a rejection of 99.6% to Remazol brilliant blue R (MW of 627 $g \cdot mol^{-1}$). And the permeability of pure acetone, acetonitrile, isopropanol and ethanol at 10 bar was 29.0, 40.7, 5.8 and 13.8 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$, respectively. In addition to chemical crosslinking with crosslinking agents, Nunes *et al.* [73] combined the typical NIPS and thermal crosslinking to prepare polytriazole asymmetric membranes with ultrathin selective layers (Fig. 5(b)). With interconnected free volume, the polytriazole polymer membrane showed high selectivity for hydrocarbons. The membrane can enrich more than 95% of hydrocarbons with less than 10 carbon atoms (MW < 140 $g \cdot mol^{-1}$), which shows great application potential for crude oil fractionation. By *in-situ* polymerization of dopamine, Zhao and co-workers [74] fabricated an interpenetrating polymer network in the PBI membrane matrix (Fig. 5(c)). By controlling the polymerization time, the pore size and the MWCO values could be adjusted. The membrane had good robustness and stability in seven polar aprotic solvents from −10 °C to 100 °C. Through Cu^{2+} crosslinking, Jin *et al.* [75] formed ISA polyimide membranes for OSN (Fig. 5(d)). The membranes showed good stability in organic solvent such as toluene, DMF, acetone, methanol, acetonitrile, *etc.*, with >99% rejection for Coomassie brilliant blue. With crosslinking with the metal ion, the compaction resistance and the polymer-chain rigidity of the membrane was greatly improved. However, the intrinsic disadvantage of the ISA membrane is that the crosslinking process increases the barrier layer thickness, resulting a higher mass transfer resistance.

2.2.2. Thin-film composite (TFC) membranes

Thin-film composite (TFC) membranes typically consist of an ultrathin dense layer and a porous support layer, which can be designed separately to optimize the membrane performance. Generally, the nature of the barrier layer plays a vital role on the separation performance [76,77]. Here, we just discuss about the selective layer. Interfacial polymerization (IP) is a large-scale method to synthesize the active layer [78]. Livingston *et al.* [79] synthesized highly cross-linked sub-10 nm polyamide nanofilms on a sacrificial layer of cadmium hydroxide nano strands by interfacial polymerization of diamine and acid chloride (Fig. 6(a)). With an ultrathin selective layer, the film showed high permeance for acetonitrile (112 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$). Increasing microporosity of selective layer to reduce the mass transfer resistance is another effective way to achieve high-performance membranes. Livingston *et al.* [80] synthesized 20 nm polyarylate nanofilms with high microporosity and interconnectivity on ultrafiltration supports via interfacial polymerization (Fig. 6(b)). Although the permeability can be increased with contorted monomers, the selectivity is usually sacrificed due to wide distribution of pore size. Therefore, some researchers turn their attention to macrocyclic molecules for the improvement of permeability and selectivity simultaneously. Peinemann *et al.* [81] employed the macrocycle, cyclodextrin (CD), as the building block for the selective layer (Fig. 6(c)). With both hydrophilic and hydrophobic domains, the β-CD film showed high permeability for polar and non-polar solvents. Interestingly, the film can discriminate small molecules based on their shapes. Chung *et al.* [82] constructed the precise molecular sieving nanofilms with Janus pathways *via* interfacial reaction between CD and TMC (Fig. 6(d)). The newly designed CD/TMC nanofilms possessed high permeances for both polar (methanol, 4.9 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) and nonpolar solvents (*n*-hexane, 6.3 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$). Solution coating is versatile and large-scale method to modify UF membranes for OSN [83]. Chuang *et al.* [84] fabricated PMIA substrates via an environmentally benign ionic liquid and followed by the thin-film selective layer for OSN (Fig. 6(e)). When the concentrations of HPEI and GA were reduced by 0.5% to 1%, the ethanol permeability of composite membranes was 3.2–21.4 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$, and the MWCO value was 470–730 $g \cdot mol^{-1}$. More importantly, this work offers a green and sustainable method to design environmentally benign

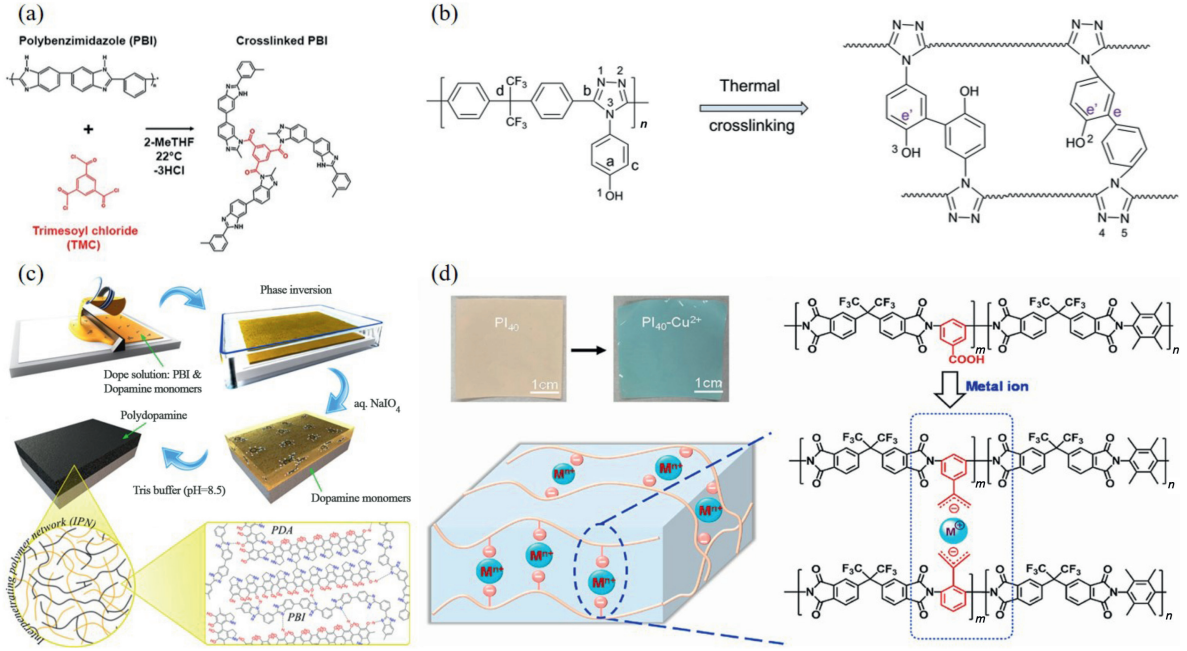

Fig. 5. (a) The crosslinking reaction mechanism of PBI membranes. Reproduced with permission [72]. (b) Thermally crosslinking mechanism of PTA-OH membranes. Reproduced with permission [73]. (c) PDA/PBI IPN membranes. Reproduced with permission [74]. (d) Polyimide membranes crosslinking with Cu^{2+}. Reproduced with permission [75].

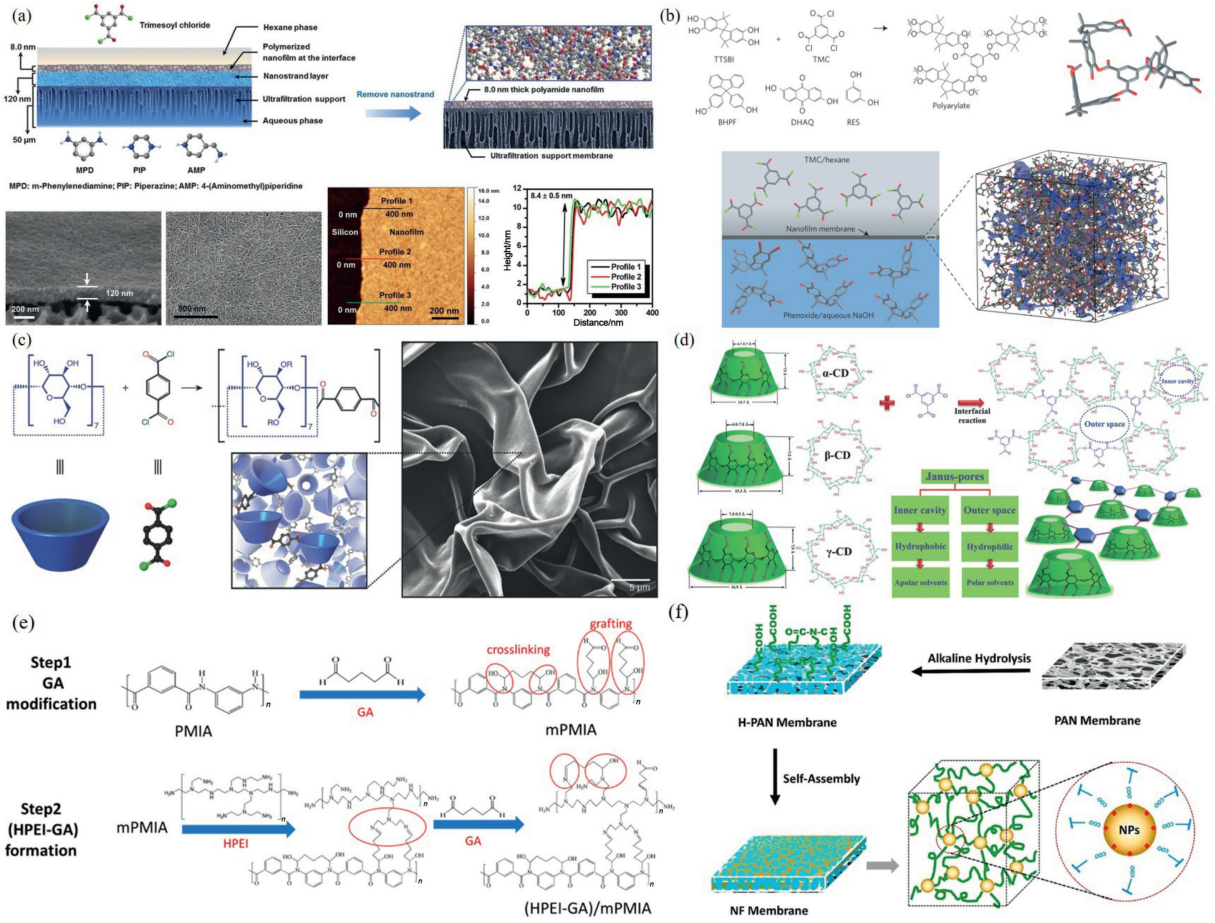

Fig. 6. (a) Description of the interfacial polymerization process for sub-10 nm nanofilms. Reproduced with permission [79]. (b) Synthesis of polyarylate nanofilms through IP. Reproduced with permission [80]. (c) β-CD films made by interfacial polymerization. Reproduced with permission [81]. (d) Chemical structures of the CD/TMC nanofilms. Reproduced with permission [82]. (e) Proposed reaction mechanism of (HPEI-GA)/mPMIA composite membranes [84]. (f) The fabrication process of the composite membrane. Reproduced with permission [85].

composite membranes for OSN. Zhu *et al.* [85] constructed separation nanochannels based on the strong electrostatic interaction between nanoparticles and the hydrolyzed PAN (HPAN) substrate *via* a one-step coating method (Fig. 6(f)). In addition, the membrane showed excellent separation performance for dyes with specific MW.

3. Strategies Developed for Permselective Nanofilms

By taking the advantages of the rapid development of new materials and chemical synthesis, several strategies have been established to regulate the separation efficiency including: (i) decreasing the thin-film thickness, (ii) designing an exact pore size/structure, (iii) improving the free volume/microporosity, (iv) regulating the membrane surface chemistry and (v) manipulating the surface morphology.

3.1. Thin-film thickness

Solvent permeance is usually inversely proportional to the thickness of the nanofilm. Therefore, the design of ultrathin films can potentially improve the permeability of the membranes. Introducing an extra layer onto the substrate layer is an effective way to manipulate the thickness of the active layer [86,87]. Livingston *et al.* [79] synthesized sub-10 nm polyamide nanofilms on a sacrificial layer of cadmium hydroxide nano strands by interfacial polymerization of diamine and acid chloride (Fig. 6(a)). Due to the controlled release of aqueous diamine, the thickness of the PA nanofilm can be controlled at sub-10 nm. Therefore, the methanol permeability of the PA nanofilm reached 52.2 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$, which was two orders of magnitude higher than that of commercially available OSN membranes. Introducing other hydrophilic nanomaterials as the interlayers can also effectively control the IP process and achieve an ultrafast solvent permeance, including graphene quantum dots (GQDs) [88], graphene oxide (GO) [89], *etc.* *Via* interfacial polymerization on the porous substrate modified by crosslinked GO nanosheets, Li *et al.* [89] reported a novel sandwich-like thin film nanocomposite OSN membranes (Fig. 7(a)). With hydrophilic selective layer and ultrathin thickness (about 15 nm), the TFN OSN membranes had a high ethanol permeance (41.47×10^5 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) and rejection for rhodamine B (>99.4%). Adjusting the reactivity of monomer with ionic liquid (IL) as the solvent is another method to manipulate the thickness of thin-film [90]. Tang *et al.* [91] synthesized polyamide nanofiltration membrane with a thickness of below 10 nm through IP of ethidium bromide (EtBr) and trimesoyl chloride (TMC) (Fig. 7(b)). Due to the extremely low solubility of the EtBr monomer in water, the polymerization process only occurred at the interface of the aqueous phase and the organic phase, thus forming a sub-10 nm thick film. When used for nanofiltration, these membranes displayed ultrahigh water permeation (40 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) and a high Congo red retention rate (~93%). Recently Zhan *et al.* [92] developed a new

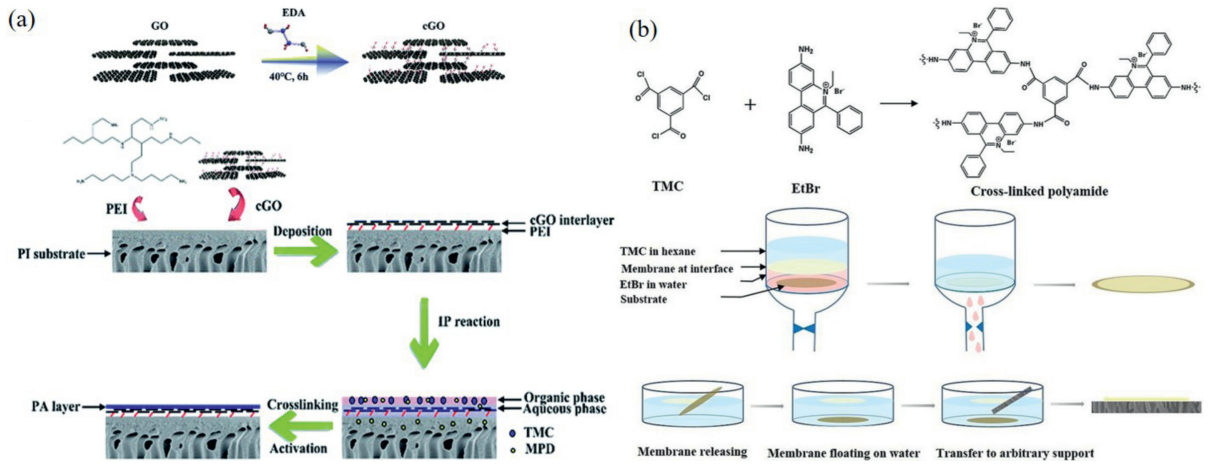

Fig. 7. (a) Schematic illustrations for the fabrication of cGO-interlayered OSN membranes. Reproduced with permission [89]. (b) The fabrication process of the ultrathin polyamide membrane. Reproduced with permission [93].

way of adding metal ions to reduce the monomer diffusion rate to form a thinner polyamide layer (~33 nm) with higher permeance (3.2 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$). However, reducing the thin-film thickness is usually at the cost of the mechanical strength.

3.2. Pore size

Since OSN is membrane separation process based on size exclusion, a well-defined pore size of the skin layer is essential for selective separation. Monomers with inherent microporosity have the potential to design precise pore structures. Peinemann *et al.* [81] employed the macrocycle, cyclodextrin (CD), as the building block for the selective layer to achieve precise separation over the size and shape (Fig. 6(c)). Interestingly, the film can discriminate small molecules based on their shapes. Similarly, Chung *et al.* [82] constructed the precise molecular sieving nanofilms with Janus pathways *via* interfacial reaction between CD and TMC (Fig. 6(d)). The newly designed CD/TMC nanofilms possessed high permeances for both polar (methanol, 4.9 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) and nonpolar solvents (*n*-hexane, 6.3 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$). However, non-functionalized macrocycles have indistinguishable reactivities and thus disordered packing in films, which hinders the interconnection of the cavity and formation of through-pores [93]. Huang *et al.* [67] fabricated an ultrathin 2D-layered macrocycle membrane using per-6-amino-β-cyclodextrin as a monomer by interfacial polymerization (Fig. 8(a)). Because the amino groups of the modified CD have high reactivity, the membrane can be quickly formed *via* interfacial polymerization with low reactant concentration under mild conditions. Based on the different reactivity of selectively functionalized macrocycles, Livingston *et al.* [94]synthesized an ultrathin nanofilm with well-defined pores (Fig. 8(b)). Compared to disordered macrocyclic membranes, aligned macrocycle membranes offered twice the methanol permeance and higher selectivity, demonstrating their potential for precise molecular separation. This method provides a viable strategy to create sub-nanometer channels in polymer membranes.

3.3. Free volume/microporosity

In addition to control the pore size/structure of the nanofilms at the molecular level, another strategy is to create more free volumes. Therefore, PIMs attract more attention for OSN. Due to the inefficient packing of the monomers, the resulting amorphous polymer chains have a contorted structure with interconnected microporosity [95]. These monomers have highly rigid and contorted structures, such as: triptycene-, spirobisindane-, ethanoanthracene-, and Tröger's base-building blocks. To achieve tunable free volumes, Ali *et al.* [96] recently reported the preparation of TFC membranes with fine-tuned sub-microporosity (pore size <0.4 nm) using a bridged-bicyclic triptycene *tetra*-acyl chloride (Trip) as organic monomer (Fig. 9(a)). Compared to current commercial membranes, the TFCs can remove small organic molecules (~200 $g \cdot mol^{-1}$) from organic solvent streams, demonstrating better retention rate and permeability in organic systems. Unlike the method of creating a rigid network skeleton, the introduction of flexible chains in the polymer films is another strategy to regulate the free volume of the skin layer. Li *et al.* [97] reported a flexible aliphatic–aromatic polyamide TFC membrane as in Fig. 9(b). The flexible aliphatic chains in the polyamide network allowed the selective layer with an adjustable free volume in different organic solvents. The membrane can accurately separate two molecules with a molar mass difference of <166 $g \cdot mol^{-1}$ in DMSO. However, due to the inherent flexibility of the backbone and reactivity of the linkers, the structural and chemical stability of these polymer membranes is still insufficient.

3.4. Surface chemistry

The interactions between the solvent and the membrane surface have an important effect on the transport efficiency. In general, the more hydrophilic the surface, the stronger its affinity to the polar solvents, and *vice versa*. Thus, modulating the membrane surface affinity is necessary to increase permeance. By filtering the TFC membrane with an activating solvent for 10 min, Livingston *et al.* [98] found that the solvent permeability of a PA membrane prepared from MPD/TMC can be greatly improved. This resulted in greatly enhanced fluxes without compromising rejection. Besides, Livingston *et al.* [99] also prepared a pollution-resistant organic solvent-stabilized PBI membranes by surface grafting with linear poly (ethylene glycol) and poly (propylene glycol). In water, the hydrophilic PEG graft modifier had good modifier-water interactions and formed a steric layer on the surface of the film. Unfortunately, it usually created an extra barrier layer that impaired the permeability of the solvent. The electrostatic repulsion between ionic solutes and membranes could also affect the molecular transportation of OSN membranes. Wu *et al.* [100] reported an oriented ionic COF membrane by stacking -SO_3 functionalized COF nanosheets layer by layer. The *oi*-COM had a

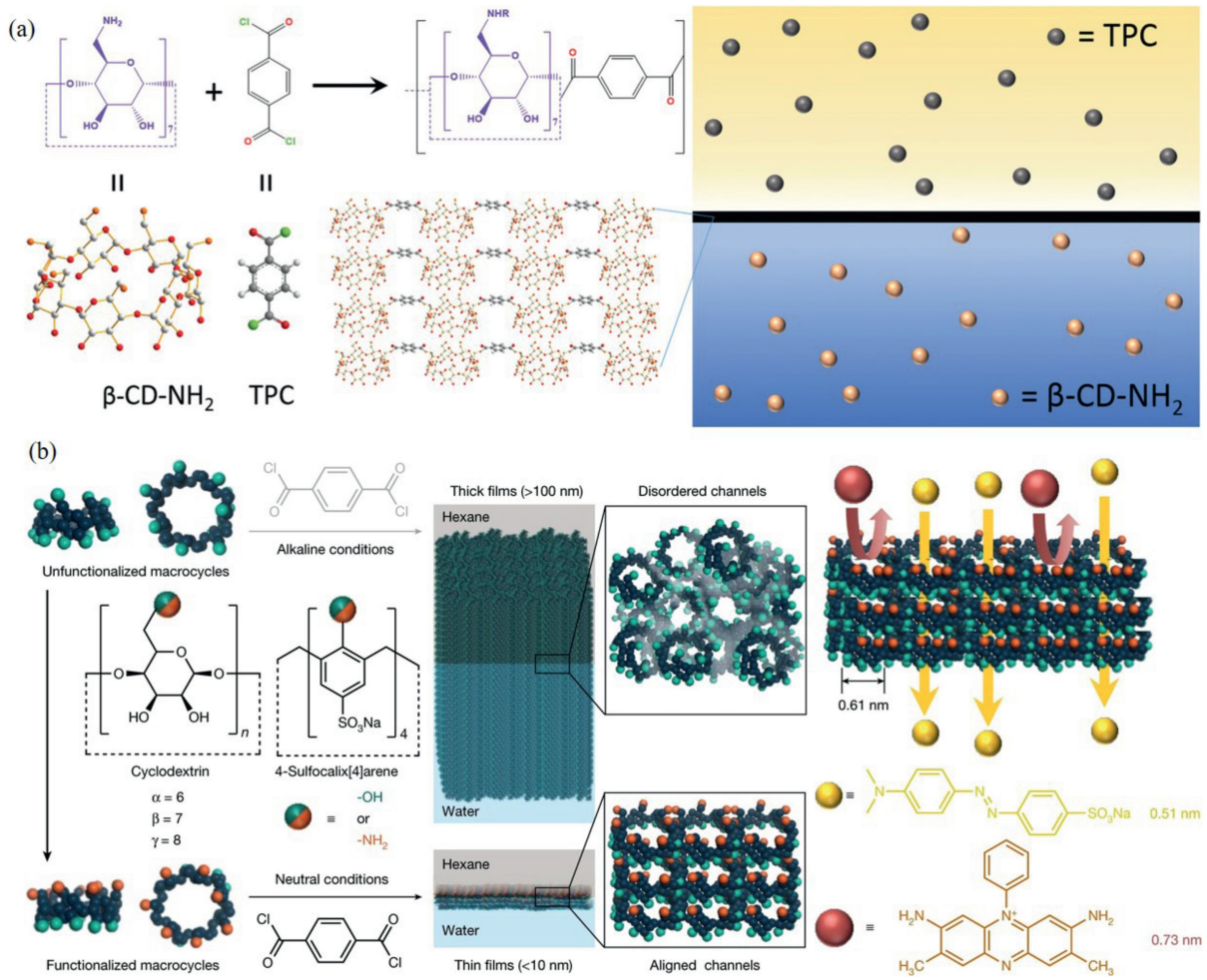

Fig. 8. (a) IP of polyamide–CD films. Reproduced with permission [66]. (b) Fabrication of ultrathin polyamide nanofilms. Reproduced with permission [94].

rejection rate of above 99% for negatively charged dyes with the solvent permeance for ethanol of 63 L $m^{-2} \cdot h^{-1} \cdot bar^{-1}$, much higher than that for positively charged dyes with similar molecular size. These results show that the OSN performance can be effectively improved by increasing the electrostatic repulsion force.

3.5. Surface morphology

The surface morphology has a significant influent on the separation efficiency of OSN. Chen *et al.* [101] proposed a method to regulate the surface morphology of the polyamide composite films

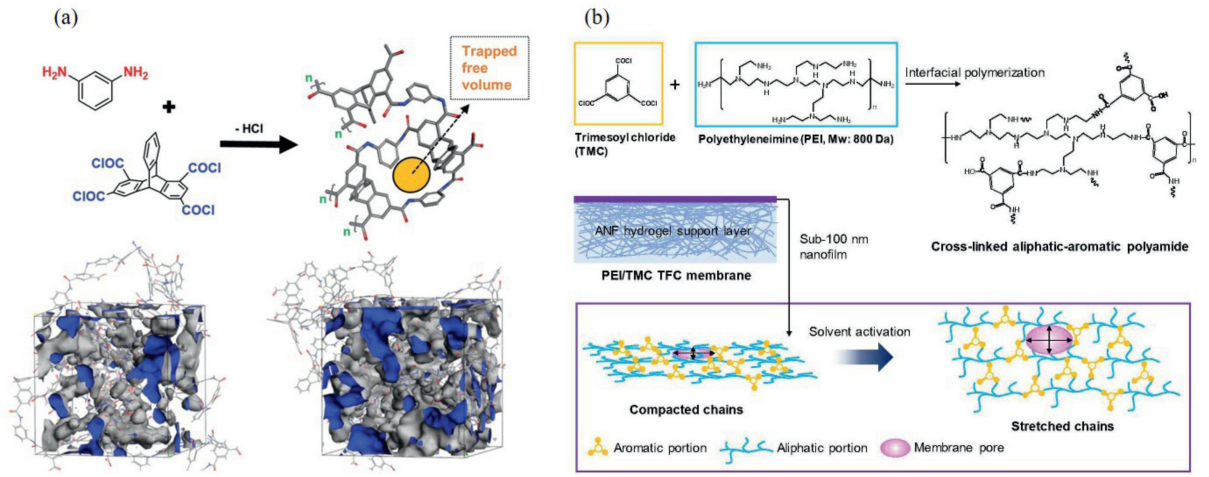

Fig. 9. (a) Scheme of interfacial polymerized polymers. Reproduced with permission [96]. (b) The fabrication of PEI/TMC TFC membrane. Reproduced with permission [97].

with ridge-valley morphology by introducing $CuCl_2$ as a reaction modifier into the IP process. The ridge-valley morphology increases the contact area between the membrane and the solvent, which lays the foundation for increased solvent permeability. The methanol permeation of the TFC-Cu_{100} membrane was 13.27 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$, which was 65.46% higher than that of the unmodified one. Gao *et al.* [88] introduced af-GQDs into the aqueous phase MPD solution to construct a smooth-surfaced baseline TFC OSN film. The af-GQDs nanomaterials could regulate the interfacial polymerization process, which provide more channels for solvent permeability. Especially, by using an ice-melting–induced ice/water phase transition, Zhang *et al.* [102] proposed an ice-confined interfacial polymerization strategy for the synthesis of a highly ionized, 3D-quasilayered PA NF membrane (Fig. 10). The IC-PANF membrane with regular wrinkled structures was coarser than the C-PANF membrane, resulting in a 2-fold increase in the surface area of the IC-PANF membrane. This led to excellent water permeability and ion selectivity, such as the separation of chloride ions from sulfate.

4. Commercial Membrane Technology for OSN

The main processes that membrane technology can implement are (i) concentration, recovery of high-value solutes from diluted solutions *(e.g.*, enrichment of solutes from chromatographic penetrants) or recovery of solvents by removal of impurities dissolved in them (solvent recovery); (ii) solvent exchange, in particular the exchange of high-boiling solvents for low-boiling solvents; (iii) purification/fractionation of high-value products, especially useful in homogeneous catalysis.

The most commercially available membranes for OSN are polydimethylsiloxane (PDMS) or polyimide-based membrane [103]. In the mid-1990s, PDMS membranes began to be used for organic solvent applications, such as Koch Membrane Systems. The membrane, which consisted of PDMS coated on crosslinked PAN support, can be used to separate triglycerides from alkanes, recover catalysts from organic solvents, and exchange solvents in pharmaceutical process. However, after continuous operation for more than 10 days, the membrane was unstable in organic solvents. In the late 1990s, polyimide OSN membranes began to be commercialized. White *et al.* [104] applied the polyimide membrane for the recovery of lube oil dewaxing in the refining industry. The membrane-based separation process provided a higher lube oil yield, while simultaneously reducing energy consumption and cooling water use, and potentially decrease volatile organic emissions from the dewaxing operation (Fig. 11). By recovering and recycling dewaxing solvents, each plant could reduce fuel oil consumption by 36000 barrels per year and greenhouse gas emissions by about 20000 tons per year [105]. This process provided a low capital method for expansion of solvent dewaxing units, but it eventually became obsolete due to changes in the lubricant oils market.

In 2008, the membrane extraction technology (MET) introduced crosslinked polyimide membranes [106]. DuraMem membrane modules were applied to purify model solutions containing product (SY7) and impurity (BB) in DMF (Case Study A), and organic synthesis solutions containing API intermediate (API-INT) from its oligomeric impurities in THF (Case Study B). The DuraMem300 membrane modules were tested in DMF for 10 days and in THF for 120 days, and the results showed that the membrane modules had

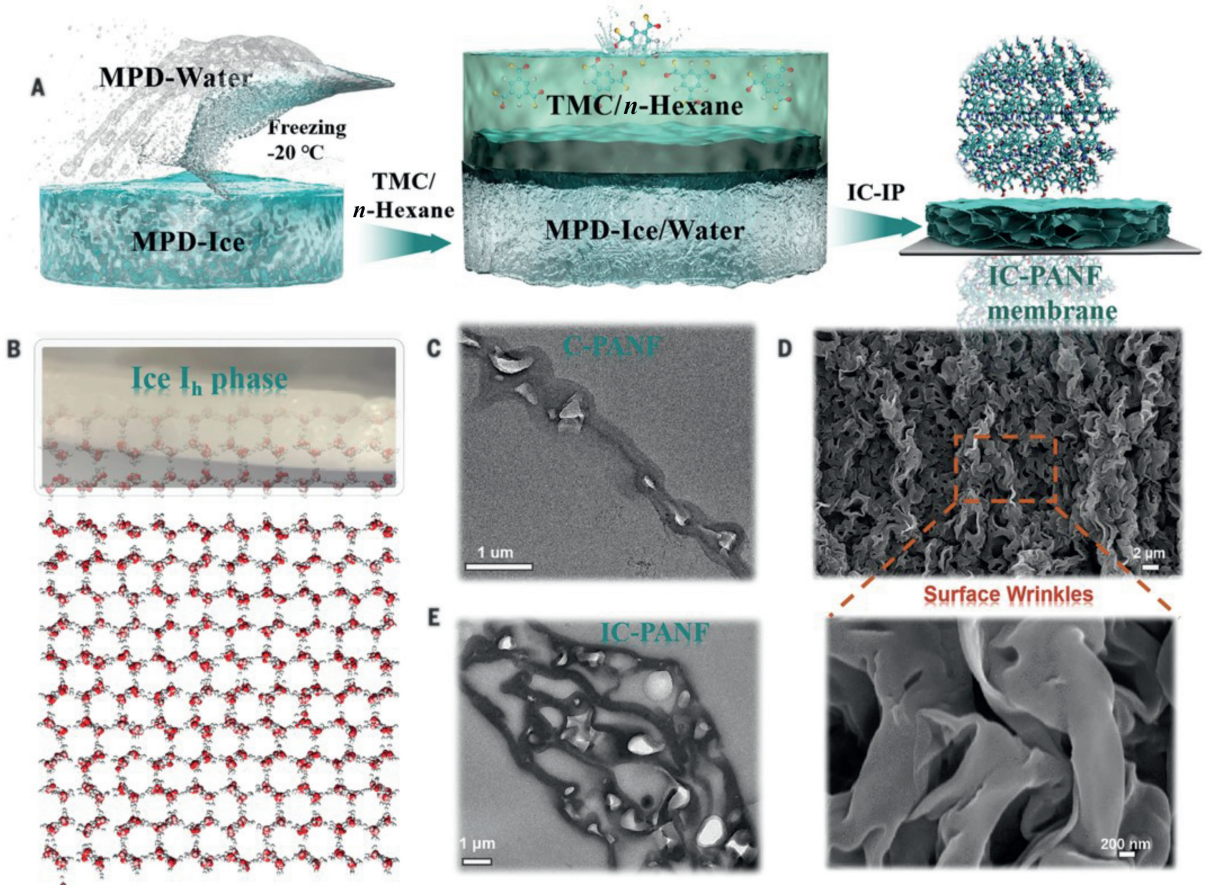

Fig. 10. Ice-confined interfacial polymerization process and PA NF membrane structure. Reproduced with permission [102].

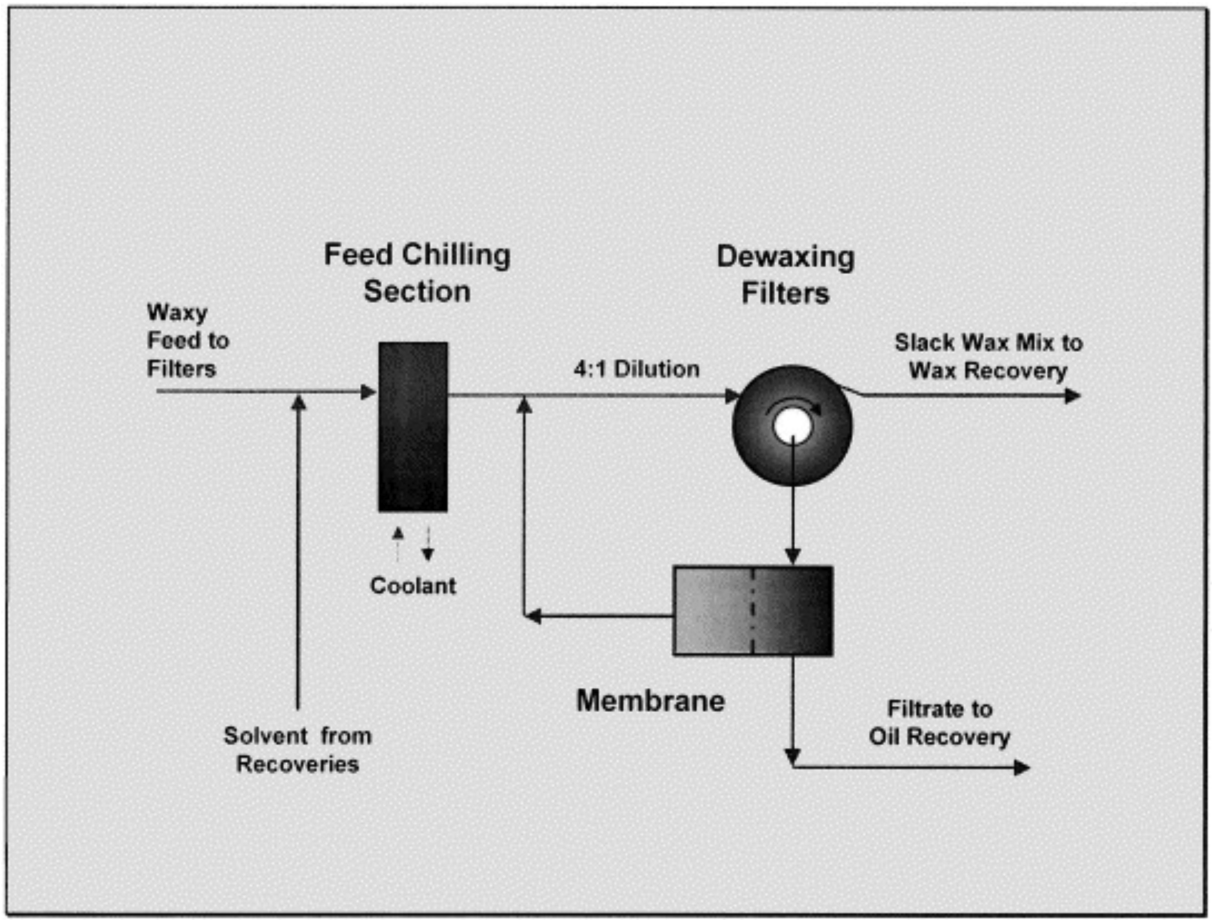

Fig. 11. Membrane separation of cold solvents from lube oil filtrate. Reproduced with permission [104].

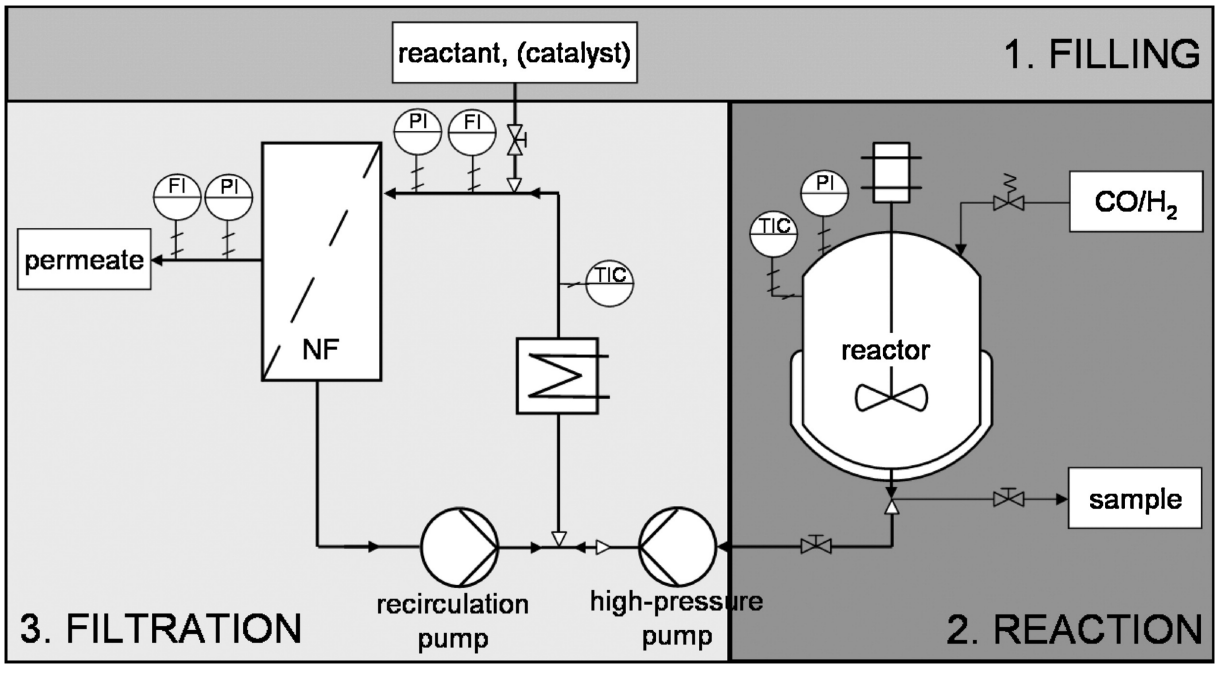

Fig. 12. Schematic diagram of hydroformylation experimental apparatus.

stable separation efficiency. In addition to PDMS and polyimide membranes, other polymers have been used industrially for membrane market. Founded in 2007, PoroGen manufactures PEEK membranes for volatile organic carbon reduction, natural gas purification, and filtration of strong solvents [107]. Perfluoro-2,2-dimethyl-1,3-dioxole copolymerized with tetrafluoroethylene (PDD-TFE) membranes from Compact Membrane Systems have been used in OSN and for OSRO separation of NMP and DMF from toluene [108].

In 2010, Nair *et al.* [109] assessed and evaluated the efficiency of palladium Heck catalysts in a cyclic intermittent recovery process using OSN membranes. Based in the findings, Priske *et al.* [110] used the single-stage membrane separation to achieve 99% rejection rate by using the OSN continuous process (Fig. 12), and recovered the Rh catalyst in the high-olefin hydrogenation reaction. This technology has been successfully applied on an industrial scale, such as Evonik Industries AG, for the removal of homogeneous catalysts.

Although great progress has been made for OSN membranes, most commercial membranes are not stable enough to meet the practical requirements. The ideal membrane needs to meet the requirements of the specific applications, such as high permeance and selectivity. In addition, polymer membranes must be able to work under challenging conditions, such as mixed organic solvents, high temperatures (above 120 °C), extreme acid or alkali conditions, and reducing/oxidizing environments. At current, the majority of commercial membranes cannot fulfill the above requirements. Therefore, there is a need to develop more stable membranes for new chemical industry processes.

5. Conclusions and Perspectives

We have summarized the recent development of polymer membranes for OSN for traditional and emerging polymer materials. Despite these advances, there are still some challenges in the application of OSN membranes, which can be summarized in the following aspects: (i) The trade-off effect between the permeance and the selectivity. It is difficult to achieve a good rejection for smaller molecules with MW < 400 Da with a high solvent permeance simultaneously [111]. (ii) Precise molecular separation. By regulating the membrane thickness and the microporosity, it is expected to achieve ultrafast permeance. However, it is still challenging to separate solvents of similar size, such as isomers or mixtures form azeotropes. (iii) Membrane stability. Most studies were focused on OSN in organic media with mild polarity, such as ketones, alcohols and aromatics. The stability in mixed organic solvents, high temperatures (above 120 °C), extreme acid or alkali conditions, and reducing/oxidizing environments is scarcely reported. (iv) Scalable fabrication process. The methods of membrane fabrication must be feasible for mass production, such as NIPS, solution-casting, and IP in seconds than minutes. There are obvious disadvantages for microporous materials with excellent properties, such as graphene, carbon nanotubes, MOFs, and COFs. Besides new stable material development, there is limited knowledge for separation mechanism. Understanding the separation mechanisms will provide guidance for rational design and synthesis of OSN membranes based on the molecules of physicochemical properties, such as size, shape, polarity, dipole moment, etc. Close interaction between the academic research and practical applications would help improve greener and more sustainable manufacturing processes.

CRediT Authorship Contribution Statement

Qianwen Su: Writing – review & editing, Writing – original draft, Investigation. Xiuming Zhang: Investigation. Daohui Zhao: Investigation. Ming Li: Writing – review & editing, Writing – original draft, Funding acquisition, Conceptualization.

Data Availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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