



Development of advanced polyamide nanofiltration membrane for water treatment

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Doctoral Dissertation

Development of advanced polyamide nanofiltration
membrane for water treatment

(水処理のための新規ポリアミドナノろ過膜の開発)

July 2023

Graduate School of Engineering
Kobe University

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宋强强

Acknowledgment

Time sure flies! Twenty two school-years were like cut-out scenes, constantly showing in my mind when I recall the moment of carrying the small schoolbag my mother gave me to go to primarily school.....

I was born in one of the poor rural areas in China. Not surprisingly, my family is not rich either. I can still recall the embarrassment of being ashamed to request relatives and friends when I was in middle school without tuition fees. At that time, I didn't know what study means. I just remember that my mother often told me to study hard so that I wouldn't work in the farmland like her. I still remember the days when I was running in the countless rainy scenes with my mother's home-made raincoat sewn from sacks; I still remember the days when I was riding bicycles and galloping on the way to home/school with friends in scorching noon; I still remember the dormitory nights when I was hungry realizing the aroma of instant noodles coming from nowhere. Always a trace of warmth comes first when I think about these days filling with laughter and pains. Now, probably I do not have sufficient courage and boldness to go through those hard days again, but those struggles Golden years always give me the strength to go on.

First of all, please allow me to show my highest respect to Prof. Matsuyama. The successful completion of this dissertation is inseparable from Matsuyama sensei's earnest teaching. Matsuyama sensei's rigorous academic attitude and profound knowledge are worth my lifelong learning. In addition, Takagi sensei seriously guided these research works included in this dissertation. Takagi sensei is knowledgeable and talented, and his insights in every academic discussion always make me feel that I am still a layman even in nanofiltration membrane field although I have been on the academic way for long time. Besides, Takagi sensei and Prof. Matsuyama care me all the time, which make me feel warm in Japan. Here, I would like to express my warmest gratitude to them two and hope they could be healthy and smooth in future life.

Secondly, I would like to express my sincere thanks to Kamio sensei, Ogino sensei and Mori sensei for their extensive efforts dedicated to this doctoral dissertation. In addition, I would like to express my gratitude to Kumagai sensei, Ms. Miyake, Ms. Kamio and Ms. Ono

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Besides, I would like to show my greatest gratitude to my family. My family's constant silent support enables me to concentrate my focus on my works without worrying about any affairs which may occur in my upcoming thirties. Now please allow me to express the highest thanks and gratitude to my mother in Chinese, sorry for any inconvenience may cause.

我的母亲是一位平凡而伟大的女性。妈妈兄弟姐妹六个，她是大姐，小时候便担负起许多本不该大姐承担的劳务。听妈妈说过，在她十几岁时，将扁担的挑子，向相反方向在扁担上缠几圈去挑水的经历；听妈妈说过，她小时候骑自行车，一前一后载着二姨舅舅去务农的经历；听妈妈说过，她读书的时候经常被煤油灯熏得鼻孔都是碳黑的经历；听妈妈说过，当我是一名嗷嗷待哺的婴儿之时，体弱多病，经常性的半夜发高烧，“强强”这个名字寄予了她希望我可以健康成长的希冀……

小时候，妈妈对我严格要求，当时觉得这真是天底下最狠心的妈妈，后来我慢慢的长大，逐渐理解即使是最严厉的苛责背后也都是浓浓的爱意。在日本的这三年，每次妈妈的电话都使我的思乡念亲的情绪得到缓解，看到母亲脸上的沟沟壑壑，也总让我觉得自己这么多年实在亏欠太多。我的母亲受了很多的苦，她的经历就像家珍一样（作家余华笔下的女性角色），其中细细，不在此详述。未来，希望这个坚强又勤劳的女性可以生活轻松，永远年轻。

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Chapter 1

General introduction

1.1 Research background

With the rapid development of social industrialization and urbanization, the world is falling into a situation of water shortage and serious pollution. In the global risk ranking released by the World Economic Forum in 2015, the freshwater resource crisis was listed as the top ten most influential crises in the world. Electroplating plants, steelmaking plants, chemical plants, etc. are all enterprises that consume a lot of water, and they also discharge large amounts of wastewater and pollute into the surrounding water environment the most. The discharge of these wastewaters poses a serious threat to human health [1].

The total volume of water in the world is about 1.4 billion cubic kilometers, of which 2.5% is fresh water. The most of fresh water are snow or ice, then only 0.4% of the fresh water (0.01% of total water) can be directly used [2]. Water resources are extremely scarce, and water resources are seriously polluted, which further exacerbates the freshwater crisis (**Fig. 1.1**). The expansion of the industrial economy around the world has increased human demand for fresh water resources. Water is basically a non-renewable resource, and nature generally relies on its own circulation to purify and reuse water resources. However, the excessive use of fresh water resources and the unrestrained discharge of wastewater have far exceeded the self-repair ability of the earth, resulting in the depletion of available water resources. In order to alleviate the shortage of water resources and improve the water pollution, effective countermeasures are urgently needed for the treatment of sewage and the recycling of industrial wastewater. Traditional separation processes (such as distillation, evaporation and extraction, etc.) have different limitations, and new low-cost and eco-friendly separation methods, such as pressure-driven membrane technologies, are increasingly favored by people [3, 4].

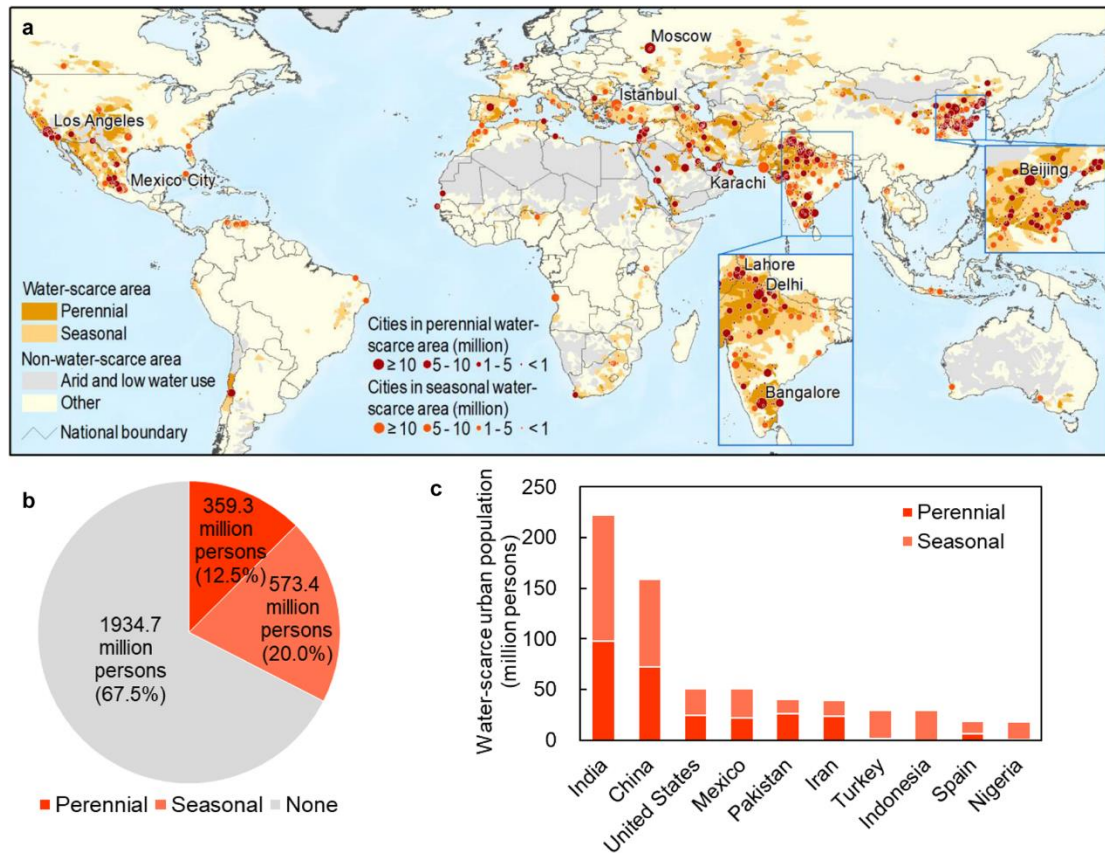


Fig. 1.1 (a) Spatial patterns of large cities in water-scarce areas (cities with population above 10 million in 2016 were labeled); (b) water-scarce urban population at the global scale; (c) water-scarce urban population at the national scale (10 countries with the largest values were listed) [5].

1.2 Membrane and membrane technology

Current membrane separation technology began with asymmetric cellulose acetate membranes by Loeb and Sourirajan in 1960 [6]. The principle of membrane separation technology is to reject or penetrate the target components of different sizes or charge properties, so as to achieve the purpose of separation. Membrane separations are commonly used for water purification or other liquid processing. It has the advantages of high separation efficiency, no phase change, no chemical change, simple design and energy saving. The membrane separation process is driven by external energy or chemical potential difference, and uses the selective permeation function of the separation membrane to separate, purify and concentrate different solutes in the mixed system. The driving force of the separation depends on the types of the

membrane separation. The concentration gradient is used in a dialysis process. The pressure gradient was used as a driving force in microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). The temperature gradient is used in a membrane distillation (MD) process. The osmotic pressure gradient is used in a forward osmosis (FO) process. The electrical potential gradient is used in an electrodialysis (ED) process (see more details in **Table 1.1**).

Table 1.1 Membrane separation processes [7].

Membrane processes	Components passed	Driving force
Microfiltration	Water and dissolved species	Pressure difference
Dialysis	Ions and low-molecular-weight organics (urea, etc.)	Concentration difference
Electro dialysis	Ions	Voltage
Reverse osmosis	Water	Pressure difference
Ultrafiltration	Water and salts	Pressure difference
Gas separation	Gases and vapors	Pressure difference
Membrane distillation	Vapor	Temperature gradient
Nanofiltration	Water, monovalent ions and small molecular-weight species	Pressure difference
Forward osmosis	Salts and water molecule	Osmotic pressure

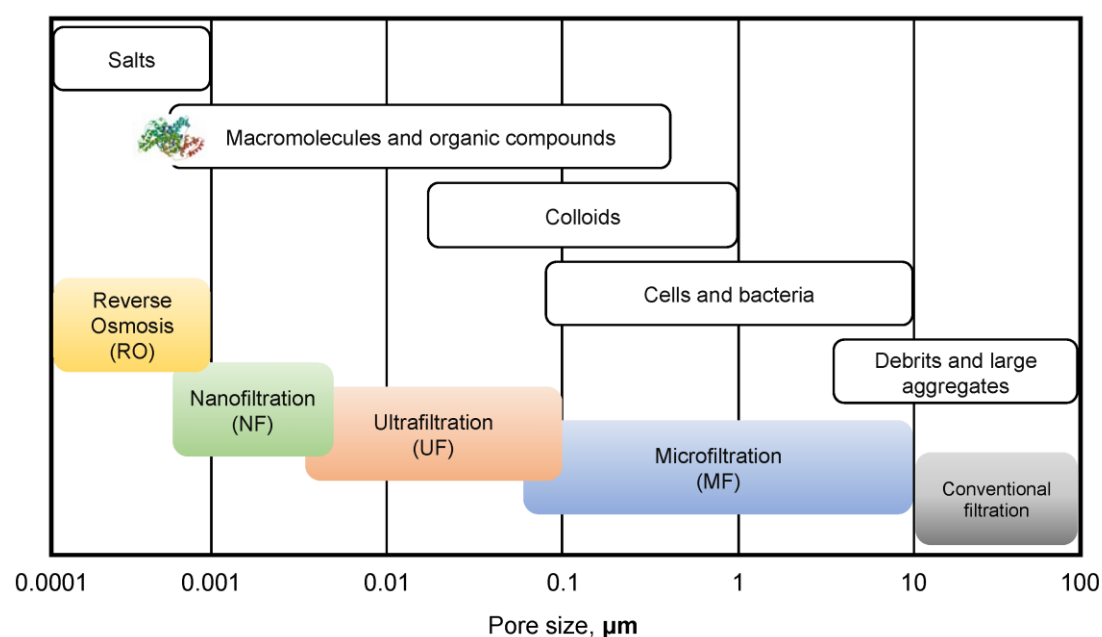


Fig. 1.2 Nominal pore size classification of membrane processes and characteristic dimensions

of various common foulants. Despite the categorization, upper and lower size limits usually overlap between two adjacent processes due to pore size distributions. The figure also shows the most suitable process for each foulant category [8].

The most common membrane process for desalination is a pressure driven membrane process.

The common pressure-driven membrane separation process can be divided into microfiltration, ultrafiltration, nanofiltration and reverse osmosis depending on the pore size (**Fig. 1.2, Table 1.2**) [7]. Due to the large pore size, microfiltration and ultrafiltration membranes only have a retention effect on large-sized components such as suspended solids, microorganisms, and organic macromolecules in wastewater. So they are often used for wastewater pretreatment. Reverse osmosis membranes have a high interception for almost components in wastewater except water molecules, so they are often used as the final operation procedure during wastewater treatment.

Nanofiltration membrane is a pressure-driven membrane separation process between ultrafiltration and reverse osmosis processes. Nanofiltration membrane has a higher rejection rate for small organic molecules within the molecular weight (Mw) of 200-1000 Da and multivalent ions (such as Ca^{2+} , Mg^{2+} , SO_4^{2-}), but the rejection for monovalent salt ions (K^+ , Na^+ , Cl^- , etc.) is low. So it has broad application prospects in the separation of ions/organic molecules [9]. Development of high-performance nanofiltration membrane is the topic of this dissertation.

Table 1.2 Membranes and membranes categories [10].

Membrane types	MWCO* (g·mol ⁻¹)	Application
Microfiltration (MF)	>100000	particles and bacteria
Ultrafiltration (UF)	1000-100000	macromolecule
Reverse osmosis (RO)	<200	seawater desalination
Organic solvent nanofiltration (OSN)	200-1000	Peptide, dye, antibody, catalyst soyben oil, lube oil
Nanofiltration (NF)	200-1000	desalination
Pervaporation		dehydration of organic solvents
Organic solvent reverse osmosis (OSRO)	<200	organic solvent

* Molecular weight cut-off

1.3 Nanofiltration membrane fabrication methods

Nanofiltration membrane is roughly divided into two types depending on material, inorganic and organic. Nanofiltration membranes with inorganic component as selective layers are particularly difficult to fabricate. This is because it is difficult for inorganic substances to form an ultra-thin, continuous, and defect-free layered structure. Therefore, there are only two successful fabrication methods for inorganic nanofiltration membranes: sol-gel method and pressure-assisted deposition method.

In contrast, the fabrication methods for organic polymeric nanofiltration membranes are diverse. Among them, phase inversion method can be used to fabricate asymmetric membranes. Compared with asymmetric membranes, the fabrication methods of thin film composite (TFC) nanofiltration membranes are more abundant, and so the selective separation layer is more diverse in materials and structures. Interfacial polymerization (IP) method is the most successful method at present and has been successfully commercialized [11]. In the conventional interfacial polymerization process, the amine monomers in an aqueous solution generally diffuse into an organic phase containing trimesoyl chloride (TMC) with vigorous stirring, thus forming a thin film at the water/organic phase interface via the Schotten-Baumann

reaction [12]. The mechanism of interfacial polymerization continues to attract considerable research interests owing to the substantial use of polyamide based nanofiltration membranes for water purification (**Fig. 1.3**) [13].

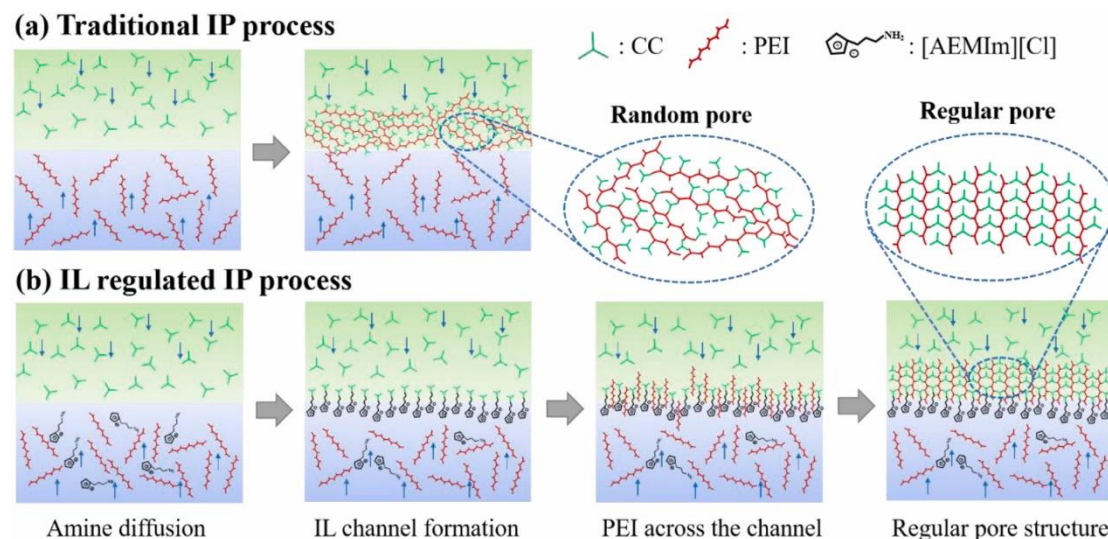


Fig. 1.3 Schematic representation of the (a) traditional interfacial polymerization and (b) ionic liquid (IL) regulated interfacial polymerization process [13]. (CC: cyanuric chloride, PEI: polyethylenimine, [AEMIm][Cl]: 1-aminopropyl-3-methylimidazolium chloride.)

The excellent performance of the interfacial polymerization nanofiltration membrane is mainly due to the following three aspects: (1) the selective separation layer of the nascent polymer formed in the early stage of interfacial polymerization inhibits the diffusion of the aqueous phase monomer into the organic phase. Therefore, the subsequent interfacial polymerization mainly occurs at the defects in the primary selective separation layer, and the generated polymer can effectively block the defects in the primary selective separation layer, while the growth of the defect-free part of the primary selective separation layer is inhibited [14]. Under such a self-limiting effect, a thin and uniform selective separation layer can often be obtained in the end; (2) in the process of interfacial polymerization, the diffusion of aqueous phase monomers into the organic phase is very rapid and violent, and the aqueous phase monomers entered the organic phase are immediately polymerized with acid chlorides. Therefore, the selective separation layer of the nanofiltration membrane often has a wrinkled structure (**Fig. 1.4**) [15], which greatly increases the effective surface area of the selective

separation layer, so that higher solvent permeance could be obtained without compromising solutes rejection rate [15]; (3) in addition, the chemical structure of the selective separation layer and its internal free volume can be regulated within a certain range by selecting monomers with different chemical structures (**Fig. 1.5**). For example, in the fabrication of nanofiltration membranes for water treatment, piperazine (PIP) is the most commonly used aqueous monomer, and the sp^3 hybridized carbon atoms makes PIP has the lowest energy conformation [16]. Therefore, the polymer polymerized with trimesoyl chloride also has a non-planar structure. This makes the free volume of resultant polymeric nanofilms smaller than most hydrated multivalent ions, but larger than water molecules. In this way, a higher water flux can be obtained while ensuring the salts rejection. In recent years, with the continuous deepening of research on the underlying mechanism of interfacial polymerization and the continuous emergence of various new materials, the performance of interfacial polymerization nanofiltration membranes has been continuously improved. For example, Livingston et al. successfully formed a selective separation layer as thin as 10 nm by adjusting the hydrophilicity and porosity of the base membrane selected in interfacial polymerization to construct an ultra-high permeable nanofiltration membrane that can be used in organic solutions [4]. Adding nanomaterials to the selective separation layer formed by interfacial polymerization to construct a mixed-matrix thin film composite nanofiltration membrane is another means to effectively improve the performance of nanofiltration membranes [17]. Nanomaterials such as carbon nanotubes and zeolite nanoparticles have also been introduced into the selective nanofilms to provide additional solvent channels. It is believed that even if the incorporated nanomaterial has a pore structure, the improvement of membrane performance mainly comes from the defects between the nanomaterial and the polymer matrix. Although the reasons for the superior performance of mixed-matrix thin film composite nanofiltration membranes are still questionable, the industrialization of mixed-matrix thin film composite membranes is already on the way [18, 19].

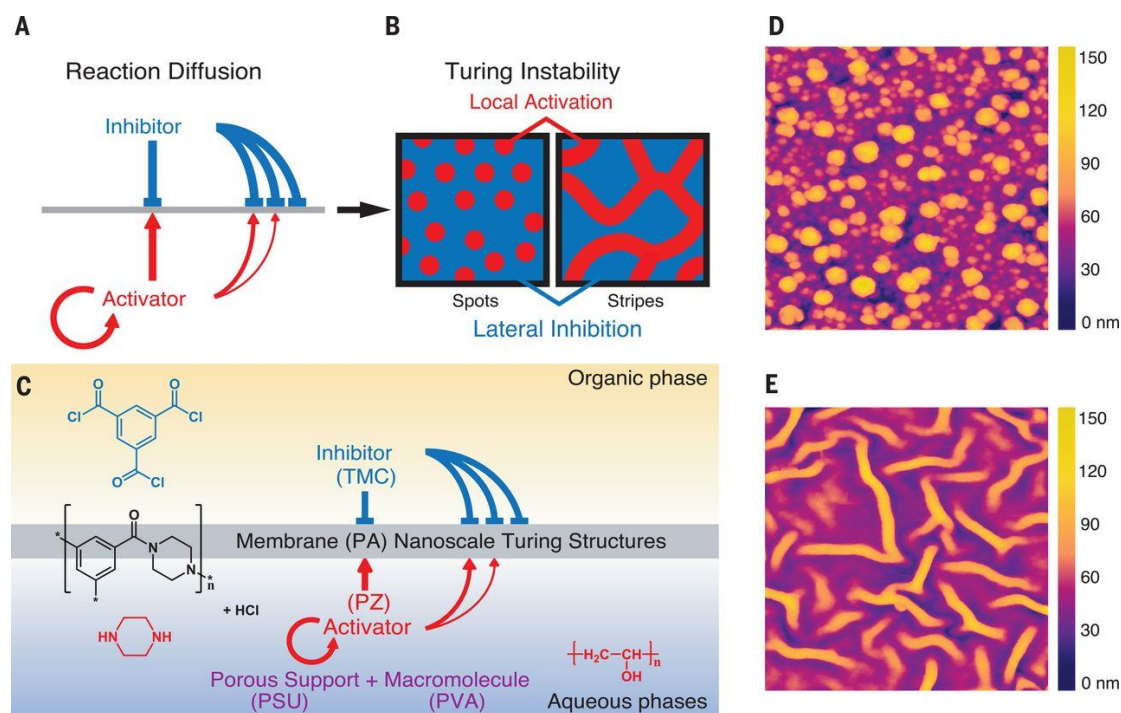


Fig. 1.4 Polyamide nanofiltration membranes with crumple structure mediated by hydrophilic aqueous additives [15]. (A: Schematic diagram of activator-inhibitor interaction in a reaction-diffusion process. Reactions leading to Turing structures rely on competing activation (red) and inhibition (blue) kinetic pathways. B: Spatial representation of local activation and lateral inhibition. In two dimensions, Turing structures generally consist of spots or stripes. C: Schematic illustration of interfacial polymerization Turing system. The inhibitor (TMC: trimesoyl chloride) is dissolved in the organic phase (top), and the activator (PZ: piperazine) and the macromolecule (PVA: polyvinyl alcohol) are dissolved in the aqueous phases (bottom). The membrane (PA: polyamide) with nanoscale Turing structures forms on the porous support (PSU: polysulfone ultrafiltration membrane). D and E: AFM topography images of the Turing-type PA membranes. Bright yellow and orange regions correspond to the formed solid-state nanoscale Turing structures.)

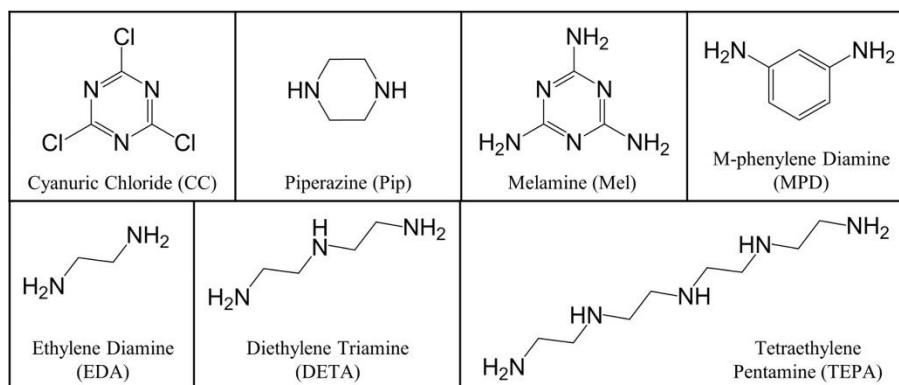


Fig. 1.5. Chemical structure of some common monomers used for interfacial polymerization [20].

1.4 Nanofiltration membrane categories

1.4.1 Organic polymeric membranes

In recent years, some polymers with high free volume represented by porous polymers have received extensive attention. These polymers have a specific molecular structure that leads to a relatively large free volume through which the solvent can pass while the solutes are trapped. The permeation flux of the solvent is related to the solubility coefficient and diffusion coefficient of the solvent in the polymer [21]. Volkov et al first applied poly 1-trimethyl-1-silapropyne (PTMSP) in the preparation of solvent-resistant nanofiltration membranes. They coated a PTMSP thin layer on cellulose acetate (CA) and polyacrylonitrile (PAN) substrates respectively, and found that this polymer had a higher permeation flux for ethanol than commercial organosiloxane nanofiltration membranes, and had a higher retention factor of 90% on reactive brilliant blue (626.5 g mol^{-1}) [22-26]. Fritsch et al. designed a series of porous polymers and coated them on PAN membrane surface to prepare composite nanofiltration membranes, which were then cross-linked with polyetherimide. It was found that the permeation flux of the cross-linked nanofiltration membrane was stable within 200 h, and the molecular weight cut-off was less than 200 Da [27].

1.4.2 Mixed matrix nanofiltration membranes

Separation membranes made of organic polymers have the advantages of good processability, low cost and excellent stability. However, the membrane structure will be

compacted as the operation time goes by, resulting in a decrease in flux. In addition, the traditional polymer nanofiltration membrane is limited by the trade-off limit between permeance and selectivity. In other words, increasing the membrane permeance will deteriorate selectivity, and vice versa [28, 29]. Mixed matrix membranes (MMMs) can combine the advantages of nanofillers and polymer by introducing nanoparticles inside polymers bulk, facilitating membranes' permeability and selectivity, as shown in **Fig. 1.6** [30]. The introduction of nanoparticles will change the chain spacing of the polymer, thereby breaking the mutual restriction of permeability and selectivity of traditional organic polymer membranes. In addition, the preparation of MMMs is applicable to the current existing traditional polymer membrane technology. At present, MMMs have been widely used in gas separation, pervaporation, nanofiltration and so on [31]. Commonly used filler particles include metal oxides, metal nanoparticles, zeolite molecular sieves, carbon nanotubes, graphene oxide, metal-organic frameworks (MOFs), etc [32-38]. However, the nanofiltration membrane fabricated by incorporating such fillers may have non-selective defects at the interface between polymer and fillers, which is a huge challenge for the commercialization of MMMs [39].

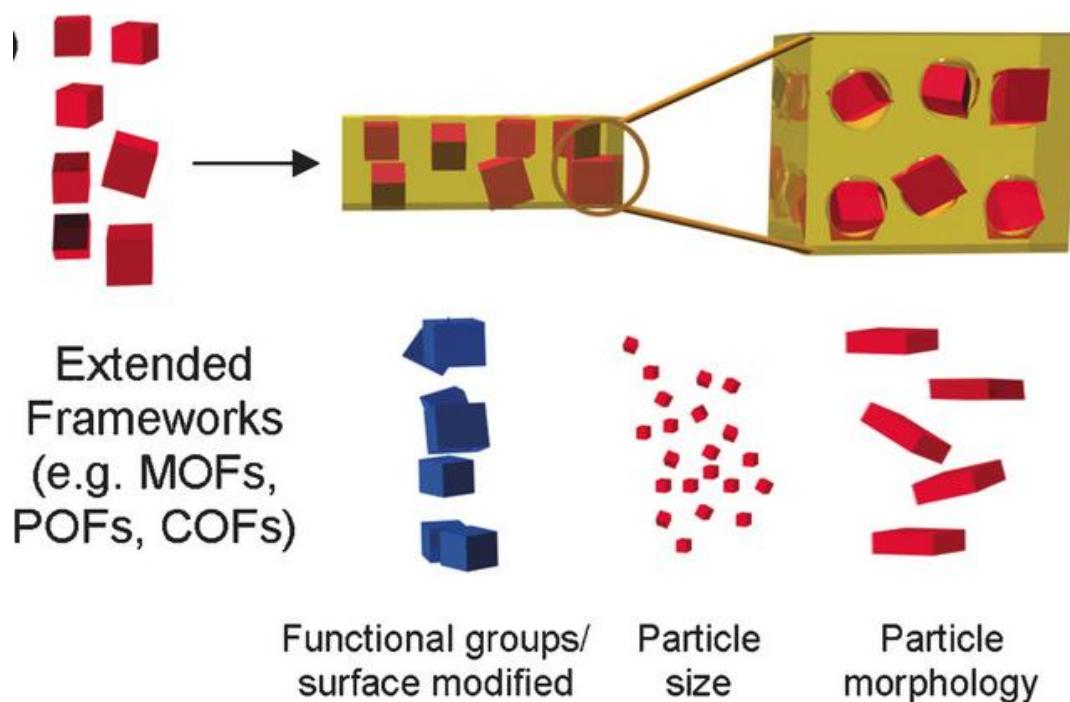


Fig. 1.6 Schematic diagram of the structures of mix-matrix membranes containing an extended framework [30]. (MOF: metal-organic frameworks, POF: porous organic frameworks; COF:

covalent organic frameworks.)

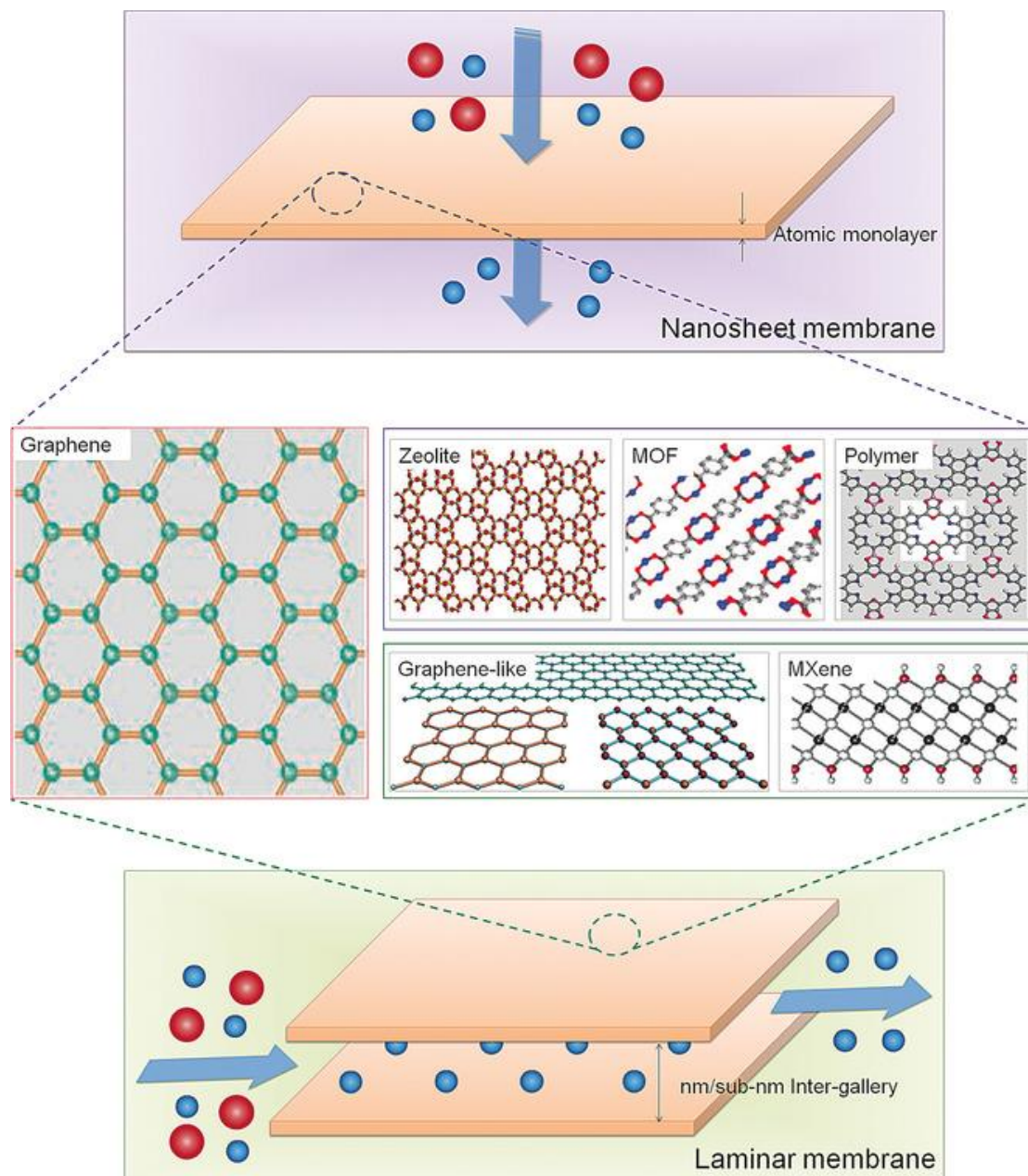


Fig. 1.7 Main types of 2D membranes materials and corresponding 2D membranes [40]. (MOF: metal organic framework.)

1.4.3 Two-dimensional layered nanofiltration membranes

After Geim et al. successfully separated and characterized graphene in 2004, two-dimensional (2D) materials began to attract great attention in the fields of physics, chemistry, and materials [41]. In the field of membrane separation, the unique structure of 2D materials

(single-atom thickness and micron-scale lateral dimensions) has led more and more researchers to try to prepare them into membranes. At present, the 2D materials including graphene and graphene oxide (GO), MXene [42], MoS₂, g-C₃N₄ [43], etc, have been processed into films successfully (**Fig. 1.7**) [40].

There are two commonly used fabrication methods for layered 2D material separation membranes (hereafter, be referred to as layered 2D membranes). The first is to fabricate separation membranes composed of single or several layers of 2D materials by in situ growth or exfoliation. Because 2D materials generally have high mechanical strength, and the thickness of a single layer is only the size of atoms, theoretical calculations show that the separation membrane formed from a single layer of 2D materials can have ultra-high flux and selectivity at the same time. However, since the 2D material has no defects, and the atomic gap cannot pass through any substance (for example, the atomic gap of graphene is only 0.064 nm), additional drilling is required to achieve the separation of substances. In terms of experimental research, researchers have successfully prepared single-layer 2D membranes by various methods for desalination and small molecule separation [44]. For example, Yang et al. used xylene as a raw material to grow single-layer graphene on the surface of copper foil by chemical vapor deposition, then covered the surface with a layer of single-walled carbon nanotubes (SWCNT), and etched away the copper foil to obtain a single-layer graphene membrane supported by SWCNTs [45]. According to the separation requirements, the surface of the membrane is covered with SiO₂ molecular sieve with a specific pore size, and holes are drilled on the graphene membrane by plasma etching. However, the existing equipment and methods cannot realize the large-scale fabrication of single-layer 2D films.

The second is to stack 2D materials layer-by-layer by means of filtration to form a multilayer 2D film [46]. Size sieving is the main mechanism for the separation of substances by multilayer 2D membranes. In addition, 2D materials are generally negatively charged, so charged substances can also be separated by electrostatic interaction [47]. Compared with single-layer 2D membranes, the formation process of multilayer separation membranes fabricated by the stacking method is simple, which is the focus and hotspot of current research [48]. As for MoS₂, since it basically does not contain additional functional groups, the interlayer

distance of MoS₂ membrane is very small and the water permeability is poor. In order to improve the separation performance of MoS₂ membrane, Ries et al. modified MoS₂ with chlorofluorocarbons, and then prepared a multilayer 2D membrane with functionalized MoS₂ [49]. The retention factor of caffeine and acetaminophen is more than 90%, and the retention factor of NaCl is 87%. MXene is a new type of 2D material composed of Ti, C and certain metal elements, which has a six-membered framework structure similar to graphene. However, similar to MoS₂, MXene basically does not contain additional functional groups. Thus when it is used for the formation of layered films, it is usually fabricated by mixing nanosheets and some other components to form a nanofilm, and then etching away the intercalation. However, since the two materials themselves basically do not contain additional functional groups, it is difficult to adjust their separation channels according to the specific needs, the application range is limited, and the preparation cost is high.

Compared with graphene, while retaining the six-membered carbon ring structure of graphene, GO also contains a large number of oxygen-containing functional groups such as hydroxyl, carboxyl, and carbonyl, which makes GO have comparable mechanical properties and chemical corrosion resistance to graphene [50]. In addition, due to the presence of oxygen-containing functional groups, the interlamellar spacing of GO nanosheets increases from 0.34 nm of graphene to 0.8 ± 0.1 nm (dry state), which makes the layered GO membrane suitable for water treatment. However, because the GO membrane is too hydrophilic, in the actual filtration process, the strong hydrogen bonding between the oxygen-containing functional groups and the water molecules will cause serious swelling of the membrane, and the stable separation performance cannot be guaranteed [51]. Under these conditions, the GO membrane may also be destroyed in water. To solve this problem, researchers usually adopt two strategies to obtain GO membranes with stable separation performance (**Fig. 1.8**). The first strategy is to partially reduce GO to decrease the number of oxygen-containing functional groups [51, 52]. The higher degree of reduction, the stronger stability of GO membrane in water. The second strategy is to graft the oxygen-containing functional groups or carbon skeleton on GO or adsorb other substances on GO via covalent or non-covalent (such as electrostatic, chelation, etc.) interaction, as shown in **Fig. 1.9** [48]. This strategy cannot only increase the stability of GO membranes, but also adjust the properties of GO membranes (such as hydrophilicity, electrical

properties, interlamellar spacing, etc.) as needed.

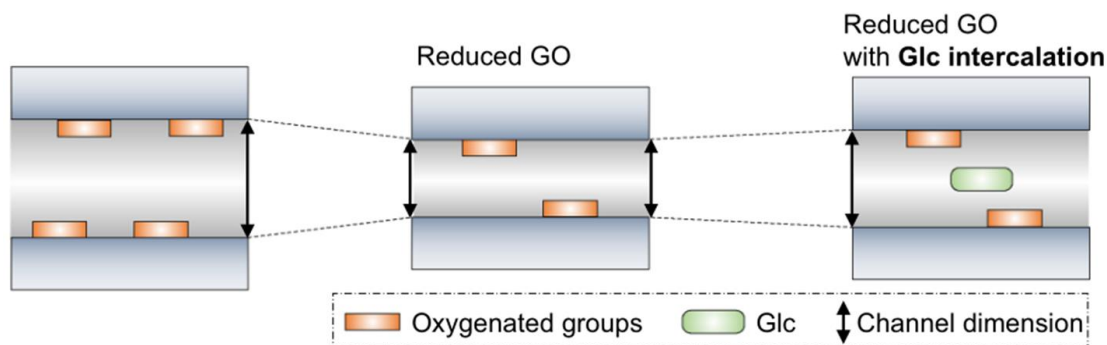


Fig. 1.8 Schematic diagram of chemical reduced GO for separation [51]. (Glc: glucose.)

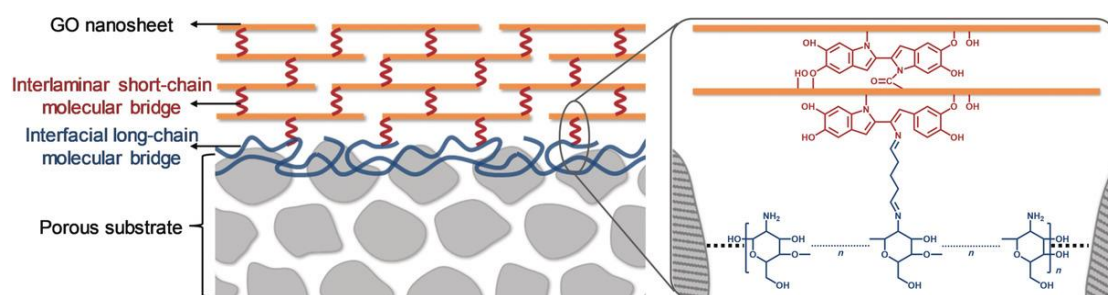


Fig. 1.9 Stabilizing a GO membrane through hierarchical interlamellar short-chain and interfacial long-chain molecular bridges. An amine monomer acted as the interlamellar short-chain molecular bridge (short wavy line in red) to interlock the GO laminate through condensation and nucleophilic addition reactions. Aldehyde-modified chitosan served as an interfacial long-chain molecular bridge (long wavy line in blue) to covalently bond with the amine-interlocked GO laminate through a Schiff base reaction while firmly adhering to a porous substrate through van der Waals forces (dotted line) [48].

1.5 Separation mechanism of nanofiltration membrane

The mass transfer behavior of solutes in nanofiltration membranes is an extremely complex process, which involves the microfluidic dynamics on the surface of nanofiltration membranes and in its nanopores, but it can be attributed to the influence of nanofiltration membrane structure on mass transfer. At present, according to the structure of nanofiltration membranes (with nanoscale pores and ionizable functional groups), researchers generally believe that the solutes interception ability of nanofiltration membranes comes from the

combined effects of size sieving, electrostatic interaction and dielectric repulsion. And based on the structure of nanofiltration membrane, a series of physical models were established to quantitatively correlate the structure of nanofiltration membrane with its separation performance, in order to realize the prediction of separation performance of nanofiltration membrane [53-55].

1.5.1 Size-sieving effect

The size sieving effect is often used to explain the mass transfer behavior of neutral particles in nanofiltration membranes. When the size of the neutral particles in the solution is larger than the pore size of the nanofiltration membrane, the neutral particles need to be deformed to reduce the size, or the membrane material needs to be deformed to increase the pore size of the membrane, so that the neutral particles can enter the membrane pores [56]. Therefore, the pore size and its distribution of the nanofiltration membrane can be indirectly understood by characterizing the rejection rate of the nanofiltration membrane to a series of neutral organic molecules with different sizes in aqueous solution or to organic molecules in organic solution. However, the deformation of both neutral particles and membrane materials needs to overcome huge energy. Therefore, the nanofiltration membrane has a good ability to repel neutral particles whose size is larger than its pore size, and achieve complete retention. When the size of the neutral particles is smaller than the pore size of the nanofiltration membrane, the neutral particles only have a certain probability to enter the pores of the nanofiltration membrane. On the other hand, due to the action of the pore wall, the diffusion and convective transfer process of the neutral particles in the pores of the nanofiltration membrane is hindered, and the degree of obstruction is related to the size of the neutral particles.

1.5.2 Electrostatic effect

Although the size sieving effect can well explain the transfer behavior of neutral particles in nanofiltration membranes, it is not fully applicable in electrolyte solutions, especially for the transmembrane of electrolytes whose size is smaller than the pore size of nanofiltration membranes. Considering that the chemical structure of nanofiltration membranes contains ionizable functional groups, when nanofiltration membranes are applied to the separation of

electrolyte solutions, there will be certain electrostatic interactions between the charged functional groups on the surface and in the pores of nanofiltration membranes and ions. The charged functional groups have a repelling effect on their co-ions and an attracting effect on their counter ions, thereby hindering or promoting the distribution of ions in the pores of the nanofiltration membrane [57, 58].

Bowen et al combined the steric-hindrance pore (SHP) model with the electrostatic interaction and proposed Donnan steric pore model (DSPM) [59, 60]. In DSPM, the nanofiltration membrane is assumed to be a charged porous membrane composed of uniform capillaries and with a constant effective volume charge density. At the same time, the model also takes into account the effect of steric hindrance on the distribution of ions on the membrane surface. According to DSPM, the interception of larger ions (larger than the membrane pore size) by the nanofiltration membrane mainly depends on the size sieving effect; smaller ions (smaller than the membrane pore size) have a certain probability to enter the nanofiltration membrane pores. The mass transfer process in the membrane pores is not only affected by the size of the ions, but also affected by the Donnan potential generated by the different ion concentrations inside and outside the membrane [61]. The charge of nanofiltration membrane in aqueous solution is determined by its chemical structure and is affected by the pH of aqueous solution. If there are amphoteric functional groups in the chemical structure of the nanofiltration membrane, such as amino acid which contains amine and carboxyl groups in a molecule, the nanofiltration membrane will have an isoelectric point (the pH value when the nanofiltration membrane is electrically neutral in aqueous solution). When the pH value is higher than the isoelectric point, ionization of carboxyl group is dominant, and the nanofiltration membrane is negatively charged in aqueous solution. When the pH value is lower than the isoelectric point (usually an acidic environment), ionization of carboxyl group is suppressed, and protonation of amino group dominates, resulting in a positive charge of membrane. However, it is difficult to measure the charge inside the pores of the nanofiltration membrane. When the electrolyte is close to the surface of the nanofiltration membrane, it will first be affected by the charge of the surface of the nanofiltration membrane. Therefore, the characterization of surface charge of the nanofiltration membrane is very important to evaluate the interaction between surface charge and ions. The zeta potential at each pH is usually evaluated as the surface charge of the

nanofiltration membrane at that pH.

1.5.3 Dielectric repulsion effect

In recent years, the effect of dielectric repulsion on the mass transfer behavior of ions in nanofiltration membranes has attracted more and more attention from researchers. At present, there are mainly two hypotheses of solute solvation energy barrier [62] and mirror force effect [63]. The hypothesis of solute solvation energy barrier is that it is due to the size of water molecules (0.28 nm) and the pore size of nanofiltration membranes. The arrangement of water molecules in the confined space of the pores of the nanofiltration membrane is different from that in the bulk solution, resulting in a lower dielectric constant of water in the pores of the nanofiltration membrane. Therefore, when ions enter the pores of nanofiltration membrane from bulk solution, they need to overcome an energy barrier, which will prevent ions from entering the nanofiltration membrane. In other words, hydrated ions prefer to stay in water with a high dielectric constant (bulk solution). In 2002, Bowen et al. introduced the dielectric repulsion effect into DSPM, revised it to DSPM-DE (Donnan steric-pore model with dielectric exclusion), and calculated the dielectric repulsion effect [62]. Compared with DSPM, DSPM-DE is more accurate in predicting the interception performance of nanofiltration membranes to divalent salts, and the prediction results of charge density of nanofiltration membranes are within a reasonable range. On the other hand, in the hypothesis of mirror force effect proposed by Bandini [63], the dielectric repulsion effect on ions is considered to be caused by the difference in dielectric constant between the nanofiltration membrane material (polymer) and water. Since the dielectric constant of water and nanofiltration membrane are different, the ions will induce a polarized charge at the nanofiltration membrane/water interface, which has a repulsive effect on the ions in the solution (called the mirror force effect). In addition, the effect of dielectric repulsion on ions caused by changes in the dielectric constant of the solvent (solute solvation energy barrier) is ignored in the mirror image force assumption [63].

1.6 Performance and structure control of TFC nanofiltration membrane

The regulation of the structure and performance of TFC nanofiltration membranes has important significance for improving separation efficiency, reducing energy consumption, and

broadening application fields. It can be seen from the structural composition that the structure and performance of the TFC nanofiltration membrane are the comprehensive reflection of its selective layer and the properties of the porous ultrafiltration support. Therefore, the selective layer and the porous ultrafiltration support have to be optimized and designed to realize the regulation and control of the structure and performance of the TFC nanofiltration membrane [28]. Among them, the optimization and design of porous supports mainly focus on the adjustment of micropores and surface chemistry, and the process is relatively simple. However, the regulation accuracy and controllability are big challenges. This section will specifically introduce the influence of different reactive monomers, additives and intermediate layer strategies on the structure and performance of TFC nanofiltration membranes during interfacial polymerization process, as well as the development of high-performance TFC nanofiltration membranes based on interfacial polymerization.

1.6.1 Different reactive monomers

The molecular structure of reactive monomers plays a crucial role in the separation properties of nanofiltration membranes [16]. At present, the most commonly used monomers for preparing polyamide nanofiltration membranes by interfacial polymerization are PIP and TMC. PIP has high solubility in n-hexane, fast reaction rate with TMC, and easy to form a complete and dense polyamide nanofilm. The surface of the film is usually negatively charged due to the hydrolysis of acid chlorides. The molecular structure of small molecular amine monomers, such as space of amine groups, chain length and conformation of amine monomer, will affect the structure of polyamide nanofiltration membrane. Some macromolecular amines can also be used in the fabrication of TFC nanofiltration membranes. The chemical environments and density of amino groups in polyethylenimine (PEI) molecules are basically the same as PIP. The difference is that PEI molecules contain tertiary amines that cannot react with acid chlorides, and some of the primary and secondary amines do not participate polymerization reaction due to steric hindrance. These unreacted amino groups can be protonated under neutral conditions, imparting the as-resultant polyamide separation layer a positive charge [64]. In recent years, PEI is mainly used to prepare positively charged polyamide nanofiltration membranes to make up the deficiency of polyvalent cations rejection

of PIP-based nanofiltration membranes. PEI can form a looser polyamide network than small molecular amine monomer, because the macromolecular diffusion is slow and it is difficult to quickly form a dense polyamide network structure; at the same time, in the subsequent stage of interfacial polymerization, the diffusion of macromolecules is hindered, and it is difficult to further densify the polyamide network (**Fig. 1.10**) [65-67].

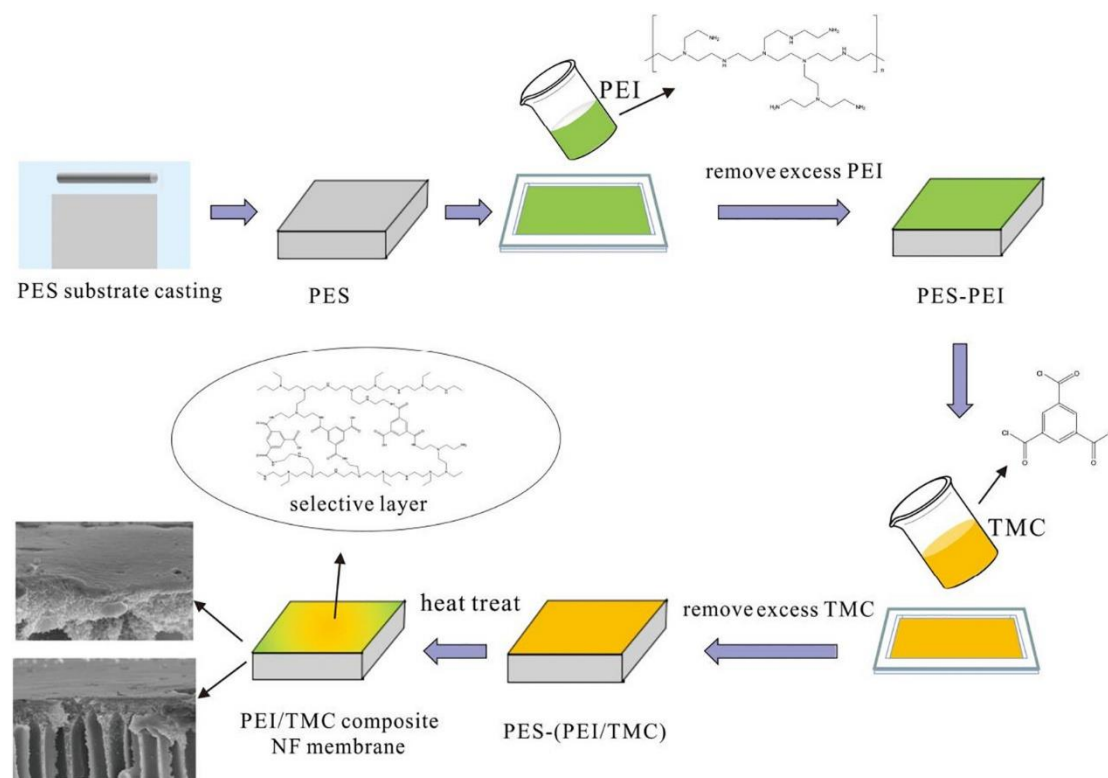


Fig. 1.10 Schematic illustration of fabrication of PEI-TMC positive nanofiltration membrane [66]. (PES: Polyethersulphone, PEI: Polyethylenimine, TMC: Trimesoyl chloride.)

1.6.2 Additives

Some additives are commonly used in the interfacial polymerization process, such as co-solvents, phase transfer catalysts, and surfactants to influence the diffusivity of amine monomers. Adding n-propanol to the water phase promoted the miscibility of water and hexane interface, and increased the roughness of the polyamide separation layer resulting in the increase of water flux [68]; however, excessively increased the miscibility of the interface would lead to separation performance failure. Additionally, they utilized a phase-transfer catalyst to facilitate the diffusion of amine monomers from the water phase to the oil phase,

thereby increasing the surface area and water flux of the separation layer [69].

Surfactants are the most commonly used additives, and their roles in the interfacial polymerization process are manifold [70]. On one hand, it helps to wet the surface of the ultrafiltration support, making the amine molecules more evenly distributed on the substrate. Secondly, it reduces the surface tension of the oil-water interface. During the polymerization of macromolecular amine monomers, the sodium dodecyl sulfate (SDS) can significantly promote the diffusion of amine molecules, thereby forming a polyamide separation layer with high degree of crosslinking [71]. Wang et al. used the SDS to promote the diffusion of PEI, and the selective layer of nanofiltration membrane formed by adding SDS to the aqueous phase solution had higher salts selectivity. In addition, in their work, the larger the molecular weight of PEI, the looser the polyamide network formed [72]. In fact, the role of SDS is more than that. Liang et al. found that the ordered monomolecular film formed by SDS at the oil-water interface can effectively regulate the diffusion behavior of amine monomers and promote the formation of polyamide nanofiltration membranes with narrower pore size distribution (**Fig. 1.11**) [71]. The sulfonic acid groups of SDS in the water phase can adsorb and enrich PIP, and increase the concentration difference of PIP in the water/oil phase, thereby increasing its diffusion rate. At the same time, according to molecular dynamics simulation and first-principle calculations, the ordered SDS monolayer can reduce the energy barrier of PIP trans-interface transport, and promote the rapid and uniform diffusion of PIP, thus forming a more uniform polyamide molecular network. Using SDS molecules to control the diffusion behavior of amine monomers during interfacial polymerization can avoid the defects caused by the inhomogeneous reaction in the polymerization process, so that the polymerization system interweaves a more intrinsic structure and exhibits optimal separation properties [73].

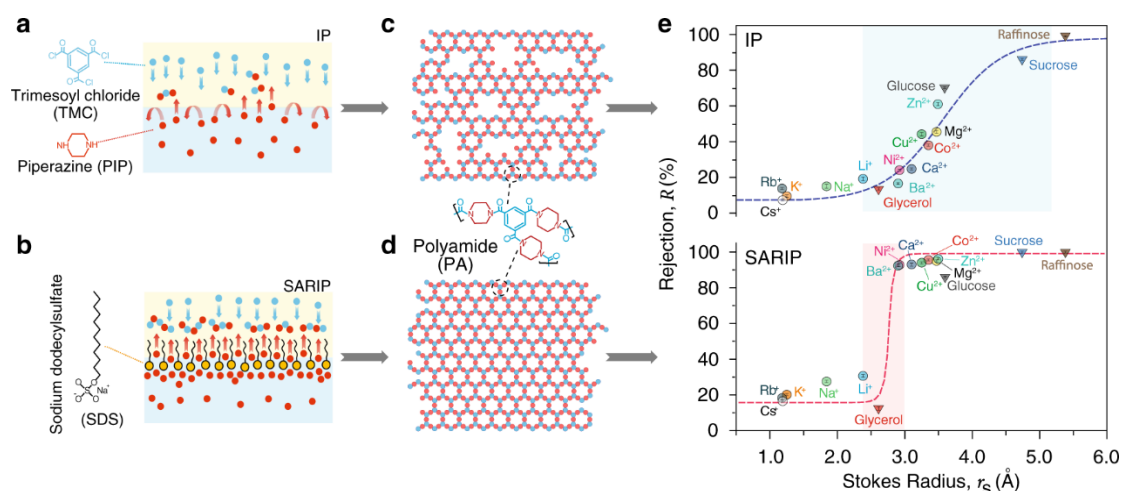


Fig. 1.11 Schematic illustration of (a, c) the conventional interfacial polymerization and (b, d) SDS assisted interfacial polymerization; (e) rejection of different solutes (circles for cations and inverted triangles for neutral organics) as a function of the Stokes radius for the polyamide membranes fabricated using conventional IP (top) and SARIP (bottom) [71]. (IP means conventional interfacial polymerization process; SARIP means surfactant assembly regulated interfacial polymerization process.)

Some rigid microporous materials, such as metal-organic frameworks (MOFs) (**Fig. 1.12**) [18, 74], zeolites [75], and biological channel proteins [76], have specific pore sizes and precise separation properties. In 2007, Hoek et al. first proposed the concept of thin-film nanocomposite (TFN) membrane (**Fig. 1.13**) [77, 78]. They doped zeolite NaA nanoparticles into the polyamide separation layer through the interfacial polymerization method, so that the water flux of the polyamide composite reverse osmosis membrane was significantly increased without loss of rejection rate. The interfacial gap between the nanoparticles and the polyamide matrix and the pore structure inside the particles may provide water transport channels. In addition to providing water channels, the hydrophilicity and negative charge of nanoparticles also enhance the water flux and anions rejection. Since then, people have been eager to dope a variety of nanomaterials with water channels or ion sieving properties into the polyamide separation layer, including inorganic nanomaterials such as zeolite particles, TiO_2 nanoparticles, carbon nanotubes, and graphene oxide, metal-organic framework (MOF) nanoparticles and so on [17]. Factors such as hydrophilicity, surface functional groups and size of nanomaterials will affect their position, distribution and compatibility with polyamide. The fabrication of TFN is

a relatively successful way in the modification and optimization of composite membranes, and there are already corresponding commercial products, such as ZIF-8. Dispersing nanomaterials in a two-phase solution and introducing them into the polyamide separation layer through an interfacial polymerization process has some problems, such as the difficulty in determining the actual doping amount, and the poor compatibility between nanomaterials and polymers leads to defects inside the nanofilm. Besides, nanomaterials are easy to aggregate, and excessive doping may destroy the compactness of the separation layer structure, resulting in a decrease in membrane rejection.

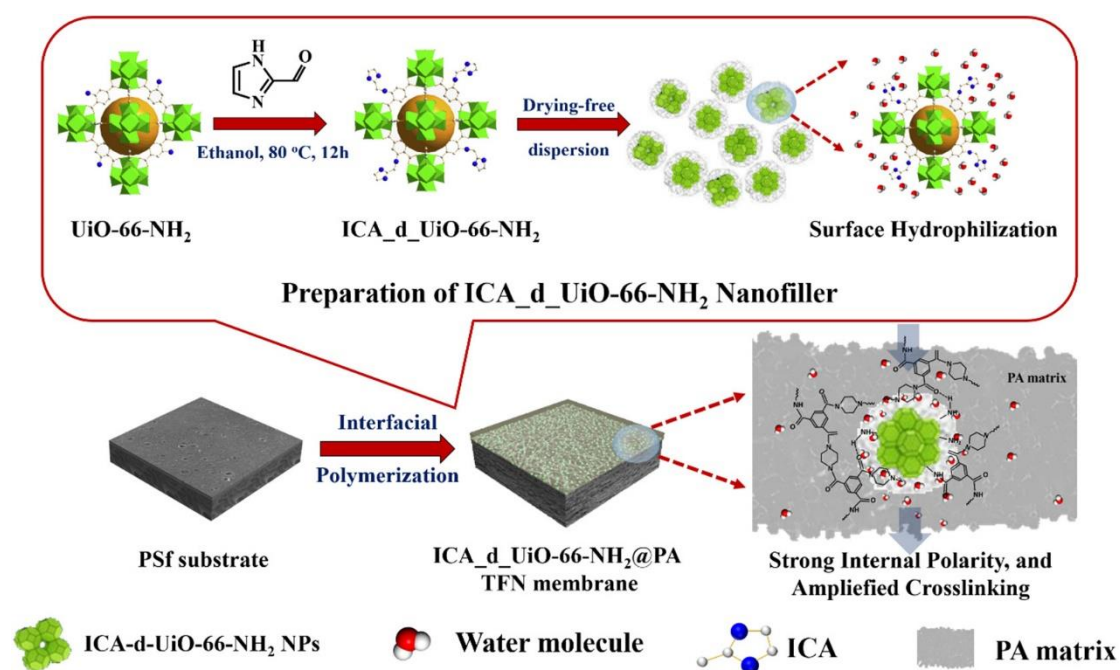


Fig. 1.12 Schematic illustration of UIO-66 (UiO-66: zirconium 1,4-dicarboxybenzene MOF) based polyamide TFN membrane for elevated nanofiltration performance [18]. (ICA means imidazole-2-carbaldehyde.)

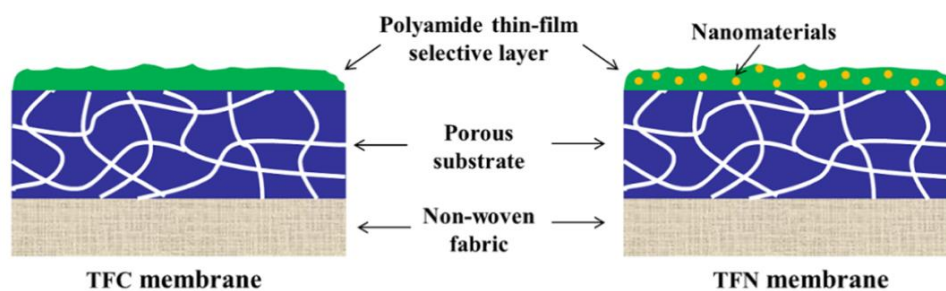


Fig. 1.13 Schematic diagram of TFN membranes [78].

1.6.3 Interlayer strategy

In recent years, the introduction of interlayers on porous support has been an effective means to regulate the interfacial polymerization process as well as the properties of selective layers [79]. Compared with the traditional polymer ultrafiltration supports, the interlayer has good hydrophilicity, high surface porosity and uniform and moderate pore size, which is conducive to the enrichment and uniform diffusion of aqueous monomer molecules, forming an ultra-thin, defect-free, dense polymer selective layer. Therefore, the TFC nanofiltration membrane fabricated based on the intermediate layer has higher permeation flux and better retention performance. In 2015, Karan et al. used cadmium hydroxide ($\text{Cd}(\text{OH})_2$) nanowires for the first time to construct a hydrophilic intermediate layer with a pore size of about 2 nm and a thickness of about 120 nm on the ultrafiltration support. A defect-free, ultra-thin (thickness < 10 nm) polyamide selective layer was prepared on the surface of $\text{Cd}(\text{OH})_2$ nanowires through interfacial polymerization [15]. In this work, the generation of ultrathin, defect-free polyamide selective layer benefited from the uniform and hydrophilic nanopore channel provided by the $\text{Cd}(\text{OH})_2$ nanowire intermediate layer to control the uniform diffusion of diamine monomer (**Fig. 1.14**) [4]. However, $\text{Cd}(\text{OH})_2$ is easily dissolved by acid, which may lead to the detachment of the polymer selective layer during interfacial polymerization [80]. Zhu et al. have constructed a hydrophilic interlayer by depositing polydopamine (PDA)-modified single-walled carbon nanotubes (SWCNT) (PDA/SWCNT) on a polyethersulfone (PES) microfiltration membrane. Then through interfacial polymerization between PIP and TMC, an ultrathin polyamide selective layer with a thickness of about 12 nm was fabricated on the PDA/SWCNT interlayer [28]. The permeance of the polyamide nanofiltration membrane fabricated in this work reaches $32 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ with comparable Na_2SO_4 rejection. At present, these intermediate layers are mostly used to modify the surface pore structure and hydrophilicity of the porous support, so as to control the diffusion of monomers in the aqueous phase (**Fig. 1.15**) [28].

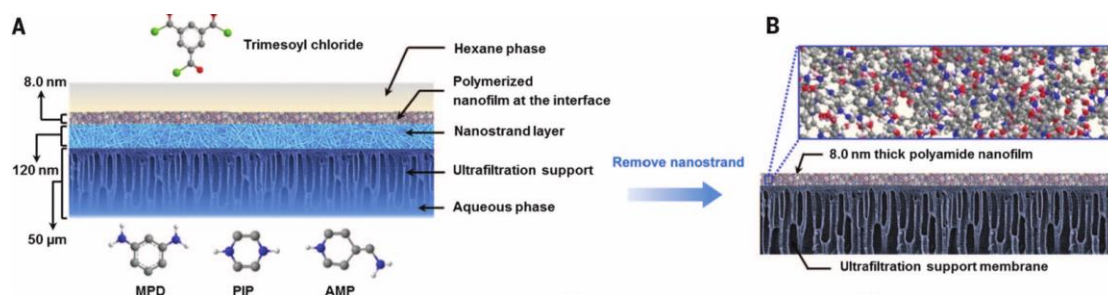


Fig. 1.14 Description of the controlled interfacial polymerization process and the resulting sub-10 nm nanofilms [4]. (A: A sacrificial $\text{Cd}(\text{OH})_2$ nanostrand layer was prepared on top of an ultrafiltration support membrane (porous alumina or cross-linked polyimide (XP84)). The nanostrand layer was saturated with an aqueous solution of diamine and contacted with a hexane layer containing trimesoyl chloride, enabling the synthesis of polyamide nanofilms via interfacial polymerization. B: The nanostrand layer was removed by acid dissolution, resulting in a free-standing nanofilm that was then attached to a support membrane. MPD: trimesoyl chloride, PIP: piperazine; AMP: 4-(aminomethyl)piperidine.

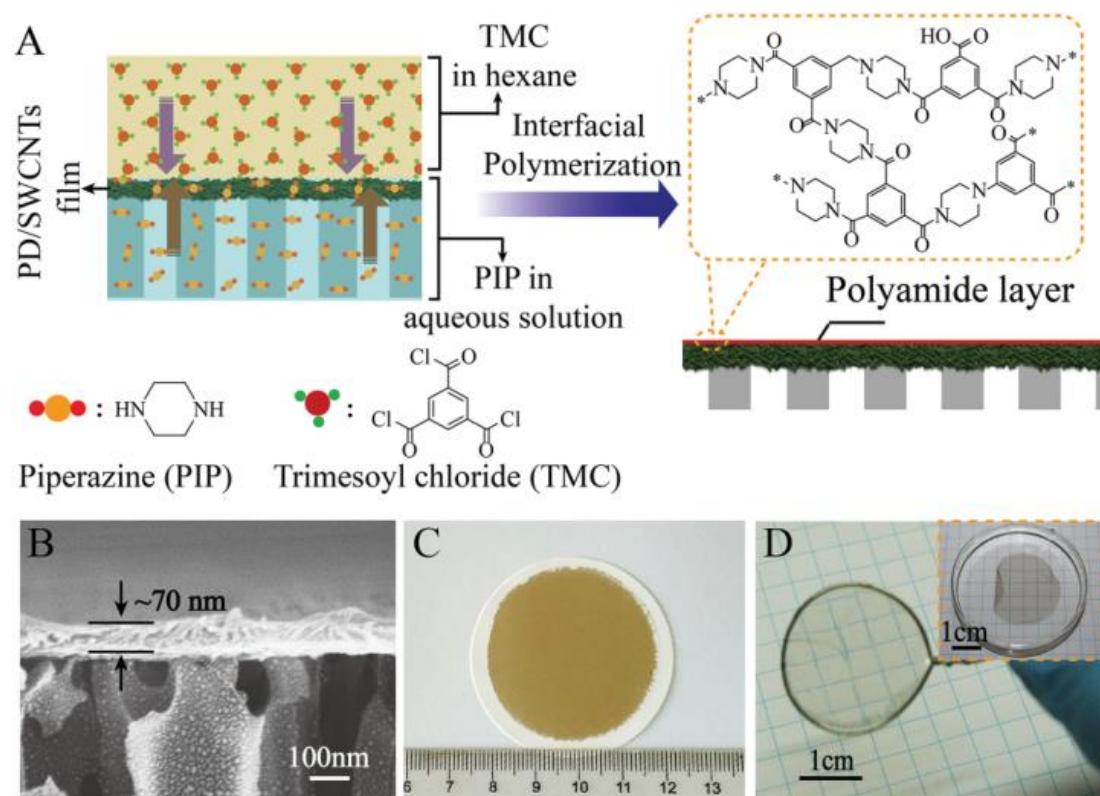


Fig. 1.15 A: A schematic of interfacial polymerization process for preparing PD/SWCNTs film supported ultrathin polyamide nanofiltration membrane. B: Cross sectional SEM image of a PD/SWCNTs film on PES membrane. C: Photograph of a PD/SWCNTs film supported ultrathin polyamide nanofiltration membrane. D: Photograph of a PD/SWCNTs film supported ultrathin polyamide nanofiltration membrane.

polyamide nanofiltration membrane. D: A free-standing polyamide layer covered PD/SWCNTs film released from PES membrane [28]. (PES: Polyethersulfone.)

1.7 Current problems faced by nanofiltration membranes

As a pressure-driven separation membrane that can remove multivalent ions and small organic molecules, nanofiltration membranes have great application value in the fields of seawater desalination, wastewater treatment, solvent recovery, and drugs concentration and purification. At present, the nanofiltration membrane mainly adopts TFC structure, which is composed of an ultra-thin selective layer and a polymer ultrafiltration support. Therefore, the performance of the TFC nanofiltration membrane could be improved by designing the selective layer and the polymer ultrafiltration support, separately. Through the structural design and optimization of the selective layer and the support membrane, a series of high-throughput TFC nanofiltration membranes have been developed. However, there are still controversies in the separation performance and stability of TFC nanofiltration membranes.

Because the permeability of the underlying support is much higher than that of the selective layer, researchers generally believe that the permeation flux of the TFC nanofiltration membrane is determined by the selective layer. However, the impacts of ultrafiltration support for interfacial polymerization cannot be ignored. In other words, even if the permeance of the TFC membrane is determined by the selective layer, the properties of the ultrafiltration support, such as porosity, surface polarity and roughness, will significantly affect the property of selective layer. As the result, the support affects the permeance and selectivity of the selective layer, thus determining the final membrane perm-selectivity of the TFC membrane [1, 17, 81]. These opinions were accepted by most of nanofiltration researchers.

Strategies to improve the permeation flux of TFC nanofiltration membranes can be mainly divided into two aspects: one is to optimize the properties of selective layers (chemical structure, porosity, surface area and thickness) through monomer structure design, doping, and interfacial polymerization regulation. Although this strategy has made some achievements in the fabrication of high-flux TFC nanofiltration membranes, it still has the disadvantages of sacrificing selectivity, poor controllability and complicated process. The second is to increase the effective filtration area of the selective layer by re-constructing the ultrafiltration support

(also termed as the interlayer strategy). Some researchers proposed that the introduction of interlayer could increase the effective filtration area of selective layer by imparting some uncertain influence [1]. Besides, some inorganic interlayer could inhibit the “funnel effect” (**Fig. 1.16**) [78] and “physical inter-locking effect” (polyamide intrusion during interfacial polymerization) (**Fig. 1.17**) [82] of TFC nanofiltration membrane, which further increase the final permeance of TFC nanofiltration membrane. This strategy can basically improve the permeation flux of TFC nanofiltration membranes while maintaining selectivity. However, although the effective filtration area of the selective layer can be increased by constructing a high surface porosity intermediate layer, its interfacial stability is still questionable, and the preparation process is often complicated and the cost is high. So it is not suitable for direct application to existing fabrication process of TFC nanofiltration membrane. More importantly, the underlying mechanism of interlayer between selective layer and ultrafiltration support is still unclear. Further investigation is needed and necessary to unveil the substantial impacts of interlayer for interfacial polymerization.

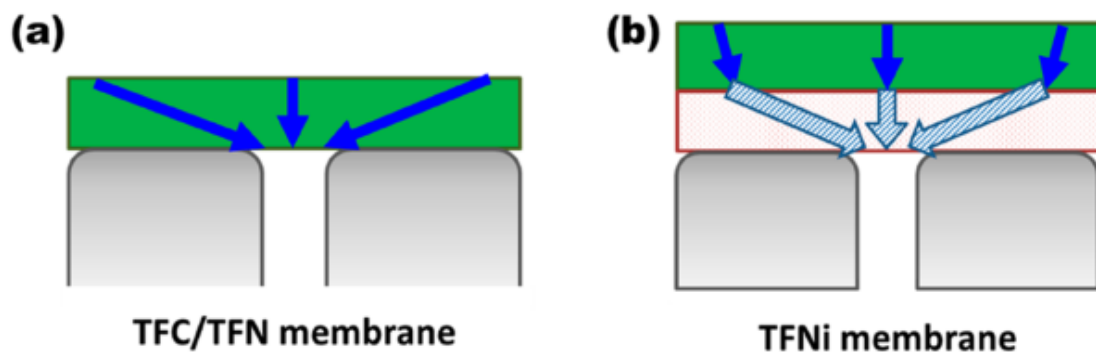


Fig. 1.16 “Funnel effect” of the existing TFC membrane, (a): the selective layer was fabricated onto an ultrafiltration support, (b): the selective layer was fabricated onto an interlayer decorated ultrafiltration support [83]. (TFC: thin film composite membrane, TFN: thin film nanocomposite membrane, TFNi: thin film nano/composite membrane engineered by interlayer strategy.)

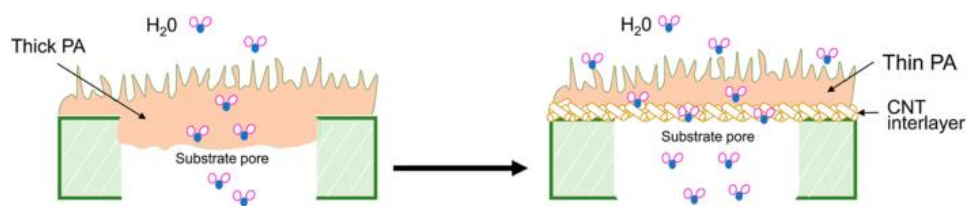


Fig. 1.17 The elimination of polyamide intrusion (also termed as the physical inter-locking effect) [82]. (PA: polyamide membrane; CNT: carbon nanotubes)

It can be seen that in order to further improve the permeation flux of TFC nanofiltration membranes, it is necessary to further design and optimize the structural relationship between the selective layer and the polymer ultrafiltration support, and develop a simple, effective, suitable method for increasing the effective filtration area of the selective layer in the fabrication process of TFC nanofiltration membrane.

In addition, as explained in the beginning of this chapter, generally, the rejection of monovalent ions of NF membrane is low. However, recently it is considered to be important to achieve a high selectivity for monovalent ions. This still remains one of the challenges for nanofiltration membranes. As a pretreatment process for reverse osmosis desalination, a higher monovalent ions retention from nanofiltration process is highly desirable to reduce the burden of the reverse osmosis stage, increase membrane lifetime, achieve higher reverse osmosis design flux and recovery in water desalination plants. Prof. Van der Bruggen revealed that the drawback of insufficient monovalent removal efficiency also challenges nanofiltration membranes in some other specific applications in separations of trace elements, such as nitrate, boron, and organic micropollutants, in applications that require a high purity of water [84]. Nanofiltration membranes with superior flux and excellent retention of di-/mono-valent ions are attractive to the contemporary market.

1.8 Purpose and overview of this dissertation

Nanofiltration membranes are suitable for the removal of multivalent ions and small molecular pollutants in water treatment, the separation of monovalent and multivalent ions, and the separation of ions and molecules due to their nanoscale pore size and charged structural characteristics. They have a wide range of application scenarios and potential application value.

Polyamide composite nanofiltration membranes occupy the membrane market due to their advantages of high flux, low cost and simple preparation process. However this kind of nanofiltration membrane usually restricted by the well-known trade-off limit, that is to say, it is inevitable to improve its permeability while losing its selectivity, and vice versa. The polyamide nanofiltration membrane based on the new substrate can improve the solvent permeance while maintaining salts selectivity. This means that for the same yield requirement, the membrane area, driving pressure and operating time can be reduced. Therefore, it is of great significance to develop new substrates and perform interfacial polymerization onto them to fabricate high performance thin-film composite nanofiltration membranes. In addition, the rejection for monovalent ion should be considered from now on. The enhanced permeance of nanofiltration membrane will inevitably results in deteriorated monovalent ion rejection due to some uncertainties. For commercial market using, the rejection for monovalent ion should not be neglected. Therefore, further increasing the monovalent ions rejection is favored in terms of the economic prospect.

This dissertation includes 6 chapters.

Chapter 1: The research background and purpose of this research are generally introduced.

Chapter 2: A high perm-selective thin-film composite (TFC) nanofilm was successfully developed via silicification interlayer-mediated interfacial polymerization. The silicification interlayer, fabricated in situ, significantly improved the surface hydrophilicity of the polysulfone (PSf) substrate and conferred the high-density uptake of amine monomers. The interlayer also served as a quasi-molecular-scale regulator that decelerated the diffusion of amine monomers into the organic phase to polymerize with the acyl chloride of 1,3,5-benzentricarbonyl (TMC). The synergistic effects triggered self-sealing and inhibited the membrane growth, which promoted the formation of ultrathin polyamide (PA) nanofilms (approx. 13 nm) with enhanced crosslinking properties. The best-performing PA₂/SiO₂/PSf membrane exhibited a high water permeance of 14.5 L m⁻²h⁻¹ bar⁻¹, which was approximately three times the permeance of the pristine PA membrane (4.8 L m⁻²h⁻¹ bar⁻¹). Furthermore, the membrane exhibited a high rejection capability toward divalent salts (98.7% against Na₂SO₄) and mono/divalent ion selectivity of 60.9. Hence, the newly-developed PA₂/SiO₂/PSf membrane exhibits a competitive separation property among the state-of-the-art desalination membranes.

The technique is applicable to the majority of conventional interfacial polymerizations, which highlights its use in the development of high-performance membranes for water remediation.

Chapter 3: Interlayered thin-film composite (TFC) membranes have a great potential for enhancing salts separation in wastewater reclamation, because of the highly permeable and selective properties. However, mechanistic insights regarding the structural features of the surface nanofilms and their corresponding interlayers, which lead to enhanced separation efficiency, remain poorly understood. Herein, I report a zwitterionic copolymer 2-methacryloyloxyethyl phosphorylcholine (MPC) and 2-amino-ethyl methacrylate hydrochloride (AEMA) (P[MPC-co-AEMA]) interlayered TFC membrane that exhibits an ultrahigh water permeance of $20.4 \text{ L m}^{-2}\text{h}^{-1} \text{ bar}^{-1}$ (almost three folds higher water permeance than that of the pristine PA membrane), together with a simultaneously enhanced rejection of inorganic salts (96.8% against Na_2SO_4). Detailed mechanistic investigations revealed that the promoted membrane separation property was mainly explained as the enriched amine monomer diffusion-driven instability induced by the P[MPC-co-AEMA] interlayer. This triggers membrane sealing and inhibits its growth, leading to the formation of an ultrathin PA nanofilm with a thickness of 12 nm, a ridge-shaped surface structure with enhanced specific surface area, and enhanced crosslinking. The fundamental mechanism revealed in this study lays a solid foundation for the engineering of the high-performance TFC membrane, which is appealing for the energy-efficient water remediation industry.

Chapter 4: Tailor-made polyamide (PA) membrane structures for ultrafast water transportation that possess excellent selectivity are promising for efficient water reclamation. In this study, an ultrathin (8 nm) and asymmetric PA nanofilm with a multilayer structure, where the back surface is a porous layer containing a spherically porous structure and the upper surface is a dense selective layer having nodular wrinkles, is engineered via amine-decorated interlayer-mediated interfacial polymerization (IP). The self-assembled network of strongly charged and highly hydrophilic ionomers exhibits strong attraction toward aqueous amine monomers, and temporally disrupts their diffusion by imposing a heterogeneous energy barrier toward the organic phase to be polymerized with acyl chloride monomers. This triggers a diffusion-driven instability that enables the formation of internal voids at the back surface of the PA nanofilm. The asymmetric PA membrane exhibits an improved water permeance of up to $12.5 \text{ L m}^{-2}\text{h}^{-1}$

bar⁻¹; this is 3-fold larger than that of the traditional PA membrane (4.4 L m⁻²h⁻¹ bar⁻¹). Further, it has a high divalent salt rejection ratio of 98.9%, thus overcoming the trade-off among state-of-the-art nanofiltration membranes. The formation mechanism of such asymmetric PA nanofilms was clarified through multiscale theoretical simulations. These findings represent advances toward developing ultrapermeable membranes for highly efficient ion/molecular separation.

Chapter 5: Nanofiltration membrane which dominated by steric hindrance (size sieving) and electrostatic exclusion (Donnan repulsion) holds great promise for water remediation and reuse. However, the single membrane chargeability and inadequate crosslinking leads to insufficient separation for micro contaminants with low molecular weight and ions with monovalent and contrary valence as that of membrane, hindering fine molecular separation. In this work, I report an electroneutral NF membrane with narrower and sharpened free volume by scale up interfacial polymerization (IP) process following post polyallylamine (PAA) chemical functionalization. The amination reaction between PAA and PA surface carboxyl groups heightened molecular crosslinking and minimized electronegativity, favoring the effective removal of solutes with varied charge abilities in nanofiltration process. The best-performing neutral charged nanofiltration membranes manifest remarkable solutes obstruction against inorganic salts (e.g. 99.6% for MgSO₄, 99.9% for MgCl₂, 92.7% for NaCl, 99.5% for Co²⁺, 99.2% for NiCl₂ and 98.7% for ZnCl₂), trace contaminants (25.2% for boron and 93.6% for phosphorus under pH 10) and emerging micro pollutants (rejection rate greater than 97.3%) along with comparable water permeance (3.8 L m⁻² h⁻¹ bar⁻¹). This denser electroneutral NF membrane provides guideline for further development of high performance membrane for precise nanofiltration.

Chapter 6: A summary of this dissertation is given.

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Chapter 2

Mechanism Insights into The Role of Support Mineralization Layer toward Ultrathin Polyamide Nanofilm for Ultrafast Molecular Separation

2.1. Introduction

In light of historical trends that demonstrate accelerated urbanization, burgeoning population, and increased water scarcity and contamination, membrane-based purification technologies have attracted increasing attention in the field of micropollutant removal and wastewater recovery because of their lower energy consumption, reduced investment costs, and higher operational efficiencies than those of conventional separation methods [1-3]. Nanofiltration (NF) technology, which separates multivalent salts and low-molecular-weight organics (200-1000 Da), is a promising candidate for mitigating the water crisis [4]. Typical NF membranes adopt thin-film composite (TFC) structures, comprising a thin polyamide (PA) nanofilm fabricated on the surface of the underlying porous substrate, which is generally fabricated via interfacial polymerization between two active monomers through the Schotten-Baumann reaction at the aqueous-organic immiscible interface [5, 6]. However, the rapid and relatively uncontrolled reaction makes the PA layer highly crosslinked, which severely restricts water transport. In other words, the improvement of water permeance will inevitably result in the deterioration of rejection performance. The membrane separation performance, in terms of permeability and selectivity, generally suffers from “trade-off” limits. New membranes that can overcome the upper bound of perm-selectivity for separating specific ions and dissolved solutes with high efficiency are still sought after; hence, advanced treatment processes garner increasing attention [7, 8].

Previous studies have focused on investigating the interfacial polymerization mechanism to optimize the microstructures of the resultant TFC membranes and realize the substantial enhancement of membrane separation properties. One viable strategy is to introduce functional nanoparticles, such as covalent organic frameworks [9], porous organic polymers [10], metal-organic frameworks [11], and nanotubes [12] into the PA polymer matrix to construct nanochannels and improve the membrane permeability [13, 14]. Nonetheless, significant improvements in permeating flux, together with a disappointing rejection ratio, have been obtained because of the poor design and mismatch (severe aggregates with poor dispersity) between the polymer matrix and embedded nanofillers, which results in the formation of non-selective voids and damages membrane integrity. Another strategy is to regulate the intrinsic structure of the PA nanofilm by manipulating the interfacial polymerization process. Significantly thin synthetic PA membranes, approaching thicknesses < 10 nm with shortest passages, have been fabricated, which exhibit high acetonitrile permeance of up to $112 \text{ L} \cdot \text{m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ [15]. These ultrathin PA membranes are first fabricated through support-free interfacial polymerization and then transferred onto a substrate; nevertheless, the complicated and meticulous fabrication process severely hampers the manufacturing of TFC membranes on an industrial scale [6, 16, 17]. Hence, these membranes have only been fabricated on the laboratory scale. However, the conventional method for developing ultrathin membranes via in situ interfacial polymerization, where the reaction directly proceeds on the underlying membrane substrate, seems inapplicable in terms of reproducibility and manufacturing scalability [18]. This is because of the incompatibility (including pore size, porosity, roughness, and wettability) between the dense active layer and the porous substrate membrane, which may cause defects forming during interfacial polymerization [1, 19, 20]. To maintain an integrated selective layer and achieve high rejection, conventional PA-NF membranes generally have a thickness of 50-100 nm [21]. These efforts render the prevention of defects formation unlikely in case of a further decrease in membrane thickness. Hence, improvements in the separation properties, achieved through the modification of the thickness-related morphological aspects, seem to reach a plateau [22]. However, very recently, ultrathin TFC membranes developed by using different amine-based monomers [23], different interfacial polymerization methods [8], or different post treatments [4] have been reported, revealing the efforts for developing ultrathin

TFC membranes toward high solvent permeances. Despite these significant progress, the very detailed information in unraveling the formation mechanism of such ultrathin nanofilm is not well understood, and to further advance the synthesis of ultrathin nanofilms is of great practical interest. Therefore, the direct synthesis of an ultrathin PA nanofilm (approx. 10 nm) by in situ deposited onto an ultrafiltration membrane surface is important for the development of high-performance nanofiltration membranes.

Recently, a new strategy for developing sandwich-structured TFC membranes, which contain an interlayer between the bottom ultrafiltration membrane substrate and the top selective layer, has been envisaged as an effective alternative to break the long-standing permeability-selectivity upper bound for the fabrication of ultrathin PA-based NF membrane [19, 24, 25]. Zhu et al. prepared a novel TFC membrane based on a polydopamine-functionalized-carbon-nanotube (PDA-CNT) interlayer, where the interlayer provided a hydrophilic platform for fabricating an ultrathin PA rejection nanofilm with a large effective surface, while preventing the intrusion of PA into the substrate pores [26]. Using this method, numerous nanomaterials, such as cellulose nanofibers [27], cellulose nanocrystals, and MXene nanosheets [28], have been used as interlayers to fabricate high-performance TFC membranes. Nevertheless, most of the nanomaterials are commonly pre-loaded to the substrate via vacuum filtration, which probably easily result in detachment of the PA layer over long-term operation because of the weak interfacial interactions [22]. Although NF membranes with sandwich structures often achieve high separation efficiency, the appropriate features of an interlayer needed to construct ultrathin PA films are still unknown and controversial. There is a scarcity of studies that systematically exploit the theoretical models describing the swing influence of interior geometry and surface functionality of the interlayers in the regulation of the uptake and release of aqueous-phase amine monomers toward the aqueous-organic interface when conducting interfacial polymerization. Consequently, performing an insightful investigation is still in demand to better understand the fundamental mechanism that governs the role of interlayers. Such an investigation should result in both ultrathin and highly crosslinked PA membranes that provide high perm-selectivity for energy-efficient water remediation and treatment applications [29].

Herein, we report the fabrication of a highly perm-selective TFC membrane via

silicification interlayer-mediated interfacial polymerization (as shown in **Fig. 2.1**). The intermediate layer comprising of ultrafine silica nanoparticles was grown in situ onto the surface of the polysulfone (PSf) ultrafiltration membrane substrate through mineralization (**Fig. 2.1a**). The silicification interlayer allows high-density enrichment of amine monomers and serves as a quasi-molecular-scale regulator to decelerate their diffusion into the organic phase to be polymerized with the acyl chloride of TMC (**Fig. 2.1b**). This realizes the simultaneous modulation of monomer adsorption and diffusion. Such synergistic effects trigger self-sealing and inhibit the membrane growth, promoting the formation of ultrathin PA nanofilms (approx. 13 nm) with significantly decreased intrinsic resistance, but enhanced crosslinking with superior separation property (**Fig. 2.1c**). The technique is applicable to the majority of conventional interfacial polymerizations, which highlights its use in the development of high-performance membranes for water remediation.

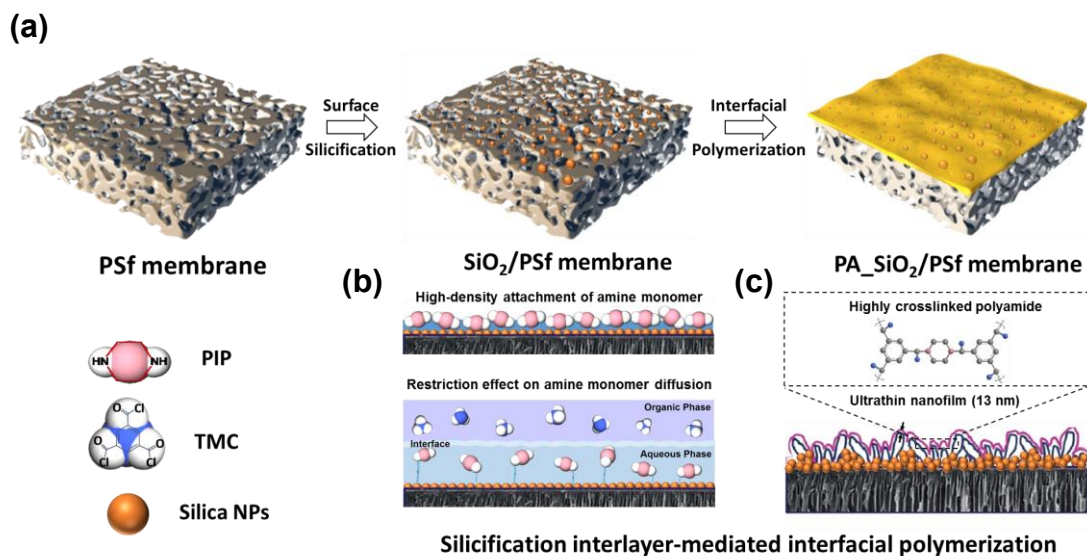


Fig. 2.1 Schematic of silicification interlayer-mediated interfacial polymerization, with (b) underlying mechanism of amine monomer adsorption enrichment and diffusion restriction toward organic phase, for (c) developing ultrathin and highly crosslinked PA nanofilm.

2.2. Experimental

2.2.1. Materials and chemicals

The commercial polysulfone ultrafiltration membrane (PSf, molecular weight cut-off

value of 30,000 Da) was supplied by Nitto Denko Corporation (Japan). Ethanol (EtOH, 99.5%), n-hexane (anhydrous), N,N-dimethylformamide (DMF, anhydrous), ammonia hydroxide (25%), (3-aminopropyl)-triethoxysilane (APTES, 98%), and tetraethyl orthosilicate (TEOS, 97%) were purchased from FUJIFILM Wako Pure Chemical Industries Co., Ltd. (Japan). D-(+)-Raffinose pentahydrate (98%), sucrose (99.5%), D-(+)-glucose (99.5%), and glycerol (99%) were purchased from Sigma-Aldrich (Japan). Inorganic salts of sodium sulfate (Na_2SO_4 , 99%), magnesium sulfate (MgSO_4 , 99%), magnesium chloride (MgCl_2 , 99%), calcium chloride (CaCl_2 , 99%), sodium chloride (NaCl , 99%), anhydrous piperazine (PIP, 99%), and 1,3,5-benzentricarbonyl (TMC 99.5%) were purchased from Tokyo Chemical Industry Co., Ltd. (Japan). Deionized (DI) water was produced by a Milli-Q water purification system (Merck, Millipore, Japan).

2.2.2. Fabrication of interlayer via in situ silicification process

The PSf substrate was first immersed in APTES aqueous solution (2.0%, w/v) for 48 h (designated APTES-d-PSf), followed by complete washing with DI water. Subsequently, the membrane substrate was immersed into a TEOS solution that comprised TEOS (1 mL), ammonia (4 mL), and EtOH (100 mL) for set times (1 h, 2 h, 4 h, or 6 h) to perform in situ silicifications. The fabrication of the ultrathin surface mineralization layer can be illustrated as follows: initially, the positively charged APTES was absorbed onto the negatively charged PSf, thereby forming a continuous polyelectrolyte layer of the APTES-d-PSf membrane after the poly-condensation process. Subsequently, the APTES-d-PSf membranes were immersed in the ethanol solutions of TEOS, and then the precursors were pre-deposited onto the surfaces of APTES-d-PSf membranes based on electrostatic interactions. Meanwhile, surface silicification occurred, whereof the side groups of silicon tetraethoxide (Si-OEt) from TEOS tended to be hydrolyzed, followed by the subsequent dehydration and condensation, and finally formed interconnected silica particles via the in situ assembly process. The newly prepared membranes with various mineralization durations were designated SiO_2 _1h/PSf, SiO_2 _2h/PSf, SiO_2 _4h/PSf, and SiO_2 _6h/PSf, respectively.

2.2.3. Fabrication of PA-based membranes via interfacial polymerization

A pristine PA membrane was prepared via interfacial polymerization. An aqueous solution containing 0.2% (w/v) PIP was poured onto the PSf substrate surface for 120 s. After draining off the aqueous solution, 0.1% (w/v) TMC solution was poured onto the substrate surface for another 30 s to form the selective layer, followed by heat curing treatment at 65 °C for 3 min. The resulting PA membranes were stored in DI water (4 °C) to finalize the hydrolysis of the unreacted chloride groups of TMC for 12 h prior to use. PA membranes supported by SiO₂/PSf membranes, designated PA_SiO₂/PSf, were fabricated by following the same procedure used for the pristine PA membrane. PA_SiO₂_xh/PSf represents a PA membrane supported by the SiO₂/PSf substrate fabricated by self-assembly for a duration of x h, where x is the surface silicification time.

The surface morphologies of the membranes were examined by field-emission scanning electron microscopy (FESEM; JSM-2100F, JEOL Ltd, Japan), and the samples were sputter-coated with platinum before characterization to inhibit the charging effect. The surface microstructures of the membranes were investigated using atomic force microscopy (AFM, SPI3800N, Hitachi, Ltd., Japan) in dynamic force microscopy (tapping) mode. The cross-sectional microstructures of the membranes were observed using field-emission transmission electron microscopy (FETEM, JEM 2100 F, JEOL). The surface chemistries of the membranes were characterized by attenuated total reflection-Fourier transform infrared spectrometry (ATR-FTIR, PerkinElmer, Spectrum One System) and X-ray photoelectron spectroscopy (XPS; JPS-9010 MC, JEOL, Japan). The surface hydrophilicity/hydrophobicity of the membranes was evaluated using a water contact angle (WCA) goniometer (Drop Master 300, Kyowa Interface Science Co., Japan). The reported WCA values were obtained by calculating the average of 5-time measurement results for three samples prepared from different batches. The surface charge of the membranes was determined using a SurPASS streaming potential analyzer (Anton Paar GmbH, Austria) at 22 °C.

2.2.4 Pore size and pore size distribution of the porous PSf supports

The mean pore size and pore size distribution of the porous pristine PSf and SiO₂/PSf substrates were evaluated using a liquid-liquid porometer (LLP-1100A, Porous Material Inc.,

Ithaca, USA). PSf membranes with a surface area of approximately $7.06 \times 10^{-4} \text{ m}^2$ were immersed in an isopropanol solution to saturate the pores before being placed into the testing cell. Galwick was selected as the displacement solution of isopropanol. It was pressurized to the upper surface of the membrane and pushed through the membrane pores by increasing the transmembrane pressure. The driving pressure and flow rates of the wet membranes were recorded. The mean pore diameter (D_p) was determined using the following equation [30]:

$$D_p = \frac{4\gamma}{P} \quad (2.1)$$

where P was the applied pressure (Pa), and γ was the interfacial tension of isopropanol ($21.7 \times 10^{-3} \text{ N m}^{-1}$). The test was performed at room temperature (298 K).

2.2.5 Membrane thickness evaluation

According to the kinetic model proposed by Freger for the polyamide nanofilms formed via interfacial polymerization, of the interfacial polymerization reaction zone is proportional to one-third of the diffusivity of the amine-based monomers [31]:

$$\delta \sim \left[\frac{LD}{k(C_a f_a + C_b f_b)} \right]^{1/3} \quad (2.2)$$

where δ (m) is the thickness of the interfacial polymerization reaction zone and hence the incipient PA layer, L (m) is the boundary zone, D ($\text{m}^2 \text{s}^{-1}$) is the diffusivity of organic amine in the organic phase, k ($\text{L} \cdot \text{mol}^{-1} \text{s}^{-1}$) is the reaction rate of the two-phase monomer, and C_i ($\text{mol} \cdot \text{L}^{-1}$) and f_i are the equilibrium concentration at reaction zone and functionality of the two-phase monomer, respectively.

2.2.6. Water permeance evaluation

Membrane performance tests of pristine PA and PA-SiO₂/PSf TFC membranes were carried out using a homemade crossflow filtration apparatus with an effective area of $8.05 \times 10^{-4} \text{ m}^2$, as reported previously [32]. The pure water permeability (J , $\text{L} \cdot \text{m}^2 \text{h}^{-1} \cdot \text{bar}^{-1}$) was calculated by measuring the weight change over a prolonged filtration time at a transmembrane pressure of 10 bar and a relatively low circulation flow rate of $0.01 \text{ L} \cdot \text{min}^{-1}$, as follows:

$$J = \frac{\Delta V}{\Delta P \times \Delta t \times A} \quad (2.3)$$

where ΔV (L) represents the permeating volume during a collection time period (Δt ; h), ΔP (bar) is the transmembrane pressure between the feed and permeate sides, and A (m²) is the effective membrane surface area. All samples were precompacted by filtration of pure water for 1 h until a stable permeating flux was reached. The reported water permeance values were obtained by calculating the average of 3-time measurement results for three samples prepared from different batches.

2.2.7 Rejection ratio evaluation

The effective rejection ratio (R , %) of membranes can be calculated as follows: [33, 34]

$$R = \left(1 - \frac{C_p}{C_f} \right) \times 100\% \quad (2.4)$$

where C_p and C_f represent the solute concentrations of the feed and permeate sides, respectively. The inorganic salts concentrations of the feed solution (Na₂SO₄, MgSO₄, MgCl₂, CaCl₂, and NaCl) were 1000 ppm, and the concentrations of the inorganic salts were measured using a conductivity meter (Ultrameter IITM 4P, Myron L Company, Japan). The reported rejection data were obtained by calculating the average of 5-time measurement results for five samples prepared from different batches.

2.2.8 Ion selectivity

The mono-/divalent ion selectivity ($\alpha_{\text{NaCl/Na}_2\text{SO}_4}$, %) of Cl⁻/SO₄²⁻ is as follows: [2]

$$\alpha_{\text{NaCl/Na}_2\text{SO}_4} = \frac{1 - R_{\text{monovalent}}}{1 - R_{\text{divalent}}} \times 100\% \quad (2.5)$$

where $R_{\text{monovalent}}$ and R_{divalent} represent the rejection ratios of NaCl and Na₂SO₄, respectively.

2.2.9 Crosslinking degree evaluation of PA membranes

The crosslinking degree of PA-based TFC membranes can be evaluated by calculating the atomic concentration of each element at the membrane surface using the following equations:

$$\text{Crosslinking degree}(\%) = \frac{m}{m+n} \times 100\% \quad (2.6)$$

where the values of m and n are derived from the ratio of oxygen to nitrogen (O/N) measured

from the XPS spectra using Equations: (2.7) and (2.8), respectively:

$$m+n = I \quad (2.7)$$

$$\frac{O}{N} = \frac{3m+4n}{3m+2n} \quad (2.8)$$

2.2.10 Molecular weight cut-off (MWCO) values and pore size distribution evaluation

The separation of neutral molecules and MWCO for PA membranes was evaluated in the aqueous feed. Four neutral saccharins, including glycerol (92 Da), glucose (180 Da), sucrose (342 Da), and raffinose (504 Da), were used in the feed solution. The concentrations of the neutral molecules were 1000 ppm, and the same experimental conditions as those for the ion selectivity tests for single salts were followed (under a transmembrane pressure of 10 bar and a circulated flow rate of 0.01 L·min⁻¹). The rejection rate was calculated using the same calculation method (Equation 2.4), except that C_p and C_f represent the sugar concentrations (determined by a total organic analyzer; TOC-VCSH, Shimadzu, Japan). Error bars represent standard deviations for at least three independent measurements toward different batches of membranes. The MWCO value is the minimum molecular weight of the polymer at a rejection ratio of 90%. The pore size distribution curve is expressed as a probability density function based on the following assumptions: (1) there are no steric or hydrodynamic interactions between the organic solutes and membrane pores, (2) the mean pore size (μ_p , nm) of the PA equals the Stokes radius of the organic solute with a measured rejection rate of 50% (d_p , nm), and (3) the distribution of membrane pore size is characterized by the geometric standard deviation of the probability density function curve, where the geometric standard deviation (σ_p) is calculated as the ratio of the Stokes radius (d_s , nm) at a rejection ratio of 84.13% to the mean pore size (d_p) at a rejection rate of 50%, as follows: [35-37]

$$\frac{dR(d_p)}{dd_p} = \frac{I}{d_p \ln \sigma_p \sqrt{2\pi}} \exp \left[-\frac{(\ln d_p - \ln \mu_p)^2}{2(\ln \sigma_p)^2} \right] \quad (2.9)$$

The Stokes radii (r_p) of these neutral organic compounds correlate with their molecular weights (Mw), which were calculated according to the following equation: [38]

$$\log(r_p) = -1.4962 + 0.4654 \log(Mw) \quad (2.10)$$

Based on the above equation, the Stokes radii for glycerol, glucose, sucrose, and raffinose were approximately 0.261 nm, 0.359 nm, 0.462 nm, and 0.538 nm, respectively.

2.2.11 Diffusion of PIP monomers into the organic phase

First, 30 mL of the PIP-based aqueous phase containing SiO₂ nanoparticles (size: 10-20 nm; Aladdin Biochemical Technology Co., Ltd, Japan) was poured into a 100 mL beaker, and 20 mL of n-hexane was carefully injected into the aqueous phase. After 30 s, 2 mL of n-hexane containing PIP was removed from the n-hexane-air interface and placed in quartz cuvettes. The diffusion of PIP from the aqueous phase to the organic phase through the interface was studied using a UV-vis absorption spectrometer (V-650KE, JASCO Company, Japan). PIP exhibited a maximum absorption peak at approximately 212.5 nm, and this peak was selected to indicate the PIP concentration (diffusion rate) in n-hexane [16, 17, 20, 39].

2.2.12 Determination of PIP adsorption and diffusion behavior of pristine PSf and SiO₂/PSf substrates

First, we immersed the pristine PSf and SiO₂/PSf substrates into the PIP solution (0.2%, w/v), followed by air drying and subsequent immersion into the n-hexane solution (without TMC), to thoroughly diffuse the PIP monomer. By investigating the PIP concentration in the organic phase using a UV-vis absorption spectrometer, the PIP adsorption amount of the substrates can be obtained based on the diffusion kinetics of PIP. The reported absorption values were attained by calculating the average of 5-time measurement results for five samples prepared from different batches. The PIP relative diffusion rate (D_r) for the first 30 s on various substrates was estimated using the following equation: [40]

$$D_r = \frac{S_{PIP-O} V_O}{C_{PIP} A} \quad (2.11)$$

where S_{PIP-O} (g L⁻¹ min⁻¹) is the diffusion rate of PIP from the membrane surface to the organic side, V_O is the volume of the organic phase (40 mL), C_{PIP} (g m⁻²) is the storage capacity of porous substrates, and A is the membrane surface area (8.05×10^{-4} m²).

2.2.13 Computational simulation

The molecular structures used in this simulation were modeled using the commercial software BIOVIA Materials Studio® 2018, and molecular dynamics (MD) simulations were performed using the same software. The condensed-phase optimized molecular potential for atomistic simulation studies II (COMPASS II) force field was used for energy minimization and MD simulations, and the effect of SiO₂ on PIP diffusivity during interfacial polymerization was investigated.

After structural optimization of these cells, MD simulations were performed under the condition of constant N (number of molecules), V (volume), and T (temperature) (NVT ensemble) for 4.0 ns at 298 K. The diffusivity of PIP was evaluated using the mean square displacement (MSD), and the diffusion coefficient, D_a , was calculated from Einstein's equation as follows: [32, 38, 39]

$$MSD = \frac{1}{N} \sum_{i=1}^N \left\langle \left[r_i(t+t_0) - r_i(t_0) \right]^2 \right\rangle = A + 6D_a t \quad (2.12)$$

where MSD was calculated for the center of gravity of the PIP in the hexane-water (hexane-water-SiO₂) system. The diffusion coefficient was calculated from the slope of the period, i.e., 1.0-3.0 ns. In addition, the atom-based interaction is investigated through the analysis of distance-dependent changes of the interaction energy between mineralization interlayer and PA active layer. The interaction energy for the PA and SiO₂ system (SiO₂-PA) is calculated according to the following equation: [41]

$$E_{inter} = E_{SiO_2+PA} - (E_{SiO_2} + E_{PA}) \quad (2.13)$$

Herein, E_{SiO_2+PA} represents the total interaction energy of the system, E_{SiO_2} and E_{PA} represent the energies of the SiO₂ and PA, respectively. For the interaction energy of the CNT-PA and CNT_{N/S}-PA, the CNT or CNT_{N/S} molecule substitutes the SiO₂ molecule, so that the E_{CNT} , $E_{CNT_{N/S}}$, E_{CNT+PA} , and $E_{CNT_{N/S}+PA}$ are hereby calculated, according to Equation (2.13). The distance-dependent variations of the interaction energy for the SiO₂-PA, CNT-PA, and CNT_{N/S}-PA were evaluated within the distance from 4.5 Å to 8 Å, wherein the critical distance of maximum intramolecular interaction force is obtained.

2.3 Results and discussion

2.3.1 Characterization of interlayer fabricated via in situ silicification

The SiO₂ interlayer is obtained via the surface silicification process on the polysulfone (PSf) substrate [42, 43], followed by interfacial polymerization between anhydrous piperazine (PIP) and 1,3,5-benzotriazin-2-one (TMC) monomers on the surface of the mineralization interlayer. The silicification interlayer, assembled in situ onto the PSf substrate, provides unique structural features and plays a significant role in the formation of an ultrathin PA-selective layer with intriguing surface architecture. After the surface silicification for 4 h, the interlayered membrane (SiO₂_4h/PSf) represents a curved topography that constitutes of ultrafine nanoparticles (50-100 nm, **Fig. 2.2b** and **2.2d**); however, the pristine PSf substrate has a smooth surface morphology (**Fig. 2.2a** and **2.2c**). This reflects the formation of a more crumpled surface architecture with higher roughness values. Notably, the pore size structures of the PSf substrate slightly decreased after surface mineralization. The average pore size decreased from 18.1 nm for the pristine PSf substrate to 16.1 nm for the SiO₂_4h/PSf membrane (**Fig. 2.2e**), which was attributed to pore blockage caused by nanoparticles surface deposition [44]. Simultaneously, the water contact angle decreased from 108° to 78°, which indicated an increase in the hydrophilicity of the surface (**Fig. 2.2f**). This was ascribed to the in situ surface silicification layer, which yielded abundant oxygen-containing groups of Si-OH with a strong polarity nature [45]. The significantly improved surface hydrophilicity enhanced the water permeance of the SiO₂_4h/PSf membrane up to 712 L·m⁻²h⁻¹·bar⁻¹ (**Fig. 2.2f**), which was an increase of 55.2% over the initial value of pristine PSf (458 L·m⁻²h⁻¹·bar⁻¹). This could be primarily attributed to the newly fabricated ultrathin silicification layer, acting as a hydrophilic nanochannel with lower mass-transfer-resistance (for more easily capturing water molecules) than that of pristine PSf. However, it should be noted the water permeance tends to decrease by continuously extending the surface silicification time over 1 h. This can be explained as the mineralization layer became denser and thicker over the prolonged treatment, which results in a more severe intrusion of agglomerated nanoparticles with increased mass-transfer resistance for the passage of water molecules throughout the membrane bulk [42, 44-46].

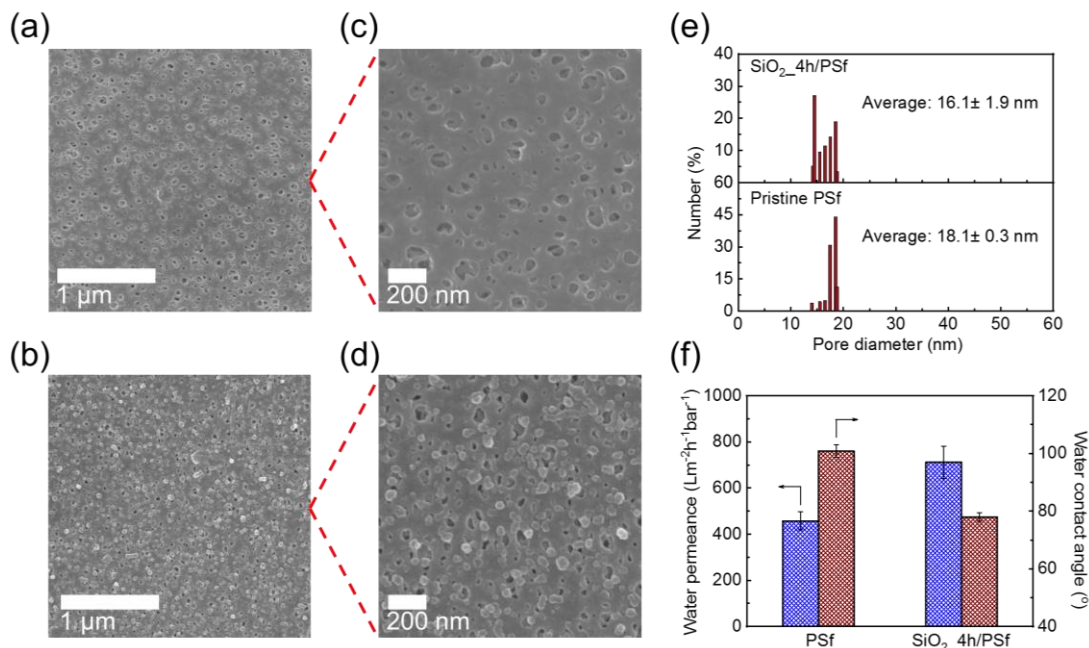


Fig. 2.2 FESEM images with low magnification (left-hand panel) and high magnification (middle panel) of pristine PSf (a, b) and SiO₂_4h/PSf (c, d) supports; (e) pore size/pore size distribution of pristine PSf and SiO₂_4h/PSf membranes; (f) water permeance and surface hydrophilicity of pristine PSf and SiO₂_4h/PSf membranes.

2.3.2 Characterization of PA_SiO₂/PSf TFC membrane

To further investigate the microstructural morphologies of the pristine PA and PA_SiO₂/PSf-TFC-NF membranes, SEM- and AFM-based characterizations were performed, and the top and bottom surfaces of the PA-based nanofilms deposited on various SiO₂/PSf substrates were analysed. It can be observed that the pristine PA membrane exhibits a conventional nodular structure with tightly dispersed granular bumps (**Fig. 2.3a**) [47]. **Fig. 2.3e** and **2.3g** present the 2D morphological features of PA_SiO₂/PSf membranes, where a distinct surface microstructure containing abundant ridge-shaped nanostrips can be observed. Interestingly, the bottom surfaces of the PA_SiO₂/PSf membranes contain a greater number of such nanostriped architectures, where more apparently Turing-like features can be observed (**Fig. 2.3f** and **2.3h**) [1, 5, 48], while the profile of the bottom surface of the pristine PA remains similar to that of its top surface (**Fig. 2.3e**). These unique structures on the bottom surfaces reflect the consistent morphologies of the top surfaces, indicating that the underlying

silicification interlayer severely affects the resultant architecture of the PA-selective nanofilm. The AFM characterization images (**Fig. 2.4**) were in accordance with the FESEM results. The AFM topography of pristine PA (**Fig. 2.4a**) shows a typical nodular-like structure with sporadic protrusions, where more crumpled volcano-like (**Fig. 2.4b**) and curved ribbon patterns (**Fig. 2.4c** and **2.4d**) surface morphologies with increased average roughness (Ra) values (9.71 nm for pristine PA to 73.26 nm for PA_SiO₂_6h/PSf) were formed (**Fig. 2.4e-2.4h**) when performing interfacial polymerization on the SiO₂/PSf membrane substrates developed over extended silicification time. AFM images of the 3D surface architectures (**Fig. 2.4i** and **2.4j**) further confirmed the effects of ultrafine mineralization layer on spatial features forming of PA nanofilm. The results of FESEM and AFM suggest that the silicification interlayer contributes to the formation of crumple ridge-shaped nanostrips with several tens of nanometers in sizes on the surface of the PA_SiO₂/PSf membranes. The nanostriped profiles in the PA nanofilms significantly increase the specific surface area (**Table 2.1**), which is superior to that of the pristine PA membrane with sporadic protrusion features. This creates a potential for improvement in the membrane permeance, which can enhance the water molecule penetration.

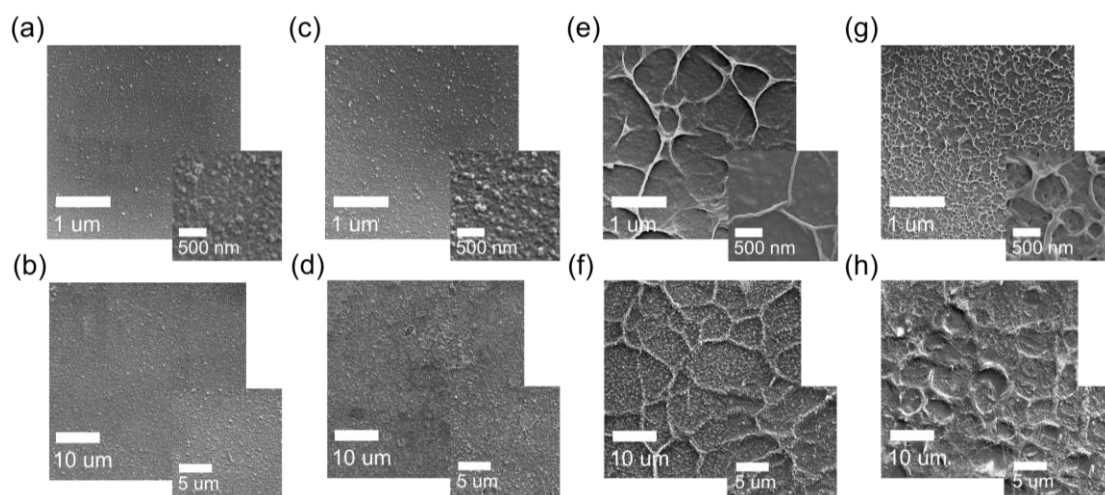


Fig. 2.3 FESEM images of top surfaces (upper panel) and bottom surfaces (bottom panel) of polyamide layers of pristine PA (a, b), PA_SiO₂_1h/PSf (c, d), PA_SiO₂_4h/PSf (e, f), and PA_SiO₂_6h/PSf (g, h) membranes.

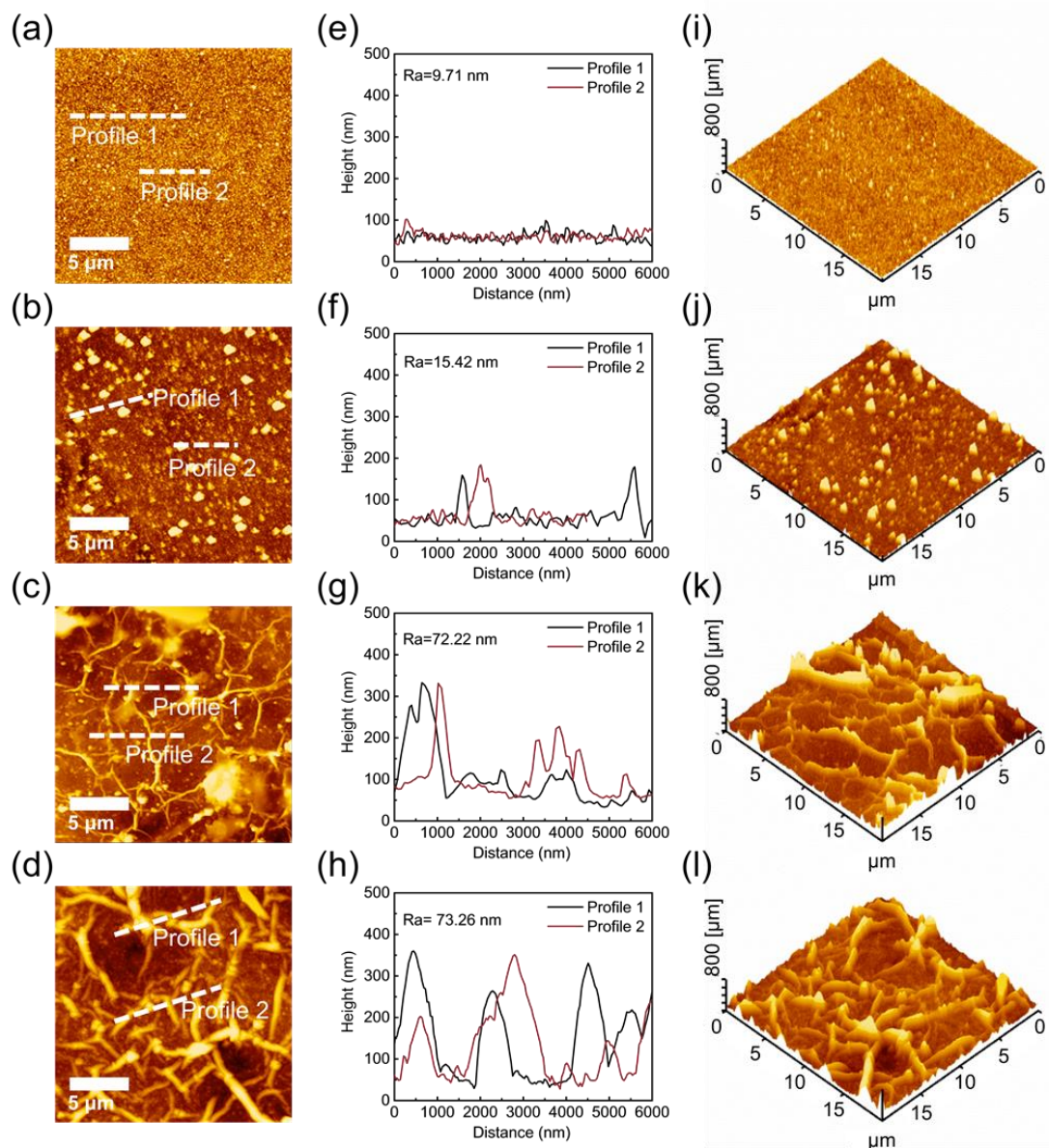


Fig. 2.4 AFM topographic images (left-hand panel), height profile (middle panel) and AFM surface 3D morphology images (right-hand panel) of pristine PA (a, e, i), SiO_2 _1h/PSf (b, f, j), SiO_2 _4h/PSf (c, g, k) and SiO_2 _6h/PSf (d, h, l) polyamide membranes.

TEM-based characterization results revealed the effects of silicification time on the internal/external microstructures of the PA_ SiO_2 /PSf membranes developed via silicification interlayer-mediated interfacial polymerization. The nanofilm thickness gradually decreased from 70 nm for pristine PA (**Fig. 2.5a**) to 13 nm for PA_ SiO_2 _4h/PSf and PA_ SiO_2 _6h/PSf membranes (**Fig. 2.5b–2.5d**). Furthermore, the silicification interlayers (tracked by the Si element in purple color), consisting of ultrafine nanoparticles of 50–100 nm, are uniformly

distributed in the proximity of the surface of the PSf substrate (**Fig. 2.5e–2.5h**). The formation of such an ultrathin PA-based active layer (approx. 13 nm) on SiO₂/PSf substrates should be explained by the enrichment of PIP on the SiO₂/PSf substrates and the hindrance of PIP transport to the TMC-based organic phase during interfacial polymerization. It should be noted that some interfacial nanovoids with interconnected curved ribbon structures between the PA active layer and the substrate inorganic nanoparticles can be observed for PA_SiO₂_4h/PSf and PA_SiO₂_6h/PSf membranes. This can be partially attributed to the highly hydrophilic silicification interlayer, which absorbs a significant number of water molecules that interrupt the normal interfacial polymerization process by hydrolysis of the acyl chloride of TMC, and thereby prevent the formation of dense PA in their vicinity [11, 32, 49]. Furthermore, the newly developed PA_SiO₂/PSf membranes, which feature a thin PA nanofilm, crumpled topography, and high specific surface area, can afford a significantly enhanced permeating flux compared to that of the traditional PA nanofilm (pristine PA) [28, 50, 51].

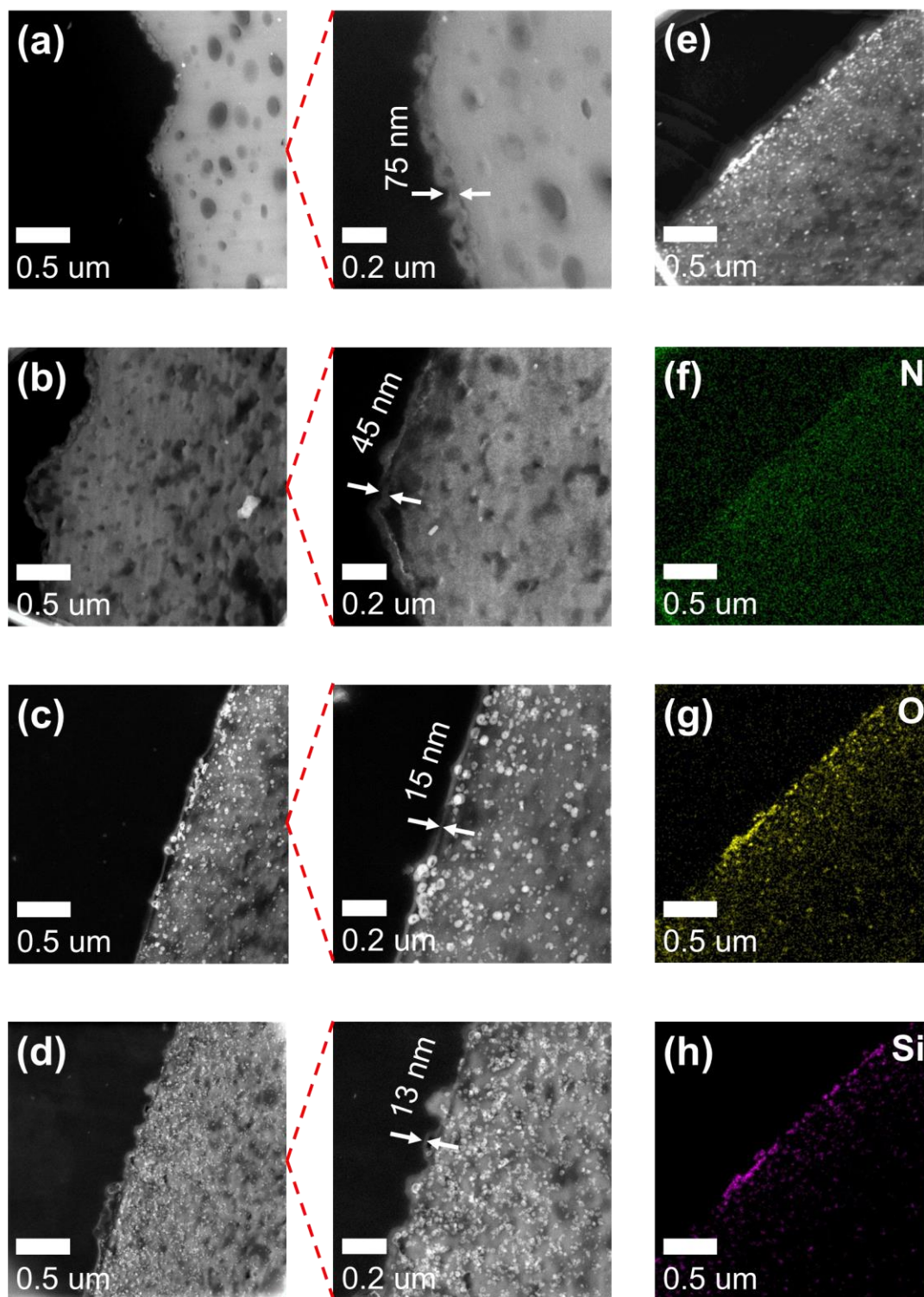


Fig. 2.5 Cross-sectional TEM images of (a) pristine PA, (b) PA_SiO₂_1h/PSf, (c) PA_SiO₂_4h/PSf, and (d) PA_SiO₂_6h/PSf-TFC membranes; TEM- and EDX-based mapping characterizations of (e) ASID mode, (f) N, (g) O, and (h) Si elements of the PA_SiO₂_4h/PSf membrane.

Table 2.1 Surface properties of pristine PA and PA_SiO₂/PSf TFC membranes. These results were acquired from AFM measurements over a scanning area of 20 $\mu\text{m} \times 20 \mu\text{m}$.

Samples	Height (nm)	Surface area (nm ²)	Ra (nm)	RMS (nm)	Surface pattern width (nm)
Pristine PA	79.3	4.245×10^8	9.71	12.61	~ 80
PA_SiO ₂ _1h/PSf	171.5	4.257×10^8	15.42	22.33	~ 180
PA_SiO ₂ _2h/PSf	180.2	4.311×10^8	24.16	38.22	~ 200
PA_SiO ₂ _4h/PSf	243.5	4.362×10^8	72.22	75.90	~ 150
PA_SiO ₂ _6h/PSf	269.9	4.417×10^8	73.26	88.71	~ 200

2.3.3 Effect of silicification interlayer on the formation of PA separation layer

To further validate our proposed mechanism of the PA nanofilm formation, molecular dynamics (MD) simulations were conducted to elucidate the diffusion kinetics of PIP monomers with and without the hindrance effects of the silicification interlayer (**Fig. 2.6a-2.6b**). More simulated details were presented in supporting information (**Fig. 2.7**). Silica particles restrict the diffusion of PIP toward the organic phase through chemical interaction (Si-O-Si/Si-OH interconnecting with PIP molecules) and steric hindrance, which results in a restricted diffusion coefficient (D_a) of $0.885 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ in hexane-water-SiO₂ system instead of a relatively rapid free diffusion behavior ($D_a = 1.671 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) in hexane-water system (**Fig. 2.6c**) [16]. The diffusion-regulated process was further investigated experimentally. **Fig. 2.6d** presents the absorbance variation of PIP in the organic phase after diffusion for 30 s. Lower trans-interface transmission rates of $0.094 \text{ g L}^{-1} \text{ min}^{-1}$ and $0.061 \text{ g L}^{-1} \text{ min}^{-1}$ are obtained for PIP_0.1 wt% SiO₂ and PIP_0.3 wt% SiO₂, respectively, and higher trans-interface transmission rate of $0.152 \text{ g L}^{-1} \text{ min}^{-1}$ is obtained for pure PIP. These results suggest a decreased diffusion rate of PIP monomers toward the organic phase during interfacial polymerization on the substrate surface with a higher density of silica nanoparticles, which corresponds to a thicker and/or denser silicification interlayer [40]. Of note, the diffusion coefficient is different from diffusion rate, but could be indicated by diffusion rate due to their positive correlation.

The enrichment of monomer (PIP storage capacity), which was integrated with the diffusion kinetics of PIP based on pristine PSf and various SiO₂/PSf substrates, was systematically measured. **Fig. 2.6e** shows that the PIP storage capacities for pristine PSf, SiO₂_4h/PSf, and SiO₂_6h/PSf substrates were in an increasing trend of 0.12 g m^{-2} , 0.39 g m^{-2} ,

and 0.36 g m^{-2} , respectively; while the measurements of the PIP concentration in the organic phase over a duration revealed that the monomer diffusion kinetics decreased (**Fig. 2.6f**), which represents the retarded the monomer diffusion toward the organic phase of TMC. The results can be ascribed to the thicker and/or denser silicification interlayer with enhanced surface hydrophilicity, where more aqueous solutions containing amine monomers were more easily captured within the nanopores of the silicification spatial structure [40]. The high density of amine monomers induces the generation of a denser PA layer with enhanced crosslinking property, which hinders PIP diffusion and the subsequent interfacial polymerization reaction between monomers and thereby promotes self-sealing and the formation of a thinner PA-based membrane. Based on Freger's equation of the supporting information, the monomer enrichment, combined with the kinetic control of PIP monomer diffusion, which is induced by the silicification interlayer, facilitates the formation of an ultrathin selective layer. This is because the thickness of the PA layer is inversely proportional to the equilibrium PIP concentration at the same diffusion time; whereas, the thickness is proportional to the one-third value of the diffusivity of amine-based PIP monomers toward the organic phase [31, 52].

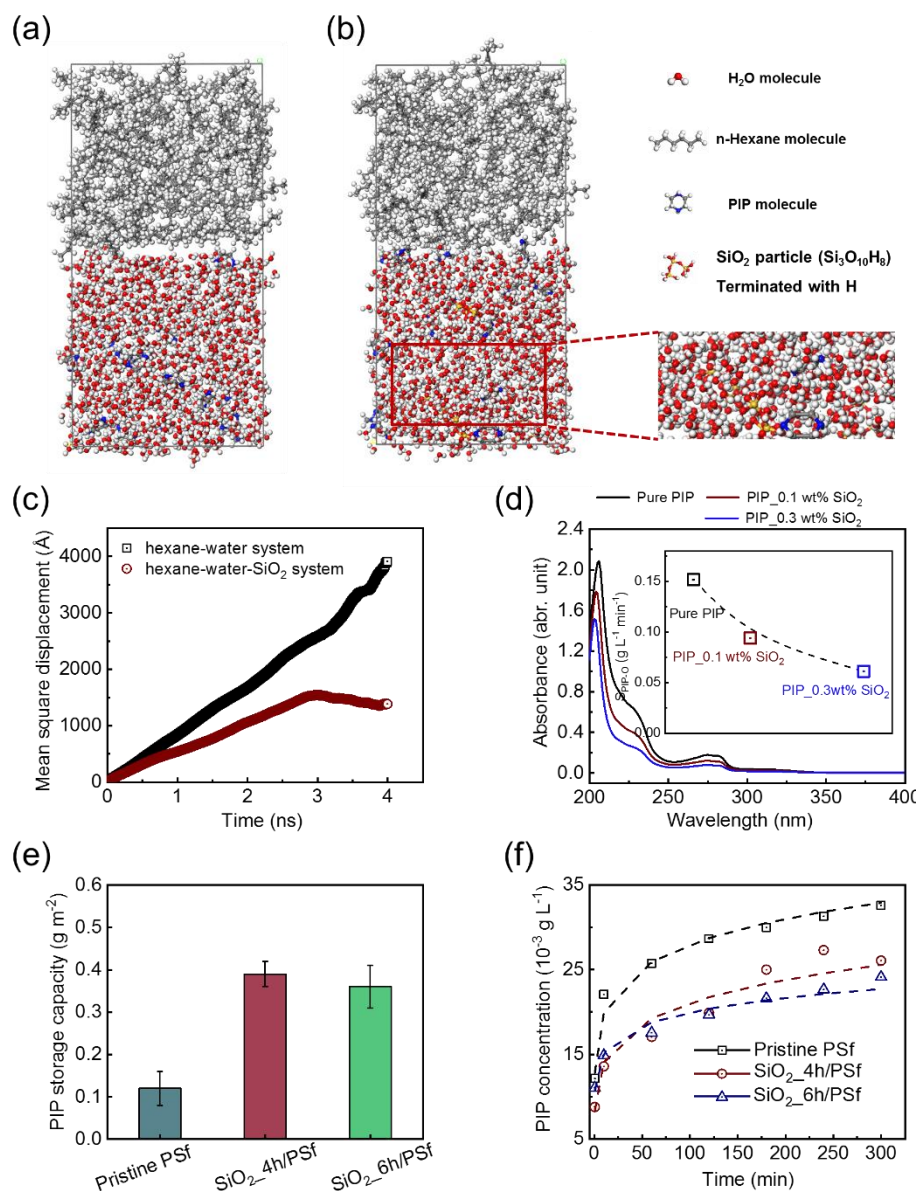


Fig. 2.6 Snapshots of the water/hexane interface in MD simulations (a) with and (b) without the SiO_2 particle; (c) MSD curves of PIP molecules in a pure water system with and without SiO_2 addition; (d) UV-vis spectra of PIP in the organic phase after 30 s of diffusion, where the inset is the transmission rate of PIP toward the organic phase, which is calculated based on the PIP standard UV-vis curve of concentration-maximum absorption peak in hexane; (e) PIP storage capacity of various PSf-based substrates; (f) detected PIP diffusion from PSf membranes to the organic phase.

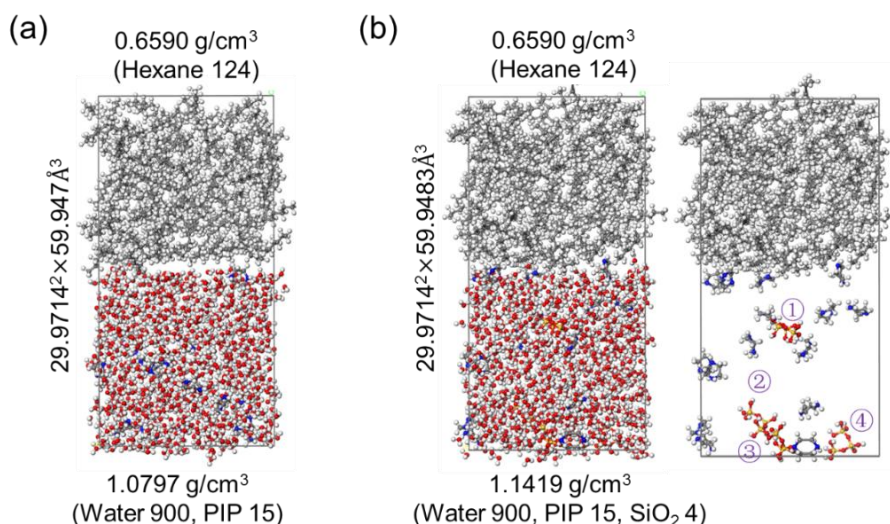


Fig. 2.7 Simulation cells with a size of 29.9714 Å × 29.9714 Å × 59.9470 Å and periodic boundaries in all directions was prepared. In the hexane-water system, 15 PIP and 900 water molecules were included to model an aqueous phase with a density of 1.0797 g cm⁻³, and 124 n-hexane molecules were included to model a hexane phase with a density of 0.6590 g cm⁻³, as shown in Fig. 2.7a. In the hexane-water-SiO₂ system, four SiO₂ molecules were distributed in the aqueous cell of the hexane-water system, as shown in Fig. 2.7b. Besides, the center coordinate of four SiO₂ particles inside the n-hexane-water-SiO₂ system are as follows: (6.09605, 15.6308, 21.2589), (20.5660, 20.3620, 5.80330), (5.88577, 16.6026, 2.13580), and (29.5996, 6.26715, 2.27770).

2.3.4 Separation properties of PA_{-SiO₂}/PSf TFC membrane

By considering the balance of the membrane separation properties in terms of permeability and selectivity, the optimum fabrication conditions, i.e., PIP 0.2% (w/v), TMC 0.1% (w/v), and interfacial polymerization duration of 30 s were selected for the fabrication of PA_{-SiO₂}/PSf TFC NF membranes. **Fig. 2.8a** shows that all PA_{-SiO₂}/PSf- TFC NF membranes exhibited increased water permeances. An exceptionally high permeating fluxes of 14.5 L m⁻²h⁻¹·bar⁻¹ and 20.6 L m⁻²h⁻¹·bar⁻¹ were obtained for PA_{-SiO₂}_4h/PSf and PA_{-SiO₂}_6h/PSf, respectively, much higher than that of the pristine PA membrane (4.8 L m⁻²h⁻¹·bar⁻¹). Such a significant enhancement (nearly three-fold) can be primarily attributed to the synergistic effects of (1) the ultrahigh specific area of the crumple microstructure with ridge-shaped nanostrips, which allows a greater number of water molecules to penetrate the membrane bulk. (2) The ultrathin

PA-based selective layer (approx. 13 nm) with a considerably shortened pore-flow distance that facilitates the permeation of water molecules. (3) The interfacial nanovoids between the silicification layer and polymer membrane, which serve as highways for quick passage of water molecules because of their low hydraulic resistance. **Fig. 2.8b** shows that the PA-SiO₂/PSf-TFC-NF membranes exhibited salt rejection ratios in the following order: Na₂SO₄ > MgSO₄ > MgCl₂ > CaCl₂ > NaCl. This result agrees with the PA-based membrane desalination properties derived from the combination of electrical (Donnan) and steric (size-sieving) exclusion effects [1]. This can be illustrated as: (1) a stronger electrostatic repulsion against the divalent ions (SO₄²⁻) than against the monovalent ions (Cl⁻) because of the negatively charged PA-based membrane surface property and (2) the hydrated radii of the monovalent ions of Na⁺ (0.358 nm) and Cl⁻ (0.332 nm), which are smaller than those of the divalent ions of SO₄²⁻ (0.379 nm), Ca²⁺ (0.412 nm), and Mg²⁺ (0.428 nm) [21]. Additionally, the formation of a ridge-shaped morphology for PA nanofilms with a surface silicification interlayer can be ascribed to the following synergistic effects: (1) The differences in the aqueous template formed on the substrate surface, which are caused by the enhanced hydrophilicity of the silicification-modified membrane, resulting in the absorption of a significant amount of aqueous microphase. The absorbed microphase assumes the shape of the substrate and directly influences the transition of the membrane surface morphology from the relatively smooth nodular structure (**Fig. 2.4a**) to the more crumple striped (**Fig. 2.4c-2.4d**) surface [51, 53]. (2) The diffusion-driven instability caused by the hindrance effect at the water/organic interface, where the surface silicification layer may alter the diffusion of the amine-dispersed aqueous phase (PIP molecules) toward the organic phase (**Fig. 2.6c-2.6d**), leads to the formation of a ridge-shaped structure consisting of closely packed hexagonal arrays or interconnected labyrinthine networks [1, 39].

The separation properties of the PA-SiO₂/PSf-TFC membranes were further investigated using carbohydrates with various molecular weights, i.e., glycerol (92 Da), glucose (180 Da), sucrose (342 Da), and raffinose (504 Da) (**Fig. 2.8c**). The PA-SiO₂/PSf-TFC membranes exhibited a negligible variation for sucrose and raffinose while performing a slightly decreased selectivity for glycerol and glucose, which indicated the formation of a greater number of homogeneous pore structures with looser (larger MWCO value of 318 Da and 334 Da for

PA_SiO₂_4h/PSf and PA_SiO₂_6h/PSf compared to that of pristine PA (304 Da), and narrower pore size (free volume) distributions compared with the pristine PA membrane. Similar experimental results can also be found in **Fig. 2.8b**, where the PA nanofilms of PA_SiO₂_1h/PSf and PA_SiO₂_2h/PSf promoted the rejection of divalent cations (Mg²⁺/Ca²⁺) and nearly retained their original rejection ratio against monovalent ion (Na⁺) solutes, resulting in improved mono/divalent ion selectivity relative to that of pristine PA. Such enhancements in the removal efficiency are attributed to the enhanced crosslinking property of the PA nanofilm. Because of the enhanced presence of aqueous amine monomers at the aqueous/organic interface, the interfacial polymerization reaction is strengthened. This promotes the formation of a dense selective layer. However, with increasing silicification time, relatively loose selective layers (with enlarged pore sizes of 0.34 nm and 0.37 nm for PA_SiO₂_4h/PSf and PA_SiO₂_6h/PSf membranes, respectively) were obtained (**Fig. 2.8d**). This indicated a slightly compromised Na₂SO₄ selectivity while allowing divalent cations (Mg²⁺ and Ca²⁺) to permeate with ease. Such a degradation of the desalination properties can be attributed to the following reasons: (1) The enlarged pore aperture architectures accompanied by the weakened size-sieving effect, with the formation of non-selective defects inside the ultrathin membrane bulk, is primarily derived from the interfacial instability in the water-organic interface because of the rugged surface profile of SiO₂/PSf substrates. (2) The ultrathin amorphous PA rejection layer (approx. 13 nm), with anomalous pore size distribution, exhibits a relatively desired water/salt perm-selectivity, which is predominantly determined by the Donnan effect (electrostatic interaction) instead of steric hindrance (size repulsion), if the thickness of the PA layer is down to several nanometers [2, 54, 55]. However, it should be noted that the PA_SiO₂_4h/PSf membrane still has a competitive selectivity, with negligible loss in the rejection ratio (98.7%) toward divalent anions (SO₄²⁻, derived from the Na₂SO₄ rejection) compared with that of the pristine PA membrane (98.8%). Although the relatively excessive silicification time (4 h) may result in defects forming on the roughened substrate, the water permeance of PA_SiO₂_4h/PSf membrane (14.5 L m⁻²h⁻¹·bar⁻¹) continues to remain significantly higher (three-fold) than that of the pristine PA membrane (4.8 L m⁻²h⁻¹·bar⁻¹). This guarantees its effectiveness in improving the separation efficiency for water remediation applications. Consequently, the PA_SiO₂_4h/PSf membrane was selected for further study because of its competitive molecular

selectivity and superior water permeability among the PA_SiO₂/PSf-based membranes.

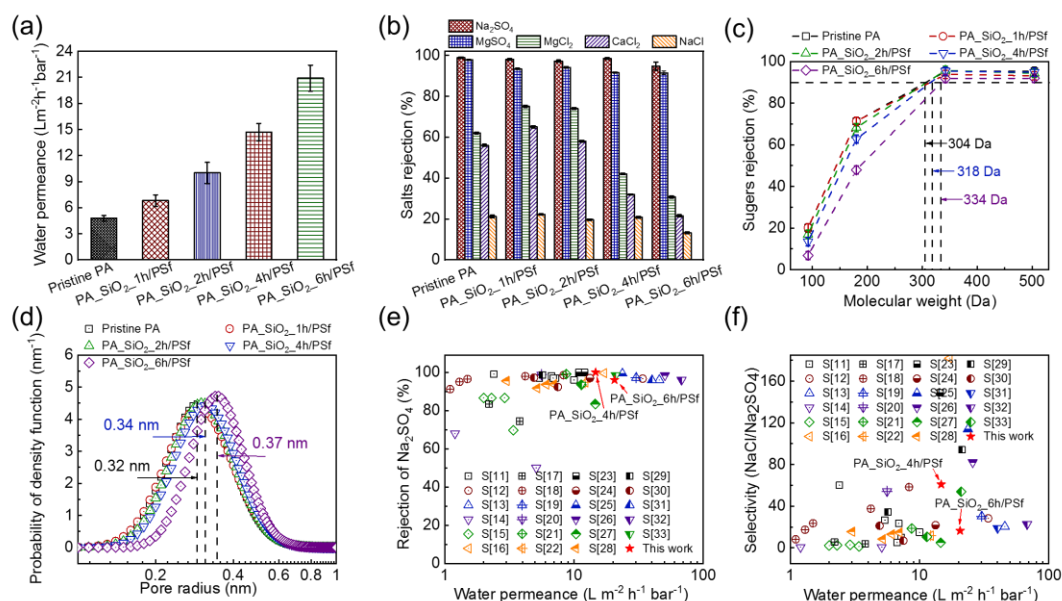


Fig. 2.8 Separation performance: (a) pure water permeance and (b) salt rejection ratio of pristine PA and PA_SiO₂/PSf membranes; (c) rejection ratios of neutral organic compounds of sugars; (d) pore size/pore size distribution of the PA-based selective layers calculated from the rejection curves; (e) comparison of the water permeances and Na₂SO₄ rejection ratios of the PA_SiO₂/PSf-TFC membranes with those of reported NF membranes; and (f) trade-off correlations between single salt selectivity (NaCl/Na₂SO₄) and water permeance for PA_SiO₂/PSf nanofilms and other reported NF membranes (further detailed information is summarized in **Table 2.2**)

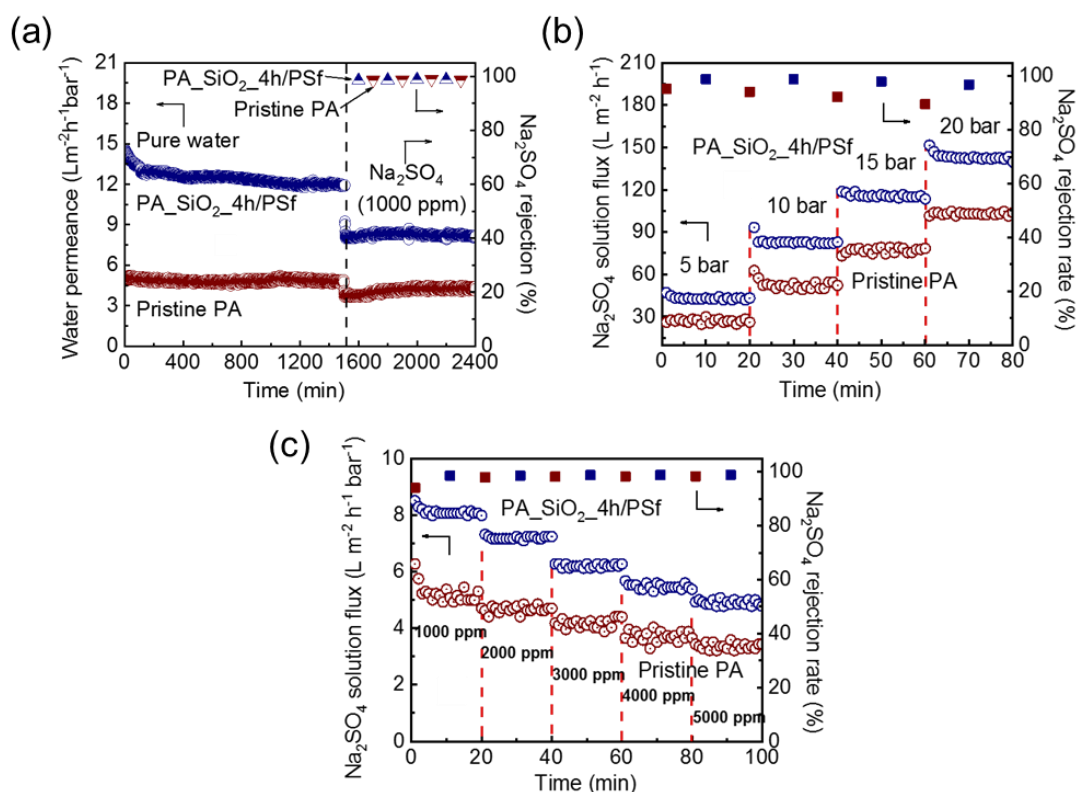


Fig. 2.9 (a) Long-term filtration of pristine PA and PA_SiO₂/PSf TFC membranes for pure water and 1000 ppm Na_2SO_4 aqueous solution; (b) Perm-selectivity of pristine PA and PA_SiO₂_4h/PSf TFC membranes toward Na_2SO_4 aqueous solution (1000 ppm) under varied transmembrane pressure (5-20 bar); Influence of Na_2SO_4 concentration on the perm-selectivity of the pristine PA and PA_SiO₂_4h/PSf TFC membranes.

The separation performance of membranes, in terms of the water/salt perm-selectivity and mono/divalent ion selectivity (for e.g., $\alpha_{\text{NaCl}/\text{Na}_2\text{SO}_4}$), is important for practical NF applications [2, 56], which requires the retention of divalent ions without any penalties associated with the extra osmotic pressure of NaCl. **Fig. 2.8e** compares the separation performance of the PA_SiO₂/PSf-TFC membrane with those of previously reported NF membranes. **Fig. 2.8f** shows the correlation between the water permeance (J) and $\alpha_{\text{NaCl}/\text{Na}_2\text{SO}_4}$ for conventional TFC desalination membranes. These results indicate that the PA_SiO₂_4h/PSf membrane presents a competitive mono/divalent ion selectivity (60.9) when compared to the state-of-the-art NF membranes (**Table 2.2**). Therefore, the silicification interlayer-mediated desalination membrane, with an excellent mono/divalent anion selectivity, is a promising candidate for future seawater softening, brine refining, and other relevant applications. For the

less competitive selectivity of Mg^{2+} , this should be attributed to the promoted transport of positively divalent ions faster than that of negatively ones when treated by PA-based membranes with negatively charged property and the weak Donnan exclusion hereby results in lower rejection ratios against cations (Mg^{2+}) compared to that against the anions (SO_4^{2-}) [9, 18, 46]. For long-term operation (2400 min), high transmembrane pressure (5-20 bar), and highly concentrated salt solution environment (1000-5000 ppm), the water permeance and Na_2SO_4 rejection ratio of the PA_ SiO_2 _4h/PSf membrane are relatively stable in comparison with that of the pristine PA membrane, as demonstrated in **Fig. 2.9**. This experiment reveals that the surface microstructures with rigid and uniform-nanostripe structures are remained, nearly without severe compaction, breaking, or tearing in harsh and long-term filtration processes, further demonstrating its long-term operation stability. To further explore the effects of the dynamic behavior between the SiO_2 interlayer and PA, in comparison with that between the pristine carbon nanotube (CNT), amino/sulfonate groups-modified CNT (CNT_ N/S) and PA layers [26, 57-61], their interfacial interactions were systematically investigated, as shown in **Fig. 2.10** and **Fig. 2.11**. The MD simulation result unveils that the SiO_2 interlayer-PA exhibits the highest interaction energy of $-23.47 \text{ kJ mol}^{-1}$ at the closest interfacial distance of $5 \text{ \AA}$, while the CNT_ N/S -PA and CNT-PA reveal the relatively weaker energy of -18.41 and $-17.61 \text{ kJ mol}^{-1}$ at a farther interfacial distance of $5.75 \text{ \AA}$ and $5.5 \text{ \AA}$, respectively. This result verifies the more intense interfacial connection between the newly-developed SiO_2 interlayer and PA layer, owing to the superior hydrophilicity with large amounts of hydroxyl groups that interconnects with the active sites (carbonyl and amine groups) of PA [59], compared to that between the relatively hydrophobic interlayers such as CNT, or CNT_ N/S with PA layer [47]. In all, these results demonstrate that such ultrathin TFC membranes with ridge-shaped nanostripe structures exhibit excellent pressure resistance and interfacial stability without breaking or tearing in harsh and long-term filtration processes.

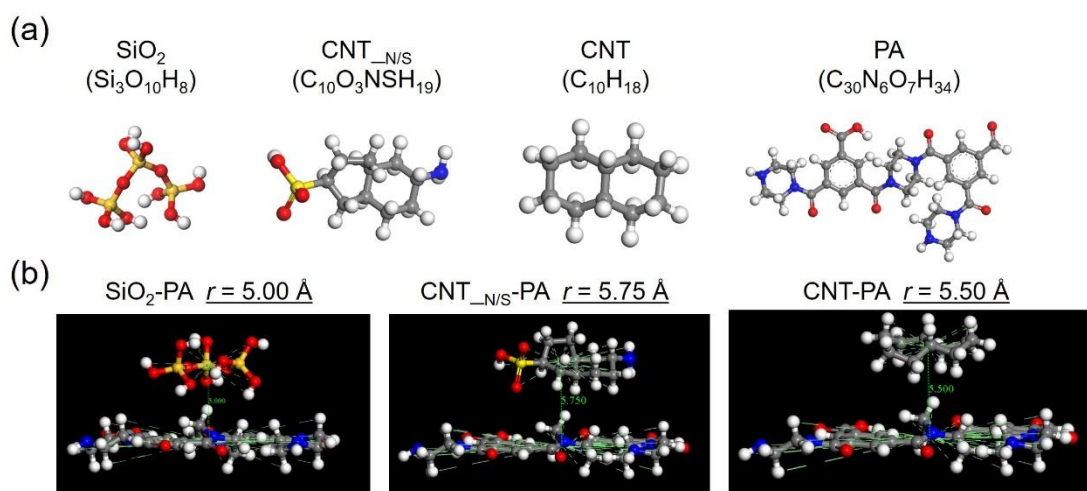


Fig. 2.10 (a) The chemical structures of SiO_2 , $\text{CNT}_{\text{N/S}}$, CNT , and PA ; (b) snapshots of $\text{SiO}_2\text{-PA}$, $\text{CNT}_{\text{N/S}}\text{-PA}$, and CNT-PA at the lowest interaction energy positions.

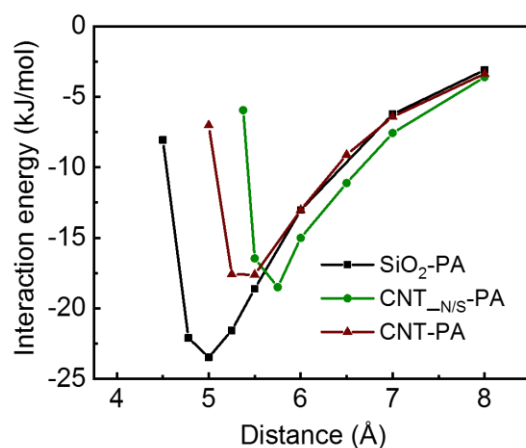


Fig. 2.11 The distance-dependent interaction energy of the $\text{SiO}_2\text{-PA}$, $\text{CNT}_{\text{N/S}}\text{-PA}$, and CNT-PA systems.

Table 2.2 Performance of reported state-of-the-art nanofiltration membranes.

Membrane and description	Membrane abbreviation	PWP ($\text{L m}^2 \text{ h}^{-1} \text{ bar}^{-1}$)	Salt rejection (%)			$\text{Cl}^-/\text{SO}_4^{2-}$ Selectivity	References
			Na_2SO_4	MgSO_4	NaCl		
Commercial membranes	DOW						
	FILMTEC™	7.2	97.0	70.0	70.0	10.0	
	NF70						
	DOW						
	FILMTEC™	6.7	98.0	90.0	90.0	5.00	[62]
	NF90						
	GE-Osmonics DL	10.0	96.0	96.0	40.0	15.0	
	GE-Osmonics HL	6.9	97.0	97.0	33.0	23.3	
	Synder NFX	2.4	99.0	99.0	40.0	60.0	

	Synder NFW	5.4	97.0	97.0	20.0	26.7	
NF membranes with cellulose nanocrystals as an interlayer	PA50/CNC/PES	34	97.7	86	6.5	40.7	[27]
MXene Nanosheet Templated Nanofiltration Membranes	TFC _n O	45.7	96.0	94	18	20.5	[28]
TFC NF membranes fabricated from polymeric amine, polyethylenimine embedded with monomeric amine, And piperazine for enhanced salt separation	PEI _{2.4} -PIP _{0.6} /TMC	5.1	50.0	74	65.0	0.70	
	PEI _{0.6} /TMC-PIP _{2.4} /TMC	1.2	68.0	94	78.0	0.69	[63]
Enhancing the performance of polyethylenimine-modified NF membranes by coating a layer of sulfonated poly(ether ketone) for removing sulfamerazine	SPEEK/PEI-PI # 5 m	3.4	69.7	> 90	57.6	1.4	
	SPEEK/PEI-PI # 10 m	2.9	86.6	> 90	60.8	2.9	
	SPEEK/PEI-PI # 30 m	2.3	86.6	> 90	66.9	2.5	[64]
	SPEEK/PEI-PI # 60 m	2.0	86.6	> 90	70.4	2.2	
Polyamide nanofiltration membrane with highly uniform sub-nanometre pores for sub-1 Å precision separation	(PIP+SDS)/TMC	17.1	99.6	98.2	27.0	182	[37]
pH-responsive NF membranes containing carboxybetaine with tunable ion selectivity for charge-based separation	PCHM1	2.2	83.4	58	5.2	5.7	
	PCHM2	3.8	74.4	56	4.4	3.7	[65]
Oligo-ethylene-glycol-based thin-film composite NF membranes for effective separation of mono-/di-valent anions	PA@EDA 0.15%	4.2	98.0	-	24.8	37.6	
	PA@EDA 1%	1.1	91.2	-	27.6	8.2	
	PA@EDA 2%	0.6	61.4	-	27.5	1.9	
	PA@DCA 0.2%	8.3	98.5	-	12.6	58.3	[56]
	PA@DCA 1.5%	1.5	96.5	-	17.5	23.6	
	PA@DCA 2.5%	1.3	95.0	-	13.2	17.4	
Alginate Hydrogel Assisted Controllable Interfacial Polymerization for High-Performance Nanofiltration Membranes	SA-15.5	30.3	97.2	82.7	15.2	30.3	[66]
TiO ₂ @graphene oxide incorporated antifouling nanofiltration membrane	NFM-3 # 0.2 wt% TiO ₂ @GO	5.6	98.8	58	35	54.17	[67]
Ultrathin PA membrane with	BTC-PIP	8.7	99.1	99.4	83.3	18.6	[68]

decreased porosity and superior antifouling properties							
Nanovoid membranes embedded with hollow zwitterionic nanocapsules	TFNM with HZN _{Cs}	12.2	94.7	93.4	38.2	11.7	[69]
MPD based nanofiltration membrane	NMP-act.	10.9	99.9	99.9	94.3	57	[70]
	DMF-act.	12.1	99.9	99.9	91.4	86	
	DMSO-act.	14.5	99.9	99.9	85.1	149	
Polydopamine-coated silica nanoparticles embedded thin-film nanocomposite nanofiltration membranes	TFN _{PDA-SiNPs}	13.3	97.0	94.0	35.0	21.7	[71]
Polyphenol intermediate layer for nanofiltration	NFM-15	23.7	99.4	99.4	33.4	114	[72]
Phosphonium modification leads to ultrapermeable antibacterial polyamide composite membranes with unreduced thickness	THPC-5	50.5	98.4	93.8	22.0	48.8	[73]
Preparation of TFC NF membranes with improved structural stability through the mediation of polydopamine	PA/PA-PES	11.4	93.5	82.4	31.0	10.6	[74]
	PA/PES	14.6	83.4	70.6	16.9	5.0	
Tuning the functional groups of carbon	PA-TFC	3.0	95.5	89.0	30.2	15.5	
quantum dots in thin-film nanocomposite membranes for nanofiltration	TFN-SCQD	7.0	93.8	82.0	8.8	14.7	[13]
	TFN-NCQD	5.2	91.7	90.0	30.5	8.4	
	TFN-CCQD	6.1	93.6	87.0	16.8	13.0	
Thin-film composite membranes with aqueous template-induced surface nanostructures for enhanced NF	TFC-R	21.3	99.4	-	43.5	94.2	[75]
	TFC-T	5.7	98.5	98.5	48.3	34.5	
	TFC-control	4.9	97.2	93.4	40.5	21.2	
SDS-intervened NF membrane	TFC-SDS	7.5	92.3	93.8	47.0	6.9	[76]
PD/SWCNTs film supported ultrathin polyamide NF membrane	PD/SWCNTs	*40.2	95.9	94.1	22.7	18.9	[26]
Sub-5 nm polyamide nanofilm	NFM #1	68.0	96	84.8	9.8	22.55	[4]
PDA inter-mediated nanofilm	PA/PD-PES	11.4	93.5	82.4	31	10.6	[77]
CNTs intermediated nanofiltration membrane	TFC-2	21	98.5	98.3	18.8	54.1	
SiO ₂ inter-modulated PA-NF membrane	PA_SiO ₂ _4h/PSf	14.5	98.7	97.9	20.8	60.9	This work
	PA_SiO ₂ _6h/PSf	20.6	94.7	91.6	13.2	16.4	

Pristine PA	4.8	98.8	91.4	21.2	65.8
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* Water permeance of NaCl feed was considered as the pure water permeance.

2.4 Conclusions

High perm-selective PA nanofilms were successfully developed via silicification interlayer-regulated interfacial polymerization process. The silicification interlayer, fabricated in situ, enhanced the surface hydrophilicity of the PSf substrate. Furthermore, it conferred the high-density attachment of amine monomers and served as a quasi-molecular-scale regulator that decelerated their diffusion into the organic phase for polymerization with the acyl chloride of TMC. These synergistic effects sealed the membrane and inhibited its growth. Consequently, ultrathin PA nanofilms (approx. 13 nm) with enhanced crosslinking properties were formed. The best-performing PA₂/SiO₂/PSf membrane showed approximately three-fold water permeance ($14.5 \text{ L m}^{-2} \text{ h}^{-1} \cdot \text{bar}^{-1}$) compared to that of the pristine PA membrane ($4.8 \text{ L m}^{-2} \text{ h}^{-1} \cdot \text{bar}^{-1}$). The best-performing membrane exhibited a high rejection rate of 98.7% toward divalent salts (without compromising the separation capability), as well as a competitive mono/divalent ion selectivity of 60.9. The outstanding nanofiltration property of the PA₂/SiO₂/PSf membrane can be attributed to the multiple integrations: the increase in the internal polarity, decrease in the active layer thickness, and increase in the specific surface area comprising a loose pore structure with a high free volume distribution.

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Chapter 3

A Zwitterionic Copolymer-Interlayered Ultrathin Nanofilm with Ridge-shaped Structure for Ultrapervious Nanofiltration

3.1. Introduction

Owing to the rapid population increase and industrialization that have caused severe water pollution and enhanced consumption, water scarcity has become a daunting challenge worldwide [1, 2]. Membrane-based purification technology plays a vital role in securing potable water through reclamation and remediation of industrial wastewater resources. Thin-film composite (TFC) membranes, consisting of an ultrathin selective layer deposited onto the substrate surface, are extensively employed in precise molecular and ionic separation processes, such as nanofiltration, reverse osmosis, and forward osmosis applications [3, 4].

Interfacial polymerization (IP), which serves as a platform technology, can be used to fabricate TFC membranes by confining amine monomers reacting with acyl chloride at the immiscible biphasic interface [5]. For the pressure-driven nanofiltration process, a polyamide (PA)-based selective layer with equivalent nanosized pore structures and charged surfaces can effectively sieve monovalent/divalent ions and thus screen small molecular organics within the range of 200-1000 Da [6]. Conventional membranes are plagued by trade-off limits in terms of permeability and selectivity, as precise control over the membrane microstructures, including molecular crosslinking degree, surface charge density, and nanofilm thickness, still remain challenging [7, 8].

Researchers have devoted extensive efforts to customizing the microstructural morphology of PA nanofilms by tuning the amine-based monomer formula, fabrication condition/process, and porous structural property [9-11]. This may generate two effects: one is the formation of a thinner PA nanofilm [12], and the other is the enhancement of the effective surface area [13]. The thinner PA nanofilm aims to decrease the hydrophilic resistance to water

molecules transporting across the selective layer, and hereby improves water permeance. It has been acknowledged that by introducing an interlayer on ultrafiltration support membrane [2, 14], including inorganic mineralization films [15], carbon nanotube network layers [16, 17], cellulose nanocrystals [18], and metal-organophosphate coordination interlayers [19], the interfacial reaction can be precisely controlled, and an ultrathin nanofilm can be developed. For instance, an ultrathin PA membranes (<10 nm thickness) with short mass transfer distances were developed on a sacrificial cadmium hydroxide nanostrand layer, and the resultant membrane exhibited a high acetonitrile permeance ($112 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) while exhibiting high rejection ratio towards various solutes with molecular weight cut-off (MWCO) values less than 300 Da [20]. Nevertheless, such complex processes hamper the industrial manufacturing of TFC membranes, whose fabrication can only be realized in the laboratory. This reflects a poor understanding of the fundamental role of the interlayer, which prompts us to investigate its underlying mechanism and develop an ultrapermeable TFC membrane via a more directly feasible approach.

Increasing the effective filtration area by creating sufficient internal nanovoids/surface ridges has been recognized as an effective way to facilitate more water cross-flow mass through the PA membrane and boost water permeance per unit area [21, 22]. Two main approaches have been developed to selectively control the formation of wrinkles on the PA surfaces. 1) Incorporating hydrophilic additives, i.e., polyvinyl alcohol (PVA) during IP, to interconnect with amine monomers via hydrogen bonding [1, 14, 22]; 2) modifying the surface properties of the substrate membrane, whose inhomogeneous surface chemistry (in terms of water wetting behavior) may impart a more uniformly distributed amine monomer, incurring diffusion-driven instability with reduced diffusion rate and further forming a crumpled PA nanofilm [7, 23]. Presumably, advanced interlayered modification can rationally promote water transport efficiency by simultaneously reducing the overall membrane thickness and enhancing the specific surface area [24]. However, such precise control of the interfacial reaction to further investigate a substrate surface structure-chemistry relationship for synergistically developing ultrathin and crumpled PA nanofilms has rarely been reported. Demand for a systematic examination of the swing influence of interlayer surface functionality and geometry via regulating the IP process is urgently needed.

In last chapter (ultrafine SiO_2 interlayer mediated interfacial polymerization), even if the as-resultant membranes show good performance in terms of membrane permeance and selectivity, there are still some room to be improved. First, the random collision (Brownian motion) usually generate larger sized SiO_2 particles, the larger sized mineralization nanoparticles on PSf support usually resulted in the interfacial polymerization process failure (**Fig. 3.1a**). Second, the limited hydrophilicity of SiO_2 layer (the WCA is approximately 80°) may also lead to the inhomogeneous distribution of diamine monomers (which may form heterogeneous pore characteristics of PA, **Fig. 3.1b**).

Herein, as schematically illustrated in **Fig. 3.2**, we report a zwitterionic copolymer, 2-methacryloyloxyethyl phosphorylcholine (MPC), and 2-amino-ethyl methacrylate hydrochloride (AEMA) (P[MPC-co-AEMA]) interlayered PA membrane to simultaneously achieve such identical advantages. The varied composition ratios of poly[MPC] and poly[AEMA] were systematically examined to unveil the underlying effects of the substrate microstructure/chemistry on the separation properties of the developed TFC membranes. Detailed mechanistic investigations revealed that the membrane separation performance was promoted, owing to the occurrence of diffusion-driven instability. This triggered membrane self-sealing and then inhibited its growth, resulting in the formation of an ultrathin PA nanofilm (down to 12 nm) with a ribbon-shaped surface structure (enhanced specific surface area) and enhanced crosslinking.

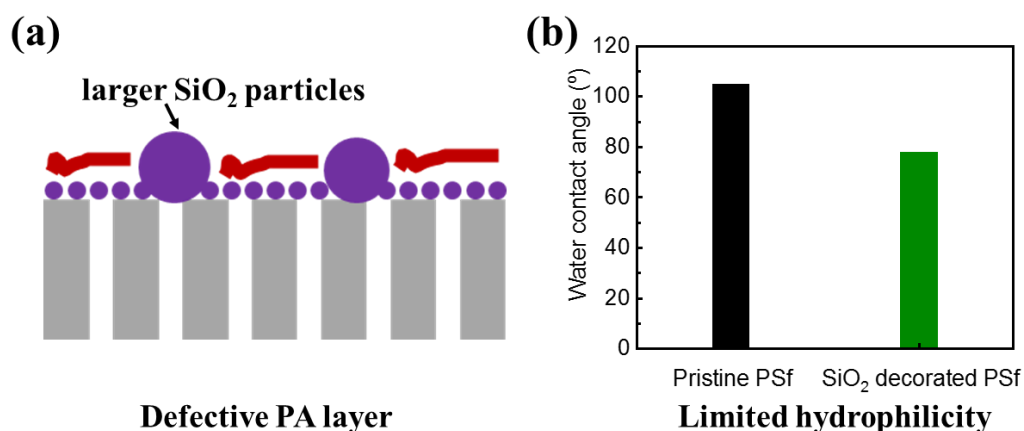


Fig. 3.1 (a) The heterogeneous distribution of SiO_2 nanoparticles on support together with the defective PA selective layer; (b) WCA values of pristine PSf and SiO_2 decorated PSf substrates.

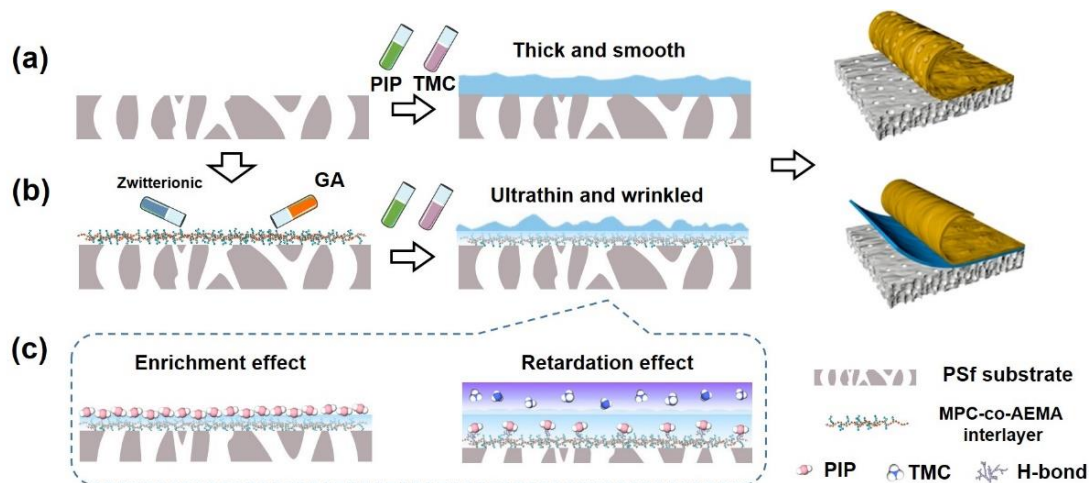


Fig. 3.2 Schematic of (a) conventional and (b) P[MPC-*co*-AEMA] inter-mediated IP with the underlying mechanism of (c) enrichment effect and (d) restricted diffusion of amine monomers for the formation of ultrathin PA membrane with a ribbon-shaped surface structure.

3.2 Experimental

3.2.1 Materials

The zwitterionic copolymers 2-methacryloyloxyethyl phosphorylcholine (MPC) and 2-aminoethyl methacrylate hydrochloride (AEMA) copolymer (P[MPC-*co*-AEMA]) was supplied by NOF Corporation (Japan). And other chemicals used in this work were same as Chapter 2.

3.2.2 Preparation of P[MPC-*co*-AEMA] interlayered PSf membrane

The commercial PSf support was treated with ethanol overnight prior to formal usage to remove pre-coated glycerol. Then, the PSf substrate was dipped into an aqueous solution (20 mL) of P[MPC-*co*-AEMA] at a certain concentration for 2 h, followed by an in-situ crosslinking reaction with GA (2.5 wt%) at 60 °C for 1 h. The resultant P[MPC-*co*-AEMA]-interlayered PSf membrane was designated as Co_x/PSf, in which x represents the copolymer concentration (wt%).

3.2.3 Fabrication of TFC nanofiltration membranes

Typically, PSf support was dipped into 0.2% (w/v) PIP aqueous solution for 30 s; then, the superficial remnant liquid was removed using an air knife and dried in air. Followed by

contacting with 0.1% (w/v) TMC hexane solution for 30 s to initiate IP reaction. The resultant PA membranes (denoted as pristine PA) were stored in pure water overnight after 70 °C treatment (3 min) prior to testing. PA_Co_x/PSf membranes were fabricated on Co_x/PSf substrates following the pristine PA membrane fabrication procedure.

3.2.4 Membrane characterization

The specific surface areas of the PSf supports were measured by N₂ sorption isotherms at 77 K using a Belsorp-Max (Bel, Japan) instrument. Using adsorption branches, Brunauer-Emmett-Teller (BET) plots were obtained. The free volume of the PA-based membranes was determined by positron annihilation lifetime spectroscopy (PALS, Toray, Research Center, Inc.). Other membranes characterization methods were listed in Chapter 2.

The evaluation of thickness of polyamide layers, water permeance, salts rejection ratio, degree of cross-linking, pore size and pore size distribution of the resultant TFC membranes were same as Chapter 2.

3.2.5 Evaluation of the PIP storage capacity of porous PSf supports

PSf and Co_x/PSf substrates were placed into the PIP aqueous solution (0.2%, wt/v) and dried in air. Subsequently, the substrates were immersed into pure water for thoroughly diffusing PIP. Finally, 2 mL solution was extracted at a different time to determine the concentration of PIP by UV-vis spectrophotometer. The PIP storage capacity (C_{PIP} , g m⁻²) can be obtained using the following equation [15, 25]:

$$C_{PIP} = \frac{m}{A} \quad (3.1)$$

where m (g) is the mass of PIP on the PSf ultrafiltration support, and A (m²) is the effective area (8.04×10^{-4} m²) of the PSf membranes. The reported absorption values were attained by calculating the average of 5-time measurement results for five samples prepared from different batches.

3.2.6 Diffusion behavior of PIP monomers into the organic phase

First, 20 mL homogeneous aqueous phase containing PIP and a certain concentration of zwitterionic copolymer was poured into a glass container and 10 mL hexane solution was

carefully poured above the PIP solution. 2 mL of hexane solution was removed from the hexane-air interface after 30 s diffusion and measured using a UV-vis spectrometer for calculating the diffusion rate of PIP [26].

3.2.7 Molecular dynamics simulation

The commercial software BIOVIA Materials Studio® 2018 was used for simulating molecular dynamics (MD). The same software was used for simulating molecular structures. The condensed-phase optimized molecular potential for atomistic simulation studies II (COMPASS II) force field was used for the energy minimization and MD simulations. In this work, zwitterionic copolymers (P[MPC-co-AEMA]) and PSf molecules were modeled using the chemical formulas $C_{28}H_{57}N_3O_{14}P_2$ (Mw: 721 g mol⁻¹) and $C_{54}H_{46}N_3O_8S_2$ (Mw: 928 g mol⁻¹), respectively. The interaction between PSf/ or MPC-co-AEMA and water/PIP molecules was investigated by analyzing the number of hydrogen bonds and the interaction energy. The distance (r) was designated as the closest distance of the center of gravity of the MPC-co-AEMA/PSf molecule to the center of gravity of the water molecules. The distance-dependent changes in the interaction energy for the water-MPC-co-AEMA and water-PSf systems were evaluated within a distance range of 3.5-9.5 Å. The interaction energy ($E_{interaction}$, kJ mol⁻¹) between water and zwitterionic copolymer (P[MPC-co-AEMA]) was calculated using the following equation [27]:

$$E_{interaction} = E_{total} - (E_{water+PIP} + E_{MPC-co-AEMA}) \quad (3.2)$$

where E_{total} is the total energy of the P[MPC-co-AEMA] system, and $E_{water+PIP}$ and $E_{MPC-co-AEMA}$ represent the energies of water/PIP and P[MPC-co-AEMA], respectively. For the interaction energy of the PSf system, the PSf molecule replaced P[MPC-co-AEMA] in every periodic unit, and E_{total} and E_{PSf} were calculated to obtain the interaction energy between the PSf substrate and water/PIP molecules in the aqueous phase.

For the water-P[MPC-co-AEMA] simulation cell, a 50.14 Å × 50.14 Å × 50.14 Å simulation cell containing 4200 water molecules and 70 PIP molecules were constructed to model an aqueous phase with a density of 1.0797 g cm⁻³. This system contained one P[MPC-co-AEMA] molecule located in the center of the aqueous phase. After structural optimization,

the water-PSf system was identical to the water-P[MPC-co-AEMA] system, barring one PSf molecule inside the cell, instead of P[MPC-co-AEMA]. The MD simulations were performed under isothermal conditions at 298 K. A constant-temperature and constant-volume (NVT) ensemble was used. The numerical integration algorithm was the velocity Verlet algorithm within the Material Studio software. The time step was set as 1 fs. The temperature of the simulation system was controlled using Nose-Hoover dynamics. An equilibrium state was obtained by a simulation of fewer than 200 ps for each model. The average data between 5 and 200 ps were employed to evaluate the interaction energy and H-bond number.

3.3 Results and discussion

3.3.1 Physicochemical characterization of P[MPC-co-AEMA] interlayered PSf membrane

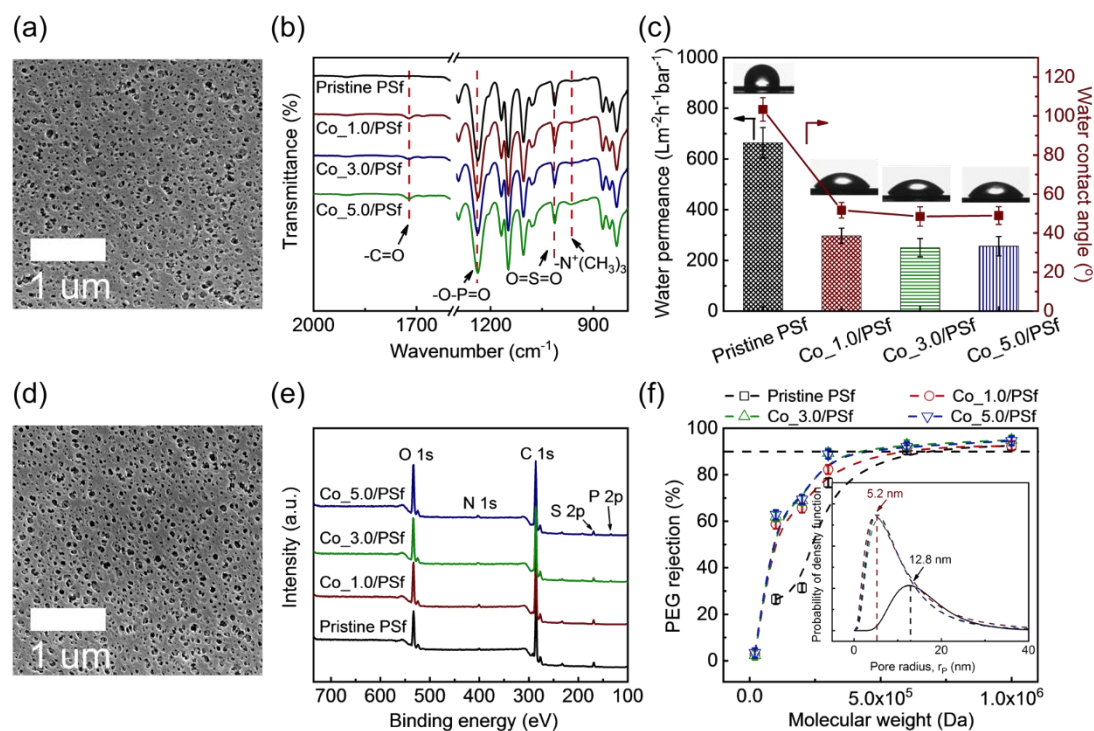


Fig. 3.3 FESEM images of (a) pristine PSf and (d) Co_3.0/PSf membranes (left-hand panel); (b) FTIR and (e) XPS spectra of pristine PSf and Co/PSf membranes (middle panel); (c) water wettability and pure water permeance of pristine PSf and Co/PSf membranes; (f) variation of neutral molecular rejection ratios of pristine PSf and Co/PSf membranes (inset: pore size and pore size distributions) (right-hand panel).

The surface morphologies of the pristine and P[MPC-co-AEMA] interlayered PSf membranes were investigated, and comparably heterogeneous surface structures (**Fig. 3.3a** and **3.3d**) were obtained before and after P[MPC-co-AEMA] modification. Contrastingly, more prominent characteristic peaks located at 1728 cm^{-1} and 963 cm^{-1} emerged, which could be ascribed to -C=O and $\text{-N}^+(\text{CH}_3)_3$ from the MPC and AEMA segments (**Fig. 3.3b**). The enhanced N and P elemental intensities (**Fig. 3.3e**) should be assigned to the enhanced $\text{-N-(CH}_3)_3$ and $\text{-C-O-PO}_3\text{-}$ groups of N 1s and P 2p. Together, these results confirm successful zwitterion surface immobilization onto the underlying PSf substrates via self-crosslinking with GA, as schematically illustrated in **Fig. 3.4** [26]. This noncovalent interaction can be explained as the electrostatic interaction between the positively charged amino and the negatively charged sulfonic groups, from the surface P[MPC-co-AEMA] modification layer and PSf substrate, respectively.

The integration of P[MPC-co-AEMA] molecules onto PSf led to a better hydrophilic property, for which the WCA decreased from 104° to 50° (**Fig. 3.3c**). This can be explained by the amassed conducting head groups of phosphate segments and quaternary groups with high polarity [28]. The MWCO and pore size distributions of the P[MPC-co-AEMA]-interlayered PSf membranes were characterized (**Fig. 3.3f**). After coating with more highly concentrated zwitterion molecules, the MWCO values gradually decreased from 590 kDa for pristine PSf to 290 kDa for Co_3.0/PSf, incorporated with smaller pore sizes (from 12.8 nm to 5.2 nm) and narrower pore size distributions. This is primarily associated with the increased crosslinking network, which results in an enhanced internal resistance against the rapid transport of water molecules across the membrane bulk, when assembling P[MPC-co-AEMA] with GA.

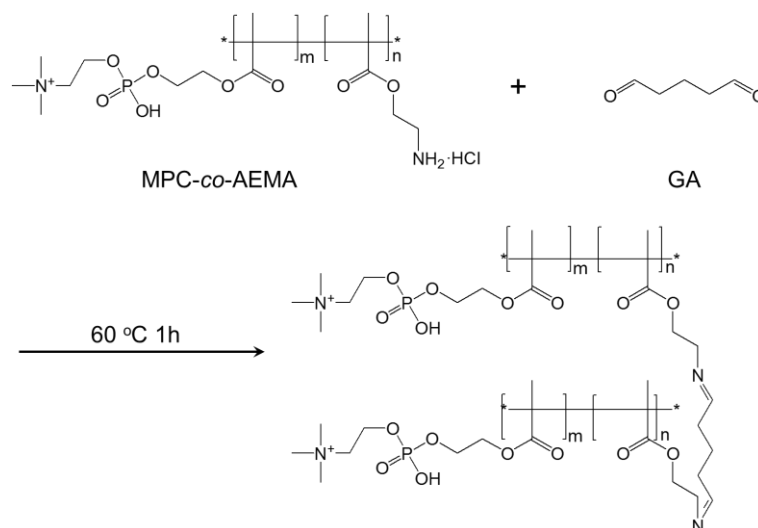


Fig. 3.4 Schematic illustration of proposed chemical crosslinking reaction between P[MPC-co-AEMA] and GA.

3.3.2 Physicochemical characterization of PA_Co/PSf membranes

The morphological properties of the PA_Co/PSf membranes were investigated via FESEM and AFM. **Fig. 3.5a** and **3.5e** represent the top surfaces of pristine PA and PA_Co_3.0/PSf membranes, respectively. Pristine PA membrane shows a typically nodular structure with tightly dispersed granular bumps, as reported in literatures [29, 30]. After introducing the P[MPC-co-AEMA] copolymer interlayer, we observed the PA_Co_3.0/PSf membrane surface morphology has close-packed hexagonal arrays or interconnected labyrinthine networks. The PA_Co_3.0/PSf membrane exhibited a roughened surface (**Fig. 3.5f** and **3.5g**) compared with that of pristine PA, which has a relatively smoother structure (**Fig. 3.5b** and **3.5c**). This is because of the differences in the diffusion coefficients of the inhibitor (organic phase) and activator (aqueous phase) induced by the P[MPC-co-AEMA] interlayer, which will be discussed later [1]. These results demonstrate that the heterogeneity of the P[MPC-co-AEMA] interlayer-mediated PA nanofilm with nanostripes possesses an enlarged effective filtration area (**Table 3.1**), because of the formation of interconnected nanovoids derived from wrinkles at the interface between the support and skin layers. It should be noted that the bottom morphologies of both pristine PA and PA_Co_3.0/PSf membranes are similar to those of the surface structures, as shown in **Fig. 3.5d** and **3.5h**, suggesting that the P[MPC-co-AEMA] interlayer induces the ridge-and-valley structural formation of the PA nanofilm more substantially than that of the

pristine PSf substrate [21, 31].

The TEM characterization results provide morphological information on the external/internal features of the PA nanofilms, fabricated via P[MPC-co-AEMA] interlayer-mediated IP. The pristine PA membrane exhibited a conventional nanofilm structure with a thickness of 65 nm (**Fig. 3.5i**). However, when preparing the PA_Co/PSf membrane based on the P[MPC-co-AEMA] interlayer, the nanofilm thickness sharply decreased to 12 nm (**Fig. 3.5j**), almost reaching the lowest limit of the thinnest PA membrane developed by IP. More importantly, unlike the tightly integrated interface between the surface nanofilm and the PSf substrate of the pristine PA membrane, we can observe many interfacial nanovoids with interconnected ribbon structures. This can be illustrated as the better hydrophilic P[MPC-co-AEMA] interlayer surface tends to absorb more PIP monomers reacting with TMC to rapidly form a highly crosslinked network of polyamide [14]. During this time, more nanosized gas (CO₂) bubbles were produced from the aqueous amine solution because of the generation of acid and heat, thereby releasing and promoting the growth of nanovoids where the amassed nanobubbles existed before the occurrence of interfacial degassing [32].

Table 3.1 Surface properties of pristine PA and PA_Co/PSfTFC membranes. These results were acquired from AFM measurements over a scanning area of 10 $\mu\text{m} \times 10 \mu\text{m}$.

Samples	Surface area (nm ²)	Ra (nm)	RMS (nm)	Surface strip width (nm)
Pristine PA	1.11×10^8	15.89	21.23	-
PA_Co_1.0/PSf	1.12×10^8	16.24	24.96	~ 210
PA_Co_3.0/PSf	1.24×10^8	26.64	34.61	~ 220
PA_Co_5.0/PSf	1.24×10^8	27.21	36.52	~ 220

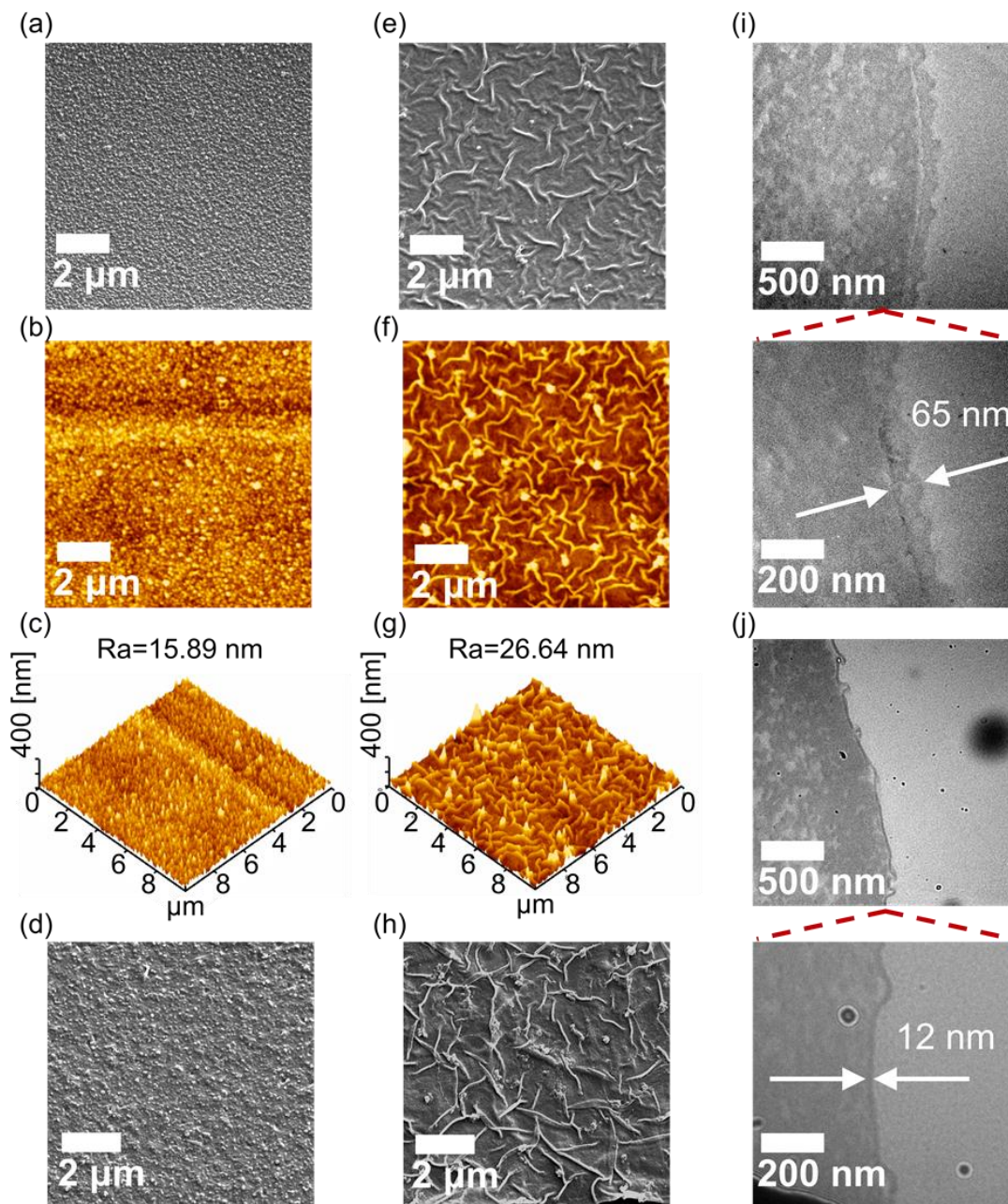


Fig. 3.5 Morphological characterization of pristine PA and PA_Co_3.0/PSf membranes: FESEM images of top polyamide layer (a, e); AFM topographic images (b, f) with corresponding 3D morphology images and height profiles (c, g); FESEM images of bottom polyamide layer (d, h); cross-section TEM images (i, j).

3.3.3 Separation performance of PA_Co/PSf based membranes

To balance the membrane separation performance in terms of solvent (water) permeability and solute (multivalent ions) selectivity, the optimum membrane fabrication condition (i.e., PIP

0.2% (wt/v), TMC 0.1% (wt/v), and reaction time of 30 s) were chosen. **Fig. 3.6a** reveals that all the PA_Co/PSf membranes exhibit considerably increased water permeance, reaching up to $20.4 \text{ L} \cdot \text{m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for PA_Co_3.0/PSf membranes by increasing nearly three-fold magnitude higher from the initial value of $5.6 \text{ L} \cdot \text{m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for the pristine PA membrane. Such a significant enhancement can be primarily attributed to the synergistic effects of (1) the ultrahigh specific area of the crumple microstructure with ridge-shaped nanostrips, which allows a greater number of water molecules to penetrate into the membrane bulk. (2) The ultrathin PA-based selective layer (approx. 12 nm) with a considerably shortened pore-flow distance that facilitates the permeation of water molecules. (3) The interfacial nanovoids between the P[MPC-co-AEMA] interlayer and polymer membrane, serves as highways for the quick passage of water molecules because of their low hydraulic resistance [1, 13, 33]. The separation performance of diva- and/or monovalent anions/cations was studied, in which Na_2SO_4 , MgSO_4 , CaCl_2 , and NaCl were used at the equal concentrations (**Fig. 3.6b**). The TFC membranes exhibited similar salt rejection trends in the order $\text{Na}_2\text{SO}_4 > \text{MgSO}_4 > \text{CaCl}_2 > \text{NaCl}$, consistent with the conventional nanofiltration membranes. All the membranes exhibit higher rejection ratios toward the divalent ions with higher valences and larger hydrated ionic sizes, which could be ascribed to the synergistic effects of electrostatic exclusion and size sieving mechanisms, as follows: 1) the stronger electrostatic repulsion against anions (SO_4^{2-}) than that of cations (Mg^{2+} , Ca^{2+}), owing to the negatively charged surface property [34], as demonstrated in **Fig. 3.7**; (2) the larger hydrated radius of divalent ion of SO_4^{2-} (0.382 nm), Mg^{2+} (0.423 nm), and Ca^{2+} (0.412 nm) than that of monovalent ion of Cl^- (0.332 nm) and Na^+ (0.358 nm) [26, 31, 35], as summarized in **Table 3.2**.

Table 3.2: Comparison of crystal, Stokes and hydrated radius of various ions.

Ions	naked ions radius (nm)	Hydrated ions radius (nm)
Na^+	0.095	0.358
Mg^{2+}	0.065	0.423
Ca^{2+}	0.099	0.412
SO_4^{2-}	0.290	0.382
Cl^-	0.181	0.332

Specifically, the PA_Co_3.0/PSf membrane exhibited a superior rejection ratio against the divalent anion Na_2SO_4 (96.8%) and a relatively reduced NaCl rejection ratio (11.8%) compared with that of the pristine PA membrane (95.7% for Na_2SO_4 and 19.3% for NaCl). The separation performance of pristine PA and PA_Co/PSf membranes were investigated by infiltrating carbohydrates with different molecular weights of glycerol (92 Da), glucose (180 Da), sucrose (342 Da), and raffinose (504 Da). According to these simulation results, all the neutral solutes exhibit an increasing trend in molecular sizes over the increased molecular weights. It can be found from **Fig. 3.6c** that the crosslinked zwitterionic interlayer brings about the nearly same MWCO values for pristine PA and PA_Co/PSf membranes with equal transition ranges. However, the PA_Co/PSf membranes show enlarged free volume distribution with expanded mean pore size of 0.34/0.31 nm for PA_Co_3.0/PSf and pristine PA (**Fig. 3.6d**) membranes, respectively. For example, the pristine PA shows rejection ratios of 75.38% and 91.63% for glucose and sucrose with Stokes radius of 0.36 nm and 0.48 nm, respectively. Nevertheless, a sharp decrease in rejection for glucose (61.79 %) was obtained for PA_Co_3.0/PSf membranes, while a relatively high rejection of 94.71% and 95.19% for sucrose and raffinose were obtained. Such a deterioration rejection ratio of ~ 33% between the two carbohydrates of glucose and sucrose with a minor difference in sizes of only ~0.12 nm verified the formation of a loose structured nanofilm that facilitates water molecules rapid transport, without a significant compromise in the membrane selectivity toward large molecular solutes [26]. This demonstrates a better ionic selectivity of the resultant PA_Co/PSf membranes, especially between mono-/divalent anions, owing to the better uniformly distributed pore structures with larger effective pore sizes, increasing from 0.31 nm for the pristine PA membrane to 0.34 nm for the PA_Co_3.0/PSf membrane, without considerable compromise (together with higher MWCO values, **Fig. 3.6c** and **3.6d**). The looser pore structure of the P[MPC-co-AEMA] interlayered membrane can be further demonstrated by PALS characterization results (**Fig. 3.6e**), which show that a relatively enlarged free volume (with enhanced S parameter value) is obtained for the PA_Co_3.0/PSf membrane compared with that obtained for the pristine PA membrane. This can be ascribed to the formation of internal nanovoids derived from the release of generated gas nanobubbles entrapped within the PA nanofilm, when conducting IP [36].

A trade-off limit is identified for all types of membranes, and the upper-bound line

represents the level of permeability and selectivity achieved by the currently fabricated membranes. **Fig. 3.6f** illustrates the superiority of our newly developed P[MPC-co-AEMA] interlayered PA membranes among the different types of nanofiltration membranes recently reported in literature (**Table 3.3**). According to this result, the PA_Co_3.0/PSf membrane synthesized in our study exhibits superior separation properties, in terms of high water permeability and high Na_2SO_4 selectivity, to most of the other nanofiltration membranes, approaching the upper-bound line of the state-of-the-art permselectivity, demonstrating a better trade-off limit. Such a significant enhancement in water permeation efficiency can be attributed to 1) a thinner and crumpled PA nanofilm with reduced transmembrane resistance and enhanced filtration area for water molecules to quickly transport across the active layer [37-39]; 2) randomly distributed nanovoids with enhanced free volumes inside the interfacial nanostrips, facilitating the water permeance per unit area.

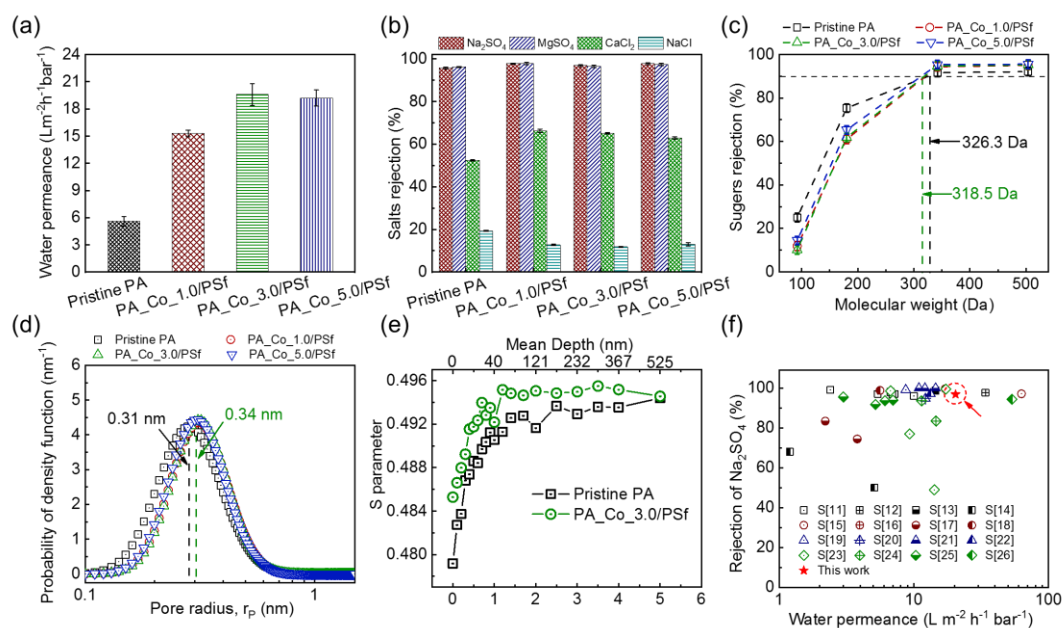


Fig. 3.6 (a) pure water permeance and (b) ionic rejection ratios of PA_Co/PSf nanofiltration membranes; (c) neutral organic compound rejection ratios; (d) pore size and pore size distribution of PA_Co/PSf nanofiltration membranes; (e) S parameter of pristine PA and PA_Co_3.0/PSf membranes obtained from the PALS characterization; and (f) comparison of the separation property with the state-of-the-art nanofiltration membranes (summarized in **Table 3.3**).

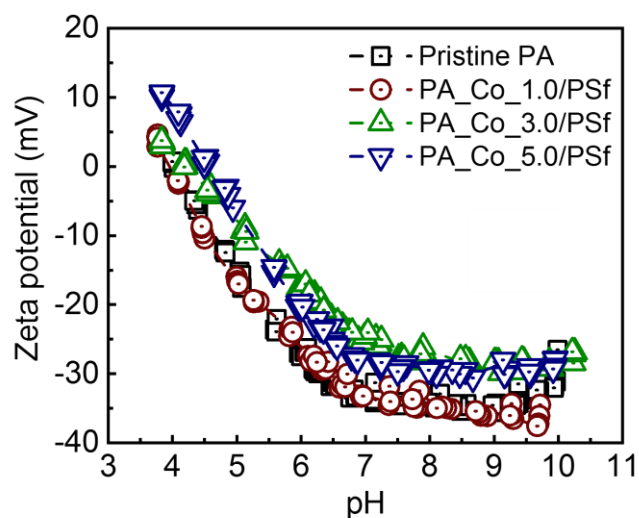


Fig. 3.7 Surface potential of pristine PA and PA_Co/PSf TFC membranes.

Table 3.3 Performance of reported state-of-the-art nanofiltration membranes.

Membrane and description	Abbreviation	PWP (L m ² h ⁻¹ bar ⁻¹)	Salt rejection (%)		Salts concentration	Pressure	References
			Na ₂ SO ₄	MgSO ₄			
Commercial membranes	DOW FILMTEC™ NF70	7.2	97.0	70.0	2000 ppm	4.8 bar	[40]
	DOW FILMTEC™ NF90	6.7	98.0	90.0	2000 ppm	4.8 bar	
	GE-Osmonics DL	10.0	96.0	96.0	5000 ppm	30 bar	
	GE-Osmonics HL	6.9	97.0	97.0	1000 ppm	7.6 bar	
	Synder NFX	2.4	99.0	99.0	2000 ppm	8.3 bar	
	Synder NFW	5.4	97.0	97.0	2000 ppm	8.3 bar	
NF membranes with cellulose nanocrystals as an interlayer	PA50/CNC/PES	34	97.7	86	1000 ppm	6 bar	[41]
In-situ mineralization interlayer regulated nanofiltration membrane	PA_SiO ₂ _4h/PSf	14.5	98.7	97.9	1000 ppm	10 bar	[15]
TFC NF membranes fabricated from polymeric amine,	PEI _{2.4} -PIP _{0.6} /TMC	5.1	50.0	74	500 ppm	10 bar	[42]

polyethylenimine embedded with monomeric amine, And piperazine for enhanced salt separation	PEI _{0.6} /TMC-PIP _{2.4} /TMC	1.2	68.0	94	500 ppm	10 bar	
Ultrathin PA layer embedded with ultrasmall UiO-66-NH ₂ for nanofiltration	TFN-0.2	63	97.1	91.2	1000 ppm	6 bar	[43]
Polyamide nanofiltration membrane with highly uniform sub-nanometer pores for sub-1 Å precision separation	(PIP+SDS)/TMC	17.1	99.6	98.2	1000 ppm	4 bar	[35]
pH-responsive NF membranes containing carboxybetaine with tunable	PCHM1	2.2	83.4	58	1000 ppm	6 bar	[44]
ion selectivity for charge-based separation	PCHM2	3.8	74.4	56	1000 ppm	6 bar	
TiO ₂ @graphene oxide incorporated antifouling nanofiltration membrane	NFM-3 # 0.2 wt% TiO ₂ @GO	5.6	98.8	58	1000 ppm	4 bar	[45]
Ultrathin PA membrane with decreased porosity and superior antifouling properties	BTC-PIP	8.7	99.1	99.4	2000 ppm	10 bar	[46]
Nanovoid membranes embedded with hollow zwitterionic nanocapsules	TFNM with HZN _{CS}	12.2	94.7	93.4	2000 ppm	6 bar	[47]
	NMP-act.	10.9	99.9	99.9	1000 ppm	10 bar	
MPD based nanofiltration membrane	DMF-act.	12.1	99.9	99.9	1000 ppm	10 bar	[48]
	DMSO-act.	14.5	99.9	99.9	1000 ppm	10 bar	
Polydopamine-coated silica nanoparticles embedded thin-film nanocomposite nanofiltration membranes	TFN _{PDA-SiNPs}	13.3	97.0	94.0	1000 ppm	6 bar	[49]
	PIP only	6.7	98.6	97.8	1000 ppm	4 bar	
Ionic dendrimer based polyamide nanofiltration membranes	G5-NH ₂ /PIP	9.3	77.0	95.5	1000 ppm	4 bar	[34]
	G5-TAC/PIP	14.2	48.9	92.6	1000 ppm	4 bar	
	G5-PS/PIP	17.3	99.5	91.2	1000 ppm	4 bar	

Preparation of TFC NF membranes with improved structural stability through the mediation of polydopamine	PA/PA-PES	11.4	93.5	82.4	1000 ppm	2 bar	[50]
	PA/PES	14.6	83.4	70.6	1000 ppm	2 bar	
Tuning the functional groups of carbon quantum dots in thin-film nanocomposite membranes for nanofiltration	PA-TFC	3.0	95.5	89.0	5 mmol/L	6 bar	[51]
	TFN-SCQD	7.0	93.8	82.0	5 mmol/L	6 bar	
	TFN-NCQD	5.2	91.7	90.0	5 mmol/L	6 bar	
	TFN-CCQD	6.1	93.6	87.0	5 mmol/L	6 bar	
Covalent organic framework modulated interfacial polymerization for ultrathin PA nanofilm	PACLS (5)	53.5	94.3	80.7	1000 ppm	2 bar	[52]
Zwitterionic copolymer inter-modulated PA-NF membrane	PA_Co_3.0/PSf	19.6	96.8	96.4	1000 ppm	10 bar	This work

Long-term (up to 2000 min) (**Fig. 3.8a**) pure water/salt solution infiltration, higher transmembrane pressure (up to 20 bar) (**Fig. 3.8b**), and a highly concentrated salt environment (up to 5000 ppm Na₂SO₄ solution) (**Fig. 3.8c**) were used to verify the operational stability of the PA_Co_3.0/PSf membrane. The results indicate that the PA_Co_3.0/PSf TFC membrane exhibits operational stability relative to that of the pristine PA membrane, showing its highly practical potential used for tough separation conditions. These characterization results demonstrate that their ridge-shaped structures are nearly remained, without severe compaction, breaking, or tearing phenomenon, further demonstrating their structural stability nature in harsh scenarios.

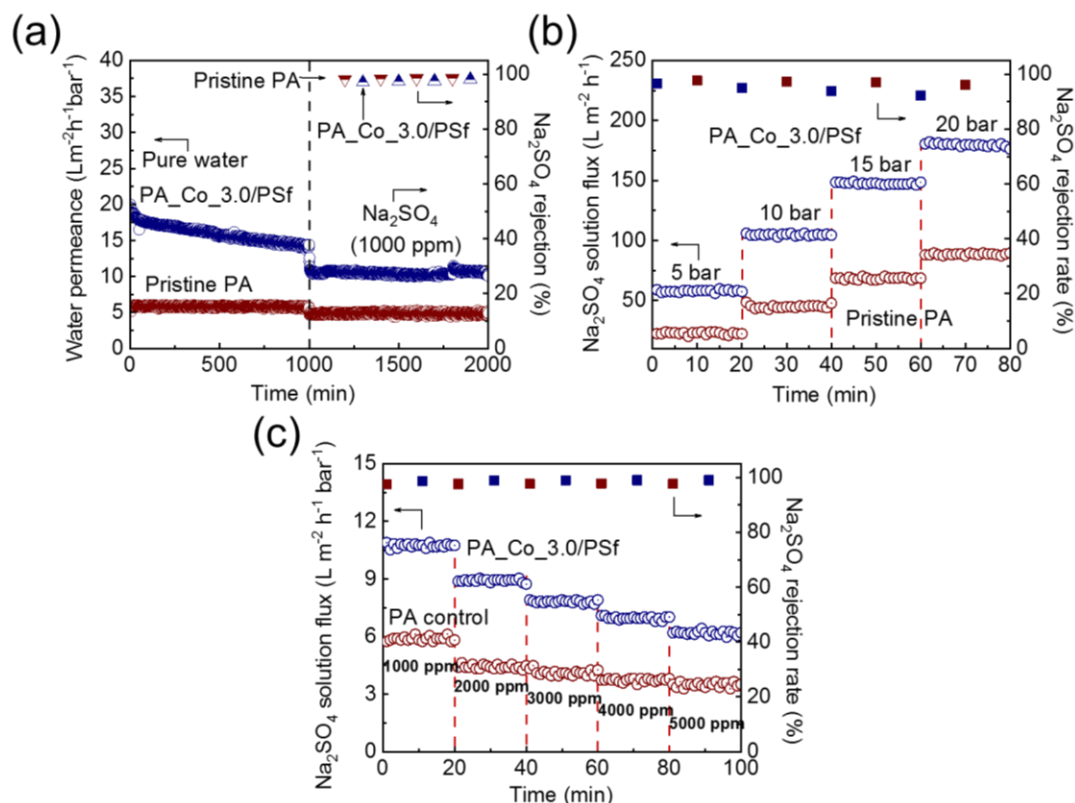


Fig. 3.8 (a) Long-term infiltration test of pristine PA and PA_Co_3.0/PSf membranes against pure water and 1000 ppm Na_2SO_4 aqueous solution; (b) perm-selectivity of pristine PA and PA_Co_3.0/PSf TFC membranes toward 1000 ppm Na_2SO_4 aqueous solution under varied trans-membrane pressure (5-20 bar); (c) perm-selectivity of pristine PA and PA_Co_3.0/PSf TFC membranes under varied concentration of Na_2SO_4 aqueous solution.

3.3.4 Formation mechanism of ridge-shaped PA nanofilm surface with an ultrathin thickness

The underlying mechanism of the formation of ridge-shaped PA nanofilms with an ultrathin thickness down to 12 nm was systematically investigated upon surface enrichment and/or diffusion transport of PIP monomers via P[MPC-co-AEMA] interlayered IP (**Fig. 3.9a**). Based on the results shown in **Fig. 3.9b**, P[MPC-co-AEMA] exhibits lower interaction energy with PIP/water molecules ($-1856.7 \text{ kJ} \cdot \text{mol}^{-1}$), by mimicking the real amine-based solution, than PSf ($-627.1 \text{ kJ} \cdot \text{mol}^{-1}$), owing to the high density of active sites (H-bond interaction) capturing more PIP/water molecules [27, 53]. Such high-density hydrophilic-hydrophilic interaction toward PIP became more severe when closing nearer to the P[MPC-co-AEMA], as shown in

Fig. 3.9c, further contributing to the spatial enrichment of PIP molecules within the simulated action range of 3.5~9.5 Å, exerted by the P[MPC-co-AEMA] interlayer with a stronger affinity to water molecules. The enrichment of PIP can be demonstrated by UV-vis analysis (**Fig. 3.9d**); large amounts of amassed PIP could be detected throughout the P[MPC-co-AEMA] interlayered PSf (0.79 g m⁻² and 0.77 g m⁻² for Co_3.0/PSf and Co_5.0/PSf, respectively) compared to that detected in the pristine PSf membrane (0.12 g m⁻²) [14, 54]. It is noted that the Co/PSf performs a comparable pore structure, including similar pore volumes and pore porosity, to that of the pristine PSf membrane (**Fig. 3.10**). This result suggests that most of the increased PIP storage capacity is retained inside the P[MPC-co-AEMA] interlayer, almost without infiltrating the underlying PSf substrate [19].

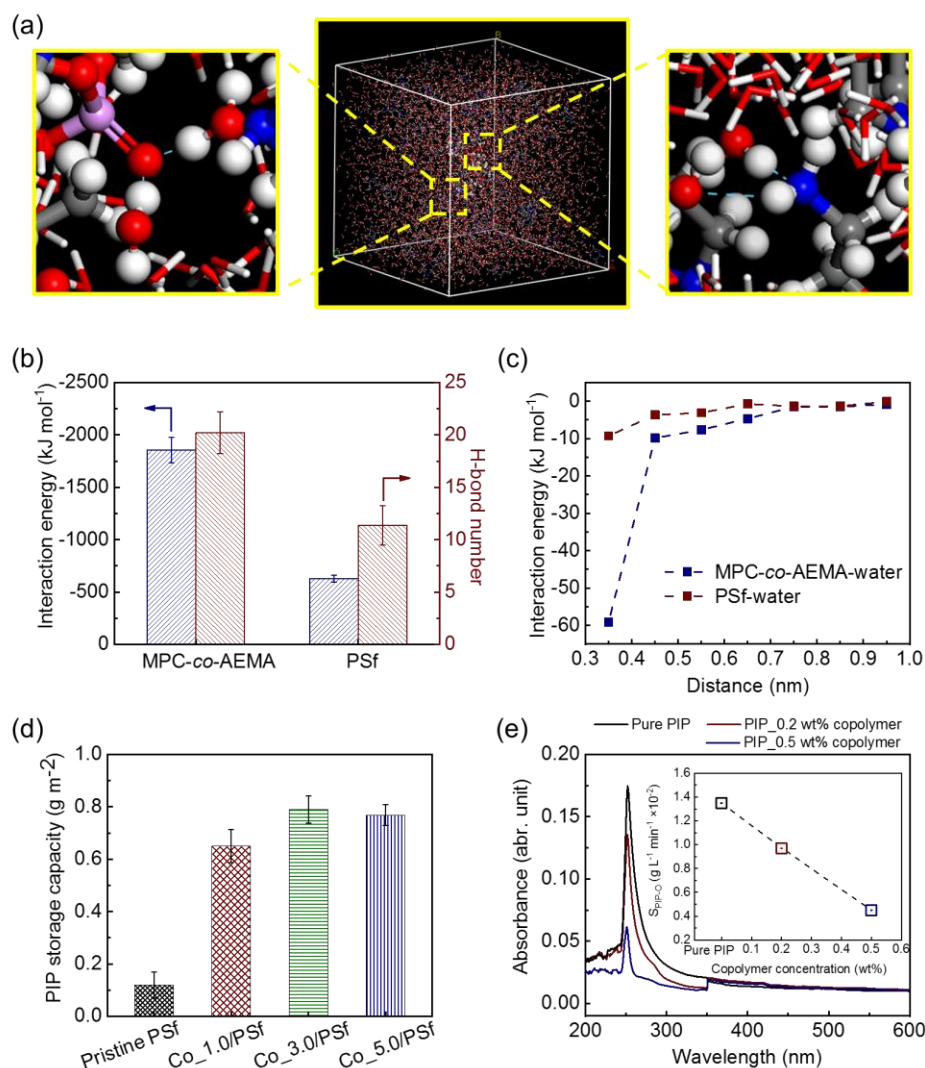


Fig. 3.9 (a) Snapshots of P[MPC-co-AEMA] in water. The interactions between molecular

P[MPC-*co*-AEMA] with water molecules are indicated by dotted lines (C, gray; H, white; O, red; N, blue; P, pink; S, yellow); (b) interaction energy and H-bond number between P[MPC-*co*-AEMA]/ or PSf and water/PIP molecules; (c) distance-dependent interaction energy variations of the P[MPC-*co*-AEMA]/ or PSf molecules with water molecules; (d) PIP storage capacity of pristine PSf and Co/PSf membranes; (e) UV-vis spectra of PIP in the organic phase after diffusion for 30 s; (inset: diffusivity rate of PIP).

Moreover, P[MPC-*co*-AEMA] not only absorbs a large number of PIP molecules onto the surface, but also imposes temporal retardation during amine monomer diffusion. As exhibited in **Fig. 3.9e**, strong hydrophilic-hydrophilic attraction tends to slow down the monomer transport across the interface, leading to a decreased diffusion coefficient ($0.97 \text{ g L}^{-1} \text{ min}^{-1} \times 10^{-2}$ and $0.45 \text{ g L}^{-1} \text{ min}^{-1} \times 10^{-2}$ for PIP_0.2 wt% and PIP_0.5 wt% solutions, respectively) than that of pure PIP ($1.35 \text{ g L}^{-1} \text{ min}^{-1} \times 10^{-2}$) [19]. These agree well with the calculating trend of the Freger equation [55], for which the incipient PA membrane thickness is proportional to one-third of the amine monomer diffusivity, whereas inversely proportional to the amine monomer concentration within the organic phase. Consequently, the enrichment of PIP storage capacity and the retarded monomer diffusion at the interface, together influence the interfacial reaction by triggering membrane sealing and inhibiting membrane growth, thus leading to the formation of an ultrathin PA nanofilm with structural integrity deposited onto the newly developed P[MPC-*co*-AEMA] interlayered substrate.

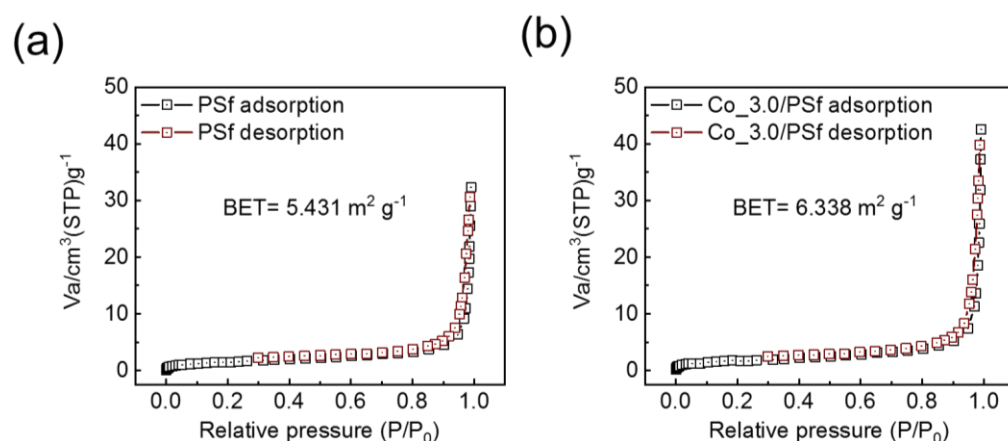


Fig. 3.10 N₂ adsorption–desorption curves at 77 K and the calculated BET surface area of the

pristine PSf and Co_3.0/PSf substrates.

At the same time, the formation of the nanostrips for the PA_Co/PSf membrane can also be explained as 1) the aqueous templates formed on the substrate surface, owing to the hydrophilic P[MPC-co-AEMA] interlayer capturing more aqueous microphases, which may directly impact the transition of the membrane surface microstructure from a relatively smooth to a more crumpled surface microstructure [37]; 2) the diffusion-driven instability induced by the retardation at the water/organic interface imposed by P[MPC-co-AEMA] interlayer, thus formed a crumpled 3D-like striped surface nanostructure comprising closely packed hexagonal arrays or interconnected labyrinthine networks; 3) the degassing of nanobubbles during IP drives the convection of monomers, and then induces the formation of ridge-and-valley structures for PA nanofilms [1, 56].

3.4 Conclusions

I hereby developed an ultrathin PA nanofilm with a thickness of 12 nm via P[MPC-co-AEMA] interlayer-mediated IP. The P[MPC-co-AEMA] copolymer acted as a “quasi-molecule-scale regulator” to precisely control the kinetics of IP reaction, in which P[MPC] was responsible for a long-range hydrophilic-hydrophilic attraction to aqueous monomers, while P[AEMA] afforded a tunable charge density by electrostatic interaction with the PSf substrate. The enhanced attraction spatially enriched the amine monomers and temporally decelerated their diffusivity into the organic phase to be polymerized with acyl chloride from TMC. Diffusion-driven instability triggered membrane sealing and inhibited its growth, thus leading to the formation of an ultrathin PA nanofilm with a ribbon-shaped surface structure and enhanced crosslinking. The resultant P[MPC-co-AEMA] interlayer-enhanced PA membrane exhibited a superior water permeance of up to $20.4 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, almost 3-fold higher than that of the pristine PA membrane ($5.6 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$), without sacrificing its ionic selectivity (96.8% against Na_2SO_4), which is superior to most of the reported state-of-the-art permselective nanofiltration membranes.

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Chapter 4

Highly Permeable Nanofilms with Asymmetric Multilayered Structure Engineered via Amine-decorated Interlayered Interfacial Polymerization

4.1. Introduction

Potable water supply is worsening worldwide owing to water-related conflicts arising from issues such as contamination and shortages caused by the dramatic growth in industrialization and the global economy [1-3]. Pressure-driven membrane technology has been widely adopted in the field of water purification and wastewater treatment owing to its low energy consumption, eco-friendliness, and easy scalability [4]. Thin-film composite (TFC) membranes that typically consist of an ultrathin selective layer deposited upon a porous support have been extensively studied and industrially applied in reverse osmosis (RO), nanofiltration (NF), and forward osmosis (FO) applications [5-7].

Interfacial polymerization (IP) can produce an essentially defect-free and highly permeable polyamide (PA) selective layer in which the amine-based monomer reacts with the acyl chloride monomer at the interface of two immiscible solvents [8]. In particular, synthetic NF membranes with pore sizes smaller than 2 nm and molecular weights of 200–1000 Da demonstrate remarkable advantages in fractionating multivalent salts or sieving micropollutant targets over freshwater production processes [9-11]. However, further improvements in the separation performance of PA-based TFC membranes are limited by the trade-off between selectivity and permeability as determined by the membrane properties, including nanofilm thickness, specific filtration area, charge density, and degree of molecular crosslinking [12, 13]. The IP process involves extremely quick reaction kinetics and uncontrollable processes at the water/hexane interface; however, producing PA membranes that afford both fast water transport

and excellent solute rejection remains technically challenging [14-16].

Enhancing the water permeance of an NF membrane without compromising its solute rejection ability can save considerable energy in the wastewater treatment process and thereby promote the practical application of PA-based TFC membranes [3, 17, 18]. To date, many studies have been conducted to enhance the separation performance [19]. On the one hand, introducing nanomaterials in the aqueous phase during IP can produce a wrinkled structure in piperazine (PIP)-based PA films with enlarged specific filtration areas, leading to a higher permeating flux while retaining the selectivity of the desired salts fractionation between monovalent and divalent ionic solutes [20]. On the other hand, nanomaterials can also be immobilized on the substrate surface, where they serve as interface modifiers between the aqueous amine and acyl chloride monomers to regulate the kinetics of the IP reaction [9, 17, 21, 22]. The spatiotemporal disruption of the aqueous monomer yields ultrathin PA membranes (thickness: 14 nm) with significantly enhanced water permeance. However, existing promising methods to precisely manipulate PA membranes seem to reach a plateau because they require complex infrastructure or procedures to develop appropriate additives such as metal-organic frameworks [23], covalent organic frameworks [24], or any other macromolecules to interact with amine molecules prior to the IP reaction [25, 26]. The time-consuming procedure hampers high-throughput water purification. Consequently, developing a facile method to fabricate high-performance PA-based TFC membranes with high permeability and precise separation abilities is of great practical significance [27].

Niu et al. recently provided a new conceptual framework to launch an underpinning mechanism for constructing asymmetric PA nanofilms, in which the back surface is highly porous with spherically ordered hollow structures but the upper selective surface is dense [3]. The highly porous structure formed inside the asymmetric PA membrane significantly increased the permeating water while maintaining its high rejection capability. Furthermore, Zhu et al. reported that internal voids within an asymmetric PA nanofilm could be constructed by initiating the inconsonant diffusion reaction of amine monomers intermediated by poly(amidoamine) (PAMAM), which provides external nanochannels between the selective PA layer and underlying PAMAM dendrimers to facilitate the transport of water molecules [28]. Fang et al. attributed the formation of highly porous nanovoids on the back surface of an

asymmetric PA nanofilm to the heterogeneous diffusion of amine monomers intervened by the amine-based PAMAM dendrimer toward the organic phase [29]. Therefore, the amine-based intermediate substances with regular and tunable surface reactivity can induce nanovoid generation at the back surface of the asymmetric PA nanofilm, thereby promoting the quick passage of water molecules. However, owing to the intractability of constructing such sub-nanostructures, fundamental studies on the effective regulation of amine monomer diffusion kinetics to develop asymmetric nanofilms with high permeability remain lacking. In last two chapters (ultrafine SiO₂ nanoparticles interlayer mediated interfacial polymerization and crosslinked zwitterionic copolymer mediated interfacial polymerization), the enhanced water permeance of as-formed nanofiltration membranes were attributed to the enhanced infiltration area and decreased selective layer thickness. Recently, researchers found that the back morphologies of PA layer should not be ignored. The PA layer will intrude into the support pore owing to the confined diamine molecular before contacting with acyl chloride. The intruded PA chains will certainly enhance the durability of TFC nanofiltration membrane, however, this physical inter-connected locking phenomenon may enhance the film thickness and deteriorate membrane flux. How to increase the membrane permeance by eliminating the back protrusion is the main target of this chapter.

Herein, we introduce a novel method to develop an asymmetric PA nanofilm with a multilayer structure, in which the back surface is a porous layer containing a spherically porous structure, and the upper selective surface is a dense layer having nodular wrinkles via amine-decorated interlayer-mediated IP (**Fig. 4.1**). The self-crosslinked poly(allylamine hydrochloride) (PAH) interlayer with regular wettability and tunable surface amination reactivity strongly attracts aqueous amine monomers and disrupts their diffusion toward the organic phase to be polymerized with acyl chloride of TMC monomers, thereby triggering a diffusion-driven instability and enabling the formation of asymmetric PA nanofilms containing spherical voids on the back surface. The asymmetric PA membrane achieves high water permeance of up to 12.5 L m⁻² h⁻¹ bar⁻¹; this is 3-fold larger than that of the traditional monolayered PA membrane. The divalent salt rejection ratio was improved to 98.9% (Na₂SO₄), through an improved trade-off among state-of-the-art nanofiltration membranes. This study opens new avenues for developing asymmetric PA nanofilms with a multilayered structure to achieve highly efficient

molecular/ion separation.

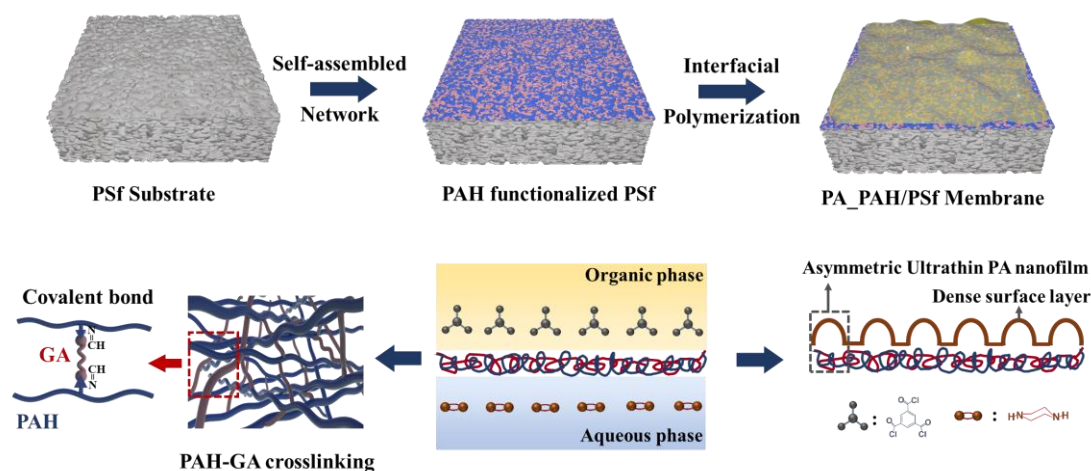


Fig. 4.1 Schematic of amine-decorated interlayer-mediated IP reaction and the mechanism of PAH-based interlayer for the formation of asymmetric PA nanofilm.

4.2 Experimental

4.2.1 Materials

PAH (Mw ~ 50,000 Da) were bought from Sigma-Aldrich (Japan). Glutaraldehyde (GA) solution (25%) and NaNO_3 (99%) were purchased from FUJIFILM Wako Chemical Co., Ltd., Japan. And other chemicals were the same as previous chapters.

4.2.2 Fabrication of PAH-functionalized PSf ultrafiltration support

To fabricate the PAH-functionalized PSf support, the PSf support was first immersed into an aqueous PAH solution with a certain concentration of 0.1 wt%, 0.2 wt% and 0.5 wt% for 3 h. Then, the excess solution was removed using an air knife, following which the crosslinking reaction with the GA solution (0.02 wt%) was performed for another 30 min. The resultant membrane was denoted as PAH_x/PSf membrane, where x represents the mass concentration of the PAH solution (0.1%, 0.2%, and 0.5%).

4.2.3 Fabrication of pristine PA and PA_PAH/PSf membranes

The PSf support was first exposed to the PIP aqueous solution (0.1 wt%) for 3 min. Next, the PIP-loaded PSf support was gently decanted and flushed with an air knife to remove the

excess solution. The membrane was treated with TMC-based hexane solution (0.05 wt%) 30 s for the IP reaction. Finally, the hexane solution was decanted, and the membrane was cured in an oven at 70°C for 3 min to complete the crosslinking process. Finally, the as-prepared membrane was stored in pure water at 4°C. The PA_PAH/PSf membranes were developed by following the same procedure as that for pristine PA, except that the pristine PSf membrane was substituted by a PAH/PSf membrane.

4.2.4 Membranes characterization

The membrane characterization was the same as previous chapters.

4.2.5 Evaluation of separation performance

The water permeance and salts rejection testing were stated in previous chapters. And the Cl⁻ and SO₄²⁻ concentrations in the mixed salt solutions were tested with an anion chromatography system (Thermo Dionex Aquion).

4.2.6 Evaluation of pore size and pore size distribution

The evaluation of pore size and pore size distribution were same as previous chapters.

4.2.7 Determination of PIP diffusion behavior

To determine the PIP monomer diffusion from the aqueous solution to the organic phase, 50 mL homogeneous PIP aqueous solutions with 0.0 wt%, 0.1 wt%, and 0.2 wt% PAH were first prepared inside a container. Then, 30 mL of hexane solution was gently poured into the aqueous solution. After 30 s, the hexane solution was removed with a pipette and put into cuvettes for characterization by ultraviolet-visible (UV-vis) spectrometry (V-650KE, JASCO Company, Japan). The maximum absorption peak at 252 nm was determined as the characteristic peak of PIP to evaluate the concentrations in hexane solution.

4.2.8 Computational simulation and dissipative particle dynamics simulation

The transport behavior of PIP molecules across the water/hexane interface was investigated by performing molecular dynamics (MD) simulation using commercial BIOVIA

Materials Studio software. The same software was used for simulating the molecular structures. The condensed-phase optimized molecular potential for atomistic simulation studies II force field was used for the energy minimization and MD simulations. For the PIP-only system, 1500 water molecules, 200 hexane molecules, and 30 PIP molecules were included in the cubic simulation box. For the PIP-PAH system, the same number of water, hexane, and PIP molecules as well as a PAH-GA crosslinking layer were included. The configurations of both systems were captured under the NVT ensemble after 2000 ps to analyze the relative abundance of PIP molecules along the z-coordinate (all simulation processes were conducted at 298.0 K). Mean square displacement (MSD) curves were obtained to indicate the mobility of PIP molecules in the PIP-only and PIP-PAH systems, and the diffusion coefficient of PIP could be estimated by the linear fitting of the slopes of MSD curves according to the Einstein relationship [1, 30].

Dissipative particle dynamics (DPD) simulations were performed using the Mesocite module in Materials Studio to investigate the IP process between PIP and TMC monomers at the water/hexane interface in the presence/absence of the PAH-GA layer. In this study, five components, namely, water, hexane, PIP, TMC, and PAH-GA, were defined and coarse-grained with different beads in the PIP-only and PIP-PAH systems. The size of both systems was $100 \times 100 \times 240 \text{ \AA}^3$, and they comprised a water slab (bottom), hexane slab (top), and middle crosslinking layer. The hexane-TMC system with a hexane: TMC ratio of 0.925: 0.075 was distributed randomly and established as the organic phase, whereas a water-PIP system with the same ratio was distributed randomly and established as the aqueous phase. For facilitating comparisons, all simulation parameters in the PIP-only system were consistent with those in the PIP-PAH system. The two slabs were independently equilibrated before being assembled for simulations [10, 16].

4.3 Results and discussion

4.3.1 Physicochemical characterization of PAH/PSf membranes

The intermediate PAH layer was developed via crosslinking with GA on the PSf substrate, which serves as a quasi-scale regulator to precisely control the kinetics of IP by prompting the diffusion-driven instability of the amine monomer reacting with acyl chlorides of TMC. Manipulating the internal structures by controlling the reaction conditions enabled the

construction of membranes with loosely packed architectures for the ultrafast transport of water molecules. FESEM characterization revealed that the surface of the PAH_0.2/PSf membrane (**Fig. 4.2d**) was more uniform and smoother but had fewer opening-pore structures compared to that of pristine PSf (**Fig. 4.2a**). Furthermore, a closer observation of the PAH_0.5/PSf membrane revealed a continuously decreased surface pore size distribution under highly concentrated PAH solution modification. The intermediate PAH layer was developed via crosslinking with GA on the PSf substrate, which serves as a quasimolecular regulator to precisely control the kinetics of IP by prompting the diffusion-driven instability of the amine monomer reacting with acyl chlorides of TMC. Manipulating the internal structures by controlling the reaction conditions enabled the construction of membranes with loosely packed architectures for the ultrafast transport of water molecules. The PAH/PSf membranes exhibited opening pore apertures with MWCO values reducing from 698.8 kDa for pristine PSf to 303.1 kDa for PAH_0.2/PSf membranes as the amount of crosslinking monomers increased (**Fig. 4.2b**). Further, a PAH_0.2/PSf membrane with a decreased mean pore size (5.3 nm) and narrower pore size distribution compared to those of pristine PSf was obtained. The results indicated a trend of a tighter surface structure, resulting in the water permeance of the PAH_0.2/PSf membrane ($115 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) decreasing greatly by more than 4 folds compared to that of the original PSf substrate ($590 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$). Synchronously, better surface wettabilities were obtained as the WCA decreased from 102.6° for the pristine PSf membrane to 43.4° for the PAH_0.2/PSf membrane (**Fig. 4.3**), owing to the amassed conducting -C=N- bonds and amino head groups with high polarity (**Fig. 4.2c** and **4.2f**) [31-33]. The active sites of amino groups from the PAH substrate tended to react with the aldehyde from GA to form a crosslinked interface layer via -C=N- interactions, as indicated by the stretching vibration at 1713 cm^{-1} (**Fig. 4.2e**) in the FTIR characterization result.

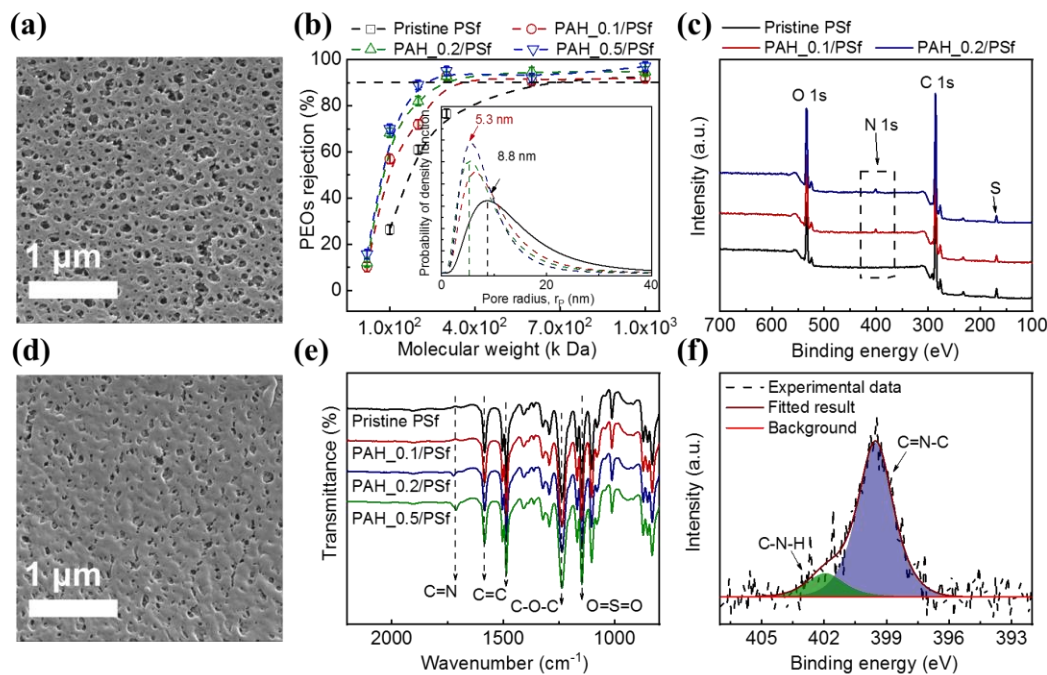


Fig. 4.2 FESEM images of (a) pristine PSf and (d) PAH_0.2/PSf membranes; (b) rejection ratio of PAH/PSf membranes against PEO solutes with different Mw values (inset: pore size and pore size distribution); (e) FTIR spectrum of PSf and PAH/PSf membranes; and (c) wide XPS spectrum and (f) high-resolution N 1s spectra of PAH_0.2/PSf membrane.

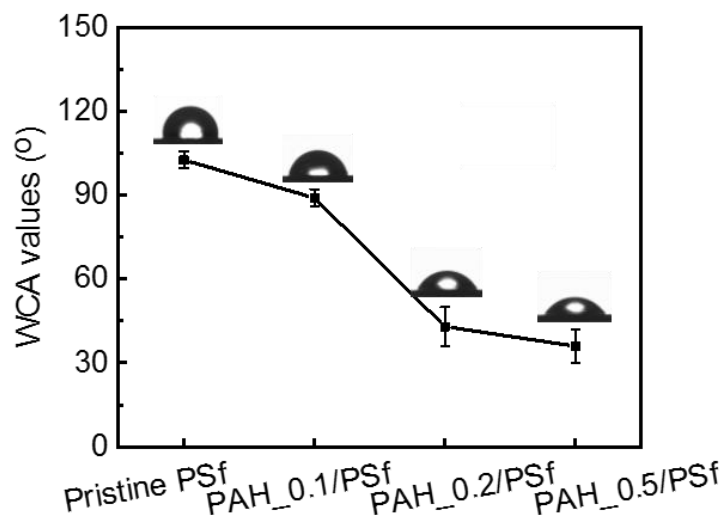


Fig. 4.3 WCAs of pristine PSf, PAH_0.1/PSf, PAH_0.2/PSf, and PAH_0.5/PSf membranes.

4.3.2 Physicochemical characterization of PA_PAH/PSf composite membrane

FTIR and XPS were used to examine the surface chemistries of PA_PAH/PSf composite

membranes. All resultant membranes exhibited the typical PA-based characteristic peaks of tertiary amide (1570 cm^{-1}) and carboxyl functional groups (1440 cm^{-1}), thus indicating the successful fabrication of PA-based membranes (**Fig. 4.4**) [34, 35]. Further, the enhanced characteristic peaks of C=O stretching in secondary amide I (1630 cm^{-1}) and coupling effects between N-H bending and C-N stretching (1570 cm^{-1}) indicated the presence of amino functional groups and an intensified IP process. The appearance of the absorption peak at 1724 cm^{-1} of C=N was attributable to the underlying in-situ crosslinked PAH. The PA_PAH/PSf composite membrane surface compositions were investigated by XPS with a probe depth of less than 10 nm, which is suitable for the as-developed ultrathin PA membranes. Also, the PA_PAH_0.2/PSf composite membrane has higher degree of crosslinking than pristine PA. This could be ascribed to the complete IP process generating highly-crosslinked PA-based membranes, as demonstrated by the increased O=C-N ratio and a decreased composition ratio of O=C-O from O 1s, respectively (**Fig. 4.5**).

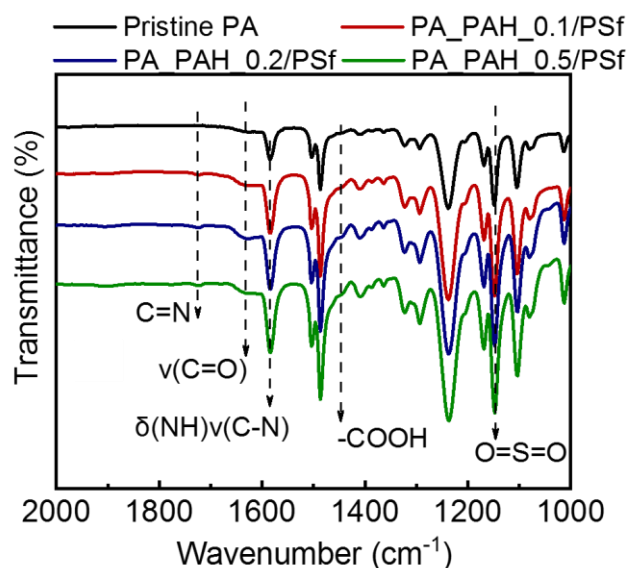


Fig. 4.4 FTIR spectrum of as-prepared PA-based TFC membranes.

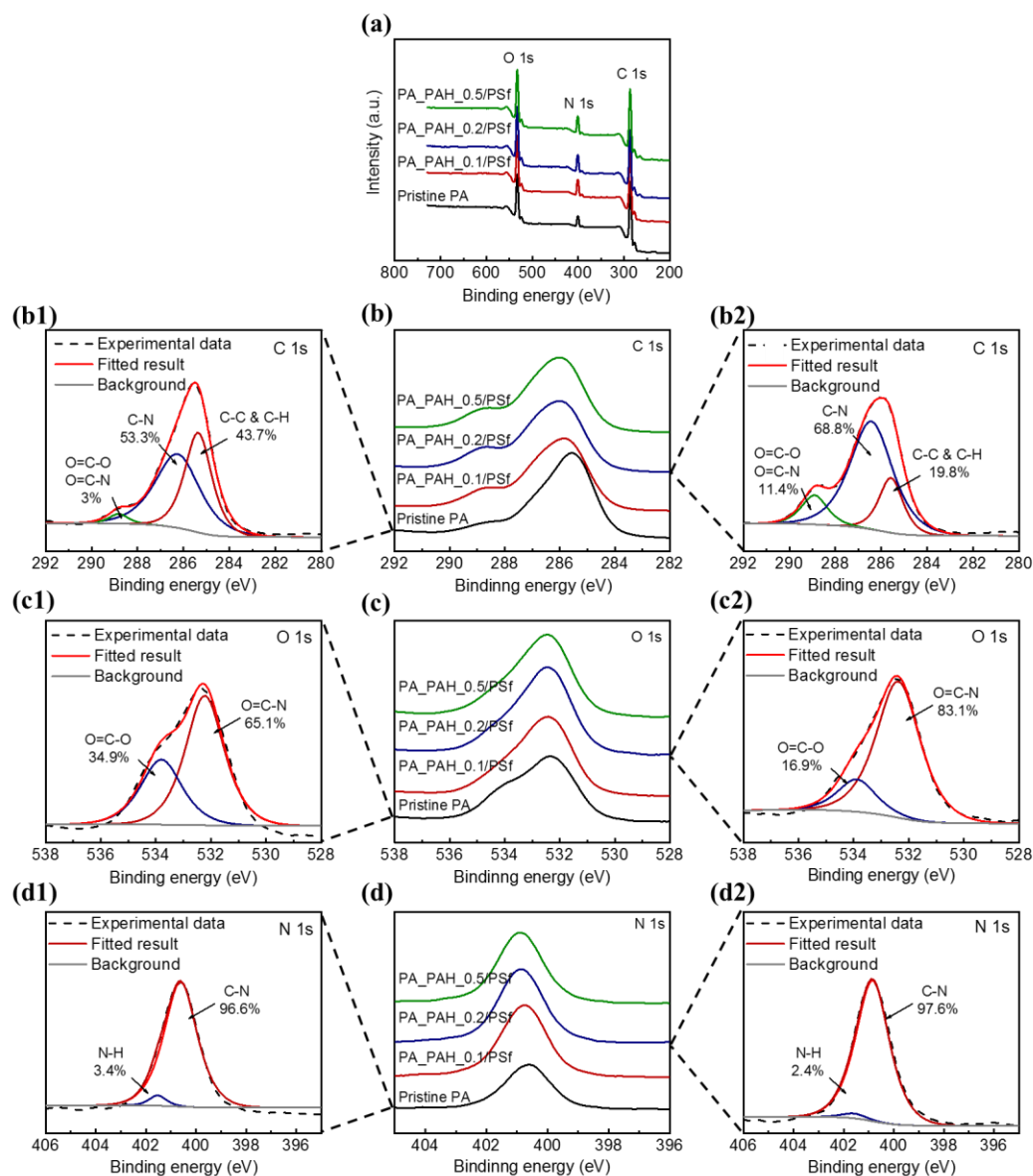


Fig. 4.5 Wide scan and core-level XPS spectra of (b), (b1), (b2) C 1s, (c), (c1), (c2) O 1s, and (d), (d1), (d2) N 1s from PA-based nanofilm.

The morphologies of the membrane surfaces were examined by FESEM and AFM. The pristine PA membrane exhibited a uniform smooth structure (**Fig. 4.6a**) with an arithmetic surface roughness of 9.5 nm (**Fig. 4.6e**), implying a moderate IP reaction [35]. The diffusion of amine monomers across the water/hexane interface was recognized as the controlling step for determining the resultant PA-based membrane structure. After preparing the PAH-based intermediate layer, the terminal amino groups with high polarity and hydrophilicity tended to absorb numerous cationic amine monomers to form PAH-PIP complexes. Such significant

amounts of distributed complexes at the water/hexane interface rapidly crosslinked with the TMC monomer at the beginning of IP reaction and then effectively impeded the subsequent diffusion of amine monomers to the interface by imposing more severe steric hindrance. The retardation effect on amine monomer transport through the organic phase induced a diffusion-driven instability that induced the formation of evenly distributed bulges on PA_PAH/PSf membranes with increased surface roughness (**Fig. 4.6b–4.6d**) [36]. Heterogeneously distributed nodular structures were obtained with increased loading amounts of intermediated PAH monomers, resulting in specific filtration areas that were enlarged by 5%, 13%, and 16% for PA_PAH_0.1/PSf, PA_PAH_0.2/PSf, and PA_PAH_0.5/PSf composite membranes, respectively, compared to that of the pristine PA membrane (**Table 4.1**).

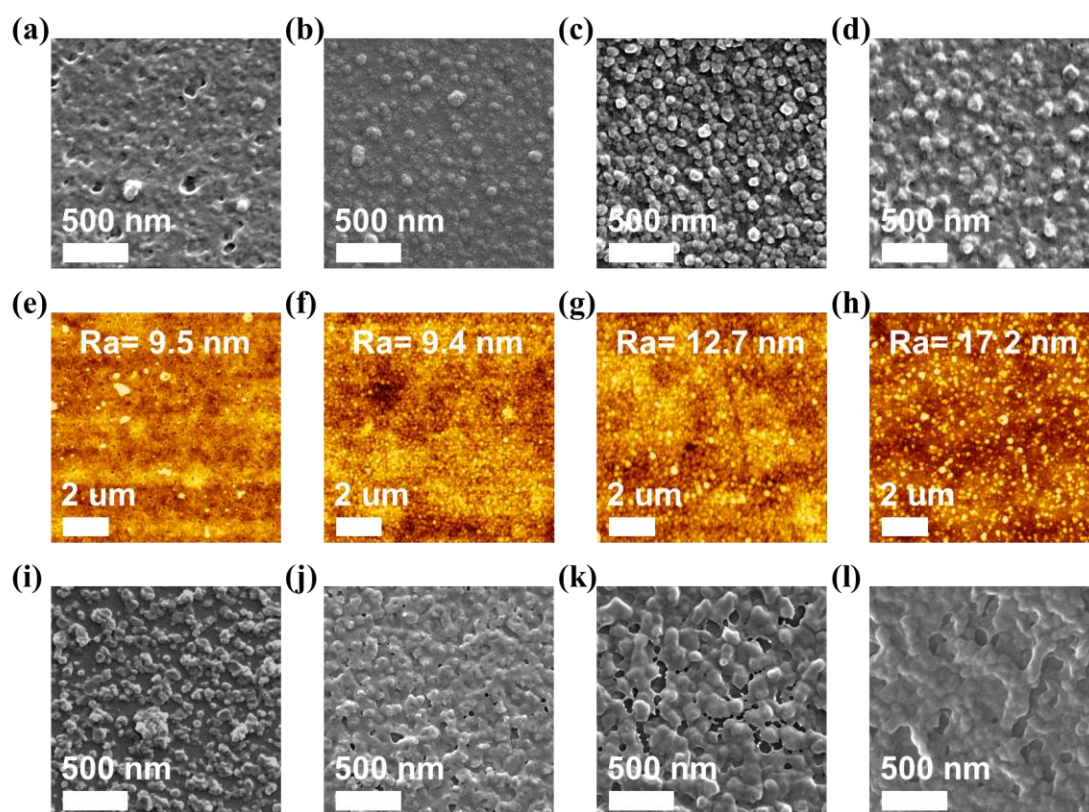


Fig. 4.6 FESEM (upper panel) and AFM images (middle panel) of the top surface morphologies, and FESEM images (lower panel) of the back surface morphologies of (a), (e), (i) pristine PA, (b), (f), (j) PA_PAH_0.1/PSf, (c), (g), (k) PA_PAH_0.2/PSf, and (d), (h), (l) PA_PAH_0.5/PSf.

Table 4.1 Top surface properties of pristine PA and PA_PAH/PSf TFC membranes. These results were acquired from AFM measurements over a scanning area of $10\ \mu\text{m} \times 10\ \mu\text{m}$.

Sample	Surface area (nm^2)	Ra (nm)	RMS (nm)
Pristine PA	1.01×10^8	9.5	11.9
PA_PAH_0.1/PSf	1.06×10^8	9.4	13.9
PA_PAH_0.2/PSf	1.14×10^8	12.7	15.5
PA_PAH_0.5/PSf	1.17×10^8	17.2	19.0

Loosened structures could be observed on the back surfaces of PA-based membranes deposited on PAH/PSf interlayered substrates (**Fig. 4.6i–4.6l**). This could be attributed to the following causes: (1) the decreased surface pore size of the support membrane weakened the pinning effect of IP by diminishing PA infiltration into the larger surface pores, resulting in the formation of a continuous layer with fewer protrusions [17]; and (2) more water molecules were absorbed at the conducting head groups of PAH, which acted as terminators to interrupt the regular IP reaction by converting the highly active acyl chlorides to carboxylic groups [23]. Consequently, the limited reaction sites resulted in a reduced covalent linkage between the underlying interlayer and PA matrix, indicating the formation of a highly porous structure at the back surface of nanofilms. The generated pore structures could serve as a gutter layer for the quick transport of water molecules without internal transport resistance [31].

The cross-sectional structures of PA nanofilms were characterized by TEM; all PA-based nanofilms were formed on the substrates, and the PA_PAH/PSf membranes were relatively thinner ($\sim 8\ \text{nm}$) than the pristine PA membranes ($\sim 12\ \text{nm}$) (**Fig. 4.7**). The mechanism of ultrathin membrane formation can be explained as follows: more amine monomers were initially stored in microvoids of the substrate, following which they slowly diffused across the water/hexane interface to react with acyl chlorides under the hindrance of the hydrophilic PAH interlayer. The passage of amine monomers would be controlled by the obstruction of the newly developed crosslinking layer, and it would form thinner nanofilms owing to the strengthened self-inhibiting nature derived from the PAH interlayer [6, 21].

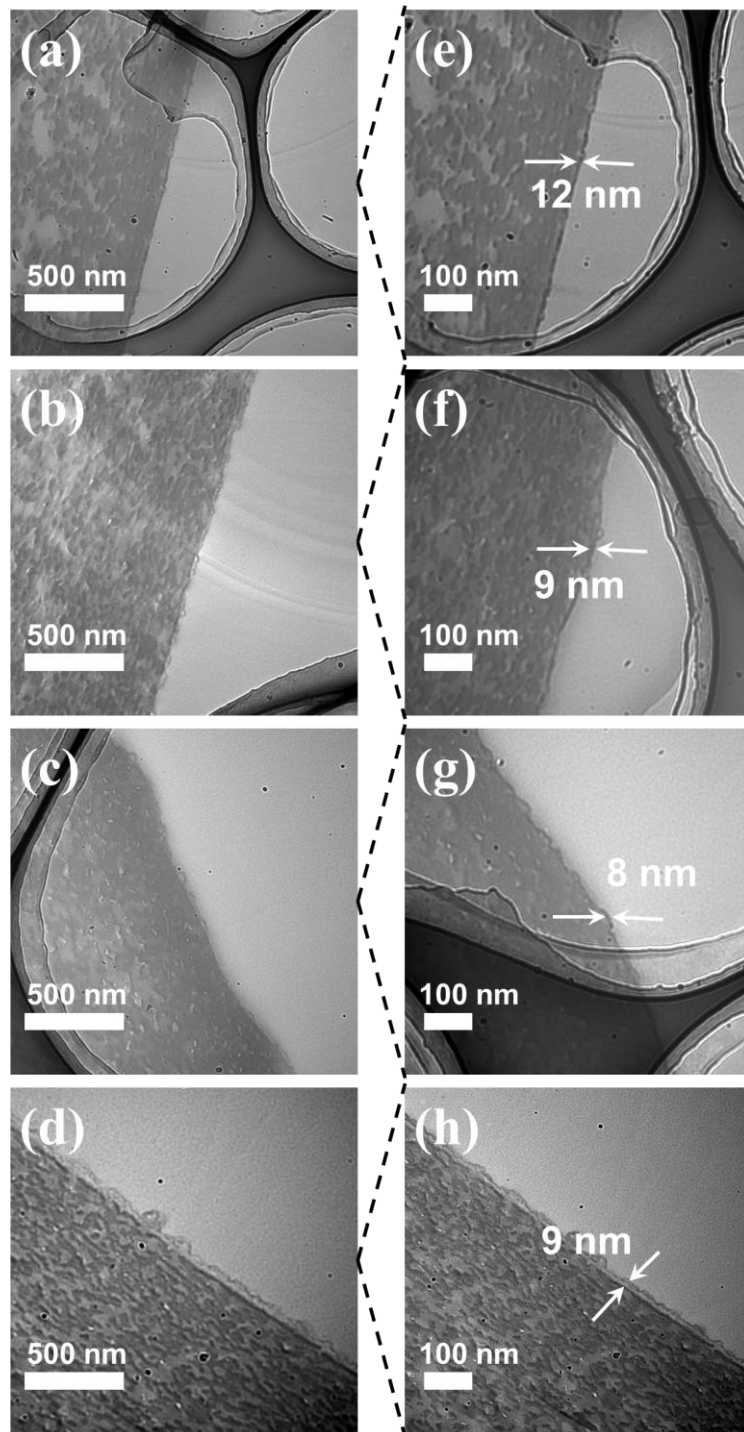


Fig. 4.7 Cross-sectional TEM images of (a), (e) pristine PA, (b), (f) PA_PAH_0.1/PSf, (c), (g) PA_PAH_0.2/PSf, and (d), (h) PA_PAH_0.5/PSf polyamide membranes.

4.3.3 Separation properties of PA_PAH/PSf composite membranes

A robust PAH_0.2/PSf membrane was constructed over the continuous operation duration of up to 7 days without performance degradation, as demonstrated in **Fig. 4.8**. The optimal IP

reaction conditions, namely, 0.1 wt% of PIP, 0.05 wt% of TMC, and IP reaction of 30 s, were investigated to reach a desired separation property in terms of water permeance and ionic selectivity. The separation performances of pristine PA and PA_PAH/PSf composite membranes are shown in **Fig. 4.9a**. The intermediate PAH layer contributes to the formation of a highly permeable PA selective layer, exhibiting improved water permeance of up to 12.5 and 17.5 L m⁻² h⁻¹ bar⁻¹ for PA_PAH_0.2/PSf and PA_PAH_0.5/PSf membranes, respectively, that is almost 3–4 folds higher than the value of 4.4 L m⁻² h⁻¹ bar⁻¹ in the case of pristine PA. This substantial enhancement of the PA_PAH/PSf membrane permeances over that of the pristine PA TFC membrane can be attributed to the as-generated thinner and rougher PA membrane with larger numbers of porous structures on the back surface [3, 37]. Furthermore, the retention capacities of PA_PAH/PSf composite membranes against various inorganic salts were examined (**Fig. 4.9b**); these membranes exhibited superior rejection ratios against Na₂SO₄, MgSO₄, and CaCl₂ relative to those of pristine PA. The superior ionic removal efficiency of divalent ions (98.9% for Na₂SO₄, 98.7% for MgSO₄, and 64.9% for CaCl₂ for PA_PAH_0.2/PSf as an example) compared to that of monovalent NaCl (20.7%) and NaNO₃ (18.3%) was attributable to the strengthened steric hindrance with larger hydrated sizes (Mg²⁺ (0.428 nm) > Ca²⁺ (0.412 nm) > SO₄²⁻ (0.379 nm) > Na⁺ (0.358 nm) > Cl⁻ (0.332 nm) ≈ NO₃⁻ (0.335 nm) together with the intensified electrostatic repulsion against ionic solutes with high valences [38, 39].

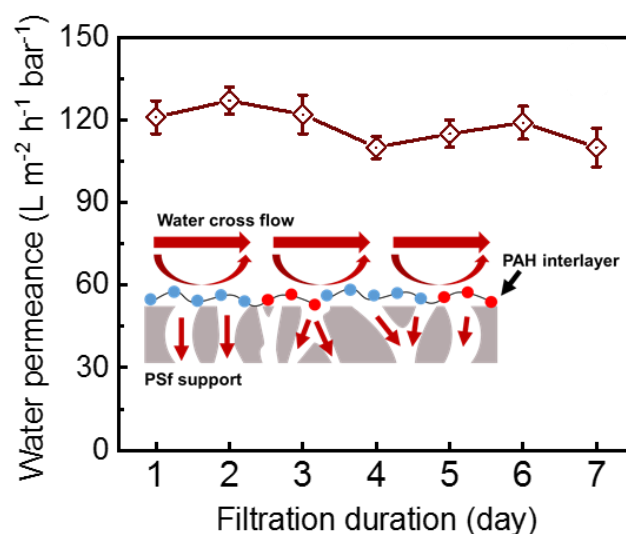


Fig. 4.8 Water permeance of variations of the PAH_0.2/PSf support operated for 7 days at 1 bar

with the flow velocity of 9.9 mL min⁻¹.

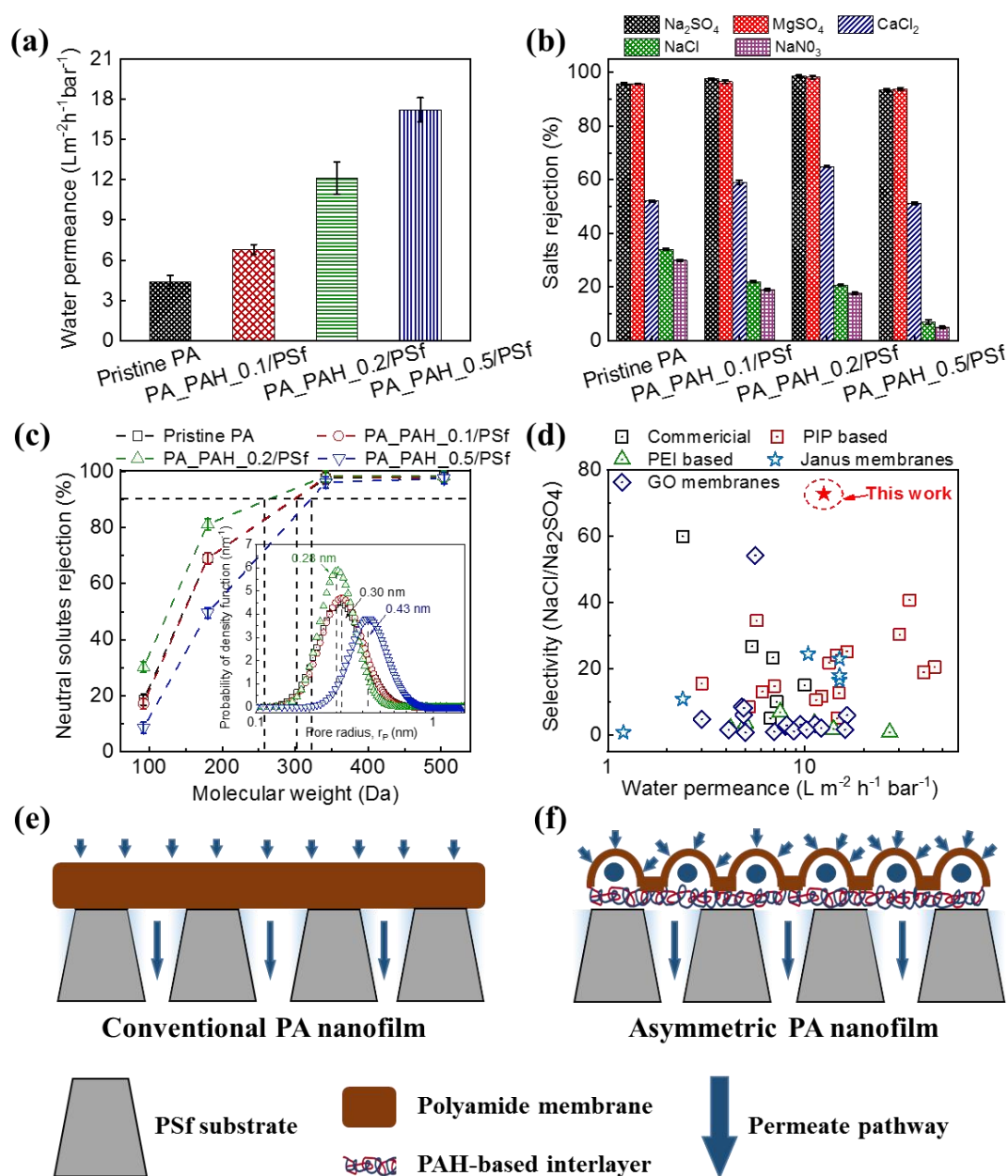


Fig. 4.9 Separation performance of (a) pure water flux and (b) salt rejection ratios of pristine PA and PA_PAH/PSf membranes; (c) neutral solutes rejection curves of PA-based membranes (inset: fitted pore size and pore size distribution curves obtained from neutral solute rejection data); (d) comparison of separation performance in terms of the water permeability and $\text{NaCl}/\text{Na}_2\text{SO}_4$ selectivity with those of other reported nanofiltration membranes (more details were listed in **Table 4.3**); schematic of water molecules permeate pathways across the (e) conventional and (f) asymmetric TFC PA nanofilms.

The retention capabilities of PA_PAH/PSf composite membranes against neutral saccharine with different molecular weights were tested, and their pore size distributions were obtained, as shown in **Fig. 4.9c**. The newly developed PA_PAH_0.2/PSf membrane had a decreased MWCO value of 257.6 Da and a smaller mean pore diameter of 0.28 nm (vs 0.30 nm) compared to those of the pristine PA membrane. More importantly, the PA_PAH_0.2/PSf membrane had a narrower pore size distribution with a lower σ_p value (**Table 4.2**). This result suggests that PA_PAH_0.2/PSf has a denser crosslinking structure than that of the pristine PA membrane. This could be explained as follows: (1) the larger concentration of amine monomers absorbed by the PAH-coated substrate produced a fully reacted PA membrane with a high degree of crosslinking, and (2) the primary amine groups from the PAH monomer participated in the reaction with acyl chloride to further promote the IP to form highly crosslinked PA nanofilms. However, further increasing the PAH concentration to 0.5 wt% may interfere with the normal reaction between PIP and TMC monomers owing to the excessive active sites of amino groups from the PAH interlayered substrate (**Fig. 4.10**) [40].

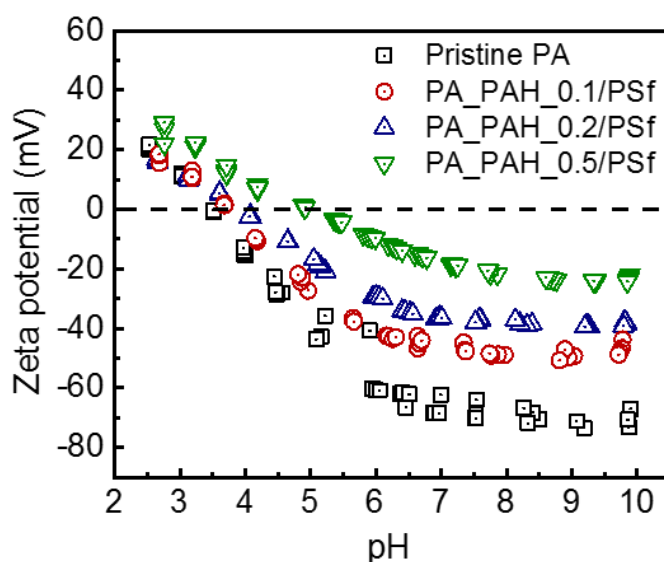


Fig. 4.10 Zeta potential of pristine PA and PA_PAH/PSf membranes.

Notably, the PA_PAH_0.2/PSf membrane has better mono-/divalent ionic solute

fractionation with a $\text{Cl}^-/\text{SO}_4^{2-}$ separation factor of 72.1 relative to that of pristine PA (15.3). Considering the slightly enhanced zeta potential of PA_PAH_0.2/PSf membrane (IEP: 4.9) than that of pristine PA (IEP: 3.5), the weakened Donnan effect was not conducive to the divalent anion rejections (SO_4^{2-}), but mainly ascribed to the substantially strengthened size exclusion effect with narrower pore size distribution and smaller most frequent pore sizes, as demonstrated in **Fig. 4.9c**. **Fig. 4.9d** and **Table 4.2** present a comparison of the separation performance of the newly developed PA_PAH/PSf membrane with different types of NF membranes, such as commercial NF membranes, PIP/PEI-based NF membranes, and 2D graphene oxide membranes. Our proposed PA_PAH/PSf membrane provides a competitive separation property with high water permeance and excellent mono-/divalent ionic sieving capability. This excellent performance could be attributed to the asymmetrical ultrathin PA nanofilm (8 nm) with a highly crosslinked surface structure and a spherically porous back surface structure that provided enlarged specific surface areas and internal transport paths for the quick transport of larger amounts of water molecules, as schematically illustrated in **Fig. 4.9e** and **4.9f**. For a 2000-min long-term filtration test performed under a high transmembrane pressure (5–20 bar) with highly concentrated Na_2SO_4 solutions (1000–5000 ppm), the PA_PAH_0.2/PSf membrane exhibited operational stability comparable to that of the pristine PA membrane (**Fig. 4.11**). This guarantees its effectiveness in retaining divalent ions without any penalties associated with the extra osmotic pressure of ionic solutes in future brine refining, seawater softening, and other relevant water treatment applications [40].

Table 4.2 MWCO value and mean pore size of as-formed PA-based membranes.

Sample	MWCO (Da)	50% rejection (Da)	84.13% rejection (Da)	d_p (nm)	d_s (nm)	σ_p
Pristine PA	302.2	148.2	266.9	0.327	0.430	1.3150
PA_PAH_0.1/PSf	302.2	148.9	266.0	0.327	0.429	1.3119
PA_PAH_0.2/PSf	257.6	125.9	208.5	0.303	0.383	1.2640
PA_PAH_0.5/PSf	323.5	182.7	300.5	0.360	0.454	1.2611

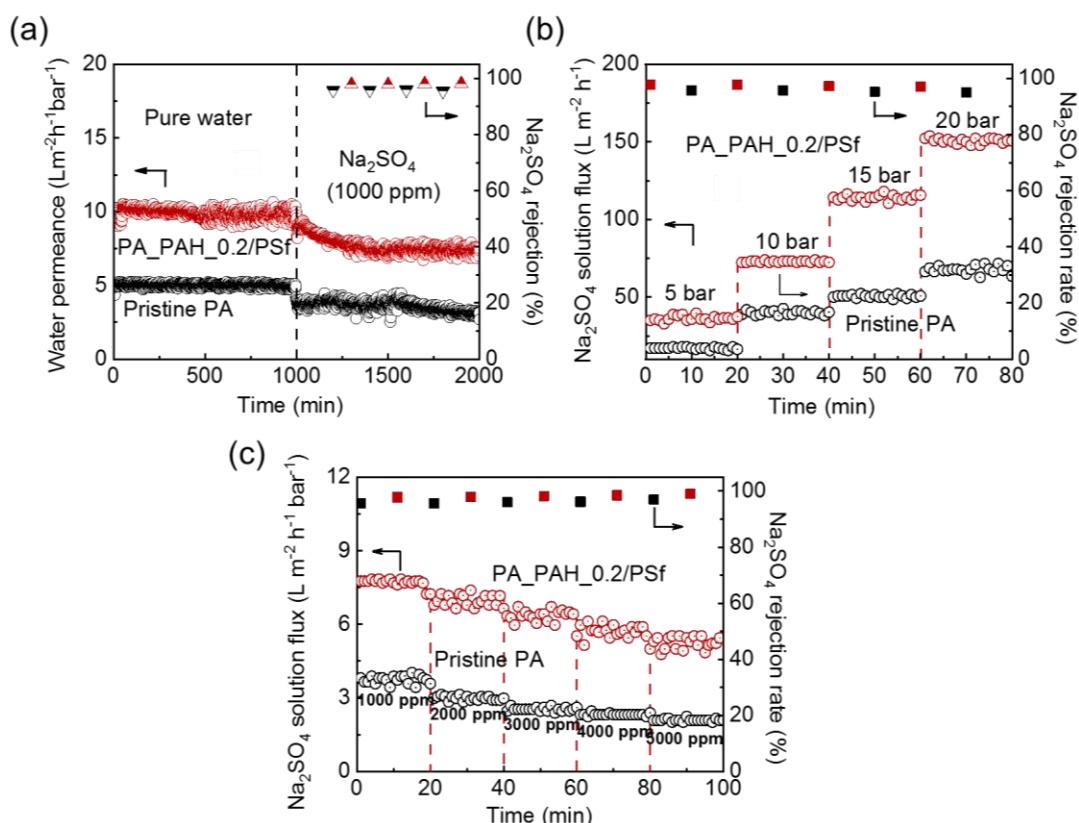


Fig. 4.11 Long-term filtration of pristine PA and PA_PAH_0.2/PSf membranes under transmembrane pressure of 10 bar for 2000 min; Separation properties of pristine PA and PA_PAH_0.2/PSf membranes toward 1000 ppm Na_2SO_4 salt solution in pressure cycling test; Separation properties of pristine PA and PA_PAH_0.2/PSf membranes toward Na_2SO_4 solutions with different concentrations under transmembrane pressure of 10 bar.

4.3.4 Mechanism implication

The diffusion-driven instability had a retardation effect on amine monomers, which enabled the formation of ultrathin nanofilms with a nodule-shaped surface and loose void structure on the back surface; the asymmetric structure is considered to confer high water permeance. To clarify the underlying mechanism such as asymmetric nanofilm formation, an MD simulation was performed to mimic the diffusion of amine monomers at the water-hexane interface with/without a PAH-based interlayer. Because the IP is an integrated diffusion-reaction process far from equilibrium, we mainly investigated the sole diffusion behavior of amine monomers in IP reactions without TMC molecules. This is because the amine monomers could be considered the indicative state of the reaction zone for the IP process.

In the PIP-PAH system, most PIP molecules were trapped into the PAH-based interlayer, where a more homogeneous distribution of monomers was obtained, indicating the IP reaction was mainly occurred at the surface of PAH-based interlayer [32]. In contrast to the pure PIP system, some monomers freely diffused into the organic phase, which results in the formation of a thicker nanofilms through the alignments of PIP molecules diffusion behavior. The positions and mean square displacements (MSD) of PIP molecules further confirm that the PAH-based interlayer obstructed the diffusion of PIP molecules through physical hindrance and chemical bonding (via hydrogen bonding interactions), thus resulting in a lower diffusion coefficient of $1.47 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ compared with that in the case of free diffusion of PIP molecules ($2.43 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) (**Fig. 4.12a**). The retardation of the movement of amine monomers could be further examined by UV-vis analysis (**Fig. 4.12b**); the thicker and denser PAH-based interlayer tended to exert a stronger attraction toward larger amounts of PIP molecules, thereby severely slowing down the movement of amine monomers across the interface and reducing the diffusion rates (inset of **Fig. 4.12b**). These results agree well with the trend of the Freger equation, in which the incipient PA membrane thickness is proportional to one-third of the amine monomer diffusivity, resulting in the deposition of an ultrathin nanofilm with thickness down to 8 nm on the PAH interlayer for ultrafast water permeating flux [41, 42].

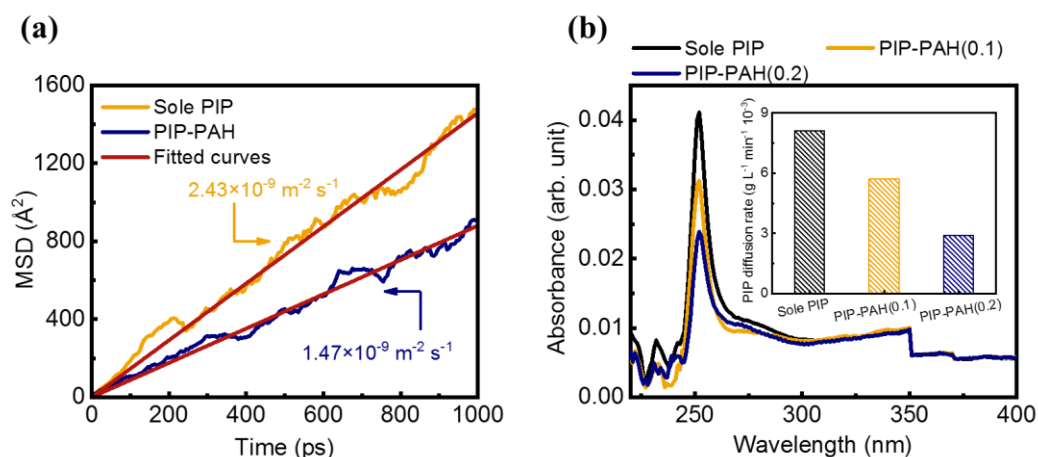


Fig. 4.12 (a) MSD profiles of PIP monomers in PIP-PAH and PIP-only systems; (b) UV-spectra of PIP in hexane solvent after diffusion for 30 s (inset: diffusion rate of PIP in the presence of various PAH concentrations).

The DPD simulations of the IP reaction with/without the PAH interlayer were conducted to reveal the underlying formation mechanism of asymmetric nanofilms. A more homogeneous surface with fewer porous structures was obtained for the nascent IP reaction (PIP-only system in **Fig. 4.13a**), in contrast to the larger number of cavities observed at the PAH-based interlayer (PIP-PAH system in **Fig. 4.13b**). The results confirmed the enlarged pore volumes on the back surface of PA nanofilms. The generated cavities could be explained as follows: (1) the absorption of more PIP molecules onto the PAH-based interlayer resulted in reduced movement of amine monomers through the water/hexane interface to react with the acyl chloride of TMC, thereby producing a less crosslinked PA nanofilm; and (2) more water molecules were captured by the highly hydrophilic PAH-based interlayer that served to interrupt the IP reaction by converting acyl chlorides to carboxyl groups to prevent the formation of a tight PA nanofilm at the PAH-based interface.

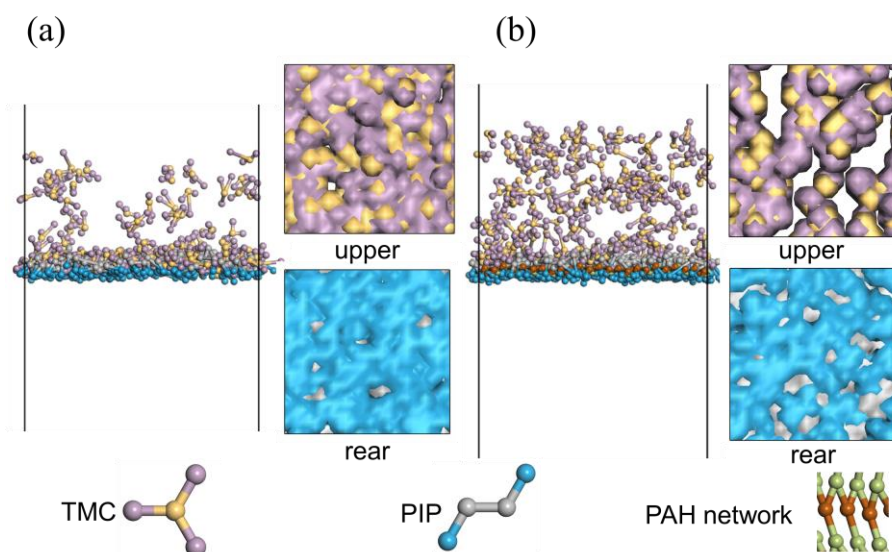


Fig. 4.13 PA nanofilm formation during IP process. Snapshots of DPD simulation of (a) conventional and (b) PAH-regulated IP reaction, and the as-formed PA structures from the bottom- and surface-side perspectives of conventional and PAH-regulated IP reactions. All the legend in this figure is from the side view perspective.

Table 4.3 Performance of reported state-of-the-art nanofiltration membranes.

Membrane	PWP (L · m ² · h ⁻¹ · bar ⁻¹)	Salt rejection (%)		Cl ⁻ /SO ₄ ²⁻ Selectivity	References
		Na ₂ SO ₄	NaCl		
Commercial NF membranes					
DOW FILMTEC™ NF70	7.2	97.0	70.0	10.0	[43]
DOW FILMTEC™ NF90	6.7	98.0	90.0	5.0	
GE-Osmonics DL	10.0	96.0	40.0	15.0	
GE-Osmonics HL	6.9	97.0	33.0	23.3	
Synder NFX	2.4	99.0	40.0	60.0	
Synder NFW	5.4	97.0	20.0	26.7	
PIP-based polyamide NF membranes					
PA50/CNC/PES	34	97.7	6.5	40.7	[44]
TFC _n O	45.7	96.0	18	20.5	[17]
SA-15.5	30.3	97.2	15.2	30.3	[45]
TFNM with HZN _{CS}	12.2	94.7	38.2	11.7	[46]
TFN _{PDA-SiNPs}	13.3	97.0	35.0	21.7	[47]
PA/PA-PES	11.4	93.5	31.0	10.6	[48]
PA/PES	14.6	83.4	16.9	5.0	
PA-TFC	3.0	95.5	30.2	15.5	[49]
TFN-SCQD	7.0	93.8	8.8	14.7	
TFN-NCQD	5.2	91.7	30.5	8.4	
TFN-CCQD	6.1	93.6	16.8	13.0	
TFC-T	5.7	98.5	48.3	34.5	[37]
PD/SWCNTs	^a 40.2	95.9	22.7	18.9	[50]
PIP/Sericin-TMC NF2	16.4	97.3	32.0	25.2	[51]
TFC2.0-5	14.5	97.0	27.7	24.1	[52]
TFN-mZIF 2	14.9	93.0	11.5	12.6	[53]
PEI-based polyamide NF membranes					
PA/SWCNT	27.0	46.0	64.0	0.7	[54]
MPMC	14.0	68.9	49.3	1.7	[55]
TFC-SDS	7.5	92.3	47.1	6.8	[56]
PEI-TMC	5.0	81.4	36.9	3.4	[57]
NF005	11.2	80.0	30.0	3.5	[58]
MTFC-70k-2	4.2	72.0	44.0	2.0	[32]
Janus membranes					
HF-NFMs	13.0~16.0	96.5	54.0	23.0	[59]
		93.2	52.0	16.5	

		82.0	46.0	18.0	
ANF1.0	2.4	96.0	57.0	10.8	[60]
PEI-TMC/PIP-TMC	1.2	68.0	78.0	0.7	[61]
G5-TAC2-PIP	10.4	97.5	39.0	24.4	[29]
GO-based NF membranes					
GO-PEI	7.0	50.0	55.0	0.9	[62]
GO-COOH	4.9	91.3	48.2	6.0	[63]
GO-EDA-HPEI	5.0	40.0	58.0	0.7	[64]
GNm	4.8	95.1	59.0	8.4	
G-CNTm(8:1)	8.0	80.9	51.4	2.5	
G-CNTm(4:1)	8.1	81.0	44.8	2.9	[65]
G-CNTm(8:3)	9.5	83.5	48.1	3.2	
G-CNTm(2:1)	11.3	81	39.7	3.2	
G-CNTm(8:5)	12.1	71.2	39.6	2.1	
PEI-GO	16.4	86.8	22.6	5.9	[66]
BPPO/EDA/GO	4.1	56.2	36.3	1.5	[67]
GO/CN/TiO ₂ -CNT	16.0	67.0	50.0	1.6	[68]
PRGO-HNTs-PSS	8.8	14.3	7.0	1.1	[69]
GO-MoS ₂	10.2	65.2	43.2	1.6	[70]
GO	4.9	95.6	64.4	8.1	[71]
GO-TEOA	3.0	85.0	30.0	4.7	[72]
NFM-3 # 0.2wt% TiO ₂ @GO	5.6	98.8	35.0	54.2	[73]
PA_PAH_0.2/PSf	12.5	98.9	20.7	72.1	This work

4.4 Conclusions

A highly permeable/selective ultrathin nanofilm (8 nm) with an asymmetrical architecture for nanofiltration was engineered via ionic amine-decorated interlayer-mediated IP. The self-assembly of the amine-based network with greater polarity conferred stronger attraction on amine monomers, thus exerting hindrance and turbulence effects on their diffusion movement toward the organic phase when conducting IP. The synergistic effects induced the formation of an asymmetric nanofilm constituting of a multilayer structure in which the back surface is a porous layer containing spherically porous structures, and the upper surface is a dense selective layer having nodular wrinkles. The best performing PA_PAH/PSf membrane provided improved water permeance of up to 12.5 L m⁻² h⁻¹ bar⁻¹, which is almost 3-fold larger than that of pristine PA (4.4 L m⁻² h⁻¹ bar⁻¹), while maintaining high Na₂SO₄ rejection of 98.9% with an

excellent $\text{Cl}^-/\text{SO}_4^{2-}$ separation factor of 72.1. This study clarifies the asymmetric structural design of multilayer nanofilms to realize breakthroughs in the existing trade-off limit of the permeability-selectivity performance in molecular fractionation, organic solvent nanofiltration, seawater desalination, and/or other separation technologies in water treatment.

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Chapter 5

Denser Electroneutral Nanofiltration Membrane for High Multiple Ions and Small Molecules Removal

5.1. Introduction

Attributing to the augmenting prevalence of reliable freshwater scarcity and pollution urged by population explosion and accelerated urbanization, global economy and social activities were constrained significantly [1-3]. To smooth away this predicament, rational management of non-conventional water resources (e.g. domestic wastewater, brackish water and seawater) presumably comprising of certain undesirable ions or regulated constituents (phosphorus, boron and other emerging micro pollutants) enables well solved water-related crisis [4]. Membrane-based purification technique especially microporous membranes featuring higher operation efficiency and environmental benefits superior to traditional depuration methods, serve as a sustainable paradigm for water reclamation and species elimination. By now, the great majority of established nanofiltration (NF) membranes present deficient arrangement for free volume cavities and surface charge, thus deteriorating precise solutes screening capacities. State-of-the-art membranes that could achieve excellent exclusion ability for ions and small organic compounds by meticulous adjusting pore structure and charge uniformity are still sought after, therefore, advanced treatment processes are gathering much more attention [5-7].

NF membrane particularly thin film composite (TFC) polyamide NF membrane termed as a pre-treatment process for reverse osmosis (RO), is one of the most promising methodologies for alleviating severe water shortage issues [8, 9]. The construction of TFC NF membranes generally necessities the extensive utilization of interfacial polymerization (IP) approach on an underlying porous support. IP is a mature and energy-efficient platform technology for

membrane preparation by constraining two reactive monomers at immiscible biphasic interface. For NF membrane preparation, amine molecules diffuse from aqueous to organic sides consisting of acyl chloride (trimesoyl chloride, TMC) monomers with intense disturbance, initializing the irreversible Schotten-Baumann polymerization for nanoscale thin film production [10, 11]. Polyamide NF membrane holds a crucial position in discriminating multivalent salts and small organic molecules via the cooperative effects of size sieving (pore properties) and electrostatic repulsion (Donnan equilibrium). However, the exceedingly fast reaction kinetics and uncontrollable diffusion-reaction rate forms highly crosslinked PA layer with multiple heterogeneity and non-uniform/broader pore characteristics (0.5-2 nm), suffering from inferior precise separation performance [12]. Membranes with a sharp pore size distribution with a tightly uniform pore structure plays a pivotal role in assuring efficient separation at the angstrom or even sub-angstrom level [13, 14]. Liang et al developed a surfactant-assembly regulated interfacial polymerization (SARIP) process, the resultant TFC membrane exhibited definite separation accuracy for hydrated ions with sub-angstrom level [15]. However, the more uniform pore structures are incapable of attain the desirable retention for monovalent salts (about 27% for NaCl). The imperfect retention for monovalent salts (generally less than 60%) of the existing NF membranes is another obstacle in some specific applications (such as clearance of trace components (boron and phosphorus) and organic micro pollutants), which call for a lower uncertainties for permeated water [4]. Besides, the self-terminating nature of IP hampers the diffusion of amine when conducting IP, and leads to the unconsumed acyl chloride groups remaining after IP. The inevitable hydrolysis of acyl chloride groups impacts the chemical and separation properties of the as-prepared selective layer. Managing membrane charge property while without sacrificing solutes selectivity is technically challenging due to the distinct protonation/deprotonation capabilities of amine/carboxyl groups. Therefore, the mostly reported NF membranes possess negative or positive charging properties, resulting in unsatisfactory retention against ions with counter ionic valence [8]. Consequently, such NF membranes couldn't meet the needs of practical cases. Molecular-modulation NF membranes with Janus chargeability enabled by temperature-assisted IP or incorporating positive macromolecular filler could simultaneously harvest the improved rejection for versatile divalent ions, which inspires us to fine-tune the balance between amine and carboxyl groups

for efficient ion separation [16].

An electroneutral NF membrane could theoretically achieve a comparable membrane rejection capability against various electrically charged solutes. For example, Xing et al invented a SAS (solvation-amination-synergy) strategy to fabricate the neutral NF membrane by synchronously suppressing residue acyl chloride hydrolysis and promoting amination reaction [17]. The as-formed electroneutral NF membrane exhibit heightened water permeance ($13.2 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) and superb anti-fouling properties, but compromised salts selectivity (less than 20% for Na_2SO_4). This is because the solvent intrusion and amination processes deteriorated degree of crosslinking and minimized Donnan impacts. Another recent work by Lin et al revealed that the electroneutral NF membrane originating from the imidazole derivative compounds (IMs) grafting could minimize the retention differences for small pollutants with identical/ or counter valences as that of membrane surface [8]. The IMs with high packing density served as an effective nanofluidic platform for solvent/ nutrients quick passing through. However, some other smaller molecules such as EMPs within the molecules weight of 350 Da approaching neutral state at pH 7 demand more precise NF membrane with high fractionation ability. Commercial NF membranes with tighter structure also preserve unsatisfied rejection for monovalent ions. Therefore, synthesis of electrostatic free nanofilm with higher separation accuracy for coexisting contaminants/small molecules and mono/multivalent ions is of paramount significance for the development of high-performance NF membranes. Alongside this concept, a paradigm shift in engineering the PA selective layer based on charged macro-molecular is thereby proposed.

Herein, we demonstrate an ultrahigh selective NF membrane by a general IP process followed by assembling macromolecular amine sources (polyethyleneimine (PEI) and polyallylamine (PAA)) chains onto nascent PA surface via amination reaction. The introduced of amine consumed surficial residue carboxyl groups and decreased membrane's electronegativity (**Fig. 5.1**). By systematically scrutinizing and optimizing reaction process (e.g. IP formula and amination duration) and amine sources, a series of charge-free NF membranes were accessed. And the ions/molecules separation were upgraded due to the charge-balance state and sharp pore features. The grafted PAA molecules regulated the membrane free volume cavities and chargeability accurately, enabling the production of electroneutral NF membrane

with high exclusion capacities. PAA is the main component discussed in this manuscript due to the following merits: 1) the amine groups ensure the steady covalent linkage on PA surface guaranteeing membrane's sharpened solvent/solutes sieving abilities; 2) higher density amino groups of PAA with excess unreacted amine after amination procedure and stronger protonation ability in solution, enabling the higher feasibility of transforming membrane surface potential. To sum up, this as-performed electroneutral high-selective NF membrane may enlighten the development of NF process for precise separation.

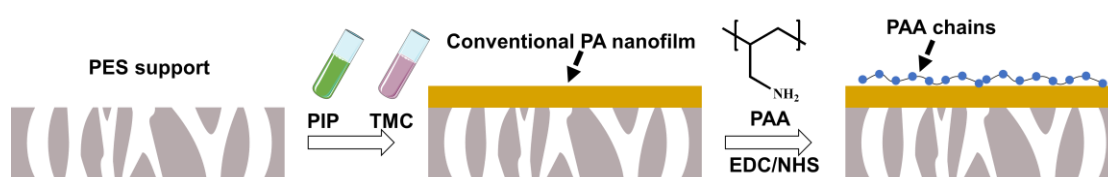


Fig. 5.1 Schematic illustration of PAA grafted PA nascent nanofilm.

5.2. Experimental

5.2.1 Materials

The commercial PES ultrafiltration membrane (MWCO: 30 kDa) was purchased from Merck Millipore. branched polyethylenimine (PEI, $M_w \sim 10000 - 20000 \text{ g mol}^{-1}$), 2-morpholinoethanesulfonic acid (MES, 99%), n-hydroxysuccinimide (NHS, 98%), n-(3-(dimethylamino)propyl)-n-ethylcarbodiimide hydrochloride (EDC·HCl, 98%) sodium hydroxide (NaOH, analytical pure) were purchased from Tokyo Chemical Industry Co., Ltd. (Japan). Polyallylamine (PAA, $MW \sim 15000 \text{ g mol}^{-1}$, 15% aqueous solution) was supplied by Polysciences, Inc. (USA). Ethylene glycol (99%), dyes of methyl orange (MO, 327.3 g mol^{-1} , 98%), methylene blue (MB, 319.9 g mol^{-1} , 95%), crystal violet (CV, 407.9 g mol^{-1} , 95%) and congo red (CR, 696.7 g mol^{-1} , 95%) were purchased from Sigma-Aldrich (Japan). Inorganic salts of lithium chloride (LiCl, 99%), cobalt chloride (CoCl_2 , 99%), sodium nitrate (NaNO_3 , 99%), copper chloride (CuCl_2 , 99%), lead chloride (PbCl_2 , 99%), zinc nitrate ($\text{Zn(NO}_3)_2$, 99%) and nickel nitrate ($\text{Ni(NO}_3)_2$, 99%), phosphoric acid (99.5%), boric acid (H_3BO_3 , 99.5%), boron standard solution, three emerging micro-pollutants (EMPs) of trimethoprim (TMP, >99%), diclofenac sodium salt (DCF, >99%) and carbamazepine (CBZ, >99%) were purchased from

FUJIFILM Wako Pure Chemical Industries Co., Ltd. (Japan). Deionized (DI) water was produced by Milli-Q water purification system (Merck, Millipore, Japan). And other chemical and reagents were the same as chapter 2 without specific notification.

5.2.2 Preparation of PEI or PAA grafted PA nanofiltration membrane

The pristine PA membrane was fabricated via typical interfacial polymerization (IP) reaction. Firstly, PES support was immersed into 0.2% (wt/wt) PIP aqueous solution for 3 min. Then, after draining off the excess PIP solution, 0.1% (wt/wt) TMC hexane solution was poured onto the PES substrate saturated with PIP solution for another 30 s to initialize the IP reaction. Finally, the resultant membrane (denoted as pristine PA) was heat cured in an oven (70 °C) for 3 min. All the TFC membranes were stored in DI water (4 °C) for 24 h to complete the hydrolysis reaction of unreacted acyl chloride of TMC prior to testing.

The specific PAA or PEI modification process were reported in previous reports [18, 19]. Specifically, for the preparation of PEI or PAA grafted PA membranes (PA-PEI or PA-PAA), the as-formed pristine PA membranes were dipped into the mixed solution containing 1 wt% MES, 2.5 wt% EDC and 1 wt% NHS (pH was adjusted to 6.0 by using 0.1 mol L⁻¹ NaOH solution) for 1h. Then putting into 0.1% (wt/wt) PEI or PAA solution for 8 h to finalize the grafting reaction.

5.2.3 Membrane characterization

The membranes characterization methods were same as chapter 2.

5.2.4 Membranes permeance evaluation

The membrane permeance test was the same as chapter 2.

5.2.5 Evaluation of rejection abilities

The sieving abilities of membranes were explored by infiltrating dyes (MO, MB, CV and CR), inorganic salts, H₃BO₃, H₃PO₄ and small organic EMPs. The ions rejection (inorganic salts) abilities of the as-performed membranes were determined with single and mixed aqueous salts solutions in the cross-flow system, and the effective salts rejection ratio (*R*, %) of the

membranes could be determined by the following equation:

$$R = \frac{C_f - C_p}{C_f} \times 100\% \quad (5.1)$$

where C_f and C_p are the saline concentrations in the feed and permeate sides, respectively. For Na_2SO_4 , MgSO_4 , MgCl_2 , NaCl and LiCl , the rejection ratio were examined by the conductivity meter (Ultrameter IITM 4P, Myron L Company, Japan); and for other heavy metal ions and trace micropollutants, the rejection ratio were determined by an inductively coupled plasma - mass spectrometer (ICP-OES, Avio 550 Max, PerkinElmer, USA). The reported rejection data was gained by calculating the average of 3-time measurement results from each, and totally three samples from distinct batches. For phosphorus and boron removal abilities evaluation, 10 ppm phosphorus acid and boric acid aqueous solution with different pH were filtered through the as-formed nanofiltration membranes under identical testing conditions as salts selectivity analysis. The phosphorus and boron contents in feed and permeate sides were investigated by inductively coupled plasma-optical emission spectrometry (ICP-OES, Avio 550 Max, PerkinElmer, USA) after necessary dilution. And the removal rates were determined by Equation 5.1, where C_f and C_p , respectively, represent the phosphorus and boron concentration in feed and permeate solutions.

5.2.6 Determination of pore size and pore size distribution

The pore size and pore size distribution of the as-formed membranes were evaluated by neutral solutes transport model, which were listed in chapter 2.

5.3. Results and discussion

5.3.1 Physicochemical properties of the as-performed membranes

ATR-FTIR characterization (**Fig. 5.2a**) was used to determine the surface chemistries of synthetic PA nanofilms. The peaks located in 1234 cm^{-1} ($-\text{C}-\text{O}-\text{C}-$) and 1146 cm^{-1} ($-\text{S}=\text{O}-$) were originated from the PES substrate. And all resultant TFC membranes exhibited identical typical polyamide characteristic peaks at 1662 cm^{-1} and 1570 cm^{-1} , which were attributed to the $-\text{C}=\text{O}$ stretching vibration (amide I) and tertiary amide in polyamide skeleton, respectively [20, 21]. These results manifest that the PA nanofilms were deposited onto the PES support successfully.

Of note, for both PA-PEI and PA-PAA membranes, the enhanced characteristic peak at 3440 cm^{-1} belonging to -NH or -NH₂ in comparison to that of PA membranes was due to the presence of PEI and PAA, thus illustrating the successful PEI and PAA grafting onto PA surface [22]. XPS characterization with a detected depth less than 10 nm was utilized to probe the surface elements composition of acquired PA nanofilms (**Fig. 5.2b**). Three peaks of C 1s, O 1s and N 1s centered at 284.6 eV, 532.5 eV and 399.5 eV, respectively, were occurred on all resultant PA membranes. The atom percentage of N in pristine PA increased from 2.16% to 3.80% and 4.37% with respect to PA-PEI and PA-PAA membranes. The enhanced N composition in PA-PEI and PA-PAA membranes are originated from the higher amino functional groups in PEI and PAA molecules. To further identify the surface chemical compositions of the synthetic membranes, the wide-scan N 1s spectra were deconvoluted (**Fig. 5.2c-5.2e**). The contents of -N< (centered at 400.8 eV) and -NH- (centered at 399.2 eV) in pristine PA are 37.2% and 67.8%, respectively. And a new peak corresponding to -NH₂ centered at 398.3 eV was detected for the spectrum of PA-PEI and PA-PAA membranes, which were assigned to the amino groups in PEI and PAA molecular chains. And it should be noted that the -NH₂ content in PA-PAA was higher than PA-PEI, manifesting the higher number of -NH₂ groups per gram of PAA molecules. The higher amino functional groups grafting density leads to a more positive charged surface with a greater isoelectric point (3.36, 5.68 and 9.45 for pristine PA, PA-PEI and PA-PAA, respectively) (**Fig. 5.3**). The consumed carboxyl groups in pristine PA outermost surface changed the polarity of PA surface and weakened the hydrophilicity of PA membranes due to the poor hydration capacity of amino groups (**Fig. 5.2f**).

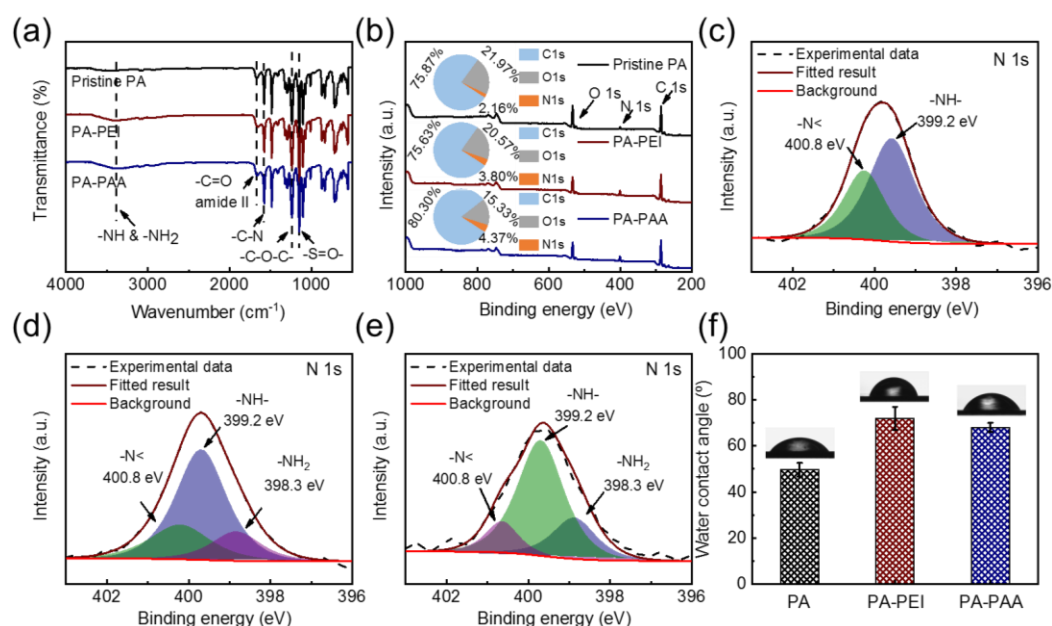


Fig. 5.2 (a) ATR-FTIR spectra and (b) wide-scan XPS spectra (inset: elemental compositions) of pristine PA, PA-PEI and PA-PAA nanofiltration membranes; Analysis of N 1s high-resolution spectrum of the PA selective layer in (c) pristine PA, (d) PA-PEI and (e) PA-PAA membranes; (f) water contact angle (WCA) measurement of pristine PA, PA-PEI and PA-PAA membranes.

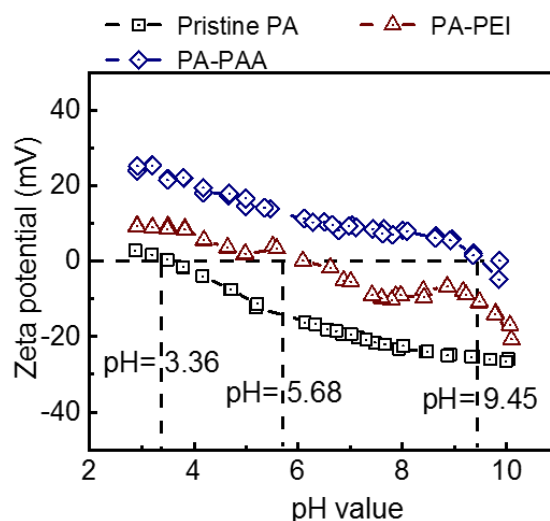


Fig. 5.3 surface zeta potential of pristine PA, PA-PEI and PA-PAA membranes.

5.3.2 Characterization of membranes structure and morphology

Interfacial polymerization reaction was conducted on PES substrate to fabricate pristine PA membrane, and PEI and PAA were grafted onto nascent PA membrane surface by amination reaction. To further explore the microscopic morphologies of the pristine PA, PA-PEI and PA-

PAA membranes, FESEM and AFM based characterizations were used and corresponding profiles are listed in **Fig. 5.4**. The pristine PA membrane shows discretely distributed globular surface topography, which was originated from the unstable diffusion-reaction behavior between diamine and acyl chloride during IP (**Fig. 5.4a**) [23]. AFM analysis of the pristine PA also presents the sporadic nodular-like structure with a roughness value of $R_a = 21.5$ nm (**Fig. 5.4d**). In comparison, pristine PA membrane decorated with PEI (**Fig. 5.4b**) and PAA (**Fig. 5.4c**) displayed a relatively flatter structure with a lower roughness values of $R_a = 17.7$ nm for PA-PEI (**Fig. 5.4e**) and $R_a = 8.8$ nm for PA-PAA (**Fig. 5.4f**) membranes. This is because that the overlay PEI and PAA with high molecular weight filled up the gully among heterogeneous nodules and hence smoothing the rough morphology of nascent PA nanofilm. These results reveal that the PEI and PAA modification enabled the creation of membrane with varied membrane topography and surface properties. TEM cross-section images demonstrate that the thickness of the PA nanofilms increased from 15 nm for the pristine PA (**Fig. 5.4g**) to 25 nm and 23 nm upon PEI (**Fig. 5.4h**) and PAA (**Fig. 5.4i**) modification. The thickness difference among pristine PA and PA-PEI/PA-PAA membranes represents the thickness of grafted PEI and PAA layers.

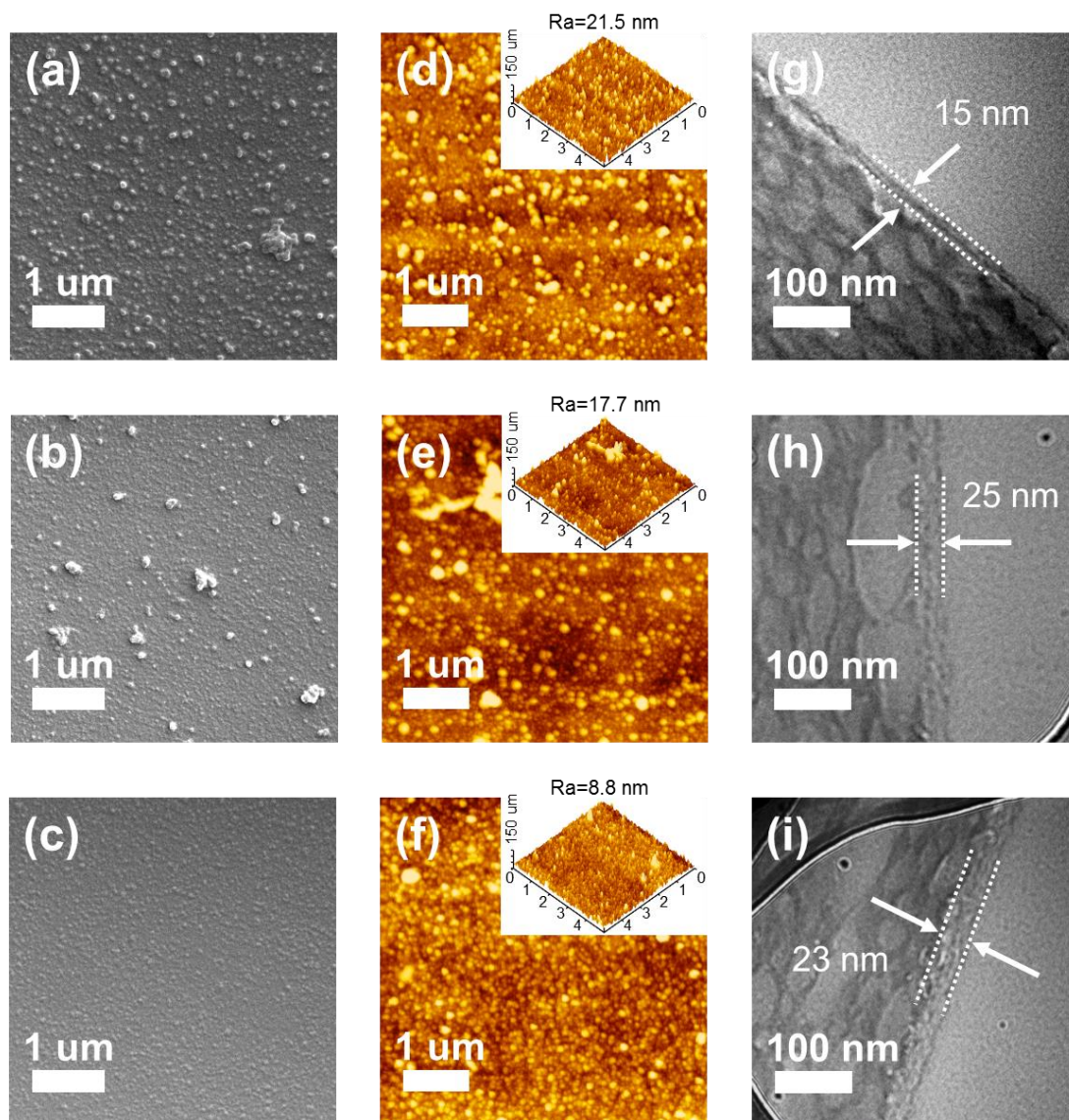


Fig. 5.4 FESEM images (left-hand panel), AFM images (middle panel, the inset represent the corresponding surface 3D morphology images) and TEM cross-section images (right-hand panel) of pristine PA (a, d, g), PA-PEI (b, e, h) and PA-PAA (c, f, i) polyamide membranes.

5.3.3 Separation performance of PA nanofilm

The filtration performance of the as-formed membranes were evaluated. As shown in **Fig. 5.5a**, the PA-PEI and PA-PAA both display decreased water permeance when compared to that of pristine PA. An water permeance of around $8.1 \text{ L m}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ were attained for PA-PEI and PA-PAA membranes, respectively, lower than that of pristine PA membrane ($15.2 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$). Such a significantly decreased water permeance could be primarily attributed to the enhancement in crosslinking degree and thickness of PA nanofilm, giving rise to the boosted

mass transfer resistance. **Fig. 5.5b** exhibit the inorganic salts rejection behavior of pristine PA, PA-PEI and PA-PAA membranes. The retention rate of pristine PA follows the order of $\text{Na}_2\text{SO}_4 > \text{MgSO}_4 > \text{MgCl}_2 > \text{LiCl} > \text{NaCl}$ consisting with the conventional negative charged PIP-based NF membranes, in which the surface charge and pore size play dominant roles for ions sieving. And the PA-PEI and PA-PAA membranes display higher rejection ratio for MgSO_4 (98.7% and 98.5% for PA-PEI and PA-PAA membranes) and MgCl_2 (97.8% and 99.3% for PA-PEI and PA-PAA membranes). Considering the larger hydrated ions size (0.428 nm and 0.379 nm for Mg^{2+} and SO_4^{2-}) and higher valence, the obviously enhanced rejection was mainly derived from the synergistic effects of decreased pore size and more positive surface charge [24, 25]. It is noteworthy that the PA-PAA membrane exhibits higher rejection ratio for monovalent salts (LiCl and NaCl) compared to that of PA-PEI but with the analogous water permeance. Similar experimental results could be found in **Fig. 5.5c**, whereof the PA-PAA membrane exhibit higher removal efficiency for heavy metal saline solutions (Pb^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+} and Ni^{2+}) relative to that of pristine PA and PA-PEI membranes. The separation properties of pristine PA, PA-PEI and PA-PAA membranes were further scrutinized by infiltrating neutral glycol and carbohydrate solutes with diverse molecular weight (M_w) in feed water solutions (**Fig. 5.5d**). The PA-PEI and PA-PAA membranes both demonstrate decreased molecular weight cutoff (MWCO) values with narrower range of transition regimes when compared to that of pristine PA membrane. For instance, relative broader rejection curve of pristine PA with rejection ratios of 19.35% and 76.74% for glycerol (92 Da / 0.261 nm) and glucose (180 Da / 0.359 nm) was obtained. While the PA-PEI and PA-PAA membranes exhibit higher rejection ratio for glycerol (32.37% and 33.67 for PA-PEI and PA-PAA membranes) and glucose (87.83% and 84.69% for PA-PEI and PA-PAA membranes) with decreased MWCO values. Pore size distribution attained from the geometric standard deviation of the probability density function curves indicate that the average pore size decreased from 0.30 nm to 0.29 nm after amino functional groups modification. The range of transition regimes in the rejection curves with a free volume distribution are narrower than pristine PA, demonstrating a highly size-dependent sieving ability for ion/molecular separation (inset of **Fig. 5.5d**). Even if the PA-PAA membrane shows a satisfactory rejection ratio for divalent cations, the Pb^{2+} still has a high permeation ability possibly probably due to the higher diffusivities ($0.95 \text{ m}^2 \text{ s}^{-1}$). Therefore, further optimizing the

IP reaction parameters to obtain best-performing membranes in terms of more precise ions sieving properties were conducted.

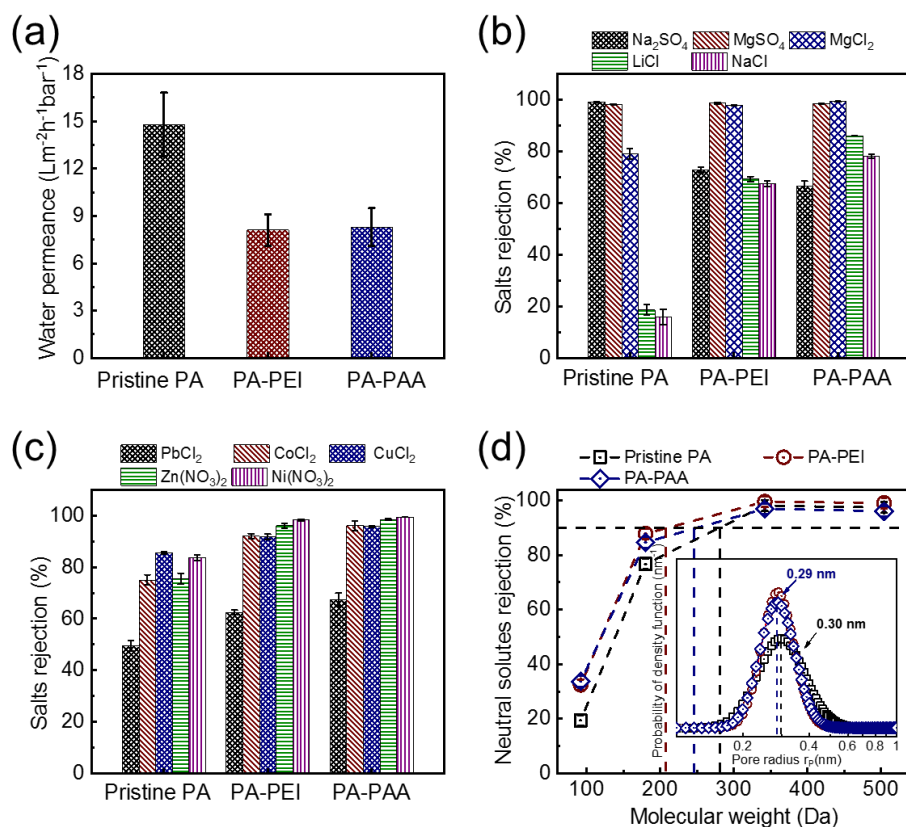


Fig. 5.5 (a) Pure water permeance, (b) inorganic salts and (c) heavy metal ions rejection ratio of pristine PA, PA-PEI and PA-PAA membranes; (d) rejection ratios for uncharged small organic compounds of the three PA-based membranes (inset: pore size and pore size distribution curves derived from the rejection data).

For practical industrial application, a higher membrane retention rate is more ordinarily favored than facilitated membrane permeability. Changing the surface carboxyl group content of polyamide NF membrane can affect the grafting density of PAA naturally [19]. In this work, the terms of IP 2min, PIP 0.5 and TMC 0.2 were used to refer to the PA membranes fabricated by extending the IP reaction time to 2 min, increasing PIP and TMC monomers concentration to 0.5% and 0.2%, respectively. Besides, the nascent membranes originated from the IP reaction were modified by PAA and are termed as m-IP 2min, m-PIP 0.5 and m-TMC 0.2, respectively. The separation properties of the as-formed membranes were systematically examined. We

found that the pure water permeance of the as-performed membranes fabricated either with higher monomers concentrations and or longer IP reaction duration are low due to the formed thicker and denser separation layers (**Fig. 5.6a**). And the salts rejection behavior matches well with the typical trend of PIP-based polyamide membranes, in which the ions selectivity follows the order of $\text{SO}_4^{2-} > \text{Mg}^{2+} > \text{Li}^+ > \text{Na}^+$ (**Fig. 5.6b**). The TMC 0.2 membrane coupon also manifests highest rejection ratio for heavy metal ions than IP 2min and PIP 0.5 membranes (**Fig. 5.6c**). This is presumably because that the higher TMC monomer content is more favorable for the construction of denser PA selective layer. After grafting with PAA compound chains, all resultant membranes with moderately reduced permeance (**Fig. 5.6d**) demonstrate augmented ions removal efficiency for almost all ions. For example, the m-TMC 0.2 membrane coupon demonstrate highly improved ions removal efficiency with a superior inorganic salts rejection (99.6% for MgSO_4 , 99.9% for MgCl_2 , 95.8% for LiCl and 92.7% for NaCl) when compared to that of TMC 0.2 membrane (98.4% for MgSO_4 , 97.1% for MgCl_2 , 48.6% for LiCl and 43.7% for NaCl), with a minimum sacrifice of Na_2SO_4 rejection (**Fig. 5.6e**). In addition, the m-TMC 0.2 membrane displayed perfect rejection properties for heavy metal ions (90.2% for Pb^{2+} , 99.5% for Co^{2+} , 97.8% for Cu^{2+} , 98.7% for Zn^{2+} and 99.2% for Ni^{2+}) (**Fig. 5.6f**). The performance results discussed above further prove that the PAA grafting significantly increased the ions retention abilities. Membranes pore size and pore size distribution were fitted by infiltrating small neutral organic compounds and surface zeta potential were detected to determine the membranes separation mechanism in case of steric (size-sieving) and electrical (Donnan) exclusion effects. As derived from the rejection curves, the MWCO values decreased from 216 Da, 217 Da and 174 Da to 168 Da, 167 Da and 158 Da for IP 2 min/m-IP 2min, PIP 0.5/m-PIP 0.5 and TMC 0.2/m-TMC 0.2 membrane pairs (**Fig. 5.7a-5.7c**), indicating the PAA grafting substantially improved membranes sieving ability with narrowed free volume cavities, of which the most frequent cavities were slightly decreased from 0.29 nm, 0.30 nm and 0.26 nm to 0.24 nm, 0.26 nm and 0.23 nm (**Fig. 5.7d-5.7f**). Additionally, the excellent organic dyes removal abilities ranging from 319.9 Da to 696.7 Da also manifest its great potential in molecular separation (**Fig. 5.8**). The membranes charge were evaluated by surface zeta potential characterization because ions sieving properties were closely related membrane charge. All resultant membranes stem from typical IP reaction exhibit negative-charged characteristic due

to the deprotonation of carboxyl groups resulting from hydrolysis reaction of unreacted acyl chloride. After modification, the membranes shows almost charge-free surface property at pH 7 (**Fig. 5.9**). This is because the grafting of PAA compounds via consumption of carboxyl groups sites, transforming the negatively charged membrane into neutral charged surface. Hence, we assumed that the superior separation abilities were mainly dominated by the size exclusion mechanism.

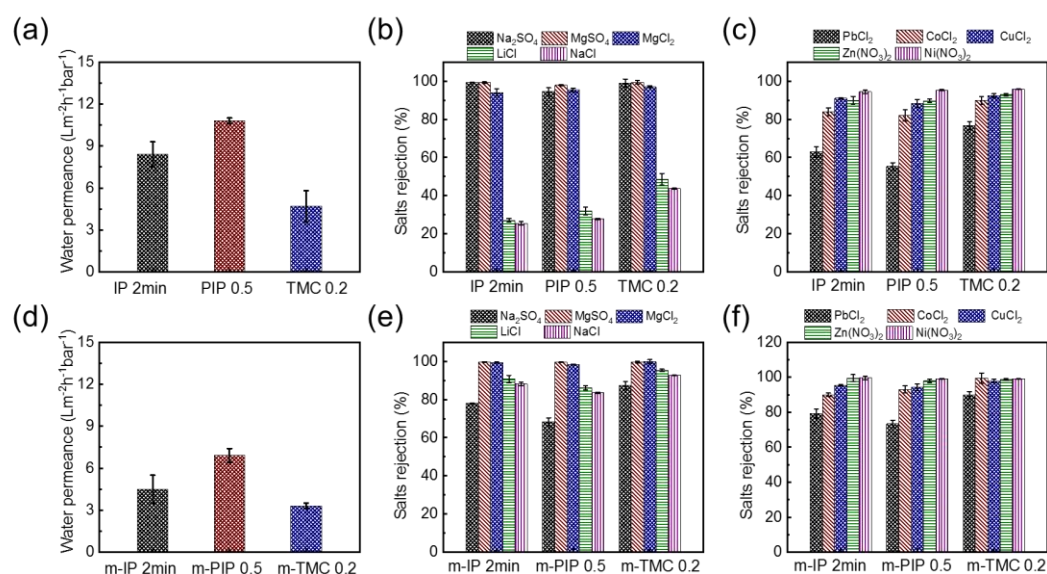


Fig. 5.6 Pure water permeance of fabricated TFC membranes (a) before and (d) after amine modification under varied IP reaction parameters; inorganic salts and heavy metal ions rejection behavior of as-formed TFC membranes (b, c) before and (e, f) after amine modification under varied IP reaction parameters.

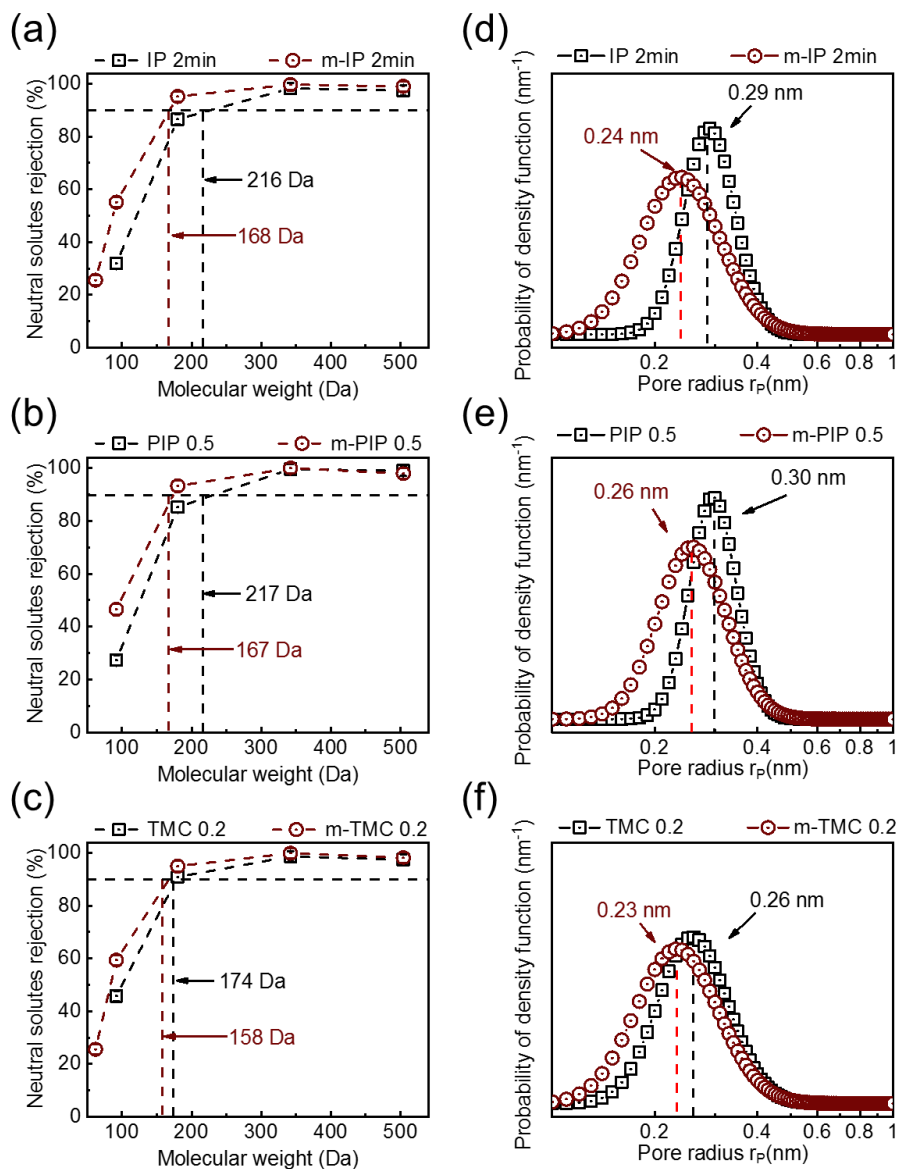


Fig. 5.7 Rejection ratios for uncharged model small molecular solutes, and pore size/pore size distribution fitted by the rejection data of as-performed (a, d) IP 2min/m-IP 2min, (b, e) PIP 0.5/m-PIP 0.5 and (c, f) TMC 0.2/m-TMC 0.2 TFC membranes.

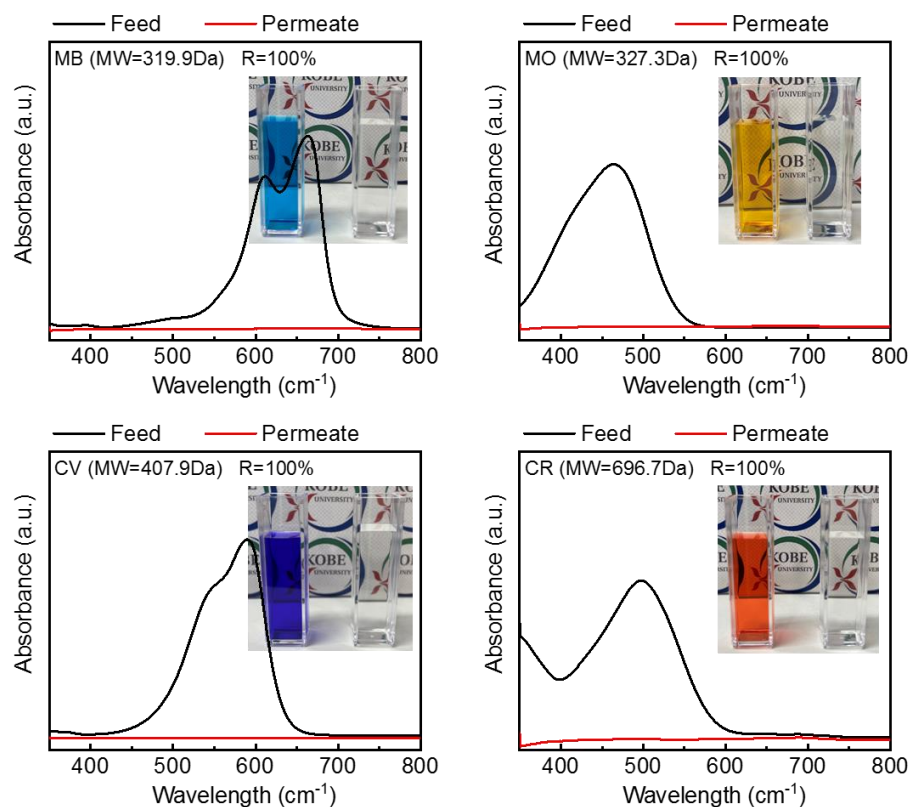


Fig. 5.8 Ultraviolet-visible absorption spectra of dyes in feed and filtrate of m-TMC 0.2 polyamide nanofiltration membrane. Inset: digital photo images of feed and permeate (dye concentration: 20 ppm).

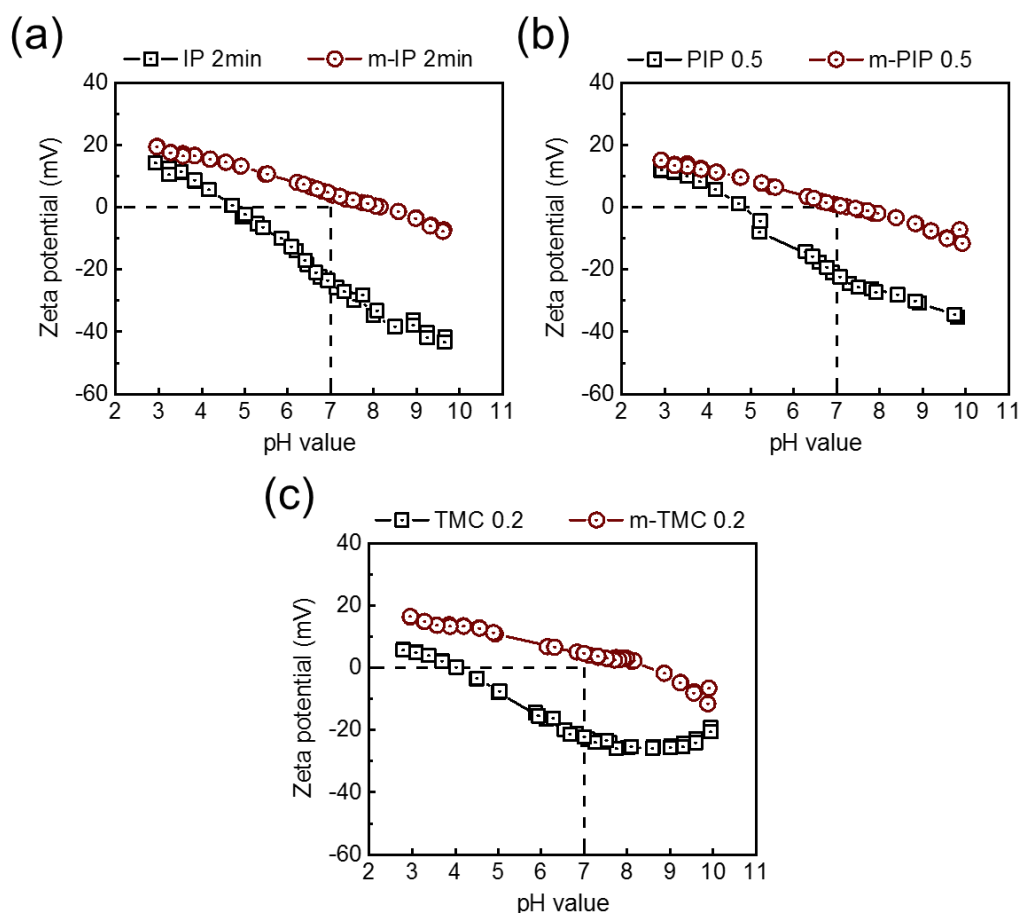


Fig. 5.9 Surface zeta potential of (a) IP 2min/m-IP 2min, (b) PIP 0.5/m-PIP 0.5 and (c) TMC 0.2/m-TMC 0.2.

The membrane separation efficiency was further scrutinized by EMPs elimination experiment, and three typical EMPs of CBZ (236 Da), DCF (318 Da) and TMP (290 Da) with diverse valences were utilized (**Fig. 5.10a**) [8]. The pristine PA membrane manifests moderate selectivity for TMP (73.3%) and CBZ (81.1%) whereof suggests high removal efficiency for DCF (92%). This is because the confined pore architectures accompanied by the negative charged membrane surface allow positive/ or neutral small compounds penetrate with ease while showing desirable refusing ability for small molecular with identical charged state. And the m-TMC 0.2 membrane exhibit excellent rejecting abilities for the three EMPs with admirable retention efficiency of 99.2%, 99.6% and 97.3% for TMP, CBZ and DCF, respectively. Guided by the pore features and membrane surface properties analysis, we deduce rationally that tighter free volume cavities and sharpened free volume cavities distributions

(size exclusion effect) of m-TMC 0.2 membrane plays pivotal role rather than the weakened Donnan repulsion for the enhanced EMPs solutes selectivity. The electroneutral dense NF membrane guarantee comparable selectivity against assorted electrically solutes in practical applications such as pollutant removal and resource recovery. In addition, the eutrophication of waterbody is a worldwide issue which could be reflected by the phosphorus concentration in water [8]. An algal bloom occurs when the content of phosphorus higher than 0.2 mg L^{-1} . From this point, strict control the concentration of phosphorus could prevent the eutrophication outbreak definitely. The dephosphorization capability of m-TMC 0.2 membrane was studied and listed in **Fig. 5.10b**. 10 ppm H_3PO_4 water was used to simulate phosphorous-containing effluent. The pH dependent separation efficiency was evaluated in view of the divergent species of phosphorus molecular/ions in water with varied pH. At pH= 7, H_2PO_4^- and HPO_4^{2-} are the predominant components (The $\text{pK}_{\text{a}1}$ of H_3PO_4 is 2.12) in H_3PO_4 solution. By adjusting the phosphorus solution with diluent sodium hydroxide (0.01 M) from 7 to 10, the HPO_4^{2-} appeared as the preeminent constituent at pH= 8 and pH= 10 (The $\text{pK}_{\text{a}2}$ and $\text{pK}_{\text{a}3}$ of H_3PO_4 is 7.2 and 12.36). The m-TMC 0.2 membrane shows satisfactory separation efficiency in selected pH range. And a slightly augmented selectivity from 73.8% (pH= 7) to 81.3% (pH= 8) and 93.6 (pH= 10) were obtained, which attributed to the more negative surface at higher pH value strengthened the electrostatic exclusion. Of note, the permeate side with phosphorus concentration far lower than the established discharge standard for safe implement (less than 2 ppm). In addition, Boron is a deleterious constituent in seawater which may motivate the bio-magnification and bio-accumulation effects, menacing the health of human beings. Another threat faced by the state-of-the-art NF membranes is the inadequate rejection of trace boron, which mainly presented as the small non-ionized H_3BO_3 molecular under pH= 7 and anionic $\text{B}(\text{OH})_4^-$ under weak alkaline circumstance ($\text{pK}_{\text{a}1}= 9.24$ and $\text{pK}_{\text{a}2}= 12.74$, $\text{pK}_{\text{a}3}= 13.4$). The small size (0.244-0.261 nm) character also facilitate its diffusion behavior through PA selective layer. The m-TMC 0.2 membrane shows low rejection of boron (1.8%) due to the charged-free H_3BO_3 compound at neutral pH. In contrast, a much higher rejection for boron was achieved in alkaline solution and even an extremely high rejection of 25.2% at pH 10 was attained (**Fig. 5.10c**). This indicates shifting the speciation towards more negative species favor boron rejection. The m-TMC 0.2 membrane shows distinctly upgraded rejection ability than that of

pristine PA. The enhanced boron efficiency could be illustrated as: (1) a stronger sieving capacity of m-TMC 0.2 membrane because of the decreased MWCO and free volume cavities distributions block boron transportation; (2) the declined surface polarity accompanied by the reduced surface energy weakened the affinity between boron and PA nanofilm, thus leading to the increment of water/boron selectivity; (3) the abundant amino-containing groups with electron-sufficient property interact with electron-deficient B atom definitely via H-bonding and electrostatic force, impeding the diffusion and mitigation of H_3BO_3 . Compared with the laboratory-made, pilot-scale and full-scale NF membranes, the m-TMC 0.2 membrane shows better competitiveness and great potential for trace boron removal while maintaining a comparable water permeance, holding potential for water-related industrial applications. For long-term pure water and salts solutions infiltration testing (1500 min), high transmembrane pressure (5- 20 bar), and highly concentrated salts solution (1000 - 4000 ppm), the m-TMC 0.2 performed exceptional structural stability without tearing or breaking in harsh and long-term filtration process, as demonstrated by the steady salts rejection (**Fig. 5.11**).

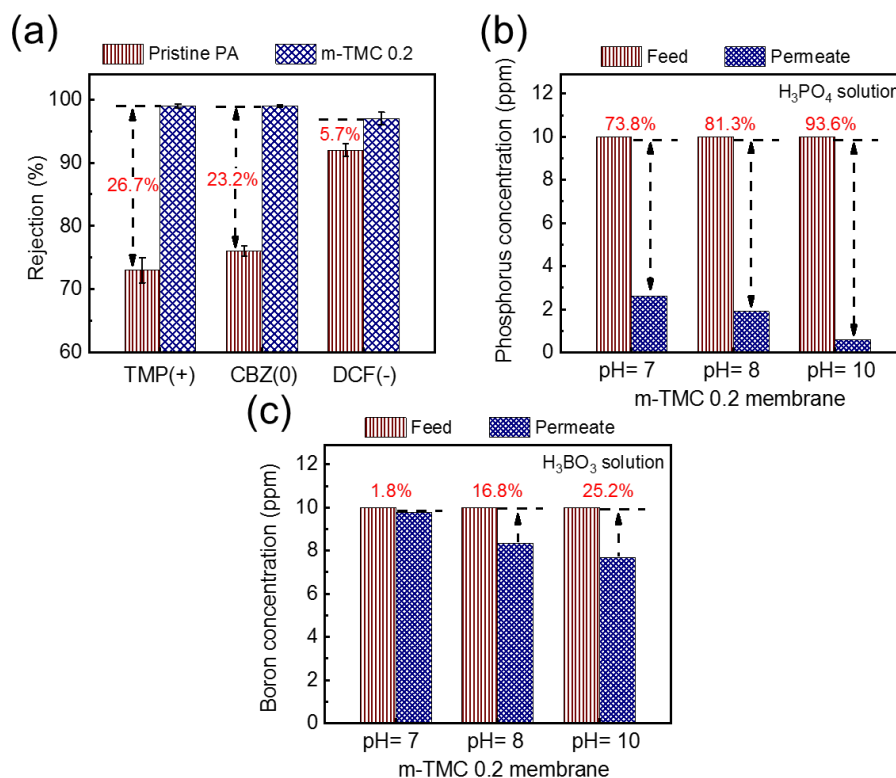


Fig. 5.10 (a) Rejection ratios against small EMPs of pristine PA and m-TMC 0.2 membranes; (b) rejection ratios of phosphorus by m-TMC 0.2 membranes under varied pH values (the feed

phosphorus is 10 ppm); (c) rejection rate of boron by m-TMC 0.2 membrane under varied pH values (the feed boron is 10 ppm);

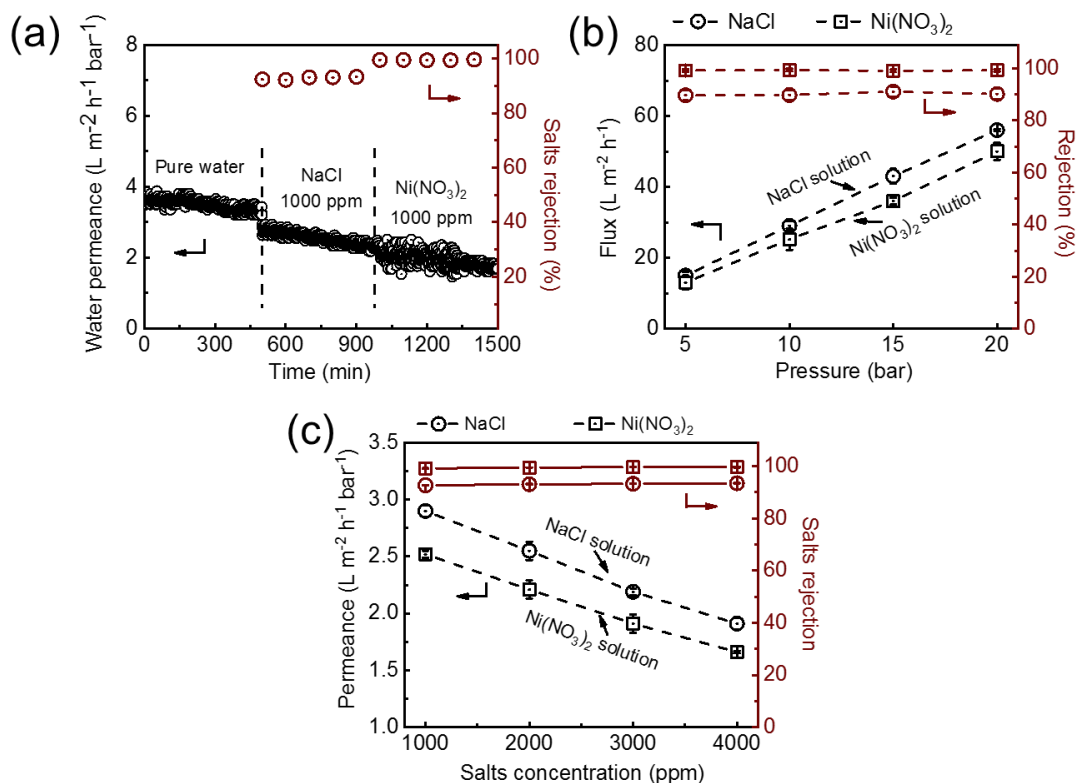


Fig. 5.11 (a) Long-term filtration of m-TMC 0.2 TFC membranes for pure water and 1000 ppm NaCl and 1000 ppm Ni(NO₃)₂ aqueous solution under 10 bar for 1500 min; (b) Perm-selectivity of m-TMC 0.2 TFC membranes toward 1000 ppm NaCl and 1000 ppm Ni(NO₃)₂ aqueous solution under varied transmembrane pressure (5–20 bar); (c) Influence of NaCl and Ni(NO₃)₂ aqueous solution concentration on the perm-selectivity of m-TMC 0.2 TFC membranes under the filtration condition of 10 bar, at 398K.

5.4 Conclusion

A better properties NF membrane was manufactured by covalently assembling the polyallylamine (PAA) onto the nascent polyamide nanofilm via amination reaction for water reclamation. The best-performing PA-PAA membrane was obtained by varying the monomer formula and optimizing the reaction conditions, demonstrating ultra-high precise separation for cation/ or anion ions (e.g. 99.2% for Ni²⁺, 99.9% for Mg²⁺ and 92.7% for Cl⁻) and upgraded

small molecules sieving abilities (e.g. 93.6% for phosphorus and 25.2% for boron). Comprehensive studies were done to elucidate the underlying mechanism for augmented separation properties. The PAA molecular bearing high charge density neutralized the negativity and narrowed the free volume cavities of PA membrane. The existence of neutral surface charge played pivotal role for ionic solutes efficacious obstruction by imposing charge-shielding effect (without electrostatic attraction and repulsion), and the denser pore structure underpinned small organic compounds exclusion by imposing reinforced steric hindrance. Furthermore, the weakened surface polarity and the enrichment of electro-donor surface groups also favored boron elimination. In summary, our proposed methodology on design of highly selectively nanofiltration membrane may shed light on future flourish of membrane and membrane process with superior specific ions/molecular separation efficiency.

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Chapter 6

Conclusions

With the rapid development of social industrialization and urbanization, the water shortage is one of the global risks, nowadays. In addition, the increased demand for freshwater due to the increase of population and the increased water pollution due to industrial activity accelerate the water shortage. Only way to fix this serious problem is purifying and recycling water resources. Membrane technology, especially nanofiltration (NF) process is one of potential way to purify and recycle water sources. NF membrane has a higher rejection rate for small organic molecules within the molecular weight (Mw) of 200-1000 Da and multivalent ions (such as Ca^{2+} , Mg^{2+} , SO_4^{2-}), but the rejection for monovalent salt ions (K^+ , Na^+ , Cl^- , etc.) are low. So, it has broad application prospects in the separation of ions/organic molecules. Generally, NF membrane is fabricated by forming a selective layer by interfacial polymerization (IP) on ultrafiltration support. The trade-off between water permeability and salt selectivity is challenging problem of NF membrane. The regulation of IP process by modifying support is considered to be one potential way to break the trade-off.

In this dissertation, in Chaps.2, 3 and 4, effective and simple methodologies to fabricate high water permeable thin film composite (TFC) polyamide nanofiltration membranes based on interlayer strategy are discussed. Some interlayers were constructed between ultrafiltration support and polyamide selective layers to regulate the interfacial polymerization process, assisting the high-permeable nanofilm with encouraging salts retention. In chapter 5, to enhance sieving effect, a new almost electro-neutral nanofiltration membrane was invented by consuming the excess carboxyl functional groups on the nascent polyamide surface after interfacial polymerization. All the results were described in Chapters 2-5, as follows:

6.1. Mechanism insights into the role of support mineralization layer toward ultrathin polyamide nanofilm for ultrafast molecular separation

In this chapter, high perm-selective PA nanofilms were successfully developed via silicification interlayer-regulated interfacial polymerization process. The silicification interlayer, fabricated in situ, enhanced the surface hydrophilicity of the PSf substrate. Furthermore, it conferred the high-density attachment of amine monomers and served as a quasi-molecular-scale regulator that decelerated their diffusion into the organic phase for polymerization with the acyl chloride of TMC. These synergistic effects sealed the membrane and inhibited its growth. Consequently, ultrathin PA nanofilms (approx. 13 nm) with enhanced crosslinking properties were formed. The best-performing PA₂/SiO₂/PSf membrane showed approximately three-fold water permeance ($14.5 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$) compared to that of the pristine PA membrane ($4.8 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$). The best-performing membrane exhibited a high rejection rate of 98.7% toward divalent salts (without compromising the separation capability), as well as a competitive mono/divalent ion selectivity of 60.9. The outstanding nanofiltration property of the PA₂/SiO₂/PSf membrane can be attributed to the multiple integrations: the increase in the internal polarity, decrease in the active layer thickness, and increase in the specific surface area comprising a loose pore structure with a high free volume distribution.

6.2. A zwitterionic copolymer-interlayered ultrathin nanofilm with ridge-shaped structure for ultrapermeable nanofiltration

In this chapter, I hereby developed an ultrathin PA nanofilm with a thickness of 12 nm via P[MPC-co-AEMA] interlayer-mediated interfacial polymerization (IP). The P[MPC-co-AEMA] copolymer acted as a “quasi-molecule-scale regulator” to precisely control the kinetics of IP reaction, in which P[MPC] was responsible for a long-range hydrophilic-hydrophilic attraction to aqueous monomers, while P[AEMA] afforded a tunable charge density by electrostatic interaction with the PSf substrate. The enhanced attraction spatially enriched the amine monomers and temporally decelerated their diffusivity into the organic phase to be polymerized with acyl chloride from TMC. Diffusion-driven instability triggered membrane sealing and inhibited its growth, thus leading to the formation of an ultrathin PA nanofilm with a ribbon-shaped surface structure and enhanced crosslinking. The resultant P[MPC-co-AEMA]

interlayer-enhanced PA membrane exhibited a superior water permeance of up to $20.4 \text{ L}\cdot\text{m}^{-2}\text{h}^{-1}\cdot\text{bar}^{-1}$, almost 3-fold higher than that of the pristine PA membrane ($5.6 \text{ L}\cdot\text{m}^{-2}\text{h}^{-1}\cdot\text{bar}^{-1}$), without sacrificing its ionic selectivity (96.8% against Na_2SO_4), which is superior to most of the reported state-of-the-art permselective nanofiltration membranes.

6.3 Highly permeable nanofilms with asymmetric multilayered structure engineered via amine-decorated interlayered interfacial polymerization

In this chapter, a high permeable/selective ultrathin nanofilm (8 nm) with an asymmetrical architecture for nanofiltration was engineered via ionic amine-decorated interlayer-mediated IP. The self-assembly of the amine-based network with greater polarity conferred stronger attraction on amine monomers, thus exerting hindrance and turbulence effects on their diffusion movement toward the organic phase when conducting IP. The synergistic effects induced the formation of an asymmetric nanofilm constituting of a multilayer structure in which the back surface is a porous layer containing spherically porous structures, and the upper surface is a dense selective layer having nodular wrinkles. The best performing PA_PAH/PSf membrane provided improved water permeance of up to $12.5 \text{ L}\cdot\text{m}^{-2}\text{h}^{-1}\cdot\text{bar}^{-1}$, which is almost 3-fold larger than that of pristine PA ($4.4 \text{ L}\cdot\text{m}^{-2}\text{h}^{-1}\cdot\text{bar}^{-1}$), while maintaining high Na_2SO_4 rejection of 98.9% with an excellent $\text{Cl}/\text{SO}_4^{2-}$ separation factor of 72.1. This study clarifies the asymmetric structural design of multilayer nanofilms to realize breakthroughs in the existing trade-off limit of the permeability-selectivity performance in molecular fractionation, organic solvent nanofiltration, seawater desalination, and/or other separation technologies in water treatment.

6.4 Denser electroneutral nanofiltration membrane for high multiple ions and small molecules removal

In this chapter, a better properties nanofiltration membrane was manufactured by covalently assembling the polyallylamine (PAA) onto the nascent polyamide nanofilm via amination reaction for water reclamation. The best-performing PA-PAA membrane was obtained by varying the monomer formula and optimizing the reaction conditions, demonstrating ultra-high precise separation for cation/ or anion ions (e.g. 99.2% for Ni^{2+} , 99.9% for Mg^{2+} and 92.7% for Cl^-) and upgraded small molecules sieving abilities (e.g. 93.6% for

phosphorus and 25.2% for boron). Comprehensive studies were done to elucidate the underlying mechanism for augmented separation properties. The PAA molecular bearing high charge density neutralized the negativity and narrowed the free volume cavities of PA membrane. The existence of neutral surface charge played pivotal role for ionic solutes efficacious obstruction by imposing charge-shielding effect (without electrostatic attraction and repulsion), and the denser pore structure underpinned small organic compounds exclusion by imposing reinforced steric hindrance. Furthermore, the weakened surface polarity and the enrichment of electro-donor surface groups also favored boron elimination. In summary, our proposed methodology on design of highly selectively nanofiltration membrane may shed light on future flourish of membrane and membrane process with superior specific ions/molecular separation efficiency.

Publication list

Chapter 2:

Song Q, Lin Y, Ueda T, et al. Mechanism insights into the role of the support mineralization layer toward ultrathin polyamide nanofilms for ultrafast molecular separation[J]. Journal of Materials Chemistry A, 2021, 9(46): 26159-26171.

Chapter 3:

Song Q, Lin Y, Ueda T, et al. A zwitterionic copolymer-interlayered ultrathin nanofilm with ridge-shaped structure for ultra-permeable nanofiltration[J]. Journal of Membrane Science, 2022, 657: 120679.

Chapter 4:

Song Q, Lin Y, Zhou S, et al. Highly permeable nanofilms with asymmetric multilayered structure engineered via amine-decorated interlayered interfacial polymerization[J]. Journal of Membrane Science, 2023: 121377.

Chapter 5:

Song Q, Denser electroneutral nanofiltration membrane for high multiple ions and small molecules removal. (To be submitted)

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