# Engineering antifouling reverse osmosis membranes: A review

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## Abstract

Over the past decades, water scarcity and security have significantly stimulated the advances of reverse osmosis (RO) technology, which dominates the global desalination market. However, deterioration of membrane separation performance caused by inevitable fouling, including organic fouling, inorganic fouling, colloidal fouling and biofouling, calls for improved RO membranes with more durable antifouling properties. In this review, we analyze the correlations between membrane properties (e.g. surface chemistry, morphology, hydrophilicity, and charge) to antifouling performance. We evaluate the three key strategies for engineering fouling resistant thin film composite RO membranes, namely: (1) substrate modification before interfacial polymerization, (2) incorporating (hydrophilic/biocidal/antifouling) additives into the selective layer during interfacial polymerization, and (3) post (surface) modification after interfacial polymerization. Finally, we offer some insights and future outlooks on the strategies for engineering next generation of high performance RO membranes with durable fouling resistance. This review provides a comprehensive, state-of-the-art assessment of the previous efforts and strategies as well as future research directions for engineering antifouling RO membranes.

***Keywords*:** RO Membrane; Desalination; Membrane Fouling; Nanomaterials; TFC membrane.

## Contents

# 1. Introduction

## *1.1. Status of reverse osmosis*

Water scarcity is one of the most concerning challenges in the world. Over 1 billion people have no access to clean drinking water and more than one-third of the world's people live in water-stressed regions [1]. Water shortages are further worsened by industrialization, population growth, water contamination and climate change. Desalination has played an increasingly important role in addressing water scarcity. Globally around 16,880 desalination plants are supplying freshwater of 97.2 million $m^3$/day in 2020 [2]. The total production capacity of freshwater has tripled since 2000 when it was less than 30 million $m^3$/day [3]. Fig. 1 shows the estimated global desalination market by technology and desalination capacity over the next few years based on the recent growth rates [2, 4]. It indicates that the desalination market is projected to double between 2015 and 2025. Reverse osmosis (RO) dominates the global desalination market in terms of both revenue and installed numbers (14,360, accounting for 85% of existing desalination plants [2]).

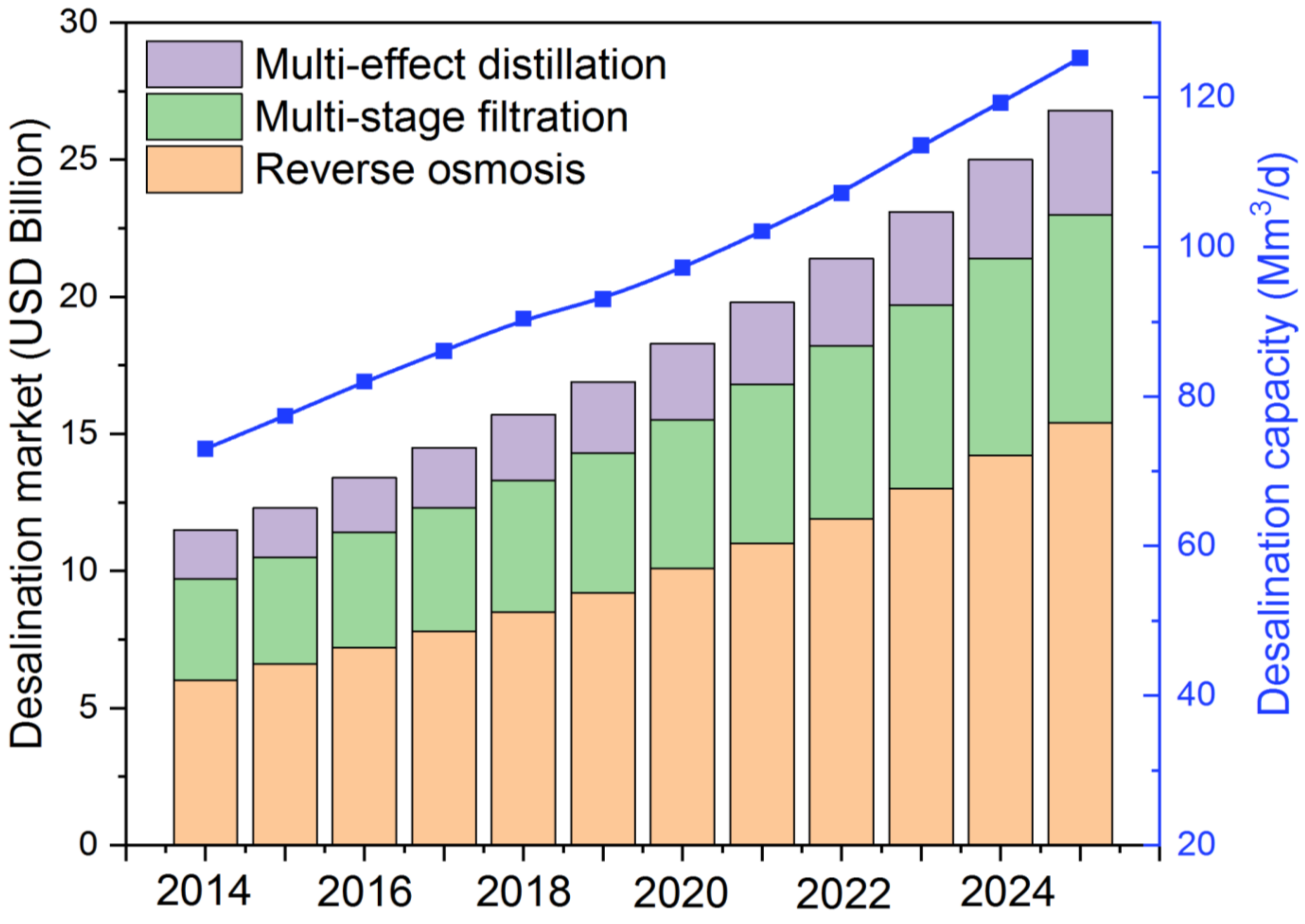

Fig. 1. The estimated global water desalination market revenue by technology and desalination capacity 2014 - 2025 based on the recent growth rates.

Fig. 2a displays the total worldwide installed desalination capacity by technologies. Obviously, as the most popular and cost-effective desalination technology, RO supplies most of the desalted freshwater. In the past few decades, the energy consumption for seawater RO desalination has dropped significantly from more than 15 kWh/m$^3$ in the 1970s to less than 2 kWh/m$^3$ in 2008 (Fig. 2b), which is close to the theoretical minimum energy requirement of 1.06 kWh/m$^3$ [5]. The reduction in energy consumption of RO is mainly caused by the advances in high performance membranes and the employment of high efficient energy recovery devices. Therefore, many countries have adopted RO for freshwater supply, particularly when they have limited access to fuel resources [6].

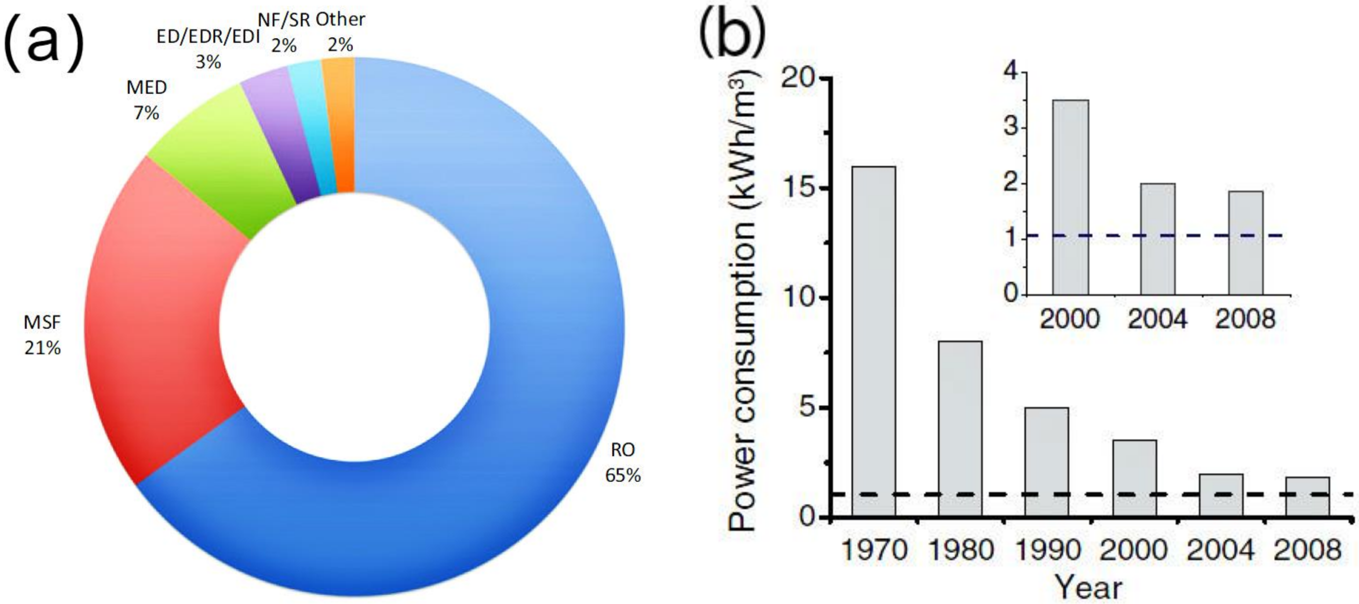

Fig. 2. (a) Total worldwide installed desalination capacity by technology [7]. (b) Reduction in power consumption of RO for seawater desalination from 1970s to 2018 [5]. The horizontal dashed line represents the theoretical minimum energy required for desalting 35 g/L seawater at 50% recovery (1.06 kWh/$m^3$). The energy data here exclude the energy used for intake, pretreatment, posttreatment, and brine discharge.

### *1.2. Challenges of reverse osmosis*

Although RO has become the dominant technology in supplying freshwater from unlimited seawater, RO also faces some challenges that affect the sustainability of the technology. In practical operation, RO is still an energy-intensive process. The state-of-the-art seawater RO plants consume 2 - 4 kWh electricity (including energy for pre-treatment, post-treatment and transportation) and release 1.4 - 1.8 kg $CO_2$ per cubic meter of produced freshwater [5, 8]. To minimise the energy consumption and greenhouse gas emissions, two effective options are developing RO membranes with reasonably high permeability and selectivity [9], and integrating renewable energy sources (e.g. solar and wind energy) in the desalination process. Higher water permeability (A) membranes could have a modest effect on energy demand. For example, Cohen-Tanugi et al. [10] estimated a 15% reduction in energy demand, or a 44% reduction in pressure vessels, for seawater RO with a

3-fold increase in A (compared with current technology) with a typical capacity and recovery ratio. Further increases in A show small energy benefit due to thermodynamic constraints. This study showed greater benefits for brackish water RO (46% less energy or 63% fewer pressure vessels). The diminishing benefit of increased A is confirmed by Werber et al. who emphasised the need to improve selectivity (lower salt permeability (B) or greater A/B ratio) [9]. Overall, modest increases in A and decreases in B would bring meaningful benefits to energy demand and product quality. Both A and B can be detrimentally affected by fouling, providing a strong incentive to improve the antifouling properties of RO membranes.

Another key problem in RO is the desalination brine. It has an increased salinity (doubled compared with seawater) and contains complex chemicals, such as coagulants, surfactants, antiscalants and chemical cleaning agents [5, 8] and, in the context of this review, all of which relate to fouling control. The most common way for brine disposal is direct discharge to the sea. However, this raises environmental concerns. In the future, more efforts may need to be devoted to minimise the environmental impacts of RO desalination brine. For example, membrane distillation (MD), with the potential to achieve zero liquid discharge [11-13], and forward osmosis [14-16] could be alternative technologies to further treat RO brine.

Lack of high performance membranes is still a long-term challenge in RO desalination, although the past decades have witnessed dramatic advances in membrane materials [17]. Table 1 summarizes the typical types of RO membranes, including thin film composite (TFC), cellulose acetate (CA), inorganic, organic/inorganic hybrids, and biomimetic RO membranes. Among these, the TFC RO membrane is the most studied and also has the largest market share in the industry for practical desalination and wastewater treatment. This is mainly because TFC RO membranes have very good salt rejection, water permeability and mechanical strength. However, TFC RO membranes still have the drawbacks of fouling and low chlorine resistance.

Table 1. Summary of the materials, advantages and disadvantages of typical RO membranes.

| RO membranes | Advantages | Disadvantages | Refs. |
|---|---|---|---|
| **TFC** | High permeability and selectivity; excellent mechanical strength; large temperature and pH tolerance range. | Susceptible to fouling; sensitive to chlorine attack and other oxidations (e.g. by chloramine, bromine, ozone). | [6, 17] |
| **CA** | Chlorine tolerant; low costs; antifouling. | Low permeability; susceptible to hydrolysis; low stability with the changes in pH, pressure and temperature. | [6, 18] |
| **Inorganic** | Excellent thermal, chemical, mechanical stabilities; antifouling; cleaning tolerant. | High costs; low rejection; low packing density. | [17, 19, 20] |
| **Organic/inorganic hybrid** | Combination of the advantages of organic and inorganic membranes (e.g. high permeability and antifouling); capable of using numerous emerging nanomaterials (e.g. 2D nanosheets). | Not commercialized at large-scale; high costs. | [19, 21] |
| **Biomimetic** | High permeability; antifouling. | Not commercialized at large-scale; high costs; limited thermal and chemical stabilities. | [17, 22] |

Engineering antifouling membranes could play a vital role in addressing the challenges of RO. Antifouling RO membranes could reduce the flux drop and extra energy requirements caused by fouling, and chemical usage (e.g. antiscalants and cleaning agents) thereby extending membrane lifespans, cutting down cleaning and shutdown frequencies, and reducing desalination costs. However, it is important that the provision of antifouling properties does not compromise the high permeability and selectivity properties of TFC RO membranes, as all these properties are required to reduced energy consumption and increase product water quality [10, 17, 23-25]. This study explores the recent research efforts on RO membrane development and modification for fouling mitigation.

### *1.3. Aim and novelty of this paper*

A number of review papers on antifouling membranes or RO membranes have been published. These review papers focus on general antifouling membranes [26-29], RO membranes [30, 31], TFC membranes [32, 33], specific surface modification [23, 34, 35], or antimicrobial membranes [36, 37]. However, no comprehensive review on antifouling engineering has been done specifically for RO desalination membranes.

This paper aims to provide a state-of-the-art assessment of research work carried out to date on engineering antifouling RO membranes, including three key strategies: (1) substrate modification before interfacial polymerization, (2) incorporating additives (e.g. nanoparticles, nanotubes, and biocidal agents) into the polyamide layer during interfacial polymerization, and (3) post (surface) modification after interfacial polymerization. Most importantly, we provide our perspectives on the current challenges, practical feasibility and future directions for each antifouling engineering strategy. This review focuses on the development of antifouling TFC RO membranes since they are the mostly studied and used RO membranes by both scientists and engineers due to their remarkable water permeability and salt selectivity.

This paper starts with exploration of the mechanisms of RO membrane fouling, followed by analysis of the membrane parameters affecting RO fouling. We summarize and analyze the three key strategies for engineering RO membranes. We also discuss the emerging nanomaterials, hydrophilic polymers and biocidal agents used for antifouling modification of RO membranes, and evaluate their feasibilities and efficiencies for practical applications. Finally, we consider the likely future of antifouling RO membranes and recommend some directions that need more research efforts. This review provides an important guide for engineering antifouling RO membranes by different methods using various nanomaterials, polymers and biocidal agents.

## 2. Mechanisms of RO membrane fouling

Membrane fouling is caused by the accumulation of a range of undesirable deposits on the membrane surface or in the membrane pores, leading to reductions in permeation flux and salt rejection. This phenomenon can significantly decrease membrane performance due to the extra mass transfer resistance from the foulants, and thus increase the costs due to increased specific energy, membrane cleaning and replacement. After fouling, the transmembrane pressure will need to increase in order to maintain a constant flux (or water flux will decrease at a constant transmembrane pressure), causing higher energy consumption [32]. Fouling can also enhance concentration polarization and thus salt permeation through the membrane, leading to reduced salt rejection [38]. Fouling can occur on the membrane surface and/or in the membrane pores. The former is surface fouling, and the latter is internal fouling. For porous microfiltration and ultrafiltration membranes, internal fouling is more common, while for dense RO membranes, surface fouling dominates the fouling process.

Several fouling mechanisms, including cake formation, concentration polarization induced deposition, organic adsorption, inorganic precipitation and biological fouling have been summarized [39]. From the thermodynamic point of view, membrane fouling is caused by the minimization of the Gibbs free energy of the system [40]. In the fouling process under convective flux, foulants move to and attach on the membrane surface via electrostatic, hydrophobic, van der Waal, hydrogen-bonding and/or other membrane-foulant interactions [34]. Subsequently, the foulants may aggregate due to foulant-foulant interactions, forming a thick fouling layer on the membrane surface.

According to the difference in foulant types, RO membrane fouling is typically classified into organic fouling, inorganic fouling (i.e. scaling), biofouling (i.e. biofilm formation) and colloidal fouling [23, 41]. Four types of foulants result in different morphologies on the membrane surface as shown in Fig. 3. Fig. 3a shows that the RO membrane was almost fully covered by organic sodium alginate [42]. Fig. 3b shows $CaSO_4$ crystal scaling on the membrane surface [43]. Fig. 3c shows a gel-like biofouling layer caused by bacterial cells embedded in extracellular polymeric substances [44]. Fig. 3d displays the colloidal fouling caused by silica particles on the RO membrane surface [45]. Colloidal and inorganic fouling are amenable to control by filtration and adjustment of water chemistry whereas organic fouling and biofouling are typically more intractable and complex.

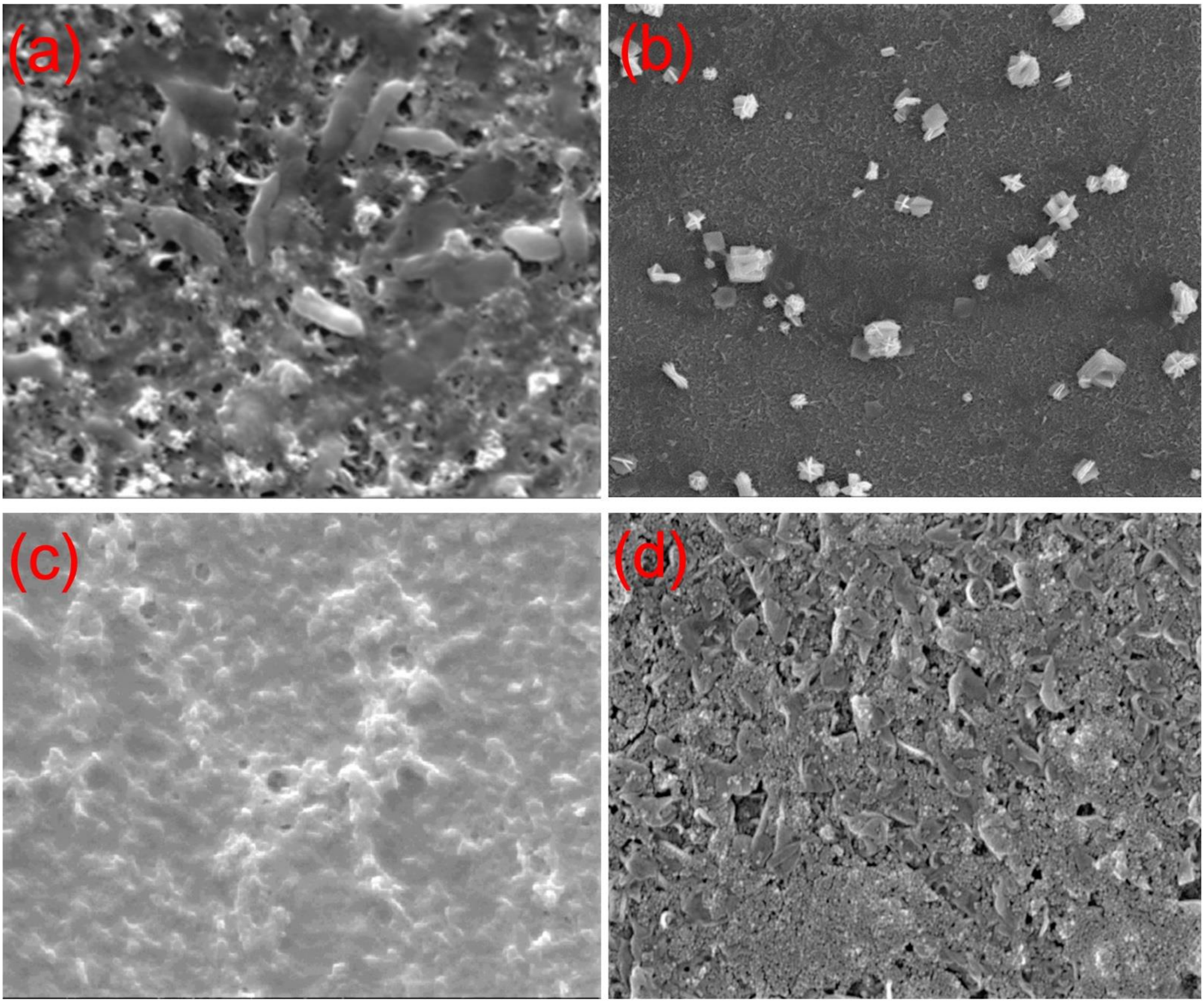

Fig. 3. SME images of different RO membrane fouling types: (a) organic fouling (by sodium alginate) [42], (b) inorganic fouling (by $CaSO_4$) [43], (c) biofouling [44], and (d) colloidal fouling (by silica) [45].

### *2.1. Organic fouling*

Organic fouling is caused by organic matter, typically including humic substances, proteins, polysaccharides, lipids, nucleic acids, amino acids, organic acids, and cell components [41]. Organic fouling is mainly caused by dissolved organic matter (DOM) that widely exists in all sorts of waters. DOM can be classified into three categories based on their origins: (1) refractory natural organic matter (NOM), (2) synthetic organic compounds from consumers and disinfection byproducts during the water disinfection process, and (3) soluble microbial products (SMPs) due to decomposition of organic compounds during the biological treatment process [46]. NOM is the key foulant for polymeric membranes in drinking water applications [39]. NOM is a complex heterogeneous mixture of compounds from the decomposition of animal and plant materials in the environment. Most NOM comprises of a range of compounds, from small hydrophobic acids, proteins and amino-acids to large humic and fulvic acids. The major fraction of NOM is composed of humic substances (HS). In brackish water or seawater RO desalination, NOM with concentrations ranging from 2 to 5 ppm is a typical foulant, while effluent organic matter (EfOM) dominates the fouling in wastewater treatment (10-20 ppm) [47, 48]. An important organic group implicated in seawater desalination fouling are transparent exopolymers (TEPs). TEPs comprise acidic polysaccharides present as particles or gels and can facilitate bio-adhesion and biofouling [49, 50].

Because of the complexity of organic matter in real waters, several model foulants are widely selected in fouling studies. For example, bovine serum albumin (BSA) is often used to represent proteins, humic acid (HA) represents humic substances, and (sodium) alginate is used as the surrogate of polysaccharides. Kim and Dempsey reported that HA was most similar to NOM in surface water and SMPs were most similar to wastewater EfOM [47]. In organic fouling, adsorption is a key fouling mechanism. Feed solution chemistry, foulant-surface interactions (initial stage), foulant-foulant interactions (fouling layer development stage), and foulant molecular weights are the important factors influencing organic fouling [39, 41, 51]. Lee et al. [51] reported that organic foulants with low to medium molecular weights (300-1,000 Da) played an important role in the initial stage of membrane fouling, while organic matters with large molecular weights (> 50,000 Da) dominated the later fouling layer development.

### *2.2. Inorganic fouling*

Inorganic fouling, also called scaling, is caused by the deposition/precipitation of inorganic salts on the membrane surface or in the membrane pores. Inorganic fouling often occurs when the concentrations of ions exceed their equilibrium solubility products and become supersaturated. Inorganic salts with very low solubilities, such as calcium sulfate ($CaSO_4$), calcium carbonate ($CaCO_3$), silica ($SiO_2$) and barium sulfate ($BaSO_4$) are the most common scalants on the membrane surface. Statistical analysis has demonstrated that ~80% of scaling studies on RO membranes were related to $CaSO_4$ and $CaCO_3$ [41]. Scaling is formed by two crystallization pathways: surface (heterogeneous) crystallization and bulk (homogeneous) crystallization [52]. Membrane scaling occurs as a result of both mechanisms, and is affected by feed properties, membrane morphology and operating conditions.

Inorganic fouling is different from other fouling types because it only occurs when the local concentration exceeds a critical saturation value. However, salt rejection and flux-induced concentration polarization (CP) can facilitate the approach to the critical saturation concentration and accelerate scaling on the membrane surface. Scaling can be mitigated by using membranes with smooth surfaces, dosing antiscalants, pH adjustment or decreasing CP by increasing the feed velocity (i.e. shear rate) and/or decreasing flux [6, 53]. The benefit of a smooth surface may be the fewer “ridge and valley” features; CP would tend to be exacerbated in the “valleys”.

### *2.3. Biofouling*

Biofouling (i.e. biological fouling) is defined as undesirable accumulation, adhesion and proliferation of microorganisms on the membrane surface. Biofoulants include bacteria, fungi, algae, viruses, higher organisms (e.g. protozoa), and biotic debris (e.g. bacterial cell wall fragments) [54, 55]. Biofilm formation can be divided into three stages: bacteria attachment, reproduction and detachment. Bacteria attachment is a dynamic process during which live bacteria move to and attach onto the membrane surface [41]. In the bacteria reproduction stage, the attached microorganisms consume nutrients in the feed solution and experience proliferation, excreting extracellular polymeric substance (EPS) that form a binding and protective matrix. The final stage is the detachment of the dead and living bacteria triggered by lack of nutrients. In RO operation, the dead bacteria could also form a biofouling layer under high hydraulic pressure, leading to decreased water flux and salt rejection through a biofilm-enhanced osmotic pressure mechanism [56], as well as providing a fouling resistance. The detached and dispersed bacteria will find new sites to grow downstream and repeat the process of biofilm formation. The formed biofilm on the membrane surface is a gel-like layer (Fig. 3c), having two key components: bacterial cells and EPS that are excreted by bacteria during metabolism. EPS is mainly made of polysaccharides, proteins, glycoproteins, lipoproteins, lipids and nucleic acids, and can protect the microorganisms from biocides and toxins, making biofouling more intractable [57].

Biofouling is one of the most severe problems in RO operations. It has the following properties: (1) it is not easily reversible; (2) it is more complicated than other fouling phenomena because the microorganisms can grow, multiply and relocate on the membrane surface; (3) it is difficult to mitigate by pretreatment unless pretreatment can remove 100% bacteria and nutrients in the feed, which is unlikely. A few surviving cells can multiply quickly under suitable conditions in the RO system, and this emphasises the need to limit nutrients in the feed. Although biofouling can be diminished by feed disinfection, it may cause extra problems for TFC polyamide membranes because of their sensitivity to chlorine degradation [58, 59]. This explains the quest for more chlorine-tolerant RO membranes [60].

### *2.4. Colloidal fouling*

Colloidal (particulate) fouling refers to the deposition of colloids or particles on the membrane surface. Colloids/particulates are regarded as fine particles roughly in the size range of 1 nm to 1 μm. Particles below this size range can diffuse away from the membrane surface via molecular diffusion, while particles above this size range can be removed by shear flow. The common colloidal foulants can be divided into two types:

inorganic foulants and organic macromolecules. The common inorganic colloids include silica, iron oxides/hydroxides and aluminium silicate minerals. Organic macromolecules are mainly composed of humic acids, polysaccharides and proteins [61]. Since colloidal foulants cover both organic and inorganic materials, in some publications colloidal fouling is integrated into organic or inorganic fouling.

## 3. Membrane properties affecting RO membrane fouling

Generally, the factors affecting membrane fouling can be classified into three groups (Fig. 4): feed solution/water characteristics, operational conditions, and membrane properties. Next, each group will be discussed briefly.

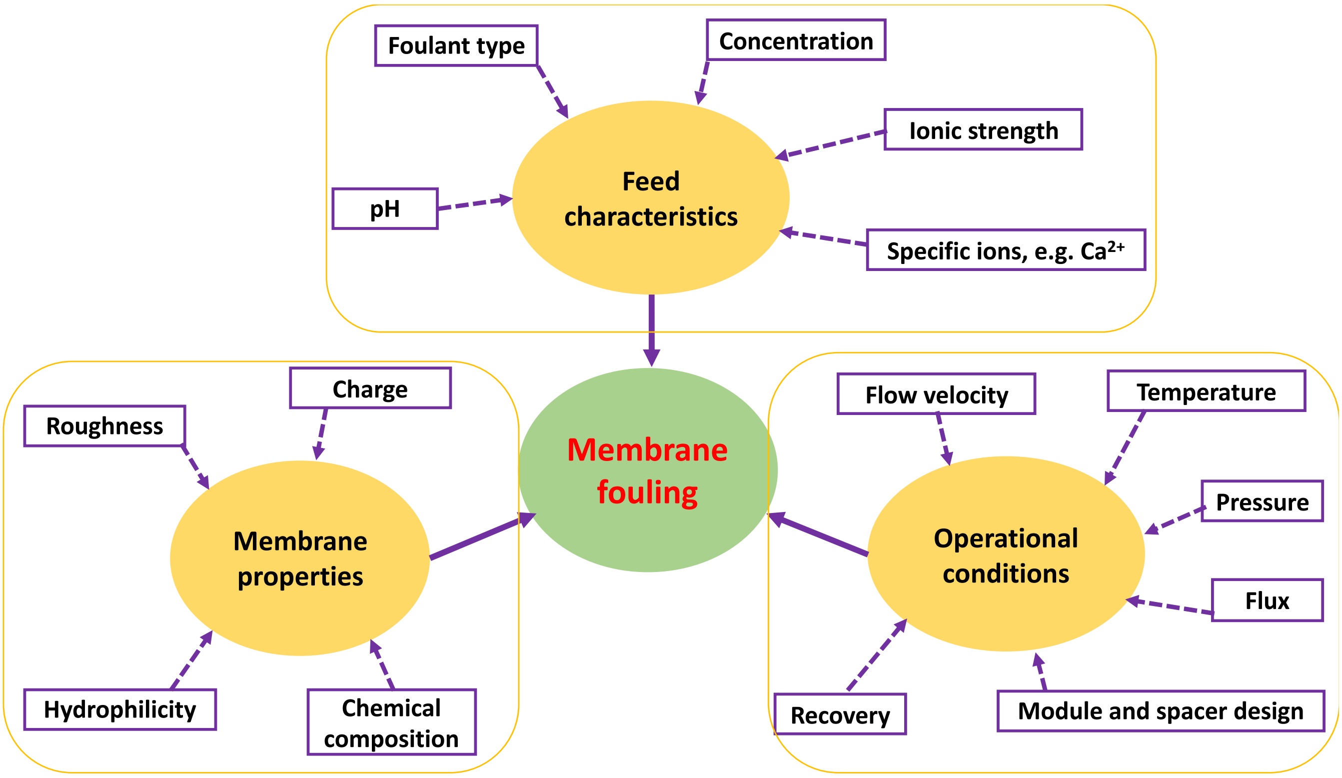

Fig. 4. Factors affecting RO membrane fouling.

(1) Feed solution/water characteristics. Membrane fouling is strongly affected by the feed chemistry (e.g. ionic strength, $Ca^{2+}$ and pH) and the foulants in the feed solution, including their types, concentrations and physiochemical properties (e.g. sizes, charges, structures, functional groups and hydrophobicity) [62-64]. For

example, RO membrane fouling by BSA was enhanced at higher $Ca^{2+}$ concentration and at pH near the BSA isoelectric point (pH 4.7) [65, 66].

(2) Operational conditions. A number of operational parameters, such as cross flow velocity, transmembrane pressure, permeation flux, and module and spacer design have significant effects on membrane fouling. This is because fouling can be linked to the degree of concentration polarization (CP) which is determined by the ratio of water flux ($J$) to the boundary layer mass transfer coefficient ($k$). The value of k depends on the crossflow velocity and the flow channel design (via module and spacer design). Therefore, membrane fouling is considered as a flux driven phenomenon and this is directly related to the transmembrane pressure [67]. In particular, the critical flux, or closely related to “threshold flux”, defined as the flux beyond which severe membrane fouling occurs, has been used to highlight the important relationship between flux and fouling [68-70]. Note that these operational parameters can affect each other, and membrane fouling is synergistically influenced by more than one parameter in practical operations. Raised temperature is another operational fouling factor as it can worsen membrane scaling [71] and biofouling by increasing bacteria growth and multiplication [57].

(3) Membrane properties. The physico-chemical properties of the membrane surface influence foulant-membrane interactions, and play an important role in RO membrane fouling [6, 61]. Since this review focuses on engineering antifouling RO membranes, these membrane properties are discussed in detail below.

### ***3.1. Surface chemical composition***

Surface chemistry of the membrane governs the membrane surface properties (e.g. charge, hydrophilicity and fouling resistance) and performance (e.g. water flux and salt rejection). In particular, functional groups and chemical compositions of the membrane surface significantly affect membrane properties. Most membrane modifications for fouling reduction essentially are to introduce oxygen-containing groups (e.g. -COOH [72-

74], -OH [75-77] and $-SO_3H$ [78]) and/or biocidal agents (e.g. Ag [79-81], Cu [82], GO [83-85], polypyrrole [86] and antibiotics [87, 88]), and thus change the membrane surface chemistry. Commercial RO membranes are often coated with hydrophilic polyvinyl alcohol (PVA, rich in -OH) to impart antifouling properties by increasing surface hydrophilicity and decreasing surface roughness. After modification, the changes in membrane surface chemical composition (e.g. functional groups and element percentages) are typically characterized by Fourier transform infrared spectroscopy (FTIR) and/or X-ray photoelectron spectroscopy (XPS).

### *3.2. Surface hydrophilicity*

Surface hydrophilicity is one of the most important parameters affecting membrane fouling. Hydrophilic membranes often have lower fouling propensities. Generally, a membrane can be attractive (hydrophilic) or repulsive (hydrophobic) to water in an aqueous solution. Hydrophilicity of a membrane is often evaluated by the water contact angle between the membrane surface and a water droplet [89], but sometimes also evaluated by the air bubble contact angle between the membrane surface and an air bubble [90]. Hydrophilic membrane surfaces have water contact angles in the range of $0° < \theta < 90°$ (i.e. $90°$ < bubble contact angles < $180°$). The membrane hydrophilicity is attributed to the presence of hydrophilic (oxygen-containing) functional groups that have the ability to form hydrogen-bonds with water molecules on the membrane surface. As a result, hydrophilic membranes tend to adsorb water molecules and thus form a hydration layer between the membrane surface and the foulant, which reduces the membrane-foulant hydrophobic interaction. This has been regarded as the key mechanism in reducing membrane surface fouling by membrane hydrophilic modification [73, 91, 92].

Compared with contact angle measurement, interfacial Gibbs free energy ($-\Delta G_{SL}$) may be a better parameter to represent membrane hydrophilicity due to the effect of membrane surface morphology (e.g. roughness) on contact angles [40]. Typically, larger values of Gibbs free energy mean more hydrophilic surfaces (i.e. lower water contact angles) as shown in Fig. 5a [93, 94]. Membrane fouling can be fundamentally explained by the minimization of interfacial Gibbs free energy [40]. Membranes after surface hydrophilic modification will have higher Gibbs free energy during fouling than the unmodified ordinary membranes (Fig. 5b). However, water contact angle measurement is much more common than Gibbs free energy for membrane surface hydrophilicity evaluation in practical applications since the former is much easier and more straightforward.

Most membrane modifications for fouling reduction are essentially hydrophilization that can be achieved by various methods, such as incorporating hydrophilic nanoparticles [95-97], plasma treatment [98-100], and introducing zwitterionic components [40, 101-103]. After hydrophilic modification, the treated membranes often become more absorptive to water but repulsive to hydrophobic foulants, leading to improve antifouling performance. However, the endowed hydrophilicity by surface modification may not be stable enough in practical long-term operations, which has been less studied and needs more research efforts in the future. A related feature of fouling is that as little as a monolayer of adsorbed foulant can change the effective membrane surface properties.

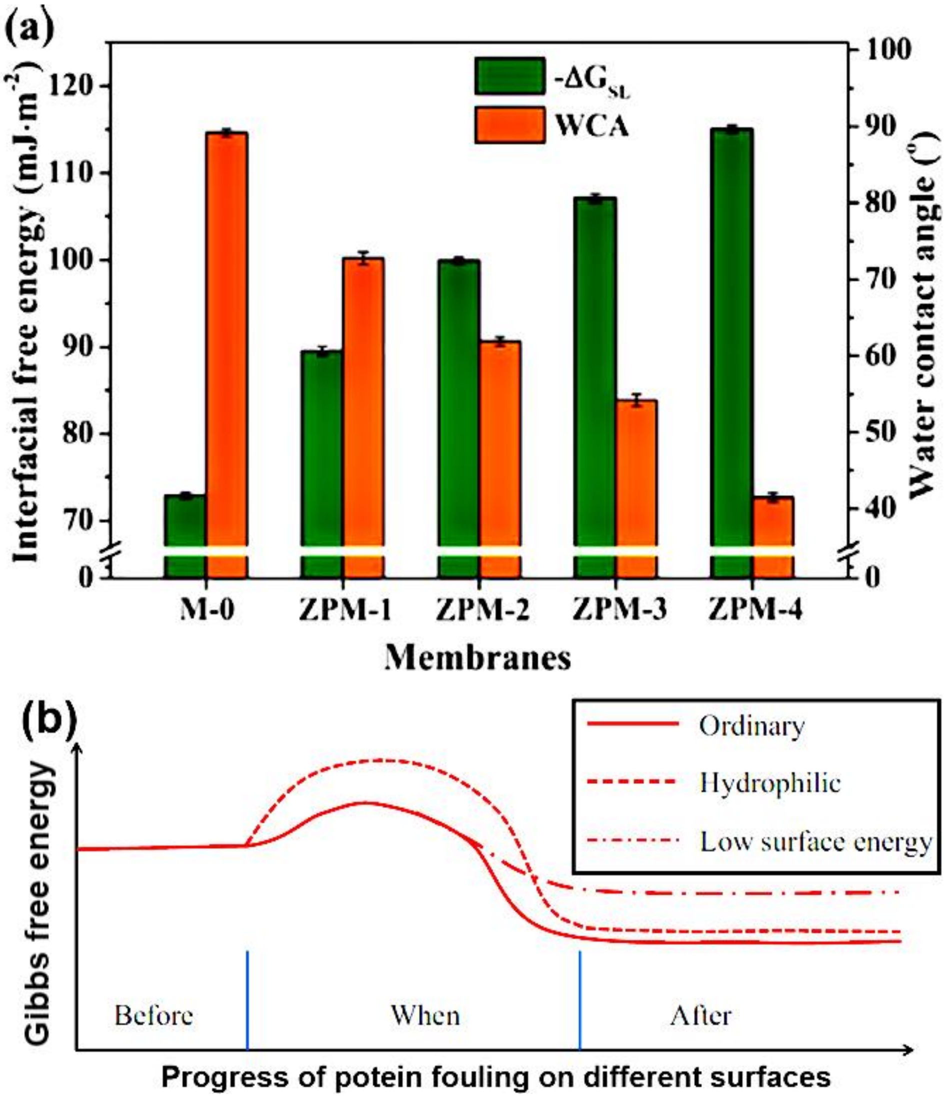

Fig. 5. (a) Relationship between interfacial free energy and water contact angle [93]. (b) Gibbs free energy changes during protein fouling on ordinary and hydrophilic membrane surfaces [40].

### *3.3. Surface charge*

The membrane surface charge has an important effect on fouling mainly via electrostatic interactions between membrane surfaces and foulants. The surface charge-induced electrostatic interactions between membranes and foulants can affect both fouling and rejection and of the membrane. Without such electrostatic interactions, severe membrane fouling and/or low rejection could occur, for instance, when the feed solution contains neutrally charged foulants or ions [104, 105]. The surface charge interactions are also dependent on the water chemistry (e.g. pH, and ionic species). RO membranes prepared by interfacial polymerization show amphoteric properties due to the unreacted carboxylic acid and amine groups on the surface [106]. The surface charge properties of RO membranes are essentially caused by the ionization of surface functional groups (e.g. -COOH and $-NH_2$ and $-SO_3H$) in aqueous media [104, 107]. As a result, most RO membranes are negatively charged under practical operation conditions (e.g. feed $pH < 8$). Desirable antifouling membranes should be close to neutral in their operations. Therefore, most TFC membranes after antifouling modification become less negatively charged [92, 108-112].

However, more negatively charged surfaces do not always suggest worse fouling resistance. Some TFC membranes may become more negatively charged, but still show better antifouling performance as the foulant types and their charge properties are complex [86]. Since most bacteria are negatively charged at neutral pH, initial adhesion of bacteria slows down on negatively charged surfaces through the repulsive force. Therefore, more negatively charged membranes after modification expect to have better anti-biofouling performance [113]. However, positively charged surfaces may have anti-microbial effects on Gram-negative bacteria, but not on Gram-positive ones [114]. A further complication of biofouling is that it is typically preceded by “surface conditioning” by organic molecules (NOM, TEP etc) and this can cause a change in effective surface charge.

### *3.4. Surface morphology (roughness)*

Another important factor that affects the performance of the RO membranes is the surface morphology. It is well known that rougher surfaces are more prone to attach foulants, while smoother surfaces have less fouling tendency but higher cleaning efficiency [115-117]. For example, Elimelech et al. [18] indicated that the TFC RO membranes had higher fouling rates than cellulose acetate RO membranes due to the higher surface roughness caused by the ridge-and-valley structures of the former. To overcome this issue, some commercial TFC RO membranes are coated with a neutral polyvinyl alcohol (PVA) layer [118]. The “ridge-and-valley” structures of TFC membranes can also be altered by coating nanomaterials in the rough structures, thereby reducing membrane surface roughness and fouling [119-121].

However, antifouling modifications do not always lead to smoother surfaces. Some antifouling modifications may result in rougher surfaces for the membranes [82, 122, 123], and other antifouling modifications may cause little change in membrane surface roughness [110, 124]. For antifouling modifications with nanoparticles, membrane surface roughness may reduce first and then increase with the rise in nanoparticle concentration, namely, a lower nanoparticle loading often causes smoother surfaces and a higher nanoparticle loading causes rougher surfaces [72, 76, 125]. The surface roughness of TFC membranes can also be influenced by the hydrophilicity and porosity of the support layer [126]. However, sometimes, the membrane surface roughness may have little effect on biofouling [127].

Overall, membrane surface chemical composition determines membrane surface hydrophilicity and surface charge properties. Improvements in oxygen content and hydrophilicity of the membrane surface often lead to better antifouling performance for the membrane. However, increasing or reducing the membrane surface charges and/or surface roughness does not necessarily improve the antifouling performance of the membrane. The modified membranes with improved fouling resistance could have increased or reduced surface charges/roughness, which will be detailed in the following section.

## 4. Modification strategies for RO membrane fouling reduction

Membrane modification for fouling reduction refers to membrane material engineering efforts implemented for slowing down the attachment of foulants onto the membrane surface, reducing flux decline and/or enhancing flux recovery. Antifouling modifications aim to alter the membrane properties that affect membrane fouling, including membrane chemistry, hydrophilicity, charge and roughness as discussed above, thereby reducing the foulant-surface interactions and thus membrane fouling [128]. Since fouling is most pronounced for TFC polyamide (PA) RO membranes among all types of RO membranes [17, 33], most antifouling modifications for RO membranes are performed on these membranes.

The most common TFC membrane has a thin selective PA layer synthesized during interfacial polymerization of m-phenylenediamine (MPD) and trimesoyl chloride (TMC) on a microporous substrate (Fig. 6a) [129]. Typical commercial TFC RO membranes have a thin selective PA layer (< 200 nm), a micro-porous substrate layer (~ 40 µm) and a thick non-woven fabric support layer (~ 120 µm) as illustrated in Fig. 6b [130]. The thin PA layer determines the membrane selectivity, while the substrate layer and the fabric support layer provide the mechanical strength and the water permeability due to their low mass transfer resistance, although the substrate properties can influence the PA layer (see below). In RO membrane applications, since the feed solution including foulants, directly contacts the selective PA layer, most antifouling engineering practice is performed for the PA layer of the RO membrane.

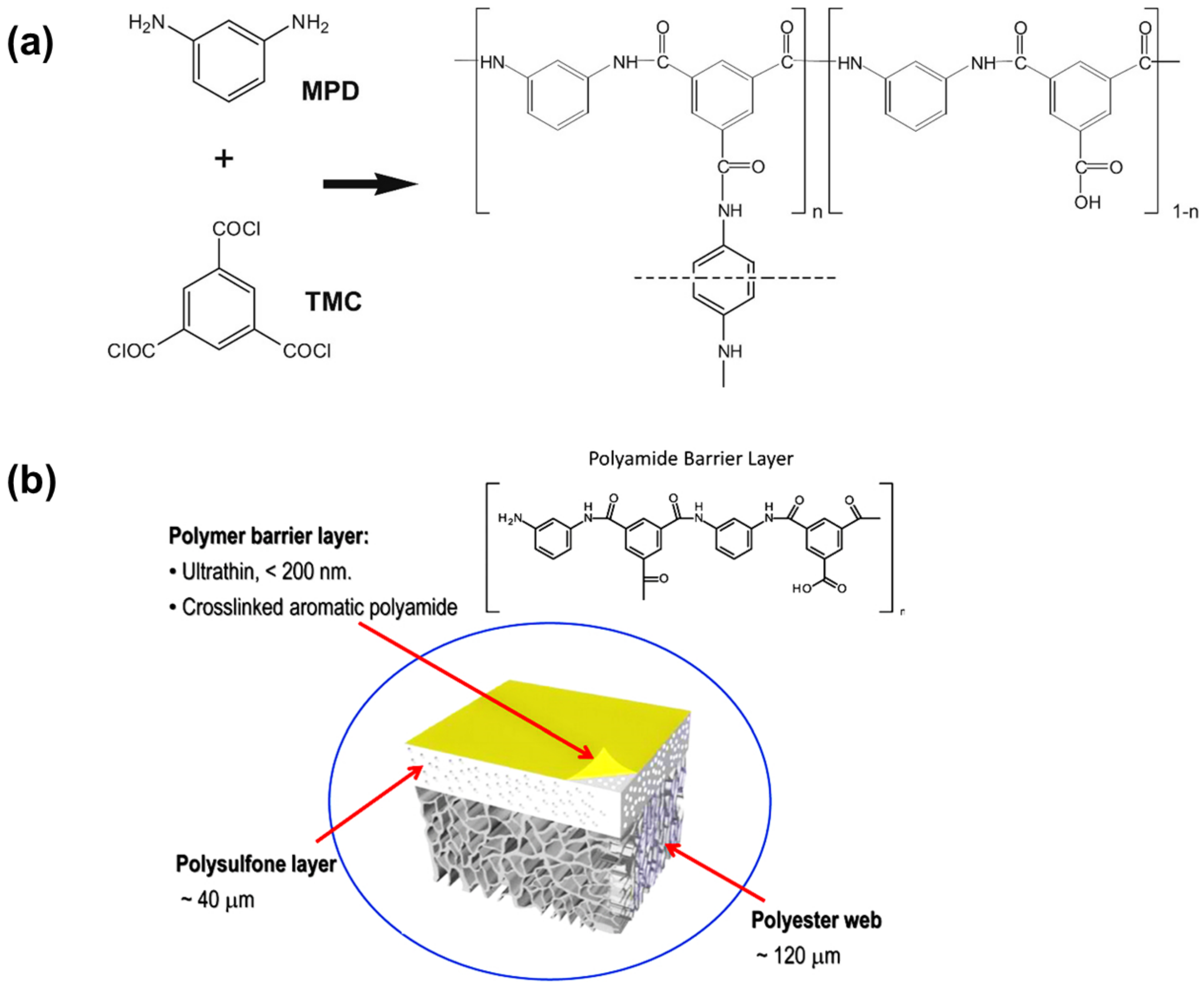

Fig. 6. (a) RO membrane polyamide layer formation by interfacial polymerization of MPD and TMC [129], and (b) different layers of TFC membranes [130].

There are three strategies for TFC RO membrane modification to reduce membrane fouling: (1) substrate (supporting layer) modification before interfacial polymerization, (2) incorporating additives (e.g. nanoparticles, nanotubes, and biocidal agents) into the polyamide layer during interfacial polymerization, (3) post (surface) modification after interfacial polymerization. These strategies are illustrated in Fig. 7, including intensively performed modification for the active layer during and after interfacial polymerization, and the less studied modification for the substrate layer [131]. Next, we will discuss these RO modification methods and applications in detail.

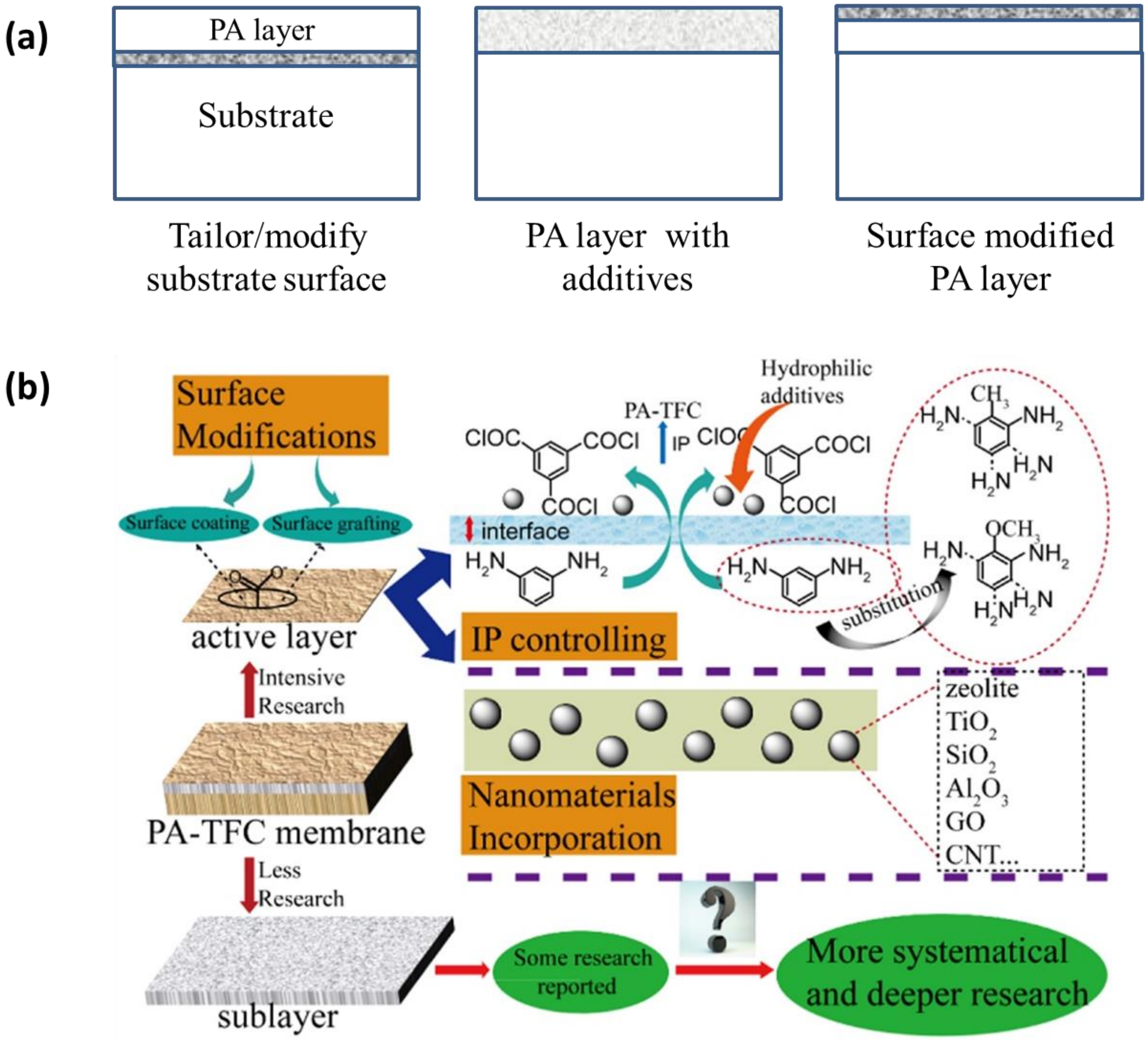

Fig. 7. Strategies for TFC membrane modification, including polyamide active layer modification and sublayer (substrate) modification: (a) simplified illustration, and (b) detailed illustration [131].

### *4.1. Substrate modification before interfacial polymerization*

The TFC RO membrane typically has a relatively thick porous substrate (supporting layer) and a thin dense PA layer. Generally, the substrate layer provides mechanical strength (i.e. pressure resistance) and the PA layer determines the membrane permeability and selectivity. However, recently researchers have started to realize the importance of the properties of the substrate in the final performance of the TFC membrane [131, 132]. In fact, the structure and characteristics of the polyamide selective layer formed by interfacial polymerization is related to the properties of the ultrafiltration support layer [133-136].

Many researchers have noticed the significant relationship between the properties (e.g. pore size, pore distribution, porosity, hydrophilicity and roughness) of the substrate and the performance (e.g. flux and rejection) of the TFC membrane. Singh et al. found that the smaller pore sizes of the substrate caused thicker polyamide active layer and thus higher salt rejection performance [137]. For TFC FO membranes, Huang and McCutcheon observed that the smaller pore sizes of the substrate caused higher crosslinking degree of the PA, leading to lower permeability but higher salt rejection performance [138]. Blending hydrophilic nanomaterials into the substrate layer typically leads to a looser surface (i.e. larger mean pore size by shifting the pore size distribution to the larger values and higher porosity) [73, 76]. Son et al. observed enlarged mean pore size, porosity and total pore area for the substrate layer after blending carbon nanotubes, which enhanced the water flux of the TFC membranes [139]. The NaA zeolite nanoparticle incorporated substrate layer became rougher and more hydrophilic, and the final TFC RO membrane had a smoother and more hydrophilic surface, and higher water flux and salt rejection [140]. However, the $TiO_2$ coated substrate layer with greater smoothness could also result in more hydrophilic and antifouling TFC membranes [141]. Therefore, roughness of the substrate layer alone has little effect on the hydrophilicity and antifouling performance of the TFC membranes, namely, there is no apparent connection between the substrate surface roughness only and the fouling resistance of a PA membrane. Surface hydrophilicity and pore areas (the combined effect of pore size, pore density and porosity) of the substrate may play a more pronounced role in the fouling properties of the TFC membranes.

According to numerical modelling, Ramon et al. reported that the substrate with higher porosity but smaller surface pores would lead to higher water permeability but lower salt selectivity of the TFC membrane [142]. This modelling also predicted that the local water flux through the composite membrane could be determined by the substrate pore morphology with local “hot spots” potentially exceeding the averaged flux by 2 times. These “hot spots” could exacerbate fouling since fouling is flux-driven. This observation argues for use of a “gutter layer” coating on top of the substrate to promote a more homogeneous local flux. Hydrophilicity of the substrate may play a more important role in the preparation and separation performance of the TFC membrane [143]. The substrate layer should be hydrophilic to facilitate interfacial polymerization, which can enhance the water flux and salt rejection performance of the TFC membrane [144]. However, hydrogen bonding between MPD and the hydrophilic substrate may limit the diffusion of MPD inside the substrate pores and some TMC may diffuse into the pores and form a thicker active PA layer with higher transfer resistance [143].

From the discussion above, it is evident that the results on effects of the substrate properties on the final performance of the TFC membrane vary significantly and sometimes may be contradictory. These inconsistent results from different researchers are mainly caused by the complex and varying experimental conditions. These varying conditions cover the substrate properties (e.g. material type, surface/cross-sectional pore size, pore distribution, surface/overall porosity, surface hydrophilicity and roughness, thickness) and the operating conditions (e.g. membrane casting temperature, humidity, speed, coagulation time, and temperature). The interfacial polymerization reaction, determined by the compositions of the MPD and TMC solutions, further increases the inconsistency between different investigations. Therefore, more comprehensive and systematic studies should be carried out to clarify the roles of the substrate in the composite membrane performance. It would be of interest to assess the reported data in terms of the potential effects of substrate-induced “hot spots”.

Although some work has been conducted to explore the relationship between the substrate properties and permeability-selectivity performance of the TFC RO membrane, much less study has examined the effect of substrate modification on fouling reduction. Chae et al. embedded graphene oxide (GO) nanosheets into the substrate layer and the PA layer of the RO membrane [145]. Compared with the single-layer incorporation with GO nanosheets, the dual-layer modification showed better performance in terms of water permeability and anti-biofouling property of the membrane. Similarly, Xie et al. incorporated modified GO into the membrane support and selective layer [146]. They found that dual-layer modification reduced the substrate pore size, but increased the porosity and hydrophilicity of the substrate layer, which led to thinner, smoother and more hydrophilic TFC membranes with higher permeability and fouling resistance. In fact, blending hydrophilic nanomaterials in the substrate layer during phase inversion often results in greater surface porosity, hydrophilicity and pore size for the substrate layer [73, 76, 147], which may prevent the aggregation of nanofillers and promote the formation of a smoother, more hydrophilic and uniform PA layer during interfacial polymerization [145]. As a result, the dual-layer modification method leads to enhanced water permeability and fouling resistance of the TFC membrane. It should also be noted that any coating layer added to the substrate would potentially help to reduce the formation of “hot spots” [142].

***Remarks on substrate modification***

Substrate modification has received much less attention in developing antifouling RO membranes among the three antifouling engineering strategies for RO membranes. This may be caused by the indirect and complicated relationship between the substrate and the antifouling surface. Indeed, from the substrate to the antifouling TFC membrane, there are many variables covering the substrate properties (e.g. material type, surface/cross-sectional pore size, pore density and distribution, surface/overall porosity, and surface hydrophilicity and roughness), the operating conditions (e.g. membrane casting temperature, humidity, speed, coagulation time, and temperature) and similar parameters for the selective layer. Sometimes, it is difficult to attribute the substrate properties to the antifouling PA surface, particularly for the lab-made RO membranes with low repeatability and large experimental errors. This may be the reason that some investigations come to contradictory conclusions. In the future, antifouling modifications for RO membranes should also include the substrate layer rather than the selective PA layer only, although the impacts of the substrate on RO membrane fouling may be more indirect and complex. However, the positive feature is that substrate modification tends to be relatively facile.

### *4.2. Incorporating additives during interfacial polymerization*

#### *4.2.1. Metals and metal oxides*

Metals and metal oxides are generally hydrophilic and have biocidal properties [23]. Incorporating these materials into the PA layer during interfacial polymerization often enhances the antifouling properties of the TFC membranes [148]. Many metals and metal oxides, such as Ag, Cu, ZnO, $Fe_3O_4$, $Al_2O_3$, $ZrO_2$ and $Mg(OH)_2$, have been widely used to develop antifouling membranes [76]. Theoretically, all of these nanomaterials can be incorporated into the PA layer of the RO membrane. In practice, however, only a few of them have been used in the PA layer of the RO membrane as the very thin selective layer has higher requirements for the nanomaterials. The TFC membranes incorporated with nanomaterials into the PA layer during interfacial polymerization are also called thin film nanocomposite (TFN) membranes. Nanomaterials have been added to both the aqueous and the organic phase.

$TiO_2$ nanoparticles, alone or with assembly of other nanomaterials have been immobilized into the PA layer of RO membranes by adding them into the aqueous phase (i.e. MPD) during interfacial polymerization [149]. Modified nanoporous titanate was added to the oil phase (i.e. TMC) to modify the PA layer of TFC membranes to improve membrane fouling resistance [150]. Copper and silver are typical biocides for engineering antifouling RO membranes thanks to their disinfection abilities [151-153]. Wang et al. dispersed cerium oxide

($CeO_2$) into the organic phase to prepare TFC membranes [154]. Hydrophilic $CeO_2$ enhanced the water flux of the TFC membrane, and endowed the membrane with excellent antifouling property by forming a hydrogen barrier layer and stronger negative charge for the membrane selective layer. The adhesion of hydrophobic and electronegative foulants to the membrane surface were inhibited by the steric hindrance and electrostatic repulsion.

Some metals and metal oxides are responsive to light or oxidants. Therefore, incorporating such nanomaterials as metal or metal oxides into the TFC membranes could make them capable of degrading organic contaminants on the membrane surface to realize the redox self-cleaning property, thereby reducing organic fouling [155, 156]. Dumée et al. encapsulated catalytic silver species into metal organic framework (MOF) nanoparticles and then incorporated the Ag-modified MOF nanofillers into the PA layer during interfacial polymerization for catalytic degradation of organic pollutants [157]. However, all polymer based catalytic membranes face two challenges in practical applications. First, the stimuli (e.g. lights and oxidants) are difficult to introduce to the membrane surface in closed membrane modules. Second, the catalytic reaction will inevitably degrade the polymeric membranes in long-term operation. These two main drawbacks significantly reduce the feasibility and practicability of catalytic RO membranes in real-world applications.

### *4.2.2. Carbon based nanomaterials*

Carbon based materials are attractive for membrane modification owing to their porous structures, biocidal activities and hydrophilic properties. A variety of carbon nanomaterials, such as carbon nanotubes (CNTs), graphene oxides (GO) and carbon dots (CDs) have been introduced to modify various membranes. Table 2 summarizes the typical carbon based nanomaterials incorporated into the PA layer of TFN membranes. Among them, GO, a type of two-dimensional (2D) nanosheet, has been the most widely studied carbon based nanomaterial for modification of various membranes (including microfiltration [158], ultrafiltration [159], nanofiltration [160], RO [161], forward osmosis [162] and gas separation membranes [163]). Abundant oxygen-containing functional groups (hydroxyl groups on the flat plane and carboxyl groups at the surface edge) providing hydrophilicity, and sharp edges, strong negative charges and laminar structures of GO are favorable intrinsic properties for engineering RO membranes. Feng et al. applied GO as nanofillers in the aqueous solution to prepare TFC membranes [164]. The GO modified TFC membrane showed an increased water flux, a salt rejection higher than 97%, and improved anti-swelling and antifouling properties. The authors attributed the enhanced performance to the hydrophilicity, negative charges and various chemical groups of the GO nanofillers. Chae et al. embedded GO in the polyamide layer by dispersing it in an aqueous solution of MPD to improve the RO membrane antifouling properties [165]. Both the size and the concentration of GO had an important effect in the performance improvement. The GO modified membranes with enhanced water flux and biofouling resistance and unchanged salt rejection were smoother and more hydrophilic.

Table 2. Typical carbon based nanomaterials used as nanofillers during interfacial polymerization to develop antifouling TFC membranes.

| Nanofillers | Modification method | Flux and rejection | Anti-fouling performance | Refs. |
|---|---|---|---|---|
| GO | Aqueous phase | 39% rise in flux; 1% decrease in rejection. | 35% higher flux recovery. | [164] |
| GO | Aqueous phase | 80% rise in flux; maintained rejection | 98% decrease of attached cells. | [166] |
| GO | Aqueous phase | 80% rise in flux and maintained rejection. | 260% higher antibacterial activity. | [167] |
| Z-CNTs | Vacuum filtration | Nearly three-fold rise in flux; comparable rejection. | 31% higher flux recovery. | [168] |
| $NH_2$-MWCNTs | Aqueous phase | Slightly increased flux and rejection. | 10% higher normalized flux. | [169] |
| GOQDs | Aqueous phase | 52% rise in flux and comparable rejection. | 20.8% higher flux recovery. | [170] |
| GOQD/AP | Aqueous phase | 54% rise in flux and comparable rejection. | 98.8% (in dark) and 99.9% (under visible light) higher sterilization rate. | [171] |
| H-OMC | Aqueous phase | 22% rise in flux; 18% decrease in rejection. | 36% lower BSA adsorption | [172] |

GO: graphene oxide; Z-CNTs: zwitterionic carbon nanotubes; $NH_2$-MWCNTs: $NH_2$ functionalized multi-walled CNTs;

GOQDs: graphene oxide quantum dots; AP: silver phosphate; H-OMC: hydrophilized ordered mesoporous carbon.

Similarly, He et al. dispersed GO in an aqueous solution of MPD to develop antibacterial TFC membranes [167]. The anti-biofouling property of the membrane was achieved due to the improved hydrophilicity, smoothness and negatively charged surface. Xia et al. reported a GO modified TFC membrane for removal of natural organic matters (NOMs) in river water [173]. The hydrophilic nature of GO increased the antifouling property by forming a hydration layer that prevented the adhesion of foulants. In addition, the GO modified TFC membrane exhibited higher removal efficiency for NOMs with different molecular weights. Inurria et al. added GO nanosheets into the organic phase (i.e. TMC solution) to prepare antifouling TFC membranes [174]. They found that increasing the GO loading in the TFC membranes increased the antifouling and antimicrobial properties, but could also reduce the water permeability of the membrane, suggesting a trade-off between water permeability and fouling resistance.

Compared with sole GO, GO-based nanocomposites seem to be more promising for RO membrane modification because of the enhancement or the synergistic effect between GO and the decoration fraction. Kim et al. incorporated GO and tannic acid (TA) modified GO (GOT) into the organic phase, and compared the performance of the TFC membranes with these two nanofillers [175]. After incorporating GO and GOT into the polyamide layer, the permeability, antimicrobial properties and chlorine resistance of the TFC membranes improved. They also observed that performance of the GOT modified membrane was superior to that of the GO modified membrane, suggesting the synergistic effect between TA and GO. In another work [176], comparisons between the TFC membranes prepared with the pristine GO and zwitterionic polymers grafted GO (Z-GO) were made. It was proved that incorporation of Z-GO into the selective layer enhanced the water permeability, selectivity and the antifouling properties. The TFN membranes fabricated with Z-GO were smoother and more hydrophilic compared with the control TFC membrane and the GO modified TFN membranes. Modification of GO can minimize the disadvantages of GO based TFN membranes, such as aggregation of GO, decreased salt rejection and increased surface roughness. Similar results were also reported by another team who prepared TFN membranes by incorporating $TiO_2$, GO and their mixture into the membrane polyamide layer [177]. The GO/$TiO_2$ TFN membranes showed better performance in terms of water flux, salt rejection, antifouling and chlorine resistance.

Wang et al. immobilized the zeolitic imidazolate framework-8 (ZIF-8) onto the GO nanosheet and the synthesized ZIF-8/GO was utilized as nanofillers for the preparation of TFN membranes [178]. The antimicrobial activity of the ZIF-8/GO TFN membrane was higher than that of the single component ZIF-8 TFN or GO TFN membranes. The better antimicrobial performance of the ZIF-8/GO TFN membrane was ascribed to the synergistic effect between ZIF-8 and GO. On the one hand, GO is a contact-based antimicrobial material, and owing to its structural characteristics, the GO nanosheets are prone to be buried under the PA layer, leading to fewer exposed effective sites. However, the stereo structure of ZIF-8 could facilitate the exposure of hybrid ZIF-8/GO composites onto the membrane surface, which would contribute to the improved antimicrobial performance. On the other hand, the coordination capacity between zinc ions and carboxyl groups of GO would be favorable for the uniform dispersion of ZIF-8 nanoparticles on GO nanosheets. The uniform dispersion of ZIF-8 is beneficial for supplying more active sites (imidazole rings and zinc ions) for the antimicrobial activity of the TFN membrane. Comparisons of the antifouling and anti-biofouling performances of the TFC, GO TFN, Ag-MOF TFN and GO-Ag-MOF TFN membranes were conducted by Firouzjaei et al. [179]. The contributions of each parameter, such as contact angle, surface roughness and charged properties were cross-compared in Fig. 8. The bacteria killing capacity of the GO-Ag-MOF TFN membrane was 16%, 30% and 92% higher than those of the Ag-MOF TFN, GO TFN and TFC membranes as demonstrated by fluorescence imaging. Besides, the water flux decrement of the GO-Ag-MOF TFN membrane was also less than other composite membranes. The explanations are probably the lower water contact angle, reduced surface roughness and lower zeta potential. Moreover, the enhanced negative charge also contributed to the higher salt rejection of the composite membrane due to the stronger Donnan effect.

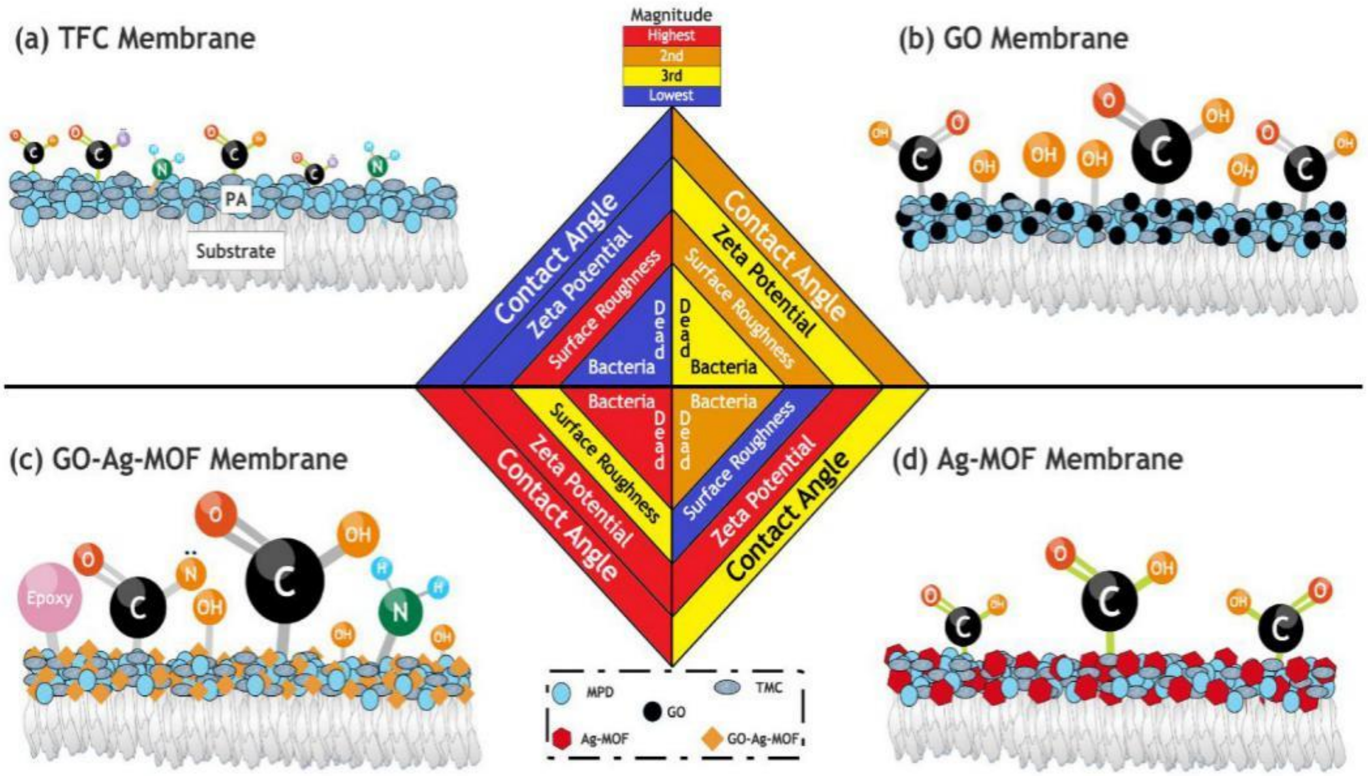

Fig. 8. Parameters contributing to anti-biofouling and antifouling properties of the membranes: (a) TFC, (b) GO TFN, (c) GO-Ag-MOF TFN, and (d) Ag-MOF TFN [179].

Apart from GO nanosheets, CNTs are also very popular for the modification of RO membranes. With the addition of multi-walled CNTs (MWNTs) into the aqueous phase, the porous structure and hydrophilic characteristics of the nanofillers are able to provide the TFN membranes with more water pathways and enhance the affinity between water and the membrane surface [180]. Besides, incorporation of negatively charged MWNTs could elevate the charge density of the membrane surface if required, although in many cases a more neutral surface is less fouling. The amelioration of hydrophilicity and charge property of the membrane could weaken the adhesion force and enhance the electrostatic repulsion between the foulant and the membrane surface. Zwitterionic CNTs (Z-CNTs) were incorporated into RO membranes via vacuum filtration during membrane synthesis [168]. The Z-CNTs appeared to form a strong hydration layer, resulting in improved surface biofouling resistance. Modified membranes had significantly reduced adsorption rate of protein foulants and better cleaning performance.

Zarrabi et al. assessed the performance of TFN membranes prepared by introducing $NH_2$ functionalized multi-walled CNTs ($NH_2$-MWCNTs) into the PA layer [169]. Owing to the hydrophilicity and tubular shape of $NH_2$-MWCNT, the flux of the TFN membrane was improved. Although the incorporation of $NH_2$-MWCNT increased the membrane roughness, which generally exacerbates the fouling propensity of the TFN membrane, the antifouling property of the TFN membrane was still better than that of the control TFC membrane. The authors attributed the improved fouling resistance to the enhanced membrane hydrophilicity, which counterbalanced the negative effect of the rougher surface. They also investigated the influence of $NH_2$-MWCNT for the modification of TFN RO membranes [181]. Similar results were reported, and the contribution of the enhanced negative charges of the TFN membrane for the elevated rejection and antifouling property was also discussed. Apart from organic fouling, CNTs are also able to mitigate the biofouling of TFN membranes. Zheng et al. prepared Z-CNTs and incorporated them into the PA layer of the TFN membrane [182]. Apart from the enhancement of water permeability and salt selectivity, better antibacterial properties of the TFN membrane were observed.

Recently, quantum dots of carbon materials, such as carbon quantum dots (CDs), graphene quantum dots (GQDs) and graphene oxide quantum dots (GOQDs) have been emerging in the fields of catalysis, sensing and energy [183]. As hydrophilic carbonaceous nanoparticles with small sizes, the quantum dots of carbon materials can be well dispersed in the aqueous solution and have excellent affinity with PA polymers. As reported by Li et al., CDs were added to the MPD aqueous solution during interfacial polymerization [184]. Results showed that the functional groups (e.g., hydroxyl, carboxyl, and epoxide) of CDs enhanced the hydrophilicity of the membrane surface. The water flux of modified membrane with 0.02% CDs loading, increased by 20%. The authors anticipated that chemically or physically modified CDs would enhance the antifouling property of the TFN membrane. Subsequently, Chung et al. made an attempt to functionalize the CDs with sodium ion to prepare TFN membranes for removal of selenium and arsenic [185]. The introduction of $Na^+$ modified CDs decreased the pore size and narrowed the pore size distribution of the TFN membrane, causing significantly enhanced selectivity. The rejection of the TFN membrane to $SeO_3^{2-}$ elevated from 82.4% to 98.6% and the rejection to $HAsO_4^{2-}$ increased from 91.3% to 99.5%. In addition, the antifouling property of the TFN membrane was also enhanced by promoting the formation of a hydration layer on the membrane surface against foulants after the incorporation of CDs.

Song et al. dispersed GOQD into the aqueous MPD solution and then deposited GOQD/MPD onto the substrate to form a cushion layer followed by interfacial polymerization [170]. The prepared RO membrane is more hydrophilic and durable in filtration experiments. After incorporation of hydrophilic GOQD, the formation of the hydration layer adjacent to the PA layer could prevent the adhesion of hydrophobic foulants, thereby increasing the antifouling property of the membrane. Moreover, the incorporated GOQD also enhanced the chlorine resistance of the TFN membrane by protecting the PA polymer from active chlorine. They also prepared a composite nanofiller by blending a biocide silver phosphate (AP) with GOQD. The incorporation of GOQD/AP conferred the TFN membrane with strong hydrophilicity and more water transport nanochannels. Besides, the synergistic antibacterial effects of AP and GOQD imparted the TFN membrane with excellent bactericidal property [171]. Moreover, the hydrophilic and negatively charged surface of the modified membrane was beneficial for the anti-adhesion of BSA by the steric hindrance of the hydrogen layer and the electrostatic repulsion between the membrane and BSA.

Similarly, GQDs are also attractive for membrane modification. For example, Bi et al. used GQDs as nanofillers for the preparation of TFN membranes [183]. The incorporation of GQDs bound with the reaction monomers and lowered the crosslinking degree, resulting in a membrane with a smoother surface. The antifouling properties were improved after the incorporation of GQDs thanks to the smooth and hydrophilic membrane surface. Xu et al. embedded GQDs into the selective layer during interfacial polymerization [186]. Electroneutral, smoother membrane surface and thinner selective layer of the TFN membrane was observed, which resulted in higher water permeability and improved antifouling properties. In addition, the covalent bonds between GQDs and PEI contributed to the stable filtration performance of the membrane.

In addition, other carbon nanomaterials, such as hydrophilized ordered mesoporous carbon (H-OMC), have also been investigated to incorporate into the PA layer of the RO membrane [172]. The hydrophilic property and porous structure of H-OMC enhanced the water flux of the TFN membrane. Meanwhile, better antifouling property of the fabricated TFN membrane was achieved by the electrical properties and hydrophilicity of the modified PA layer after the introduction of H-OMC.

Overall, incorporation of carbon based nanomaterials into the selective PA layer of RO membranes can enhance the water permeability of the membrane thanks to the hydrophilic membrane surface and additional water transport pathways (channels). Furthermore, the smoother, and more hydrophilic membrane surfaces after the modification by carbon based nanomaterials are favorable for antifouling properties. The shape edges of carbon nanomaterials also render the TFC RO membranes with better antibacterial activity. However, the difficulty in controlling aggregation of the nanomaterials, defects in the thin PA layer, the limited thickness of the PA layer, and nanoparticle leaching after interfacial polymerization should be carefully considered in practical applications. More investigations on these issues are highly recommended for future research.

#### *4.2.3. Silica based nanomaterials*

Silica based nanomaterials, such as zeolites [187, 188], non-permeable silica nanoparticles [189] and porous silica nanospheres [190, 191] have been used to develop antifouling membranes due to their hydroxyl groups and active sites [190, 192, 193]. Meanwhile, most silica based nanomaterials are porous. The porous structures of silica based nanomaterials also expect to increase the membrane water permeability [187, 194].

Ang et al. synthesized silica nanoparticles with varying sizes of 50, 200, and 500 nm, and incorporated them into the PA layer to prepare TFN membranes during interfacial polymerization [195]. The results showed that the membrane surface roughness of the TFN membranes was larger than that of the pristine TFC membrane, and the introduced hydrophilic silica nanoparticles significantly strengthened the membrane hydrophilicity, leading to higher flux recovery ratios and thus enhanced antifouling properties. They also investigated influences of hollow silica nanoparticles with various shapes and dimensions on the performance of TFC membranes [196]. They found that the spherical silica nanoparticles were more suitable for the modification of TFC membranes, owing to the highest separation performance of the membrane compared with other cubic, or rod-like hollow silica nanoparticles. More importantly, because of the strong hydrophilicity, the spherical silica nanoparticles also enhanced antifouling properties to both positively charged cetyltrimethylammonium bromide (CTAB) foulant and negatively charged BSA foulant.

Most TFN RO membranes with higher permeability and antifouling performance are related to hydrophilic nanocomposites. However, in nature, water permeates faster in hydrophobic pores (e.g. aquaporin) due to lower affinity (friction force) between water and the hydrophobic wall of the pore. Methyltrichlorosilane ($MeSiCl_3$) is an interesting silica based nanomaterial with hydrophobic nanochannels. Shen et al. reported an antifouling TFN membrane prepared by interfacial polymerization of aqueous amine and organic methyltrichlorosilane/acyl chloride solutions [197]. They attributed the increased water flux and salt rejection to the hydrophobic nanochannels of $MeSiCl_3$, which could reduce the friction force between water molecules and nanochannels and facilitate the mass transfer. Meanwhile, the prepared TFN membrane showed improved antifouling property compared with the control TFC membrane.

The nanofillers discussed above mostly belong to inorganic nanomaterials. The polymer chains generally have poor compatibilities with inorganic nanomaterials. As a result, interfacial defects between polymers and inorganic nanofillers occur, lowering the membrane selectivity [86]. In addition, the incorporated nanofillers in TFN membranes are prone to leach into the solution, resulting in secondary pollution during water treatment.

### *4.2.4. Polymer based nanomaterials*

Surface modification/functionalization of nanofillers is an effective strategy to enhance the compatibility between the fillers and polymers [198, 199]. Endowing organic segments and chemical groups to the nanofillers are desirable to improve the compatibility and stability of the composite membranes. Zhu et al. utilized zwitterions grafted GO as nanofillers to prepare composite membranes [200]. Surface modification of GO promoted the dispersion and the interfacial compatibility of nanofillers, improving the homogeneity of the composite membranes. Hence, the modified composite membrane presents higher selectivity and permeability. In addition, the favorable effect on membrane hydrophilicity and surface roughness led to better antifouling properties.

Because of the better compatibility between organic nanomaterials and PA polymers, recently polymer nanoparticles have attracted growing interest in membrane development. Compared with the inorganic nanomaterials for TFN membranes, polymer nanoparticles are more compatible with the PA chains [201]. Apart from the excellent compatibility, organic nanomaterials are prone to form strong bonds with the chains of PA, which is favorable for the stability of the composite membrane. Zwitterionic monomer N-aminoethyl piperazine propane sulfonate (AEPPS) has been added into aqueous MPD solution to react with TMC via interfacial polymerization to fabricate zwitterionic TFC RO membranes [202]. The surface hydrophilicity and antifouling properties of the modified membranes were greatly improved after introducing AEPPS into membranes. Jeon et al. designed a star-shaped polymer and incorporated it into the PA layer for preparation of RO membrane [203]. The prepared RO membrane displayed improved permeability owing to the thinner selective layer, and lower fouling tendency due to the smoother surface and higher surface charge density.

Zwitterionic colloid nanoparticles were added into aqueous MPD solution to prepare TFN membranes via interfacial polymerization, and the prepared membrane showed enhanced antifouling properties due to the improved hydrophilicity and negative charge density of the membrane surface [93]. Liao et al. introduced organic polypyrrole nanospheres into the PA layer of RO membranes via dispersing the fillers into the organic phase [86]. After the incorporation of organic polypyrrole, the water permeability and antibacterial property of the membrane significantly improved because of the positive charge of the embedded nanospheres. Liao et al. also prepared hydrophilic and hollow nanocubes (HHNs) via etching ZIF-8 with tannic acid, and introduced the HHNs into the PA layer during interfacial polymerization [204]. Compared with the hydrophobic and positively charged ZIF-8, the highly hydrophilic and negatively charged HHNs significantly enhanced the membrane hydrophilicity and charge property, leading to weakened adhesion and strengthened electrostatic repulsion of the surface to hydrophobic and negatively charged pollutants (Fig. 9ab). Therefore, the prepared TFC membrane had improved antifouling performance (Fig. 9cd). Most recently, Liao et al. further modified the membrane hydrophilicity and charge property by introducing resorcinol-formaldehyde nanobowls into the PA layer of the TFC membrane, which reduced the flux decline during filtrating feed solution containing organic pollutants [205].

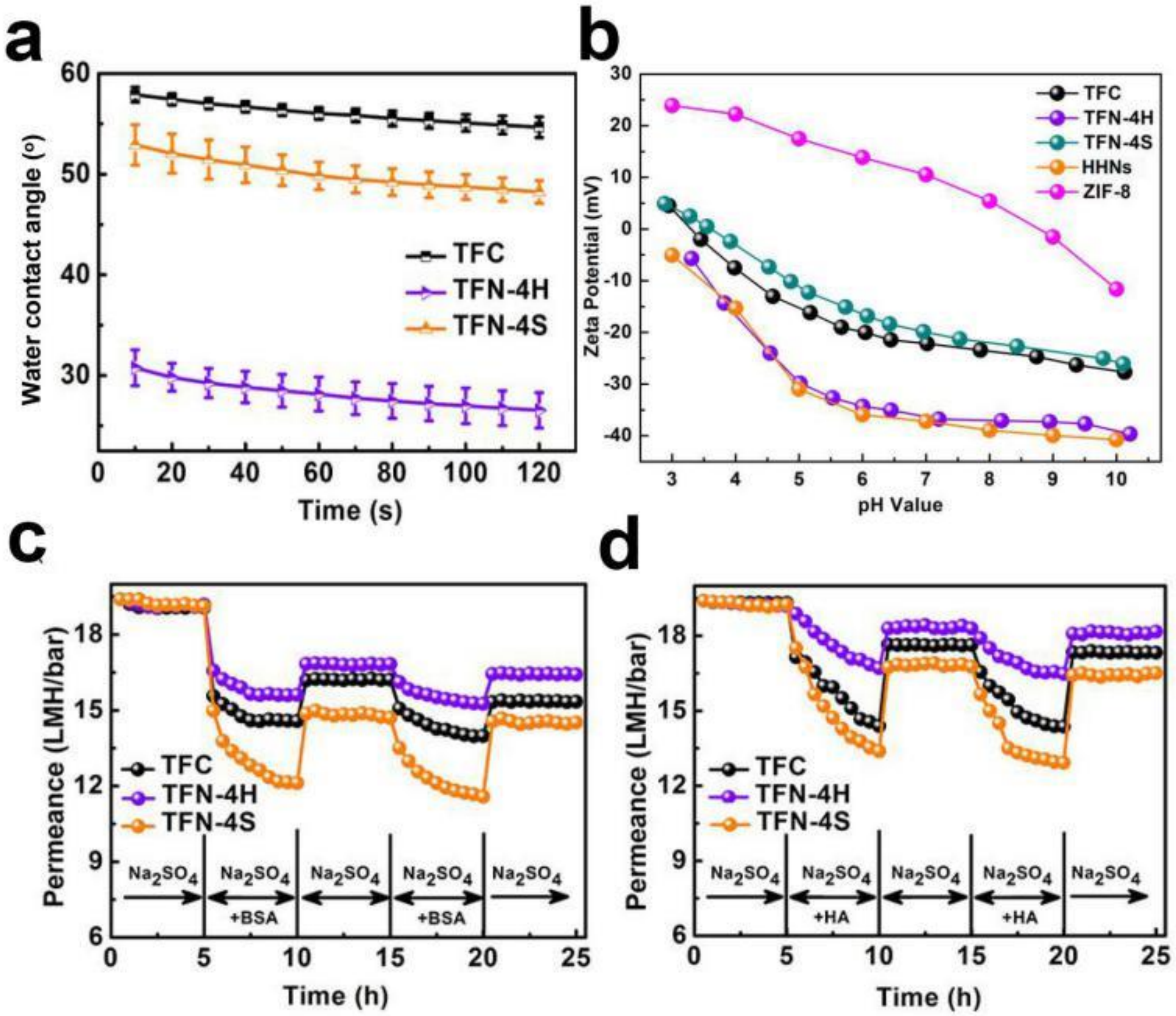

Fig. 9. (a) Water contact angles, (b) zeta potential properties, (c) long-term filtration performance using 1 g/L $Na_2SO_4$ and 1 g/L humic acid solution as the feed, and (d) using 1 g/L $Na_2SO_4$ and 1 g/L BSA solution as the feed [204]. TFN-4H: the thin film nanocomposite membrane prepared by adding 0.04 wt% hollow nanocubes into the organic solution during interfacial polymerization; TFN-4S: the thin film nanocomposite membrane prepared by adding 0.04 wt% solid ZIF-8 into the organic solution during interfacial polymerization.

Apart from the nanofillers mentioned above, some other nanofillers have also been reported for elevating the antifouling property of RO membranes. Dong et al. prepared two different TFN RO membranes by incorporating two oppositely charged nanoclays (a cationic clay: montmorillonite and an anionic clay: layered double hydroxide) into the PA layers [206]. Interestingly, both TFN membranes showed increased hydrophilicity, improved desalination performance and better fouling resistance to proteins, cationic surfactants, and natural organic matters, although they had different negative charge densities on the membrane surfaces.

### *4.2.5. Remarks on incorporating additives*

Table 3. Comparison of various parameters of the four types of nanofillers used for TFC RO membrane modification during interfacial polymerization.

| Parameters | Ranking of different nanofillers | | | |
|---|---|---|---|---|
| | Metals and metal oxides | Carbon based | Silica based | Polymer based |
| Antifouling properties | * | *** | ** | ** |
| Separation (flux and rejection) performance | * | *** | *** | ** |
| Robustness/compatibility | * | ** | * | *** |
| Simplicity of preparation | *** | ** | ** | * |
| Leaching and its environmental risks | * | ** | *** | *** |
| Cost | *** | * | ** | * |
| Research popularity | * | *** | ** | *** |
| Commercialization | * | ** | ** | * |
| Overall performance | 12* | 18* | 17* | 16* |

*** means beneficial property (high or low); ** means intermediate; * means negative property (high or low).

Table 3 compares different parameters of the four types of nanofillers used for TFC RO membrane modification during interfacial polymerization. Considering all the parameters of these nanofillers, the estimated ranking in terms of potential could be: carbon based > silica based > polymer based > metals and metal oxides. Metals and metal oxides are easy to prepare, and have relatively low costs but also have low popularity likely due to their high leaching potential and low content of hydrophilic groups; insufficient hydrophilic groups adversely affect their antifouling properties, separation performance and robustness in the polymer membrane. Carbon based nanofillers often lead to excellent antifouling properties and separation performance due to their rich and diverse hydrophilic functional groups. The great diversity of carbon based nanomaterials makes them attract significant research popularity. However, costs of emerging carbon based nanomaterials are usually not low. Silica based nanofillers often provide high separation performance due to their intrinsic pores. They face similar low compatibility with polymers and thus leaching issues with metals and metal oxides. However, silica based nanofillers have lower environmental risks after leaching compared with metals and metal oxides as well as carbon based materials. Polymer based nanofillers have high compatibility with the PA layer and thus low leaching risks, but their costs are typically high due to the complex preparation procedure. Recently, polymer based materials have attract growing research interest for engineering TFC RO membranes [198, 199]. Although all of these nanofillers display improved antifouling performance for RO membranes to some extent in lab-scale research, most of them have very low commercialization potential in the current stage. "Don't start a business to commercialise a technology just because it seems great in the lab" [207] as lessoned by Professor Eric Hoek who commercialised his TFN RO membranes (Nano$H_2O$™) containing silica based nanofillers [208].

When incorporating nanomaterials into the very thin PA layer (50 - 200 nm) of TFN membranes, there should be some requirements for the nanomaterials, such as particle sizes, loadings, density of hydrophilic functional groups and compatibility between the nanomaterials and the polymers. However, these questions have not been well answered. A general guideline on these parameters for engineering next generation of high performance antifouling RO membranes should be developed. Most recently, Yeo et al. attempted to reveal the effects of nanofiller parameters, e.g. particle size, pore size and loading on TFN membrane performance by surveying 31 journal papers via machine learning [209]. They concluded that porous nanoparticles performed better than nonporous ones and the ideal situations are hydrophilic porous nanofillers with pore sizes between 5-7 Å, particle sizes ~150 nm, and loadings ~0.1 wt%. This conclusion was reached based on a relatively small data set (31 journal papers) and only applicable for some nanoporous particles. One of the challenges in such a comparison is that fouling protocols tend to differ between researchers. In the future, more extensive studies in this area should be done since there are numerous nanomaterials with diverse shapes, dimensions and properties available for membrane development.

### *4.3. Post (surface) modification after interfacial polymerization*

Surface modification of existing (commercial or lab-prepared) membranes is another widely studied method to develop antifouling RO membranes [210]. Various physical and chemical post modification methods, such as surface adsorption [211], plasma treatment [212], radical grafting [213] and chemical coupling [214], have been employed to enhance the fouling resistance of RO membranes [129]. In physical modification, the coating materials attach to the active layers of RO membranes via electrostatic interaction, hydrogen bonding or van de Waals force [6]. These interactions are relatively weak, leading to unstable coatings in long-term operations. Therefore, physical modification is often combined with chemical modification. For example, plasma treatment is a physical irradiation method for surface modification, while it is often used together with chemical modification (e.g. graft polymerization) for RO membrane surface engineering [215, 216]. In chemical modification, the functional group of the coating material reacts with those of the active layer by covalent bonding and thus the modified membrane has better chemical and structural stabilities.

The surfaces of most commercial RO membranes have been treated to improve their performances (e.g. antifouling and antioxidation) [118]. Most commercial RO membranes also have preservatives (e.g. glycerin) to prevent them from undesirable reactions in air (e.g. oxidation). Therefore, these membranes are often soaked in or washed with deionized water or chemical agents (e.g. isopropanol) for some time to remove these preservatives or destroy the extra coating before further surface modification [217]. For the lab-prepared TFC RO membranes, these actions are not required since there is no coating after interfacial polymerization.

Four types of materials, including inorganic nanomaterials, organic polymers, hybrid inorganic/organic materials, and non-metal based biocides have been employed to modify RO membrane surfaces for fouling reduction. Typical inorganic materials are similar to those that have been used during interfacial polymerization for TFC RO membranes, such as metals and metal oxides, mineral salts, carbon based nanomaterials, and polymer/nanoparticle composites. However, inorganic materials often have relatively low compatibilities with the PA surface, and it is not easy to form uniform stable layers on the smooth dense PA surface. Therefore, organic polymers are more desirable for antifouling surface modification for RO membranes considering their practicability and long-term stability. These widely used organic polymers include ordinary hydrophilic polymers, zwitteronic polymers, quaternary ammonium polymers, hyperbranched polymers, amphiphilic polymers, and thermo-responsive polymers. Next, we will briefly introduce these inorganic nanomaterials and organic polymers.

### *4.3.1. Inorganic nanomaterials*

Table 4. Summary of inorganic nanomaterials used for surface antifouling modification of TFC membranes.

| Modification materials | Modification methods | Target fouling | Remarks | Refs. |
|---|---|---|---|---|
| Ag nanoparticles | Dip-coating by adsorption and reduction. | Biofouling | Improved biofouling resistance in real desalination plant test; Ag-modified spacer had more lasting antibacterial performance. | [218] |
| Ag nanoparticles | $AgNO_3$ was in situ reduced into Ag by $NaBH_4$ | Biofouling | Reduced water flux; increased surface roughness; improved biofouling resistance. | [151] |
| Ag nanoparticles | Covalent bonding by a bridging agent cysteamine. | Biofouling | Higher water flux but slightly lower salt rejection due to the effects of ethanol solution; enhanced biofouling resistance. | [81] |
| Ag nanoparticles | Surface grafted through hydrolysis, ion exchange and thermal reduction. | Biofouling and organic fouling | Rougher and more hydrophobic surface; improved anti-biofouling and anti-organic fouling properties. | [219] |
| Ag nanoparticles | In situ reduced by PDA. | Biofouling | More hydrophilic; slightly reduced water flux; improved salt rejection; enhanced biofouling resistance. | [153] |

| | | | | |
|---|---|---|---|---|
| Ag-decorated silica | Covalent bonding by cysteamine. | Biofouling | Maintained water flux and salt rejection; Significantly enhanced antibacterial properties against *E. coli*, *Pseudomonas aeruginosa* and *Staphylococcus aureus.* | [80] |
| TA-Fe-Ag | In situ reduced by TA-Fe | Biofouling | Increased hydrophilicity; increased water flux and salt rejection; 100% bacteria mortalities against *E. coli* and *B. subtilis.* | [220] |
| Cu | In situ reduced by $NaBH_4$. | Biofouling | Slightly increased water and salt permeability with comparable surface properties; 90% reduction of live *E. coli.* | [152] |
| Cysteamine- and GO-mediated Cu | $CuSO_4$ was in situ reduced into Cu by $NaBH_4$, during which bridging agents cysteamine and GO were used. | Biofouling | More hydrophilic; slightly reduced water flux; comparable salt rejection; significantly improved antifouling performance. | [217] |
| $Cu(OH)_2$ | Chelation with GO and mineralization under alkanes. | Organic fouling | Smoother and more hydrophilic membrane surface; higher flux with comparable rejection; weakened foulant deposition. | [221] |
| Silica nanoparticles | Silica was functionalized with APTMS, and then dip-coating. | Organic fouling and biofouling | Improved hydrophilicity, organic fouling and biofouling resistance; reduced water flux; comparable salt rejection. | [222] |
| GO nanosheets | Layer-by-layer assembly of GO and aminated-GO. | Organic fouling | More hydrophilic and smoother; increased water flux; comparable salt rejection; improved fouling and chlorine resistance. | [223] |
| $TiO_2$ and GO | Layer-by-layer self-assembly by hydrogen bonding and physical adsorption. | Biofouling | Improved hydrophilicity and biofouling resistance; the modified membrane with layer number $\leqslant 6$ showed increased water flux and salt rejection. | [77] |
| Photocatalytic $TiO_2$ | Self-assembly through coordination and H-bond interaction with the COOH group by dip-coating. | Biofouling | Reduced water flux; increased salt rejection; photocatalytic bactericidal effect. | [224] |
| Catalytic CuO nanoparticles | PEI-assisted coating | Colloidal fouling, organic fouling and biofouling | Bubble generation and oxidation reduced colloidal fouling, organic and biofouling. | [225] |
| $BaSO_4$ | Surface coating by dip-coating. | Organic fouling | Uniformly distribution of $BaSO_4$; enhanced hydrophilicity and charge; elevated permeability and selectivity; reduced foulant deposition. | [226] |

PDA: polydopamine; TA: tannic acid; GO: graphene oxide; PEI: polyethylenimine; APTMS: 3-aminopropyl trimethoxysilane.

As summarized in Table 4, a number of inorganic nanomaterials, including Ag [151], Cu [152], Ag- and Cu-based nanomaterials [217, 220], $Cu(OH)_2$ [221], CuO [225], silica [222], $TiO_2$ [224], GO [223] and $BaSO_4$ [226] have been used for surface antifouling modification of TFC RO membranes. Most of these inorganic nanomaterials have biocidal properties. Therefore, they are often used to improve the biofouling resistance of the surfaces of TFC RO membranes, although they may also increase the resistance to organic fouling and colloidal fouling of RO membranes [225].

Most surface antifouling modifications of RO membranes with metal nanoparticles are realized by the in situ generation methods. Ben-Sasson *et al.* immersed a commercial TFC RO membrane into silver nitrate ($AgNO_3$) solution and left a thin layer of solution on the membrane surface (Fig. 10a). Subsequently, the sodium borohydride ($NaBH_4$) solution was poured onto the top layer of the membrane for *in situ* coating silver [151]. The final membrane was imparted with excellent antibacterial activity. Similarly, they introduced Cu nanoparticles onto the RO membrane surface via the same strategy [152]. The antibacterial activity of the modified RO membrane was strengthened, and the water permeability and selectivity of the composite membrane were less affected. Yang *et al.* pre-coated a commercial RO membrane with polydopamine (PDA) (Fig. 10b), and the modified membrane was subsequently soaked in $AgNO_3$ solution for *in situ* reduction of silver nanoparticles with PDA [227]. The thickness of the coated silver (Ag) nanoparticles was around 15 nm. After surface modification, salt rejection significantly enhanced with comparable water flux. In addition, the modified RO membrane showed excellent antimicrobial properties.

Dong *et al.* coated a commercial RO membrane with tannic acid (TA)-Fe-PEI complex, and then the modified membrane was immersed into silver ammonia environment for *in situ* generation of Ag nanoparticles (Fig. 10c) [220]. Owing to the decorations of the nano-Ag, the fabricated membrane was furnished with elevated permeability and higher anti-biofouling property. Besides, the force between TA and silver is also favorable for alleviating the leaching of Ag. Compared with the post-synthesized method, the *in-situ* formation of metal nanoparticles on the membrane surface generally leads to smaller particle sizes and uniform dispersion of the nanobiocides, which is more effective for the utilization of nanoparticles. Moreover, the *in-situ* strategy avoids the agglomeration of the nanoparticles, which could reduce the formation of unselective defects in the selective layer.

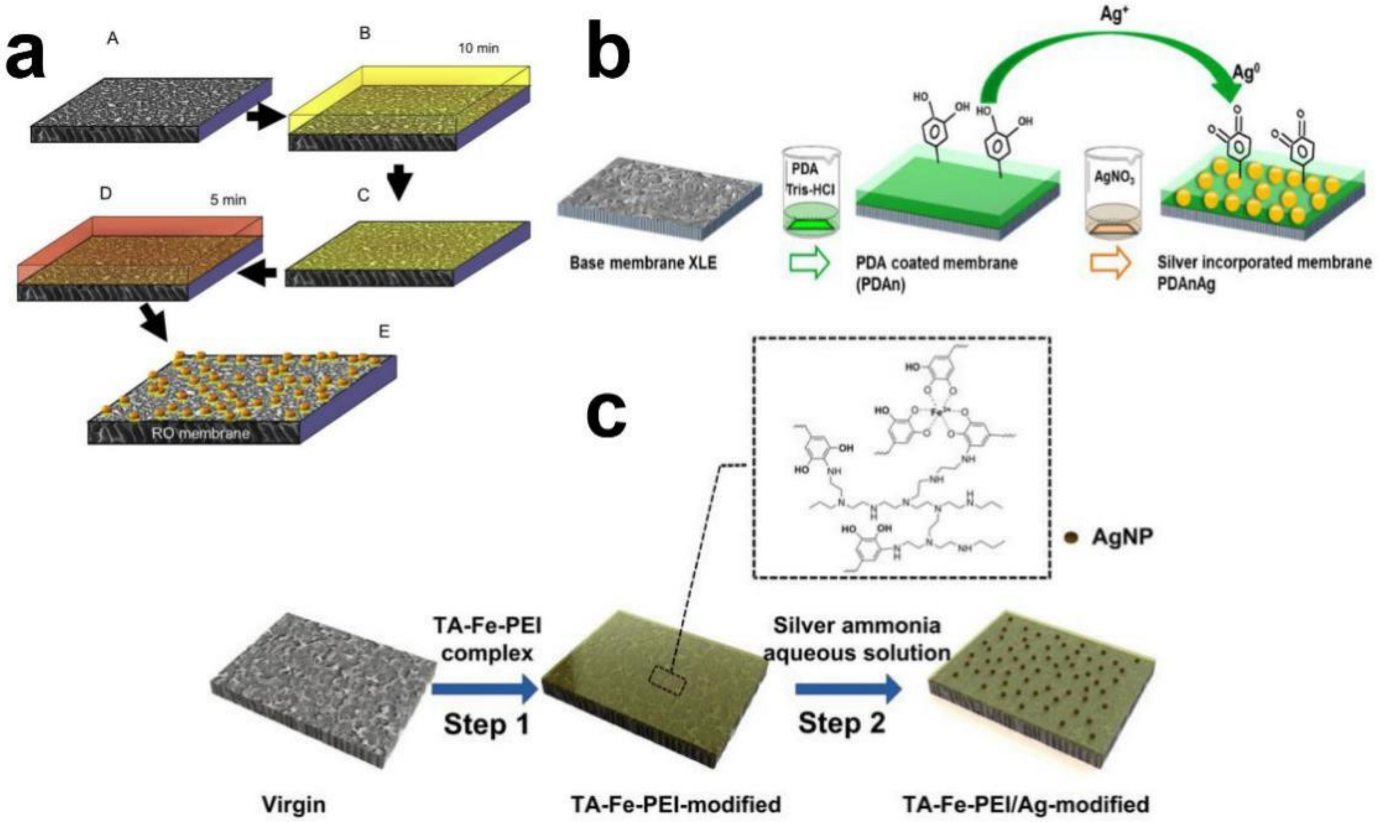

Fig. 10. Schematic diagram of in situ modifying RO membrane: (a) schematic diagram of in situ formation of Ag-NPs on a TFC RO membrane - first, the pristine TFC membrane (A) is covered by $AgNO_3$ solution (B); then, the $AgNO_3$ solution is removed leaving a thin layer of the AgNO3 solution on the surface (C); next, the membrane is contacted with $NaBH_4$ solution (D) to form the Ag-modified membrane (E) [151]. (b) In situ formation of Ag NPs on a TFC membrane [227]. (c) In situ immobilization of Ag NPs on the RO membrane surface [220].

Guha et al. anchored catalytic CuO nanoparticles on a commercial TFC RO membrane surface by the bioinspired PDA polymer as shown in Fig. 11 [225]. The coated CuO nanoparticle layer generated hydroxyl radicals (HO·) and $O_2$ that were able to degrade and sweep away the deposited organic foulants on the membrane surface by the Fenton-like reaction between the CuO and hydrogen peroxide. Besides, the formation of *E. coli* biofilm on the membrane surface was also inhibited by the introduced CuO nanoparticles. However, the exposed CuO nanoparticles tend to leach from the PA layer under crossflow shearing because of the weak interaction between CuO and the membrane surface. Also, the antifouling process consumes new chemical $H_2O_2$, and the catalytic oxidation reaction would likely damage the membrane in long-term operation. Therefore, imparting RO membranes self-cleaning and thus antifouling properties by using catalytic agents may not be feasible in practical applications.

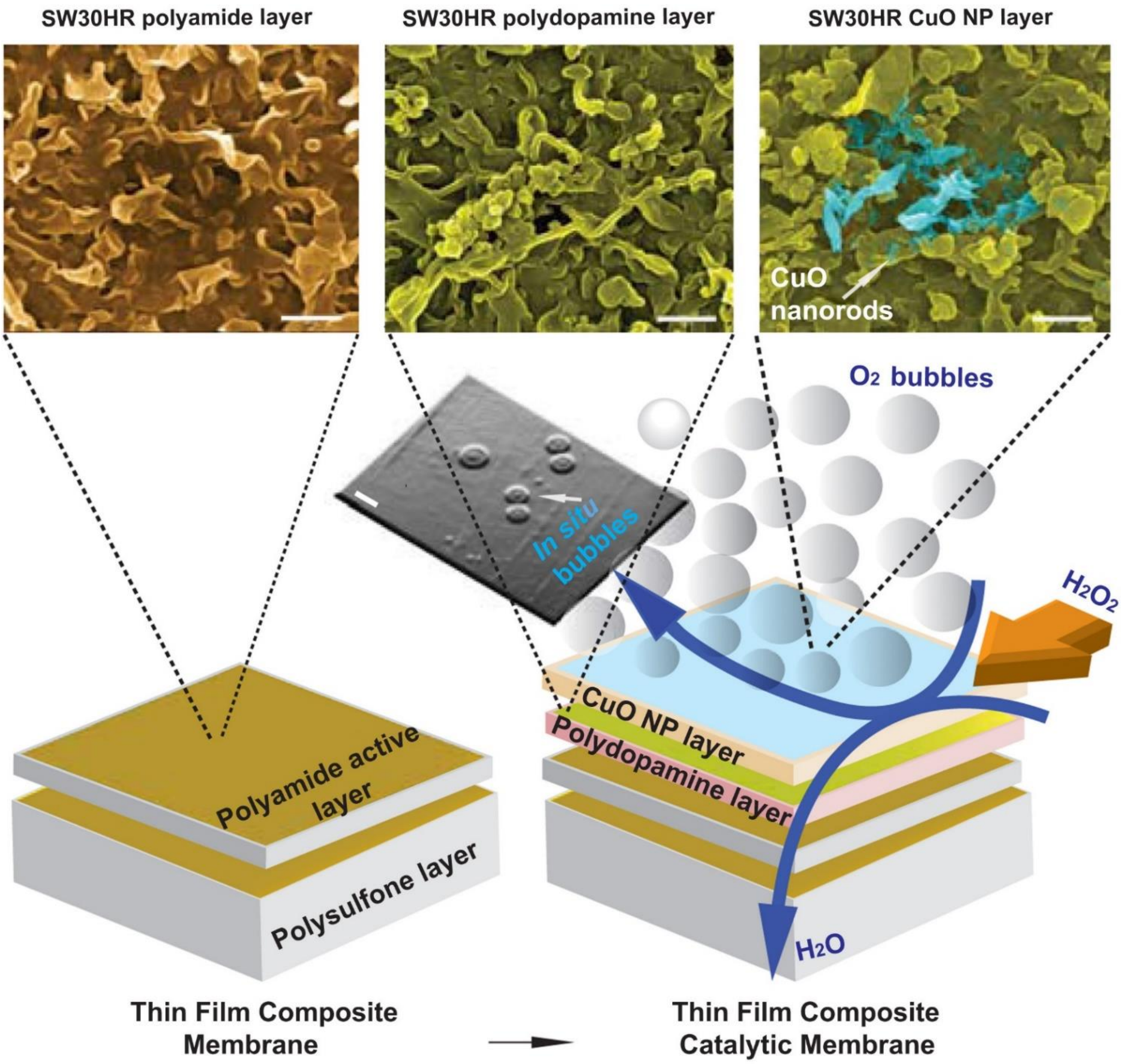

Fig. 11. Schematic of catalytic TFC RO membrane assembly and antifouling mechanism. The active polyamide layer was coated with polydopamine. Cupric oxide (CuO) nanoparticles were thereafter deposited on the polydopamine layer. Hydrogen peroxide ($H_2O_2$) was added to this membrane which on dissociation to molecular oxygen and water, generated in situ bubbles on the membrane surface sweeping away deposited foulants and disrupting concentration polarization. The SEM images have scale bars of 500 nm and the in situ bubbles image has scale bar of 150 µm.

Although various inorganic nanoparticles have been used for surface antifouling modification of RO membranes, the long-term stability of the coated nanoparticles on the membrane surface has not be well studied. Because the dense surfaces of RO membranes are much smoother than other pressure-driven (e.g. UF and NF) membranes, it is very challenging to coat a uniform, stable, long-lasting, fouling resistant layer with inorganic nanoparticles on the RO membrane surface, particularly under the requirement of not sacrificing water permeability of the membrane. This may be the reason that few commercial RO membranes have antifouling surfaces modified with inorganic nanomaterials.

### *4.3.2. Organic polymers*

Compared with inorganic nanomaterials, organic polymers are more desirable for RO membrane surface modification due to the better compatibility between the polymer chains. These polymers can be classified into four types: (1) ordinary hydrophilic polymers, (2) zwitteronic polymers, (3) biomimetic polydopamine (PDA), and (4) other polymers (e.g. hyperbranched polymers, thermo-responsive polymers, and amphiphilic polymers). These polymers have been coated onto RO membrane surfaces for fouling reduction by various methods, such as layer-by-layer assembly [228], contact coating (either via dip-coating or filtration coating) [229], polymerization [213], crosslinking [230] and combination of different techniques [231]. The PA membrane surfaces have unreacted carboxylic acid and amine groups that can be utilized for grafting. Grafting, refers to the addition of polymer chains onto a surface. Most of the chemical surface modification methods belong to surface grafting that can be induced by various mechanisms, such as UV, plasma, redox, cationic, anionic, free radical, enzyme, chemical vapor deposition, and atom transfer radical polymerization (ATRP) [23]. These polymer types, surface modification methods and their performance are summarized in Table 5. Next, we briefly discuss these typical polymers.

Table 5. Summary of organic polymers used for surface antifouling modification of TFC membranes.

| Modification materials | Modification methods | Target fouling | Remarks after surface modification | Refs. |
|---|---|---|---|---|
| PEI | Electrostatic self-assembly. | Organic fouling | Increased hydrophilicity and salt rejection; reduced water flux; improved fouling resistance with cationic surfactants. | [232] |

| | | | | |
|---|---|---|---|---|
| PEI | Carbodiimide-induced grafting with PEI. | Organic fouling | Changed the membrane from negative charge to positive charge; more hydrophilic; little change in surface roughness and salt rejection; reduced water flux; improved fouling resistance. | [233] |
| Poly(GHPEI) | PDA immobilization. | Biofouling and organic fouling | More hydrophilic and smoother; Lower flux; increased salt rejection; improved biofouling and organic fouling resistance. | [234] |
| Tobramycin and PAA | Layer-by-layer assembly. | Organic fouling and biofouling | Slightly enhanced water flux and salt rejection; significantly improved performance in organic fouling and biofouling resistance. | [228] |
| Polyelectrolyte (PSS and PAH) | Layer-by-layer assembly. | Organic fouling | More hydrophilic and smoother; increased salt rejection; reduced water flux; improved fouling resistance; the optimal layer number is 4. | [235] |
| PVP onto a metal-polyphenol precursor layer | Two-step dip-coating: self-assembly of TA and Fe(III) ions; PVP was immobilized by PEI. | Organic fouling | Slightly reduced water flux; unchanged salt rejection; improved organic fouling resistance; stable performance for 15 days. | [229] |
| ADMH | Free-radical graft polymerization | Biofouling | Improved water flux; slightly reduced salt reject; enhanced chlorine and biofouling resistance. | [213] |
| PVA | Thermally initiated free radial grafting | Organic fouling | More hydrophilic, smoother and less charged; increased salt rejection and slightly reduced water flux; improved fouling and chlorine resistance. | [236] |
| Sulfonated PVA | Contact coating and thermal crosslinking. | Organic fouling | More hydrophilic, smoother and more negatively charged; increased salt rejection and reduced water flux; improved fouling resistance. | [231] |
| PVA and cationic PHMG | Dispersion coating and thermal crosslinking. | Biofouling | Coating layer thickness: 100 - 250 nm; more hydrophilic and smoother; increased salt rejection and reduced water flux; improved biofouling resistance. | [214] |
| PVA and MPTES | Organic-inorganic hybrid gel fabricated by PVA and MPTES; coating and then thermal crosslinking. | Organic fouling | More hydrophilic, smoother and less charged; increased salt rejection and reduced water flux; improved fouling resistance. | [237] |
| PVAm | Surface grafting via amide bonding. | Organic fouling | Reduced water flux but increased salt rejection; improved antifouling performance. | [238] |
| Thermo-responsive polymer | Surface coating with poly(N-isopropylacrylamide-co-acrylamide) copolymer by hydrogen bonding | Organic fouling | Unchanged salt rejection; improved water permeability and fouling resistance. | [239] |

| | | | | |
|---|---|---|---|---|
| ASA, DEA and PIP | In-situ surface grafting small molecular monomers with amino groups. | Organic fouling | Unchanged surface roughness; increased hydrophilicity; slightly increased salt rejection and reduced water permeability; increased fouling resistance. | [240] |
| P(MDBAC-r-Am-r-HEMA) copolymer | Dip-coating followed by GA crosslinking. | Organic fouling and biofouling | More hydrophilic; rougher surface; slightly increased salt rejection; reduced water flux; less flux decline during BSA fouling; less bacterial adhesion. | [106] |
| P(ADMH-co-VAm) copolymer | Contact coating. | Biofouling | Similar rejections; water flux increased first and then decreased with increasing coating solution concentration; improved fouling resistance; coating layer thickness: ~ 8 nm. | |
| PEG | Surface grafting with aminopolyethylene glycol monomethylether (MPEG-$NH_2$) as the monomer. | Organic fouling | Increased surface roughness; reduced fouling indicated by less flux decline. | [241] |
| PEG | Surface grafting by crosslinker EGDMA. | Mineral scaling | Increased hydrophilicity; increased scaling resistance without organic matters in the feed; promoted $CaSO_4$ scaling if organic matters existed in the feed. | [242] |
| PEG acrylate | Layer-by-layer assembly. | Organic fouling | Increased surface hydrophilicity and roughness; reduced water flux; increased salt rejection; improved fouling resistance. | [243] |
| PEG derivatives | Carbodiimide-induced grafting. | Organic fouling | More hydrophilic and rougher; decreased water flux; unchanged salt rejection; improved fouling resistance. | [244] |
| SPM and PEGMA | Crossflow coating. | Fouling with real sea water. | PEGMA seemed to have a stronger anti-fouling effect than SPM; stable flux for 3 months. | [245] |
| PEGDE | Surface grafting | Organic fouling | Lower concentrations of higher molecular weight PEG caused better fouling resistance. | [123] |
| PEG-based hydrogels: PEGDA and PEGA | Surface crosslinking | Organic fouling | Reduced water flux; improved salt rejection and fouling resistance. | [230] |
| NIPAm and AA | Redox initiated graft polymerization of NIPAm followed by AA | Organic fouling | More hydrophilic; more negatively charged; slightly increased surface roughness and salt rejection; reduced water flux; less flux decline during BSA fouling. | [124] |
| PMAA and PAA | Plasma-induced graft polymerization | Mineral scaling, organic fouling and biofouling | More hydrophilic and smoother; improved water permeability and scaling resistance; unchanged salt rejection and organic fouling resistance; enhanced biofouling resistance. | [215, 216, 246] |

| | | | | |
|---|---|---|---|---|
| Triethylene glycol dimethyl ether (PEG-like) | Plasma polymerization | Organic fouling | More hydrophilic and rougher; slightly reduced water flux and salt rejection; improved fouling resistance. | [98] |
| Block copolymer of PEG and Nylon-6 | Dip-coating | Organic fouling | Significantly dropped water flux; comparable salt rejection; improved fouling resistance; increased fouling resistance was not sufficient to compensate for the flux reduction. | [247] |
| Silane | Dip-coating and quaternization | Biofouling | More hydrophilic and smoother; increased water flux; comparable salt rejection; improved biofouling resistance. | [248] |
| Silane coupling agents | Sol–gel process | Organic fouling | Less hydrophilic and rougher; significant flux drop; comparable salt rejection; less flux decline during fouling. | [249] |
| Sericin | In-situ deposition by cross-flow circulation. | Organic fouling | Smoother and more hydrophilic; increased salt rejection and reduced water permeability; increased fouling resistance. | [250] |
| Zwitterionic pSBMA | Grafting by surface-initiated ATRP. | Organic fouling | Unchanged salt rejection; significantly improved water flux (by ~65%) and fouling resistance (irreversible fouling reduced by ∼97%). | [121] |
| Zwitterionic coating | p(4VP-co-EGDA) co-polymerization via initiated chemical vapor deposition | Organic fouling; biofouling | Reduced water flux but slightly increased salt rejection; improved fouling resistance. | [42, 251] |
| Zwitterionic L-DOPA | Dip coating | Organic fouling | Improved water permeability and unchanged salt rejection; improved antifouling performance. | [252] |
| Zwitterionic amino acid L-cysteine | Covalent bonding by the thiol-ene reaction. | Organic fouling | Smoother and more hydrophilic surface; increased salt rejection; reduced water flux; less flux decline during organic fouling test. | [253] |
| Zwitterionic MPC | Grafting by surface-initiated ATRP. | Biofouling | Reduced water flux and salt rejection; improved biofouling resistance. | [254] |
| zwitterionic CBMA | Redox initiated graft polymerization of DMAEMA, followed by quaternization with 3-BPA. | Biofouling | Similar surface hydrophilicity and roughness; changed from negative charge to positive charge at pH7.0; increased water flux; comparable salt rejection; anti-adhesive and anti-microbial properties. | [255] |
| Zwitterionic PSVBP | Surface-initiated free radical polymerization. | Organic fouling | More negatively charged; increased hydrophilicity; less flux decline and improved cleaning during BSA fouling. | [256] |
| PDA assisted polyzwitterion (MPC-*co*-AEMA) | PDA coating; dip-coating in MPC-co-AEMA copolymer solution. | Biofouling | Neutrally charged surface; reduced water flux; comparable salt rejection; improved biofouling resistance. | [257] |
| HPOEM and zwitterionic carboxylated PEI | Dip coating, crosslinking with glutaraldehyde, and | Organic fouling | HPOEM-coated RO membranes showed salt-out effect and thus better fouling resistance in brackish water desalination; carboxylated PEI | [258] |

|  |  |  |  |  |
|---|---|---|---|---|
|  | PEI carboxylation. |  | coated membranes had salt-in effect and thus better fouling resistance in seawater desalination. |  |
| PDA | UV-accelerated PDA coating | Organic fouling | More hydrophilic and smoother surface; reduced water permeability; increased salt rejection; less flux decline under alginate fouling. | [259] |
| PDA | Surface deposition | Biofouling | Little change in hydrophilicity; reduced water flux; comparable salt rejection; improved biofouling resistance. | [260] |
| PDA and PDA-*g*-PEG | Contact coating | Organic fouling | PDA coating led to little flux decline; PDA-*g*-PEG coating led to significant flux decline; BSA adhesion reduction for the two coated membranes. | [261] |
| PDA-*g*-PEI | PDA coating followed by grafting of PEI. | Organic fouling and biofouling | More hydrophilic and rougher surface; reduced water permeability; comparable salt rejection; improved organic fouling and biofouling resistance. | [262] |
| Hyperbranched PAMAM | Spray coating | Organic fouling | Little change in surface roughness; less negatively charged; increased water flux; slightly reduced salt rejection; less flux decline during BSA fouling. | [263] |
| Thermo-responsive polymer P(NIPAM-co-Am) | Crossflow coating by hydrogen bonding. | Organic fouling | More hydrophilic; increased water flux and salt rejection; less flux decline during BSA fouling; higher efficiency at higher temperature. | [239, 264] |
| Amphiphilic MMA-HPOEM copolymer | The copolymer was synthesized by free radical polymerization; then dip-coating. | Organic fouling, biofouling. | Less negatively charged; reduced water flux; salt rejection was not reported; slightly increased fouling resistance. | [265] |
| Amphiphilic HEMA-*co*-PFDA copolymer | Initiated chemical vapor deposition | Organic fouling | More hydrophobic; large drop in water flux; salt rejection was not reported; the antifouling performance was not significant. | [266] |
| Amphiphilic HEMA-*co*-PFDA copolymers | Initiated chemical vapor deposition | Biofouling | More hydrophobic; rougher surface; comparable salt reject; large drop in water flux; reduced static bacterial adhesion. | [267, 268] |

PEI: polyethylenimine; Poly(GHPEI): poly(guanidine-hexamethylenediamine-PEI); PDA: polydopamine; PAA: poly(acrylic acid); PSS: Poly(sodium 4-styrenesulfonate); PAH: poly(allylamine hydrochloride); PVP: poly(N-vinylpyrrolidone); ADMH: 3-allyl-5,5-dimethylhydantoin; PVA: polyvinyl alcohol; PHMG: polyhexamethylene guanidine hydrochloride; MPTES: 3-mercaptopropyltrimethoxysilane; PVAm: polyvinylamine; ASA: amidosulfonic acid; DEA: diethanolamine; PIP: piperazine; P(MDBAC-r-Am-r-HEMA): poly(methylacryloxyethyldimethyl benzyl ammonium chloride-r-acrylamide-r-2-hydroxyethyl methacrylate); P(ADMH-co-VAm): poly(3-allyl-5,5-dimethylhydantoin-co-vinylamine); PEG: poly(ethylene glycol); EGDMA: ethylene glycol dimethacrylate; SPM: sulfopropylmethacrylate; PEGMA: PEG ester of methacrylic acid; PEGDE: poly(ethylene glycol) diglycidyl ether; PEGDA: poly(ethylene glycol) diacrylate; PEGA: poly(ethylene glycol) acrylate; NIPAm: N-isopropylacrylamide; PMAA: poly(methacrylic acid); PAAm: poly(acrylamide); pSBMA: poly(sulfobetaine methacrylate); ATRP: atom transfer radical polymerization; p(4VP-co-EGDA): poly(4-vinylpyridine-co-ethylene glycol diacrylate); L-DOPA: amino acid 3-(3,4-dihydroxyphenyl)-l-alanine; MPC: methacryloyloxyethyl phosphorylcholine; CBMA: carboxybetaine methacrylate; DMAEMA: N,N-dimethylaminoethyl methacrylater; 3-BPA: 3-bromopropionic acid; PSVBP: poly (4-(2-sulfoethyl)-1-(4-vinylbenzyl) pyridinium betaine); AEMA: 2-aminoethyl methacrylate; PAMAM: poly(amido amine); P(NIPAM-co-Am): poly(N-isopropylacrylamide-co-acrylamide); MMA: methyl methacrylate-hydroxy; HPOEM: hydroxyl poly(oxyethylene) methacrylate homopolymer; HEMA: hydroxyethyl methacrylate; PFDA: perfluorodecyl acrylate.

*Ordinary hydrophilic polymers*. Several ordinary hydrophilic polymers, including PVA, poly(ethylene glycol) (PEG), acrylic acid (AA), polyacrylic acid (PAA), polyethylenimine (PEI), and their derivatives, have been used for antifouling surface modification of RO membranes. PVA is a water-soluble, neutrally charged, hydrophilic polymer with rich hydroxyl groups (-HO) and water-loving and film forming properties. Therefore, PVA and its derivatives (e.g. sulfonated PVA and polyvinylamine) have been used to modify the RO membrane surface for fouling minimization (Table 5) [236-238]. PEG is another common water-soluble, uncharged polymer having flexible long chains, large exclusion volume, and strong ability to prevent the adsorption of hydrophobic or organic molecules onto the membrane surface. PEG, PEG-based polymers/hydrogels and PEG-like polymers are also popular in RO membrane surface modification for fouling reduction [98, 123, 230, 241, 242, 244].

AA is the simplest unsaturated carboxylic acid and it often reacts with other materials to form new hydrophilic agents, such as PAA [215, 216, 246] and AA-grafted CNTs [269] for antifouling modification. PAA is a hydrophilic anionic polymer having hydroxyl groups (-HO), while typical PEI is a branched cationic polymer with primary, secondary and tertiary amine bonds rich in amine groups ($-NH_2$). Because of their charge properties, PAA and PEI have been employed for membrane antifouling modification or functionalization via electrostatic interaction (e.g. layer-by-layer assembly) [228, 232, 270]. Hydrophilic poly(sodium 4-styrenesulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) have also been used to modify TFC RO membranes by layer-by-layer assembly for fouling reduction [235]. However, as a physical approach the assembly modification based on relatively weak electrostatic interaction cannot provide long-lasting stability for the prepared membranes, which may limit their applications for practical desalination and water treatment. Utilizing the hydrophilic and cationic properties, PEI has also been grafted onto negatively charged TFC RO membrane surfaces to prepare positively charged antifouling membranes by carbodiimide-induced grafting [233]. Sericin, a hydrophilic natural polymer with groups of hydroxyl, carboxyl and amino groups, has also been used for surface modification of RO membranes by dip-coating followed by in situ cross-linking with glutaraldehyde (GA) [271].

*Zwitterionic polymers* with the same number of cations and anions along their polymer chains have been widely used for various antifouling membrane developments [90, 272]. Zwitterionic polymers endow membrane surface with antifouling properties mainly through two mechanisms as illustrated in Fig. 12 [40]. The first mechanism is to form a hydration layer via electrostatic interactions on the membrane surface. Compared with PEG and its derivatives, zwitterionic polymers can bond with much more water molecules for each unit (Fig. 12ab) and thus form denser and thicker hydration layers on the membrane surface. Therefore, zwitterionic polymers may perform better than PEG-based polymers in repelling bio-foulants [273]. Another mechanism is the steric hindrance effect (Fig. 12c). Zwitterionic polymer chains act as brushes with high mobility and hydrophilicity on the membrane surface, which tend to maintain a swelling state and thus repulse foulants from attaching to the membrane surface. The antifouling properties of zwitterionic polymers are closely related to their charge distribution. The zwitterions with balanced charges and minimized dipoles can fully bind water molecules and repel charged proteins via electrostatic interactions [274].

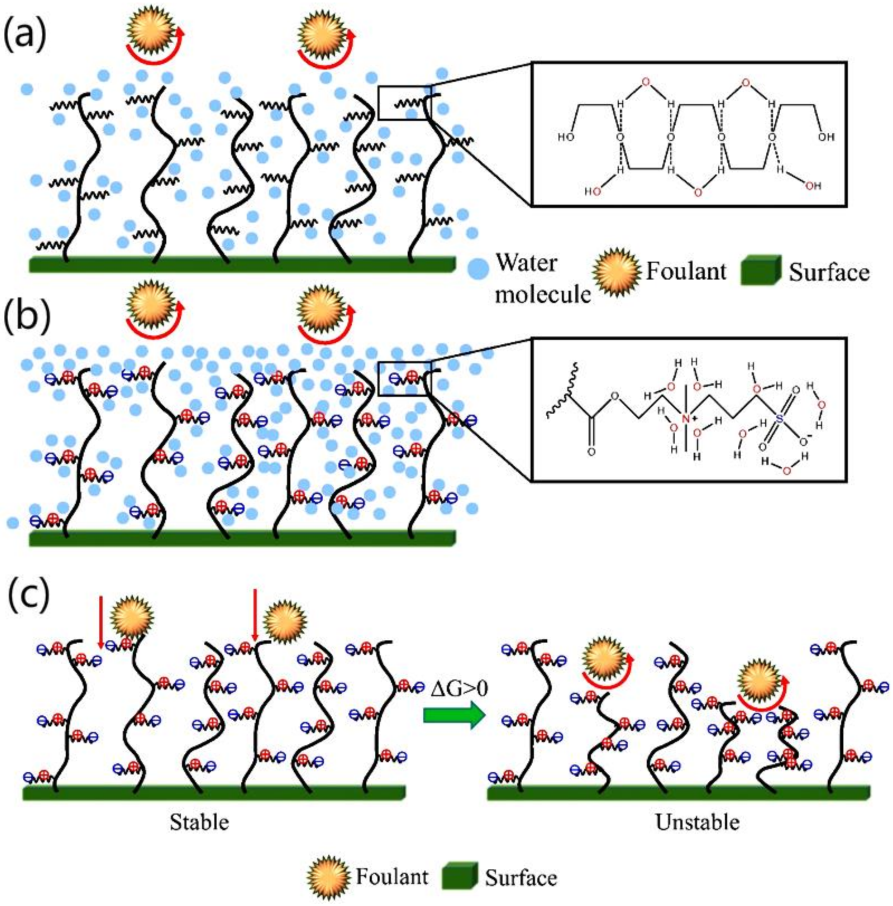

Fig. 12. Schematic illustration of antifouling mechanisms of zwitterionic polymers. (a) Each unit of PEG polymers bonding with one water molecule, (b) each unit of zwitterionic polymers bonding with eight water molecules, and (c) the steric hindrance effect: the unstable compression state of the zwitterionic polymer by foulants tends to go back to the stable swelling state and thus repulse foulants from attaching to the membrane surface [40].

As summarized in Table 5, various zwitterion-based materials have been applied for surface antifouling modification of RO membranes by different methods. These methods mainly include surface grafting [255], surface coating [275] and biomimetic PDA-assisted coating [252]. Surface grafting refers to the anchoring of polymer chains onto a solid surface (e.g. a membrane surface) through chemical bonding. Surface grafting can be induced by either "grafting from" or "grafting to" strategy [276]. For RO membranes, most surface modifications are performed via "grafting from", including conventional radical polymerization [277] and living radical polymerization [254]. Surface coating refers to the deposition or self-assembly of polymers, nanoparticles, or other modifying agents onto the membrane surface via nonspecific interactions, and the typical methods for surface coating include adsorption, self-assembly and initiated chemical vapor deposition. Surface coating tends to form dense smooth membrane surfaces with improved selectivity and reduced water permeability [40].

*Biomimetic polydopamine.* Recently, PDA and its derivatives have attracted growing interests for various membrane modifications due to its versatile adhesive properties [95, 278-281]. PDA is a highly hydrophilic because of the catechol, quinone and amino groups in its structure, and highly adhesive to almost all types of substrates via covalent bonding, hydrogen bonding, and electrostatic and hydrophobic interactions [279, 282]. PDA acting as a bio-glue can attach to different substrates even with opposite properties for surface functionalization [283]. Antifouling surface modification with PDA is often realized in two ways. First, PDA itself can be coated onto RO membranes to increase the surface hydrophilicity, thereby reducing membrane fouling [261, 284-286]. However, PDA coating through dopamine polymerization often requires a long time (a few hours to even 16 hours) [261]. UV [259] and tobramycin (TOB) [88] have been used to accelerate the antifouling surface coating with PDA.

Second, PDA can also be used as an adhesive agent to increase the surface functionalization and immobilization with other antifouling materials. Recently, PDA has been used to immobilize $TiO_2$ nanoparticles [287-289], PEG [261, 290], and zwitterionic polymers [257] to the RO membrane surface. Generally, a thin pure PDA layer generated in a short polymerization time will not introduce large mass transfer resistance and thus significantly affect the RO membrane separation performance in terms of water permeability and salt selectivity. Immobilizing extra antifouling and/or hydrophilic materials (e.g. macromolecules) would inevitably increase the mass transfer resistance and thus reduce the water permeability of the membrane [261]. Therefore, there is a balance between the water permeability decline and the flux maintenance after antifouling modification during the foulant filtration.

*Hyperbranched polymers* are highly branched three-dimensional (3D) macromolecules with globular and dendritic architectures and unique properties, such as abundant functional groups, intramolecular cavities, low viscosity, and high solubility [291]. Although hyperbranched polymers have been used to modify MF [292], UF [293], NF [294] and FO [295] membranes, few studies have been focused on surface antifouling modification of TFC RO membranes. Nikolaeva et al. chemically coupled a hydrophilic hyperbranched poly(amido amine) (PAMAM) onto the active PA-layer of a RO membrane by spray coating [263]. Interestingly, the modified RO membrane showed increased water flux but slightly reduced salt rejection, which was likely caused by the incomplete formation of the PA layer after introducing PAMAM. Less water flux decline was observed for the modified RO membrane. After hyperbranched polymer coating, the 3D globular and dendritic architectures are typically thick (300 - 400 nm) [263] and loose, the stability of the coating layer could be an issue under high crossflow velocity and high pressure conditions. Therefore, surface antifouling modification with hyperbranched polymers may not be practically feasible for high pressure dense RO membranes.

*Thermo-responsive polymers* with low critical solution temperature (LCST) have been employed to engineer antifouling membranes. Yu et al. synthesized two thermo-responsive copolymers N-isopropylacrylamide-co-acrylic acid (P(NIPAm-co-AA)) [264] and poly(N-isopropylacrylamide-co-acrylamide) (P(NIPAM-co-Am)) [239] by free radical copolymerization, and coated them onto the RO membrane surface by hydrogen bonding. Interestingly, the coated RO membranes showed improved water permeability and salt rejection when using coating solutions of lower concentration. The surface modification with thermo-responsive polymers also reduced the flux decline during BSA fouling and improved the cleaning efficiency at temperature above the LCST. The fouling resistance and cleaning efficiency of the modified membranes were respectively imparted by the enhanced hydrophilicity and the phase transition property of the thermo-responsive coating layer. However, phase change surfaces for RO membranes are not desirable as a highly stable (both thermally and chemically) and selective layer is of great importance for RO membranes. Also, altering the temperature for membrane cleaning is not technically feasible in practical operations.

*Amphiphilic polymers* with both hydrophilic and hydrophobic components have also been synthesized and used to develop antifouling membranes. Although amphiphilic polymers showed excellent performance in engineering antifouling resistant surfaces [296, 297], their applications for antifouling surface modification of RO membranes is not promising. For example, amphiphilic methyl methacrylate-hydroxy poly(oxyethylene) methacrylate (MMA-HPOEM) and hydroxyethyl methacrylate-*co*-perfluorodecyl acrylate (HEMA-*co*-PFDA) copolymers were grafted onto RO membrane surfaces for fouling reduction [265-268]. However, more hydrophobic and rougher surfaces were observed and the slightly improved antifouling performance might not be able to compensate the significant flux decline due to the extra mass transfer resistance after surface grafting. These limited attempts suggests amphiphilic copolymers may not be effective for antifouling surface modification of RO membranes due to the relatively dense surface of the membrane and the large and complex repeating units of the copolymers.

### *4.3.3. Combination of inorganic nanomaterials and organic polymers*

Table 6. Summary of antifouling surface modifications of TFC membranes with hybrid organic and inorganic materials.

| **Coating materials** | **Modification methods** | **Target fouling** | **Remarks** | **Refs.** |
|---|---|---|---|---|
| PEI-coated Ag and hydrophilic polymer brushes (i.e. poly(sulfobetaine) and PDMS). | Layer-by-layer self-assembled with PAA and PEI; and then functionalized by grafting of polymer brushes. | Biofouling | Increased surface hydrophilicity and roughness; decreased water flux and increased selectivity; 95% inactivation of attached bacteria and around 90% decrease in cell adhesion. | [298] |
| PEMs/Ag/ polyzwitterion | Layer-by-layer assembly by PAH and PSS; NaNO3 in situ reduction by $NaBH_4$; polyzwitterion deposition. | Biofouling | More hydrophilic; 15% Reduction in water permeability; comparable salt rejection; improved biofouling resistance. | [299] |

|  |  |  |  |  |
|---|---|---|---|---|
| PDA-Ag | In situ reduction by precoated PDA. | Biofouling | Uniformly dispersed Ag with more hydrophilic surface; increased rejection with decreased flux; more than 40% higher bacteria inactivation. | [300] |
| PSBMA-Ag | Surface grafting with in situ reduction by $NaBH_4$. | Biofouling and organic fouling | Rougher and more hydrophilic surface; 95% higher antimicrobial activity with 8% lower flux decline. | [301] |
| Zwitterion-Ag | Surface grafting with zwitterions and then in situ immobilization of Ag by $NaBH_4$. | Biofouling and organic fouling | Increased hydrophilicity; improved flux and salt rejection; significantly improved antimicrobial and antifouling properties. | [302] |
| PEI modified Cu | Cu was modified with positively charged PEI, and then applied to negatively charged RO membrane for functionalization by electrostatic interaction. | Biofouling | Enhanced positive charge; maintained membrane transport parameters; 80-95% reduction in the number of attached live bacteria. | [82] |
| PEI modified Cu | Spray- and spin-assisted layer-by-layer assembly. | Biofouling | Achieved uniform coating layer; maintained salt reject but slightly (13.3%) reduced water flux; excellent antimicrobial property. | [270] |
| Chitosan linked Cu | In situ formed and fixed via reduction and crosslinking of carboxylated chitosan. | Biofouling and organic fouling | Elevated hydrophilicity; lower water flux and higher salt rejection; more than 99% antibacterial efficiency and higher protein fouling resistance. | [303] |
| AA+ COOH-MWCNTs | Surface grafting. | Organic fouling | Increased hydrophilicity and salt rejection; reduced water flux; improved fouling resistance. | [269] |

PDMS: poly(dimethylsiloxane); PSBMA: Poly(sulfobetaine methacrylate); COOH-MWCNTs: carboxylated multi-walled carbon nanotubes.

Inorganic nanomaterials often have low compatibility with the PA layer of the TFC RO membrane. Therefore, they are often combined with organic polymers for surface antifouling modification of RO membranes. Table 6 summarizes antifouling surface modifications of TFC RO membranes with hybrid organic and inorganic materials. Obviously, the dominant inorganic nanomaterials used are Ag and Cu and these surface modifications mainly target for improving the biofouling resistance of the RO membranes. Generally, there are three strategies for the hybrid inorganic/organic materials to modify TFC RO membrane surfaces for fouling reduction, including: (1) inorganic nanomaterial modification with organic polymers followed by coupling the functionalized nanomaterials onto the PA layer (Fig. 13a), (2) PA layer surface modification with organic polymers followed by bridging/growing inorganic nanomaterials onto the treated surface (Fig. 13b), and (3) PA layer surface modification with inorganic nanomaterials followed by organic polymer deposition (e.g. crosslinking or grafting) (Fig. 13c).

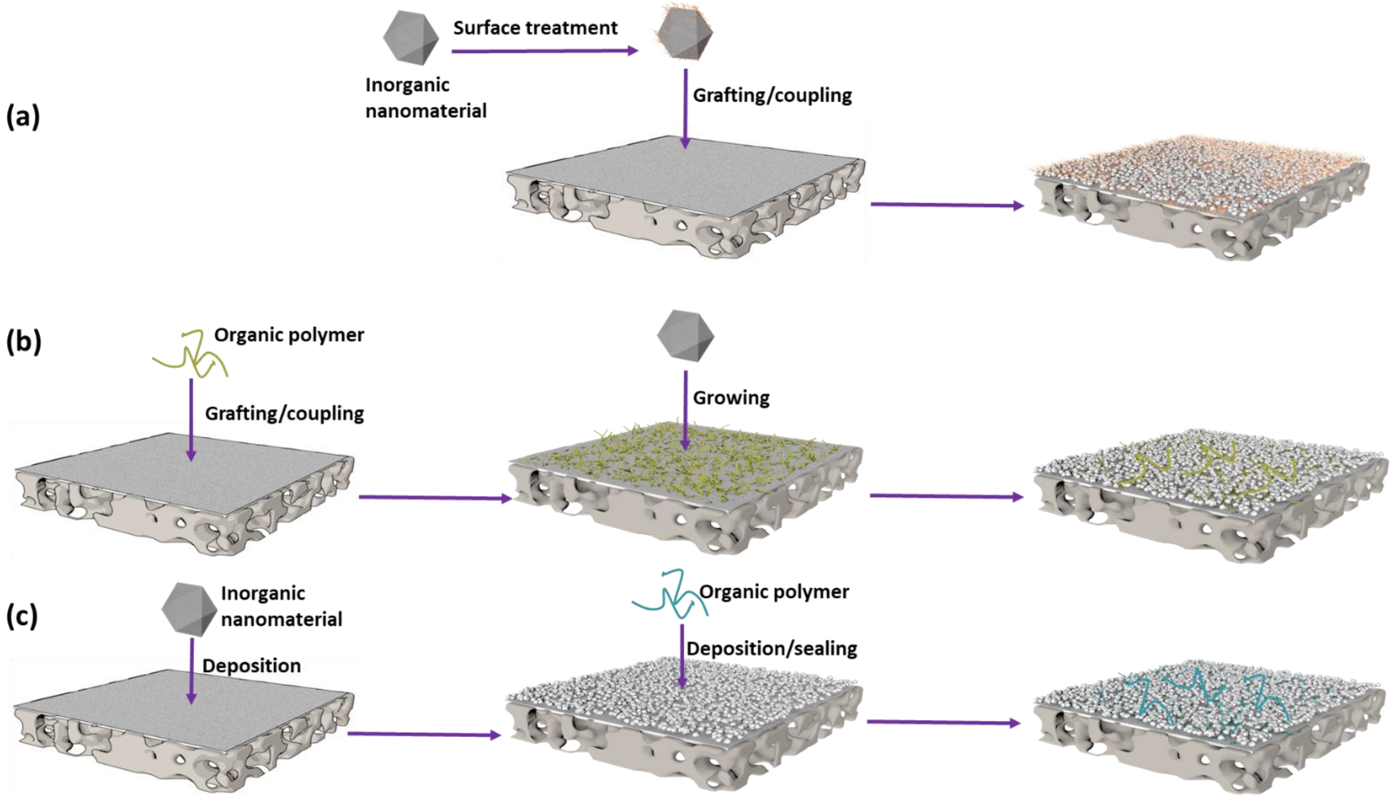

Fig. 13. Typical strategies for surface modification of TFC membranes using hybrid organic and inorganic materials.

### *4.3.4. Other biocidal agents*

Apart from metal-based biocidal agents, other antibacterial agents have also been used for surface modification of RO membranes with the target of biofouling control. Tobramycin (TOB) is a potent antimicrobial agent with a broad antibacterial spectrum, and it is chemically stable. Wang et al. developed TFC RO membrane with enhanced biofouling resistance by surface modification via layer-by-layer assembly of PAA and TOB [228]. Under optimal modification conditions, the treated membrane showed slightly increased permeability and selectivity, and achieved more than 99.6% killing ratio for both Gram-negative *E. coli* and Gram-positive *B. subtilis*. Later, they developed another RO membrane with fouling release, fouling resistant and biocidal properties by grafting a low-surface-energy fluorine-based material 2,2,3,4,4,4-hexauorobutyl methacrylate (HFBM) first and then TOB on the membrane surface (Fig. 14) [87]. The prepared RO membrane displayed excellent organic fouling and biofouling resistance due to the anti-adhesion, self-cleaning and antimicrobial characteristics. Zhao et al. coated TOB and PDA onto a commercial RO membrane surface and found that TOB could not only accelerate the polymerization of dopamine, but also avoid the use of the tris buffer solution during the surface coating [88]. The modified RO membrane also showed significantly improved organic fouling and biofouling resistance.

Quaternary ammonium (QA) is a class of cationic disinfectants with excellent biocidal properties against both Gram-positive and Gram-negative bacteria [304]. Hibbs et al. attempted to use QA functionalized polymer to develop biofouling resistant RO membranes by spray coating [305]. The QA modified surface showed hydrophobic properties, but excellent biocidal performance and killed 100% of the *E. coli* cells. However, it seemed that the QA functionalized polymer was not promising for RO surface modification because of the significantly reduced water flux.

N-halamine has durable and regenerable antimicrobial activities against a wide spectrum of microorganisms without causing environmental concerns [306]. A hydantoin derivative 3-monomethylol-5,5-dimethylhydantoin (MDMH) has been used as the precursor to prepare N-halamine biocides for engineering biofouling resistant RO membranes via surface grafting [307]. The grafted MDMH moieties with high reaction activity and free chlorine could play as sacrificial pendant groups when membranes suffer from chlorine attacks, and the chlorination products of N-halamines with strong antimicrobial function could sterilize microorganisms on membrane surfaces and then regenerate to MDMH. Similarly, 3-allyl-5,5-

dimethylhydantoin (ADMH) with high reaction activity with free chlorine to generate antimicrobial N-halamines has also been grafted onto the PA RO membrane surface by free-radical graft polymerization for biofouling control [213, 308]. However, the chlorination reaction on the membrane surface could damage the membrane integrity and thus reduce membrane selectivity.

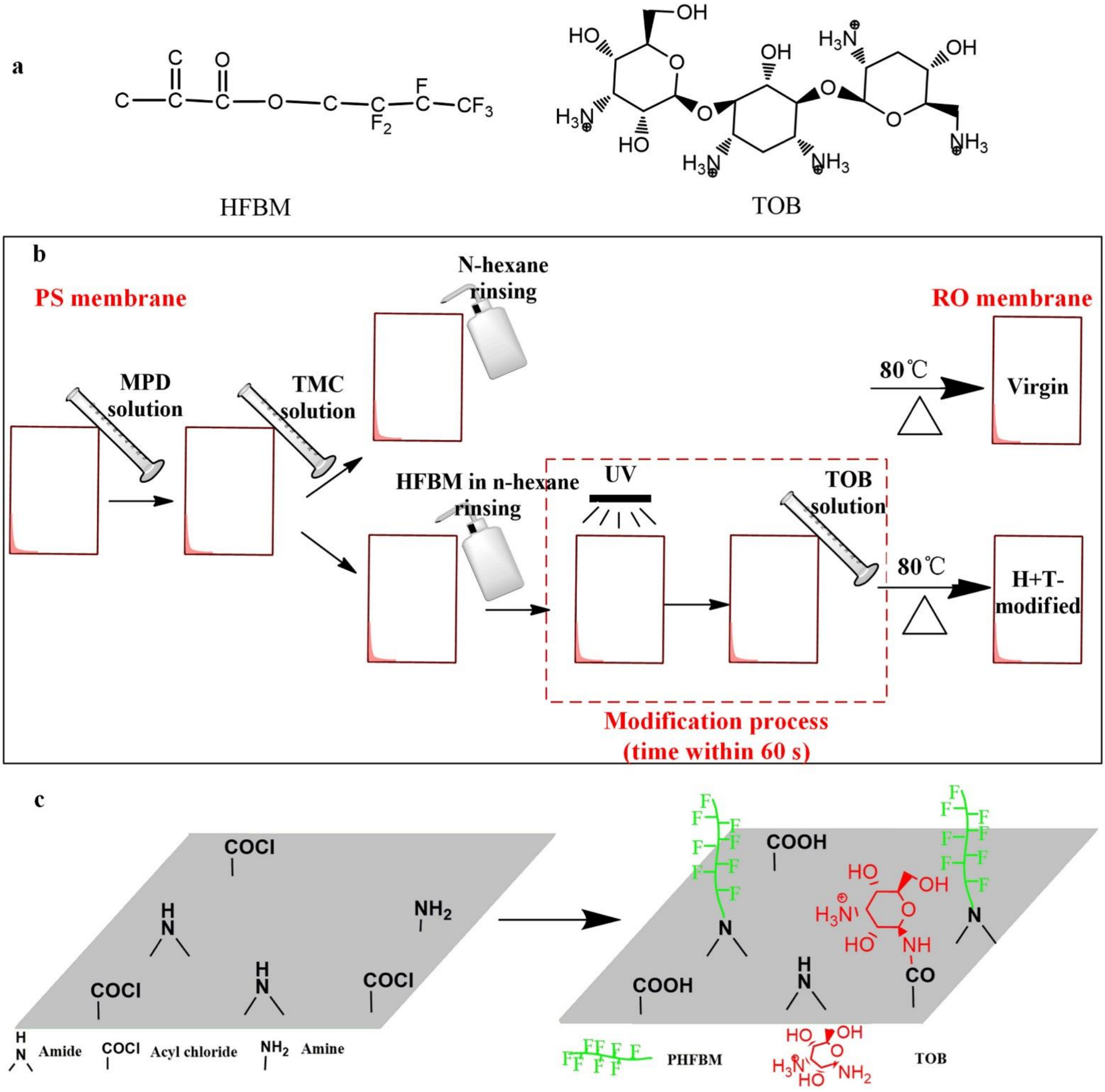

Fig. 14. (a) Chemical structures of HFBM and TOB, (b) schematic diagram of membrane fabrication process, and (c) modification mechanism [87].

The antimicrobial properties of [2-(methacryloyloxy)ethyl]trimethylammonium chloride (MTAC) have been employed to develop biofouling resistant materials [309]. Blok et al. coated PDA-g-MTAC onto a commercial TFC RO membrane surface by the electron transfer-ATRP method [310]. Before coating, the RO membrane was treated by isopropanol for 30 min. As a result, the coated membrane showed increased water flux and comparable salt rejection. Six-day incubation tests with nutrient solution confirmed a 93.2% reduction in bacteria on the modified PA RO membrane compared with the unmodified one, suggesting the excellent biocidal performance of the PDA-g-MTAC coating layer. The coating process required a long time (up to 24 h), which may impede their practical applications.

### *4.3.5. Remarks on surface modification*

Table 7. Comparison of various parameters of the four types of nanomaterials used for surface modification of TFC RO membranes.

| Parameters | Ranking of different nanomaterials | | | |
|---|---|---|---|---|
| | Inorganic | Organic polymers | Hybrid organic-inorganic | Organic biocides |
| Antifouling properties | *** | *** | ** | ** |
| Separation (flux and rejection) performance | ** | * | ** | * |
| Robustness/compatibility | * | *** | ** | *** |
| Simplicity of preparation | *** | Varies | * | * |
| Leaching and its environmental risks | * | *** | ** | ** |
| Cost | *** | Varies | ** | * |
| Research popularity | ** | *** | ** | * |
| Commercialization | * | *** | ** | * |

|  |  |  |  |  |
|---|---|---|---|---|
| Overall performance | 16* | >18* | 15* | 12* |

*** means beneficial property (high or low); ** means intermediate; * means negative property (high or low).

Table 7 compares different parameters of the four types of nanomaterials used for surface modification of TFC RO membranes. Considering all the parameters of these nanomaterials, the estimated ranking in terms of potential could be: organic polymer > inorganic > hybrid organic-inorganic > organic biocides. Interestingly, this ranking order well agrees with the research popularity order of these nanomaterials. For surface modification with inorganic nanomaterials, particle leaching and aggregation are always issues that need more attention. Such modification has low commercial potential, although it has low cost and intermediate popularity due to its simple preparation. In the future, long-term tests for biofouling evaluation by inorganic nanomaterials should be carried out. For example, a biocidal coating layer inactivates (or kills) incoming bacteria that could accumulate on the membrane surface. Once the coating has leached sufficiently, the surface would then promote bacterial growth.

Most surface modifications of RO membranes have been focused on fouling reduction, although they often decrease the membrane permeability and increase the selectivity. It seems that the benefit of the increased selectivity has been underestimated. A recent study called for research efforts to increase RO membrane selectivity rather than the permeability [9]. It is true that further increasing permeability brings limited benefit for specific energy cost reduction for seawater desalination. However, RO membranes are used in many other applications, such as water reuse and brackish water treatment. For feed solutions of low osmotic pressures, high-permeability membranes are more beneficial for reducing energy consumption for a fixed plant size or reducing plant size at fixed energy consumption [10, 311]. Therefore, critical assessment and research efforts are required to evaluate the synergetic effects of reduced fouling, modestly increased selectivity and decreased or unchanged permeability after surface modification of RO membranes.

The great diversity of organic polymers makes their simplicity of preparation and cost vary a lot, attracting significant research popularity. Organic polymers often lead to excellent antifouling properties for RO membranes, but also decrease water permeability. Some hydrophilic polymers (e.g. PVA) have been commercialized for surface coating of RO membranes. Most parameters for hybrid organic-inorganic nanomaterials are intermediate except extra steps for fabricating the hybrids. Organic biocides have similar performance with other organic polymers, but they have less types and may cause environmental concerns, leading to their low research popularity and commercialization potential.

Compared with other pressure driven (e.g. MF, UF and NF) membranes, the surfaces of RO membranes are much denser and smoother. Consequently, some nanomaterials and modification methods that have been widely used for engineering MF, UF and NF membrane surfaces may not be feasible for surface modification of RO membranes. Surface modification often inevitably causes extra mass transfer resistance and thus reduce water permeability of the RO membrane. Particularly, some macromolecules with complex structures and large molecular weights (e.g. hyperbranched polymers, amphiphilic polymers and other copolymers) often require tedious synthesis procedures, involve many hazardous chemicals and complex experimental facilities, and tend to result in relatively thick coating layers that will significantly reduce the water flux of the coated RO membranes. Such polymers may not be technically and economically feasible for engineering antifouling RO membranes. After surface antifouling modification, there should be a balance between the water permeability reduction and the improvement of the antifouling performance (i.e. flux conservation under fouling conditions). Developing a general guideline to quantify the balance between the water permeability reduction and the flux conservation during fouling based on the energy cost analysis will be highly important. Such work will guide how much flux decline and fouling flux maintenance after surface modification would be acceptable in practical operation.

## 5. Concluding remarks and prospects

Concerns over water scarcity and security have provided powerful stimuli for the advance and development of membrane separation technology over the past decades. In particular, RO membrane based desalination plants will continue growing due to the increasing demand for freshwater and the decreasing energy cost of RO. However, separation performance reduction of the membranes caused by inevitable fouling, including organic fouling, inorganic fouling, colloidal fouling and biofouling, calls for new RO membranes with durable antifouling properties. Antifouling RO membranes can be achieved by optimizing several membrane properties, including surface chemistry (e.g. functional groups), surface morphology (roughness), hydrophilicity, and charge properties. Therefore, we have assessed the correlations between these properties and antifouling membrane performance.

This review provides a comprehensive, state-of-the-art assessment of the efforts and strategies for engineering antifouling RO membranes. The three key strategies for engineering fouling resistant TFC RO membranes include: (1) substrate modification before interfacial polymerization, (2) incorporating (hydrophilic/biocidal/antifouling) additives into the PA layer during interfacial polymerization, and (3) post (surface) modification after interfacial polymerization. For each strategy, we have ranked the various approaches in terms of performance and practical aspects, such as simplicity of preparation, robustness and likely cost.

Substrate modification has received much less attention in developing antifouling RO membranes. This may be caused by the indirect and complex relationship between the substrate and the antifouling surface. Indeed, from the substrate to the antifouling TFC membrane, there are many variables covering the substrate properties (e.g. material type, surface/cross-sectional pore size, pore distribution, surface/overall porosity, surface hydrophilicity and roughness, and thickness), the operating conditions (e.g. membrane casting temperature, humidity, speed, coagulation time, temperature) and similar parameters for the PA layer. It is difficult to contribute the substrate properties to the antifouling PA surface, particularly for the lab-made RO membranes with low repeatability and large experimental errors. This may be the reason that some relevant investigations have come to contradictory conclusions. In the future, more systematic investigations exploring the relationship between substrate modification and antifouling PA RO membranes under well-controlled conditions with high repeatability should be carried out, although they may be challenging.

Incorporating nanomaterials into the PA layer during interfacial polymerization is highly promising for engineering fouling resistant TFC RO membranes. Various metal based biocides, carbon based nanomaterials, silica based nanomaterials and hydrophilic nanopolymers have been used to improve the antifouling properties of TFC RO membranes during interfacial polymerization. There would be optimal requirements for these nanomaterials, such as particle sizes, loadings, density of hydrophilic functional groups and compatibility between the nanomaterials and the polymers. However, these questions have not been well answered yet. Future work should focus on the development of general guidelines on these parameters for engineering next generation of high performance antifouling RO membranes, and then we can use the developed guidelines to screen and design most desirable nanomaterials. Fortunately, the emerging machine learning based artificial intelligence technology makes this target technically achievable.

Post (surface) modification of existing RO membranes is relatively simple and it is easy to obtain antifouling surfaces. Therefore, numerous investigations have taken the surface modification strategy for engineering antifouling RO membranes. Typical materials for surface antifouling modification include inorganic nanomaterials, ordinary hydrophilic polymers, zwitterionic polymers, biomimetic polymers, amphiphilic polymers, biocidal agents or combinations of the materials above. For surface modification with inorganic nanomaterials, particle leaching and aggregation are the common issues that need more attention. Compared with other pressure driven (e.g. MF, UF and NF) membranes, the surfaces of RO membranes are much denser and smoother, and some nanomaterials that have been widely used for engineering these membrane surfaces may not be easily and stably anchored onto the surfaces of RO membranes.

Most surface modifications would inevitably induce extra mass transfer resistance and thus reduce water permeability of the RO membrane. In particular, some macromolecules with complex structures and large molecular weights (e.g. hyperbranched polymers, amphiphilic polymers and other copolymers) often require tedious synthesis procedures and tend to introduce relatively thick coating layers that will significantly reduce the water flux of the coated RO membranes. Such polymers may not be the desirable materials for surface antifouling modification. After surface antifouling modification, there should be a balance between the water permeability reduction and the improvement of the antifouling performance (i.e. flux conservation under fouling conditions). Developing a general guideline to quantify the balance between the water permeability reduction and the flux conservation during fouling based on the energy cost analysis will be important. Such work will guide how much flux decline and fouling flux maintenance after surface modification would be acceptable.

To summarize, these key guidelines and directions can be followed to engineer the next generation of antifouling RO membranes:

- Nanomaterials with desirable properties, such as reasonable particle sizes, low tendency to aggregate, high density of hydrophilic functional groups and good compatibility with contacting polymers, are promising in developing antifouling TFC RO membranes during interfacial polymerization.
- Surface modification with hydrophilic polymers has more industrialization interest than incorporation of hydrophilic nanomaterials during interfacial polymerization, since the former operation is simple and does not require significant modification for the existing production line.

- Macromolecules with complex structures and large molecular weights (e.g. hyperbranched polymers, amphiphilic polymers and other copolymers) may not be the desirable materials for surface antifouling modification of RO membranes because of their tedious synthesis procedures, high costs and high tendency to introduce high mass transfer resistance thereby reducing water permeability of the membranes.
- Substrates are potentially important and there would be benefit in optimizing the substrate properties to facilitate antifouling behaviors, such as to minimize "hot spots" at the RO membrane surface. Substrate optimization can accompany antifouling via the PA layer or surface modification.

Overall, engineering the next generation of antifouling RO membranes is important for our future water security. Recent advances in emerging nanomaterials, such as 2D nanosheets and porous nanoparticles with intrinsic water pathways, have significantly diversified the selection of materials for engineering antifouling RO membranes using various preparation methods. Some general guidelines for nanomaterials selection and performance evaluation are needed, since they will make the development of antifouling RO membranes more targeted and efficient. This will require joint efforts from membrane and polymer scientists, engineers and end-users.

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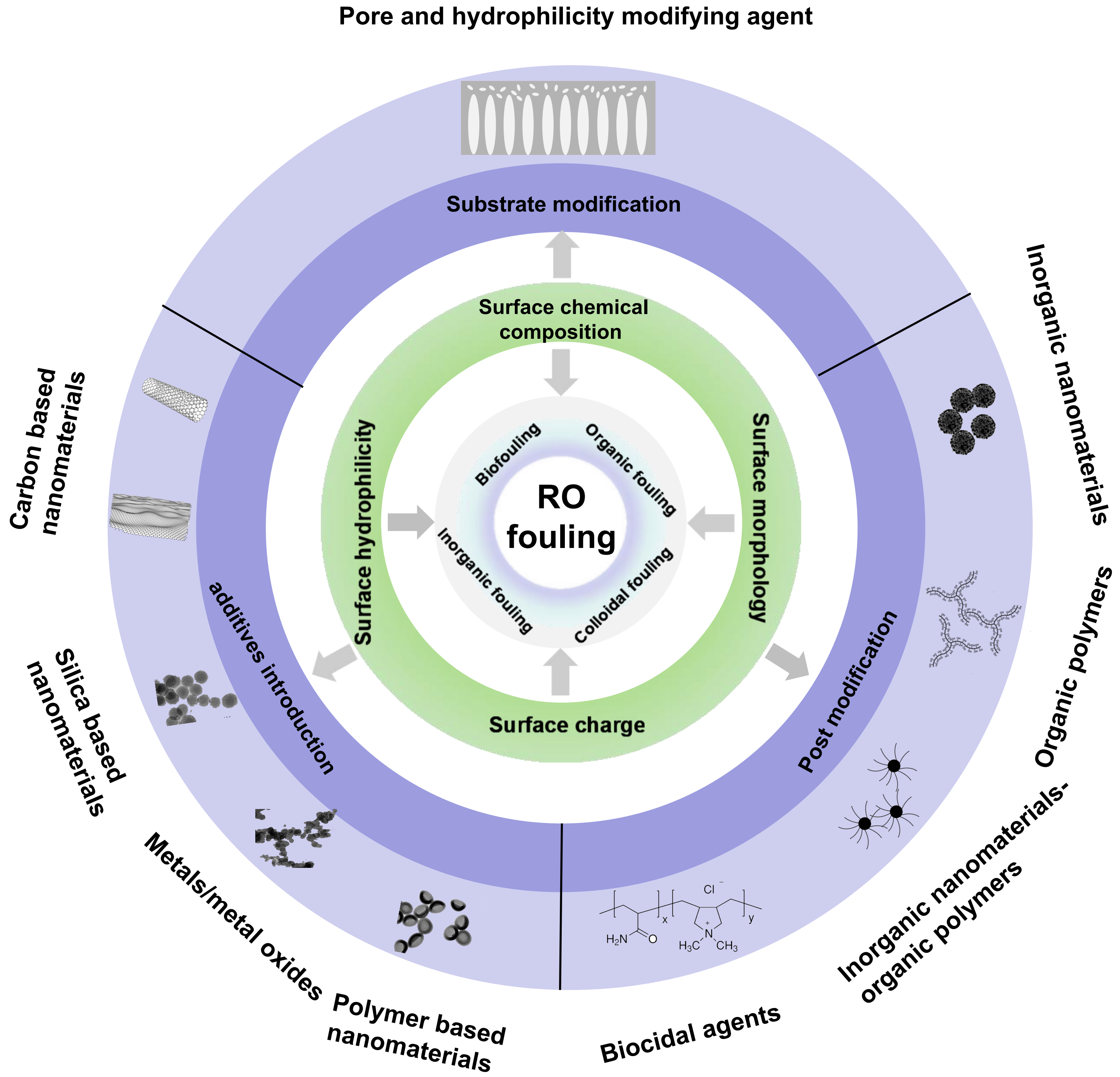
Graphical Abstract



# Engineering antifouling reverse osmosis membranes: A review

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## Abstract

Over the past decades, water scarcity and security have significantly stimulated the advances of reverse osmosis (RO) technology, which dominates the global desalination market. However, deterioration of membrane separation performance caused by inevitable fouling, including organic fouling, inorganic fouling, colloidal fouling and biofouling, calls for improved RO membranes with more durable antifouling properties. In this review, we analyze the correlations between membrane properties (e.g. surface chemistry, morphology, hydrophilicity, and charge) to antifouling performance. We evaluate the three key strategies for engineering fouling resistant thin film composite RO membranes, namely: (1) substrate modification before interfacial polymerization, (2) incorporating (hydrophilic/biocidal/antifouling) additives into the selective layer during interfacial polymerization, and (3) post (surface) modification after interfacial polymerization. Finally, we offer some insights and future outlooks on the strategies for engineering next generation of high performance RO membranes with durable fouling resistance. This review provides a comprehensive, state-of-the-art assessment of the previous efforts and strategies as well as future research directions for engineering antifouling RO membranes.

***Keywords*:** RO Membrane; Desalination; Membrane Fouling; Nanomaterials; TFC membrane.

**Contents**

# 1. Introduction

## *1.1. Status of reverse osmosis*

Water scarcity is one of the most concerning challenges in the world. Over 1 billion people have no access to clean drinking water and more than one-third of the world's people live in water-stressed regions [1]. Water shortages are further worsened by industrialization, population growth, water contamination and climate change. Desalination has played an increasingly important role in addressing water scarcity. Globally around 16,880 desalination plants are supplying freshwater of 97.2 million $m^3$/day in 2020 [2]. The total production capacity of freshwater has tripled since 2000 when it was less than 30 million $m^3$/day [3]. Fig. 1 shows the estimated global desalination market by technology and desalination capacity over the next few years based on the recent growth rates [2, 4]. It indicates that the desalination market is projected to double between 2015 and 2025. Reverse osmosis (RO) dominates the global desalination market in terms of both revenue and installed numbers (14,360, accounting for 85% of existing desalination plants [2]).

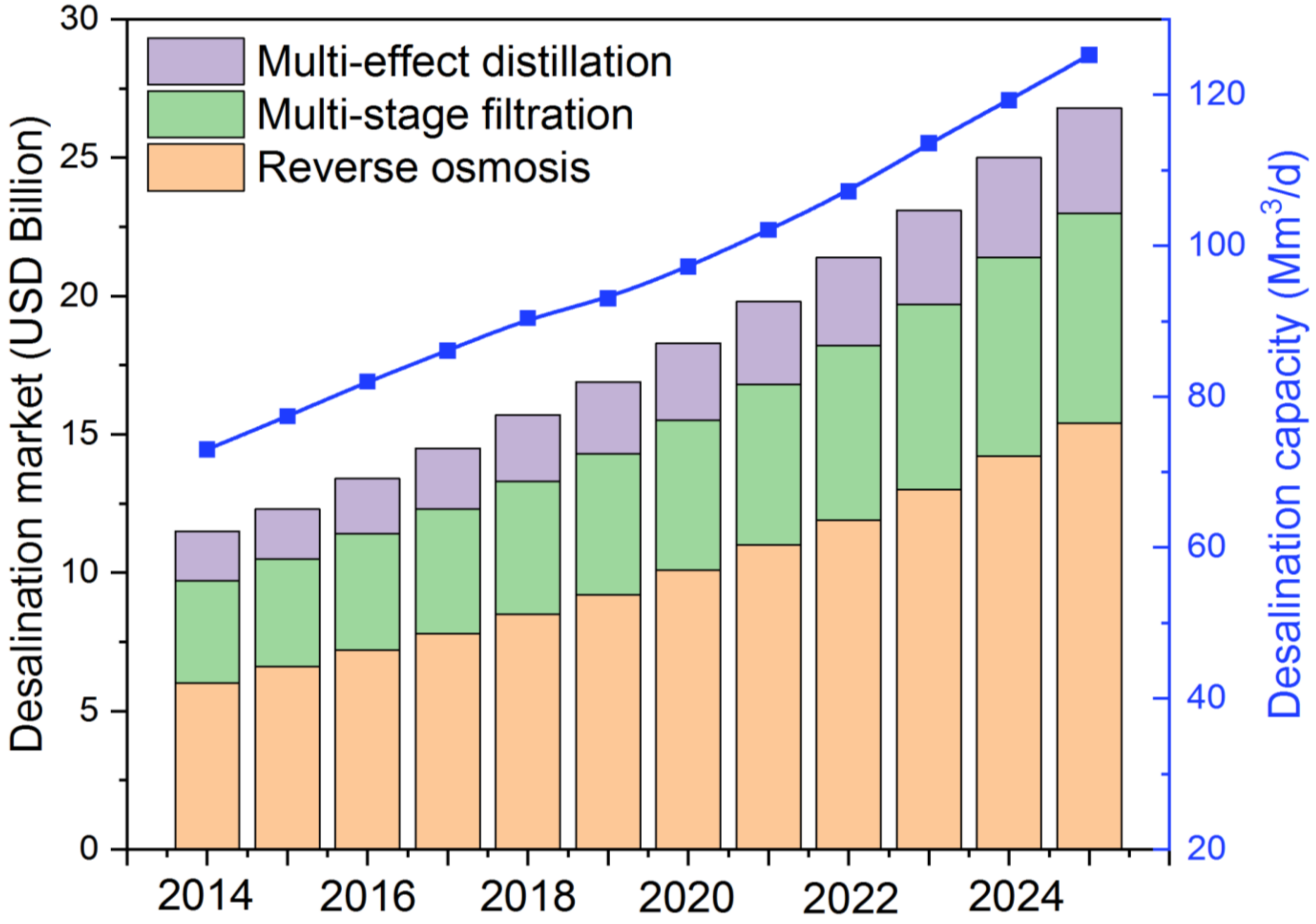

Fig. 1. The estimated global water desalination market revenue by technology and desalination capacity 2014 - 2025 based on the recent growth rates.

Fig. 2a displays the total worldwide installed desalination capacity by technologies. Obviously, as the most popular and cost-effective desalination technology, RO supplies most of the desalted freshwater. In the past few decades, the energy consumption for seawater RO desalination has dropped significantly from more than 15 kWh/m$^3$ in the 1970s to less than 2 kWh/m$^3$ in 2008 (Fig. 2b), which is close to the theoretical minimum energy requirement of 1.06 kWh/m$^3$ [5]. The reduction in energy consumption of RO is mainly caused by the advances in high performance membranes and the employment of high efficient energy recovery devices. Therefore, many countries have adopted RO for freshwater supply, particularly when they have limited access to fuel resources [6].

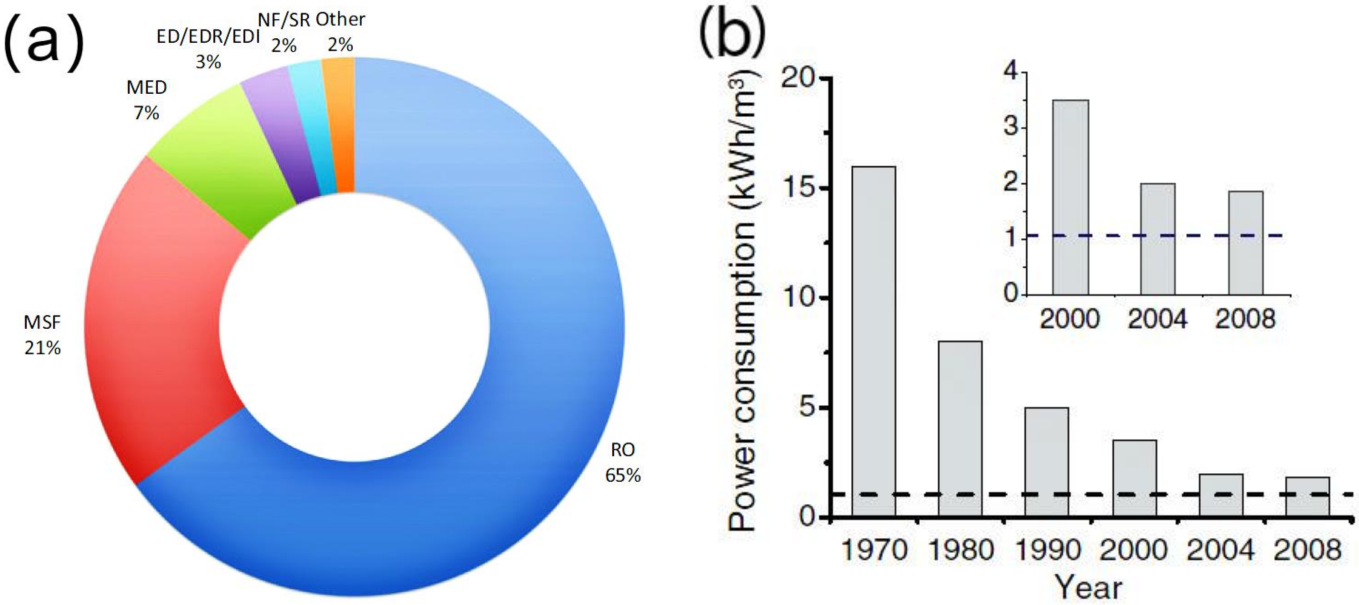

Fig. 2. (a) Total worldwide installed desalination capacity by technology [7]. (b) Reduction in power consumption of RO for seawater desalination from 1970s to 2018 [5]. The horizontal dashed line represents the theoretical minimum energy required for desalting 35 g/L seawater at 50% recovery (1.06 kWh/m$^3$). The energy data here exclude the energy used for intake, pretreatment, posttreatment, and brine discharge.

### *1.2. Challenges of reverse osmosis*

Although RO has become the dominant technology in supplying freshwater from unlimited seawater, RO also faces some challenges that affect the sustainability of the technology. In practical operation, RO is still an energy-intensive process. The state-of-the-art seawater RO plants consume 2 - 4 kWh electricity (including energy for pre-treatment, post-treatment and transportation) and release 1.4 - 1.8 kg $CO_2$ per cubic meter of produced freshwater [5, 8]. To minimise the energy consumption and greenhouse gas emissions, two effective options are developing RO membranes with reasonably high permeability and selectivity [9], and integrating renewable energy sources (e.g. solar and wind energy) in the desalination process. Higher water permeability (A) membranes could have a modest effect on energy demand. For example, Cohen-Tanugi et al. [10] estimated a 15% reduction in energy demand, or a 44% reduction in pressure vessels, for seawater RO with a

3-fold increase in A (compared with current technology) with a typical capacity and recovery ratio. Further increases in A show small energy benefit due to thermodynamic constraints. This study showed greater benefits for brackish water RO (46% less energy or 63% fewer pressure vessels). The diminishing benefit of increased A is confirmed by Werber et al. who emphasised the need to improve selectivity (lower salt permeability (B) or greater A/B ratio) [9]. Overall, modest increases in A and decreases in B would bring meaningful benefits to energy demand and product quality. Both A and B can be detrimentally affected by fouling, providing a strong incentive to improve the antifouling properties of RO membranes.

Another key problem in RO is the desalination brine. It has an increased salinity (doubled compared with seawater) and contains complex chemicals, such as coagulants, surfactants, antiscalants and chemical cleaning agents [5, 8] and, in the context of this review, all of which relate to fouling control. The most common way for brine disposal is direct discharge to the sea. However, this raises environmental concerns. In the future, more efforts may need to be devoted to minimise the environmental impacts of RO desalination brine. For example, membrane distillation (MD), with the potential to achieve zero liquid discharge [11-13], and forward osmosis [14-16] could be alternative technologies to further treat RO brine.

Lack of high performance membranes is still a long-term challenge in RO desalination, although the past decades have witnessed dramatic advances in membrane materials [17]. Table 1 summarizes the typical types of RO membranes, including thin film composite (TFC), cellulose acetate (CA), inorganic, organic/inorganic hybrids, and biomimetic RO membranes. Among these, the TFC RO membrane is the most studied and also has the largest market share in the industry for practical desalination and wastewater treatment. This is mainly because TFC RO membranes have very good salt rejection, water permeability and mechanical strength. However, TFC RO membranes still have the drawbacks of fouling and low chlorine resistance.

Table 1. Summary of the materials, advantages and disadvantages of typical RO membranes.

| RO membranes | Advantages | Disadvantages | Refs. |
|---|---|---|---|
| **TFC** | High permeability and selectivity; excellent mechanical strength; large temperature and pH tolerance range. | Susceptible to fouling; sensitive to chlorine attack and other oxidations (e.g. by chloramine, bromine, ozone). | [6, 17] |
| **CA** | Chlorine tolerant; low costs; antifouling. | Low permeability; susceptible to hydrolysis; low stability with the changes in pH, pressure and temperature. | [6, 18] |
| **Inorganic** | Excellent thermal, chemical, mechanical stabilities; antifouling; cleaning tolerant. | High costs; low rejection; low packing density. | [17, 19, 20] |
| **Organic/inorganic hybrid** | Combination of the advantages of organic and inorganic membranes (e.g. high permeability and antifouling); capable of using numerous emerging nanomaterials (e.g. 2D nanosheets). | Not commercialized at large-scale; high costs. | [19, 21] |
| **Biomimetic** | High permeability; antifouling. | Not commercialized at large-scale; high costs; limited thermal and chemical stabilities. | [17, 22] |

Engineering antifouling membranes could play a vital role in addressing the challenges of RO. Antifouling RO membranes could reduce the flux drop and extra energy requirements caused by fouling, and chemical usage (e.g. antiscalants and cleaning agents) thereby extending membrane lifespans, cutting down cleaning and shutdown frequencies, and reducing desalination costs. However, it is important that the provision of antifouling properties does not compromise the high permeability and selectivity properties of TFC RO membranes, as all these properties are required to reduced energy consumption and increase product water quality [10, 17, 23-25]. This study explores the recent research efforts on RO membrane development and modification for fouling mitigation.

### *1.3. Aim and novelty of this paper*

A number of review papers on antifouling membranes or RO membranes have been published. These review papers focus on general antifouling membranes [26-29], RO membranes [30, 31], TFC membranes [32, 33], specific surface modification [23, 34, 35], or antimicrobial membranes [36, 37]. However, no comprehensive review on antifouling engineering has been done specifically for RO desalination membranes.

This paper aims to provide a state-of-the-art assessment of research work carried out to date on engineering antifouling RO membranes, including three key strategies: (1) substrate modification before interfacial polymerization, (2) incorporating additives (e.g. nanoparticles, nanotubes, and biocidal agents) into the polyamide layer during interfacial polymerization, and (3) post (surface) modification after interfacial polymerization. Most importantly, we provide our perspectives on the current challenges, practical feasibility and future directions for each antifouling engineering strategy. This review focuses on the development of antifouling TFC RO membranes since they are the mostly studied and used RO membranes by both scientists and engineers due to their remarkable water permeability and salt selectivity.

This paper starts with exploration of the mechanisms of RO membrane fouling, followed by analysis of the membrane parameters affecting RO fouling. We summarize and analyze the three key strategies for engineering RO membranes. We also discuss the emerging nanomaterials, hydrophilic polymers and biocidal agents used for antifouling modification of RO membranes, and evaluate their feasibilities and efficiencies for practical applications. Finally, we consider the likely future of antifouling RO membranes and recommend some directions that need more research efforts. This review provides an important guide for engineering antifouling RO membranes by different methods using various nanomaterials, polymers and biocidal agents.

## 2. Mechanisms of RO membrane fouling

Membrane fouling is caused by the accumulation of a range of undesirable deposits on the membrane surface or in the membrane pores, leading to reductions in permeation flux and salt rejection. This phenomenon can significantly decrease membrane performance due to the extra mass transfer resistance from the foulants, and thus increase the costs due to increased specific energy, membrane cleaning and replacement. After fouling, the transmembrane pressure will need to increase in order to maintain a constant flux (or water flux will decrease at a constant transmembrane pressure), causing higher energy consumption [32]. Fouling can also enhance concentration polarization and thus salt permeation through the membrane, leading to reduced salt rejection [38]. Fouling can occur on the membrane surface and/or in the membrane pores. The former is surface fouling, and the latter is internal fouling. For porous microfiltration and ultrafiltration membranes, internal fouling is more common, while for dense RO membranes, surface fouling dominates the fouling process.

Several fouling mechanisms, including cake formation, concentration polarization induced deposition, organic adsorption, inorganic precipitation and biological fouling have been summarized [39]. From the thermodynamic point of view, membrane fouling is caused by the minimization of the Gibbs free energy of the system [40]. In the fouling process under convective flux, foulants move to and attach on the membrane surface via electrostatic, hydrophobic, van der Waal, hydrogen-bonding and/or other membrane-foulant interactions [34]. Subsequently, the foulants may aggregate due to foulant-foulant interactions, forming a thick fouling layer on the membrane surface.

According to the difference in foulant types, RO membrane fouling is typically classified into organic fouling, inorganic fouling (i.e. scaling), biofouling (i.e. biofilm formation) and colloidal fouling [23, 41]. Four types of foulants result in different morphologies on the membrane surface as shown in Fig. 3. Fig. 3a shows that the RO membrane was almost fully covered by organic sodium alginate [42]. Fig. 3b shows $CaSO_4$ crystal scaling on the membrane surface [43]. Fig. 3c shows a gel-like biofouling layer caused by bacterial cells embedded in extracellular polymeric substances [44]. Fig. 3d displays the colloidal fouling caused by silica particles on the RO membrane surface [45]. Colloidal and inorganic fouling are amenable to control by filtration and adjustment of water chemistry whereas organic fouling and biofouling are typically more intractable and complex.

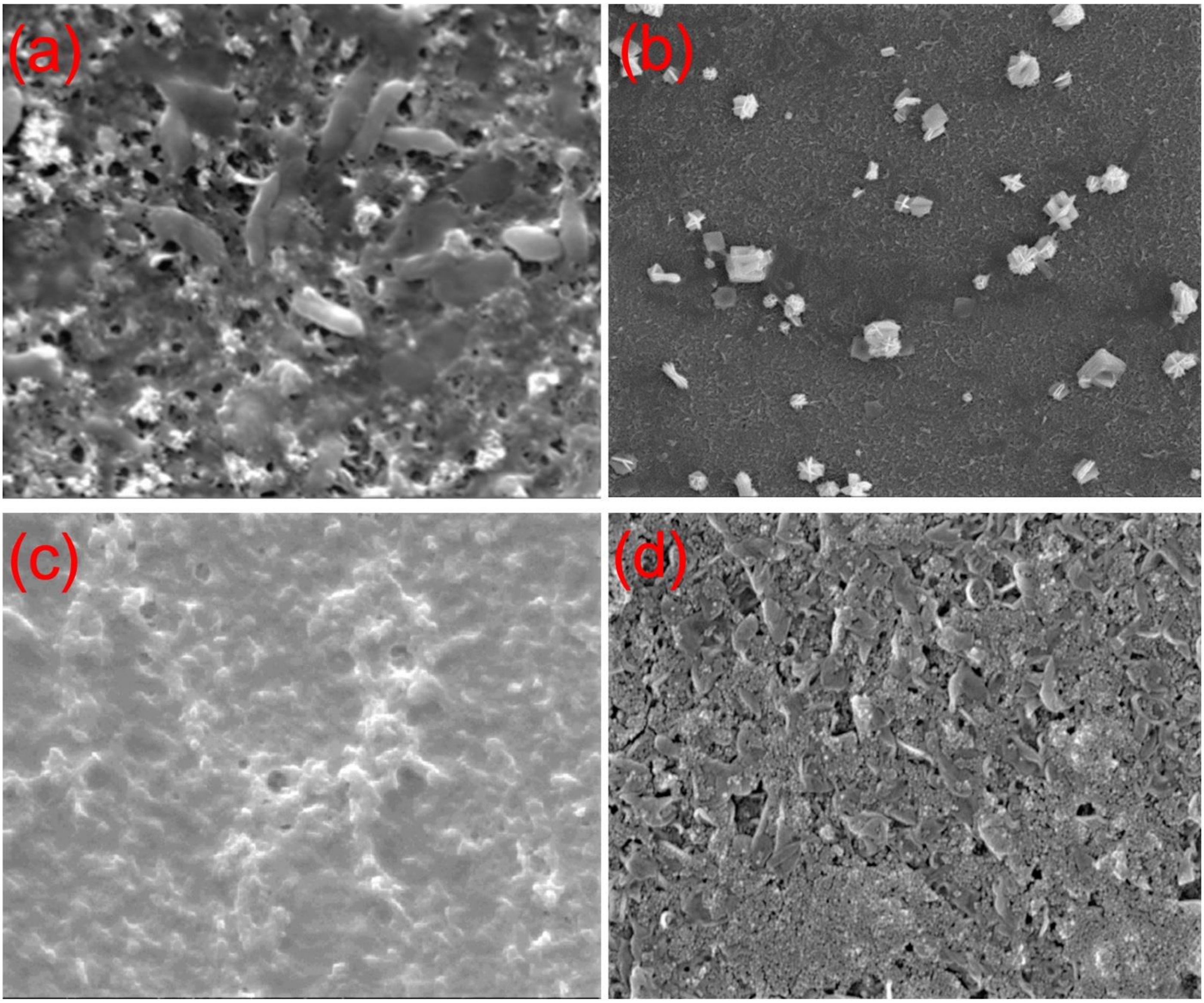

Fig. 3. SME images of different RO membrane fouling types: (a) organic fouling (by sodium alginate) [42], (b) inorganic fouling (by $CaSO_4$) [43], (c) biofouling [44], and (d) colloidal fouling (by silica) [45].

### *2.1. Organic fouling*

Organic fouling is caused by organic matter, typically including humic substances, proteins, polysaccharides, lipids, nucleic acids, amino acids, organic acids, and cell components [41]. Organic fouling is mainly caused by dissolved organic matter (DOM) that widely exists in all sorts of waters. DOM can be classified into three categories based on their origins: (1) refractory natural organic matter (NOM), (2) synthetic organic compounds from consumers and disinfection byproducts during the water disinfection process, and (3) soluble microbial products (SMPs) due to decomposition of organic compounds during the biological treatment process [46]. NOM is the key foulant for polymeric membranes in drinking water applications [39]. NOM is a complex heterogeneous mixture of compounds from the decomposition of animal and plant materials in the environment. Most NOM comprises of a range of compounds, from small hydrophobic acids, proteins and amino-acids to large humic and fulvic acids. The major fraction of NOM is composed of humic substances (HS). In brackish water or seawater RO desalination, NOM with concentrations ranging from 2 to 5 ppm is a typical foulant, while effluent organic matter (EfOM) dominates the fouling in wastewater treatment (10-20 ppm) [47, 48]. An important organic group implicated in seawater desalination fouling are transparent exopolymers (TEPs). TEPs comprise acidic polysaccharides present as particles or gels and can facilitate bio-adhesion and biofouling [49, 50].

Because of the complexity of organic matter in real waters, several model foulants are widely selected in fouling studies. For example, bovine serum albumin (BSA) is often used to represent proteins, humic acid (HA) represents humic substances, and (sodium) alginate is used as the surrogate of polysaccharides. Kim and Dempsey reported that HA was most similar to NOM in surface water and SMPs were most similar to wastewater EfOM [47]. In organic fouling, adsorption is a key fouling mechanism. Feed solution chemistry, foulant-surface interactions (initial stage), foulant-foulant interactions (fouling layer development stage), and foulant molecular weights are the important factors influencing organic fouling [39, 41, 51]. Lee et al. [51] reported that organic foulants with low to medium molecular weights (300-1,000 Da) played an important role in the initial stage of membrane fouling, while organic matters with large molecular weights (> 50,000 Da) dominated the later fouling layer development.

## *2.2. Inorganic fouling*

Inorganic fouling, also called scaling, is caused by the deposition/precipitation of inorganic salts on the membrane surface or in the membrane pores. Inorganic fouling often occurs when the concentrations of ions exceed their equilibrium solubility products and become supersaturated. Inorganic salts with very low solubilities, such as calcium sulfate ($CaSO_4$), calcium carbonate ($CaCO_3$), silica ($SiO_2$) and barium sulfate ($BaSO_4$) are the most common scalants on the membrane surface. Statistical analysis has demonstrated that ~80% of scaling studies on RO membranes were related to $CaSO_4$ and $CaCO_3$ [41]. Scaling is formed by two crystallization pathways: surface (heterogeneous) crystallization and bulk (homogeneous) crystallization [52]. Membrane scaling occurs as a result of both mechanisms, and is affected by feed properties, membrane morphology and operating conditions.

Inorganic fouling is different from other fouling types because it only occurs when the local concentration exceeds a critical saturation value. However, salt rejection and flux-induced concentration polarization (CP) can facilitate the approach to the critical saturation concentration and accelerate scaling on the membrane surface. Scaling can be mitigated by using membranes with smooth surfaces, dosing antiscalants, pH adjustment or decreasing CP by increasing the feed velocity (i.e. shear rate) and/or decreasing flux [6, 53]. The benefit of a smooth surface may be the fewer “ridge and valley” features; CP would tend to be exacerbated in the “valleys”.

### *2.3. Biofouling*

Biofouling (i.e. biological fouling) is defined as undesirable accumulation, adhesion and proliferation of microorganisms on the membrane surface. Biofoulants include bacteria, fungi, algae, viruses, higher organisms (e.g. protozoa), and biotic debris (e.g. bacterial cell wall fragments) [54, 55]. Biofilm formation can be divided into three stages: bacteria attachment, reproduction and detachment. Bacteria attachment is a dynamic process during which live bacteria move to and attach onto the membrane surface [41]. In the bacteria reproduction stage, the attached microorganisms consume nutrients in the feed solution and experience proliferation, excreting extracellular polymeric substance (EPS) that form a binding and protective matrix. The final stage is the detachment of the dead and living bacteria triggered by lack of nutrients. In RO operation, the dead bacteria could also form a biofouling layer under high hydraulic pressure, leading to decreased water flux and salt rejection through a biofilm-enhanced osmotic pressure mechanism [56], as well as providing a fouling resistance. The detached and dispersed bacteria will find new sites to grow downstream and repeat the process of biofilm formation. The formed biofilm on the membrane surface is a gel-like layer (Fig. 3c), having two key components: bacterial cells and EPS that are excreted by bacteria during metabolism. EPS is mainly made of polysaccharides, proteins, glycoproteins, lipoproteins, lipids and nucleic acids, and can protect the microorganisms from biocides and toxins, making biofouling more intractable [57].

Biofouling is one of the most severe problems in RO operations. It has the following properties: (1) it is not easily reversible; (2) it is more complicated than other fouling phenomena because the microorganisms can grow, multiply and relocate on the membrane surface; (3) it is difficult to mitigate by pretreatment unless pretreatment can remove 100% bacteria and nutrients in the feed, which is unlikely. A few surviving cells can multiply quickly under suitable conditions in the RO system, and this emphasises the need to limit nutrients in the feed. Although biofouling can be diminished by feed disinfection, it may cause extra problems for TFC polyamide membranes because of their sensitivity to chlorine degradation [58, 59]. This explains the quest for more chlorine-tolerant RO membranes [60].

### *2.4. Colloidal fouling*

Colloidal (particulate) fouling refers to the deposition of colloids or particles on the membrane surface. Colloids/particulates are regarded as fine particles roughly in the size range of 1 nm to 1 μm. Particles below this size range can diffuse away from the membrane surface via molecular diffusion, while particles above this size range can be removed by shear flow. The common colloidal foulants can be divided into two types:

inorganic foulants and organic macromolecules. The common inorganic colloids include silica, iron oxides/hydroxides and aluminium silicate minerals. Organic macromolecules are mainly composed of humic acids, polysaccharides and proteins [61]. Since colloidal foulants cover both organic and inorganic materials, in some publications colloidal fouling is integrated into organic or inorganic fouling.

## 3. Membrane properties affecting RO membrane fouling

Generally, the factors affecting membrane fouling can be classified into three groups (Fig. 4): feed solution/water characteristics, operational conditions, and membrane properties. Next, each group will be discussed briefly.

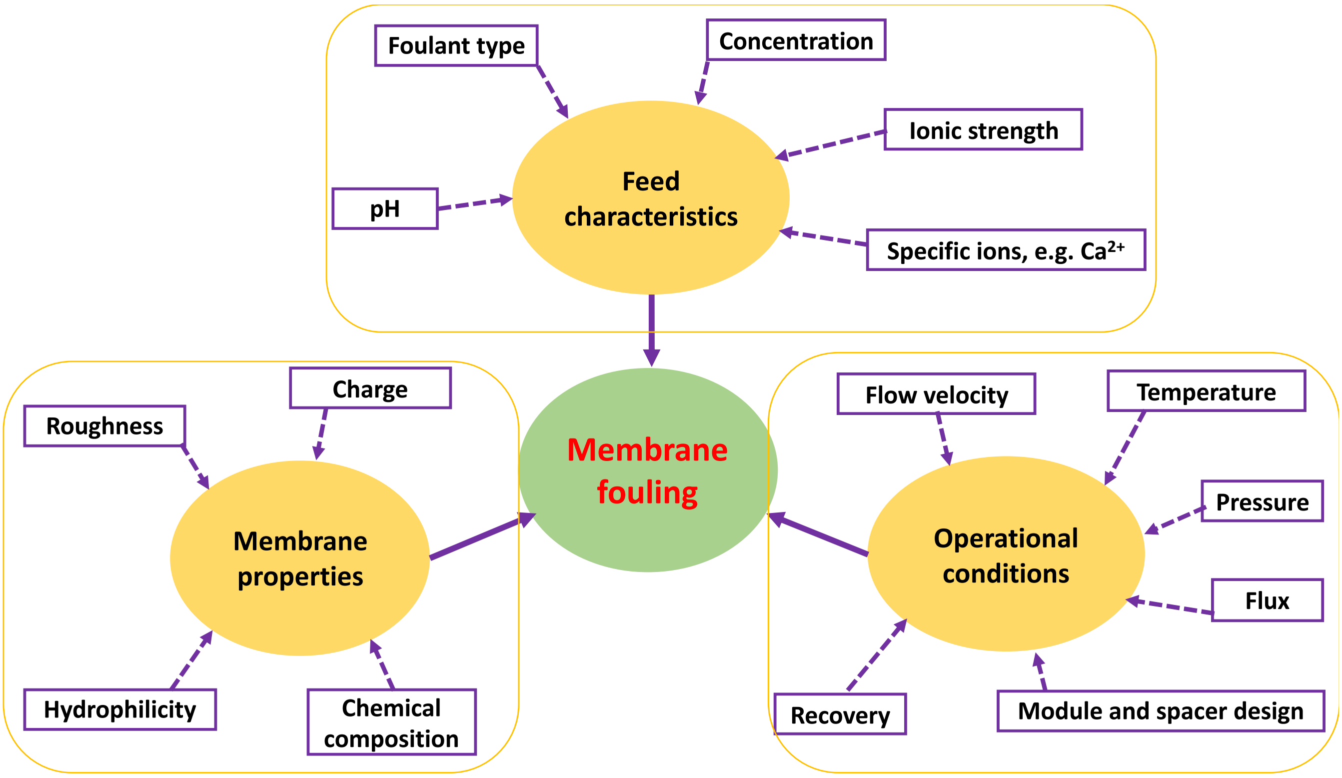

Fig. 4. Factors affecting RO membrane fouling.

(1) Feed solution/water characteristics. Membrane fouling is strongly affected by the feed chemistry (e.g. ionic strength, $Ca^{2+}$ and pH) and the foulants in the feed solution, including their types, concentrations and physiochemical properties (e.g. sizes, charges, structures, functional groups and hydrophobicity) [62-64]. For

example, RO membrane fouling by BSA was enhanced at higher $Ca^{2+}$ concentration and at pH near the BSA isoelectric point (pH 4.7) [65, 66].

(2) Operational conditions. A number of operational parameters, such as cross flow velocity, transmembrane pressure, permeation flux, and module and spacer design have significant effects on membrane fouling. This is because fouling can be linked to the degree of concentration polarization (CP) which is determined by the ratio of water flux ($J$) to the boundary layer mass transfer coefficient ($k$). The value of k depends on the crossflow velocity and the flow channel design (via module and spacer design). Therefore, membrane fouling is considered as a flux driven phenomenon and this is directly related to the transmembrane pressure [67]. In particular, the critical flux, or closely related to “threshold flux”, defined as the flux beyond which severe membrane fouling occurs, has been used to highlight the important relationship between flux and fouling [68-70]. Note that these operational parameters can affect each other, and membrane fouling is synergistically influenced by more than one parameter in practical operations. Raised temperature is another operational fouling factor as it can worsen membrane scaling [71] and biofouling by increasing bacteria growth and multiplication [57].

(3) Membrane properties. The physico-chemical properties of the membrane surface influence foulant-membrane interactions, and play an important role in RO membrane fouling [6, 61]. Since this review focuses on engineering antifouling RO membranes, these membrane properties are discussed in detail below.

### ***3.1. Surface chemical composition***

Surface chemistry of the membrane governs the membrane surface properties (e.g. charge, hydrophilicity and fouling resistance) and performance (e.g. water flux and salt rejection). In particular, functional groups and chemical compositions of the membrane surface significantly affect membrane properties. Most membrane modifications for fouling reduction essentially are to introduce oxygen-containing groups (e.g. -COOH [72-

74], -OH [75-77] and $-SO_3H$ [78]) and/or biocidal agents (e.g. Ag [79-81], Cu [82], GO [83-85], polypyrrole [86] and antibiotics [87, 88]), and thus change the membrane surface chemistry. Commercial RO membranes are often coated with hydrophilic polyvinyl alcohol (PVA, rich in -OH) to impart antifouling properties by increasing surface hydrophilicity and decreasing surface roughness. After modification, the changes in membrane surface chemical composition (e.g. functional groups and element percentages) are typically characterized by Fourier transform infrared spectroscopy (FTIR) and/or X-ray photoelectron spectroscopy (XPS).

### *3.2. Surface hydrophilicity*

Surface hydrophilicity is one of the most important parameters affecting membrane fouling. Hydrophilic membranes often have lower fouling propensities. Generally, a membrane can be attractive (hydrophilic) or repulsive (hydrophobic) to water in an aqueous solution. Hydrophilicity of a membrane is often evaluated by the water contact angle between the membrane surface and a water droplet [89], but sometimes also evaluated by the air bubble contact angle between the membrane surface and an air bubble [90]. Hydrophilic membrane surfaces have water contact angles in the range of $0° < \theta < 90°$ (i.e. 90° < bubble contact angles < 180°). The membrane hydrophilicity is attributed to the presence of hydrophilic (oxygen-containing) functional groups that have the ability to form hydrogen-bonds with water molecules on the membrane surface. As a result, hydrophilic membranes tend to adsorb water molecules and thus form a hydration layer between the membrane surface and the foulant, which reduces the membrane-foulant hydrophobic interaction. This has been regarded as the key mechanism in reducing membrane surface fouling by membrane hydrophilic modification [73, 91, 92].

Compared with contact angle measurement, interfacial Gibbs free energy ($-\Delta G_{SL}$) may be a better parameter to represent membrane hydrophilicity due to the effect of membrane surface morphology (e.g. roughness) on contact angles [40]. Typically, larger values of Gibbs free energy mean more hydrophilic surfaces (i.e. lower water contact angles) as shown in Fig. 5a [93, 94]. Membrane fouling can be fundamentally explained by the minimization of interfacial Gibbs free energy [40]. Membranes after surface hydrophilic modification will have higher Gibbs free energy during fouling than the unmodified ordinary membranes (Fig. 5b). However, water contact angle measurement is much more common than Gibbs free energy for membrane surface hydrophilicity evaluation in practical applications since the former is much easier and more straightforward.

Most membrane modifications for fouling reduction are essentially hydrophilization that can be achieved by various methods, such as incorporating hydrophilic nanoparticles [95-97], plasma treatment [98-100], and introducing zwitterionic components [40, 101-103]. After hydrophilic modification, the treated membranes often become more absorptive to water but repulsive to hydrophobic foulants, leading to improve antifouling performance. However, the endowed hydrophilicity by surface modification may not be stable enough in practical long-term operations, which has been less studied and needs more research efforts in the future. A related feature of fouling is that as little as a monolayer of adsorbed foulant can change the effective membrane surface properties.

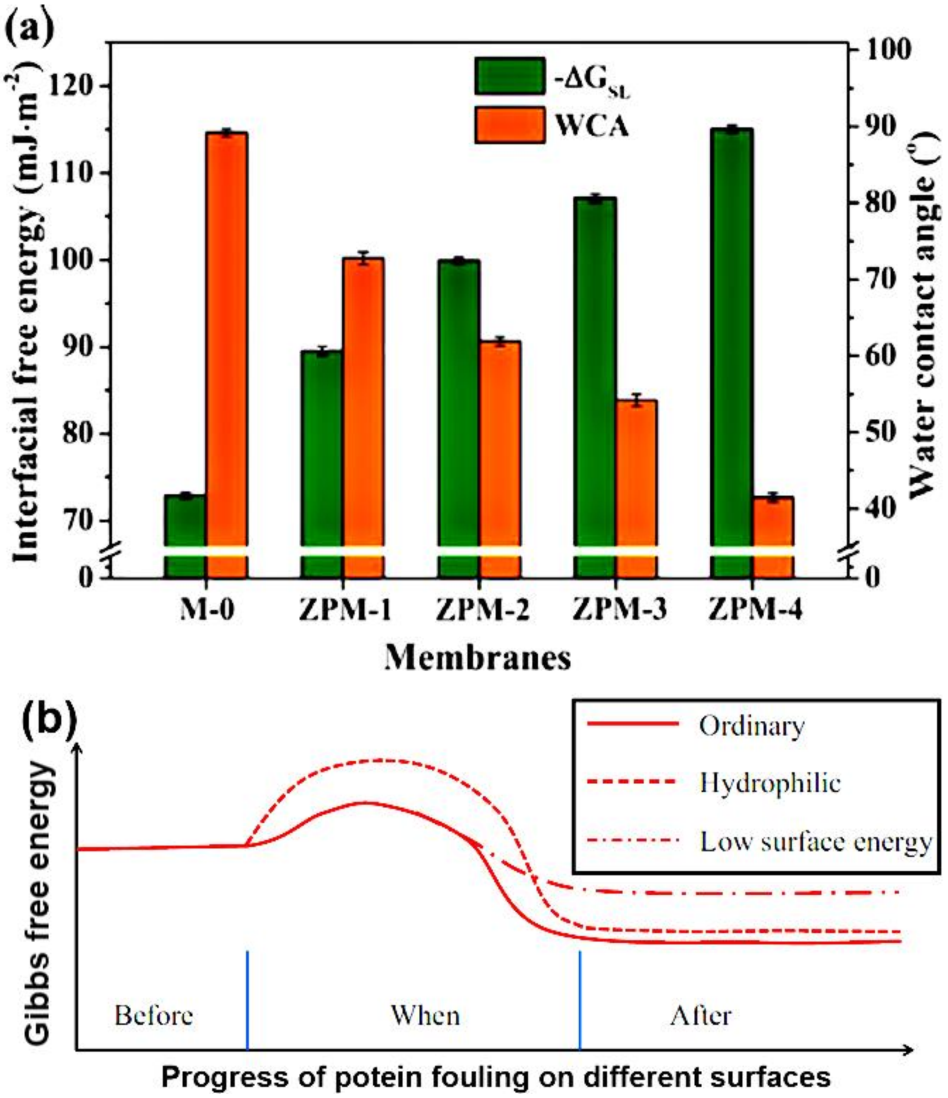

Fig. 5. (a) Relationship between interfacial free energy and water contact angle [93]. (b) Gibbs free energy changes during protein fouling on ordinary and hydrophilic membrane surfaces [40].

### *3.3. Surface charge*

The membrane surface charge has an important effect on fouling mainly via electrostatic interactions between membrane surfaces and foulants. The surface charge-induced electrostatic interactions between membranes and foulants can affect both fouling and rejection and of the membrane. Without such electrostatic interactions, severe membrane fouling and/or low rejection could occur, for instance, when the feed solution contains neutrally charged foulants or ions [104, 105]. The surface charge interactions are also dependent on the water chemistry (e.g. pH, and ionic species). RO membranes prepared by interfacial polymerization show amphoteric properties due to the unreacted carboxylic acid and amine groups on the surface [106]. The surface charge properties of RO membranes are essentially caused by the ionization of surface functional groups (e.g. -COOH and -$NH_2$ and -$SO_3H$) in aqueous media [104, 107]. As a result, most RO membranes are negatively charged under practical operation conditions (e.g. feed $pH < 8$). Desirable antifouling membranes should be close to neutral in their operations. Therefore, most TFC membranes after antifouling modification become less negatively charged [92, 108-112].

However, more negatively charged surfaces do not always suggest worse fouling resistance. Some TFC membranes may become more negatively charged, but still show better antifouling performance as the foulant types and their charge properties are complex [86]. Since most bacteria are negatively charged at neutral pH, initial adhesion of bacteria slows down on negatively charged surfaces through the repulsive force. Therefore, more negatively charged membranes after modification expect to have better anti-biofouling performance [113]. However, positively charged surfaces may have anti-microbial effects on Gram-negative bacteria, but not on Gram-positive ones [114]. A further complication of biofouling is that it is typically preceded by “surface conditioning” by organic molecules (NOM, TEP etc) and this can cause a change in effective surface charge.

### *3.4. Surface morphology (roughness)*

Another important factor that affects the performance of the RO membranes is the surface morphology. It is well known that rougher surfaces are more prone to attach foulants, while smoother surfaces have less fouling tendency but higher cleaning efficiency [115-117]. For example, Elimelech et al. [18] indicated that the TFC RO membranes had higher fouling rates than cellulose acetate RO membranes due to the higher surface roughness caused by the ridge-and-valley structures of the former. To overcome this issue, some commercial TFC RO membranes are coated with a neutral polyvinyl alcohol (PVA) layer [118]. The “ridge-and-valley” structures of TFC membranes can also be altered by coating nanomaterials in the rough structures, thereby reducing membrane surface roughness and fouling [119-121].

However, antifouling modifications do not always lead to smoother surfaces. Some antifouling modifications may result in rougher surfaces for the membranes [82, 122, 123], and other antifouling modifications may cause little change in membrane surface roughness [110, 124]. For antifouling modifications with nanoparticles, membrane surface roughness may reduce first and then increase with the rise in nanoparticle concentration, namely, a lower nanoparticle loading often causes smoother surfaces and a higher nanoparticle loading causes rougher surfaces [72, 76, 125]. The surface roughness of TFC membranes can also be influenced by the hydrophilicity and porosity of the support layer [126]. However, sometimes, the membrane surface roughness may have little effect on biofouling [127].

Overall, membrane surface chemical composition determines membrane surface hydrophilicity and surface charge properties. Improvements in oxygen content and hydrophilicity of the membrane surface often lead to better antifouling performance for the membrane. However, increasing or reducing the membrane surface charges and/or surface roughness does not necessarily improve the antifouling performance of the membrane. The modified membranes with improved fouling resistance could have increased or reduced surface charges/roughness, which will be detailed in the following section.

## 4. Modification strategies for RO membrane fouling reduction

Membrane modification for fouling reduction refers to membrane material engineering efforts implemented for slowing down the attachment of foulants onto the membrane surface, reducing flux decline and/or enhancing flux recovery. Antifouling modifications aim to alter the membrane properties that affect membrane fouling, including membrane chemistry, hydrophilicity, charge and roughness as discussed above, thereby reducing the foulant-surface interactions and thus membrane fouling [128]. Since fouling is most pronounced for TFC polyamide (PA) RO membranes among all types of RO membranes [17, 33], most antifouling modifications for RO membranes are performed on these membranes.

The most common TFC membrane has a thin selective PA layer synthesized during interfacial polymerization of m-phenylenediamine (MPD) and trimesoyl chloride (TMC) on a microporous substrate (Fig. 6a) [129]. Typical commercial TFC RO membranes have a thin selective PA layer (< 200 nm), a micro-porous substrate layer (~ 40 µm) and a thick non-woven fabric support layer (~ 120 µm) as illustrated in Fig. 6b [130]. The thin PA layer determines the membrane selectivity, while the substrate layer and the fabric support layer provide the mechanical strength and the water permeability due to their low mass transfer resistance, although the substrate properties can influence the PA layer (see below). In RO membrane applications, since the feed solution including foulants, directly contacts the selective PA layer, most antifouling engineering practice is performed for the PA layer of the RO membrane.

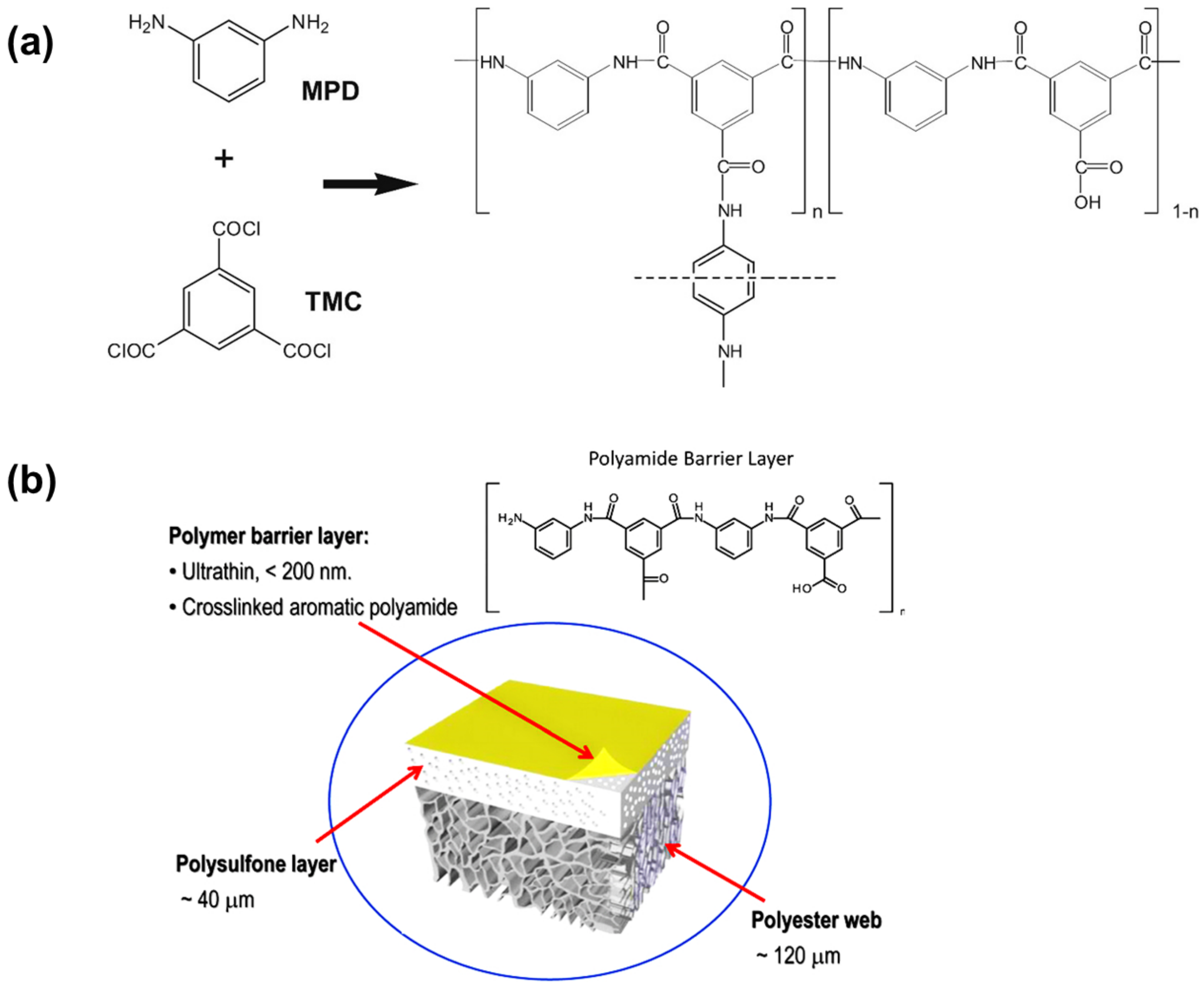

Fig. 6. (a) RO membrane polyamide layer formation by interfacial polymerization of MPD and TMC [129], and (b) different layers of TFC membranes [130].

There are three strategies for TFC RO membrane modification to reduce membrane fouling: (1) substrate (supporting layer) modification before interfacial polymerization, (2) incorporating additives (e.g. nanoparticles, nanotubes, and biocidal agents) into the polyamide layer during interfacial polymerization, (3) post (surface) modification after interfacial polymerization. These strategies are illustrated in Fig. 7, including intensively performed modification for the active layer during and after interfacial polymerization, and the less studied modification for the substrate layer [131]. Next, we will discuss these RO modification methods and applications in detail.

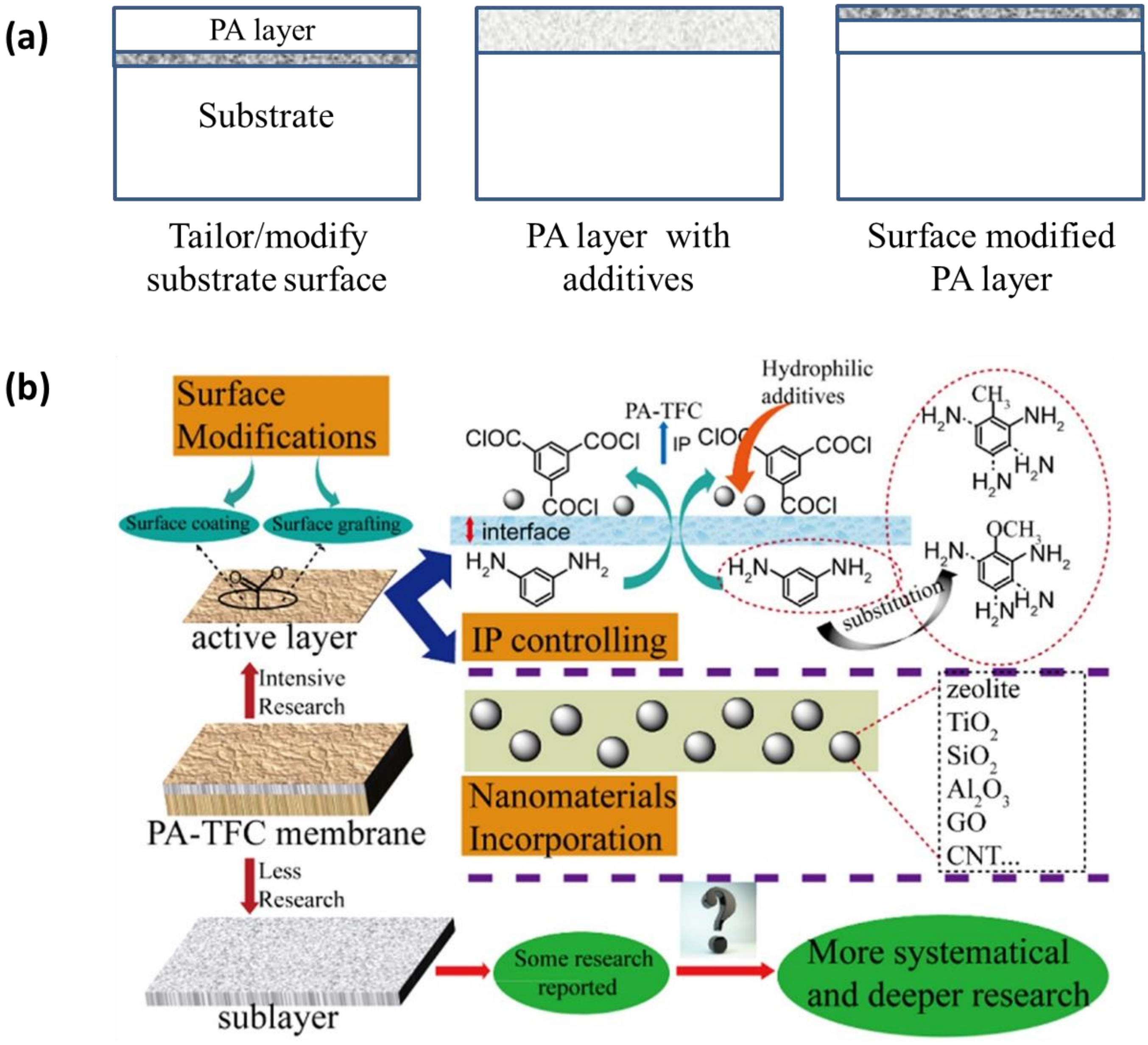

Fig. 7. Strategies for TFC membrane modification, including polyamide active layer modification and sublayer (substrate) modification: (a) simplified illustration, and (b) detailed illustration [131].

### *4.1. Substrate modification before interfacial polymerization*

The TFC RO membrane typically has a relatively thick porous substrate (supporting layer) and a thin dense PA layer. Generally, the substrate layer provides mechanical strength (i.e. pressure resistance) and the PA layer determines the membrane permeability and selectivity. However, recently researchers have started to realize the importance of the properties of the substrate in the final performance of the TFC membrane [131, 132]. In fact, the structure and characteristics of the polyamide selective layer formed by interfacial polymerization is related to the properties of the ultrafiltration support layer [133-136].

Many researchers have noticed the significant relationship between the properties (e.g. pore size, pore distribution, porosity, hydrophilicity and roughness) of the substrate and the performance (e.g. flux and rejection) of the TFC membrane. Singh et al. found that the smaller pore sizes of the substrate caused thicker polyamide active layer and thus higher salt rejection performance [137]. For TFC FO membranes, Huang and McCutcheon observed that the smaller pore sizes of the substrate caused higher crosslinking degree of the PA, leading to lower permeability but higher salt rejection performance [138]. Blending hydrophilic nanomaterials into the substrate layer typically leads to a looser surface (i.e. larger mean pore size by shifting the pore size distribution to the larger values and higher porosity) [73, 76]. Son et al. observed enlarged mean pore size, porosity and total pore area for the substrate layer after blending carbon nanotubes, which enhanced the water flux of the TFC membranes [139]. The NaA zeolite nanoparticle incorporated substrate layer became rougher and more hydrophilic, and the final TFC RO membrane had a smoother and more hydrophilic surface, and higher water flux and salt rejection [140]. However, the $TiO_2$ coated substrate layer with greater smoothness could also result in more hydrophilic and antifouling TFC membranes [141]. Therefore, roughness of the substrate layer alone has little effect on the hydrophilicity and antifouling performance of the TFC membranes, namely, there is no apparent connection between the substrate surface roughness only and the fouling resistance of a PA membrane. Surface hydrophilicity and pore areas (the combined effect of pore size, pore density and porosity) of the substrate may play a more pronounced role in the fouling properties of the TFC membranes.

According to numerical modelling, Ramon et al. reported that the substrate with higher porosity but smaller surface pores would lead to higher water permeability but lower salt selectivity of the TFC membrane [142]. This modelling also predicted that the local water flux through the composite membrane could be determined by the substrate pore morphology with local “hot spots” potentially exceeding the averaged flux by 2 times. These “hot spots” could exacerbate fouling since fouling is flux-driven. This observation argues for use of a “gutter layer” coating on top of the substrate to promote a more homogeneous local flux. Hydrophilicity of the substrate may play a more important role in the preparation and separation performance of the TFC membrane [143]. The substrate layer should be hydrophilic to facilitate interfacial polymerization, which can enhance the water flux and salt rejection performance of the TFC membrane [144]. However, hydrogen bonding between MPD and the hydrophilic substrate may limit the diffusion of MPD inside the substrate pores and some TMC may diffuse into the pores and form a thicker active PA layer with higher transfer resistance [143].

From the discussion above, it is evident that the results on effects of the substrate properties on the final performance of the TFC membrane vary significantly and sometimes may be contradictory. These inconsistent results from different researchers are mainly caused by the complex and varying experimental conditions. These varying conditions cover the substrate properties (e.g. material type, surface/cross-sectional pore size, pore distribution, surface/overall porosity, surface hydrophilicity and roughness, thickness) and the operating conditions (e.g. membrane casting temperature, humidity, speed, coagulation time, and temperature). The interfacial polymerization reaction, determined by the compositions of the MPD and TMC solutions, further increases the inconsistency between different investigations. Therefore, more comprehensive and systematic studies should be carried out to clarify the roles of the substrate in the composite membrane performance. It would be of interest to assess the reported data in terms of the potential effects of substrate-induced “hot spots”.

Although some work has been conducted to explore the relationship between the substrate properties and permeability-selectivity performance of the TFC RO membrane, much less study has examined the effect of substrate modification on fouling reduction. Chae et al. embedded graphene oxide (GO) nanosheets into the substrate layer and the PA layer of the RO membrane [145]. Compared with the single-layer incorporation with GO nanosheets, the dual-layer modification showed better performance in terms of water permeability and anti-biofouling property of the membrane. Similarly, Xie et al. incorporated modified GO into the membrane support and selective layer [146]. They found that dual-layer modification reduced the substrate pore size, but increased the porosity and hydrophilicity of the substrate layer, which led to thinner, smoother and more hydrophilic TFC membranes with higher permeability and fouling resistance. In fact, blending hydrophilic nanomaterials in the substrate layer during phase inversion often results in greater surface porosity, hydrophilicity and pore size for the substrate layer [73, 76, 147], which may prevent the aggregation of nanofillers and promote the formation of a smoother, more hydrophilic and uniform PA layer during interfacial polymerization [145]. As a result, the dual-layer modification method leads to enhanced water permeability and fouling resistance of the TFC membrane. It should also be noted that any coating layer added to the substrate would potentially help to reduce the formation of “hot spots” [142].

### *Remarks on substrate modification*

Substrate modification has received much less attention in developing antifouling RO membranes among the three antifouling engineering strategies for RO membranes. This may be caused by the indirect and complicated relationship between the substrate and the antifouling surface. Indeed, from the substrate to the antifouling TFC membrane, there are many variables covering the substrate properties (e.g. material type, surface/cross-sectional pore size, pore density and distribution, surface/overall porosity, and surface hydrophilicity and roughness), the operating conditions (e.g. membrane casting temperature, humidity, speed, coagulation time, and temperature) and similar parameters for the selective layer. Sometimes, it is difficult to attribute the substrate properties to the antifouling PA surface, particularly for the lab-made RO membranes with low repeatability and large experimental errors. This may be the reason that some investigations come to contradictory conclusions. In the future, antifouling modifications for RO membranes should also include the substrate layer rather than the selective PA layer only, although the impacts of the substrate on RO membrane fouling may be more indirect and complex. However, the positive feature is that substrate modification tends to be relatively facile.

### *4.2. Incorporating additives during interfacial polymerization*

#### *4.2.1. Metals and metal oxides*

Metals and metal oxides are generally hydrophilic and have biocidal properties [23]. Incorporating these materials into the PA layer during interfacial polymerization often enhances the antifouling properties of the TFC membranes [148]. Many metals and metal oxides, such as Ag, Cu, ZnO, $Fe_3O_4$, $Al_2O_3$, $ZrO_2$ and $Mg(OH)_2$, have been widely used to develop antifouling membranes [76]. Theoretically, all of these nanomaterials can be incorporated into the PA layer of the RO membrane. In practice, however, only a few of them have been used in the PA layer of the RO membrane as the very thin selective layer has higher requirements for the nanomaterials. The TFC membranes incorporated with nanomaterials into the PA layer during interfacial polymerization are also called thin film nanocomposite (TFN) membranes. Nanomaterials have been added to both the aqueous and the organic phase.

$TiO_2$ nanoparticles, alone or with assembly of other nanomaterials have been immobilized into the PA layer of RO membranes by adding them into the aqueous phase (i.e. MPD) during interfacial polymerization [149]. Modified nanoporous titanate was added to the oil phase (i.e. TMC) to modify the PA layer of TFC membranes to improve membrane fouling resistance [150]. Copper and silver are typical biocides for engineering antifouling RO membranes thanks to their disinfection abilities [151-153]. Wang et al. dispersed cerium oxide

($CeO_2$) into the organic phase to prepare TFC membranes [154]. Hydrophilic $CeO_2$ enhanced the water flux of the TFC membrane, and endowed the membrane with excellent antifouling property by forming a hydrogen barrier layer and stronger negative charge for the membrane selective layer. The adhesion of hydrophobic and electronegative foulants to the membrane surface were inhibited by the steric hindrance and electrostatic repulsion.

Some metals and metal oxides are responsive to light or oxidants. Therefore, incorporating such nanomaterials as metal or metal oxides into the TFC membranes could make them capable of degrading organic contaminants on the membrane surface to realize the redox self-cleaning property, thereby reducing organic fouling [155, 156]. Dumée et al. encapsulated catalytic silver species into metal organic framework (MOF) nanoparticles and then incorporated the Ag-modified MOF nanofillers into the PA layer during interfacial polymerization for catalytic degradation of organic pollutants [157]. However, all polymer based catalytic membranes face two challenges in practical applications. First, the stimuli (e.g. lights and oxidants) are difficult to introduce to the membrane surface in closed membrane modules. Second, the catalytic reaction will inevitably degrade the polymeric membranes in long-term operation. These two main drawbacks significantly reduce the feasibility and practicability of catalytic RO membranes in real-world applications.

#### *4.2.2. Carbon based nanomaterials*

Carbon based materials are attractive for membrane modification owing to their porous structures, biocidal activities and hydrophilic properties. A variety of carbon nanomaterials, such as carbon nanotubes (CNTs), graphene oxides (GO) and carbon dots (CDs) have been introduced to modify various membranes. Table 2 summarizes the typical carbon based nanomaterials incorporated into the PA layer of TFN membranes. Among them, GO, a type of two-dimensional (2D) nanosheet, has been the most widely studied carbon based nanomaterial for modification of various membranes (including microfiltration [158], ultrafiltration [159], nanofiltration [160], RO [161], forward osmosis [162] and gas separation membranes [163]). Abundant oxygen-containing functional groups (hydroxyl groups on the flat plane and carboxyl groups at the surface edge) providing hydrophilicity, and sharp edges, strong negative charges and laminar structures of GO are favorable intrinsic properties for engineering RO membranes. Feng et al. applied GO as nanofillers in the aqueous solution to prepare TFC membranes [164]. The GO modified TFC membrane showed an increased water flux, a salt rejection higher than 97%, and improved anti-swelling and antifouling properties. The authors attributed the enhanced performance to the hydrophilicity, negative charges and various chemical groups of the GO nanofillers. Chae et al. embedded GO in the polyamide layer by dispersing it in an aqueous solution of MPD to improve the RO membrane antifouling properties [165]. Both the size and the concentration of GO had an important effect in the performance improvement. The GO modified membranes with enhanced water flux and biofouling resistance and unchanged salt rejection were smoother and more hydrophilic.

Table 2. Typical carbon based nanomaterials used as nanofillers during interfacial polymerization to develop antifouling TFC membranes.

| Nanofillers | Modification method | Flux and rejection | Anti-fouling performance | Refs. |
|---|---|---|---|---|
| GO | Aqueous phase | 39% rise in flux; 1% decrease in rejection. | 35% higher flux recovery. | [164] |
| GO | Aqueous phase | 80% rise in flux; maintained rejection | 98% decrease of attached cells. | [166] |
| GO | Aqueous phase | 80% rise in flux and maintained rejection. | 260% higher antibacterial activity. | [167] |
| Z-CNTs | Vacuum filtration | Nearly three-fold rise in flux; comparable rejection. | 31% higher flux recovery. | [168] |
| $NH_2$-MWCNTs | Aqueous phase | Slightly increased flux and rejection. | 10% higher normalized flux. | [169] |
| GOQDs | Aqueous phase | 52% rise in flux and comparable rejection. | 20.8% higher flux recovery. | [170] |
| GOQD/AP | Aqueous phase | 54% rise in flux and comparable rejection. | 98.8% (in dark) and 99.9% (under visible light) higher sterilization rate. | [171] |
| H-OMC | Aqueous phase | 22% rise in flux; 18% decrease in rejection. | 36% lower BSA adsorption | [172] |

GO: graphene oxide; Z-CNTs: zwitterionic carbon nanotubes; $NH_2$-MWCNTs: $NH_2$ functionalized multi-walled CNTs;

GOQDs: graphene oxide quantum dots; AP: silver phosphate; H-OMC: hydrophilized ordered mesoporous carbon.

Similarly, He et al. dispersed GO in an aqueous solution of MPD to develop antibacterial TFC membranes [167]. The anti-biofouling property of the membrane was achieved due to the improved hydrophilicity, smoothness and negatively charged surface. Xia et al. reported a GO modified TFC membrane for removal of natural organic matters (NOMs) in river water [173]. The hydrophilic nature of GO increased the antifouling property by forming a hydration layer that prevented the adhesion of foulants. In addition, the GO modified TFC membrane exhibited higher removal efficiency for NOMs with different molecular weights. Inurria et al. added GO nanosheets into the organic phase (i.e. TMC solution) to prepare antifouling TFC membranes [174]. They found that increasing the GO loading in the TFC membranes increased the antifouling and antimicrobial properties, but could also reduce the water permeability of the membrane, suggesting a trade-off between water permeability and fouling resistance.

Compared with sole GO, GO-based nanocomposites seem to be more promising for RO membrane modification because of the enhancement or the synergistic effect between GO and the decoration fraction. Kim et al. incorporated GO and tannic acid (TA) modified GO (GOT) into the organic phase, and compared the performance of the TFC membranes with these two nanofillers [175]. After incorporating GO and GOT into the polyamide layer, the permeability, antimicrobial properties and chlorine resistance of the TFC membranes improved. They also observed that performance of the GOT modified membrane was superior to that of the GO modified membrane, suggesting the synergistic effect between TA and GO. In another work [176], comparisons between the TFC membranes prepared with the pristine GO and zwitterionic polymers grafted GO (Z-GO) were made. It was proved that incorporation of Z-GO into the selective layer enhanced the water permeability, selectivity and the antifouling properties. The TFN membranes fabricated with Z-GO were smoother and more hydrophilic compared with the control TFC membrane and the GO modified TFN membranes. Modification of GO can minimize the disadvantages of GO based TFN membranes, such as aggregation of GO, decreased salt rejection and increased surface roughness. Similar results were also reported by another team who prepared TFN membranes by incorporating $TiO_2$, GO and their mixture into the membrane polyamide layer [177]. The GO/$TiO_2$ TFN membranes showed better performance in terms of water flux, salt rejection, antifouling and chlorine resistance.

Wang et al. immobilized the zeolitic imidazolate framework-8 (ZIF-8) onto the GO nanosheet and the synthesized ZIF-8/GO was utilized as nanofillers for the preparation of TFN membranes [178]. The antimicrobial activity of the ZIF-8/GO TFN membrane was higher than that of the single component ZIF-8 TFN or GO TFN membranes. The better antimicrobial performance of the ZIF-8/GO TFN membrane was ascribed to the synergistic effect between ZIF-8 and GO. On the one hand, GO is a contact-based antimicrobial material, and owing to its structural characteristics, the GO nanosheets are prone to be buried under the PA layer, leading to fewer exposed effective sites. However, the stereo structure of ZIF-8 could facilitate the exposure of hybrid ZIF-8/GO composites onto the membrane surface, which would contribute to the improved antimicrobial performance. On the other hand, the coordination capacity between zinc ions and carboxyl groups of GO would be favorable for the uniform dispersion of ZIF-8 nanoparticles on GO nanosheets. The uniform dispersion of ZIF-8 is beneficial for supplying more active sites (imidazole rings and zinc ions) for the antimicrobial activity of the TFN membrane. Comparisons of the antifouling and anti-biofouling performances of the TFC, GO TFN, Ag-MOF TFN and GO-Ag-MOF TFN membranes were conducted by Firouzjaei et al. [179]. The contributions of each parameter, such as contact angle, surface roughness and charged properties were cross-compared in Fig. 8. The bacteria killing capacity of the GO-Ag-MOF TFN membrane was 16%, 30% and 92% higher than those of the Ag-MOF TFN, GO TFN and TFC membranes as demonstrated by fluorescence imaging. Besides, the water flux decrement of the GO-Ag-MOF TFN membrane was also less than other composite membranes. The explanations are probably the lower water contact angle, reduced surface roughness and lower zeta potential. Moreover, the enhanced negative charge also contributed to the higher salt rejection of the composite membrane due to the stronger Donnan effect.

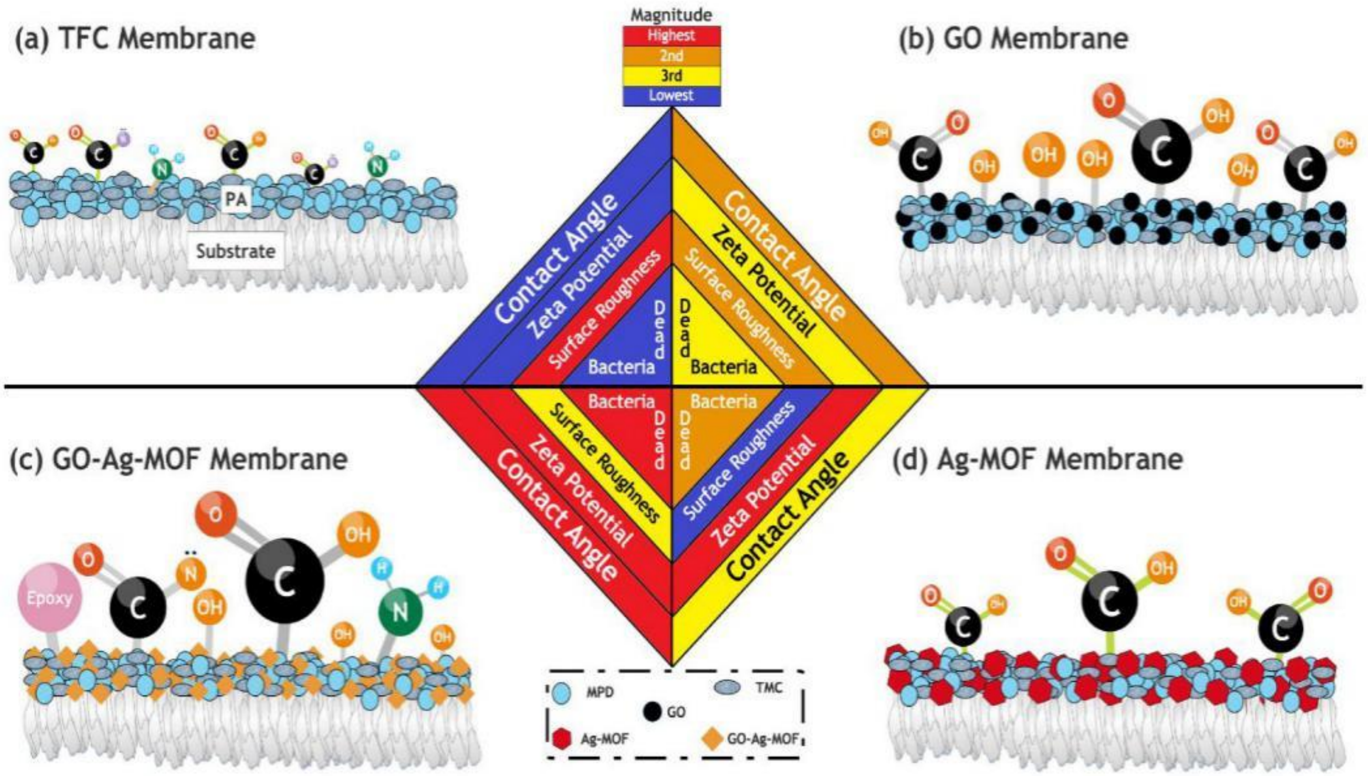

Fig. 8. Parameters contributing to anti-biofouling and antifouling properties of the membranes: (a) TFC, (b) GO TFN, (c) GO-Ag-MOF TFN, and (d) Ag-MOF TFN [179].

Apart from GO nanosheets, CNTs are also very popular for the modification of RO membranes. With the addition of multi-walled CNTs (MWNTs) into the aqueous phase, the porous structure and hydrophilic characteristics of the nanofillers are able to provide the TFN membranes with more water pathways and enhance the affinity between water and the membrane surface [180]. Besides, incorporation of negatively charged MWNTs could elevate the charge density of the membrane surface if required, although in many cases a more neutral surface is less fouling. The amelioration of hydrophilicity and charge property of the membrane could weaken the adhesion force and enhance the electrostatic repulsion between the foulant and the membrane surface. Zwitterionic CNTs (Z-CNTs) were incorporated into RO membranes via vacuum filtration during membrane synthesis [168]. The Z-CNTs appeared to form a strong hydration layer, resulting in improved surface biofouling resistance. Modified membranes had significantly reduced adsorption rate of protein foulants and better cleaning performance.

Zarrabi et al. assessed the performance of TFN membranes prepared by introducing $NH_2$ functionalized multi-walled CNTs ($NH_2$-MWCNTs) into the PA layer [169]. Owing to the hydrophilicity and tubular shape of $NH_2$-MWCNT, the flux of the TFN membrane was improved. Although the incorporation of $NH_2$-MWCNT increased the membrane roughness, which generally exacerbates the fouling propensity of the TFN membrane, the antifouling property of the TFN membrane was still better than that of the control TFC membrane. The authors attributed the improved fouling resistance to the enhanced membrane hydrophilicity, which counterbalanced the negative effect of the rougher surface. They also investigated the influence of $NH_2$-MWCNT for the modification of TFN RO membranes [181]. Similar results were reported, and the contribution of the enhanced negative charges of the TFN membrane for the elevated rejection and antifouling property was also discussed. Apart from organic fouling, CNTs are also able to mitigate the biofouling of TFN membranes. Zheng et al. prepared Z-CNTs and incorporated them into the PA layer of the TFN membrane [182]. Apart from the enhancement of water permeability and salt selectivity, better antibacterial properties of the TFN membrane were observed.

Recently, quantum dots of carbon materials, such as carbon quantum dots (CDs), graphene quantum dots (GQDs) and graphene oxide quantum dots (GOQDs) have been emerging in the fields of catalysis, sensing and energy [183]. As hydrophilic carbonaceous nanoparticles with small sizes, the quantum dots of carbon materials can be well dispersed in the aqueous solution and have excellent affinity with PA polymers. As reported by Li et al., CDs were added to the MPD aqueous solution during interfacial polymerization [184]. Results showed that the functional groups (e.g., hydroxyl, carboxyl, and epoxide) of CDs enhanced the hydrophilicity of the membrane surface. The water flux of modified membrane with 0.02% CDs loading, increased by 20%. The authors anticipated that chemically or physically modified CDs would enhance the antifouling property of the TFN membrane. Subsequently, Chung et al. made an attempt to functionalize the CDs with sodium ion to prepare TFN membranes for removal of selenium and arsenic [185]. The introduction of $Na^+$ modified CDs decreased the pore size and narrowed the pore size distribution of the TFN membrane, causing significantly enhanced selectivity. The rejection of the TFN membrane to $SeO_3^{2-}$ elevated from 82.4% to 98.6% and the rejection to $HAsO_4^{2-}$ increased from 91.3% to 99.5%. In addition, the antifouling property of the TFN membrane was also enhanced by promoting the formation of a hydration layer on the membrane surface against foulants after the incorporation of CDs.

Song et al. dispersed GOQD into the aqueous MPD solution and then deposited GOQD/MPD onto the substrate to form a cushion layer followed by interfacial polymerization [170]. The prepared RO membrane is more hydrophilic and durable in filtration experiments. After incorporation of hydrophilic GOQD, the formation of the hydration layer adjacent to the PA layer could prevent the adhesion of hydrophobic foulants, thereby increasing the antifouling property of the membrane. Moreover, the incorporated GOQD also enhanced the chlorine resistance of the TFN membrane by protecting the PA polymer from active chlorine. They also prepared a composite nanofiller by blending a biocide silver phosphate (AP) with GOQD. The incorporation of GOQD/AP conferred the TFN membrane with strong hydrophilicity and more water transport nanochannels. Besides, the synergistic antibacterial effects of AP and GOQD imparted the TFN membrane with excellent bactericidal property [171]. Moreover, the hydrophilic and negatively charged surface of the modified membrane was beneficial for the anti-adhesion of BSA by the steric hindrance of the hydrogen layer and the electrostatic repulsion between the membrane and BSA.

Similarly, GQDs are also attractive for membrane modification. For example, Bi et al. used GQDs as nanofillers for the preparation of TFN membranes [183]. The incorporation of GQDs bound with the reaction monomers and lowered the crosslinking degree, resulting in a membrane with a smoother surface. The antifouling properties were improved after the incorporation of GQDs thanks to the smooth and hydrophilic membrane surface. Xu et al. embedded GQDs into the selective layer during interfacial polymerization [186]. Electroneutral, smoother membrane surface and thinner selective layer of the TFN membrane was observed, which resulted in higher water permeability and improved antifouling properties. In addition, the covalent bonds between GQDs and PEI contributed to the stable filtration performance of the membrane.

In addition, other carbon nanomaterials, such as hydrophilized ordered mesoporous carbon (H-OMC), have also been investigated to incorporate into the PA layer of the RO membrane [172]. The hydrophilic property and porous structure of H-OMC enhanced the water flux of the TFN membrane. Meanwhile, better antifouling property of the fabricated TFN membrane was achieved by the electrical properties and hydrophilicity of the modified PA layer after the introduction of H-OMC.

Overall, incorporation of carbon based nanomaterials into the selective PA layer of RO membranes can enhance the water permeability of the membrane thanks to the hydrophilic membrane surface and additional water transport pathways (channels). Furthermore, the smoother, and more hydrophilic membrane surfaces after the modification by carbon based nanomaterials are favorable for antifouling properties. The shape edges of carbon nanomaterials also render the TFC RO membranes with better antibacterial activity. However, the difficulty in controlling aggregation of the nanomaterials, defects in the thin PA layer, the limited thickness of the PA layer, and nanoparticle leaching after interfacial polymerization should be carefully considered in practical applications. More investigations on these issues are highly recommended for future research.

### *4.2.3. Silica based nanomaterials*

Silica based nanomaterials, such as zeolites [187, 188], non-permeable silica nanoparticles [189] and porous silica nanospheres [190, 191] have been used to develop antifouling membranes due to their hydroxyl groups and active sites [190, 192, 193]. Meanwhile, most silica based nanomaterials are porous. The porous structures of silica based nanomaterials also expect to increase the membrane water permeability [187, 194].

Ang et al. synthesized silica nanoparticles with varying sizes of 50, 200, and 500 nm, and incorporated them into the PA layer to prepare TFN membranes during interfacial polymerization [195]. The results showed that the membrane surface roughness of the TFN membranes was larger than that of the pristine TFC membrane, and the introduced hydrophilic silica nanoparticles significantly strengthened the membrane hydrophilicity, leading to higher flux recovery ratios and thus enhanced antifouling properties. They also investigated influences of hollow silica nanoparticles with various shapes and dimensions on the performance of TFC membranes [196]. They found that the spherical silica nanoparticles were more suitable for the modification of TFC membranes, owing to the highest separation performance of the membrane compared with other cubic, or rod-like hollow silica nanoparticles. More importantly, because of the strong hydrophilicity, the spherical silica nanoparticles also enhanced antifouling properties to both positively charged cetyltrimethylammonium bromide (CTAB) foulant and negatively charged BSA foulant.

Most TFN RO membranes with higher permeability and antifouling performance are related to hydrophilic nanocomposites. However, in nature, water permeates faster in hydrophobic pores (e.g. aquaporin) due to lower affinity (friction force) between water and the hydrophobic wall of the pore. Methyltrichlorosilane ($MeSiCl_3$) is an interesting silica based nanomaterial with hydrophobic nanochannels. Shen et al. reported an antifouling TFN membrane prepared by interfacial polymerization of aqueous amine and organic methyltrichlorosilane/acyl chloride solutions [197]. They attributed the increased water flux and salt rejection to the hydrophobic nanochannels of $MeSiCl_3$, which could reduce the friction force between water molecules and nanochannels and facilitate the mass transfer. Meanwhile, the prepared TFN membrane showed improved antifouling property compared with the control TFC membrane.

The nanofillers discussed above mostly belong to inorganic nanomaterials. The polymer chains generally have poor compatibilities with inorganic nanomaterials. As a result, interfacial defects between polymers and inorganic nanofillers occur, lowering the membrane selectivity [86]. In addition, the incorporated nanofillers in TFN membranes are prone to leach into the solution, resulting in secondary pollution during water treatment.

#### *4.2.4. Polymer based nanomaterials*

Surface modification/functionalization of nanofillers is an effective strategy to enhance the compatibility between the fillers and polymers [198, 199]. Endowing organic segments and chemical groups to the nanofillers are desirable to improve the compatibility and stability of the composite membranes. Zhu et al. utilized zwitterions grafted GO as nanofillers to prepare composite membranes [200]. Surface modification of GO promoted the dispersion and the interfacial compatibility of nanofillers, improving the homogeneity of the composite membranes. Hence, the modified composite membrane presents higher selectivity and permeability. In addition, the favorable effect on membrane hydrophilicity and surface roughness led to better antifouling properties.

Because of the better compatibility between organic nanomaterials and PA polymers, recently polymer nanoparticles have attracted growing interest in membrane development. Compared with the inorganic nanomaterials for TFN membranes, polymer nanoparticles are more compatible with the PA chains [201]. Apart from the excellent compatibility, organic nanomaterials are prone to form strong bonds with the chains of PA, which is favorable for the stability of the composite membrane. Zwitterionic monomer N-aminoethyl piperazine propane sulfonate (AEPPS) has been added into aqueous MPD solution to react with TMC via interfacial polymerization to fabricate zwitterionic TFC RO membranes [202]. The surface hydrophilicity and antifouling properties of the modified membranes were greatly improved after introducing AEPPS into membranes. Jeon et al. designed a star-shaped polymer and incorporated it into the PA layer for preparation of RO membrane [203]. The prepared RO membrane displayed improved permeability owing to the thinner selective layer, and lower fouling tendency due to the smoother surface and higher surface charge density.

Zwitterionic colloid nanoparticles were added into aqueous MPD solution to prepare TFN membranes via interfacial polymerization, and the prepared membrane showed enhanced antifouling properties due to the improved hydrophilicity and negative charge density of the membrane surface [93]. Liao et al. introduced organic polypyrrole nanospheres into the PA layer of RO membranes via dispersing the fillers into the organic phase [86]. After the incorporation of organic polypyrrole, the water permeability and antibacterial property of the membrane significantly improved because of the positive charge of the embedded nanospheres. Liao et al. also prepared hydrophilic and hollow nanocubes (HHNs) via etching ZIF-8 with tannic acid, and introduced the HHNs into the PA layer during interfacial polymerization [204]. Compared with the hydrophobic and positively charged ZIF-8, the highly hydrophilic and negatively charged HHNs significantly enhanced the membrane hydrophilicity and charge property, leading to weakened adhesion and strengthened electrostatic repulsion of the surface to hydrophobic and negatively charged pollutants (Fig. 9ab). Therefore, the prepared TFC membrane had improved antifouling performance (Fig. 9cd). Most recently, Liao et al. further modified the membrane hydrophilicity and charge property by introducing resorcinol-formaldehyde nanobowls into the PA layer of the TFC membrane, which reduced the flux decline during filtrating feed solution containing organic pollutants [205].

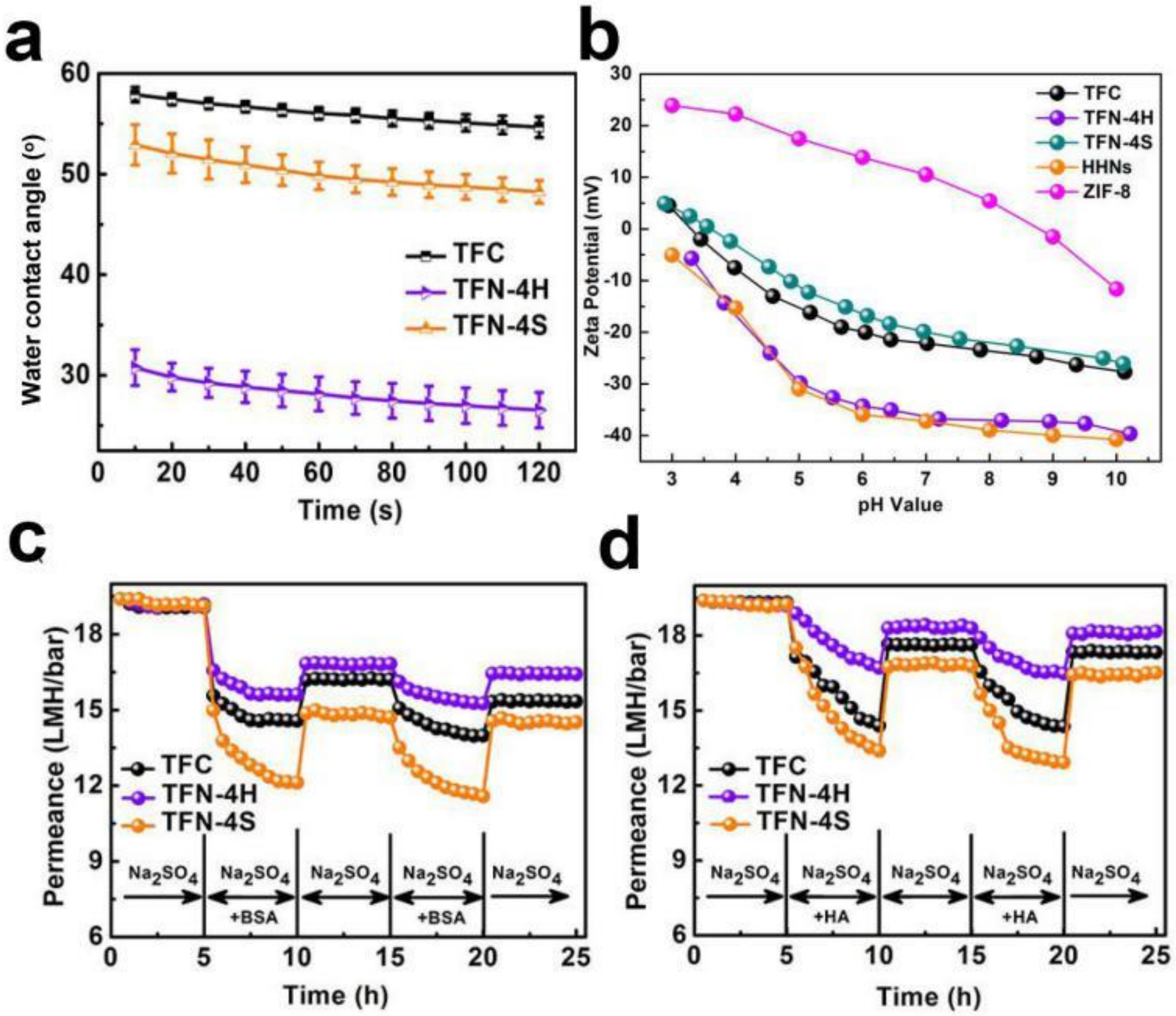

Fig. 9. (a) Water contact angles, (b) zeta potential properties, (c) long-term filtration performance using 1 g/L $Na_2SO_4$ and 1 g/L humic acid solution as the feed, and (d) using 1 g/L $Na_2SO_4$ and 1 g/L BSA solution as the feed [204]. TFN-4H: the thin film nanocomposite membrane prepared by adding 0.04 wt% hollow nanocubes into the organic solution during interfacial polymerization; TFN-4S: the thin film nanocomposite membrane prepared by adding 0.04 wt% solid ZIF-8 into the organic solution during interfacial polymerization.

Apart from the nanofillers mentioned above, some other nanofillers have also been reported for elevating the antifouling property of RO membranes. Dong et al. prepared two different TFN RO membranes by incorporating two oppositely charged nanoclays (a cationic clay: montmorillonite and an anionic clay: layered double hydroxide) into the PA layers [206]. Interestingly, both TFN membranes showed increased hydrophilicity, improved desalination performance and better fouling resistance to proteins, cationic surfactants, and natural organic matters, although they had different negative charge densities on the membrane surfaces.

### *4.2.5. Remarks on incorporating additives*

Table 3. Comparison of various parameters of the four types of nanofillers used for TFC RO membrane modification during interfacial polymerization.

| Parameters | Ranking of different nanofillers | | | |
|---|---|---|---|---|
| | Metals and metal oxides | Carbon based | Silica based | Polymer based |
| Antifouling properties | * | *** | ** | ** |
| Separation (flux and rejection) performance | * | *** | *** | ** |
| Robustness/compatibility | * | ** | * | *** |
| Simplicity of preparation | *** | ** | ** | * |
| Leaching and its environmental risks | * | ** | *** | *** |
| Cost | *** | * | ** | * |
| Research popularity | * | *** | ** | *** |
| Commercialization | * | ** | ** | * |
| Overall performance | 12* | 18* | 17* | 16* |

*** means beneficial property (high or low); ** means intermediate; * means negative property (high or low).

Table 3 compares different parameters of the four types of nanofillers used for TFC RO membrane modification during interfacial polymerization. Considering all the parameters of these nanofillers, the estimated ranking in terms of potential could be: carbon based > silica based > polymer based > metals and metal oxides. Metals and metal oxides are easy to prepare, and have relatively low costs but also have low popularity likely due to their high leaching potential and low content of hydrophilic groups; insufficient hydrophilic groups adversely affect their antifouling properties, separation performance and robustness in the polymer membrane. Carbon based nanofillers often lead to excellent antifouling properties and separation performance due to their rich and diverse hydrophilic functional groups. The great diversity of carbon based nanomaterials makes them attract significant research popularity. However, costs of emerging carbon based nanomaterials are usually not low. Silica based nanofillers often provide high separation performance due to their intrinsic pores. They face similar low compatibility with polymers and thus leaching issues with metals and metal oxides. However, silica based nanofillers have lower environmental risks after leaching compared with metals and metal oxides as well as carbon based materials. Polymer based nanofillers have high compatibility with the PA layer and thus low leaching risks, but their costs are typically high due to the complex preparation procedure. Recently, polymer based materials have attract growing research interest for engineering TFC RO membranes [198, 199]. Although all of these nanofillers display improved antifouling performance for RO membranes to some extent in lab-scale research, most of them have very low commercialization potential in the current stage. “Don’t start a business to commercialise a technology just because it seems great in the lab” [207] as lessoned by Professor Eric Hoek who commercialised his TFN RO membranes (Nano$H_2O$™) containing silica based nanofillers [208].

When incorporating nanomaterials into the very thin PA layer (50 - 200 nm) of TFN membranes, there should be some requirements for the nanomaterials, such as particle sizes, loadings, density of hydrophilic functional groups and compatibility between the nanomaterials and the polymers. However, these questions have not been well answered. A general guideline on these parameters for engineering next generation of high performance antifouling RO membranes should be developed. Most recently, Yeo et al. attempted to reveal the effects of nanofiller parameters, e.g. particle size, pore size and loading on TFN membrane performance by surveying 31 journal papers via machine learning [209]. They concluded that porous nanoparticles performed better than nonporous ones and the ideal situations are hydrophilic porous nanofillers with pore sizes between 5-7 Å, particle sizes ~150 nm, and loadings ~0.1 wt%. This conclusion was reached based on a relatively small data set (31 journal papers) and only applicable for some nanoporous particles. One of the challenges in such a comparison is that fouling protocols tend to differ between researchers. In the future, more extensive studies in this area should be done since there are numerous nanomaterials with diverse shapes, dimensions and properties available for membrane development.

### ***4.3. Post (surface) modification after interfacial polymerization***

Surface modification of existing (commercial or lab-prepared) membranes is another widely studied method to develop antifouling RO membranes [210]. Various physical and chemical post modification methods, such as surface adsorption [211], plasma treatment [212], radical grafting [213] and chemical coupling [214], have been employed to enhance the fouling resistance of RO membranes [129]. In physical modification, the coating materials attach to the active layers of RO membranes via electrostatic interaction, hydrogen bonding or van de Waals force [6]. These interactions are relatively weak, leading to unstable coatings in long-term operations. Therefore, physical modification is often combined with chemical modification. For example, plasma treatment is a physical irradiation method for surface modification, while it is often used together with chemical modification (e.g. graft polymerization) for RO membrane surface engineering [215, 216]. In chemical modification, the functional group of the coating material reacts with those of the active layer by covalent bonding and thus the modified membrane has better chemical and structural stabilities.

The surfaces of most commercial RO membranes have been treated to improve their performances (e.g. antifouling and antioxidation) [118]. Most commercial RO membranes also have preservatives (e.g. glycerin) to prevent them from undesirable reactions in air (e.g. oxidation). Therefore, these membranes are often soaked in or washed with deionized water or chemical agents (e.g. isopropanol) for some time to remove these preservatives or destroy the extra coating before further surface modification [217]. For the lab-prepared TFC RO membranes, these actions are not required since there is no coating after interfacial polymerization.

Four types of materials, including inorganic nanomaterials, organic polymers, hybrid inorganic/organic materials, and non-metal based biocides have been employed to modify RO membrane surfaces for fouling reduction. Typical inorganic materials are similar to those that have been used during interfacial polymerization for TFC RO membranes, such as metals and metal oxides, mineral salts, carbon based nanomaterials, and polymer/nanoparticle composites. However, inorganic materials often have relatively low compatibilities with the PA surface, and it is not easy to form uniform stable layers on the smooth dense PA surface. Therefore, organic polymers are more desirable for antifouling surface modification for RO membranes considering their practicability and long-term stability. These widely used organic polymers include ordinary hydrophilic polymers, zwitteronic polymers, quaternary ammonium polymers, hyperbranched polymers, amphiphilic polymers, and thermo-responsive polymers. Next, we will briefly introduce these inorganic nanomaterials and organic polymers.

### *4.3.1. Inorganic nanomaterials*

Table 4. Summary of inorganic nanomaterials used for surface antifouling modification of TFC membranes.

| Modification materials | Modification methods | Target fouling | Remarks | Refs. |
|---|---|---|---|---|
| Ag nanoparticles | Dip-coating by adsorption and reduction. | Biofouling | Improved biofouling resistance in real desalination plant test; Ag-modified spacer had more lasting antibacterial performance. | [218] |
| Ag nanoparticles | $AgNO_3$ was in situ reduced into Ag by $NaBH_4$ | Biofouling | Reduced water flux; increased surface roughness; improved biofouling resistance. | [151] |
| Ag nanoparticles | Covalent bonding by a bridging agent cysteamine. | Biofouling | Higher water flux but slightly lower salt rejection due to the effects of ethanol solution; enhanced biofouling resistance. | [81] |
| Ag nanoparticles | Surface grafted through hydrolysis, ion exchange and thermal reduction. | Biofouling and organic fouling | Rougher and more hydrophobic surface; improved anti-biofouling and anti-organic fouling properties. | [219] |
| Ag nanoparticles | In situ reduced by PDA. | Biofouling | More hydrophilic; slightly reduced water flux; improved salt rejection; enhanced biofouling resistance. | [153] |

| | | | | |
|---|---|---|---|---|
| Ag-decorated silica | Covalent bonding by cysteamine. | Biofouling | Maintained water flux and salt rejection; Significantly enhanced antibacterial properties against *E. coli*, *Pseudomonas aeruginosa* and *Staphylococcus aureus.* | [80] |
| TA-Fe-Ag | In situ reduced by TA-Fe | Biofouling | Increased hydrophilicity; increased water flux and salt rejection; 100% bacteria mortalities against *E. coli* and *B. subtilis.* | [220] |
| Cu | In situ reduced by NaBH$_4$. | Biofouling | Slightly increased water and salt permeability with comparable surface properties; 90% reduction of live *E. coli.* | [152] |
| Cysteamine- and GO-mediated Cu | CuSO$_4$ was in situ reduced into Cu by NaBH$_4$, during which bridging agents cysteamine and GO were used. | Biofouling | More hydrophilic; slightly reduced water flux; comparable salt rejection; significantly improved antifouling performance. | [217] |
| Cu(OH)$_2$ | Chelation with GO and mineralization under alkanes. | Organic fouling | Smoother and more hydrophilic membrane surface; higher flux with comparable rejection; weakened foulant deposition. | [221] |
| Silica nanoparticles | Silica was functionalized with APTMS, and then dip-coating. | Organic fouling and biofouling | Improved hydrophilicity, organic fouling and biofouling resistance; reduced water flux; comparable salt rejection. | [222] |
| GO nanosheets | Layer-by-layer assembly of GO and aminated-GO. | Organic fouling | More hydrophilic and smoother; increased water flux; comparable salt rejection; improved fouling and chlorine resistance. | [223] |
| TiO$_2$ and GO | Layer-by-layer self-assembly by hydrogen bonding and physical adsorption. | Biofouling | Improved hydrophilicity and biofouling resistance; the modified membrane with layer number $\leqslant$ 6 showed increased water flux and salt rejection. | [77] |
| Photocatalytic TiO$_2$ | Self-assembly through coordination and H-bond interaction with the COOH group by dip-coating. | Biofouling | Reduced water flux; increased salt rejection; photocatalytic bactericidal effect. | [224] |
| Catalytic CuO nanoparticles | PEI-assisted coating | Colloidal fouling, organic fouling and biofouling | Bubble generation and oxidation reduced colloidal fouling, organic and biofouling. | [225] |
| BaSO$_4$ | Surface coating by dip-coating. | Organic fouling | Uniformly distribution of BaSO$_4$; enhanced hydrophilicity and charge; elevated permeability and selectivity; reduced foulant deposition. | [226] |

PDA: polydopamine; TA: tannic acid; GO: graphene oxide; PEI: polyethylenimine; APTMS: 3-aminopropyl trimethoxysilane.

As summarized in Table 4, a number of inorganic nanomaterials, including Ag [151], Cu [152], Ag- and Cu-based nanomaterials [217, 220], $Cu(OH)_2$ [221], CuO [225], silica [222], $TiO_2$ [224], GO [223] and $BaSO_4$ [226] have been used for surface antifouling modification of TFC RO membranes. Most of these inorganic nanomaterials have biocidal properties. Therefore, they are often used to improve the biofouling resistance of the surfaces of TFC RO membranes, although they may also increase the resistance to organic fouling and colloidal fouling of RO membranes [225].

Most surface antifouling modifications of RO membranes with metal nanoparticles are realized by the in situ generation methods. Ben-Sasson *et al.* immersed a commercial TFC RO membrane into silver nitrate ($AgNO_3$) solution and left a thin layer of solution on the membrane surface (Fig. 10a). Subsequently, the sodium borohydride ($NaBH_4$) solution was poured onto the top layer of the membrane for *in situ* coating silver [151]. The final membrane was imparted with excellent antibacterial activity. Similarly, they introduced Cu nanoparticles onto the RO membrane surface via the same strategy [152]. The antibacterial activity of the modified RO membrane was strengthened, and the water permeability and selectivity of the composite membrane were less affected. Yang *et al.* pre-coated a commercial RO membrane with polydopamine (PDA) (Fig. 10b), and the modified membrane was subsequently soaked in $AgNO_3$ solution for *in situ* reduction of silver nanoparticles with PDA [227]. The thickness of the coated silver (Ag) nanoparticles was around 15 nm. After surface modification, salt rejection significantly enhanced with comparable water flux. In addition, the modified RO membrane showed excellent antimicrobial properties.

Dong *et al.* coated a commercial RO membrane with tannic acid (TA)-Fe-PEI complex, and then the modified membrane was immersed into silver ammonia environment for *in situ* generation of Ag nanoparticles (Fig. 10c) [220]. Owing to the decorations of the nano-Ag, the fabricated membrane was furnished with elevated permeability and higher anti-biofouling property. Besides, the force between TA and silver is also favorable for alleviating the leaching of Ag. Compared with the post-synthesized method, the *in-situ* formation of metal nanoparticles on the membrane surface generally leads to smaller particle sizes and uniform dispersion of the nanobiocides, which is more effective for the utilization of nanoparticles. Moreover, the *in-situ* strategy avoids the agglomeration of the nanoparticles, which could reduce the formation of unselective defects in the selective layer.

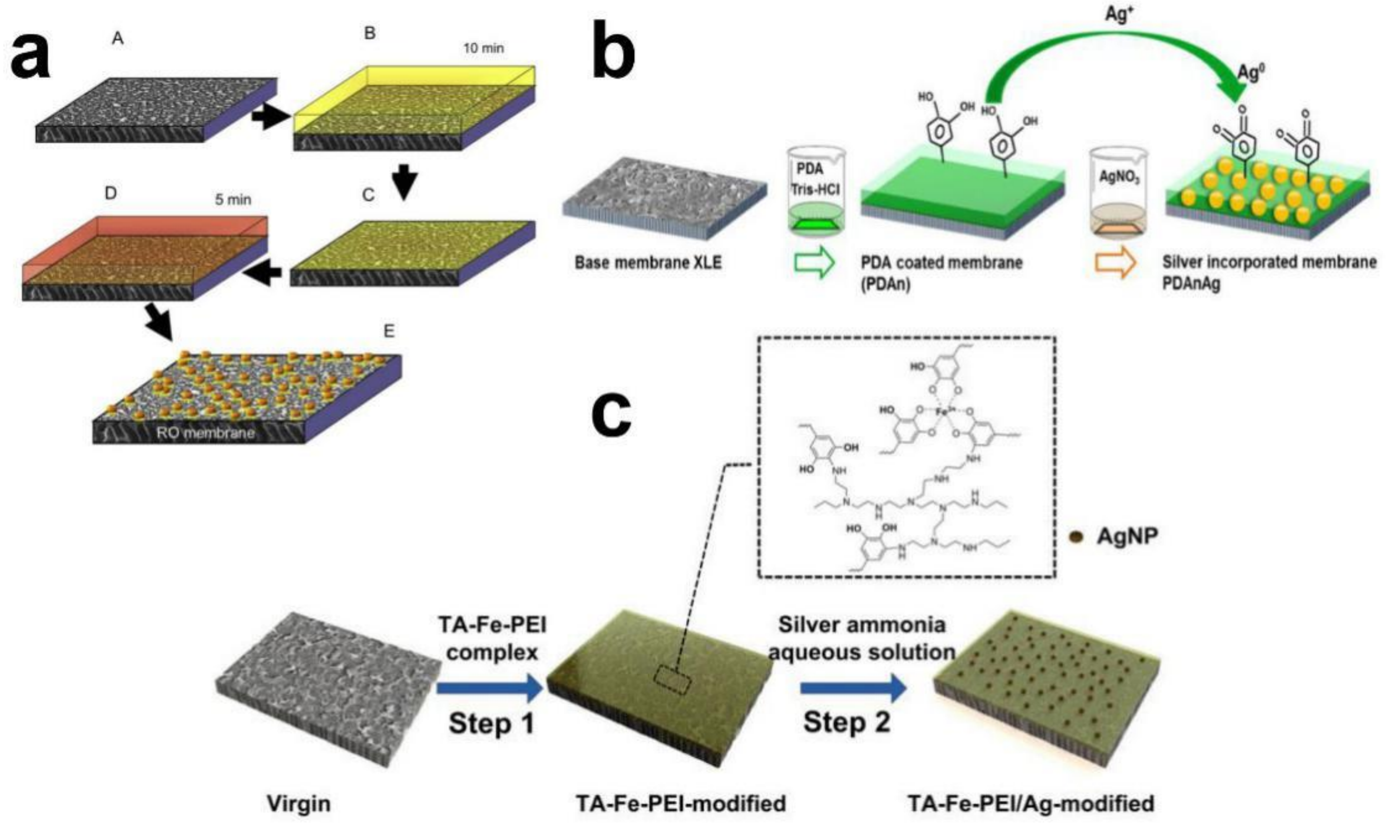

Fig. 10. Schematic diagram of in situ modifying RO membrane: (a) schematic diagram of in situ formation of Ag-NPs on a TFC RO membrane - first, the pristine TFC membrane (A) is covered by $AgNO_3$ solution (B); then, the $AgNO_3$ solution is removed leaving a thin layer of the AgNO3 solution on the surface (C); next, the membrane is contacted with $NaBH_4$ solution (D) to form the Ag-modified membrane (E) [151]. (b) In situ formation of Ag NPs on a TFC membrane [227]. (c) In situ immobilization of Ag NPs on the RO membrane surface [220].

Guha et al. anchored catalytic CuO nanoparticles on a commercial TFC RO membrane surface by the bioinspired PDA polymer as shown in Fig. 11 [225]. The coated CuO nanoparticle layer generated hydroxyl radicals (HO·) and $O_2$ that were able to degrade and sweep away the deposited organic foulants on the membrane surface by the Fenton-like reaction between the CuO and hydrogen peroxide. Besides, the formation of *E. coli* biofilm on the membrane surface was also inhibited by the introduced CuO nanoparticles. However, the exposed CuO nanoparticles tend to leach from the PA layer under crossflow shearing because of the weak interaction between CuO and the membrane surface. Also, the antifouling process consumes new chemical $H_2O_2$, and the catalytic oxidation reaction would likely damage the membrane in long-term operation. Therefore, imparting RO membranes self-cleaning and thus antifouling properties by using catalytic agents may not be feasible in practical applications.

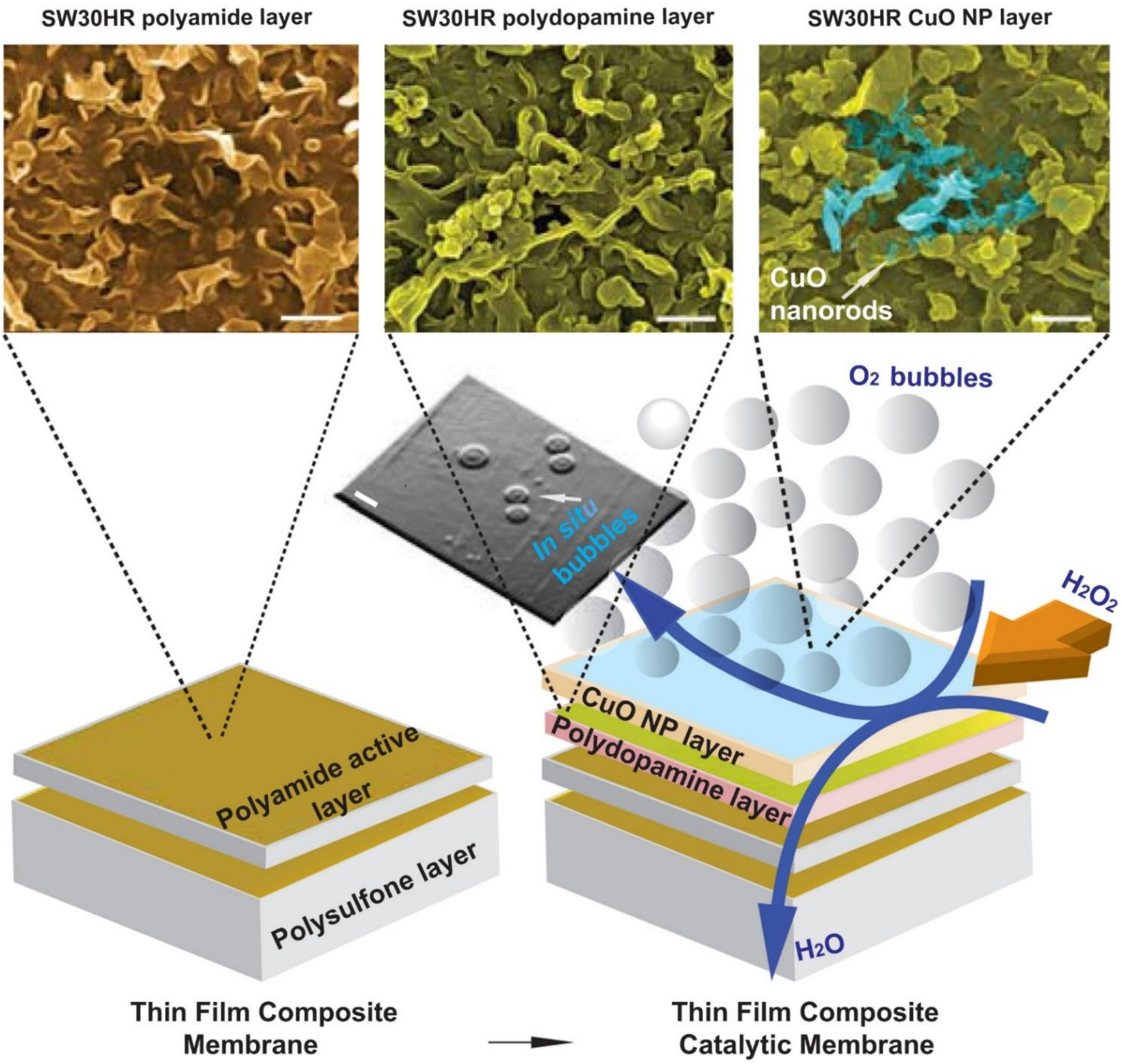

Fig. 11. Schematic of catalytic TFC RO membrane assembly and antifouling mechanism. The active polyamide layer was coated with polydopamine. Cupric oxide (CuO) nanoparticles were thereafter deposited on the polydopamine layer. Hydrogen peroxide ($H_2O_2$) was added to this membrane which on dissociation to molecular oxygen and water, generated in situ bubbles on the membrane surface sweeping away deposited foulants and disrupting concentration polarization. The SEM images have scale bars of 500 nm and the in situ bubbles image has scale bar of 150 µm.

Although various inorganic nanoparticles have been used for surface antifouling modification of RO membranes, the long-term stability of the coated nanoparticles on the membrane surface has not be well studied. Because the dense surfaces of RO membranes are much smoother than other pressure-driven (e.g. UF and NF) membranes, it is very challenging to coat a uniform, stable, long-lasting, fouling resistant layer with inorganic nanoparticles on the RO membrane surface, particularly under the requirement of not sacrificing water permeability of the membrane. This may be the reason that few commercial RO membranes have antifouling surfaces modified with inorganic nanomaterials.

### *4.3.2. Organic polymers*

Compared with inorganic nanomaterials, organic polymers are more desirable for RO membrane surface modification due to the better compatibility between the polymer chains. These polymers can be classified into four types: (1) ordinary hydrophilic polymers, (2) zwitteronic polymers, (3) biomimetic polydopamine (PDA), and (4) other polymers (e.g. hyperbranched polymers, thermo-responsive polymers, and amphiphilic polymers). These polymers have been coated onto RO membrane surfaces for fouling reduction by various methods, such as layer-by-layer assembly [228], contact coating (either via dip-coating or filtration coating) [229], polymerization [213], crosslinking [230] and combination of different techniques [231]. The PA membrane surfaces have unreacted carboxylic acid and amine groups that can be utilized for grafting. Grafting, refers to the addition of polymer chains onto a surface. Most of the chemical surface modification methods belong to surface grafting that can be induced by various mechanisms, such as UV, plasma, redox, cationic, anionic, free radical, enzyme, chemical vapor deposition, and atom transfer radical polymerization (ATRP) [23]. These polymer types, surface modification methods and their performance are summarized in Table 5. Next, we briefly discuss these typical polymers.

Table 5. Summary of organic polymers used for surface antifouling modification of TFC membranes.

| Modification materials | Modification methods | Target fouling | Remarks after surface modification | Refs. |
|---|---|---|---|---|
| PEI | Electrostatic self-assembly. | Organic fouling | Increased hydrophilicity and salt rejection; reduced water flux; improved fouling resistance with cationic surfactants. | [232] |

| | | | | |
|---|---|---|---|---|
| PEI | Carbodiimide-induced grafting with PEI. | Organic fouling | Changed the membrane from negative charge to positive charge; more hydrophilic; little change in surface roughness and salt rejection; reduced water flux; improved fouling resistance. | [233] |
| Poly(GHPEI) | PDA immobilization. | Biofouling and organic fouling | More hydrophilic and smoother; Lower flux; increased salt rejection; improved biofouling and organic fouling resistance. | [234] |
| Tobramycin and PAA | Layer-by-layer assembly. | Organic fouling and biofouling | Slightly enhanced water flux and salt rejection; significantly improved performance in organic fouling and biofouling resistance. | [228] |
| Polyelectrolyte (PSS and PAH) | Layer-by-layer assembly. | Organic fouling | More hydrophilic and smoother; increased salt rejection; reduced water flux; improved fouling resistance; the optimal layer number is 4. | [235] |
| PVP onto a metal-polyphenol precursor layer | Two-step dip-coating: self-assembly of TA and Fe(III) ions; PVP was immobilized by PEI. | Organic fouling | Slightly reduced water flux; unchanged salt rejection; improved organic fouling resistance; stable performance for 15 days. | [229] |
| ADMH | Free-radical graft polymerization | Biofouling | Improved water flux; slightly reduced salt reject; enhanced chlorine and biofouling resistance. | [213] |
| PVA | Thermally initiated free radial grafting | Organic fouling | More hydrophilic, smoother and less charged; increased salt rejection and slightly reduced water flux; improved fouling and chlorine resistance. | [236] |
| Sulfonated PVA | Contact coating and thermal crosslinking. | Organic fouling | More hydrophilic, smoother and more negatively charged; increased salt rejection and reduced water flux; improved fouling resistance. | [231] |
| PVA and cationic PHMG | Dispersion coating and thermal crosslinking. | Biofouling | Coating layer thickness: 100 - 250 nm; more hydrophilic and smoother; increased salt rejection and reduced water flux; improved biofouling resistance. | [214] |
| PVA and MPTES | Organic-inorganic hybrid gel fabricated by PVA and MPTES; coating and then thermal crosslinking. | Organic fouling | More hydrophilic, smoother and less charged; increased salt rejection and reduced water flux; improved fouling resistance. | [237] |
| PVAm | Surface grafting via amide bonding. | Organic fouling | Reduced water flux but increased salt rejection; improved antifouling performance. | [238] |
| Thermo-responsive polymer | Surface coating with poly(N-isopropylacrylamide-co-acrylamide) copolymer by hydrogen bonding | Organic fouling | Unchanged salt rejection; improved water permeability and fouling resistance. | [239] |

| | | | | |
|---|---|---|---|---|
| ASA, DEA and PIP | In-situ surface grafting small molecular monomers with amino groups. | Organic fouling | Unchanged surface roughness; increased hydrophilicity; slightly increased salt rejection and reduced water permeability; increased fouling resistance. | [240] |
| P(MDBAC-r-Am-r-HEMA) copolymer | Dip-coating followed by GA crosslinking. | Organic fouling and biofouling | More hydrophilic; rougher surface; slightly increased salt rejection; reduced water flux; less flux decline during BSA fouling; less bacterial adhesion. | [106] |
| P(ADMH-co-VAm) copolymer | Contact coating. | Biofouling | Similar rejections; water flux increased first and then decreased with increasing coating solution concentration; improved fouling resistance; coating layer thickness: ~ 8 nm. | |
| PEG | Surface grafting with aminopolyethylene glycol monomethylether (MPEG-$NH_2$) as the monomer. | Organic fouling | Increased surface roughness; reduced fouling indicated by less flux decline. | [241] |
| PEG | Surface grafting by crosslinker EGDMA. | Mineral scaling | Increased hydrophilicity; increased scaling resistance without organic matters in the feed; promoted $CaSO_4$ scaling if organic matters existed in the feed. | [242] |
| PEG acrylate | Layer-by-layer assembly. | Organic fouling | Increased surface hydrophilicity and roughness; reduced water flux; increased salt rejection; improved fouling resistance. | [243] |
| PEG derivatives | Carbodiimide-induced grafting. | Organic fouling | More hydrophilic and rougher; decreased water flux; unchanged salt rejection; improved fouling resistance. | [244] |
| SPM and PEGMA | Crossflow coating. | Fouling with real sea water. | PEGMA seemed to have a stronger anti-fouling effect than SPM; stable flux for 3 months. | [245] |
| PEGDE | Surface grafting | Organic fouling | Lower concentrations of higher molecular weight PEG caused better fouling resistance. | [123] |
| PEG-based hydrogels: PEGDA and PEGA | Surface crosslinking | Organic fouling | Reduced water flux; improved salt rejection and fouling resistance. | [230] |
| NIPAm and AA | Redox initiated graft polymerization of NIPAm followed by AA | Organic fouling | More hydrophilic; more negatively charged; slightly increased surface roughness and salt rejection; reduced water flux; less flux decline during BSA fouling. | [124] |
| PMAA and PAA | Plasma-induced graft polymerization | Mineral scaling, organic fouling and biofouling | More hydrophilic and smoother; improved water permeability and scaling resistance; unchanged salt rejection and organic fouling resistance; enhanced biofouling resistance. | [215, 216, 246] |

| | | | | |
|---|---|---|---|---|
| Triethylene glycol dimethyl ether (PEG-like) | Plasma polymerization | Organic fouling | More hydrophilic and rougher; slightly reduced water flux and salt rejection; improved fouling resistance. | [98] |
| Block copolymer of PEG and Nylon-6 | Dip-coating | Organic fouling | Significantly dropped water flux; comparable salt rejection; improved fouling resistance; increased fouling resistance was not sufficient to compensate for the flux reduction. | [247] |
| Silane | Dip-coating and quaternization | Biofouling | More hydrophilic and smoother; increased water flux; comparable salt rejection; improved biofouling resistance. | [248] |
| Silane coupling agents | Sol–gel process | Organic fouling | Less hydrophilic and rougher; significant flux drop; comparable salt rejection; less flux decline during fouling. | [249] |
| Sericin | In-situ deposition by cross-flow circulation. | Organic fouling | Smoother and more hydrophilic; increased salt rejection and reduced water permeability; increased fouling resistance. | [250] |
| Zwitterionic pSBMA | Grafting by surface-initiated ATRP. | Organic fouling | Unchanged salt rejection; significantly improved water flux (by ~65%) and fouling resistance (irreversible fouling reduced by ∼97%). | [121] |
| Zwitterionic coating | p(4VP-co-EGDA) co-polymerization via initiated chemical vapor deposition | Organic fouling; biofouling | Reduced water flux but slightly increased salt rejection; improved fouling resistance. | [42, 251] |
| Zwitterionic L-DOPA | Dip coating | Organic fouling | Improved water permeability and unchanged salt rejection; improved antifouling performance. | [252] |
| Zwitterionic amino acid L-cysteine | Covalent bonding by the thiol-ene reaction. | Organic fouling | Smoother and more hydrophilic surface; increased salt rejection; reduced water flux; less flux decline during organic fouling test. | [253] |
| Zwitterionic MPC | Grafting by surface-initiated ATRP. | Biofouling | Reduced water flux and salt rejection; improved biofouling resistance. | [254] |
| zwitterionic CBMA | Redox initiated graft polymerization of DMAEMA, followed by quaternization with 3-BPA. | Biofouling | Similar surface hydrophilicity and roughness; changed from negative charge to positive charge at pH7.0; increased water flux; comparable salt rejection; anti-adhesive and anti-microbial properties. | [255] |
| Zwitterionic PSVBP | Surface-initiated free radical polymerization. | Organic fouling | More negatively charged; increased hydrophilicity; less flux decline and improved cleaning during BSA fouling. | [256] |
| PDA assisted polyzwitterion (MPC-*co*-AEMA) | PDA coating; dip-coating in MPC-co-AEMA copolymer solution. | Biofouling | Neutrally charged surface; reduced water flux; comparable salt rejection; improved biofouling resistance. | [257] |
| HPOEM and zwitterionic carboxylated PEI | Dip coating, crosslinking with glutaraldehyde, and | Organic fouling | HPOEM-coated RO membranes showed salt-out effect and thus better fouling resistance in brackish water desalination; carboxylated PEI | [258] |

| | | | | |
|---|---|---|---|---|
| | PEI carboxylation. | | coated membranes had salt-in effect and thus better fouling resistance in seawater desalination. | |
| PDA | UV-accelerated PDA coating | Organic fouling | More hydrophilic and smoother surface; reduced water permeability; increased salt rejection; less flux decline under alginate fouling. | [259] |
| PDA | Surface deposition | Biofouling | Little change in hydrophilicity; reduced water flux; comparable salt rejection; improved biofouling resistance. | [260] |
| PDA and PDA-*g*-PEG | Contact coating | Organic fouling | PDA coating led to little flux decline; PDA-*g*-PEG coating led to significant flux decline; BSA adhesion reduction for the two coated membranes. | [261] |
| PDA-*g*-PEI | PDA coating followed by grafting of PEI. | Organic fouling and biofouling | More hydrophilic and rougher surface; reduced water permeability; comparable salt rejection; improved organic fouling and biofouling resistance. | [262] |
| Hyperbranched PAMAM | Spray coating | Organic fouling | Little change in surface roughness; less negatively charged; increased water flux; slightly reduced salt rejection; less flux decline during BSA fouling. | [263] |
| Thermo-responsive polymer P(NIPAM-co-Am) | Crossflow coating by hydrogen bonding. | Organic fouling | More hydrophilic; increased water flux and salt rejection; less flux decline during BSA fouling; higher efficiency at higher temperature. | [239, 264] |
| Amphiphilic MMA-HPOEM copolymer | The copolymer was synthesized by free radical polymerization; then dip-coating. | Organic fouling, biofouling. | Less negatively charged; reduced water flux; salt rejection was not reported; slightly increased fouling resistance. | [265] |
| Amphiphilic HEMA-*co*-PFDA copolymer | Initiated chemical vapor deposition | Organic fouling | More hydrophobic; large drop in water flux; salt rejection was not reported; the antifouling performance was not significant. | [266] |
| Amphiphilic HEMA-*co*-PFDA copolymers | Initiated chemical vapor deposition | Biofouling | More hydrophobic; rougher surface; comparable salt reject; large drop in water flux; reduced static bacterial adhesion. | [267, 268] |

PEI: polyethylenimine; Poly(GHPEI): poly(guanidine-hexamethylenediamine-PEI); PDA: polydopamine; PAA: poly(acrylic acid); PSS: Poly(sodium 4-styrenesulfonate); PAH: poly(allylamine hydrochloride); PVP: poly(N-vinylpyrrolidone); ADMH: 3-allyl-5,5-dimethylhydantoin; PVA: polyvinyl alcohol; PHMG: polyhexamethylene guanidine hydrochloride; MPTES: 3-mercaptopropyltrimethoxysilane; PVAm: polyvinylamine; ASA: amidosulfonic acid; DEA: diethanolamine; PIP: piperazine; P(MDBAC-r-Am-r-HEMA): poly(methylacryloxyethyldimethyl benzyl ammonium chloride-r-acrylamide-r-2-hydroxyethyl methacrylate); P(ADMH-co-VAm): poly(3-allyl-5,5-dimethylhydantoin-co-vinylamine); PEG: poly(ethylene glycol); EGDMA: ethylene glycol dimethacrylate; SPM: sulfopropylmethacrylate; PEGMA: PEG ester of methacrylic acid; PEGDE: poly(ethylene glycol) diglycidyl ether; PEGDA: poly(ethylene glycol) diacrylate; PEGA: poly(ethylene glycol) acrylate; NIPAm: N-isopropylacrylamide; PMAA: poly(methacrylic acid); PAAm: poly(acrylamide); pSBMA: poly(sulfobetaine methacrylate); ATRP: atom transfer radical polymerization; p(4VP-co-EGDA): poly(4-vinylpyridine-co-ethylene glycol diacrylate); L-DOPA: amino acid 3-(3,4-dihydroxyphenyl)-l-alanine; MPC: methacryloyloxyethyl phosphorylcholine; CBMA: carboxybetaine methacrylate; DMAEMA: N,N-dimethylaminoethyl methacrylater; 3-BPA: 3-bromopropionic acid; PSVBP: poly (4-(2-sulfoethyl)-1-(4-vinylbenzyl) pyridinium betaine); AEMA: 2-aminoethyl methacrylate; PAMAM: poly(amido amine); P(NIPAM-co-Am): poly(N-isopropylacrylamide-co-acrylamide); MMA: methyl methacrylate-hydroxy; HPOEM: hydroxyl poly(oxyethylene) methacrylate homopolymer; HEMA: hydroxyethyl methacrylate; PFDA: perfluorodecyl acrylate.

*Ordinary hydrophilic polymers*. Several ordinary hydrophilic polymers, including PVA, poly(ethylene glycol) (PEG), acrylic acid (AA), polyacrylic acid (PAA), polyethylenimine (PEI), and their derivatives, have been used for antifouling surface modification of RO membranes. PVA is a water-soluble, neutrally charged, hydrophilic polymer with rich hydroxyl groups (-HO) and water-loving and film forming properties. Therefore, PVA and its derivatives (e.g. sulfonated PVA and polyvinylamine) have been used to modify the RO membrane surface for fouling minimization (Table 5) [236-238]. PEG is another common water-soluble, uncharged polymer having flexible long chains, large exclusion volume, and strong ability to prevent the adsorption of hydrophobic or organic molecules onto the membrane surface. PEG, PEG-based polymers/hydrogels and PEG-like polymers are also popular in RO membrane surface modification for fouling reduction [98, 123, 230, 241, 242, 244].

AA is the simplest unsaturated carboxylic acid and it often reacts with other materials to form new hydrophilic agents, such as PAA [215, 216, 246] and AA-grafted CNTs [269] for antifouling modification. PAA is a hydrophilic anionic polymer having hydroxyl groups (-HO), while typical PEI is a branched cationic polymer with primary, secondary and tertiary amine bonds rich in amine groups ($-NH_2$). Because of their charge properties, PAA and PEI have been employed for membrane antifouling modification or functionalization via electrostatic interaction (e.g. layer-by-layer assembly) [228, 232, 270]. Hydrophilic poly(sodium 4-styrenesulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) have also been used to modify TFC RO membranes by layer-by-layer assembly for fouling reduction [235]. However, as a physical approach the assembly modification based on relatively weak electrostatic interaction cannot provide long-lasting stability for the prepared membranes, which may limit their applications for practical desalination and water treatment. Utilizing the hydrophilic and cationic properties, PEI has also been grafted onto negatively charged TFC RO membrane surfaces to prepare positively charged antifouling membranes by carbodiimide-induced grafting [233]. Sericin, a hydrophilic natural polymer with groups of hydroxyl, carboxyl and amino groups, has also been used for surface modification of RO membranes by dip-coating followed by in situ cross-linking with glutaraldehyde (GA) [271].

*Zwitterionic polymers* with the same number of cations and anions along their polymer chains have been widely used for various antifouling membrane developments [90, 272]. Zwitterionic polymers endow membrane surface with antifouling properties mainly through two mechanisms as illustrated in Fig. 12 [40]. The first mechanism is to form a hydration layer via electrostatic interactions on the membrane surface. Compared with PEG and its derivatives, zwitterionic polymers can bond with much more water molecules for each unit (Fig. 12ab) and thus form denser and thicker hydration layers on the membrane surface. Therefore, zwitterionic polymers may perform better than PEG-based polymers in repelling bio-foulants [273]. Another mechanism is the steric hindrance effect (Fig. 12c). Zwitterionic polymer chains act as brushes with high mobility and hydrophilicity on the membrane surface, which tend to maintain a swelling state and thus repulse foulants from attaching to the membrane surface. The antifouling properties of zwitterionic polymers are closely related to their charge distribution. The zwitterions with balanced charges and minimized dipoles can fully bind water molecules and repel charged proteins via electrostatic interactions [274].

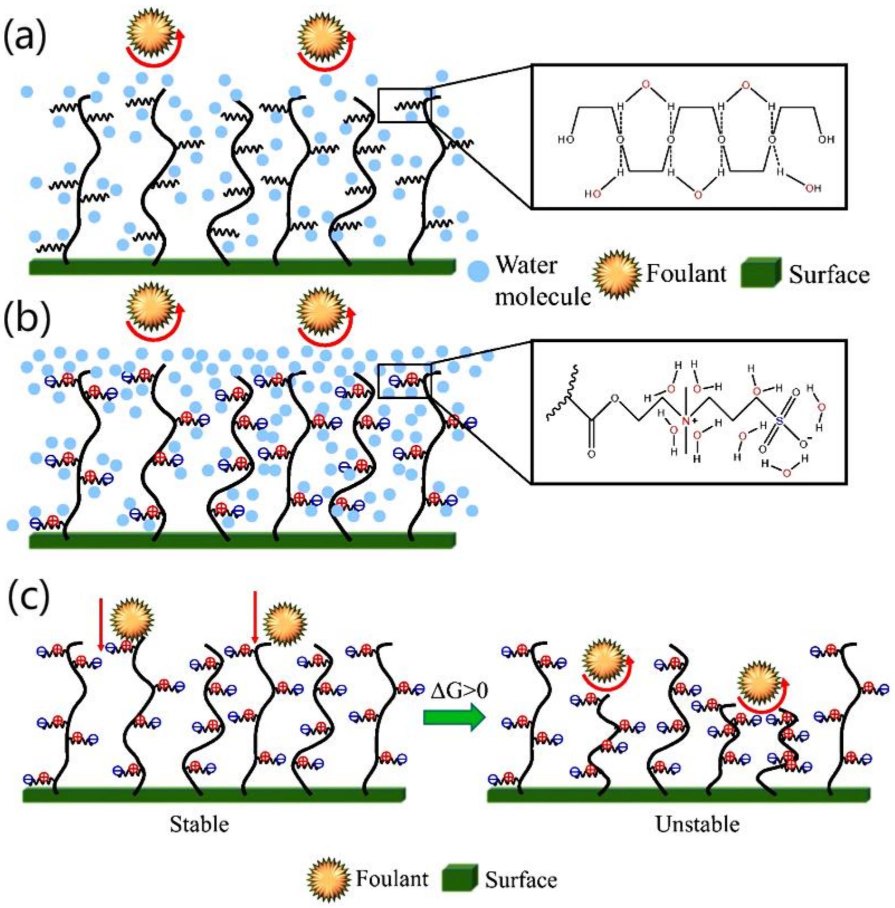

Fig. 12. Schematic illustration of antifouling mechanisms of zwitterionic polymers. (a) Each unit of PEG polymers bonding with one water molecule, (b) each unit of zwitterionic polymers bonding with eight water molecules, and (c) the steric hindrance effect: the unstable compression state of the zwitterionic polymer by foulants tends to go back to the stable swelling state and thus repulse foulants from attaching to the membrane surface [40].

As summarized in Table 5, various zwitterion-based materials have been applied for surface antifouling modification of RO membranes by different methods. These methods mainly include surface grafting [255], surface coating [275] and biomimetic PDA-assisted coating [252]. Surface grafting refers to the anchoring of polymer chains onto a solid surface (e.g. a membrane surface) through chemical bonding. Surface grafting can be induced by either “grafting from” or “grafting to” strategy [276]. For RO membranes, most surface modifications are performed via “grafting from”, including conventional radical polymerization [277] and living radical polymerization [254]. Surface coating refers to the deposition or self-assembly of polymers, nanoparticles, or other modifying agents onto the membrane surface via nonspecific interactions, and the typical methods for surface coating include adsorption, self-assembly and initiated chemical vapor deposition. Surface coating tends to form dense smooth membrane surfaces with improved selectivity and reduced water permeability [40].

*Biomimetic polydopamine.* Recently, PDA and its derivatives have attracted growing interests for various membrane modifications due to its versatile adhesive properties [95, 278-281]. PDA is a highly hydrophilic because of the catechol, quinone and amino groups in its structure, and highly adhesive to almost all types of substrates via covalent bonding, hydrogen bonding, and electrostatic and hydrophobic interactions [279, 282]. PDA acting as a bio-glue can attach to different substrates even with opposite properties for surface functionalization [283]. Antifouling surface modification with PDA is often realized in two ways. First, PDA itself can be coated onto RO membranes to increase the surface hydrophilicity, thereby reducing membrane fouling [261, 284-286]. However, PDA coating through dopamine polymerization often requires a long time (a few hours to even 16 hours) [261]. UV [259] and tobramycin (TOB) [88] have been used to accelerate the antifouling surface coating with PDA.

Second, PDA can also be used as an adhesive agent to increase the surface functionalization and immobilization with other antifouling materials. Recently, PDA has been used to immobilize $TiO_2$ nanoparticles [287-289], PEG [261, 290], and zwitterionic polymers [257] to the RO membrane surface. Generally, a thin pure PDA layer generated in a short polymerization time will not introduce large mass transfer resistance and thus significantly affect the RO membrane separation performance in terms of water permeability and salt selectivity. Immobilizing extra antifouling and/or hydrophilic materials (e.g. macromolecules) would inevitably increase the mass transfer resistance and thus reduce the water permeability of the membrane [261]. Therefore, there is a balance between the water permeability decline and the flux maintenance after antifouling modification during the foulant filtration.

*Hyperbranched polymers* are highly branched three-dimensional (3D) macromolecules with globular and dendritic architectures and unique properties, such as abundant functional groups, intramolecular cavities, low viscosity, and high solubility [291]. Although hyperbranched polymers have been used to modify MF [292], UF [293], NF [294] and FO [295] membranes, few studies have been focused on surface antifouling modification of TFC RO membranes. Nikolaeva et al. chemically coupled a hydrophilic hyperbranched poly(amido amine) (PAMAM) onto the active PA-layer of a RO membrane by spray coating [263]. Interestingly, the modified RO membrane showed increased water flux but slightly reduced salt rejection, which was likely caused by the incomplete formation of the PA layer after introducing PAMAM. Less water flux decline was observed for the modified RO membrane. After hyperbranched polymer coating, the 3D globular and dendritic architectures are typically thick (300 - 400 nm) [263] and loose, the stability of the coating layer could be an issue under high crossflow velocity and high pressure conditions. Therefore, surface antifouling modification with hyperbranched polymers may not be practically feasible for high pressure dense RO membranes.

*Thermo-responsive polymers* with low critical solution temperature (LCST) have been employed to engineer antifouling membranes. Yu et al. synthesized two thermo-responsive copolymers N-isopropylacrylamide-co-acrylic acid (P(NIPAm-co-AA)) [264] and poly(N-isopropylacrylamide-co-acrylamide) (P(NIPAM-co-Am)) [239] by free radical copolymerization, and coated them onto the RO membrane surface by hydrogen bonding. Interestingly, the coated RO membranes showed improved water permeability and salt rejection when using coating solutions of lower concentration. The surface modification with thermo-responsive polymers also reduced the flux decline during BSA fouling and improved the cleaning efficiency at temperature above the LCST. The fouling resistance and cleaning efficiency of the modified membranes were respectively imparted by the enhanced hydrophilicity and the phase transition property of the thermo-responsive coating layer. However, phase change surfaces for RO membranes are not desirable as a highly stable (both thermally and chemically) and selective layer is of great importance for RO membranes. Also, altering the temperature for membrane cleaning is not technically feasible in practical operations.

*Amphiphilic polymers* with both hydrophilic and hydrophobic components have also been synthesized and used to develop antifouling membranes. Although amphiphilic polymers showed excellent performance in engineering antifouling resistant surfaces [296, 297], their applications for antifouling surface modification of RO membranes is not promising. For example, amphiphilic methyl methacrylate-hydroxy poly(oxyethylene) methacrylate (MMA-HPOEM) and hydroxyethyl methacrylate-*co*-perfluorodecyl acrylate (HEMA-*co*-PFDA) copolymers were grafted onto RO membrane surfaces for fouling reduction [265-268]. However, more hydrophobic and rougher surfaces were observed and the slightly improved antifouling performance might not be able to compensate the significant flux decline due to the extra mass transfer resistance after surface grafting. These limited attempts suggests amphiphilic copolymers may not be effective for antifouling surface modification of RO membranes due to the relatively dense surface of the membrane and the large and complex repeating units of the copolymers.

### *4.3.3. Combination of inorganic nanomaterials and organic polymers*

Table 6. Summary of antifouling surface modifications of TFC membranes with hybrid organic and inorganic materials.

| **Coating materials** | **Modification methods** | **Target fouling** | **Remarks** | **Refs.** |
|---|---|---|---|---|
| PEI-coated Ag and hydrophilic polymer brushes (i.e. poly(sulfobetaine) and PDMS). | Layer-by-layer self-assembled with PAA and PEI; and then functionalized by grafting of polymer brushes. | Biofouling | Increased surface hydrophilicity and roughness; decreased water flux and increased selectivity; 95% inactivation of attached bacteria and around 90% decrease in cell adhesion. | [298] |
| PEMs/Ag/ polyzwitterion | Layer-by-layer assembly by PAH and PSS; NaNO3 in situ reduction by $NaBH_4$; polyzwitterion deposition. | Biofouling | More hydrophilic; 15% Reduction in water permeability; comparable salt rejection; improved biofouling resistance. | [299] |

| | | | | |
|---|---|---|---|---|
| PDA-Ag | In situ reduction by precoated PDA. | Biofouling | Uniformly dispersed Ag with more hydrophilic surface; increased rejection with decreased flux; more than 40% higher bacteria inactivation. | [300] |
| PSBMA-Ag | Surface grafting with in situ reduction by $NaBH_4$. | Biofouling and organic fouling | Rougher and more hydrophilic surface; 95% higher antimicrobial activity with 8% lower flux decline. | [301] |
| Zwitterion-Ag | Surface grafting with zwitterions and then in situ immobilization of Ag by $NaBH_4$. | Biofouling and organic fouling | Increased hydrophilicity; improved flux and salt rejection; significantly improved antimicrobial and antifouling properties. | [302] |
| PEI modified Cu | Cu was modified with positively charged PEI, and then applied to negatively charged RO membrane for functionalization by electrostatic interaction. | Biofouling | Enhanced positive charge; maintained membrane transport parameters; 80-95% reduction in the number of attached live bacteria. | [82] |
| PEI modified Cu | Spray- and spin-assisted layer-by-layer assembly. | Biofouling | Achieved uniform coating layer; maintained salt reject but slightly (13.3%) reduced water flux; excellent antimicrobial property. | [270] |
| Chitosan linked Cu | In situ formed and fixed via reduction and crosslinking of carboxylated chitosan. | Biofouling and organic fouling | Elevated hydrophilicity; lower water flux and higher salt rejection; more than 99% antibacterial efficiency and higher protein fouling resistance. | [303] |
| AA+ COOH-MWCNTs | Surface grafting. | Organic fouling | Increased hydrophilicity and salt rejection; reduced water flux; improved fouling resistance. | [269] |

PDMS: poly(dimethylsiloxane); PSBMA: Poly(sulfobetaine methacrylate); COOH-MWCNTs: carboxylated multi-walled carbon nanotubes.

Inorganic nanomaterials often have low compatibility with the PA layer of the TFC RO membrane. Therefore, they are often combined with organic polymers for surface antifouling modification of RO membranes. Table 6 summarizes antifouling surface modifications of TFC RO membranes with hybrid organic and inorganic materials. Obviously, the dominant inorganic nanomaterials used are Ag and Cu and these surface modifications mainly target for improving the biofouling resistance of the RO membranes. Generally, there are three strategies for the hybrid inorganic/organic materials to modify TFC RO membrane surfaces for fouling reduction, including: (1) inorganic nanomaterial modification with organic polymers followed by coupling the functionalized nanomaterials onto the PA layer (Fig. 13a), (2) PA layer surface modification with organic polymers followed by bridging/growing inorganic nanomaterials onto the treated surface (Fig. 13b), and (3) PA layer surface modification with inorganic nanomaterials followed by organic polymer deposition (e.g. crosslinking or grafting) (Fig. 13c).

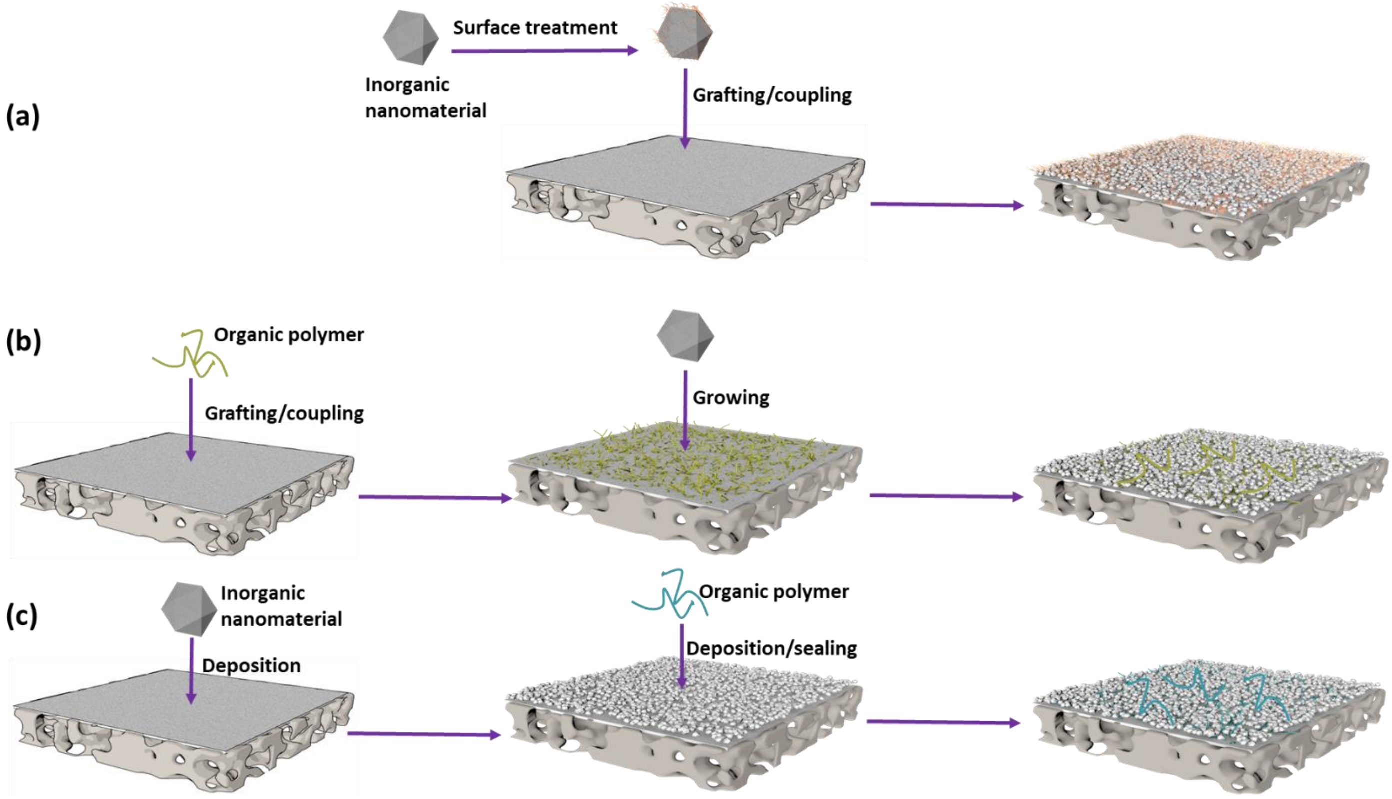

Fig. 13. Typical strategies for surface modification of TFC membranes using hybrid organic and inorganic materials.

### *4.3.4. Other biocidal agents*

Apart from metal-based biocidal agents, other antibacterial agents have also been used for surface modification of RO membranes with the target of biofouling control. Tobramycin (TOB) is a potent antimicrobial agent with a broad antibacterial spectrum, and it is chemically stable. Wang et al. developed TFC RO membrane with enhanced biofouling resistance by surface modification via layer-by-layer assembly of PAA and TOB [228]. Under optimal modification conditions, the treated membrane showed slightly increased permeability and selectivity, and achieved more than 99.6% killing ratio for both Gram-negative *E. coli* and Gram-positive *B. subtilis*. Later, they developed another RO membrane with fouling release, fouling resistant and biocidal properties by grafting a low-surface-energy fluorine-based material 2,2,3,4,4,4-hexauorobutyl methacrylate (HFBM) first and then TOB on the membrane surface (Fig. 14) [87]. The prepared RO membrane displayed excellent organic fouling and biofouling resistance due to the anti-adhesion, self-cleaning and antimicrobial characteristics. Zhao et al. coated TOB and PDA onto a commercial RO membrane surface and found that TOB could not only accelerate the polymerization of dopamine, but also avoid the use of the tris buffer solution during the surface coating [88]. The modified RO membrane also showed significantly improved organic fouling and biofouling resistance.

Quaternary ammonium (QA) is a class of cationic disinfectants with excellent biocidal properties against both Gram-positive and Gram-negative bacteria [304]. Hibbs et al. attempted to use QA functionalized polymer to develop biofouling resistant RO membranes by spray coating [305]. The QA modified surface showed hydrophobic properties, but excellent biocidal performance and killed 100% of the *E. coli* cells. However, it seemed that the QA functionalized polymer was not promising for RO surface modification because of the significantly reduced water flux.

N-halamine has durable and regenerable antimicrobial activities against a wide spectrum of microorganisms without causing environmental concerns [306]. A hydantoin derivative 3-monomethylol-5,5-dimethylhydantoin (MDMH) has been used as the precursor to prepare N-halamine biocides for engineering biofouling resistant RO membranes via surface grafting [307]. The grafted MDMH moieties with high reaction activity and free chlorine could play as sacrificial pendant groups when membranes suffer from chlorine attacks, and the chlorination products of N-halamines with strong antimicrobial function could sterilize microorganisms on membrane surfaces and then regenerate to MDMH. Similarly, 3-allyl-5,5-

dimethylhydantoin (ADMH) with high reaction activity with free chlorine to generate antimicrobial N-halamines has also been grafted onto the PA RO membrane surface by free-radical graft polymerization for biofouling control [213, 308]. However, the chlorination reaction on the membrane surface could damage the membrane integrity and thus reduce membrane selectivity.

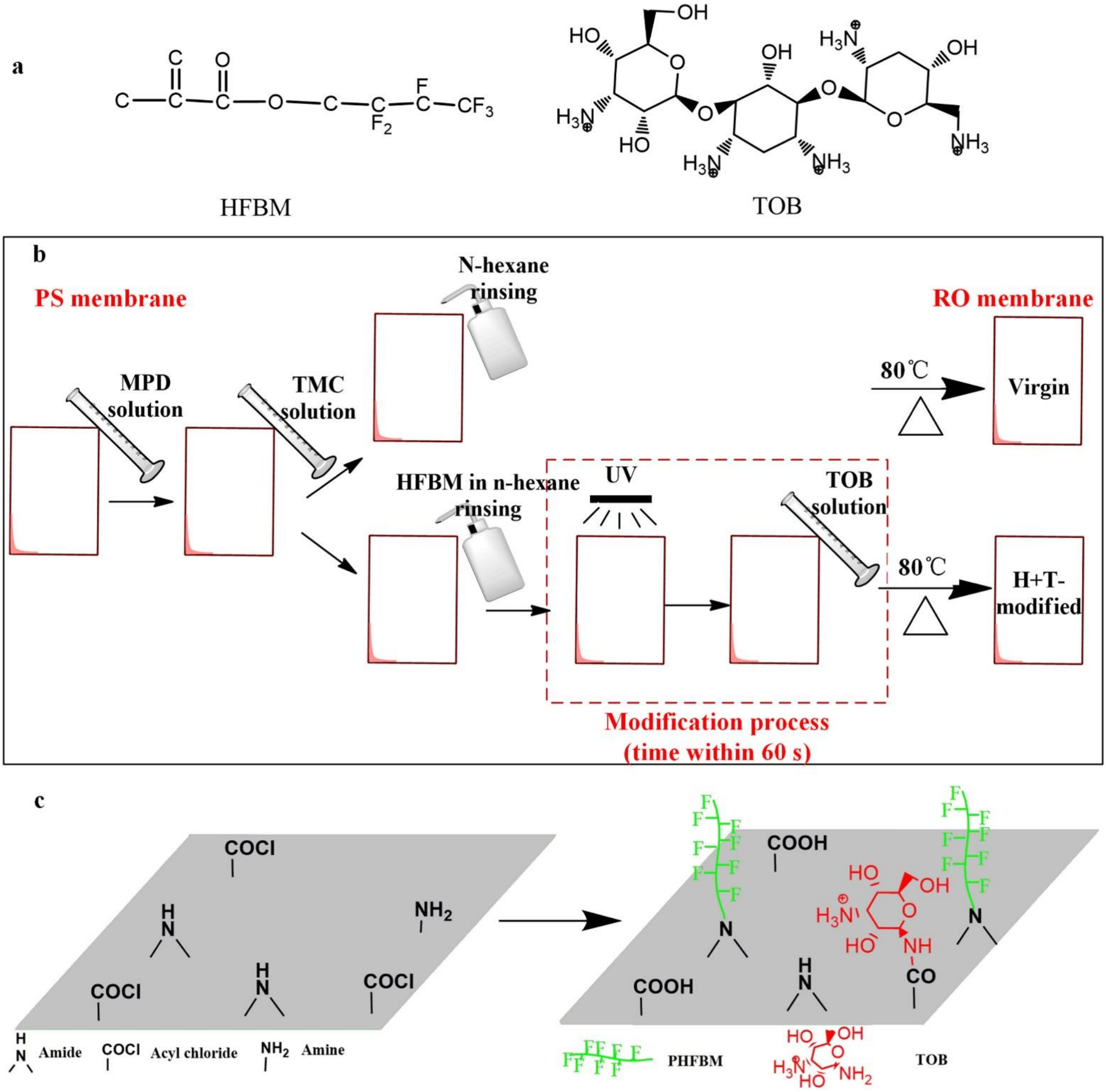

Fig. 14. (a) Chemical structures of HFBM and TOB, (b) schematic diagram of membrane fabrication process, and (c) modification mechanism [87].

The antimicrobial properties of [2-(methacryloyloxy)ethyl]trimethylammonium chloride (MTAC) have been employed to develop biofouling resistant materials [309]. Blok et al. coated PDA-g-MTAC onto a commercial TFC RO membrane surface by the electron transfer-ATRP method [310]. Before coating, the RO membrane was treated by isopropanol for 30 min. As a result, the coated membrane showed increased water flux and comparable salt rejection. Six-day incubation tests with nutrient solution confirmed a 93.2% reduction in bacteria on the modified PA RO membrane compared with the unmodified one, suggesting the excellent biocidal performance of the PDA-g-MTAC coating layer. The coating process required a long time (up to 24 h), which may impede their practical applications.

### *4.3.5. Remarks on surface modification*

Table 7. Comparison of various parameters of the four types of nanomaterials used for surface modification of TFC RO membranes.

| Parameters | Ranking of different nanomaterials | | | |
|---|---|---|---|---|
| | Inorganic | Organic polymers | Hybrid organic-inorganic | Organic biocides |
| Antifouling properties | *** | *** | ** | ** |
| Separation (flux and rejection) performance | ** | * | ** | * |
| Robustness/compatibility | * | *** | ** | *** |
| Simplicity of preparation | *** | Varies | * | * |
| Leaching and its environmental risks | * | *** | ** | ** |
| Cost | *** | Varies | ** | * |
| Research popularity | ** | *** | ** | * |
| Commercialization | * | *** | ** | * |

| | | | | |
|---|---|---|---|---|
| Overall performance | 16* | >18* | 15* | 12* |

*** means beneficial property (high or low); ** means intermediate; * means negative property (high or low).

Table 7 compares different parameters of the four types of nanomaterials used for surface modification of TFC RO membranes. Considering all the parameters of these nanomaterials, the estimated ranking in terms of potential could be: organic polymer > inorganic > hybrid organic-inorganic > organic biocides. Interestingly, this ranking order well agrees with the research popularity order of these nanomaterials. For surface modification with inorganic nanomaterials, particle leaching and aggregation are always issues that need more attention. Such modification has low commercial potential, although it has low cost and intermediate popularity due to its simple preparation. In the future, long-term tests for biofouling evaluation by inorganic nanomaterials should be carried out. For example, a biocidal coating layer inactivates (or kills) incoming bacteria that could accumulate on the membrane surface. Once the coating has leached sufficiently, the surface would then promote bacterial growth.

Most surface modifications of RO membranes have been focused on fouling reduction, although they often decrease the membrane permeability and increase the selectivity. It seems that the benefit of the increased selectivity has been underestimated. A recent study called for research efforts to increase RO membrane selectivity rather than the permeability [9]. It is true that further increasing permeability brings limited benefit for specific energy cost reduction for seawater desalination. However, RO membranes are used in many other applications, such as water reuse and brackish water treatment. For feed solutions of low osmotic pressures, high-permeability membranes are more beneficial for reducing energy consumption for a fixed plant size or reducing plant size at fixed energy consumption [10, 311]. Therefore, critical assessment and research efforts are required to evaluate the synergetic effects of reduced fouling, modestly increased selectivity and decreased or unchanged permeability after surface modification of RO membranes.

The great diversity of organic polymers makes their simplicity of preparation and cost vary a lot, attracting significant research popularity. Organic polymers often lead to excellent antifouling properties for RO membranes, but also decrease water permeability. Some hydrophilic polymers (e.g. PVA) have been commercialized for surface coating of RO membranes. Most parameters for hybrid organic-inorganic nanomaterials are intermediate except extra steps for fabricating the hybrids. Organic biocides have similar performance with other organic polymers, but they have less types and may cause environmental concerns, leading to their low research popularity and commercialization potential.

Compared with other pressure driven (e.g. MF, UF and NF) membranes, the surfaces of RO membranes are much denser and smoother. Consequently, some nanomaterials and modification methods that have been widely used for engineering MF, UF and NF membrane surfaces may not be feasible for surface modification of RO membranes. Surface modification often inevitably causes extra mass transfer resistance and thus reduce water permeability of the RO membrane. Particularly, some macromolecules with complex structures and large molecular weights (e.g. hyperbranched polymers, amphiphilic polymers and other copolymers) often require tedious synthesis procedures, involve many hazardous chemicals and complex experimental facilities, and tend to result in relatively thick coating layers that will significantly reduce the water flux of the coated RO membranes. Such polymers may not be technically and economically feasible for engineering antifouling RO membranes. After surface antifouling modification, there should be a balance between the water permeability reduction and the improvement of the antifouling performance (i.e. flux conservation under fouling conditions). Developing a general guideline to quantify the balance between the water permeability reduction and the flux conservation during fouling based on the energy cost analysis will be highly important. Such work will guide how much flux decline and fouling flux maintenance after surface modification would be acceptable in practical operation.

## 5. Concluding remarks and prospects

Concerns over water scarcity and security have provided powerful stimuli for the advance and development of membrane separation technology over the past decades. In particular, RO membrane based desalination plants will continue growing due to the increasing demand for freshwater and the decreasing energy cost of RO. However, separation performance reduction of the membranes caused by inevitable fouling, including organic fouling, inorganic fouling, colloidal fouling and biofouling, calls for new RO membranes with durable antifouling properties. Antifouling RO membranes can be achieved by optimizing several membrane properties, including surface chemistry (e.g. functional groups), surface morphology (roughness), hydrophilicity, and charge properties. Therefore, we have assessed the correlations between these properties and antifouling membrane performance.

This review provides a comprehensive, state-of-the-art assessment of the efforts and strategies for engineering antifouling RO membranes. The three key strategies for engineering fouling resistant TFC RO membranes include: (1) substrate modification before interfacial polymerization, (2) incorporating (hydrophilic/biocidal/antifouling) additives into the PA layer during interfacial polymerization, and (3) post (surface) modification after interfacial polymerization. For each strategy, we have ranked the various approaches in terms of performance and practical aspects, such as simplicity of preparation, robustness and likely cost.

Substrate modification has received much less attention in developing antifouling RO membranes. This may be caused by the indirect and complex relationship between the substrate and the antifouling surface. Indeed, from the substrate to the antifouling TFC membrane, there are many variables covering the substrate properties (e.g. material type, surface/cross-sectional pore size, pore distribution, surface/overall porosity, surface hydrophilicity and roughness, and thickness), the operating conditions (e.g. membrane casting temperature, humidity, speed, coagulation time, temperature) and similar parameters for the PA layer. It is difficult to contribute the substrate properties to the antifouling PA surface, particularly for the lab-made RO membranes with low repeatability and large experimental errors. This may be the reason that some relevant investigations have come to contradictory conclusions. In the future, more systematic investigations exploring the relationship between substrate modification and antifouling PA RO membranes under well-controlled conditions with high repeatability should be carried out, although they may be challenging.

Incorporating nanomaterials into the PA layer during interfacial polymerization is highly promising for engineering fouling resistant TFC RO membranes. Various metal based biocides, carbon based nanomaterials, silica based nanomaterials and hydrophilic nanopolymers have been used to improve the antifouling properties of TFC RO membranes during interfacial polymerization. There would be optimal requirements for these nanomaterials, such as particle sizes, loadings, density of hydrophilic functional groups and compatibility between the nanomaterials and the polymers. However, these questions have not been well answered yet. Future work should focus on the development of general guidelines on these parameters for engineering next generation of high performance antifouling RO membranes, and then we can use the developed guidelines to screen and design most desirable nanomaterials. Fortunately, the emerging machine learning based artificial intelligence technology makes this target technically achievable.

Post (surface) modification of existing RO membranes is relatively simple and it is easy to obtain antifouling surfaces. Therefore, numerous investigations have taken the surface modification strategy for engineering antifouling RO membranes. Typical materials for surface antifouling modification include inorganic nanomaterials, ordinary hydrophilic polymers, zwitterionic polymers, biomimetic polymers, amphiphilic polymers, biocidal agents or combinations of the materials above. For surface modification with inorganic nanomaterials, particle leaching and aggregation are the common issues that need more attention. Compared with other pressure driven (e.g. MF, UF and NF) membranes, the surfaces of RO membranes are much denser and smoother, and some nanomaterials that have been widely used for engineering these membrane surfaces may not be easily and stably anchored onto the surfaces of RO membranes.

Most surface modifications would inevitably induce extra mass transfer resistance and thus reduce water permeability of the RO membrane. In particular, some macromolecules with complex structures and large molecular weights (e.g. hyperbranched polymers, amphiphilic polymers and other copolymers) often require tedious synthesis procedures and tend to introduce relatively thick coating layers that will significantly reduce the water flux of the coated RO membranes. Such polymers may not be the desirable materials for surface antifouling modification. After surface antifouling modification, there should be a balance between the water permeability reduction and the improvement of the antifouling performance (i.e. flux conservation under fouling conditions). Developing a general guideline to quantify the balance between the water permeability reduction and the flux conservation during fouling based on the energy cost analysis will be important. Such work will guide how much flux decline and fouling flux maintenance after surface modification would be acceptable.

To summarize, these key guidelines and directions can be followed to engineer the next generation of antifouling RO membranes:

- Nanomaterials with desirable properties, such as reasonable particle sizes, low tendency to aggregate, high density of hydrophilic functional groups and good compatibility with contacting polymers, are promising in developing antifouling TFC RO membranes during interfacial polymerization.
- Surface modification with hydrophilic polymers has more industrialization interest than incorporation of hydrophilic nanomaterials during interfacial polymerization, since the former operation is simple and does not require significant modification for the existing production line.

- Macromolecules with complex structures and large molecular weights (e.g. hyperbranched polymers, amphiphilic polymers and other copolymers) may not be the desirable materials for surface antifouling modification of RO membranes because of their tedious synthesis procedures, high costs and high tendency to introduce high mass transfer resistance thereby reducing water permeability of the membranes.
- Substrates are potentially important and there would be benefit in optimizing the substrate properties to facilitate antifouling behaviors, such as to minimize “hot spots” at the RO membrane surface. Substrate optimization can accompany antifouling via the PA layer or surface modification.

Overall, engineering the next generation of antifouling RO membranes is important for our future water security. Recent advances in emerging nanomaterials, such as 2D nanosheets and porous nanoparticles with intrinsic water pathways, have significantly diversified the selection of materials for engineering antifouling RO membranes using various preparation methods. Some general guidelines for nanomaterials selection and performance evaluation are needed, since they will make the development of antifouling RO membranes more targeted and efficient. This will require joint efforts from membrane and polymer scientists, engineers and end-users.

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**Declaration of interests**

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

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: