

A review on membrane fouling: membrane modification

Farzin Saffarimiandoab^{a,b}, Bahar Yavuzturk Gul^{a,b}, Reyhan Sengur Tasdemir^{b,c}, Selda Erkoc Ilter^d, Serkan Unal^{d,e}, Bahadir Tunaboynu^f, Yusuf Z. Menciloglu^{d,e}, İsmail Koyuncu^{a,b,*}

^aDepartment of Environmental Engineering, Istanbul Technical University, Maslak 34469, Istanbul, Turkey, emails: koyuncu@itu.edu.tr/koyuncu@itu.edu.tr (İ. Koyuncu), saffari101@gmail.com (F. Saffarimiandoab), baharyavuzturk@yahoo.com (B. Yavuzturk Gul)

^bNational Research Center on Membrane Technologies, Istanbul Technical University, Maslak 34469, Istanbul, Turkey, email: reyhansengur@gmail.com

^cDepartment of Nanoscience and Nanoengineering, Istanbul Technical University, Maslak 34469, Istanbul, Turkey

^dIntegrated Manufacturing Technologies Research and Application Center & Composite Technologies Center of Excellence, Sabanci University, Pendik 34906, Istanbul, Turkey, emails: serkanunal@sabanciuniv.edu (S. Unal), yusufm@sabanciuniv.edu (Y.Z. Menciloglu)

^eNanotechnology Research and Application Center, Sabanci University, Tuzla 34956, Istanbul, Turkey

^fDepartment of Materials Science and Engineering, Marmara University Göztepe Campus, Istanbul, Turkey, email: bahadir.tunaboynu@marmara.edu.tr

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ABSTRACT

Membrane separation has become a prevalent technique in water and wastewater treatment. However, fouling is still the most challenging issue in case of membranes. Fouling causes flux decline, loss in rejection performance, increased energy consumption, etc. Different modification techniques have been applied to mitigate fouling on the membrane surface. In this study, the insights for state-of-the-art approaches in membrane modification using nanoparticles, organic modifiers such as hydrophilic, amphiphilic, and zwitterionic materials were critically reviewed. Detailed information about the methods blending, interfacial polymerization, grafting, coating, etc. were provided. Furthermore, the effects of membrane modification on membrane morphology and membrane performance were discussed. Finally, the obstacles for the scale-up of the studied techniques are analyzed.

Keywords: Membrane fouling; Membrane modification; Nanoparticles; Hydrophilic modifiers; Amphiphilic modifiers; Zwitterionic modifiers

1. Introduction

Membrane fouling is the most challenging issue in water and wastewater treatment membrane processes. Fouling could be categorized as organic fouling, colloidal fouling, scaling, and biofouling. The fouling layer is removed by cyclic cleaning between filtration steps. However, what makes fouling a serious problem is its irreversibility in

which bacteria or foulant no longer can be removed from the membrane surface. Dissolved and particulate foulants are brought and pushed onto the membrane surface by hydrodynamic forces and attractive physicochemical interactions, which causes fouling [1]. Developing an antifouling membrane is mainly aimed by engineering its surface properties including surface roughness, hydrophobicity, surface charge, and toxicity against foulants using

* Corresponding author.

the incorporation of either nanoparticle (NP) or organic molecules. Numerous techniques have been applied for membrane modification including surface coating, matrix blending, chemically induced graft polymerization, photoinduced graft polymerization, plasma graft copolymerization, initiated chemical vapor deposition (iCVD), interfacial polymerization (IP), and high energy photo irradiation.

In this contribution, the modification methods and their associated limitations were discussed by focusing on the effect of modifier type, its concentration, and modification methods on the membrane performance and fouling propensity. Finally, the obstacles for up-scaling the modification techniques were introduced.

2. Membrane modification approaches to control fouling

Regular membrane cleaning and feed water pretreatment are the commonly practiced ways of reducing fouling in the membrane process. However, cleaning can adversely impact the longevity of the membrane. Moreover, survived microorganisms from the pretreatment step can easily cause colonization on the membrane surface. Hence, it necessitates tackling the fouling by tailoring the membrane properties without sacrificing its performance. Surface characteristics of membranes such as hydrophilicity/hydrophobicity, charge, and roughness are the factors playing an important role in the interaction of foulant and membrane surface. Hence, membrane modification tries to halt the mechanisms by which fouling occurs. Fig. 1 illustrates different materials, techniques, and

mechanisms by which fouling is tried to be inhibited on the membrane. In this section, the mechanisms, techniques, and materials used for this purpose were reviewed.

2.1. Membrane modification through nanoparticles

The addition of NP tends to change the properties of membranes by influencing separation performances such as increased permeability, rejection, etc.; structural properties such as pore volume, pore size distribution, hydrophobicity, roughness, etc.; mechanical, thermal, and electrical properties and also fouling propensity. As the size of particle decreases, properties of particles such as surface area, etc. change. By introducing NPs into the membrane matrix, it is possible to take advantage of their properties. To date, numerous studies have been conducted using different types of NPs such as silver (Ag) [2–4], titanium dioxide (TiO₂) [5], carbon nanotubes (CNTs) [6], graphene oxide (GO) [7,8], zinc oxide (ZnO) [9], aluminum oxide (Al₂O₃) [10], copper oxide (CuO) [11], lipophilic bismuth (BisBAL) [12], clay nanoparticles [13], etc.

NP incorporation is possible by (1) mixing into polymeric membrane matrix, (2) coating on the membrane surface as a film layer (self-assembling or directly depositing on the membrane), or (3) incorporating into a thin-film layer of thin-film-composite (TFC) membranes via IP, etc.

2.1.1. Titanium dioxide NP

Titanium dioxide (TiO₂) NPs are mainly found in rutile, anatase, and brookite forms. Rutile and anatase, which possess photocatalytic activity, are usually incorporated inside or on the membranes for simultaneous disinfection and separation applications. TiO₂ NP is commercially available; it is cheap and has a nearly endless lifetime.

The photocatalytic activity of titania is activated by UV or sunlight to degrade organic compounds by redox reactions. In photocatalysis, titania absorbs a photon with enough wavelength and an electron-hole pair is generated via excitation of electrons from conductive to the valence band. These electron-hole pairs can end up with either recombination or can go under redox reactions with the surrounding media and generate strong oxidizing hydroxyl radicals to degrade organic components as Eqs. (1)–(6). Normally, in bulk titania, either hole or electron is available while in nanoscale both of them could be found, which enables its high efficiencies [14].

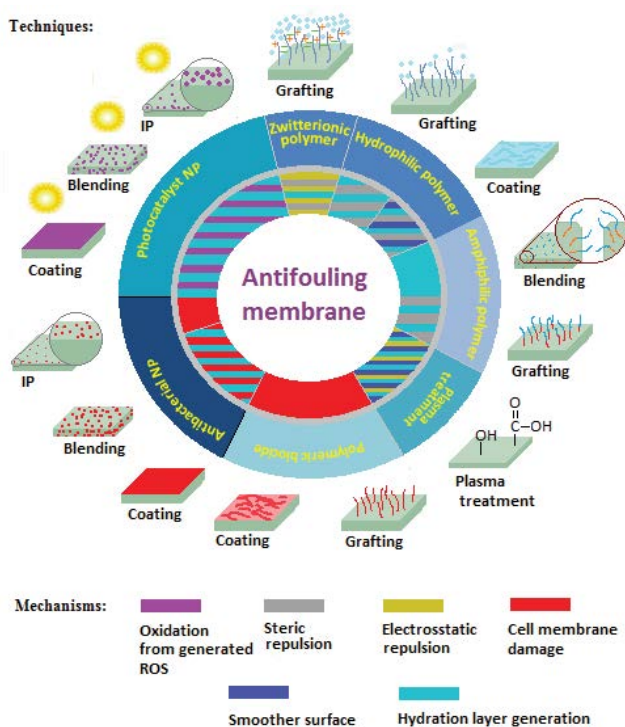
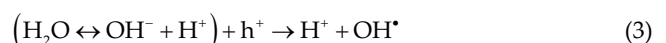
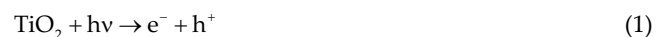


Fig. 1. Schematic representation of antifouling membrane modification techniques, materials, and mechanisms (defined by colors in the middle layer).

Photo-induced super-hydrophilicity of TiO_2 NP is another important feature, which was first introduced by Wang et al. [15]. Hence both super-hydrophilicity and photocatalytic activity made TiO_2 NP as a unique and promising substance for developing anti-biofouling membranes.

Damodar et al. [16] incorporated TiO_2 NPs inside the polyvinylidene fluoride (PVDF) membrane to develop anti-bacterial and photocatalytic membrane. Different membranes with 0–4% PVDF/ TiO_2 concentrations were used to test their *E. coli* removal under the dark and under 15 W UV lamp. Membranes were held at the bottom of the Petri dishes, and bacteria suspension was placed on the membranes and the UV lamp was held at 15 cm top to Petri dishes. An increase in TiO_2 concentration at longer durations showed better efficiency in the removal of bacteria, whose best removal efficiency was obtained at 4% PVDF/ TiO_2 .

Rahimpour et al. [17] analyzed organic fouling and biofouling propensity of TiO_2 /PVDF/sulfonated polyethersulfone (SPES) membranes and found the membrane with 4 wt.% TiO_2 concentration with minimum fouling propensity against Bovine Serum Albumin (BSA). Moreover, an inhibition zone was formed around the TiO_2 NP incorporated membranes in disk diffusion tests against *E. coli* under UV light after 24 h.

Besides mixing NP inside the matrix, TiO_2 NP can also be incorporated into the TFC membrane in different ways via self-assembly on the membrane [18–20], entrapment inside the PA layer [21,22], and chemical binding [23]. Self-assembly can be done by soaking the TFC membrane into TiO_2 NP colloidal solution [18–20]. Kim et al. [18] self-assembled TiO_2 NP on polyamide (PA) TFC membrane by dipping the membrane in a colloidal TiO_2 NP solution for 1 h. The hydrogen bonding between hydroxyl groups on the TiO_2 NPs and carbonyl groups on the membrane. In addition, bidentate coordination of the Ti^{4+} took place with $-\text{COOH}$ functional groups on the PA layer of the membrane. The flux variation and bacterial survival experiments were carried out for UV exposed and unexposed neat and coated membranes. According to the results, UV light-exposed TiO_2 NP-incorporated membranes could successfully remove microorganisms and showed lower fouling propensity as exposure duration against UV light increased.

TiO_2 NPs could also be embedded onto the TFC membrane during IP. Unlike self-assembling on the surface, in this case, the TiO_2 NPs are less susceptible to be lost and leak into the medium. However, the TiO_2 NP inside the thin-film PA layer does not offer considerable photocatalytic activity and super-hydrophilicity due to its residence inside the polymeric matrix and limited exposure to light. Based on TiO_2 NPs concentration, a rejection-antifouling trade-off relation occurs. In fact, increasing embedded TiO_2 NPs concentration can lead to structural variation and consequently lead to a reduction in rejection. In the IP technique, embedding TiO_2 NPs can be done by dispersing them either in the aqueous phase [22] or organic phase [21] of the solution during polymerization of the PA thin film layer, which can end up with two different performances. Mansourpanah and Habili [22] attempted to compare Na_2SO_4 rejection and the sugar separation performances of two different membranes, which were prepared by dissolving TiO_2 NP in (1) the organic phase and (2) in the aqueous phase. For the TiO_2 NPs dissolved in

the aqueous phase, coordination and hydrogen bonding occurred between N–H groups of piperazine (PIP) with Ti^{4+} and hydroxyl group of TiO_2 . TiO_2 NPs were entrapped under the PA layer and resulted higher flux. On the other hand, by dispersing TiO_2 NPs in the organic phase, the coordination interaction and hydrogen bonding were formed between carboxylic group with Ti^{4+} and $-\text{OH}$ of Ti atom.

The water flux, Na_2SO_4 and sugar rejections were improved for the membrane prepared by TiO_2 NPs dispersion in aqueous solution. However, no significant improvement was obtained in the case of the membrane with TiO_2 NPs dispersed in the organic phase.

One of the serious challenges that photocatalytic TiO_2 NP composite polymeric membranes faces is TiO_2 NP release by polymer chain degradation by oxidative UV light illumination or hydroxyl radical generation. This was observed by Lee et al. [23] after TiO_2 -PVDF hollow fiber membrane exposed to the UV light. Fracture and collapse in structure, C–N and C–C bond dissociation, and the decrease in the performance were reported. Considering this issue, to protect the PA layer from TiO_2 -catalyzed UV degradation in TiO_2 -coated PA TFC membrane, Mo et al. [24] developed a protective SiO_2 NPs layer between the lower PA and upper TiO_2 NP layers. A cross-linked thin PA layer was developed after the IP of piperazine (PIP) and trimethyl chloride (TMC) solutions on the PS support layer. Then 3-aminopropyltrimethoxysilane (APTMS) was used for making amide linkage by utilizing unreacted $-\text{COCl}$ groups. Later APTMS was reacted with titanium(IV) isopropoxide (TIP) and finally SiO_2 and TiO_2 layers were formed by adding TiO_2 NPs colloid in aqueous solution. Fabricated membrane performance was found to be stable after several times of permeation while keeping its antifouling property.

Leaching of NPs could also occur by sweeping hydrodynamic force of fluid in a cross-flow filtration mode of reverse osmosis (RO) and NF membrane processes. Hence to tackle such a problem, Zhang et al. [25] utilized polydopamine as bio-glue to bind TiO_2 NP irreversibly on the PA TFC membrane. However, its stability under UV light operation was not investigated.

It is noteworthy to mention that research efforts trying to study the photocatalytic activity of TiO_2 NP in RO and nanofiltration (NF) membrane processes are not applicable for real-life applications. The limitations in the RO and NF membranes module design and the vessel containing the modules inhibit applying UV light illumination.

2.1.2. Silver composite membranes

As an anti-bacterial matter, silver (Ag) has attracted great interest for a long time. The capacity of Ag NPs and Ag^+ ion to attack bacteria has been used for developing anti-biofouling membranes. The high antibacterial efficiency and its zero cytotoxicity at concentrations up to 0.1 mg/L on human being makes this material applicable for commercial uses [26,27]. Based on the study of López-Heras et al. [28] on the antibacterial activity of Ag NP, the activity of bacteria is reduced due to the synergistic effect between direct particle-specific biological impacts and the release of Ag^+ ions. Furthermore, Ag NPs can interact with sulfur-containing proteins of the cytoplasmic cell

membrane and subsequently can penetrate the cell. Also, the Ag^+ ions released from Ag NP interact with thiol groups ($-\text{SH}$) in cysteine and other cell components that can interrupt the transportation and respiratory system of bacteria. All these are enough for bacterial cell death [29–32]. Ag NPs can be synthesized by various routes, including chemical reduction, laser beam irradiation, nano templates, sonochemical deposition, and gas condensation [33]. Considering all methods, chemical reduction of Ag^+ ions to form Ag NPs is the most commonly practiced way in membrane modification. Sodium tetrahydroborate, formaldehyde CH_2O , hydrazine, and polyols are common reducing agents.

The antibacterial property of Ag NP stimulated the interest of many researchers to develop various Ag-based antifouling composite membranes [2,34,35]. Blending as a basic method of NP incorporation primarily is used to change membrane matrix and porous structure. However, Ag NPs have been used also to render antibacterial activity to the membrane. Taurozzi et al. [36] applied two different ways of Ag NP blending in the PSf membrane. Ag NPs were either synthesized ex-situ and used as an organosol in casting solution or produced in casting solution via in situ reductions of Ag^+ ions by a polymer-solvent. For ex-situ Ag NP blended membrane, larger NPs are preferentially located in the skin layer while for in situ Ag NP blended membrane, small NPs are distributed homogeneously in the membrane matrix. Better accessibility of Ag NPs at ex-situ Ag blended membrane resulted in more biofilm growth inhibition as shown in Fig. 2.

More accessible Ag NPs result in more antibacterial activity. The polymer and NP interaction defines the NPs location in mixed matrix membrane during the solvent-nonsolvent exchange at the phase inversion process. Sileyuksel et al. [34] studied the Ag NPs location inside three different polymeric membranes of cellulose acetate (CA), PSf, and PES. Ag NPs were homogeneously located at the skin and top layers of PSf and PES membranes; whereas, for the CA membrane, the Ag NPs were located at the bottom layer as illustrated in Fig. 3. Better accessibility of Ag NPs in the PSf membrane resulted in higher antibacterial activity by having higher Ag^+ ion diffusivity.

Generally, NP leakage from the membrane is considered a challenge for the longevity of the membrane. However, the release of Ag^+ ions is a key step for its antibacterial activity. Koseoglu-Imer et al. [27] investigated Ag^+ ions leaching from Ag NP mixed PSf membrane. The DI water was permeated and the amount of Ag^+ ions at the permeate side was analyzed by the ICP. The inductively coupled plasma (ICP) analysis revealed the increased Ag^+ ion amount in the permeate side at higher Ag NP concentrations inside the membrane. This Ag^+ ion release generated an inhibition zone around the membrane in the disk diffusion test against *E. coli*. However, after the biofouling test, the results from polymerase chain reaction – denaturing gradient gel electrophoresis revealed that the bacterial community and consortium were not significantly different for both bare and modified membrane.

Mollahosseini et al. [37] related the size of blended Ag NPs (30 and 70 nm) to the membrane performance, antibacterial activity, and NPs leakage out of the PSf ultrafiltration (UF) membrane. Ag NPs with 30 nm in diameter were shown to leach totally out of the membrane, while the Ag NPs with 70 nm in diameter stopped leaching after 72 h. More leakage for NPs with 30 nm in diameter was attributed to the lower crystallinity of the prepared membrane. More hydrophilic, smoother surface, and higher Ag NP release for the 30 nm Ag NPs mixed membrane, resulted in less biofouling propensity.

The role of Ag NPs extends beyond its antibacterial property since it can also enhance the hydrophilicity of the membrane. Liu et al. [38] used the direct observation technique to monitor bacterial deposition and detachment from Ag-blended PSf membrane surfaces. Even though the bacterial adhesion amount was the same for both the bare and blended membranes, the adhesion on the blended membrane was highly reversible, which 75% of bacteria were detached compared with 18% for bare membrane. The hydrophilicity of Ag NP can also help reduce organic fouling. Hoek et al. [35] observed a lower flux decline for Ag NP blended PSF membrane over the BSA solution filtration compared with the bare membrane.

Cao et al. [39] tried to immobilize silver NPs onto sulfonated PES membranes by taking advantage of the interaction

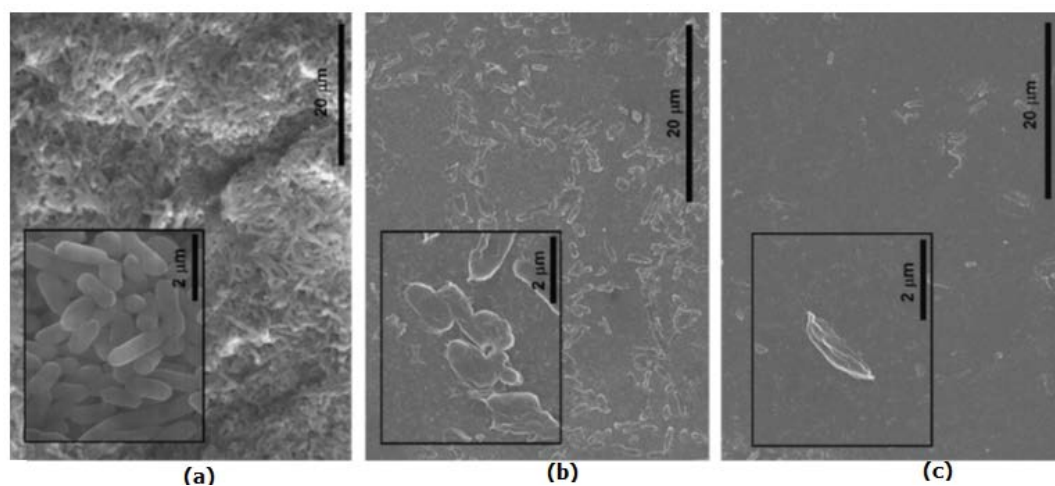


Fig. 2. Biofouling visualization by SEM images, silver-free (a) PSf/ Ag_m (b), and PSf/ Ag_{ex} (c) membrane [36].

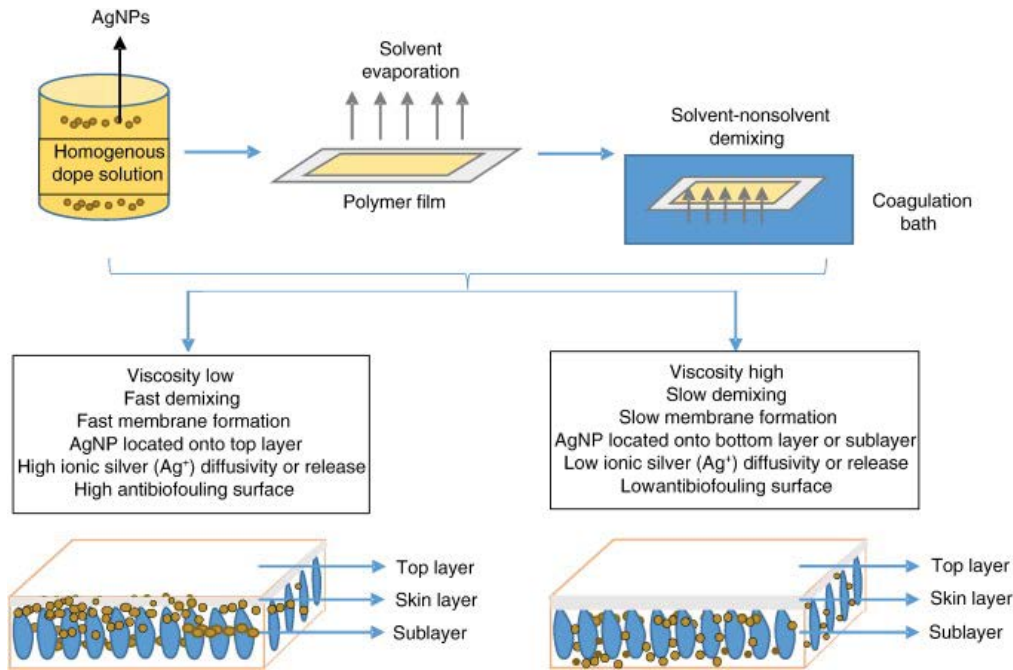


Fig. 3. Schematic representation of Ag NP location in nanocomposite membrane matrix for different polymer types [34].

between sulfonated groups and silver ions. Vitamin C was used as a reducing agent as shown in Fig. 4. The blended membrane was found to have bacteriostatic (growth inhibition) and bactericidal (antibacterial) impact on *Staphylococcus aureus*, *Staphylococcus albus*, and *Escherichia coli*.

Ben-Sasson et al. [40] tried to load Ag NPs onto the TFC RO membrane matrix by a novel and facile procedure. The reaction between NaBH_4 as a reducing agent and Ag salt enabled homogeneous Ag NP coverage on the membrane surface. Ag NP addition did not affect the salt selectivity, surface roughness, and the hydrophilicity of membranes; however, the permeability decreased by 17%. Confocal laser scanning microscopy (CLSM) analyses showed that Ag NPs effectively suppressed biofilm formation, with a 41% reduction in biovolume and a significant reduction in EPS, dead, and live bacteria.

Yin et al. [41] covalently bonded Ag NPs on the PA TFC membrane using cysteamine. First, thiol groups were

formed on the membrane surface by soaking it into the cysteamine ($\text{H}_2\text{N}[\text{CH}_2]_2\text{SH}$) solution in ethanol for sufficient time, then the active surface of the TFC-SH membrane was exposed to Ag NPs suspension to covalently bind Ag NPs on the membrane. The addition of thiol groups and Ag NP increased water permeability. The Ag^+ ion release was controlled and minimized due to the covalent bonding of Ag NPs onto the membrane while maintaining its antibacterial activity against *E. coli*. The grafting caused a decline in water permeability and slight enhancement in salt rejection.

2.1.3. CNT-based membrane

CNT has become a highly preferred material for a variety of applications due to its high aspect ratio, extreme hardness, electrical conductivity, thermal conductivity, specific optical property, and partial antibacterial activity [42]. CNTs can be synthesized through CVD, laser ablation, and

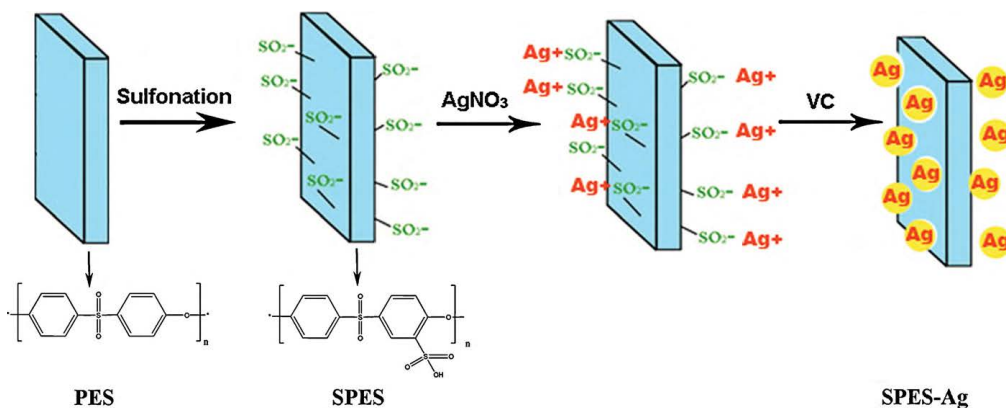


Fig. 4. Process of the Ag NP incorporation onto sulfonated PES membrane [39].

arc-discharge methods. The structure of CNTs can be classified as single-walled (SWCNT) or multi-walled CNT (MWCNT). Antibacterial activity of CNT is a function of their diameter-dependent penetration and length-dependent wrapping on the lysis of the microbial membranes. SWCNT is proved to be more lethal than MWCNT to the bacteria [43]. CNT can be incorporated into membranes by vertically aligning, blending, and surface coating ways. For antibacterial purposes, vertical alignment has not been practiced yet.

Kar et al. [44] investigated the anti-biofouling efficiency of SWCNT (1.2–1.5 nm in diameter) and MWCNT (7–15 nm and 110–170 nm in diameter) impregnated PSf membranes. SWCNT embedded and MWCNT (7–15 nm) embedded membranes were shown to possess more antibacterial behavior than bare PSf membrane. However, MWCNT (110–170 nm) embedded membrane was found to have the worst anti-biofouling property. It was confirmed that the increase in the diameter of CNT results in a lower anti-biofouling activity of the membrane surface.

Brady-Estévez et al. [45] examined the SWCNT-coated PVDF membrane to evaluate the viability and the ability in retaining the viral and bacterial pathogens. SWCNTs (1.2 nm in diameter, 10 to 20 μm in length with $407 \text{ m}^2 \text{ g}^{-1}$ specific surface area) were suspended in dimethyl sulfoxide (DMSO) and a layer was formed on the membrane by vacuum filtration. *E. coli* was completely retained by carbon bundles inside the SWCNT layer. It was seen also that the morphology and size of the *E. coli* cell inside the SWCNT layer were significantly different than the morphology of *E. coli* in the control membrane. SWCNT-coated membrane showed $79\% \pm 9\%$ cell inactivation in comparison with only 10% inactivation obtained in the control membrane. Membranes also have exceptionally high virus removal (5–7 log) when operated at low pressure.

Fouling mitigation and membrane cleaning can be improved by benefiting from the electrical conductivity of incorporated CNTs and by overcoming the intrinsic electrical resistance of polymers. Electrostatic repulsion and electrochemical redox reactions can be conducted by engineering the chemistry of CNTs to mitigate fouling. Incorporation of CNT improves separation performance, water flux, and brittleness of membrane by making the polymer conductive [46–49]. Dudchenko et al. [50] have prepared conductive CNT-polyvinyl alcohol (PVA) UF membrane to mitigate fouling. The membrane was modified with carboxylated CNT at a 3:1 PVA to carboxylated CNT ratio by crosslinking with glutaraldehyde. Alginate (AA) and polyethylene oxide (PEO) were chosen as negative and neutral fouling agents, respectively. Applying 3–5 V cell potentials and the 9–15 V/cm cell potential fields, AA fouling was greatly reduced by electrostatic repulsive force.

In the electrochemical redox reaction, the membrane can be used as an anode for oxidation or a cathode where foulants are removed by generating bubbles. Vecitis et al. [51] applied MWCNT-coated PTFE membrane to develop combined filtration and anodic oxidation of bacteria and viruses. The modified membrane itself could remove bacteria and viruses; however, when 2 or 3 V electrical potential was applied to the membrane, the number of bacteria and viruses was decreased dramatically. Electrochemical inactivation of *E. coli* and MS2 viruses occurred by direct

oxidation of pathogen in contact with MWCNT anode or indirect oxidation of pathogen by generated anodic oxidants (Cl_2 , HO^\bullet , etc.).

Hashaikeh et al. [52] conducted similar work by developing a self-cleaning MWCNT-coated PVDF MF membrane and applying it in an electrochemical filtration cell. However, the membrane acted as a cathode and the fouling layer was removed by cathodic gas bubble generation during the electrochemical reaction. The gas bubbles generated during a 2–3 min electrochemical reaction at 2 V on the cathode could successfully remove the CaCO_3 and yeast fouling layer and the flux almost was retained back.

2.1.4. Graphene oxide NP composite membrane

Graphene and its other forms (graphite [Gt], graphite oxide [GtO], graphene oxide [GO], and reduced graphene oxide [rGO]) have great fatality against bacteria. Antibacterial activity of GO and rGO is attributed to the sharp edges of graphene nanosheets that induce stress on the cell membrane, leading to the loss of bacterial membrane integrity and the leakage of RNA [53]. Furthermore, the fatality of the GO nanosheets can be attributed to chemical interaction, cellular oxidative stress, and lipid peroxidation [54,55]. Moreover, incorporation of GO can increase the hydrophilicity of the membrane due to the carboxylic, epoxy, and hydroxyl functional groups that exist in GO structure [56]. GO nanosheets are usually blended in a polymeric membrane matrix or coated on the membrane surface. Lee et al. [57] investigated the fouling propensity of GO incorporated PSf membrane in membrane bioreactor. GO incorporation improved hydrophilicity, permeability and could impede biofouling probably by creating low energy interfacial energy between surface and water. Also, functional groups within the GO structure increased the negativity of surface charge which disabled the biofouling attachment and their accumulation. In this case, increasing GO concentration decreased the biofilm formation on the membrane surface.

Before incorporation, pre-functionalization on GO can be performed to render the desired properties. Xu et al. [58] functionalized GO (f-GO) by 3-aminopropyltriethoxysilane before blending with PVDF to investigate its effect on the antifouling properties of membranes. The f-GO blended PVDF membranes exhibited superior hydrophilicity and consequently lower fouling propensity against BSA. After a few BSA filtration cycles and cleaning, f-GO embedded membranes maintained its initial flux, unlike the pristine membrane. Zhao et al. [59] treated GO with isocyanate (iGO) to improve the homogeneity of GOs within the PSf membrane matrix. Carboxylic iGO migrated toward the membrane surface during the phase inversion process perhaps due to its affinity to aqueous nonsolvent and this made the membrane surface hydrophilic. However increasing iGO concentration within polymer solution beyond a specific level, resulted in an increase in surface roughness and consequently increased the fouling propensity and decreased the flux recovery ratio (FRR). Yu et al. [60] modified GO with hyperbranched polyethyleneimine (HPEI) to improve the antifouling and antibacterial performance of

PES membranes. Water permeability and BSA adsorption resistance were enhanced by increasing HPEI-GO content in the membrane matrix. The images from the morphology variation of the *E. coli* filtrated membranes proved clear damage in the cytoplasmic cell membrane. HPEI-GO/PES showed the high antibacterial property.

Perreault et al. [61] tried to covalently attach GO to TFC polyamide membranes to render antimicrobial properties. Covalent attachment was done by treating membrane and GO with 1-ethyl-3-(3-[dimethylamino] propyl) carbodiimide (EDC) and N-hydroxysuccinimide (NHS) to transform the carboxylic group into the amine-reactive esters. Then, ethylenediamine (ED) was applied to bind the modified GO onto the membrane surface. Modified membranes achieved bacterial cell inactivation by 59% without altering permeability and its salt rejection performance. Cell damage was visible for the modified membrane in SEM images. Mokkaapati et al. [62] fabricated GO modified PSf membranes to determine the changes that occurred in the anti-bacterial/anti-biofouling activity of membranes. In the study, to keep GO content in the membrane matrix at a specific level, the aqueous coagulation bath in phase inversion contained GO^+ . The study showed that 74.5% bacterial inhibition was possible with 0.048% GO concentration. The addition of GO in the membrane matrix can act as a protective layer for membrane pores due to decreased pore resistances in activated sludge filtration.

2.1.5. Other nanoparticles

In addition to the aforementioned NPs, copper [63], zinc [9], lipophilic bismuth (BisBAL) [64], quantum dots [65], clay [66], nanocarbon black [67] nanoparticles have been also used for the modification of membrane surface to benefit their antibacterial properties.

Akar et al. [68] prepared polyethersulfone (PES) UF membranes containing Cu NPs and Se NPs via phase inversion method and investigated their biofouling properties. In the casting solution including 18 wt.% PES, nanoparticle (Cu, Zn) concentrations increased from 0.002 to 0.050 Se/PES or Cu/PES. Anti-fouling and protein rejection performances of the modified membranes were evaluated by using activated sludge as a biological suspension and BSA solution, respectively. As a result, all modified PES membranes (especially 0.05 Se/PES and Cu/PES membranes) had better antifouling properties with a high rejection rate than the neat PES membranes. 0.05 Se/PES or Cu/PES membranes showed the highest protein rejection ratio (80.0% for nSe and 86.3% for nCu) when compared with other modified membranes and neat membranes.

Table 1 summarizes studies (based on the last 4 years) concentrated on the modification of membranes for improving anti-fouling, biofouling, microbial properties in terms of modification method, nanoparticle type, the base polymer used, and nanoparticle size, diameter, concentration.

2.2. Membrane modification by organic modifiers

Organic molecules due to their specific hydrophilic or antibacterial properties can be applied for membrane modification to mitigate fouling. These molecules can be

tailored on the membrane surface or incorporated into the membrane matrix by various methods such as blending, grafting, physical coating, initiated iCVD, etc. In this section, methods used to modify membranes by organic modifiers are discussed and the literature related to developing membrane modification techniques and materials by organic molecules are presented.

2.2.1. Blending

Blending is one of the facile methods, which can modify the polymeric membrane in bulk. In this method, generally, an amphiphilic copolymer having hydrophobic and hydrophilic segments is blended in membrane casting solution and during phase inversion, hydrophilic segments segregate toward the membrane surface, and the hydrophobic segment is anchored to the polymer matrix. Amphiphilic copolymers can block copolymers, comb copolymers, and branched copolymers. Efforts on applying this type of material are increasing in number due to the stable self-assembly of synthesized copolymers in the membrane and imparting hydrophilicity [89]. Pluronic is a common triblock amphiphilic copolymer that is applied for blending with the polymeric solution [90,91]. This triblock copolymer is composed of two external hydrophilic polyethylene oxide segments and a hydrophobic polypropylene oxide (PEO-PPO-PEO) segment. Zhao et al. [92] blended pluronic F127 into PES solution at different concentrations (0.72–3.60 wt.%) for fabricating the antifouling membrane. This additive increased the pore size and the permeability of the membranes without a remarkable increase in BSA rejections. Membrane properties were affected due to (1) pluronic wrapping by PES as PPO segments connected to PES. (2) Fast phase separation by pluronic location at the interface of solvent and non-solvent, which leads to the bigger pore size formation and (3) misallocation of pluronic with orientation of PEO to corona side; micelles were trapped in skin layer of the membrane, which determines pore size. Increasing pluronic concentration lead to an increase in pore size, anti-fouling capacity and water permeability of the membranes.

Wang et al. [93] synthesized the pluronic 123 triblock copolymer and blended with PEG400 and PES to make a casting solution for the phase inversion membrane fabrication process. Water permeability of the prepared membrane was affected by the combination of the surface hydrophilicity and pore structure change. The formed PEG rich and poor parts during the phase separation process resulted in pore formation. The amphiphilic pluronic-b-PEG located at the interface with PPO orientation toward the PEG rich and PPO stretched toward PEG poor, which resulted in the pore structure change. Introducing Pluronic 123 did not change mechanical stability significantly. PEO segment increased the BSA fouling resistivity and FRR. FRR showed great dependency on the pluronic 123 content and operating pressure.

PEG is a non-ionic, hydrophilic, and flexible material that has also been applied in blending technique for enhancing membrane hydrophilicity [93,94]. Shi et al. [95] synthesized PEGylated PES membranes by blending PEG into a casting solution to fabricate antifouling membranes. It was shown that an increase in PEGylated PES content

Table 1
Summary of membrane modification by nanoparticle studies published in the last 4 years

Membrane type	NP type	NP size (nm)	Modification method	Ref.
PES UF	Sulfonated TiO ₂	25–80	Blending-phase inversion	[69]
PVDF UF	TiO ₂	416	Blending-phase inversion	[70]
PA TFC NF	Ag	10–20	In situ reduction on surface	[71]
TFC PA	Ag	28.5–32.7	Plasma-enhanced magnetron sputtering	[72]
PVDF-co-hexafluoro propylene UF	Ag	10.2 ± 3.8	Electrospinning	[4]
PEI UF	Ag	40	In situ reduction on surface	[73]
PA TFC NF	Biogenic Ag ⁰ -6	–	IP	[74]
PA TFC NF	TiO ₂ /GO	5	IP	[75]
PES UF	GO	56.21	Blending-phase inversion	[76]
PVDF UF	ZnO	30–200	Blending-phase inversion	[77]
PES UF	CuO	–	Blending-phase inversion	[11]
PA TFC RO	Cu	10–50	In situ reduction on surface	[63]
PVDF, UF	MWCNT-COOH	L: 0.5–2 μm D: 5–15 nm	Blending-phase inversion	[13]
Polypropylene (PP)	Nanoclay	–	Blending-phase inversion	[66]
PVDF, UF	SiO ₂	46.3	Blending-phase inversion	[78]
PES NF	Fe ₃ O ₄	60	Crosslinking dip-coating	[79]
CA, UF	Fe ₃ O ₄	151.8 ± 8.2	Physical coating	[80]
PES, UF	Ce(III) metal-organic framework	60	Blending-phase inversion	[81]
PSf, UF	Au	50	Blending-phase inversion	[82]
PES, UF	Antimony tin oxide	18	Blending-phase inversion	[83]
PAN, UF	ZrO	25–80	Blending-phase inversion	[84]
PSf, UF	Oxidized nano carbon black	40–60	Blending-phase inversion	[67]
TFC PA	Polyrhodanine	6–18	IP	[85]
PES, UF	Activated carbon-chitosan	14–24	Blending-phase inversion	[86]
Cellulose ester	Cu(OH) ₂ nanowires - GO	–	Physical vacuum coating	[87]
PES, UF	Carbon quantum dots	3.2	Chemical dip-coating	[65]
PAN, UF	Chitosan-coated iron oxide	32–78	Blending-phase inversion	[88]
PSf, UF	Lipophilic bismuth (BisBAL)	–	Self-assembling by dip-coating and UVA treatment	[64]

L: length; D: diameter.

resulted in an exponential decrease in BSA adsorption. Apart from endowing antifouling property to the membrane, enhancing water permeability is considered to be a key advantage for blending PEG.

Ma et al. [96] have studied the effect of chemical structures of amphiphilic poly(poly(ethylene glycol) methyl ether methacrylate-methyl methacrylate) [P(PEGMA-MMA)] copolymer on hydrophilicity and antifouling properties of PVDF membrane. Initial PEGMA/MMA monomer ratios, PEG side chain lengths, and copolymer/PVDF blend ratios were considered as parameters. Fig. 5 shows the route of membrane formation according to the different parameters used in the study. The fouling property and flux value of amphiphilic copolymer blended membranes improved compared with the pristine PVDF membrane. Air bubble contact angle of membranes increased in cases of increased P(PEGMA-MMA)/PVDF blend ratio, PEGMA/MMA monomer ratio of the copolymer, and PEG side chain length of the copolymer. Also, change in monomer ratio and PEG

length enhanced the antifouling property of the membranes slightly more than changes in copolymer/PVDF blend ratio of membranes.

Zwitterionic material has become a new class of antifouling material due to its strong affinity for water molecules via electrostatic interactions. This electrostatic force generates a hydration layer around its positively and negatively charged molecules rendering its resistance against protein and microorganism adsorption as illustrated in Fig. 6. The generated hydration layer around zwitterionic materials is more stable and stronger than the hydration layer generated from other hydrophilic materials. Also, their positively charged group heads can show antibacterial property and cause death in bacteria as reported previously by Saffarimiandoab et al. [97]. Poor miscibility of zwitterionic materials in the casting solution makes them not suitable for applying blending technique. Hence, only a limited number of studies can be found on zwitterionic blended antifouling membranes [89].

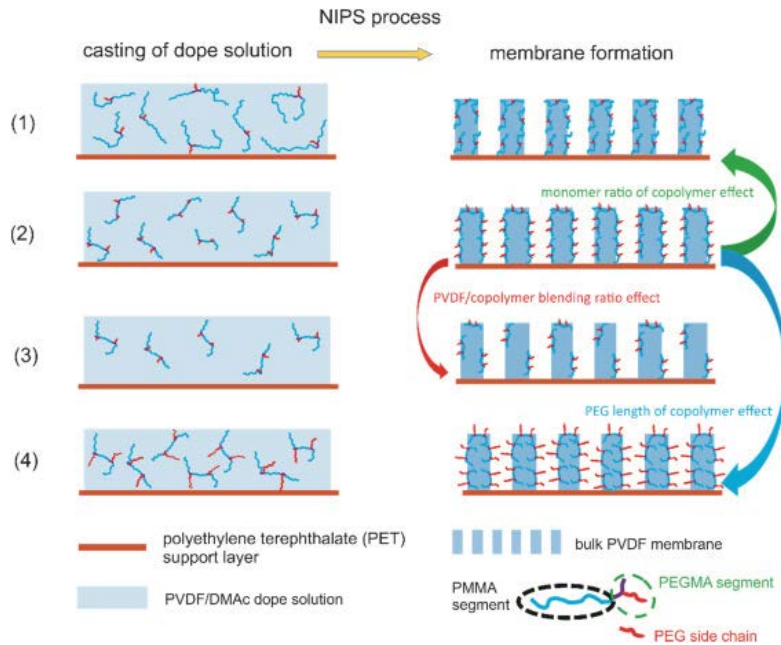


Fig. 5. Schematic of P(PEGMA-MMA)/PVDF blend membrane formation by non-solvent induced phase separation process. Route (1): PEGMA/MMA monomer ratio (low), PEG side chain length (short), copolymer/PVDF blend ratio (high); route (2): PEGMA/MMA monomer ratio (high), PEG side chain length (short), copolymer/PVDF blend ratio (high); route (3): PEGMA/MMA monomer ratio (high), PEG side chain length (short), copolymer/PVDF blend ratio (low); route (4): PEGMA/MMA monomer ratio (high), PEG side chain length (long), copolymer/PVDF blend ratio (high) [96].

Wang et al. [98] prepared highly efficient antifouling zwitterionic poly([3-(methacryloylamino)propyl]-dimethyl(3-sulfopropyl)ammonium hydroxide) (PAN-MPDSA) blended UF membrane. PAN-MPDSA was synthesized by the water-phase suspension polymerization. Zwitterionic PAN-based membranes showed higher hydrophilicity and wettability and lower protein adsorption compared with the PAN membrane. Ultrafiltration experiments revealed irreversible fouling properties decreased for zwitterionic PAN-based membranes due to the existence of PMPDSA segments on the membrane surface. Moreover, reversible membrane fouling during the UF membrane process can be easily washed away by simple water cleaning. Table 2 summarizes studies done with amphiphilic and zwitterionic copolymers by blending method to mitigate fouling in membranes in terms of membrane materials, the zwitterionic polymer used, and general conclusions.

2.2.2. Physical coating

Physical coating of surfactants or hydrophilic polymers on the membrane surface is a simple and efficient method for antifouling modification of the membrane by which surface gets smoother, more hydrophilic, and electrostatically repellent against foulants. The physical coating is possible through adhesion/adsorption with binding energy improved by manifold interactions between functional groups in the macromolecular layer and on membrane surface; interpenetration by combining functional material and base polymer in interphase; and macroscopic entanglement of functional group and pore structure of membrane [1]. The main challenge for physical coating is the

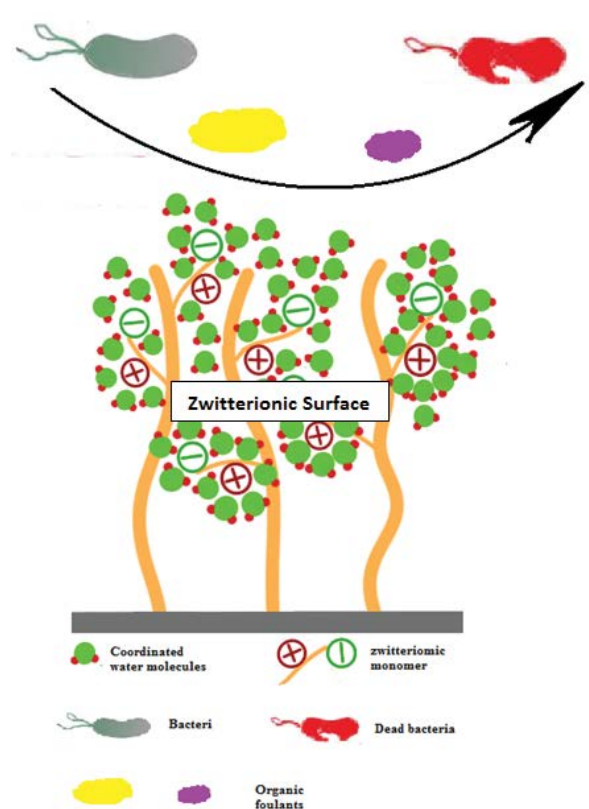
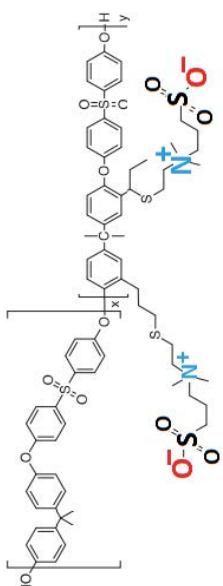
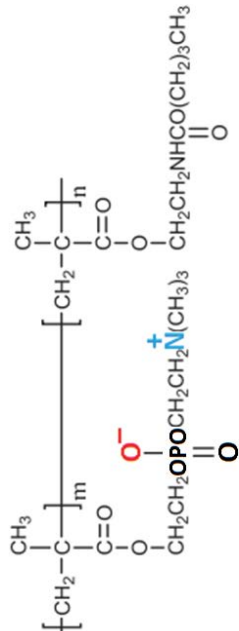
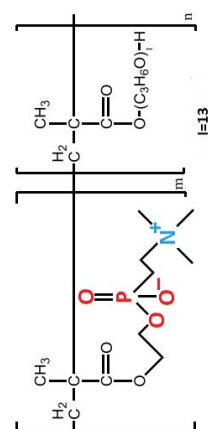
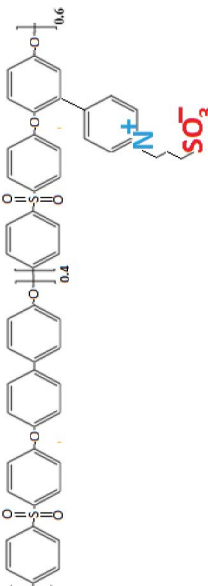









Fig. 6. Schematic illustration of zwitterionic material coated membrane and antifouling effect of the hydration layer and antibacterial effect of positively charged groups.

Table 2
Summary of Zwitterionic material blended membrane modification to mitigate antifouling

Membrane material	Zwitterionic polymer type	General conclusions	Ref.
	Zwitterionic polymer structure		
PSf	<p>Poly(arylene ether sulfone-co-sulfobetaine arylene ether sulfone)</p> 	<ul style="list-style-type: none"> • Water contact angles decreased dramatically • Water permeability increased • BSA fouling propensity decreased • Showed chlorine resistance 	[99]
PVDF	<p>Poly(2-methacryloyloxyethyl phosphorylcholine-co-methacryloyloxyethyl butylurethane)</p> 	<ul style="list-style-type: none"> • Water contact angles decreased but remained hydrophobic • The decrease in fibrinogen protein fouling level • <i>Escherichia coli</i> adhesion almost was mitigated • Permeability decreased dramatically over the humic acid fouling process • Flux recovery rate increased even though the fouling was high for humic acid 	[100]
PVC	<p>(methacryloyloxyethylphosphorylcholine-co-poly(propylene glycol) methacrylate)</p> 	<ul style="list-style-type: none"> • Air bubble contact angles increased revealing increased hydrophilicity • BSA adsorption was suppressed in the adsorption test • Pure water permeability increased • Flux dramatically decreased by BSA fouling • Flux recovery increased 	[101]
Polyphenylsulfone	<p>poly(arylene ether sulfone) (PAES)</p> 	<ul style="list-style-type: none"> • Water contact angles decreased dramatically • BSA adsorption decreased by 80% • Pure water permeability increased • BSA and humic acid rejection decreased • FRR increased up to 96% for BSA fouling 	[102]

Sulfonated poly(amine) (SPANI)		<ul style="list-style-type: none"> • Water contact angles decreased • BSA adsorption decreased by 57% • BSA rejection decreased • Pure water permeability increased • FRR increased up to 93% for BSA fouling 	[103]
Polyphenyl sulfone			
PVDF	<p>Poly(methyl methacrylate [3-(methacryloylamino) propyl] dimethyl(3-sulfopropyl)ammonium-hydroxide)</p> 	<ul style="list-style-type: none"> • Water contact angles decreased dramatically • BSA adsorption decreased by 50% 	[104]
PVDF	<p>PVDF-b-poly[2-(N,N-dimethylamino) ethyl methacrylate]</p> 	<ul style="list-style-type: none"> • Water contact angles decreased dramatically • BSA rejection decreased • Pure water permeability increased • FRR increased for BSA fouling 	[105]
PVDF	<p>Poly(tetrafluoroethylene-co-vinylpyrrolidone)</p> 	<ul style="list-style-type: none"> • Air bubble contact angles increased • Flux reduced less by BSA fouling • Pure water permeability increased 	[106]
PVDF	<p>Pluronic 127</p> 	<ul style="list-style-type: none"> • Water contact angles increased • Water uptake increased • Flux reduced less by BSA and humic acid fouling • FRR for BSA increased • Pure water permeability increased • BSA rejection increased 	[107]
PSf/sulfonated poly(ether ether ketone)			

instability of physical bonds, which make them not unstable especially for operations under crossflow with high pressures such as RO and NF membrane separations.

PE-PA block copolymer was dip-coated on the PA RO by Louie et al. [108] membrane for improving membrane fouling resistance. Nylon 6 and PEG species with high hydrophilicity and swelling up to 130% in room temperature have opted as surface modifying material. The mechanism for fouling mitigation was surface smoothening and improving surface wettability. The coating was carried by dip coating in the coating solution. The decline in pure-water flux was observed due to the pore size shrinkage. Permeate flux of the control membrane in 120 d surfactant oil–water mixture fouling became less than the flux of the coated membranes after about 30 d on average for the membranes. However, the foulant was removed from the fouled coated membranes after cleaning. Reddy et al. [109] took the filtration approach for coating negatively charged poly (sodium 4-styrene sulfonate; PSS) on the PES membrane to introduce the SO_3^- groups on the surface. The membranes with higher molecular weight cutoff allowed the solution to be treated inside the pores. The FRR for all the modified membranes was enhanced up to around 90% over the dextran/PEG fouling. In Table 3, some of the surface modifiers used in antifouling coating are given.

2.2.3. Grafting

Although blending and physical coating are convenient methods to modify membrane properties, they are facing some challenges such as aging and instability in and on the membrane. In this respect, grafting offers a more efficient alternative approach for membrane modification. Stronger and stable hydrophilic membranes can be fabricated by grafting since monomers covalently bond to the sites on or at the end of the polymeric chain [110]. Polymerizable hydrophilic or bactericidal monomers can be employed in grafting methods to modify and develop new antifouling membranes. “Grafting to” and “grafting from” methods are two possible routes of grafting, but the latter is the most applicable method in modifying membrane surfaces. In the “grafting to” the functional branch is anchored on the membrane surface [111]. In this approach, an end-functionalized monomer can be covalently bonded on reactive groups on the membrane surface. Branching can be occurred having a narrow molecular weight distribution, which limits the employment of this technique in membrane surface

modification. On the other hand, in the “grafting from,” method, the introduction of functional macromolecules can be initiated and propagated from the active sites on the polymer backbone of the membrane matrix [112]. Active sites can be made either on polymer backbone before grafting or pre-existed on the copolymer itself. The grafting-from process is usually carried by chemical, photochemical-, radiation-, and plasma-induced grafting [113–115].

2.2.3.1. Chemical-induced grafting

In the chemical grafting process, initiators create free radical and ionic active sites on the polymer backbone for functional groups formed on the membrane surface. Common chemical grafting methods are (1) free radical graft polymerization and (2) living graft polymerization. The compatibility of grafted monomers with mild reaction conditions in free radical graft polymerization is an advantage. However, low control on reaction, homopolymerization, and high polydispersity index (M_w/M_n) polymer molecular weight distribution are disadvantages of this technique. On the other hand, the living graft polymerization technique plays an efficient role in overcoming the aforementioned problems since termination and chain transfer do not exist in living polymerization [1,116]. Initiators play a significant role in determining the route of the reaction [117]. The initiation can be performed by chemical means such as redox initiation. Hydrogen abstraction and radical creation are possible by $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ [118], Ce^{4+} salts [119], $\text{K}_2\text{S}_2\text{O}_8/\text{K}_2\text{S}_2\text{O}_5$ [120], $\text{NaHSO}_3/(\text{NH}_4)_2\text{S}_2\text{O}_8$ [121]. Living-free radical graft polymerization is a type of living graft polymerization in which the active end groups are free radical. This method enables chemists to develop well-defined graft polymers by overcoming issues associated with conventional free radical polymerization and living polymerization.

Atom transfer radical polymerization (ATRP) and reversible addition–fragmentation chain transfer (RAFT) are the most commonly used techniques in controlled living-free radical polymerization for membrane surface grafting. ATRP utilizes alkyl halides as initiators and a transition metal catalyst, which is considered to have a significant role. Yao et al. [122] grafted block copolymer of poly(ethylene glycol) monomethacrylate (PEGMA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) (PPHF-g-(PPEGMA-b-PDMAEMA)) on PP HF membrane through surface-initiated ATRP. Results showed that the pore size of membranes can be controlled by adjusting graft chain

Table 3
Some of the surface modifiers used in coating for antifouling improvement [1]

Surface coating modifier	Base polymer
Chitosan coating	PA membrane
Macroinitiators photoreactive coating from PEG-based hydrogel	PA layer on PSf membrane
PDMA-b-PMMA-b-PDMA copolymer micelles and gel coating	PSf membrane
Silver-PEGylated dendrimer nanocomposite coating	TFC membranes
Carboxymethyl chitosan/ Fe_3O_4 nanoparticle	PES membrane
PDMS/PMMA copolymers	PDMS membrane
Zwitterionic coating (poly(4-vinylpyridine-co-ethylene glycol diacrylate))	TFC membrane

length or ATRP time. To give an antibacterial effect on the PP HF membrane, PDMAEMA quaternized and antibacterial property of membranes found effective against *E. coli* and *S. aureus*. Besides block copolymers' bactericidal properties, the surface of the grafted membrane exhibited a non-adhesive property against bacteria due to the hydrophilic nature of the P(PEGMA) block.

RAFT technique enables preparing of well-defined polymers with specific polymer architectures. Peng et al. [123] applied the RAFT polymerization technique for grafting the poly(N-vinyl-2-pyrrolidone) (PNVP) on the PVDF membrane. PVDF solution in the DMF was treated by O₃/O₂ gas for introducing the peroxide groups to the polymer. Then the solution was reacted with 1-phenylethyl dithiobenzoate (PDB) as a chain transfer agent under 60°C. The PVDF-g-PNVP copolymer was precipitated in ethanol. Then the membrane was fabricated by the wet-phase inversion process. Results showed that even a low surface coverage by PNVP chains, a significant reduction in BSA adsorption was achieved. PVDF-g-PNVP membrane showed very low mortality on the *E. coli* while significant antibacterial activity was observed for QAS-functionalized (PVDF-g-PNVP)-b-PDMAEMA membranes.

2.2.3.2. Photoinduced grafting

In the photochemical grafting process, reactive radicals for further polymerization are initiated by excitation of the functional groups on the membrane via light illumination. The grafting process can be initiated through sensitizer or without sensitizer. Photo-initiated grafting can be done by (I) pre-irradiation; (II) peroxidation; and (III) mutual irradiation [117]. In pre-irradiation, free radicals were formed on the polymer backbone before immersion in the interested monomer solution. Irradiation is done under vacuum or in inert gas. But in the peroxidation method, high energy irradiation is performed under air or oxygen for peroxide product formation. Then, grafting is initiated by treatment with a monomer solution in which temperature is high enough to form free radicals by cleaving the peroxides. In the mutual irradiation technique, interested monomers and polymer backbone are illuminated by UV together. Photo-induced grafting parameters are polymer backbone [124], monomer type [125], solvent type [126], initiators and its concentration [127], additives [128], temperature [129], applied UV intensity and distance from the membrane surface [130]. The bactericidal property of the membrane is determined by the grafted monomer nature. The density of the grafted chains and their length are also important for determining membrane properties.

2.2.3.3. Photo-induced grafting without a photosensitizer

If a polymer is photosensitive enough, backbone molecules will be excited and free reactive radicals will be formed by applying UV illumination. The main challenges are the photo-degradation of polymer chains and block copolymerization. Grafting without a photosensitizer can be performed in two ways: dip and immersion methods. In the dip method, the membrane is dipped in a monomer solution then UV illumination is carried out in the inert environment,

but in the immersion method, UV illumination takes place while the membrane is soaked in monomer solution [131]. Immersion consumes a large amount of the solution, which makes it an inappropriate method on an industrial scale, in addition, the degree of the modification in the immersion method is also less than in the dip method [131].

Malaisamy et al. [132] modified PES membranes to mitigate biofouling by anchoring (2-[acryloyloxy] ethyl) trimethyl ammonium chloride (AETMA) and acrylic acid (AA) by UV grafting. A photosensitizer was not necessary since PES and AETMA are photo-sensitive. The degree of grafting is adjusted by changing the UV exposure time. The water contact angle decreased by increasing UV exposure time. Biofouling results showed that *E. coli* filtration fluxes were 25%–70% higher for modified membranes. The bacterial adhesion was lower for AETMA grafted membrane, which also showed antibacterial activity.

2.2.3.4. Photo-induced grafting with a photosensitizer

If the molecules of the polymer backbone are not photosensitive enough to go into an excitation state by UV irradiation, a photosensitizer is needed. A photosensitizer can be either incorporated into monomer bulk solution or deposited on the membrane surface. Low photoinitiator concentration formation on the membrane can be formed in a monomer solution containing the photosensitizer. Furthermore, side reactions and homo-polymerization may take place at a higher concentration of photosensitizer. Aromatic ketones such as xanthone, isopropylthioxanthone, and benzophenone, benzoin ethyl ether and dyes such as Na-2,7 anthraquinone sulphonate or acrylated azo dye isopropyl thioxanthone, xanthone, anthraquinone, benzoyl peroxide and 2,2-azobisisobutyronitrile (AIBN) can be applied as photosensitizers, but the benzophenone (BP) is the most practiced one in the membrane surface photografting polymerization [133]. Benzophenone (BP) molecules go into an excitation state upon UV irradiation, which extracts hydrogen from the substrate molecules. The generated free radicals (R^{*}) initiate the graft polymerization.

Ulbricht and Yang [134] developed the “entrapping” method for BP photosensitizer incorporation on the PP membrane and compared it with the pre-existing “adsorption method”. In the developed method, branching and crosslinking are probable mechanisms but in the adsorption method, homo-polymerization may occur. In the BP photosensitizer “entrapping” method, the membrane was pre-swelled in the heptane and then the BP was “entrapped” in the surface layer by further solvent exchange. Then the carboxyl brushes were grafted by UV illumination in the monomer solution. Less dense and long grafted brushes resulted from the “entrapping” method (Fig. 7).

Yang et al. [91] modified polypropylene membranes by PDMAEMA using UV-initiated grafting, where BP was a photosensitizer to mitigate biofouling. The membrane was swelled for “entrapping” the BP in the heptane solution and for post UV exposure. In order to elucidate the antibacterial mechanisms of the brushes and understand the effect of their mobility on the destroying bacteria, quaternization and quaternization-crosslinking were performed on the grafted membranes. Monofunctional benzyl chloride (BC) or iodomethane

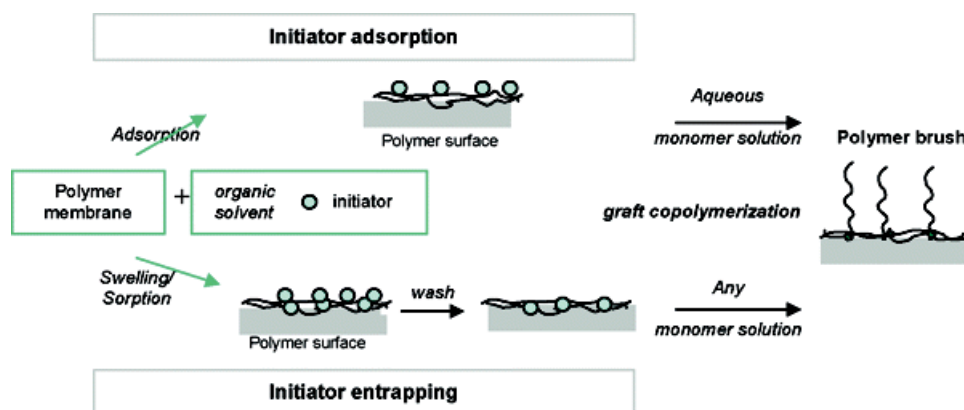


Fig. 7. Schematic description of surface-initiated graft copolymerization via adsorption and entrapment methods for initiator immobilization [134].

were applied for quaternization to make PDMAEMA permanent. The bifunctional p-xylylene dichloride (XDC) or 1,2-bis(2-iodoethoxy)ethane (BIEE) was used for quaternization-crosslinking as shown in Fig. 8. Quaternized membrane showed bacterial reduction and this antibacterial activity got higher by increasing the degree of the polymerization (DP) because of increasing surface density of the positive charge (SDPC). Antibacterial activity of quaternized iodomethane toward *E. coli* and *S. aureus* was higher than BC due to its higher hydrophilicity and higher SDPC. Quaternized cross-linked membranes lose their bactericidal efficiency due to the interconnection between the grafted chains.

2.2.3.5. Plasma graft copolymerization

Plasma is an ionized medium with an overall neutral charge that can generate free radicals on the polymeric membrane surface to react with reactive molecules in a gas environment. After plasma exposure, the membrane can be treated by oxygen or air to form peroxides to induce grafting of vinyl groups on the membrane [135]. Two substrate polymer destruction reactions and new brush grafting reactions take place to form new structures on the membrane. Ulbricht and Belfort [136] grafted acrylic monomers on PAN and PSf membranes by taking advantage of their high radical polymerization capability. Membranes were treated with water plasma and He/water plasma at low temperatures. Plasma treatment altered PSf membrane pore size, unlike for the PAN membrane. After the oxidation by air and peroxide formation, hydroxyethyl methacrylate (H*EMA), acrylic acid, and methacrylic acid monomers were grafted on the plasma-activated membranes through thermal decomposition of the peroxides at 323 K. PSf showed a lower degree of polymerization, which was ascribed to inefficient peroxide decomposition for inducing polymerization in the aromatic part of PSf. Considering protein fouling, modified PAN membranes showed higher fluxes and rejection as compared with pristine membranes but results for the PSf were not desirable due to pore etching. Wavhal and Fisher [137] grafted acrylamide (AAM) on the PES membrane by the Ar-plasma route. The grafting step was performed in the vapor phase, which leads to better grafting and no homo-polymerization

in comparison with the solution-based plasma grafting. The grafting yield of AAM on the PES membrane was in linear relation with grafting time. Increased hydrophilicity and low protein fouling were observed for the modified membrane without noteworthy alteration in the polymeric structure of the membrane.

Investigating the role of grafting structure on membrane performance and fouling behavior, Chang et al. [138] grafted two brush-like and network-like structures of the PEGMA on the PVDF membrane. Low-pressure plasma grafting was applied for developing a network-like structure and surface-initiated thermal and ATRP polymerization were utilized for developing the brush-like structure as shown in Fig. 9. The hydration capacity for the membranes, which is a determining factor in the membrane tendency to resist fouling, is attributed to the following three factors: (1) entrapping water inside the pores; (2) binding of water to the grafted brushes; (3) binding the water in confined spaces between the chains. The membrane with a network-grafted membrane showed lower protein adsorption and the high FRR in comparison with other grafted and pristine membranes.

2.2.3.6. Initiated chemical vapor deposition

iCVD can also be used to create thin-film polymers on the membrane surfaces. iCVD is a solventless free-radical polymerization technique performed at low temperatures and low operating pressures. In the system, free radical initiator species are thermally cracked over a heated filament and they induce vapor phase monomers to deposit on the surface at high rates. Deposition from the vapor phase provides conformal coatings. Film thickness can be controlled by changing deposition conditions [139].

2.2.3.7. Other grafting techniques

Apart from the previously mentioned grafting techniques, the initiation can also be carried out by other means such as gamma (γ) ray [140], electron beam [141] and ozone [111,142] have been reported in membrane surface grafting. Active site generation on the polymeric backbone by the γ -ray and electron beam happens due to their high

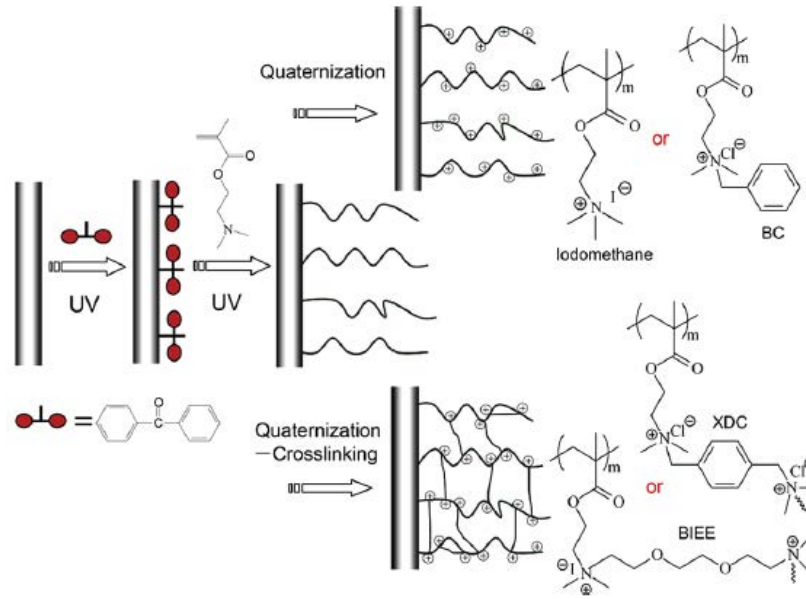


Fig. 8. UV-induced grafting of the DMAEMA and further quaternization or quaternization-cross linking of the PDMAEMA [91].

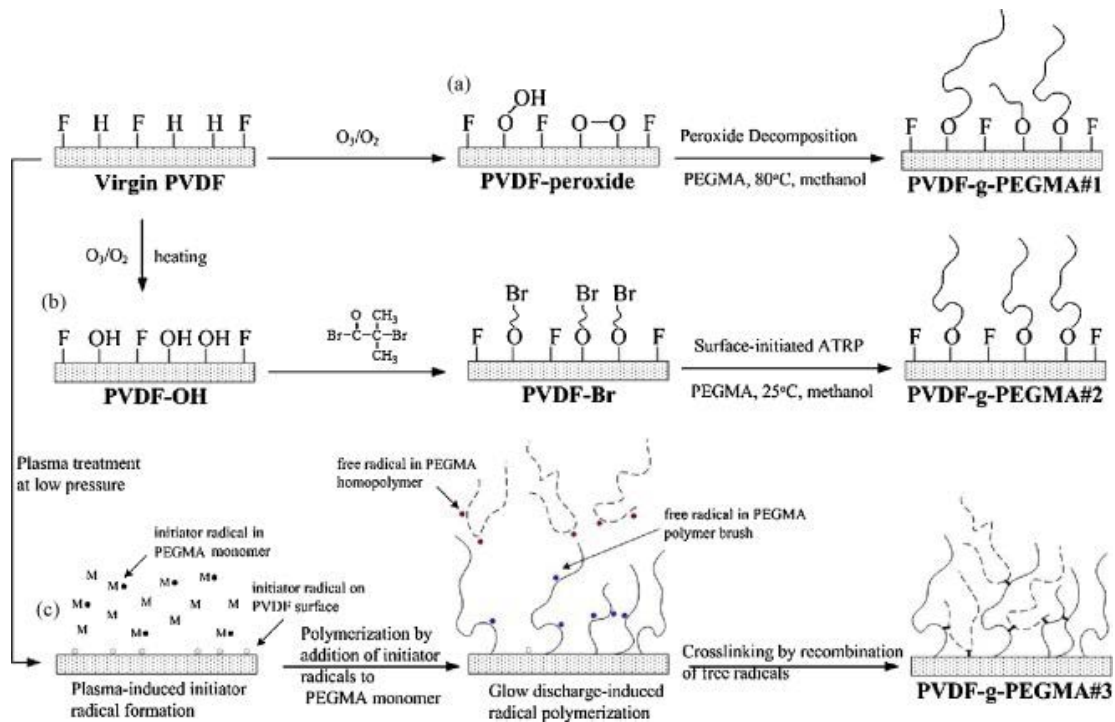


Fig. 9. Schematic illustration of the preparation process of the PVDF-g-PEGMA UF membranes via surface-initiated radical graft copolymerization: (a) ozone surface activation followed by thermal-induced radical polymerization, (b) ozone treatment and bromide activation followed by surface-initiated ATRP, and (c) low-pressure plasma treatment for plasma-induced graft-polymerization [138].

energy, but in the case of the ozone, this originates from its oxidizing property.

Table 4 summarizes the recent studies based on different grafting methods to modify membranes for fouling mitigation in terms of grafting method; initiator used in grafting; copolymer type, structure, and improved properties.

2.3. Interfacial polymerization

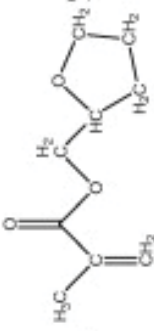
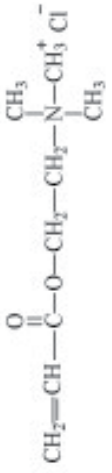

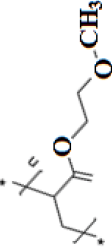
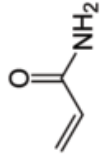
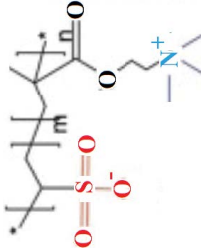
Apart from NP incorporation during IP, some hydrophilic, zwitterionic, or antimicrobial organic compounds can also be incorporated as a monomer or as additives during IP to improve the antifouling property of NF and RO membranes.

Table 4
Antifouling membrane modification by grafting methods

Membrane material	Grafting method	Initiator	Grafted copolymer type		Improved properties	Ref.
			Structure			
PAN	Free radical	Ce ^{IV}	(PAN-g-PVA)		<ul style="list-style-type: none"> • Surface roughness ↑ • Pore size ↑ • Pure water permeation ↑ • Protein rejection ↓ • Hydrophilicity ↑ 	[143]
PVC	ATRP	CuCl	Poly(methacrylic acid)		<ul style="list-style-type: none"> • BSA adsorption ↓ • Hydrophilicity ↑ • BSA solution permeance ↑ • BSA rejection x • Porosity ↑ 	[144]
PES/Torlon	Modified free radical	2,2'-Azobis(2-methylpropionitrile)	2-Methacryloyloxyethyl 1-phosphorylcholine-co-2-aminoethyl methacrylate hydrochloride		<ul style="list-style-type: none"> • Hydrophilicity ↑ • Pore size ↓ • Pure water permeation ↑ • Flux decline by fouling ↓ • FRR ↑ 	[145]
PVC	ATRP	CuCl	PVC-g-Poly(oxyethylene methacrylate)/titanium isopropoxide (TTIP)		<ul style="list-style-type: none"> • Porosity ↑ • BSA rejection ↓ • FRR ↑ • BSA solution permeance ↑ 	[146]

(Continued)

Table 4 Continued

Membrane material	Grafting method	Initiator	Grafted copolymer type Structure	Improved properties	Ref.
PVDF	RDRP	Cu ^{II}	Tetrahydrofurfuryl methacrylate 	<ul style="list-style-type: none"> Hydrophilicity ↑ Pure water flux ↑ BSA rejection ↑ FRR ↑ 	[147]
PES	Photo (UV)	-	AETMA 	<ul style="list-style-type: none"> Hydrophilicity ↑ Pure water permeation ↓ <i>Escherichia coli</i> solution permeance ↑ FRR ↑ Antibacterial activity ↑ 	[132]
PVDF	ATRP/plasma-induced	Br	Poly(ethylene glycol) methacrylate 	<ul style="list-style-type: none"> Hydrophilicity ↑ BSA adsorption ↓ 	[138]
PE	Plasma	-	Poly(2-methoxyethylacrylate) 	<ul style="list-style-type: none"> BSA solution permeance ↑ 	[148]
PES	Plasma	Ar	Acrylamide 	<ul style="list-style-type: none"> Thermal stability ↑ Hydrophilicity ↑ Water flux ↑ 	[137]
PES	Photo (UV)	-	Vinyl sulfonic acid-co-[2-(methacryloyloxy) ethyl] trimethylammonium chloride 	<ul style="list-style-type: none"> Pure water permeation ↓ BSA, sodium alginate, humic acid fouling ↓ FRR of BSA, Sodium alginate, humic acid fouling ↑ 	[149]

↑: increase; ↓: decrease; x: negligible change.

Bera et al. [150] incorporated both triazine ring and PEG into TFC RO membranes. The PA active layer was prepared on the PSf support membrane via IP using *m*-phenylenediamine (MPD), melamine and MPD-terminated PEG (MeO-PEG-MPD) and TMC. PEGylated membranes showed higher surface hydrophilicity, lower surface roughness, and superior overall antifouling properties compared with corresponding non-PEGylated membranes. Recently, An et al. [151] prepared a fouling resistant NF membrane incorporating zwitterionic amine monomer during IP. Zwitterionic amine functional N-aminoethyl piperazine propane sulfonate, AEPPS monomer was synthesized and used in the aqueous phase in IP with PIP. Results showed that as AEPPS content (0–5.91 mol% AEPPS/PIP) increased in membrane matrix, surface hydrophilicity and surface roughness increased. Resulting membranes showed excellent separation performance, good antifouling and antibacterial properties. Moreover, the water flux and salt rejection were stable during 288 h filtration.

2.4. Plasma treatment

Plasma, an ionized medium, can be utilized for changing the physicochemical property of the membrane surfaces, making them permanently hydrophilic and in some cases more smooth. Apart from the aforementioned plasma-induced graft polymerization technique, plasma treatment can be carried out by a non-polymerizable gas; the gas forms functional groups on the plasma-generated active sites. An important challenge associated with the utilization of the plasma is the aging and hydrophobic recovery by over-exposing plasma and subsequent polar group reorientation [1]. Table 5 lists different plasma treatment works with different plasmas.

3. Concluding remarks and future perspective

Recent advances in developing antifouling membranes along with their mechanisms to halt fouling were investigated. There are various review studies on membrane biofouling focusing on process factors [155] and different applications [156–158], while this study makes a holistic and critical review on the state of the art strategies and materials for developing antifouling membrane by covering all the UF, NF, and RO processes. In general, increasing wettability, reducing surface roughness, rendering electrostatic repulsion, incorporating antibacterial monomer or NPs, and photocatalyst NPs are the main approaches to inhibit organic molecules or microorganisms from approaching, attaching, accumulation, and growing (in the case of bacteria) on the membrane surface. Rendering these properties to the membrane has been sought by numerous promising techniques including polymer and NP coating, blending, grafting, IP, plasma treatment, etc. While many techniques and materials were shown to successfully minimize fouling, most of their applicability for real-life applications and commercial use at large scale is under question. Table 6 summarizes the different modification techniques that have been carried for various applications in the lab scale. In addition, it provides the main obstacles for the scale-up of these techniques. In order to solve these challenges different questions need to be answered could be categorized as below:

3.1. Technical feasibility

The majority of studies did answer the question of how the proposed method can be covered for commercial use and even whether the idea suits for the interested application. For example, numerous studies applied photocatalytic TiO₂-PA TFC RO or NF membranes. However, designing a new module that allows light passage on the membrane is rife with serious questions. Also, synthesizing copolymers, zwitterionic polymers and NP requires multiple synthesis steps, intensive labor work, precise control, and time.

3.2. Performance and membrane properties

Trying to minimize fouling by membrane modification should not sacrifice rejection and water flux performance. Introducing a new layer on the membrane by spin-/dip-coating can reduce the permeability. This is more critical in RO and NF membranes which thickness of the thin film is a key factor for membrane permeability. TiO₂ blended or coated UF membranes can be applied for the pretreatment step of desalination and wastewater treatment. However, the membrane can go under structural deterioration and polymeric chain degradation from UV light and generated reactive oxygen species from photocatalyst NPs. Plasma treatment of membrane under nonreactive environment can induce the pore structure variation, aging, and hydrophobic recovery by over-exposing plasma and subsequent polar group reorientation.

3.3. Stability

Stability of NP and polymeric modifiers on/in the membranes under hydrodynamic, chemical, and oxidative stresses are still considered a challenge. NP leaching and release of hydrophilic polymers out of the blended and physically coated membrane have swayed researches toward approaches that anchor modifiers covalently in/on the membrane. Apart from studying the stability of modifiers during membrane filtration, it is necessary to evaluate it during cyclic membrane cleaning, which only a limited number of researches have pointed out this.

3.4. Safety

Safety and sustainability of the modification process and organic and NP modifiers are other factors to be considered large-scale applications. Management of hazardous solvents during and after membrane fabrication can impact adversely on humans and the environment. Less toxic and bio-based green solvents have been recently explored but still are limited to the lab-scale synthesis. Light-induced graft polymerization is considered to be more sustainable due to the less usage of solvent compared with chemical graft polymerization, which uses a huge amount of toxic solvent. Leakage and release of NPs and polymeric biocides out of the membrane can lead to serious problems in the food chain by bioaccumulation and biomagnification. In addition, the impact could even be more complex if the microorganisms can develop to resist against the biocides.

Table 5
Different plasma treatments for membrane surface modification with and without the presence of reactive monomers

Plasma type	Membrane type	Contact angle change	Water permeability improvement (%)	Introduced functional group	Ref.
Ar/O ₂	PES	57 to 8.6	40	Not mentioned	[152]
CO ₂	PP	128.2 to 73	27	O containing groups	[60]
H ₂ O	PES	69.5 to 30	28.29	O contained groups	[153]
O ₂ /NH ₃	PES	96 to 0	63	Hydroxyl	[154]

Table 6
Summary of modification techniques for different applications and challenges for their scale-up

Modification technique	Application	Challenges for up-scaling and real-life applications
Blending and surface coating (polymer, NP)	<ul style="list-style-type: none"> Wastewater treatment (UF, MF) Desalination pretreatment (UF) 	Membrane leaching
Blending or surface coating with photocatalyst NP	<ul style="list-style-type: none"> Photocatalytic membrane reactor for wastewater treatment (UF) 	Membrane leaching, structural variation from oxidation, module design
Physical coating (polymer, NP)	UF and MF processes	Instability
Graft copolymerization	<ul style="list-style-type: none"> Wastewater treatment (UF, MF) Pretreatment of desalination (UF) Desalination (RO) 	RAFT, ATRP: the extensive amount of solvent usage, costly, hard handling of reactive and water-soluble monomers and catalysts
IP – photocatalyst NP	RO, NF	Module design
IP – (NP, polymer)	RO, NF	Challenge for monomer or NP preparation, instability
iCVD	MF, UF, NF, RO	Hard accurate operational parameters, deposition rate variation, the hard measurement for partial pressure of initiator and monomer
Plasma treatment	MF, UF, NF, RO	Hard control on surface chemistry, costly due to the needed vacuum, aging, hydrophobic recovery

3.5. Cost

The cost is one of the most important factors for the development and commercialization of modification techniques. The applied technique used reagents and materials, labor cost, energy cost are the main factors for the cost-benefit analysis of techniques. The step in which surface modification is performed at the membrane fabrication process has also a high impact on determining the economical feasibility of the method. Regarding this, usually in situ modifications and techniques which are carried at the final steps of membrane fabrication are less costly.

The blending technique is simple and can improve mechanical stability, porous structure, and permeability. However, surface modification of membrane is more effective in terms of reducing fouling propensity. Anchored modifier on the surface can repel foulant or can damage the approaching cell better than imbedded ones due to their better accessibility. Surface physical coating and UV/redox grafting have a high capacity for commercial purposes and scale-up due to their simple steps, feasible cost, easily controllable reactions under mild conditions, and capability to be applied at the final steps of membrane synthesis. However, for desalination RO and NF membranes, polymeric brush grafting or IP modification could be more efficient in terms of maintaining permeability while the chemical coating of

the polymeric network on the membrane can dramatically decrease the permeability. For UF wastewater treatment separation membranes, more or less are applicable as the mild operation conditions are applied. Future researches have to point out the applicability of their suggested methods in large-scale applications and researches on removing these barriers for scaling-up of the modification techniques are needed. Moreover, studies on evaluating the modification techniques have mainly been carried against model foulants such as *E. coli*, *S. aureus*, humic acid, and BSA for a short time. However, further researches with long-term experiments under real conditions and multifoulants are very important to get better insights.

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References

- [1] J. Ayyavoo, T.P.N. Nguyen, B.-M. Jun, I.-C. Kim, Y.-N. Kwon, Protection of polymeric membranes with antifouling surfacing via surface modifications, *Colloids Surf. A*, 506 (2016) 190–201.

- [2] T. Turken, R. Sengur-Tasdemir, D.Y. Koseoglu-Imer, I. Koyuncu, Determination of filtration performances of nanocomposite hollow fiber membranes with silver nanoparticles, *Environ. Eng. Sci.*, 32 (2015) 656–665.
- [3] X. Fan, Y. Liu, X. Wang, X. Quan, S. Chen, Improvement of antifouling and antimicrobial abilities on silver-carbon nanotube based membranes under electrochemical assistance, *Environ. Sci. Technol.*, 53 (2019) 5292–5300.
- [4] V. Anand Ganesh, B. Kundukad, D. Cheng, S. Radhakrishnan, S. Ramakrishna, K.J. Van Vliet, Engineering silver-zwitterionic composite nanofiber membrane for bacterial fouling resistance, *J. Appl. Polym. Sci.*, 136 (2019) 47580.
- [5] A.L. Ahmad, W.Y. Pang, Z.M.H. Mohd Shafie, N.D. Zaulkiflee, PES/PVP/TiO₂ mixed matrix hollow fiber membrane with antifouling properties for humic acid removal, *J. Water Process Eng.*, 31 (2019) 100827.
- [6] R. Sengur-Tasdemir, V.R.S.S. Mokkapati, D.Y. Koseoglu-Imer, I. Koyuncu, Effect of polymer type on characterization and filtration performances of multi-walled carbon nanotubes (MWCNT)-COOH-based polymeric mixed matrix membranes, *Environ. Technol. (United Kingdom)*, 39 (2017) 1226–1237.
- [7] T.A. Makhetha, R.M. Moutloali, Antifouling properties of Cu(tpa)@GO/PES composite membranes and selective dye rejection, *J. Membr. Sci.*, 554 (2018) 195–210.
- [8] A. Modi, J. Bellare, Efficient removal of dyes from water by high flux and superior antifouling polyethersulfone hollow fiber membranes modified with ZnO/cGO nanohybrid, *J. Water Process Eng.*, 29 (2019) 100783.
- [9] S. Zinadini, S. Rostami, V. Vatanpour, E. Jalilian, Preparation of antibiofouling polyethersulfone mixed matrix NF membrane using photocatalytic activity of ZnO/MWCNTs nanocomposite, *J. Membr. Sci.*, 529 (2017) 133–141.
- [10] N. Maximous, G. Nakhla, W. Wan, K. Wong, Preparation, characterization and performance of Al₂O₃/PES membrane for wastewater filtration, *J. Membr. Sci.*, 341 (2009) 67–75.
- [11] N. Nasrollahi, S. Aber, V. Vatanpour, N.M. Mahmoodi, Development of hydrophilic microporous PES ultrafiltration membrane containing CuO nanoparticles with improved antifouling and separation performance, *Mater. Chem. Phys.*, 222 (2019) 338–350.
- [12] F.N.S. Yavuz, R. Sengur Tasdemir, T. Turken, G.M. Urper, I. Koyuncu, Improvement of anti-biofouling properties of hollow fiber membranes with bismuth-BAL chelates (BisBAL), *Environ. Technol. (United Kingdom)*, 40 (2017) 19–28.
- [13] M.H.D.A. Farahani, V. Vatanpour, A comprehensive study on the performance and antifouling enhancement of the PVDF mixed matrix membranes by embedding different nanoparticulates: clay, functionalized carbon nanotube, SiO₂ and TiO₂, *Sep. Purif. Technol.*, 197 (2018) 372–381.
- [14] M.M. Pendergast, E.M.V. Hoek, A review of water treatment membrane nanotechnologies, *Energy Environ. Sci.*, 4 (2011) 1946.
- [15] R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe, Light-induced amphiphilic surfaces [4], *Nature*, 388 (1997) 431–432.
- [16] R.A. Damodar, S.-J. You, H.-H. Chou, Study the self cleaning, antibacterial and photocatalytic properties of TiO₂ entrapped PVDF membranes, *J. Hazard. Mater.*, 172 (2009) 1321–1328.
- [17] A. Rahimpour, M. Jahanshahi, B. Rajaeian, M. Rahimnejad, TiO₂ entrapped nano-composite PVDF/SPES membranes: preparation, characterization, antifouling and antibacterial properties, *Desalination*, 278 (2011) 343–353.
- [18] S.H. Kim, S.-Y. Kwak, B.-H. Sohn, T.H. Park, Design of TiO₂ nanoparticle self-assembled aromatic polyamide thin-film-composite (TFC) membrane as an approach to solve biofouling problem, *J. Membr. Sci.*, 211 (2003) 157–165.
- [19] S.-Y. Kwak, S.H. Kim, S.S. Kim, Hybrid organic/inorganic reverse osmosis (RO) membrane for bactericidal anti-fouling. 1. Preparation and characterization of TiO₂ nanoparticle self-assembled aromatic polyamide thin-film-composite (TFC), *Membrane, Environ. Sci. Technol.*, 35 (2001) 2388–2394.
- [20] S.S. Madaeni, N. Ghaemi, Characterization of self-cleaning RO membranes coated with TiO₂ particles under UV irradiation, *J. Membr. Sci.*, 303 (2007) 221–233.
- [21] H.S. Lee, S.J. Im, J.H. Kim, H.J. Kim, J.P. Kim, B.R. Min, Polyamide thin-film nanofiltration membranes containing TiO₂ nanoparticles, *Desalination*, 219 (2008) 48–56.
- [22] Y. Mansourpanah, E.M. Habibi, Investigation and characterization of TiO₂-TFC nanocomposite membranes; membrane preparation and UV studies, *J. Membr. Sci.*, 1 (2015) 26–33.
- [23] M.J. Lee, C.S. Ong, W.J. Lau, B.C. Ng, A.F. Ismail, S.O. Lai, Degradation of PVDF-based composite membrane and its impacts on membrane intrinsic and separation properties, *J. Polym. Eng.*, 36 (2016) 261–268.
- [24] J. Mo, S.-H. Son, J. Jegal, J. Kim, Y.H. Lee, Preparation and characterization of polyamide nanofiltration composite membranes with TiO₂ layers chemically connected to the membrane surface, *J. Appl. Polym. Sci.*, 105 (2007) 1267–1274.
- [25] R.-X. Zhang, L. Braeken, T.-Y. Liu, P. Luis, X.-L. Wang, B. Van der Bruggen, Remarkable anti-fouling performance of TiO₂-modified TFC membranes with mussel-inspired polydopamine binding, *Appl. Sci.*, 7 (2017) 81–95.
- [26] P. Maheswari, D. Prasannadevi, D. Mohan, Preparation and performance of silver nanoparticle incorporated poly-etherethersulfone nanofiltration membranes, *High Perform. Polym.*, 25 (2013) 174–187.
- [27] D.Y. Koseoglu-Imer, B. Kose, M. Altinbas, I. Koyuncu, The production of polysulfone (PS) membrane with silver nanoparticles (AgNP): physical properties, filtration performances, and biofouling resistances of membranes, *J. Membr. Sci.*, 428 (2013) 620–628.
- [28] M. López-Heras, I.G. Theodorou, B.F. Leo, M.P. Ryan, A.E. Porter, Towards understanding the antibacterial activity of Ag nanoparticles: electron microscopy in the analysis of the materials-biology interface in the lung, *Environ. Sci. Nano*, 2 (2015) 312–326.
- [29] Q.L. Feng, J. Wu, G.Q. Chen, F.Z. Cui, T.N. Kim, J.O. Kim, A mechanistic study of the antibacterial effect of silver ions on *Escherichia coli* and *Staphylococcus aureus*, *J. Biomed. Mater. Res.*, 52 (2000) 662–668.
- [30] S.Y. Liao, D.C. Read, W.J. Pugh, J.R. Furr, A.D. Russell, Interaction of silver nitrate with readily identifiable groups: relationship to the antibactericidal action of silver ions, *Lett. Appl. Microbiol.*, 25 (1997) 279–283.
- [31] J.R. Morones-Ramirez, A. Camacho, J. Tapia, M.J. Yacaman, J.R. Morones, J. Luis Elechiguerra, K. Holt, J.B. Kouri, J. Tapia Ramírez, The bactericidal effect of silver nanoparticles view project multifunctional nanoplatfor for cancer theranostics view project SEE PROFILE The bactericidal effect of silver nanoparticles, *Nanotechnology*, 16 (2005) 2346–2353.
- [32] I. Sondi, B. Salopek-Sondi, Silver nanoparticles as antimicrobial agent: a case study on *E. coli* as a model for Gram-negative bacteria, *J. Colloid Interface Sci.*, 275 (2004) 177–182.
- [33] H.-L. Yang, J.C.-T. Lin, C. Huang, Application of nanosilver surface modification to RO membrane and spacer for mitigating biofouling in seawater desalination, *Water Res.*, 43 (2009) 3777–3786.
- [34] M. Sile-Yuksel, B. Tas, D.Y. Koseoglu-Imer, I. Koyuncu, Effect of silver nanoparticle (AgNP) location in nanocomposite membrane matrix fabricated with different polymer type on antibacterial mechanism, *Desalination*, 347 (2014) 120–130.
- [35] E.M.V. Hoek, A.K. Ghosh, X. Huang, M. Liang, J.I. Zink, Physical-chemical properties, separation performance, and fouling resistance of mixed-matrix ultrafiltration membranes, *Desalination*, 283 (2011) 89–99.
- [36] J.S. Taurozzi, H. Arul, V.Z. Bosak, A.F. Burban, T.C. Voice, M.L. Bruening, V.V. Tarabara, Effect of filler incorporation route on the properties of polysulfone-silver nanocomposite membranes of different porosities, *J. Membr. Sci.*, 325 (2008) 58–68.
- [37] A. Mollahosseini, A. Rahimpour, M. Jahanshahi, M. Peyravi, M. Khavarpour, The effect of silver nanoparticle size on performance and antibactericidal activity of polysulfone ultrafiltration membrane, *Desalination*, 306 (2012) 41–50.

- [38] Y. Liu, E. Rosenfield, M. Hu, B. Mi, Direct observation of bacterial deposition on and detachment from nanocomposite membranes embedded with silver nanoparticles, *Water Res.*, 47 (2013) 2949–2958.
- [39] X. Cao, M. Tang, F. Liu, Y. Nie, C. Zhao, Immobilization of silver nanoparticles onto sulfonated polyethersulfone membranes as antibacterial materials, *Colloids Surf. B*, 81 (2010) 555–562.
- [40] M. Ben-Sasson, X. Lu, E. Bar-Zeev, K.R. Zodrow, S. Nejati, G. Qi, E.P. Giannelis, M. Elimelech, In situ formation of silver nanoparticles on thin-film composite reverse osmosis membranes for biofouling mitigation, *Water Res.*, 62 (2014) 260–270.
- [41] J. Yin, Y. Yang, Z. Hu, B. Deng, Attachment of silver nanoparticles (AgNPs) onto thin-film composite (TFC) membranes through covalent bonding to reduce membrane biofouling, *J. Membr. Sci.*, 441 (2013) 73–82.
- [42] C. Ursino, R. Castro-Muñoz, E. Drioli, L. Gaara, M. Albeirutty, A. Figoli, C. Ursino, R. Castro-Muñoz, E. Drioli, L. Gaara, M.H. Albeirutty, A. Figoli, Progress of nanocomposite membranes for water treatment, *Membranes (Basel)*, 8 (2018) 18.
- [43] A. Amiri, H. Zare-Zardini, M. Shanbedi, S.N. Kazi, A. Taheri-Kafrani, B.T. Chew, A. Zarrabi, *Microbial Toxicity of Different Functional Groups-Treated Carbon Nanotubes*, Surface Chemistry Nanobiomaterials, William Andrew Publishing, USA, New York, 2016, pp. 33–70.
- [44] S. Kar, M. Subramanian, A. Pal, A.K. Ghosh, R.C. Bindal, S. Prabhakar, J. Nuwad, C.G.S. Pillai, S. Chattopadhyay, P.K. Tewari, Preparation, Characterisation and Performance Evaluation of Anti-biofouling Property of Carbon Nanotube-Polysulfone Nanocomposite Membranes, in: AIP Conference Proceedings, American Institute of Physics, 2013, pp. 181–185.
- [45] A.S. Brady-Estévez, S. Kang, M. Elimelech, A single-walled-carbon-nanotube filter for removal of viral and bacterial pathogens, *Small*, 4 (2008) 481–484.
- [46] L. Liu, J. Liu, B. Gao, F. Yang, S. Chellam, Fouling reductions in a membrane bioreactor using an intermittent electric field and cathodic membrane modified by vapor phase polymerized pyrrole, *J. Membr. Sci.*, 394–395 (2012) 202–208.
- [47] I.-H. Loh, R.A. Moody, J.C. Huang, Electrically conductive membranes: synthesis and applications, *J. Membr. Sci.*, 50 (1990) 31–49.
- [48] J. Mansouri, R.P. Burford, Novel membranes from conducting polymers, *J. Membr. Sci.*, 87 (1994) 23–34.
- [49] W.E. Price, C.O. Too, G.G. Wallace, D. Zhou, Development of membrane systems based on conducting polymers, *Synth. Met.*, 102 (1999) 1338–1341.
- [50] A.V. Dudchenko, J. Rolf, K. Russell, W. Duan, D. Jassby, Organic fouling inhibition on electrically conducting carbon nanotube-polyvinyl alcohol composite ultrafiltration membranes, *J. Membr. Sci.*, 468 (2014) 1–10.
- [51] C.D. Vecitis, M.H. Schnoor, M.S. Rahaman, J.D. Schiffman, M. Elimelech, Electrochemical multiwalled carbon nanotube filter for viral and bacterial removal and inactivation, *Environ. Sci. Technol.*, 45 (2011) 3672–3679.
- [52] R. Hashaikheh, B.S. Lalia, V. Kochkodan, N. Hilal, A novel in situ membrane cleaning method using periodic electrolysis, *J. Membr. Sci.*, 471 (2014) 149–154.
- [53] S. Liu, T.H. Zeng, M. Hofmann, E. Burcombe, J. Wei, R. Jiang, J. Kong, Y. Chen, Antibacterial activity of graphite, graphite oxide, graphene oxide, and reduced graphene oxide: membrane and oxidative stress, *ACS Nano*, 5 (2011) 6971–6980.
- [54] O. Akhavan, E. Ghaderi, Toxicity of graphene and graphene oxide nanowalls against bacteria, *ACS Nano*, 4 (2010) 5731–5736.
- [55] Y. Zhang, S.F. Ali, E. Dervishi, Y. Xu, Z. Li, D. Casciano, A.S. Biris, Cytotoxicity effects of graphene and single-wall carbon nanotubes in neural pheochromocytoma-derived PC12 cells, *ACS Nano*, 4 (2010) 3181–3186.
- [56] H. He, J. Klinowski, M. Forster, A. Lerf, A new structural model for graphite oxide, *Chem. Phys. Lett.*, 287 (1998) 53–56.
- [57] J. Lee, H.-R. Chae, Y.J. Won, K. Lee, C.-H. Lee, H.H. Lee, I.-C. Kim, J. Lee, Graphene oxide nanoplatelets composite membrane with hydrophilic and antifouling properties for wastewater treatment, *J. Membr. Sci.*, 448 (2013) 223–230.
- [58] Z. Xu, J. Zhang, M. Shan, Y. Li, B. Li, J. Niu, B. Zhou, X. Qian, Organosilane-functionalized graphene oxide for enhanced antifouling and mechanical properties of polyvinylidene fluoride ultrafiltration membranes, *J. Membr. Sci.*, 458 (2014) 1–13.
- [59] H. Zhao, L. Wu, Z. Zhou, L. Zhang, H. Chen, Improving the antifouling property of polysulfone ultrafiltration membrane by incorporation of isocyanate-treated graphene oxide, *Phys. Chem. Chem. Phys.*, 15 (2013) 9084.
- [60] L. Yu, Y. Zhang, B. Zhang, J. Liu, H. Zhang, C. Song, Preparation and characterization of HPEI-GO/PES ultrafiltration membrane with antifouling and antibacterial properties, *J. Membr. Sci.*, 447 (2013) 452–462.
- [61] F. Perreault, M.E. Tousley, M. Elimelech, Thin-film composite polyamide membranes functionalized with biocidal graphene oxide nanosheets, *Environ. Sci. Technol. Lett.*, 1 (2014) 71–76.
- [62] V.R.S.S. Mokkapati, D.Y. Koseoglu-Imer, N. Yilmaz-Devenci, I. Mijakovic, I. Koyuncu, Membrane properties and antibacterial/anti-biofouling activity of polysulfone-graphene oxide composite membranes phase inverted in graphene oxide non-solvent, *RSC Adv.*, 7 (2017) 4378–4386.
- [63] A. Zhang, Y. Zhang, G. Pan, J. Xu, H. Yan, Y. Liu, In situ formation of copper nanoparticles in carboxylated chitosan layer: preparation and characterization of surface modified TFC membrane with protein fouling resistance and long-lasting antibacterial properties, *Sep. Purif. Technol.*, 176 (2017) 164–172.
- [64] M. Li, J.C. Bradley, A.R. Badireddy, H. Lu, Ultrafiltration membranes functionalized with lipophilic bismuth dimercap-topropanol nanoparticles: anti-fouling behavior and mechanisms, *Chem. Eng. J.*, 313 (2017) 293–300.
- [65] D.L. Zhao, S. Das, T.-S. Chung, Carbon quantum dots grafted antifouling membranes for osmotic power generation via pressure-retarded osmosis process, *Environ. Sci. Technol.*, 51 (2017) 14016–14023.
- [66] S. Taghaddosi, A. Akbari, R. Yegani, Preparation, characterization and anti-fouling properties of nanoclays embedded polypropylene mixed matrix membranes, *Chem. Eng. Res. Des.*, 125 (2017) 35–45.
- [67] A. Khan, T.A. Sherazi, Y. Khan, S. Li, S.A.R. Naqvi, Z. Cui, Fabrication and characterization of polysulfone/modified nanocarbon black composite antifouling ultrafiltration membranes, *J. Membr. Sci.*, 554 (2018) 71–82.
- [68] N. Akar, B. Asar, N. Dizge, I. Koyuncu, Investigation of characterization and biofouling properties of PES membrane containing selenium and copper nanoparticles, *J. Membr. Sci.*, 437 (2013) 216–226.
- [69] S. Ayyaru, Y.-H. Ahn, Fabrication and separation performance of polyethersulfone/sulfonated TiO₂ (PES-STiO₂) ultrafiltration membranes for fouling mitigation, *J. Ind. Eng. Chem.*, 67 (2018) 199–209.
- [70] H. Dzinun, M.H.D. Othman, A.F. Ismail, M.H. Puteh, M.A. Rahman, J. Jaafar, N. Adrus, N.A. Hashim, Antifouling behavior and separation performance of immobilized TiO₂ in dual layer hollow fiber membranes, *Polym. Eng. Sci.*, 58 (2018) 1636–1643.
- [71] Y. Zhang, Y. Wan, Y. Shi, G. Pan, H. Yan, J. Xu, M. Guo, L. Qin, Y. Liu, Facile modification of thin-film composite nanofiltration membrane with silver nanoparticles for anti-biofouling, *J. Polym. Res.*, 23 (2016) 105.
- [72] U.M. Hirsch, N. Teuscher, M. Rühl, A. Heilmann, Plasma-enhanced magnetron sputtering of silver nanoparticles on reverse osmosis membranes for improved antifouling properties, *Surf. Interfaces*, 16 (2019) 1–7.
- [73] M.S.S.A. Saraswathi, D. Rana, S. Alwarappan, S. Gowrishankar, P. Vijayakumar, A. Nagendran, Polydopamine layered poly (ether imide) ultrafiltration membranes tailored with silver nanoparticles designed for better permeability, selectivity and antifouling, *J. Ind. Eng. Chem.*, 76 (2019) 141–149.
- [74] S. Liu, M. Zhang, F. Fang, L. Cui, J. Wu, R. Field, K. Zhang, Biogenic silver nanocomposite TFC nanofiltration membrane with antifouling properties, *Desal. Water Treat.*, 57 (2016) 10560–10571.

- [75] J. Wang, Y. Wang, J. Zhu, Y. Zhang, J. Liu, B. Van der Bruggen, Construction of TiO₂@graphene oxide incorporated antifouling nanofiltration membrane with elevated filtration performance, *J. Membr. Sci.*, 533 (2017) 279–288.
- [76] S. Aditya Kiran, Y. Lukka Thuyavan, G. Arthanareeswaran, T. Matsuura, A.F. Ismail, Impact of graphene oxide embedded polyethersulfone membranes for the effective treatment of distillery effluent, *Chem. Eng. J.*, 286 (2016) 528–537.
- [77] H. Jia, Z. Wu, N. Liu, Effect of nano-ZnO with different particle size on the performance of PVDF composite membrane, *Plast. Rubber Compos.*, 46 (2017) 1–7.
- [78] M.Y. Wahab, S. Muchtar, S. Jeon, L. Fang, S. Rajabzadeh, R. Takagi, N. Arahman, S. Mulyati, M. Riza, H. Matsuyama, Synergistic effects of organic and inorganic additives in preparation of composite poly(vinylidene fluoride) antifouling ultrafiltration membranes, *J. Appl. Polym. Sci.*, 136 (2019) 47737.
- [79] E. Bagheripour, A.R. Moghadassi, F. Parvizian, S.M. Hosseini, B. Van der Bruggen, Tailoring the separation performance and fouling reduction of PES based nanofiltration membrane by using a PVA/Fe₃O₄ coating layer, *Chem. Eng. Res. Des.*, 144 (2019) 418–428.
- [80] S.C. Low, Q.H. Ng, L.S. Tan, Study of magnetic-responsive nanoparticle on the membrane surface as a membrane antifouling surface coating, *J. Polym. Res.*, 26 (2019) 70.
- [81] F. Mohammadnezhad, M. Feyzi, S. Zinadini, A novel Ce-MOF/PES mixed matrix membrane; synthesis, characterization and antifouling evaluation, *J. Ind. Eng. Chem.*, 71 (2019) 99–111.
- [82] M.R. Esfahani, N. Koutahzadeh, A.R. Esfahani, M.D. Firouzjaei, B. Anderson, L. Peck, A novel gold nanocomposite membrane with enhanced permeation, rejection and self-cleaning ability, *J. Membr. Sci.*, 573 (2019) 309–319.
- [83] B. Khorshidi, S.A. Hosseini, G. Ma, M. McGregor, M. Sadrzadeh, Novel nanocomposite polyethersulfone-antimony tin oxide membrane with enhanced thermal, electrical and antifouling properties, *Polymer (Guildf)*, 163 (2019) 48–56.
- [84] K. Monsef, M. Homayoonfal, F. Davar, Coating carboxylic and sulfate functional groups on ZrO₂ nanoparticles: antifouling enhancement of nanocomposite membranes during water treatment, *React. Funct. Polym.*, 131 (2018) 299–314.
- [85] A. Rahimpour, S.F. Seyedpour, S. Aghapour Aktij, M. Dadashi Firouzjaei, A. Zirehpour, A. Arabi Shamsabadi, S. Khoshhal Salestan, M. Jabbari, M. Soroush, Simultaneous improvement of antimicrobial, antifouling, and transport properties of forward osmosis membranes with immobilized highly-compatible polyrhodanine nanoparticles, *Environ. Sci. Technol.*, 52 (2018) 5246–5258.
- [86] E. Bagheripour, A.R. Moghadassi, S.M. Hosseini, M.B. Ray, F. Parvizian, B. Van der Bruggen, Highly hydrophilic and antifouling nanofiltration membrane incorporated with water-dispersible composite activated carbon/chitosan nanoparticles, *Chem. Eng. Res. Des.*, 132 (2018) 812–821.
- [87] Y. Feng, Z. Wang, R. Zhang, Y. Lu, Y. Huang, H. Shen, X. Lv, J. Liu, Anti-fouling graphene oxide based nanocomposites membrane for oil-water emulsion separation, *Water Sci. Technol.*, 77 (2018) 1179–1185.
- [88] M. Mukherjee, S. De, Investigation of antifouling and disinfection potential of chitosan coated iron oxide-PAN hollow fiber membrane using Gram-positive and Gram-negative bacteria, *Mater. Sci. Eng. C*, 75 (2017) 133–148.
- [89] J. Wang, L. Liu, Z. Qu, Z. Qu, C. He, Outstanding antifouling performance of poly(vinylidene fluoride) membranes: novel amphiphilic brushlike copolymer blends and one-step surface zwitterionization, *J. Appl. Polym. Sci.*, 136 (2019) 47637.
- [90] J.S. Beril Melbiah, P. Joseph, D. Rana, A. Nagendran, N. Nagendra Gandhi, D.R. Mohan, Customized antifouling polyacrylonitrile ultrafiltration membranes for effective removal of organic contaminants from aqueous stream, *J. Chem. Technol. Biotechnol.*, 94 (2019) 859–868.
- [91] Y.-F. Yang, H.-Q. Hu, Y. Li, L.-S. Wan, Z.-K. Xu, Membrane surface with antibacterial property by grafting polycation, *J. Membr. Sci.*, 376 (2011) 132–141.
- [92] W. Zhao, Y. Su, C. Li, Q. Shi, X. Ning, Z. Jiang, Fabrication of antifouling polyethersulfone ultrafiltration membranes using Pluronic F127 as both surface modifier and pore-forming agent, *J. Membr. Sci.*, 318 (2008) 405–412.
- [93] Y. Wang, Y. Su, Q. Sun, X. Ma, X. Ma, Z. Jiang, Improved permeation performance of Pluronic F127–polyethersulfone blend ultrafiltration membranes, *J. Membr. Sci.*, 282 (2006) 44–51.
- [94] L.F. Hancock, S.M. Fagan, M.S. Ziolo, Hydrophilic, semipermeable membranes fabricated with poly(ethylene oxide)–polysulfone block copolymer, *Biomaterials*, 21 (2000) 725–733.
- [95] Q. Shi, Y. Su, S. Zhu, C. Li, Y. Zhao, Z. Jiang, A facile method for synthesis of pegylated polyethersulfone and its application in fabrication of antifouling ultrafiltration membrane, *J. Membr. Sci.*, 303 (2007) 204–212.
- [96] W. Ma, S. Rajabzadeh, A.R. Shaikh, Y. Kakihana, Y. Sun, H. Matsuyama, Effect of type of poly(ethylene glycol) (PEG) based amphiphilic copolymer on antifouling properties of copolymer/poly(vinylidene fluoride) (PVDF) blend membranes, *J. Membr. Sci.*, 514 (2016) 429–439.
- [97] F. Saffarimiandoab, B. Yavuzturk Gul, S. Erkoc-Ilter, S. Guclu, S. Unal, B. Tunaboylu, Y.Z. Menciloglu, I. Koyuncu, Evaluation of biofouling behavior of zwitterionic silane coated reverse osmosis membranes fouled by marine bacteria, *Prog. Org. Coat.*, 134 (2019) 303–311.
- [98] L. Wang, Y. Su, L. Zheng, W. Chen, Z. Jiang, Highly efficient antifouling ultrafiltration membranes incorporating zwitterionic poly([3-(methacryloylamino)propyl]-dimethyl(3-sulfopropyl) ammonium hydroxide), *J. Membr. Sci.*, 340 (2009) 164–170.
- [99] Y. Yang, T.L. Ramos, J. Heo, M.D. Green, Zwitterionic poly(arylene ether sulfone) copolymer/poly(arylene ether sulfone) blends for fouling-resistant desalination membranes, *J. Membr. Sci.*, 561 (2018) 69–78.
- [100] A. Venault, C.-H. Hsu, K. Ishihara, Y. Chang, Zwitterionic bi-continuous membranes from a phosphobetaine copolymer/poly(vinylidene fluoride) blend via VIPS for biofouling mitigation, *J. Membr. Sci.*, 550 (2018) 377–388.
- [101] L.-F. Fang, S. Jeon, Y. Kakihana, J. Kakehi, B.-K. Zhu, H. Matsuyama, S. Zhao, Improved antifouling properties of polyvinyl chloride blend membranes by novel phosphate based-zwitterionic polymer additive, *J. Membr. Sci.*, 528 (2017) 326–335.
- [102] G. Rong, D. Zhou, X. Han, J. Pang, Preparation and characterization of novel zwitterionic poly(arylene ether sulfone) ultrafiltration membrane with good thermostability and excellent antifouling properties, *Appl. Surf. Sci.*, 427 (2018) 1065–1075.
- [103] G. Rong, D. Zhou, J. Pang, Preparation of high-performance antifouling polyphenylsulfone ultrafiltration membrane by the addition of sulfonated polyaniline, *J. Polym. Res.*, 25 (2018) 66.
- [104] K. Tu, P. Shen, J. Li, B. Fan, C. Yang, R. Du, Preparation of enduringly antifouling PVDF membrane with compatible zwitterionic copolymer via thermally induced phase separation, *J. Appl. Polym. Sci.*, 132 (2015) n/a-n/a.
- [105] L. Zhang, Z. Zhu, U. Azhar, J. Ma, Y. Zhang, C. Zong, S. Zhang, Synthesis of well-defined PVDF-based amphiphilic block copolymer via iodine transfer polymerization for antifouling membrane application, *Ind. Eng. Chem. Res.*, 57 (2018) 8689–8697.
- [106] Y. Sun, S. Rajabzadeh, L. Fang, S. Jeon, Z. Zhou, Y. Ohmukai, J. Miki, X. Wang, H. Matsuyama, Poly(vinylidene difluoride)/poly(tetrafluoroethylene-co-vinylpyrrolidone) blend membranes with antifouling properties, *Mater. Sci. Eng. C*, 75 (2017) 79–87.
- [107] S.B. Teli, A. Benamor, M. Nasser, A. Hawari, S.J. Zaidi, M. Ba-abbad, A.W. Mohammad, Effects of amphiphilic pluronic F127 on the performance of PS/SPEEK blend ultrafiltration membrane: characterization and antifouling study, *J. Water Process Eng.*, 18 (2017) 176–184.

- [108] J.S. Louie, I. Pinnau, I. Ciobanu, K.P. Ishida, A. Ng, M. Reinhard, Effects of polyether–polyamide block copolymer coating on performance and fouling of reverse osmosis membranes, *J. Membr. Sci.*, 280 (2006) 762–770.
- [109] A.V. Reddy, D. Mohan, A. Bhattacharya, V. Shah, P. Ghosh, Surface modification of ultrafiltration membranes by preadsorption of a negatively charged polymer: I. Permeation of water soluble polymers and inorganic salt solutions and fouling resistance properties, *J. Membr. Sci.*, 214 (2003) 211–221.
- [110] P. Phomdum, S. Gassara, A. Deratani, W. Chinpa, Enhancement of resistance to protein fouling of poly(ether imide) membrane by surface grafting with PEG under organic solvent-free condition, *Chin. J. Polym. Sci.*, 36 (2018) 1157–1167.
- [111] Y. Wang, J.-H. Kim, K.-H. Choo, Y.-S. Lee, C.-H. Lee, Hydrophilic modification of polypropylene microfiltration membranes by ozone-induced graft polymerization, *J. Membr. Sci.*, 169 (2000) 269–276.
- [112] Y. Ikada, Comparison of surface modification of polymers by different methods, *Int. J. Radiat. Appl. Instrum. Part C*, 39 (1992) 509–511.
- [113] S. Belfer, Y. Purinson, R. Fainshtein, Y. Radchenko, O. Kedem, Surface modification of commercial composite polyamide reverse osmosis membranes, *J. Membr. Sci.*, 139 (1998) 175–181.
- [114] M. Taniguchi, J.E. Kilduff, G. Belfort, Low fouling synthetic membranes by UV-assisted graft polymerization: monomer selection to mitigate fouling by natural organic matter, *J. Membr. Sci.*, 222 (2003) 59–70.
- [115] Y. Uyama, K. Kato, Y. Ikada, Surface Modification of Polymers by Grafting, in: *Grafting/Characterization Techniques/Kinetic Modelling*, Springer Berlin Heidelberg, Berlin, Heidelberg, 1998, pp. 1–39.
- [116] Y.-F. Zhao, P.-B. Zhang, J. Sun, C.-J. Liu, Z. Yi, L.-P. Zhu, Y.-Y. Xu, Versatile antifouling polyethersulfone filtration membranes modified via surface grafting of zwitterionic polymers from a reactive amphiphilic copolymer additive, *J. Colloid Interface Sci.*, 448 (2015) 380–388.
- [117] A. Bhattacharya, B.N. Misra, Grafting: a versatile means to modify polymers: techniques, factors and applications, *Prog. Polym. Sci.*, 29 (2004) 767–814.
- [118] X. Yuan, J. Sheng, N. Shen, Surface modification of acrylonitrile copolymer membranes by grafting acrylamide. III. Kinetics and reaction mechanism initiating by $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, *J. Appl. Polym. Sci.*, 69 (1998) 1917–1921.
- [119] J. Zhang, J. Yuan, Y. Yuan, J. Shen, S. Lin, Chemical modification of cellulose membranes with sulfo ammonium zwitterionic vinyl monomer to improve hemocompatibility, *Colloids Surf. B*, 30 (2003) 249–257.
- [120] A. Ben-David, R. Bernstein, Y. Oren, S. Belfer, C. Dosoretz, V. Freger, Facile surface modification of nanofiltration membranes to target the removal of endocrine-disrupting compounds, *J. Membr. Sci.*, 357 (2010) 152–159.
- [121] T. Jimbo, A. Tanioka, N. Minoura, Characterization of an amphoteric-charged layer grafted to the pore surface of a porous membrane, *Langmuir*, 14 (1998) 7112–7118, <https://doi.org/10.1021/LA9800295>.
- [122] F. Yao, G.-D. Fu, J. Zhao, E.-T. Kang, K.G. Neoh, Antibacterial effect of surface-functionalized polypropylene hollow fiber membrane from surface-initiated atom transfer radical polymerization, *J. Membr. Sci.*, 319 (2008) 149–157.
- [123] Q. Peng, S. Lu, D. Chen, X. Wu, P. Fan, R. Zhong, Y. Xu, Poly(vinylidene fluoride)-graft-Poly(N-vinyl-2-pyrrolidone) copolymers prepared via a RAFT-mediated process and their use in antifouling and antibacterial membranes, *Macromol. Biosci.*, 7 (2007) 1149–1159.
- [124] Y.Y. Durmaz, G. Yilmaz, Y. Yagci, Polymers with side chain N-Alkoxy pyridinium ions as precursors for photoinduced grafting and modification processes, *Macromol. Chem. Phys.*, 208 (2007) 1737–1743.
- [125] L.-T. Ng, J.L. Garnett, E. Zilic, D. Nguyen, Effect of monomer structure on radiation grafting of charge transfer complexes to synthetic and naturally occurring polymers, *Radiat. Phys. Chem.*, 62 (2001) 89–98.
- [126] P. Guo, J.D. Anderson, J.J. Bozell, S. Zivanovic, The effect of solvent composition on grafting gallic acid onto chitosan via carbodiimide, *Carbohydr. Polym.*, 140 (2016) 171–180.
- [127] A.E. Ofomaja, S.L. Ngema, E.B. Naidoo, The grafting of acrylic acid onto biosorbents: effect of plant components and initiator concentration, *Carbohydr. Polym.*, 90 (2012) 201–209.
- [128] T. Shiojima, Y. Inoue, M. Kyomoto, K. Ishihara, High-efficiency preparation of poly(2-methacryloyloxyethyl phosphorylcholine) grafting layer on poly(ether ether ketone) by photoinduced and self-initiated graft polymerization in an aqueous solution in the presence of inorganic salt additives, *Acta Biomater.*, 40 (2016) 38–45.
- [129] C.V. Chaudhari, R.K. Mondal, K.A. Dubey, V. Grover, L. Panicker, Y.K. Bhardwaj, L. Varshney, Ethylene vinyl acetate based radiation grafted hydrophilic matrices: process parameter standardization, grafting kinetics and characterization, *Radiat. Phys. Chem.*, 125 (2016) 213–219.
- [130] Y.T. Chung, L.Y. Ng, A.W. Mohammad, Sulfonated-poly-sulfone membrane surface modification by employing methacrylic acid through UV-grafting: optimization through response surface methodology approach, *J. Ind. Eng. Chem.*, 20 (2014) 1549–1557.
- [131] J. Pieracci, D.W. Wood, J.V. Crivello, G. Belfort, UV-assisted graft polymerization of N-vinyl-2-pyrrolidinone onto Poly(ether sulfone) ultrafiltration membranes: comparison of dip versus immersion modification techniques, *Chem. Mater.*, 12 (2000) 2123–2133.
- [132] R. Malaisamy, D. Berry, D. Holder, L. Raskin, L. Lepak, K.L. Jones, Development of reactive thin film polymer brush membranes to prevent biofouling, *J. Membr. Sci.*, 350 (2010) 361–370.
- [133] B. Pan, K. Viswanathan, C.E. Hoyle, R.B. Moore, Photoinitiated grafting of maleic anhydride onto polypropylene, *J. Polym. Sci. Part A*, 42 (2004) 1953–1962.
- [134] M. Ulbricht, H. Yang, Porous polypropylene membranes with different carboxyl polymer brush layers for reversible protein binding via surface-initiated graft copolymerization, *Chem. Mater.*, 17 (2005) 2622–2631.
- [135] D. Tyszler, R.G. Zytner, A. Batsch, A. Brügger, S. Geissler, H. Zhou, D. Klee, T. Melin, Reduced fouling tendencies of ultrafiltration membranes in wastewater treatment by plasma modification, *Desalination*, 189 (2006) 119–129.
- [136] M. Ulbricht, G. Belfort, Surface modification of ultrafiltration membranes by low temperature plasma II. Graft polymerization onto polyacrylonitrile and polysulfone, *J. Membr. Sci.*, 111 (1996) 193–215.
- [137] D.S. Wayhal, E.R. Fisher, Membrane surface modification by plasma-induced polymerization of acrylamide for improved surface properties and reduced protein fouling, *Langmuir*, 19 (2002) 79–85.
- [138] Y. Chang, C.-Y. Ko, Y.-J. Shih, D. Quémener, A. Deratani, T.-C. Wei, D.-M. Wang, J.-Y. Lai, Surface grafting control of PEGylated poly(vinylidene fluoride) antifouling membrane via surface-initiated radical graft copolymerization, *J. Membr. Sci.*, 345 (2009) 160–169.
- [139] S.J. Zaidi, K.A. Mauritz, M.K. Hassan, *Membrane Surface Modification and Functionalization*, Springer, Cham, 2018, pp. 1–26.
- [140] J.K. Shim, H.S. Na, Y.M. Lee, H. Huh, Y.C. Nho, Surface modification of polypropylene membranes by γ -ray induced graft copolymerization and their solute permeation characteristics, *J. Membr. Sci.*, 190 (2001) 215–226.
- [141] J.R. Varcoe, R.C.T. Slade, An electron-beam-grafted ETFE alkaline anion-exchange membrane in metal-cation-free solid-state alkaline fuel cells, *Electrochem. Commun.*, 8 (2006) 839–843.
- [142] S.X. Liu, J.-T. Kim, S. Kim, Effect of polymer surface modification on polymer–protein interaction via hydrophilic polymer grafting, *J. Food Sci.*, 73 (2008) E143–E150.
- [143] N.A.M. Nazri, W.J. Lau, M. Padaki, A.F. Ismail, A facile modification approach for polyacrylonitrile-based UF hollow fiber membrane utilizing polyacrylonitrile-g-poly(vinyl alcohol) graft copolymer, *J. Polym. Res.*, 21 (2014) 594.

- [144] L.-F. Fang, M.-Y. Zhou, N.-C. Wang, B.-K. Zhu, L.-P. Zhu, Improving the antifouling property of poly(vinyl chloride) membranes by poly(vinyl chloride)-g-poly(methacrylic acid) as the additive, *J. Appl. Polym. Sci.*, 132 (2015) n/a–n/a.
- [145] G. Han, J.T. Liu, K.J. Lu, T.-S. Chung, Advanced anti-fouling membranes for osmotic power generation from wastewater via pressure retarded osmosis (PRO), *Environ. Sci. Technol.*, 52 (2018) 6686–6694.
- [146] M.S. Park, B.J. Park, N.U. Kim, J.T. Park, J.H. Kim, Ultrafiltration membranes based on hybrids of an amphiphilic graft copolymer and titanium isopropoxide, *J. Appl. Polym. Sci.*, 135 (2018) 45932.
- [147] H. Lei, L. Liu, L. Huang, W. Li, W. Xing, Novel anti-fouling PVDF-g-THFMA copolymer membrane fabricated via photoinduced Cu(II)-mediated reversible deactivation radical polymerization, *Polymer (Guildf)*, 157 (2018) 1–8.
- [148] K. Akamatsu, T. Furue, F. Han, S. Nakao, Plasma graft polymerization to develop low-fouling membranes grafted with poly(2-methoxyethylacrylate), *Sep. Purif. Technol.*, 102 (2013) 157–162.
- [149] W. Zhang, Z. Yang, Y. Kaufman, R. Bernstein, Surface and anti-fouling properties of a polyampholyte hydrogel grafted onto a polyethersulfone membrane, *J. Colloid Interface Sci.*, 517 (2018) 155–165.
- [150] A. Bera, R.M. Gol, S. Chatterjee, S.K. Jewrajka, PEGylation and incorporation of triazine ring into thin film composite reverse osmosis membranes for enhancement of anti-organic and anti-biofouling properties, *Desalination*, 360 (2015) 108–117.
- [151] Q.-F. An, W.-D. Sun, Q. Zhao, Y.-L. Ji, C.-J. Gao, Study on a novel nanofiltration membrane prepared by interfacial polymerization with zwitterionic amine monomers, *J. Membr. Sci.*, 431 (2013) 171–179.
- [152] N. Saxena, C. Prabhavathy, S. De, S. DasGupta, Flux enhancement by argon–oxygen plasma treatment of polyethersulfone membranes, *Sep. Purif. Technol.*, 70 (2009) 160–165.
- [153] M.L. Steen, A.C. Jordan, E.R. Fisher, Hydrophilic modification of polymeric membranes by low temperature H₂O plasma treatment, *J. Membr. Sci.*, 204 (2002) 341–357.
- [154] K.R. Kull, M.L. Steen, E.R. Fisher, Surface modification with nitrogen-containing plasmas to produce hydrophilic, low-fouling membranes, *J. Membr. Sci.*, 246 (2005) 203–215.
- [155] K.L. Jepsen, M.V. Bram, S. Pedersen, Z. Yang, Membrane fouling for produced water treatment: a review study from a process control perspective, *Water*, 10 (2018) 847–874.
- [156] S. Jiang, Y. Li, B.P. Ladewig, A review of reverse osmosis membrane fouling and control strategies, *Sci. Total Environ.*, 595 (2017) 567–583.
- [157] X. Shi, G. Tal, N.P. Hankins, V. Gitis, Fouling and cleaning of ultrafiltration membranes: a review, *J. Water Process Eng.*, 1 (2014) 121–138.
- [158] W. Zhang, L. Ding, J. Luo, M.Y. Jaffrin, B. Tang, Membrane fouling in photocatalytic membrane reactors (PMRs) for water and wastewater treatment: a critical review, *Chem. Eng. J.*, 302 (2016) 446–458.