A Tweak in Puzzle: Tailoring Membrane Chemistry and Structure Towards Targeted Removal of Organic Micropollutants for Water Reuse

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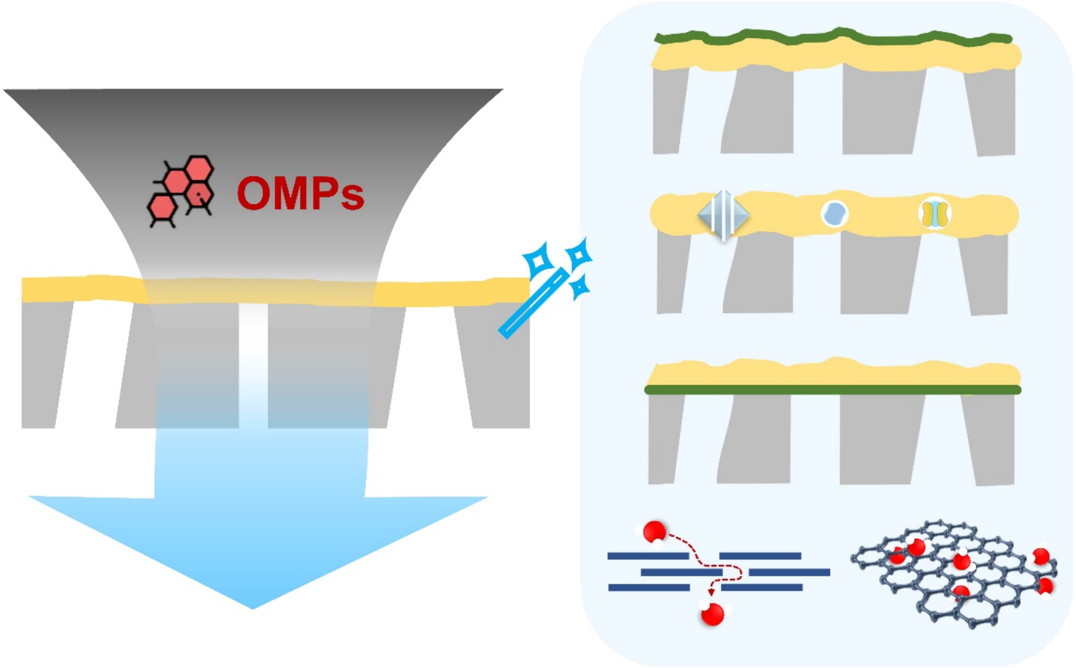

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■ ABSTRACT

Membrane-based water reuse through reverse osmosis (RO) and nanofiltration (NF) faces the critical challenge from organic micropollutants (OMPs). Conventional polyamide RO and NF membranes often lack adequate selectivity to achieve sufficient removal of toxic and harmful OMPs in water. Tailoring membrane chemistry and structure to allow highly selective removal of OMPs has risen as an important topic in membrane-based water reuse. However, a critical literature gap remains to be addressed: how to design membranes for more selective removal of OMPs. In this review, we critically analyzed the roles of membrane chemistry and structure on the removal of OMPs and highlighted opportunities and strategies towards more selective removal of OMPs in the context of water reuse. Specifically, we statistically analyzed rejection of OMPs by conventional polyamide membranes to illustrate their drawbacks on OMPs removal, followed by a discussion on the underlying fundamental mechanisms. Corresponding strategies to tailor membrane properties for improving membrane selectivity against OMPs, including surface modification, nano-architecture construction, and deployment of alternative membrane materials, were systematically assessed in terms of water permeance, OMPs rejection, and water-OMPs selectivity. In the end, we discussed the potential and challenges of various strategies for scale up in real applications.

Keywords: membrane, organic micropollutants, water reuse, selectivity, surface modification, membrane nano-architecture, alternative membrane materials.

■ SYNOPSIS

This review highlights the fundamental mechanisms and overarching design principles to tailor membrane selectivity for the effective removal of organic micropollutants in water reuse.

INTRODUCTION

Water scarcity in many parts of the world is the underlying driver for dedicated scientific efforts to develop new, sustainable, and reliable technologies for a secured water supply.[1, 2] Water reuse through advanced membrane technology is a promising strategy to augment alternative water resource, which has been successfully implemented in many countries including the United States, Singapore, Australia, and several European nations.[3-6] The state-of-the-art plants for potable water reuse generally employ thin film composite (TFC) polyamide reverse osmosis (RO) and nanofiltration (NF) membranes.[7-9] These polyamide-based membranes have been historically developed and optimized for desalination, showing superior rejection of inorganic salts and a range of other contaminants.[10]

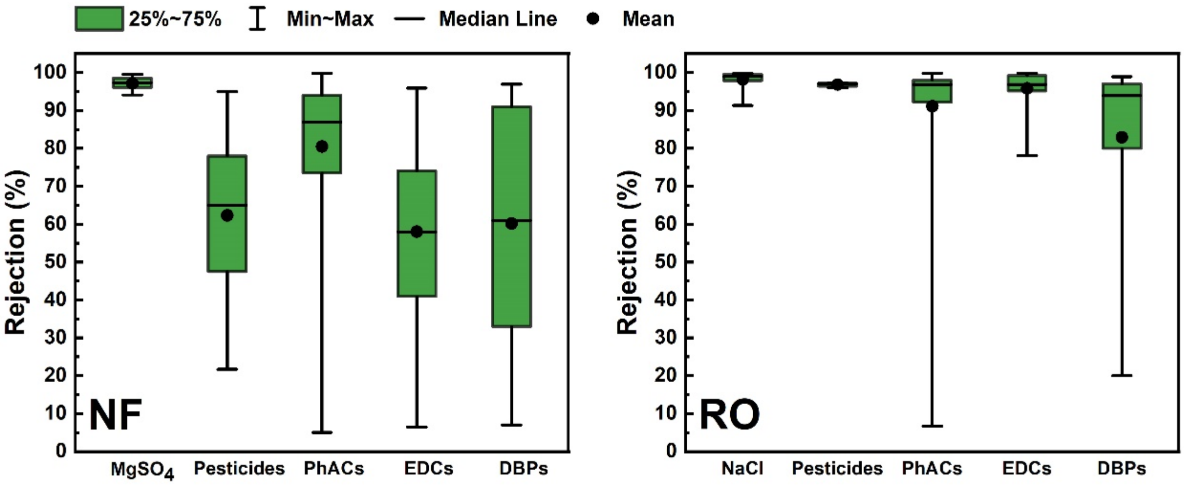

Figure 1. Boxplot of rejection values of mineral salts and different types of OMPs with MW < 500 Da by commercially available polyamide RO and NF membranes. The data were extracted from 50 references (*Supporting Information S1*). The quartile was calculated by the OriginLab software. PhACs, EDCs, and DBPs stand for pharmaceutically active compounds, endocrine disrupting compounds, and disinfection by-products, respectively.

A critical deficit of commercially available polyamide RO and NF membranes is their insufficient rejection of neutral and small molecular weight (MW) organic micropollutants (OMPs), especially those highly hydrophobic or highly polar (Figure 1). For example, hydrophobic EDCs often show low rejections by NF/RO membranes as a result of their strong hydrophobic interaction with the membrane,[11-15] even though they typically have larger MWs compared to NaCl. Similarly, poor membrane rejections as low as < 50% were also observed for *N*-nitrosodimethylamine (NDMA) due to its high polarity in addition to the small molecule size.[16-18] Intrinsic defects within the ultrathin rejections layer of the membrane[19] can further reduce the removal efficiency. Consequently, membrane rejection of some toxic OMPs is below 50%,[11-15, 17, 20] raising critical concerns over the safety of recycled water.[6, 21, 22] Improving membrane rejection of OMPs deserves to be a prioritized research pillar for membrane-based water reuse.

This paper reviews the recent progress of tailoring membrane chemistry and structure towards targeted removal of OMPs. Various strategies, including tailoring[23-27] and modification[15, 28-32] of polyamide membranes as well as developing non-polyamide membranes,[33, 34] are summarized, and the governing mechanisms are systematically highlighted. Our work paves a paradigm shift towards designing membranes for OMPs removal based on first principles and provides important perspectives on its future development.

■ BASIC PRINCIPLES

Typical TFC membranes consist of a top thin rejection layer (e.g., polyamide), a microporous supporting layer, and a non-woven substrate.[10] The thin polyamide layer governs the transport of water and solutes (e.g., OMPs) through the membrane. Following the classical solution-diffusion theory,[35] the rejection of a solute R is given by:[36]

$$R = \frac{\frac{A}{B}(\Delta P - \Delta\pi)}{\frac{A}{B}(\Delta P - \Delta\pi) + \exp\left(\frac{J_{\mathrm{w}}}{k}\right)} \tag{1}$$

where A is the water permeance, ΔP is the applied hydraulic pressure, $\Delta\pi$ is the osmotic pressure difference across the membrane, B is the solute permeability coefficient, J_w is the water flux, k is the mass transfer coefficient, and the term $\exp(J_w/k)$ accounts for the effect of concentration polarization (CP). Under relatively mild CP ($J_w << k$), Eq. (1) shows that the rejection of an OMP is governed by the competition of water permeation and solute transport through the membrane. A high water permeation at a given B value would effectively dilute the solute concentration in the permeate water and thus enhance its rejection. From membrane design point of view, this may be achieved by increasing the membrane water permeance (the A value), e.g., through the incorporation of porous nanofillers with selective water channels in the case of thin film nanocomposite (TFN) membranes.[8, 37-40] However, the applied water flux in many practical applications is constrained by CP and fouling,[41] so that the dilution strategy is only effective up to a certain “sustainable flux”.[42-44]

An effective way to enhance the rejection of an OMP is to reduce the solute permeability coefficient (B value) of the membrane. Solute transport through a polyamide NF/RO membrane is governed by solute partitioning into the membrane rejection layer. This is influenced by size exclusion, electrostatic repulsion, and a range of physiochemical interactions between the solute and the polymeric matrix of the rejection layer such as hydrophobic interaction and polar interaction (Figure 2A).[45] In general, tighter membrane pores[46-48] and enhanced solute-membrane electrostatic repulsion[49, 50] are beneficial in reducing OMPs permeation. On the other hand, stronger hydrophobic interaction[11, 12] or polar interaction[51] tends to reduce membrane rejection. Accordingly, the properties of a polyamide layer can be tuned by controlling its formation during interfacial polymerization (IP)[52] or deploying post-treatment. For example, increasing crosslinking degree of polyamide by extending IP reaction time can effectively enhance solute rejection owing to improved size exclusion.[53] However, this approach often results in a reduction in membrane water permeance, a phenomenon wellknown in the membrane field as the "upper bound" tradeoff relationship.[36] The rejection of OMPs is also hampered by the highly heterogeneous nature of polyamide rejection layers,[54-56] which creates localized "hot spots" for solute transport (e.g., through hydrophobic moieties[11, 15] and/or nanosized defects[19]). Techniques to synthesize more homogeneous and defect-free polyamide rejection layer could be beneficial for enhanced rejection of OMPs.

■ STRATEGIES FOR IMPROVED SELECTIVITY OF OMPs

As discussed above, the key to improve membrane rejection of OMPs of a membrane is to enhance its selectivity (i.e., the A/B value) by facilitating its water transport and/or suppressing the passage of target compounds. Generally, membrane water permeance A can be improved through tuning its nano-architecture (e.g., creating additional water transport pathways by nanofillers,[26, 40, 57] Figure 2B). On the other hand, solute permeability coefficient B can be tailored via controlling membrane-solute interactions (e.g., surface modification,[15, 30, 58] panel 3, Figure 2C). Towards a better improved selectivity, membrane chemistry and structure can be altered via introducing an interlayer[59] (panel 4, Figure 2C) or deploying alternative membrane materials[60-65] (panel 1 & 2, Figure 2C) to achieve simultaneously enhanced A and reduced B.

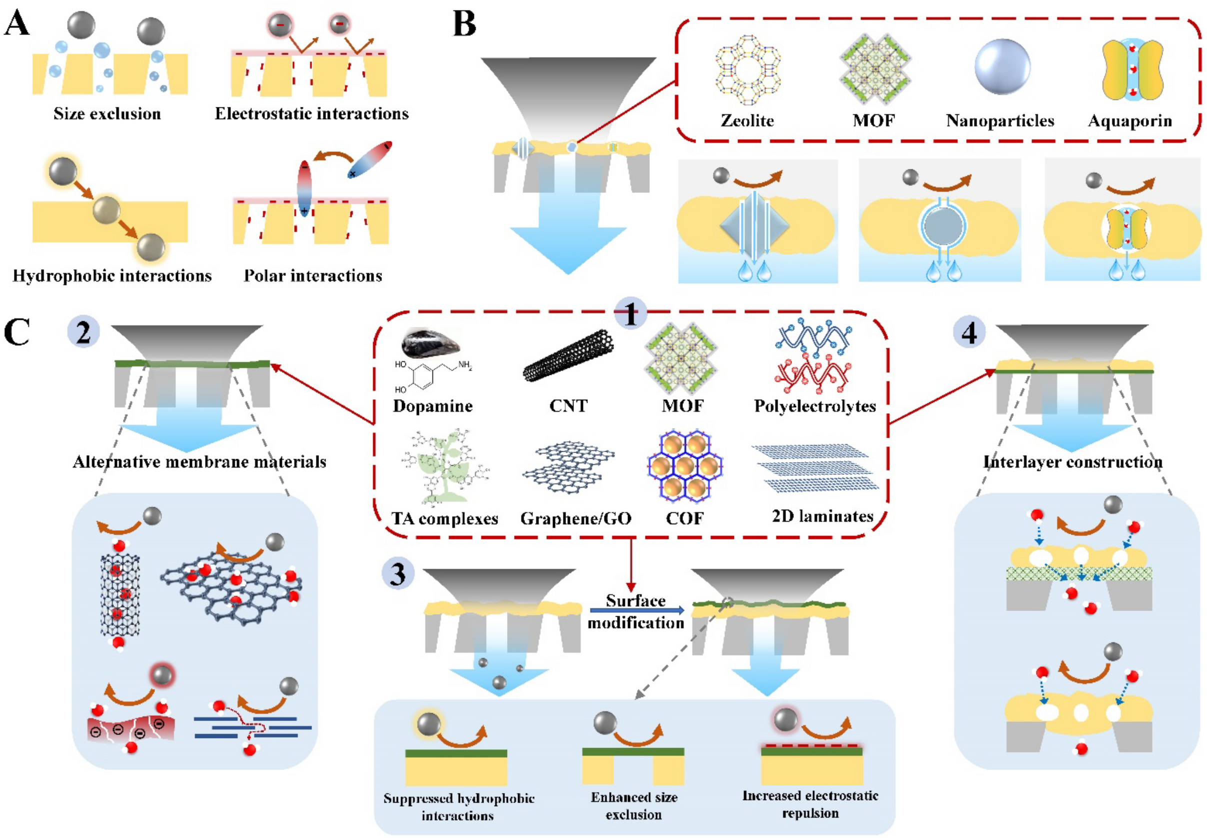

Figure 2. **(A)** Schematic illustration of membrane-solute interactions including size exclusion, electrostatic interactions, hydrophobic interactions, and polar interactions. **(B)** Incorporation of various nanofillers in TFN membranes to introduce additional water channels (e.g., intrinsic nanochannels within porous nanofillers,[37, 57] induced nanochannels around hydrophilic nanofillers,[25, 26] and selective water channels inside aquaporins[23, 24]) for accelerated water transport. **(C)** Materials and potential strategies for tailoring membrane chemistry and structure with improved selectivity against OMPs. (Panel 1) Materials used for membrane modification and construction.[62, 65] (Panel 2) Ideal water transport and solutes retention by alternative membrane materials, e.g., carbon nanotube (CNT),[61] nanosheet with well-defined pores,[64] polyelectrolyte film,[63] and stacked 2D laminates.[33] (Panel 3) Mechanistic illustration of enhanced membrane rejection of OMPs through controlling membrane-OMPs interactions (e.g., suppressed hydrophobic interactions,[15, 30] enhanced size exclusion,[30, 58] and increased electrostatic repulsion[28]) using surface coating. (Panel 4) Water pathways and OMPs rejection by interlayered thin film nanocomposite (TFNi) membranes in the cases of using gutter layer[66] and sacrificial nanofillers[67].

Surface modification

Commonly adopted strategies for surface modification include surface coating and grafting.[68] In principal, a coating/grafting layer could introduce additional barrier to resist the transport of both water and solutes according to the resistance-in-series model (*Supporting Information S2*).[69] Specifically, the overall resistance of a modified membrane for water ($1/A_{\text{overall}}$) and solutes ($1/B_{\text{overall}}$) can be simplified as the sum of resistance from the base membrane and that of the coating/grafting layer as:

$$\frac{1}{A_{\text{overall}}} = \frac{1}{A_{\text{base}}} + \frac{1}{A_{\text{c}}} \tag{2}$$

$$\frac{1}{B_{\text{overall}}} = \frac{1}{B_{\text{base}}} + \frac{1}{B_{\text{c}}} \tag{3}$$

where the subscripts overall, base, and c represent the modified membrane, base membrane, and coating/grafting layer, respectively.

Figure 3A presents the permeance enhancement factor ($A_{\text{overall}}/A_{\text{base}}$ or $B_{\text{overall}}/B_{\text{base}}$) on the basis of Eqs. (2) and (3). According to this figure, an ideal coating/grafting layer should have a high water permeance ($A_{\text{c}} >> A_{\text{base}}$) to minimize its adverse impact on overall water permeance. At the same time, a low solute permeance of the layer (e.g., $B_{\text{c}} << B_{\text{base}}$) is essential to reduce solute permeation and thus enhance its rejection (Eq. (1)). To achieve lower B_{c} values, the coating/grafting components need be highly resistant to the target compounds by tailoring solute-membrane interactions. For example, coating the NF membrane with hydrophilic polydopamine (PDA) has shown improved rejection of hydrophobic EDCs despite little change in effective membrane pore size, but long-duration PDA coating decreased water permeance (e.g., nearly 50% reduction for 4 hours coating).[15] Other hydrophilic surface coating/grafting materials such as polyvinyl alcohol,[70] polyethylene glycol,[71] and zwitterionic polymer[72] could also be potentially exploited to enhance membrane rejection of hydrophobic OMPs, a direction that requires further systematic investigations. Surface modification can also be used to tailor membrane effective pore size and surface charge properties (*Supporting Information S3*).

However, reducing solute permeance alone is not sufficient to ensure an enhanced rejection of OMP. According to Eq. (1), the rejection is governed by the water to solute selectivity ($S = A/B$), which is dependent on both water permeance and solute permeation. High solute rejection calls for membranes with improved overall selectivity ($A_{\mathrm{overall}}/B_{\mathrm{overall}}$) against OMPs.[73] As shown in Figure 3B, membrane selectivity can be enhanced (i.e., $S_{\mathrm{overall}}/S_{\mathrm{base}} > 1$) if and only if the selectivity of coating/grafting layer (S_c) is greater than that of base membrane (S_{base}). Indeed, for a coating layer whose S_c is identical to that of the base membrane, both the water permeance and the solute permeance of the resulting membrane will be reduced by the same degree, leading to an unchanged overall selectivity (also see Eq. S8 and related derivations in *Supporting information S2*). In addition, a more selective coating/grafting layer is generally beneficial for the improvement of the overall selectivity. For example, compared to a pure PDA coating on a base NF90 membrane without post-treatment, the more selective silver-nitrate-treated PDA coating could achieve much more effective enhancement in water-EDC selectivity (more than one order of magnitude enhancement), resulting in better rejection of EDCs.[30]

Figure 3B also shows a strong dependence of the selectivity enhancement ($S_{\mathrm{overall}}/S_{\mathrm{base}}$) on the water permeance of the coating/grafting layer relative to that of the base membrane (A_c/A_{base}). A highly permeable ($A_c >> A_{\mathrm{base}}$) and highly selective ($S_c >> S_{\mathrm{base}}$) coating layer has relatively limited contribution to improve membrane selectivity (e.g., blue line, Figure 3B) despite that it can minimize the overall water permeance loss for the coated membrane. In comparison, a less permeable but highly selective coating layer can significantly enhance the overall selectivity of the coated membrane (e.g., red line, Figure 3B). These results reveal an inherent trade-off relationship between water permeance and selectivity for the surface modified membranes. The results presented in Figure 3A&B suggest coatings with moderate water permeance (A_c/A_{base} of 3-10) and high selectivity (S_c/S_{base} ~ or > 10) are preferred for enhancing solute rejection while avoiding severe reduction in water permeance.

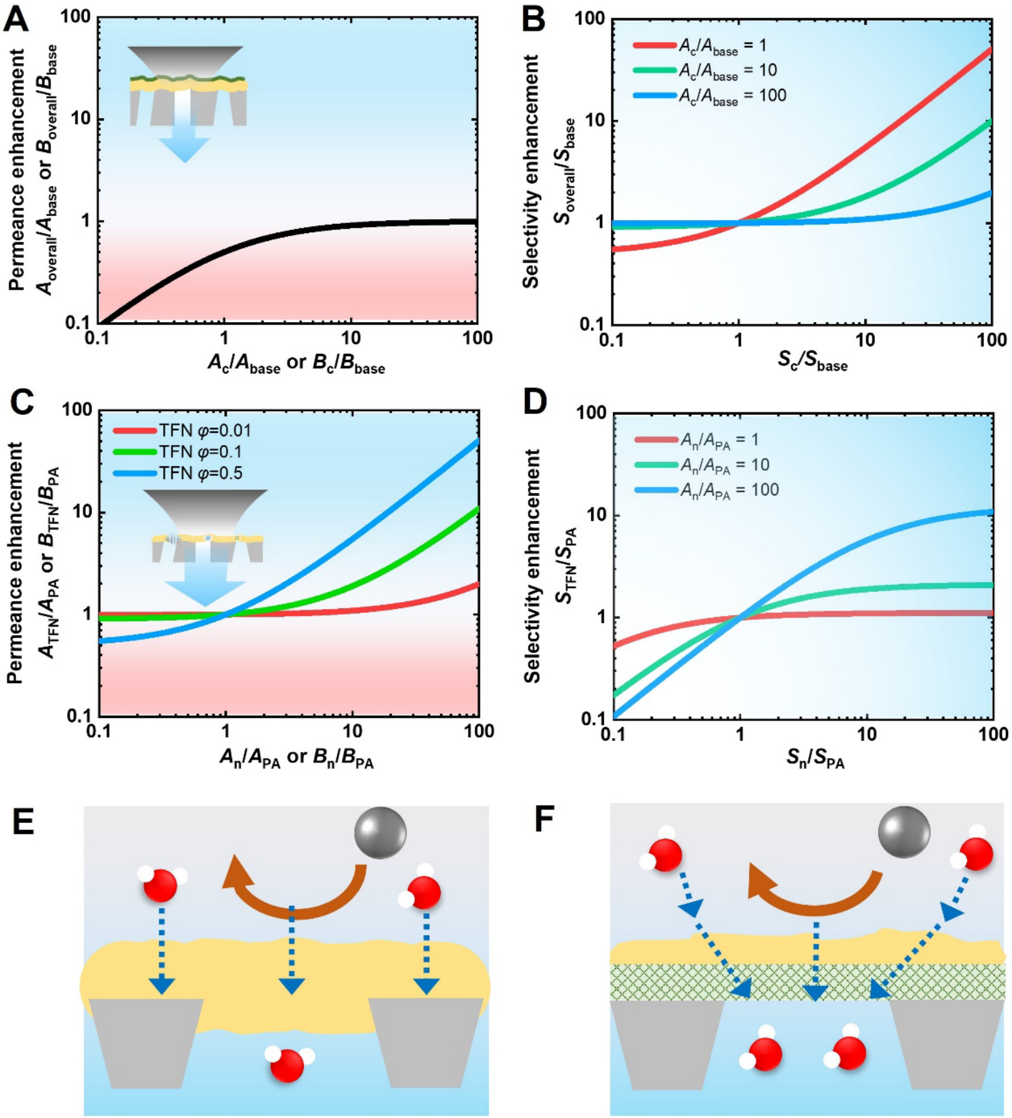

Figure 3. **(A)** The dependence of permeability enhancement factor ($A_{overall}/A_{base}$ or $B_{overall}/B_{base}$) on the ratio of A_c/A_{base} or B_c/B_{base} for surface modified membranes (based on Eq. S8). **(B)** The dependence of selectivity enhancement factor ($S_{overall}/S_{base}$) on the ratio of coating layer selectivity over the base membrane selectivity (S_c/S_{base}) for surface modified membranes. Three cases were analyzed, namely, the ratio of coating/grafting layer water permeance (A_c) over base membrane water permeance (A_{base}) equals to 1, 10, and 100, respectively. **(C)** The dependence of the permeability enhancement factor (A_{TFN}/A_{PA} or B_{TFN}/B_{PA}) on the ratio of A_n/A_{PA} or B_n/B_{PA} for TFN membranes based on Eqs. S9 and S10. The red, green, and blue lines represent the TFN membranes with the coverage ratio φ of 0.01, 0.1, and 0.5 for nanofiller-containing regions, respectively. Detailed derivations of Eqs. S8, S9, and S10 can be found in *Supporting information S2*. **(D)** The dependence of selectivity enhancement factor (S_{TFN}/S_{PA}) on the ratio of selectivity of nanofillers over the polyamide membrane selectivity (S_n/S_{PA}) for TFN membranes with a coverage φ of 0.1 for nanofiller-containing regions. It was analyzed in three cases, namely, the ratio of intrinsic water permeance for nanofillers (A_n) over polyamide membrane water permeance (A_{PA}) equals to 1, 10, and 100, respectively. Results in parts A-D were simulated based on Eq. (2)-(5). **(E)** Schematic illustration of water and solutes transport through a TFC membrane and (**F**) a TFNi membrane. Interlayer could enhance the formation of polyamide layer and thus improve membrane separation performance.[66] In addition, the presence of interlayer could also facilitate selective water transport through the membrane by creating additional nanosized water channel[25, 26] and providing gutter effect[66], thereby improving membrane water-solute selectivity.

Membrane nano-architecture

Polyamide structure

Polyamide membrane nano-architectural features such as roughness,[74, 75] pore size and distribution,[76] and interior voids/channels[25, 77] play important roles in its water permeance and solutes rejection. Controlling IP reaction conditions could tailor membrane nano-architecture to enhance the separation performance. For example, the addition of $NaHCO_3$ into aqueous amine solution (as a precursor for CO_2 nanobubbles)[75] or the use of more volatile organic solvents[78] in the IP process could enhance the formation of nanovoids in polyamide layer as a result of promoted interfacial degassing/vaporization,[77, 78] leading to the improved water permeance. Introducing additional reactive monomer (e.g., zwitterionic compound,[79] polyethyleneimine,[80, 81] bipiperidine,[82] or melamine[83]) into aqueous amine solution could also affect the IP reaction and thus shape membrane nanostructure to achieve high rejections of OMPs. For instance, adding polyethyleneimine into aqueous piperazine solution during IP could tune the pore size and distribution of formed NF membrane thereby enabling highly selective removal of antibiotics from nutrient water.[81]

TFN membranes

A more popular approach to tailor membrane nano-architecture is to incorporate nanofillers into polyamide matrix to form the TFN membrane (Figure 2B).[37, 84] These nanofillers often have intrinsic nanochannels, which could introduce additional pathways for selective water transport to enhance membrane water permeance. Meanwhile, the specific properties (e.g., well-defined pore size, hydrophilicity, and charge) of the nanofillers could be tailored to reduce the passage of OMPs through the TFN membrane (thus enhance rejections).[26, 85] Therefore, the overall water permeance (A_{TFN}) and solute permeability coefficient (B_{TFN}) of a TFN membrane are greatly affected by the intrinsic properties of the nanofillers and their loadings in the polyamide layer. The water and solute permeation for a TFN membrane can be analyzed using a resistance-in-parallel model:

$$A_{\mathrm{TFN}} = \varphi A_{\mathrm{n}} + (1 - \varphi) A_{\mathrm{PA}} \tag{4}$$

$$B_{\mathrm{TFN}} = \varphi B_{\mathrm{n}} + (1 - \varphi) B_{\mathrm{PA}} \tag{5}$$

where φ is the coverage ratio of the nanofiller-containing regions, and the subscripts n and PA represent the nanofiller-containing regions and polyamide layer, respectively.

Figure 3C shows the permeance enhancement factor for a TFN membrane over the TFC polyamide counterpart ($A_{\mathrm{TFN}}/A_{\mathrm{PA}}$ or $B_{\mathrm{TFN}}/B_{\mathrm{PA}}$). As expected, highly water-permeable nanofillers ($A_{\mathrm{n}} >> A_{\mathrm{PA}}$) with high coverage ratio φ are desirable to improve the overall membrane water permeance A_{TFN}. In practice, however, an over-dosage of nanofillers often results in more defects (typically caused by severe aggregation of nanofillers[59]), which affects membrane integrity and compromises rejection of solutes.[86] As shown in Figure 3D, to enhance the selectivity of a TFN membrane, it is essential that nanofillers shall have higher selectivity than the polyamide matrix ($S_{\mathrm{n}} > S_{\mathrm{PA}}$). This is possible through the careful design of the selective channels of nanofiller to promote water transport ($A_{\mathrm{n}} > A_{\mathrm{PA}}$) and/or reduce solute passage ($B_{\mathrm{n}} < B_{\mathrm{PA}}$). For example, a hydrophilic MOF of MIL-101(Cr) with precise openings of 1.2/1.6 nm had low permeation of hydrophobic EDCs together with fast permeation of water, such that the corresponding TFN membrane demonstrated significantly enhanced EDC rejection.[57] Negatively charged MOFs (e.g., MIL-53 and NH_2-UiO-66) could increase the negative charge of TFN membranes thereby enhancing their rejection for anionic pharmaceuticals as a result of enhanced electrostatic repulsion.[87] A proper design of the charge for nanofillers (e.g., dually charged MOF[85]) could further allow the TFN membrane to simultaneously better reject both cationic and anionic OMPs. In some cases, the addition of nanofillers could impact the membrane formation process, thus affecting the crosslinking and effective pore size of polyamide layer.[87, 88] Unlike the case of surface coating, Figure 3C&D shows that more permeable nanofillers (e.g., $A_n >> A_{PA}$) are generally preferred for simultaneously enhancing the selectivity and permeance of the resultant TFN membranes. More permeable nanofillers would allow a greater portion of water to permeate through their selective water channels instead of the bare polyamide regions, resulting in increased production and improved quality of permeate water.

In addition to porous nanofillers, non-porous nanofillers (e.g., solid nanoparticles) have also been used to fabricate TFN membranes.[84, 86] These non-porous nanofillers are often used as sacrificial templates for nanovoids generation[89] or as precursors for interfacial nanochannel formation[25]. For example, the incorporation of silver nanoparticles could induce the formation of interfacial nanochannels (~2.5 nm in channel gap) by suppressing the formation of polyamide around the nanoparticles.[25] These nanochannels tripled the membrane water permeance while significantly enhancing the rejection of EDCs and antibiotics at the same time.

Integrating biomimetic water channels such as aquaporin[90] and artificial water channels[91] into membrane matrix has also been explored for selective removal of OMPs. For the case of aquaporins, their channels allow ultrafast transport of water molecules (at a rate of approximately 1 billion water molecules per second through each single channel) while virtually rejecting all solutes,[90] resulting in an ultrahigh water-solute selectivity. An early attempt by Madson and co-workers[23] demonstrated >97% rejection for three pesticides by an aquaporin-incorporated forward osmosis membrane. The removal of a wider range of OMPs (30 compounds in total, including EDCs, PhACs, and pesticides) using another aquaporin-based biomimetic membrane were reported in wastewater treatment[24] and in an osmotic membrane bioreactor,[92] and the membrane showed high rejection (>90%) for most OMPs accompanying with a moderate water permeance of 2.1 $Lm^{-2}h^{-1}bar^{-1}$. Compared to aquaporins, artificial water channels offer potential advantages such as lower cost, easier incorporation, higher loading, and better material stability.[93] Future studies are needed to further investigate their feasibility in simultaneously enhancing membrane water permeance and improving OMP removal. Despite the apparent success of aquaporin-incorporated TFN membranes for enhancing the removal of OMPs, its polyamide matrix generally dominates the overall membrane resistance and allow the "leakage" of OMPs at the same time, which limits the overall water permeance and selectivity of the membrane. This observation calls for the further optimization of membrane structure to fully unleash the unique features of biomimetic water channels for highly selective separation of OMPs.

TFNi membranes

In recent years, an emerging type of TFN membrane prepared on an interlayered substrate (TFNi) has drawn increasing attention.[59, 94] The presence of an interlayer during IP reaction has multiple impacts on the formation of polyamide, including: (1) improved interfacial conditions, (2) increased storage of amine monomer, (3) controlled release of amine monomer during IP reaction, and (4) eliminated polyamide intrusion in the substrate pores.[66, 95, 96] As a result, the resultant TFNi membrane often showed a thinner rejection layer featuring with a higher water permeance, better selectivity, and more regulated solutes passage (Figure 3F) than that of a conventional TFC membrane (Figure 3E). In addition, the interlayer could play as a gutter to further facilitate water transport through the membrane (Figure 3F). For example, a polydopamine interlayered TFNi membrane demonstrated simultaneously enhanced water permeance and rejection of OMPs in comparison with the control TFC membrane, leading to its significantly improved water-OMP selectivity.[66] These results indicate that TFNi membranes are promising for selective removal of OMPs from contaminated water. Nevertheless, how the interlayer regulates the transmembrane behavior of OMPs still needs to be quantitatively modelled in future studies.

Alternative membrane chemistry

In recent decades, the rapid development of alternative desalination materials offers unprecedented opportunities to synthesize novel membranes for highly efficient water treatment (panel 2, Figure 2C).[97] Carbon-based materials (e.g., CNT,[98] graphene, and graphene oxide (GO)[99, 100]), MOF,[101] and covalent organic framework (COF)[102, 103] have been considered as promising materials to fabricate next-generation high-performance membranes for replacing existing polyamide-based membranes. These novel materials often possess tailored pore structure and chemistry, offering great potential to overcome the permeability-selectivity trade-off through achieving significantly higher water permeance and better regulated rejection of solutes.[36] Although some materials have relatively large intrinsic pore size (e.g., 0.8-4.7 nm for COF), improving the monomer design during the fabrication process could effectively adjust the pore size (e.g., < 0.6 nm) to achieve precise separation of solutes.[103] The pore chemistry could also be tuned through a modification step to tailor its interaction with OMPs thereby enabling highly selective removal of OMP. Indeed, well designed pores with uniformly distributed size could greatly benefit membrane separation performance. For example, Yuan et al. reported a single layer graphene membrane with well-defined sub-nanometer pores (~ 0.63 nm), which exhibited a high water permeance up to ~37 $Lm^{-2}h^{-1}bar^{-1}$ and a NaCl rejection of ~ 98% for high-efficiency separation.[104] These results demonstrated its remarkable water-solute selectivity compared to existing polyamide membranes.[36] Nevertheless, the fabrication of such intact single layer graphene membrane in large-scale remains as a critical challenge and thus severely limits its applications in practice. Compared with single layer membrane, stacked graphene/GO membranes are much easier to prepare through the vacuum-assisted deposition or layer-by-layer assembly of these 2D materials.[33, 99, 105] Nevertheless, the stacked membrane often had small imperfections within its lamellar structure, which could result in the formation of defects that significantly impair membrane integrity and selectivity.[106]

In addition, thin films assembled through metal-ligand complex,[34, 107] self-polymerization,[108] chemical crosslinking,[109, 110], and layer-by-layer deposition[111] were also explored to remove OMPs from water. Compared with traditional polyamide membrane, these membranes often had unique physicochemical properties to regulate the partitioning of OMPs into membrane thereby improving the rejection of OMPs. For example, a tannic acid-iron (TA-Fe) complexed thin film (~ 30 nm) showed a two orders of magnitude reduction for the sorption of EDCs compared to a commercial polyamide membrane, leading to its remarkably high EDCs rejection of up to 99.7%.[34] Such novel thin films often have better flexibility to allow further membrane modification and optimization for targeted removal of OMPs.[111] Apart from the above novel membrane materials, other emerging materials such as novel 2D nanosheets (e.g., MoS_2, MXene, and graphite carbon nitride),[112] porous organic cage,[113] etc. can also be considered as potential candidates. Some materials have been successfully used in membranes for gas separation and ion-sieving liquid separation,[114] which drives the research efforts to further explore their capability for the selective removal of OMPs in water treatment and reuse.

■ PERSPECTIVES AND OUTLOOK

Tailoring membrane chemistry and structure for highly selective removal of OMPs is essential for further progress in membrane-based water reuse over the coming decades. To achieve this target, we shall shift the current membrane design focus from historically emphasized high salt rejection to reduced permeation of OMPs through RO and NF membranes. Figure 4A summarizes the relative enhancement in both water-OMP selectivity and water permeance by surface modified TFC membranes, TFN membranes, and TFNi membranes. Similar to conventional TFC membranes, these three types of membranes can be relatively easy to scale up using existing polyamide RO/NF production lines (with possibly minor modifications). Indeed, TFN membranes and surface coated TFC membranes have already been commercialized.[84, 115] Compared with TFN and TFNi membranes, surface modified TFC membranes could potentially offer better enhancement in water-OMP selectivity (up to an order of magnitude). An extra advantage of this approach is that a well-designed surface modification could also impart antifouling properties, which happens to be the main reason for existing commercially coated TFC membranes (e.g., BW30 from Dupont FilmTec^{TM} and LFC3 from Hydranautics^{TM}/Nitto Denko[115]). Nevertheless, as predicted by the simple model in this study (Figure 3A and Eq. S5 in *Supporting information S2*), surface modified TFC membranes tend to suffer from reduced water permeance (up to 50%, see Figure 4A), which could translate into significantly increased specific energy consumption. Future studies shall choose more OMP-selective coating materials and optimize coating conditions to further improve OMP selectivity without major loss in water permeance.

TFNi membranes provide another promising strategy for enhancing OMP selectivity (Figure 4A). Due to the beneficial gutter layer effect, this approach enables simultaneously enhanced water permeance and selectivity against inorganic salts, OMPs, and other contaminants (e.g., boron and arsenic).[59] In addition, a recent study has also revealed the possibility of reduced membrane fouling tendency by including an interlayer to achieve more uniform flux distribution over the membrane surface.[116] Nevertheless, the number of studies on the design of TFNi membranes for OMP removal are still limited, which calls for more systematic investigations. For example, comparing a continuous interlayer (e.g., a PDA interlayer) with an interlayer staggered by discrete nanomaterials (e.g., a CNT interlayer), which form is preferred? How to ensure the long-term stability of TFNi membranes through proper interlayer design? These critical issues need to be experimentally investigated. In addition, analytical models need to be developed to further understand the transport phenomena in TFNi membranes. Although TFN membranes could also potentially improve OMP selectivity in addition to water permeance, these beneficial effects are not as promising as their TFNi counterparts (Figure 4A). This is partly due to the relatively low dosage of nanofillers (Figure 3C and D). In addition, severe aggregation of nanofillers in TFN membranes could even result in reduced membrane selectivity/integrity in some cases.[59] Some studies have also reported the use of aquaporin-based TFN membranes for OMP removal.[23, 24] Nevertheless, these bench-scale studies (often conducted in forward osmosis experiments) are not fully supported by a recent pilot scale RO test.[117] The cost-benefit and long-term performance of these membranes also need to be systematically investigated to verify their suitability for water reuse applications.

In addition of the state-of-the-art polyamide membranes, a wide range of alternative membrane materials are also available, such as polyphenols, polyelectrolytes, COF, MOF, graphene, and GO (Figure 4B). Among them, polyphenols have demonstrated excellent selectivity of OMPs in a recent study.[34] The scale up of polyphenol-based membranes also deem to be easier compared to other emerging materials (e.g., single layer porous graphene/GO membranes). Nevertheless, there has not been any report on the full-scale production of such membranes, and their long-term stability for water reuse application has not been verified. Indeed, scale up and stability issues are the two most critical concerns facing the emerging membrane materials. For example, despite that single layer porous graphene/GO membranes show good potential in bench-scale tests, these membranes generally involve stringent fabrication conditions, high cost, and difficult for producing large membrane areas, making them unlikely suitable for water reuse applications at current stage. Similar constraints are also applicable to COF and MOF membranes, though to a lesser degree. In view of the limited stability (for the case of stacked 2D laminates of GO) or the lack of report on long-term stability (for single layer porous graphene/GO membranes or COF/MOF membranes), it will take a long way to translate these novel materials from lab research into practical applications. Nevertheless, the potential reward of precise selectivity along with ultrahigh water permeability warrantees the continued search for the next-generation RO/NF membrane materials.

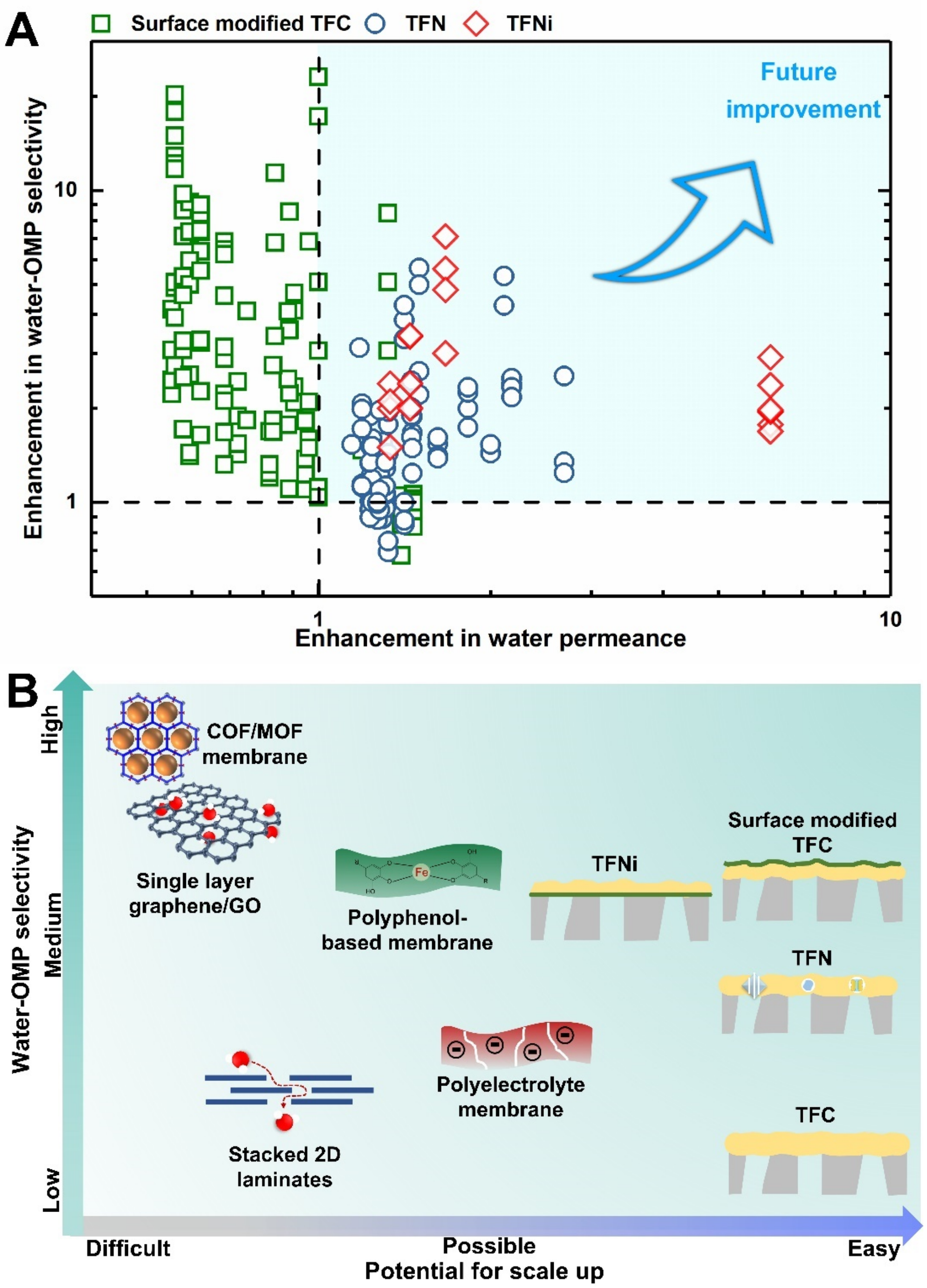

Figure 4. **(A)** The enhancement in water permeance and water-OMP selectivity for surface modified TFC, TFN, and TFNi membranes over that of conventional TFC membranes (represented by the dash lines). The data were extracted from 17 references.[15, 25, 26, 28-32, 57, 66, 85, 87, 88, 118-121] **(B)** Outlook of various membranes for selective removal of OMPs. The horizontal axis represents the difficulties of full scale manufacturing for the different membranes. The vertical axis represents the water-OMP selectivity for the different membranes.

■ SUPPORTING INFORMATION

The Supporting Information is available free of charge at https://pubs.acs.org/.

S1. Rejection of salts and OMPs by commercial polyamide RO and NF membranes; S2. Membrane transport models; S3. Surface modification for tailoring membrane effective pore size and surface charge.

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NOTES

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