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Engineering advance

Recent advances in the development of (bio)fouling resistant thin film composite membranes for desalination☆

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ABSTRACT

Membrane (bio)fouling is a major obstacle to many separation and purification processes. Due to the inherent physicochemical properties of some thin film composite membrane surfaces such as polyamide, these are prone to (bio)fouling. Hence, this review highlights recent advances in the design and development of highly resistant thin film composite membrane through surface modification by either coating or grafting with antifouling polymers and/or antimicrobial polymers/biocidal inorganic nanoparticles.

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1. Introduction

(Bio)fouling, denoted as the “Achilles heel” of membrane process, still remains as one of the most technical challenges in the desalination industry, resulting in a decrease of permeate flux, shortens the

membrane lifespan and subsequently increases the operational cost [1,2]. Membrane (bio)fouling is a dynamic process of microbial colonization and growth at the membrane surface [3,4]. Once permanently attached, these organisms start to produce extracellular polymeric secretions (EPS) comprising proteins, glycoproteins, lipoproteins, polysaccharides and other biomacromolecules [5]. The accumulation of EPS and reproduction of bacteria would lead to the formation of mature biofilm [6–8].

In particular, thin film composite (TFC) membranes have currently been used as the primary choice to desalinate seawater. They generally consist of an ultra-thin polyamide (PA) layer which is interfacially polymerized onto a microporous substrate [2,9]. The inherent membrane

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surface characteristics of the PA TFC membrane such as surface roughness, hydrophilicity and surface charge are, therefore, reported to be strongly related to foulant adhesion. It is generally well-acknowledged that foulants can adsorb to the membrane surface by hydrophobic interaction, van der Waals attraction, hydrogen bonding, Lewis acid-base interaction and electrostatic repulsion [10,11]. Owing to the aforementioned issues, prevention or reduction of undesired interactions between foulants and the membrane surface can be an imperative method to control the adhesion of foulants. This could be achieved through surface modification of commercial TFC PA membrane with the aim to increase the PA surface hydrophilicity, reduce membrane surface roughness and to modify membrane surface charge that has the same electrical charge as the foulants [4]. Hence, this review highlights recent advances in the development of TFC membranes through surface modification. To date, several routes have been proposed to improve fouling resistance including, physical adsorption or coating over the membrane surfaces, covalent attachment of anti (bio)fouling polymers, and incorporation of biocidal inorganic particles on the membrane surface.

2. Surface modification strategies for TFC membranes

2.1. Anti-adhesion approaches

2.1.1. Polyethylene GLYCOL (PEG)ylated polymers

Imparting PEGylated materials has been commonly employed due to their superlow-fouling ability to combat the nonspecific protein adsorption and cell adhesion [12–14]. PEG is highly hydrophilic and neutrally charged. It is also able to form hydrogen bonds with water that could increase surface hydrophilicity and lower the interaction with nonspecific foulants [12,15].

In recent advances, novel low fouling TFC membranes were successfully fabricated by in situ PEGylation of polyamide composite membranes [15,16]. Resembling the *m*-phenylenediamine (MPD) structure, commonly used monomer to prepare polyamide RO membrane, amine terminated hydrophilic PEG (MPD – PEG – MPD or MeO – PEG – MPD) monomers as shown in Fig. 1 were used to react with trimesoyl chloride (TMC) during the composite membrane fabrication [16]. Similarly, in situ PEGylation of poly(piperazineamide) TFC nanofiltration membranes was performed by interfacial polymerization between TMC and poly(piperazine) (PIP) + PIP – terminated PEG (PIP – PEG – PIP) and PIP + MPD-terminated PEG (MPD – PEG – MPD) and PIP + alkyl amine terminated – PEG (H₂N – PEG – H₂N) mixtures (as can be seen in Fig. 1), respectively [15]. The PEGylated TFC membranes exhibited superior antifouling property owing to the hydrophilization of polyamide network by PEG, reduced surface roughness and probably due to effect of steric hindrance by covalently attached PEG chains than that of non-PEGylated TFC membranes [15,16].

However, some problems still need to be addressed. Although PEGylated materials demonstrated excellent protein resistance ability, PEG could decompose in the presence of oxygen and transition metal ions found in most biochemically relevant solutions [13,17,18].

2.1.2. Natural hydrophilic polymer sericin

Natural hydrophilic polymer sericin, as shown in Fig. 2, is a water-soluble globular protein having polar side groups of hydroxyl, carboxyl and amino groups [19,20]. The polymer sericin was coated on the

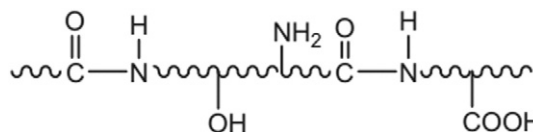


Fig. 2. Schematic diagram of natural polymer sericin chemical structure [19,20].

surface of commercial TFC RO membranes followed by cross-linking with glutaraldehyde (GA) [19]. The sericin-coated membrane showed decreased water permeability due to the additional hydraulic resistance, but improved salt rejection as a result of the enhancement of surface negative charge. Resistance to BSA fouling was improved due to enhanced surface hydrophilicity, increased surface negative charge and smoothed surface morphology [19]. Besides, Zhou et al. [20] used the natural hydrophilic polymer sericin to react with TMC during the interfacial polymerization process. The fouling experiment demonstrated that the sericin-TMC composite membrane possessed better fouling resistances to both BSA and sodium alginate (SA) when compared to the commercial composite nanofiltration membrane (NF270). This is mainly due to the higher electrostatic repulsion between the foulant molecules and negatively charged sericin-TMC membrane that resulted in less adsorption of foulant molecules on the membrane surface [20].

2.1.3. Hyperbranched polymers

Surface coating with polymers possessing hydrophilic end groups, dendritic or hyperbranched polymers, is of great interest to researchers in order to impart protein resistance to the surface of TFC membrane [21,22]. A large number of functional groups and low solution viscosity cause the hyperbranched polymers to be advantageous for various applications [22]. Nikolaeva et al. [22] used hydrophilic hyperbranched poly(amido amine) (PAMAM) for the surface modification as represented in Fig. 3. Highly reactive acid chloride groups are, therefore, used for the covalent bonding of PAMAM to the PA layer by the formation of amide linkages between TMC moieties of the PA layer and amine groups of PAMAM molecules. The modification is accomplished by spraying a 10 wt.% solution of PAMAM onto the PA surface of using either methanol (PAMAM1) or water (PAMAM2) as solvent. In comparison to the unmodified membranes, both modifications led to a significant increase in water flux which is attributed to the suppression of subsequent cross-linking during the final curing step. In view of salt rejection and protein adsorption, the use of water (PAMAM2) has been found to be beneficial over the use of methanol (PAMAM1). This is primarily due to the formation of an additional highly hydrophilic PAMAM layer, which can be recognized as a hydrogel layer when in contact with water. Additionally, PAMAM can be synthesized in a simple one-pot polymerization and is also easily purified, making it a low cost material [22].

2.1.4. Zwitterionic polymers

Zwitterionic polymers have also drawn great attention as a new generation of fouling resistant material in recent years [23–25]. They comprise both positive and negative charged units that can create stronger and more stable electrostatic bonds with water than hydrophilic materials [23]. Inspired from the adhesive proteins found in mussel, a multi-functional zwitterionic amino acid L-DOPA (3-(3,4-Dihydroxyphenyl)-

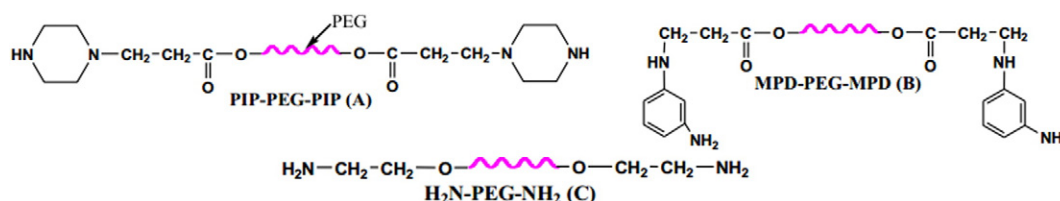


Fig. 1. Amine terminated hydrophilic PEG monomers [15,16].

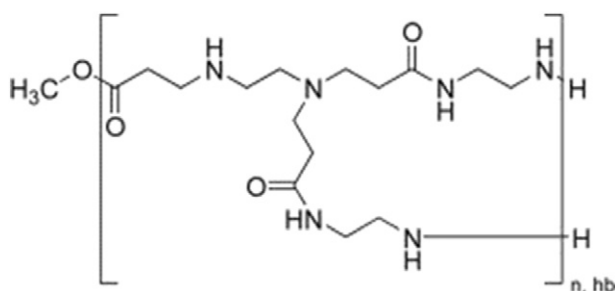


Fig. 3. Basic structure of hyperbranched poly(amido amine) (PAMAM) [22].

L-alanine) has been successfully anchored on the surface of RO membrane to resist protein fouling [23]. In general, L-DOPA contains functional groups such as amino, hydroxyl, and carboxylate or acid groups [23]. After the L-DOPA treatment, a remarkable increase in membrane hydrophilicity has been observed resulting in the enhancement of water flux. The salt rejection remains unchanged. Further deposition of L-DOPA, however, resulted in a marginal decrease in water flux owing to the formation of a diffusion resistant layer. During dynamic filtration experiments using BSA and alginate sodium salt solution as the feed, unmodified membrane retained only 62% of its initial flux while the modified membrane maintained about 82% after 16 h of fouling test [23].

Besides, Zhang et al. [25] successfully grafted a zwitterionic poly(sulfobetaine methacrylate) (pSBMA) onto the polyamide membrane surface via surface-initiated atom transfer radical polymerization. The resulting pSBMA-coated PA membrane exhibited a tremendous increment in water flux of about 65% and the adsorption amount of irreversible proteins is significantly reduced by ~97%, as compared to the untreated membrane. The decrease in ionic rejection was observed which is mainly due to membrane defects caused by the presence of pSBMA between the aromatic polyamide sheets. At high operating pressure, however, the pSBMA-coated PA membrane consistently retained a much higher water flux and enhanced the rejection rate of sodium chloride (NaCl).

Very recently, Meng et al. [24] developed a novel salt-responsive TFC RO membrane having easy-cleaning properties by tethering a zwitterionic poly(4-(2-sulfoethyl)-1-(4-vinylbenzyl) pyridinium betaine) (PSVBP) onto the polyamide surface. The PSVBP was successfully grafted via redox initiated graft polymerization as depicted in Fig. 4. The polyamide-grafted-PSVBP (PA-g-PSVBP) demonstrated a significant increase in the salt rejection but lost its permeation flux of about 20%. A cross-flow protein fouling test for about 100 h indicates that the PA-g-PSVBP membrane had superior antifouling property in the short term but lost the advantage for long-term operation. Nevertheless, the PA-g-PSVBP membrane can restore 90% of the initial flux by rinsing with brine. Besides it can form a hydration layer on the membrane surface, the salt-responsive property of the PSVBP brush is also believed to provide the driving force for the release of protein foulants.

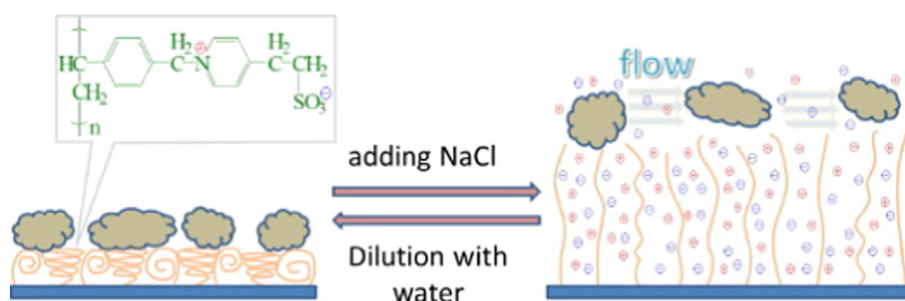


Fig. 4. Synthesis of the salt-responsive TFC RO membrane having antifouling and easy-cleaning properties [24].

2.2. Antimicrobial approaches

2.2.1. Antimicrobial polymers

Immobilizing antimicrobial polymers as biocidal agents on the TFC membrane surface is another approach to preventing biofilm growth and (bio)fouling. Examples of antimicrobial polymers, include poly-amino acids, polylactams and polymers containing tertiary and/or quaternary ammonium groups [26]. In an effort to develop TFC membrane with improved chlorine resistance and anti-(bio)fouling property, a commercial aromatic polyamide RO membrane was modified by free-radical graft polymerization of 3-allyl-5,5-dimethylhydantoin (ADMH) (see Fig. 5) [27,28]. The ADMH-functionalized materials are well-known to exhibit antimicrobial functions by producing the strong biocide N-halamines after chlorination [27,29]. After chlorination, the reduction ratios of *Escherichia coli* in grafted membrane were observed to be above 90% in three sterilization processes as compared to the unmodified membrane. The repeatable chlorine resistances and anti-(bio)fouling properties of the membranes modified by ADMH and N,N'-Methylenebis (acrylamide) (MBA), as a crosslinker, were significantly enhanced [27].

Recently, a novel hydrophilic random copolymer poly(methylacryloxyethyl dimethyl benzyl ammonium chloride - *r* - acrylamide - *r* - 2-hydroxyethyl methacrylate) (P(MDBAC-*r*-AM-*r*-HEMA)) used as a coating material was synthesized via simple free-radical copolymerization [30]. The terpolymer was coated on a commercial RO membrane followed by glutaraldehyde (GA) cross-linking. The highly hydrophilic coated membranes can significantly retain its flux under BSA filtration compared to that of pristine membranes. The coated membranes showed excellent antimicrobial activity to *E. coli*. It is reported that the ammonium moiety, which exists in the coating terpolymer matrix, could inhibit bacterial growth since a very clean surface of the coated membranes was observed without any visible cell aggregates [30].

2.2.2. Incorporation of antimicrobial nanoparticles (NPs)

Modification of TFC membrane by imparting biocidal nanoparticles (NPs) is a promising approach to enhancing antimicrobial activity and hence, (bio)fouling resistance. This is mainly due to the fact that inactivated microorganisms would not be able to grow and create a biofilm on the membrane surface, which is a form of irreversible fouling [31]. For instance, silver (Ag) NPs that have excellent biocidal properties are commonly used materials to prepare antimicrobial coatings, plastics, and wound dressings. Owing to the advantages of using Ag-based compounds to combat fouling, AgNPs were effectively attached to the surface of PA TFC membrane via covalent bonding with cycteamine as a bridging agent [32]. The PA surface was first thiol-derivatized by reacting with $\text{NH}_2-(\text{CH}_2)_2-\text{SH}$ in ethanol solution, following by attachment of AgNPs onto the membrane surface via the Ag-S chemical bonding (TFC-S-AgNPs). It is observed that TFC-S-AgNPs membrane was toxic to *E. coli* as there was no evidence of bacterial growth on the membrane surface. The AgNPs possess antimicrobial properties due to several mechanisms. At first, released Ag^+ could interact with disulfide or thiol groups of enzymes of DNA and disrupt metabolic processes

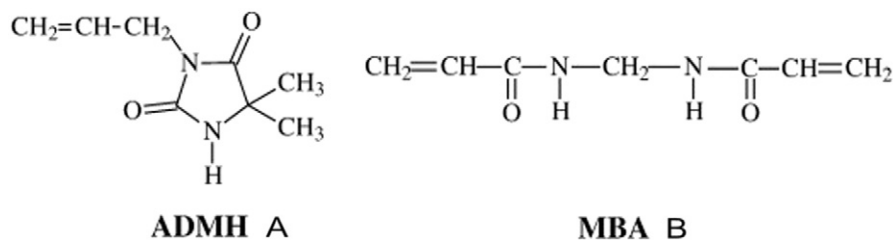


Fig. 5. Chemical structures of ADMH (a) and MBA (b) [27].

which generate reactive oxygen species or interrupt replication of DNA. These processes could lead to damage or death of bacterial cells. Additionally, AgNPs can also be attached to the surface of the cells and disturb their proper function. Finally, AgNPs with particle size ranging between 1–10 nm, are able to penetrate inside the bacteria and result in further damage by interacting with sulfur- and phosphorus-containing compounds [31–33]. After 14 days of silver release test, the TFC-S-AgNPs demonstrated a good inhibition capability towards *E. coli* which makes them a potential candidate to reduce membrane (bio)-fouling [32]. On the other hand, Ben-Sasson et al. [34] applied biocidal copper (Cu) on the PA surface through Cu-NP binding. A simple binding procedure was employed by dip-coating the pristine TFC membrane in the Cu-NP suspension as presented in Fig. 6. The Cu-NPs with multiple positively charged polyethylenimine (PEI) molecules were believed to have strong electrostatic attraction to the negatively charged PA surface. Through SEM measurement, it is confirmed that the Cu-NPs were successfully bound. No significant changes in water permeability coefficient and salt rejections were observed. Functionalization with Cu-NPs resulted in tremendously decreased number of viable bacteria attached to the TFC RO membrane by $87\% \pm 0.2\%$, $96\% \pm 3\%$, and $79.5\% \pm 13\%$ for *E. coli*, *Pseudomonas aeruginosa*, and *Staphylococcus aureus*, respectively,

after 1 h contact relative to the control. The results were mainly associated with the toxicity of the bound Cu-NPs. Additionally, it is reported that the Cu-NPs are able to be recharged on the PA membrane surface [34].

The incorporation of biocidal nanoparticles and antifouling/fouling release polymer brushes has recently been introduced [31,35]. Rahaman et al. [31] developed novel surface coatings for TFC RO membrane functionalized with silver nanoparticles (AgNPs) and antifouling polymer brushes via polyelectrolyte layer-by-layer (LBL) self-assembly. As shown in Fig. 7, the commercial RO membranes were spray coated with dilute polymer solutions of positively charged polyethylene imine (PEI) or Ag-PI, and negatively charged polyacrylic acid (PAA). Subsequently, coatings were further functionalized by grafting either hydrophilic poly(sulfobetaine) or low surface energy poly(dimethylsiloxane) (PDMS). It is observed that the grafted membrane (sulfobetaine-Ag-LBL, PDMS-LBL and PDMS-Ag-LBL) demonstrated relatively decreased water flux and higher salt rejection than the unmodified membranes. Modified membranes exhibited remarkably low adhesion in a microbial adhesion test with *E. coli*. Moreover, improved bacterial inactivation was observed by coating with the PAA/Ag-PEI which achieved up to 95% inactivation of bacteria attached to the

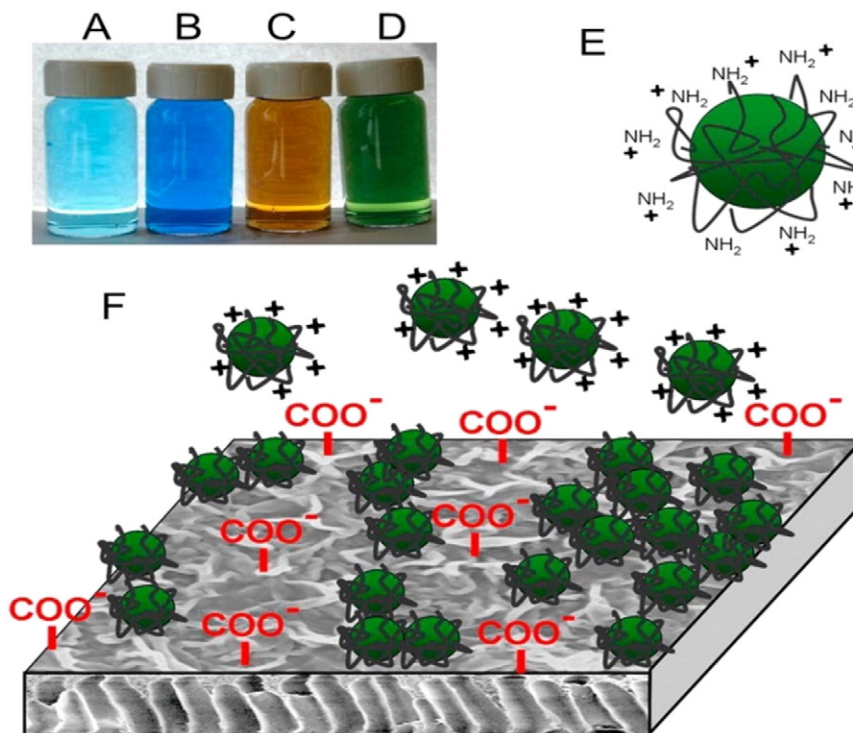


Fig. 6. Preparation and binding of Cu-NP to the TFC membrane active layer. The colors of the Cu-NP suspension at the various synthesis stages are shown for: (A) CuSO₄ solution, (B) after addition of PEI and formation of Cu-PEI complexes, (C) after reduction with sodium borohydride, and (D) after 20-h dialysis and oxidation of the Cu-NPs. The amine groups of the PEI impart a positive charge to the Cu-NPs (E). The positively charged Cu-NPs electrostatically bind to the negatively charged native carboxyl groups on the membrane active layer (F) [34].

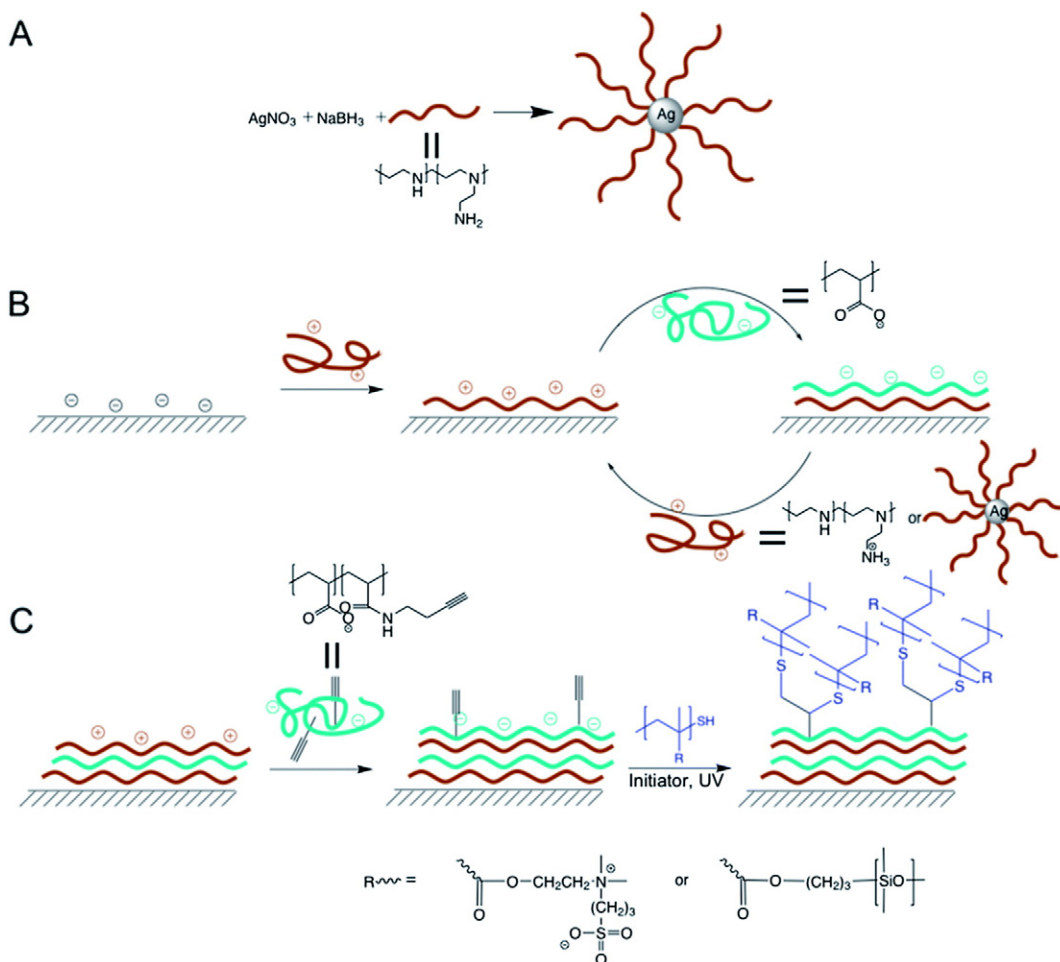


Fig. 7. Synthetic scheme for the membrane modification. (A) Preparation of PEI coated AgNPs. (B) Formation of the LBL film. (C) Grafting of the polymer brushes [31].

surface within 1 h of contact time [31]. Apart from that, Zhang et al. [35] incorporated both PEGylated dendrimer having different functionalities, and AgNPs on the PA membrane surface [35]. The AgNPs are formed within the PEG modified dendrimer matrix by the photolysis of the trapped silver nitrate. After modifications, improved hydrophilicity and desired electrochemical characteristics have been obtained. Among all the modified surfaces, coating with silver-PEGylated dendrimer nanocomposite membrane was reported to effectively decrease fouling susceptibility. The adhesion forces for PEG and AgNP modified

membranes were small, which explained the lessened protein fouling of the membrane [35].

Nevertheless, biocidal nanoparticles are not sustainable for a long-term application owing to a decline in its antimicrobial activity over time [36]. Therefore, carbon-based nanomaterials, such as carbon nanotubes (CNTs) and graphene have been introduced as an alternative strategy since they have been demonstrated to inactivate bacteria upon contact with bacterial cells [36–38]. Graphene, comprising single-atom-thick sheets of sp^2 -bonded carbon, has received much

Graphene oxide functionalization → Antimicrobial properties

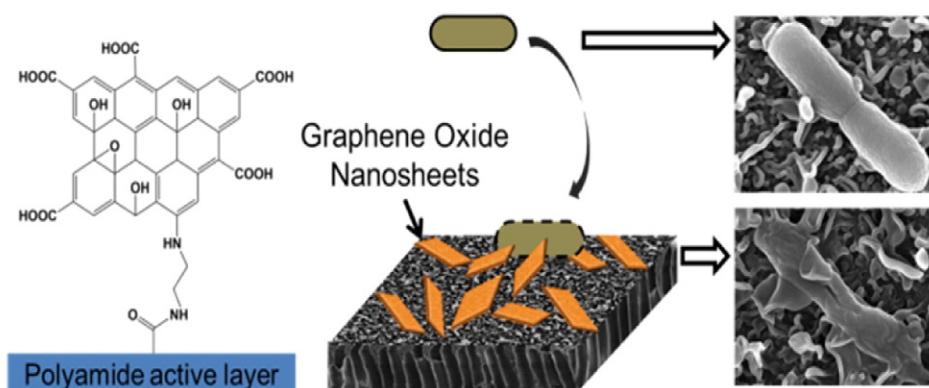


Fig. 8. Functionalization of graphene oxide nanosheets onto the TFC membrane [36].

attention for a new generation of carbon nanomaterials due to its inherent smoothness, atomic-level thickness, and high water slip length [36, 39,40]. Recently, functionalization of graphene oxide on the active layer TFC membrane was successfully employed as presented in Fig. 8 [36]. The resulting graphene oxide-functionalized TFC (GO-TFC) membranes showed equivalent performance to control-TFC membrane. The number of viable *E. coli* cells was reduced up to 64.5% after direct contact with the GO-TFC membrane for 1 h. Antimicrobial graphene oxide inactivates bacteria by inducing membrane damage, mediated by physical disruption, charge transfer, and formation of reactive oxygen species, and extraction of lipid from the cell membrane [36,41,42]. SEM images, as shown in Fig. 8, proved that the cells attached to the GO-TFC membrane demonstrate compromised integrity and appear to be flattened or shrunk compared to cells attached to the control-TFC membrane. On the other hand, CNTs have also been selected to be applied on the PA surface due to the biocidal properties that can damage the membranes of microorganisms and disrupt their metabolic pathways accompanied by oxidative stress, subsequent inactivation and/or death of the microorganisms [38]. Kim et al. [38] prepared TFC RO membranes having anti-(bio)fouling properties by the deposition of oxidized CNTs followed by coating with poly(vinyl alcohol) (PVA). The PA-CNT-PVA membrane showed enhanced durability and mechanical properties relative to the control membrane. Upon optimization, the PA-CNT-PVA membrane exhibited reasonably high water flux and salt rejection, and excellent anti-(bio)fouling properties. By increasing the CNT loadings, however, the anti-(bio)fouling property of the PA-CNT-PVA membrane was decreased due to the formation of aggregated CNT clusters.

3. Conclusions

In summary, various strategies have been recently proposed in developing (bio)fouling resistant thin film composite membranes, particularly through either surface coating or grafting with hydrophilic, brush, hyperbranched, hydrogels and zwitterionic polymers. Such techniques are very promising due to the improvement of antifouling property. Of these, coating with PEGylated polymers is a commonly used approach to reduce fouling propensity due to its simplicity. This post-surface modification technique, however, leads to a lower water permeability and/or smaller salt rejections in many cases. Besides, among the important factors that need to be considered are the chemical and mechanical stability and durability of such coatings for long-run applications.

Recently, there is increasing attention to modify TFC membrane having antifouling and/or antimicrobial activities for combating microbial contaminants. Thus, surface functionalization with either biocidal polymer and/or inorganic particles has been successfully employed to polyamide membrane surfaces. The use of biocidal inorganic particles includes silver nanoparticles, copper nanoparticles, carbon nanotubes and graphene. Owing to the biocide-releasing mechanism, the inorganic nanoparticles could lose their functionality over time. Besides, it is expected that these nanoparticles could leach out after a long time of operation. Therefore, it is still very challenging to develop TFC membranes with both improved resistance to fouling and increased separation performance as well. New materials and strategies need to be developed in order to overcome the shortcomings particularly for water desalination application.

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