

Journal of Membrane Science & Research

journal homepage: www.msrjournal.com

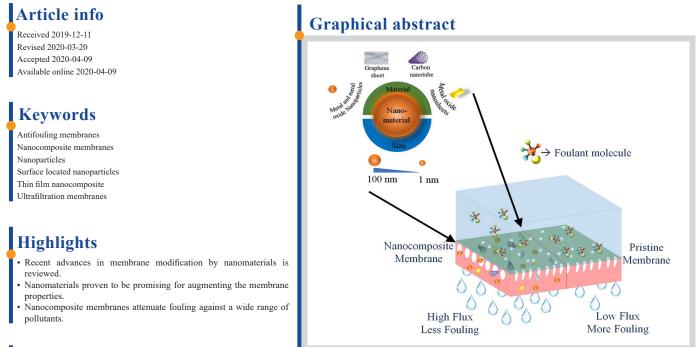
Review Paper

Progress and Perspective of Antifouling, Pressure Driven, Flat-Sheet Nanocomposite, Polymeric Membranes in Water Treatment

Hassan Younas¹, Zohaib Ur Rehman Afridi², Yue Zhou¹, Zhaoliang Cui^{1,3,4,*}

¹ The State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 210009, China ² Energy Management and Sustainability, U.S. Pakistan Centre for Advanced Studies in Energy, University of Engineering and Technology Peshawar, Peshawar, Pakistan

³ Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University, Nanjing 210009, China
⁴ National Engineering Research Center for Special Separation Membrane, Nanjing Tech University, Nanjing 210009, China



Abstract

Membrane filtration, especially based on the size exclusion phenomenon, has long been established due to its abilities to addressing the growing demands of the clean water of the world's population. However, widespread applications of the membranes face several challenges including chemical vulnerability, thermal deterioration, and biological degradation of the membranes that transpire while recovering the membrane flux after fouling. Therefore, developing antifouling membranes for water treatment purposes immensely increased in the past few years and inorganic nanoparticles played a significant role in this era. By considering the great potential of nanoparticles in the field of developing robust and small foot-print membranes, this study reviews the application of nanoparticles in pressure driven flat-sheet membranes and their impact on membrane characteristics and performance. It has been demonstrated that the application of nanoparticles has greatly improved the water permeability and antifouling potential of the membrane without compromising the selectivity of the membranes.

© 2020 MPRL. All rights reserved.

Membrane

Contents

1. Introduction	320
2. Membrane modifications for fouling mitigation	320
3. Nanomaterials as membrane modifiers	
3.1. Nanocomposite or hybrid membranes	321
3.1.1. Impact of physical blending on nanocomposite membranes	321



3.1.2. Effect on membrane porous structure	
3.1.2. Effect on membrane porous structure. 3.1.3. Effect on hydrophilicity.	
3.1.4. Effect on surface charge	
3.1.5. Effect on mechanical strength	323
3.1.6. Effect on surface roughness	
3.2. Thin film nanocomposite membrane	
3.2.1. Interfacial polymerization	
3.2. Thin film nanocomposite membrane. 3.2.1. Interfacial polymerization. 3.3. Surface located nanocomposite. 3.3.1. Self-assembly. 3.3.2. Coating/deposition.	
3.3.1. Self-assembly	
3.3.2. Coating/deposition	
3.3.3. Electrostatic attraction	
3.3.4. Layer-by-layer assembly 3.3.5. Chemical grafting	
3.3.5. Chemical grafting	
4. Challenges and future perspectives.	
Acknowledgements	
References	

1. Introduction

A continuously increasing demand of fresh water is one of the threatening issues to the world. The world's water resources are distributed into conventional water resources (ground water, rivers, and lakes) providing clean water for direct utilization including drinking or industrial purposes and unconventional water resources (polluted water, wastewater, brackish water and sea water) that need treatment prior to use. The huge utilization of conventional water resources in everyday life by individuals (drinking, cleaning, flushing), agriculturalists and industrialists has promptly depleting the conventional water resources. According to an estimate, a large amount of water is utilized by industrial and agricultural activities: 70% of the surface water and ground water, rest is served for domestic use [1]. The main challenges that are afflicting the world into sever water crisis include but not limited to population growth, food security demand, and mining activities [2-5]. Due to extensive use of freshwater for agricultural and industrial activities nearly 750 million people lack access to the safe drinking water [6]. Many are forced to rely on contaminated water for potable use, which tends them prone to waterborne diseases like Typhoid, hepatitis A and hepatitis E, polio and cholera, birth defects, bladder cancer, and spontaneous abortion. Moreover, ~ 80% of the used water is directly discharged into the conventional water resources (lakes and rivers) that reduces the availability of fresh water for direct use [6]. In developing countries around half of the population is exposed to polluted water sources, which along with inadequate water supplies for personal hygiene and poor sanitation contribute to an estimated 4 billion cases of diarrheal disease each year. Consequently, ca 2.2 million deaths occur annually with high proportion of children under five years. These problems motivated the researchers to develop new water treatment technologies, or to improve conventional water treatment systems resulting in adequate supply of clean and safe water by utilizing unconventional water resources. The low production rate of conventional water treatment technologies fails to meet the world's demand of clean water, therefore, to address the global scarcity of clean water, substitution of conventional water treatment technology is required with key features of sustainability, robustness, and low usage of chemicals during water treatment.

Water filtration has long been used in the history to meet the safe water demand of the world, whereas, the old techniques are insufficient to meet the current demand of water, both in terms of quality and quantity, of the world. The membrane-based industry is a rapidly growing domain in recent advances of water treatment due to its substantiality and robustness [7]. The low operational cost, high quality water and adequate output, compliance with stringent environmental parameters, and small foot-print deemed the membrane technology as the most suitable pathway for water treatment than other conventional counterparts such as chemical oxidation, disinfection, adsorption, distillation, or conventional media filtration. The membrane-based processes are easy to scale up due to minimized spatial requirements and potentially applicable in widespread domains including, water treatment, wastewater treatment, and industrial wastewater treatment (pharmaceutical, dyes, and metal recovery), because it provides good quality effluent, instant removal of pollutants, and high output in terms of treated water [8]. Therefore, membrane-based water purification technology has been targeted as a dominant future technology.

The membranes filtration process is mainly dependent on the applied pressure across the membrane. Based on the applied pressure, the membranes can be categorized as: (*i*) the pressure driven membrane processes (e.g. microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), pervaporation (PVP), and forward osmosis (FO)), and (*ii*) the non-pressure driven membrane processes (e.g. dialysis, electrodialysis, and membrane distillation) [9]. Now days, pressure driven membranes are of great importance owing to spontaneous production of large amount of clean water.

Based on the size exclusion principal (characteristics pore size), chemistry of active layer, and potential applications, pressure driven membranes are available as MF (for suspended solids, protozoa and bacteria removal), UF (for virus, dissolved organic matter, and colloid removal), NF (for hardness, heavy metals and dissolved organic matter removal) and RO (for desalination, water reuse and ultrapure water production).

Although, some degree of successful commercialization has been achieved for membrane filtration but fouling of the membrane limits its widespread commercialization [7]. The fouling of the membrane is the most considerable issue that occurs on the surface of the membrane or inside pores [10]. Depending upon the foulant type, the fouling could be organic fouling (foulants: organic pollutants), biofouling (foulants: protozoa, bacteria, and viruses), scaling (foulants: salt minerals). Due to fouling of the membrane the permeate flux of the membrane reduces that increase the operational cost in various terms including cleaning of the membrane (mostly, at commercial scale, cleaning is attained using chemical oxidation), more energy requirements in lieu of to increased transmembrane pressure due to clogging of the pores, replacement of the membranes, and the most important, skilled labor to perform all these tasks. Moreover, if the membrane cleaning or replacement is not timely performed, it reduces the water quality, which itself is a concerning issue. Therefore, excellent fouling resistant membranes need to be developed to mitigate fouling of the membrane.

The main reason of the fouling is the intrinsic properties of the membrane materials, i.e., the membranes fabricated by hydrophobic polymers are hydrophobic in nature and are more prone to the fouling, especially organic fouling [7, 11, 12]. Most of the industrial effluents contain high amount of organic foulants and rapidly fouls the hydrophobic membranes by deposition on the surface, or adsorption into the pores and pore walls. The hydrophobicity of the polymer depends on the surface energy: the polymers with lower than water surface energy produces hydrophobic membranes [13]. Therefore, the modification of the intrinsic membrane properties is of paramount preference. The fouling could be either irreversible or reversible, irreversible fouling is fouling that could not be cleaned from the membrane by any means and it reduces the life of the membrane. Hence, hydrophilic membrane allows less foulant to be adsorbed on the membrane fouling and increase the membrane life span by reducing cleaning frequency [14].

2. Membrane modifications for fouling mitigation

For several years, a huge devotion is employed for altering the membrane properties to reduce membrane fouling [9, 14-16]. Different researchers use different methods to alter membrane properties, which can produce fouling resistant membranes with longer life spans. Based on the particular requirement, various modifications are performed by adding new additives, including hydrophilic polymers (polydopamine, poly(ethylene glycol), etc.) [17, 18], amphiphilic copolymers (PVD-g-P(PEGMA), poly(vinylidene fluoride)-graft-poly(N,N-dimethylamino-2-ethylmethacrylate) (PVDF-g-PDMAEMA), etc.) [19, 20], inorganic nanoparticles (SiO₂, ZnO, TiO₂, graphene oxide, etc.) [16, 17, 21-23] or some other charged molecules. The modification techniques can be broadly categorized into pre-modification and post-modification. In pre-modification, membrane properties are altered before fabrication of the membrane i.e. alteration of polymer backbone to use for membrane fabrication or modifiers are applied to membrane solution before membrane fabrication. In post-modification, membrane properties are altered after the fabrication of the membrane. A detailed summary is given in Table 1 about the types of modifications, polymer, and modifier used in

different researches.

3. Nanomaterials as membrane modifiers

The technical innovation introduces new methods for incorporation of NPs into the membrane to fabricate membranes with desirable properties. The location of NPs in membrane categorizes the prepared membrane as well as the preparation procedure. The incorporation of NPs not only improves the intrinsic properties of the membrane (e.g. hydrophilicity, surface charge, and surface roughness), but also introduces some additional properties to the membrane. Such properties include mechanical strength, thermal stability, change in pore size and porosity, and specific properties of respective NPs i.e. photocatalysis, antibacterial property, adsorption etc. The prepared membrane could be a nanocomposite or hybrid membrane in which NPs are dispersed throughout the membrane matrix; thin-film nanocomposite membrane in which NPs are incorporated at the surface of the membrane but dispersed in a thin-film of polymer; surface located nanocomposite membrane in which NPs are located at the surface. Each type of membrane modification, method to prepare such membranes, and advantages of these modification will be discussed in details in the following sections.

3.1. Nanocomposite or hybrid membranes

It is the simplest method used to incorporate NPs into the membrane to improve membrane fouling characteristics: NPs are dispersed throughout the membrane matrix and improve antifouling properties of the membranes. In order to prepare such membranes, NPs are blended in polymer solution, and polymer-NPs blend is used to prepare the membrane. Thus, the process is largely known as physical blending process. The membrane preparation could be through phase inversion process (PIP) or by electrospinning process. In both cases, the NPs are incorporated into the membrane matrix. A schematic of physical blending followed by phase inversion method is given in Figure 1.

Oh et al. [24] prepared flat-sheet PVDF UF membranes by dispersing TiO₂ NPs into casting solution. The membranes were prepared on a nonwoven solid support by adding 2% P25 TiO₂ NPs into casting solution. A shift of membrane surface property was found from hydrophobic to hydrophilic: the contact angle was decreased from 80° to 69°. They further found that the addition of NPs decreased the average pore size (~0.24 to 0.12 μ m) and surface roughness. The membrane fouling index was determined using casein solution that showed reduced fouling of modified membrane, which was attributed to the increase in hydrophilicity, decrease in pore size and surface roughness of the membrane. Yan et al. [25] prepared Alumina (Al₂O₃) PVDF nanocomposite UF membrane by PIP. The prepared membranes were used for the rejection of oil from an oil field. More than 90% and 98% retention of chemical oxygen demand and total organic carbon (TOC) and less than 1 g L^{-1} oil content was found in the permeate. Moreover, 100% of flux recovery ratio (FRR) of Al₂O₃-PVDF nanocomposite membranes was reported after cleaning with 1 wt.% OP-10 surfactant treatment at pH 10.

Cui et al. [26] prepared PVDF/SiO₂/dibutyl phthalate UF membrane using thermally induced phase separation (TIPS) and found that the presence of SiO₂ largely affected the membrane internal morphology. In more details, they reported that the porosity continuously decreased by increasing the concentration of SiO₂. The membrane flux increased by increasing the SiO₂ concentration and reached at maximum point i.e. 120 L.m⁻².h⁻¹ at 0.1 MPa corresponding to 5 wt.% SiO₂, but a further increase in SiO₂ reduced the flux. Tensile strength also showed the similar trend as of flux, but the optimized concentration of SiO₂ was reported as 3 wt.% for tensile strength.

Shuai et al. [23] prepared PVDF nanocomposite membrane with a wide concentration range of Nano-ZnO (6.7% to 26.7 wt.%) as membrane modifier to fabricate anti-irreversible fouling membranes. They found almost 100% FRR for all the modified membranes whereas pristine PVDF membrane achieved only 78% FRR. Finally, the optimized dosage of nano-ZnO was determined as 6.7%, which increased the flux of the membrane almost double than that of pristine PVDF.

Another very interesting study was reported by Nang et al. [27]: PVDF-TiO₂ mixed matrix membrane was prepared and the modified membrane dramatically improved PWP i.e., $392.81\pm10.93 \text{ Im}^{-2} \text{ h}^{-1}$ bar⁻¹ compared to that of the neat membrane ($76.99\pm4.87 \text{ L.m}^{-2}.\text{h}^{-1}.\text{bar}^{-1}$). The rejection coefficient was reported as 99% for methylene blue (MB) dye with modified membranes. Moreover, they induced the self-cleaning potential of the membrane under UV light, which showed 100% FRR.

The nanocomposite membranes showed an improvement in the basic characteristics of the membranes (hydrophilicity, pore size, porosity), which are considered crucial for the filtration purposes. The detailed properties of the nanocomposite membranes are discussed hereafter.

3.1.1. Impact of physical blending on nanocomposite membranes

There are several advantages of nanocomposite membranes, some are specific to the applied NPs (antibacterial activity, oxidative behavior etc.) and some are irrespective of the NPs (hydrophilicity, surface roughness, tensile strength etc.). Some of the important modifications encountered after incorporation of NPs are mentioned below:

Table 1

Types of modification to the membranes and changes in membrane properties acquired after modification.

Polymer	Modifier	Modification technique	Application/ foulant	Membrane properties and performance evaluation
PVDF	TiO ₂	Pre-modification (blending)	UF/ HA	hydrophilicity [↑] , PWP [↑] , fouling [↓] , S value [↓] , fouling resistance [↑] , rejection coefficient [↑] , irreversible fouling [↓] [28]
PSf	GO- TiO ₂	Pre-modification (blending)	UF/ HA	hydrophilicity [↑] , PWP [↑] , fouling [↓] , surface charge: more negative, fouling resistance [↑] , rejection coefficient [↑] , surface roughness [↓] [29]
PVDF	CA	Pre-modification (blending)	UF/BSA and sewage waste water	hydrophilicity \uparrow , PWP \uparrow , porosity \uparrow , fouling \downarrow , fouling resistance \uparrow , flux recovery ratio \downarrow , tensile strength \downarrow , pore size \uparrow , rejection coefficient \uparrow [30]
PSf	Isocyanated-GO	Pre-modificatoin (blending)	UF/BSA	hydrophilicity [↑] , PWP [↓] , fouling [↓] , surface charge: more negative, surface roughness [↓] , pore size [↓] , fouling resistance [↑] , flux recovery [↑] [31]
PVDF	PVC-g-P(PEGMA)*	Pre-modification (blending)	UF/BSA solution	hydrophilicity↑, PWP↑, pore size↑, porosity↑, fouling resistance↓ but higher absolute flux was recorded, rejection coefficient↑ [19]
PVDF	PVP-carboxylated TiO ₂	Post-modification (TFN)	NF/ BSA	hydrophilicity↑, PWP↑, fouling↓, rejection coefficient↑, flux recovery↑, surface roughness↓ [32]
PVDF	ZnO	Post-modification (Atomic layer deposition)	MF/SA	hydrophilicity [↑] , PWP [↑] , fouling [↓] , pore size [↓] , surface charge: more negative, total surface energy [↑] , fouling resistance [↑] , rejection coefficient [↑] [33]
PVDF	Acrylic and amino monomer	Post-modification (dip coating)	UF/non-skim milk	hydrophilicity [↑] , PWP [↓] , fouling [↓] , fouling resistance [↑] , rejection coefficient [↑] , flux recovery [↑] [34]
SMA/PVDF	TiO ₂	Post-modification (self- assembly)	UF/BSA	hydrophilicity↑, PWP↑, fouling↓, rejection coefficient↓, flux recovery↑, MWCO↓ [35]
PCTE**	Al ₂ O ₃	Post-modificatoin (atomic layer deposition)	UF/BSA	hydrophilicity↑, PWP↓, fouling↓, pore size↓, rejection coefficient↑ [36]

*PVC-g-P(PEGMA): Poly(vinyl chloride)-grafted-poly(ethylene glycol) methylether methacrylate **PCTE: track-etched polycarbonate membranes

HA: humic acid

BSA: bovine serum albumin

PWP: pure water permeance S value: structural parameter value

3.1.2. Effect on membrane porous structure

Incorporation of NPs into polymer membrane alters the morphology of the membrane. Most of the studies found that porosity and pore size are largely affected by the incorporation of NPs into the membrane [37, 38]. Besides pore size and porosity, the type of interconnected porous network of the membrane is also influenced by NPs [28].

Zhang et al. [39] found that addition of TiO_2 NPs into PVDF membrane tailored the membrane porous structure and a shift was observed from fingerlike voids to spongy voids with an increase in NPs concentration. However, they found that a transformation of inherent porous network is dependent on optimized concentration of NPs.

Dong et al. [40] found that addition of Al₂O₃ NPs or Linda type L (LTL) zeolite NPs changed the pore size of the PSf membrane. Alpatova et al. [41] reported an insignificant change in the pore size of the PVDF membranes by incorporation of Fe₂O₃ NPs, but porosity of membrane was highly affected and linearly related to the concentration of Fe2O3 NPs. The addition of ZnO NPs also tailored the porosity and pore size of the membrane [23], but optimized concentration of NPs to be applied serves an important factor. The role of ZnO NPs for changing the porosity and pore size is shown in Figures 2a,b. Likewise, MgOH NPs also increased the porosity of the membrane that is directly correlated to the concentration of MgCl2 in casting solution (Figure 2c), which reacted with NaOH in coagulation bath and produced MgOH NPs in membrane. In another study, CuO NPs were also found responsible for increase in membrane pore size, but after certain concentration of CuO, the pore size started to decrease. Similar trend was observed with porosity change caused by the addition of CuO NPs (Figure 2d). It was described that the hydrophilicity of NPs increased the water penetration during solventnonsolvent exchange period and more water rapidly entered the membrane, which increased the pore size and porosity. Conversely, by increasing the

concentration of NPs from specific range, the dope solution became more viscous and reduced the penetration of water into membrane during phase transformation. As a result, smaller pore size and less porosity was recorded with high concentration of NPs [42].

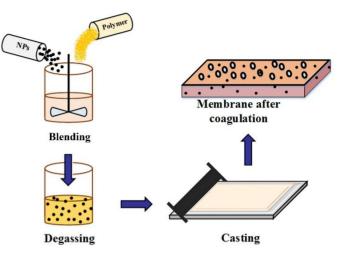


Fig. 1. Physical blending of NPs into membrane casting solution followed by PIP for membrane fabrication.

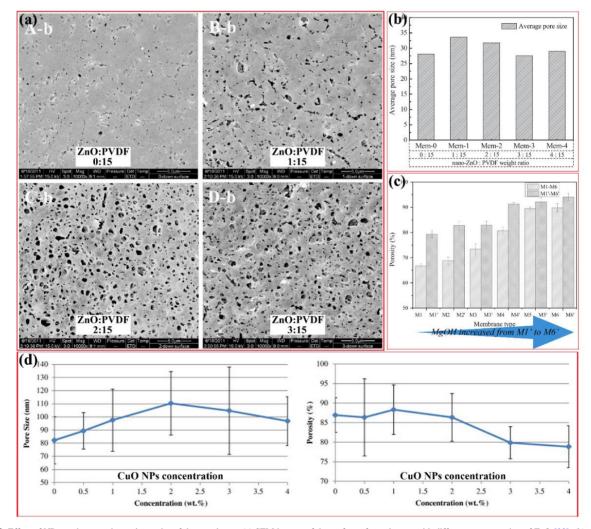


Fig. 2. Effect of NPs on the pore size and porosity of the membrane, (a) SEM images of the surface of membranes with different concentration of ZnO [23]; (b) average pore size of the membranes of ZnO containing membranes [23]; (c) effect of MgOH NPs concentration on the porosity of the membranes [43]; (d) effect of different concentrations of CuO NPs on the pore size and porosity of the membrane [42].

3.1.3. Effect on hydrophilicity

Hydrophilicity is another major attribution of membrane affected by incorporation of NPs. The membrane imbedded NPs attract more water molecules because of their high surface energy by producing hydrogen bonds with water molecules resulting in the formation of tight hydration layer on the membrane. The hydrophilicity of the membrane is assessed using the contact angel measurement of the membrane, where a smaller contact angle represents more hydrophilicity. As a water drop gets into contact with the hydrophilic surface with high energy NPs, the water drop readily dispersed by attraction of the adjacent high energy particles on the surface and produce a smaller CA. Alternatively, the hydrophobic surface does not attract the water molecule and large CA is formed on the surface of the membrane [44]. Zhang et al. [45] prepared PVDF membranes with addition of SiO₂ NPs and phosphorylated silica nanotubes (PSNTs) and found that contact angle of the membrane decreased in the following order:

PVDF > PVDF/SiO₂ NPs > PVDF/PSNTs,

which can also be observed in Figure 3a. The maximum hydrophilicity was recorded for the membranes prepared with PSNTs. Song et al. [46] found an increase in hydrophilicity of PVDF-LiCl membrane after addition of TiO₂ NPs and contact angle declined from 80° to 75°. In another study, PES based hybrid membranes were prepared by blending SiO₂-Ag NPs in casting solution and CA was found to be decreased corresponding to NPs concentration [47], i.e. CA decreased from 67.7° to 52.6° for PES membrane and 4% SiO₂-Ag PES membrane, respectively. Zhang et al. [22] studied the antifouling behavior of modified PVDF membrane with addition of different ratio of GO/oxidized multi-walled carbon nanotubes (OMWCNTs) and recorded a least CA and highest hydrophilicity by adding 1:9 proportion of GO/OMWCNTs, which can be observed in the Figure 3d. The reason of low CA was described as owing the hydration effect between carboxyl group of low dimensional carbon material and water.

A serious consideration during physical blending is the masking effect of NPs by polymer. It is largely accepted that most of the NPs remain unexposed due to masking by polymer during preparation of nanocomposite membranes.

3.1.4. Effect on surface charge

Surface charge density of the membranes could also be affected by the incorporation of NPs. Sometimes, NPs are functionalized with charged groups to induce charge on the membrane, which helps in reducing the fouling propensity of the membrane. Zhao et al. [31] prepared the PSF membranes with different concentration of isocyanate-treated GO (iGO) NPs. First, they analyzed the zeta potential of GO and iGO at different pH and found that zeta potential of both, GO and iGO, decreased continuously as pH increased from 2 to 11, but increased after pH 11. After incorporation of iGO into PSF membrane, the surface charge of the membrane was dramatically decreased and showed a linear relationship with iGO content in the membrane demonstrating more exposure of iGO to the surface by increasing the concentration of iGO in the dope solution.

3.1.5. Effect on mechanical strength

Mechanical strength influences the life-span of the membranes. A membrane with higher mechanical strength can resist the harsh conditions produced by the feed solution i.e. increase in transmembrane pressure. The mechanical strength of the membrane largely depends on the membrane morphology e.g. macroporous membrane has less mechanical strength and microporous membrane has higher mechanical strength. A good compatibility is usually found between NPs and polymer that increases the interaction (physical or chemical) among NPs and polymer molecules. As a result, membrane morphology is transformed from macroporous to microporous structure and membrane become mechanically strong [49]. Liang et al. [23] reported a linear relationship between the concentration of ZnO NPs present in membrane and mechanical strength of the membrane (Figure 4a).

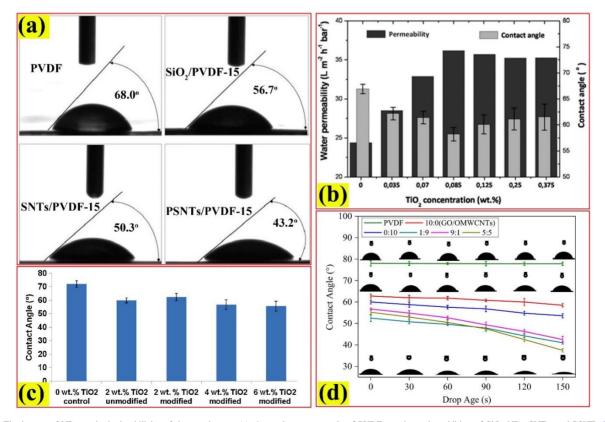


Fig. 3. The impact of NPs on the hydrophilicity of the membranes, (a) change in contact angle of PVDF membrane by addition of SiO₂ NPs, SNTs, and PSNTs [45]; (b) correlation between contact angle and water permeability by addition of TiO₂ NPs to the PES membrane [44]; (c) effect of different concentrations of TiO₂ NPs (modified and unmodified) on the contact angle of the membrane [48]; (d) a decrease in contact angle of PVDF membrane by adding GO/OMWCNTs to the membrane, and temporal behavior of contact angle by varied concentration of said modifiers [22].

The increase in mechanical strength was attributed to the shrinking of fingerlike voids beneath skin layer of the PVDF membrane by addition of ZnO NPs. Wang et al. [50] prepared nano Al₂O₃/EPDM composite and reported an increase in tensile strength and elongation at brake with increase in nano Al₂O₃ concentration in membrane matrix. In another study, PVDF-LiClO₄-TiO₂ membrane was prepared by adding TiO₂ NPs into PVDF-LiClO₄ membrane [51]. It was found that the addition of LiClO₄ decreased the membrane strength but the addition of TiO2 NPs increased the mechanical strength of the membrane, which was exclusively attributed to strongly interconnected voids as an effect of TiO₂ NPs (Figures 4c,d). The thorough study on the stress and strain of the membranes with and without NPs strongly supports that addition of NPs in membrane adds mechanical strength to the membrane system, which could enhance the membrane resistance against harsh conditions i.e. high pressure, strong flow rate, mechanical cleaning. Sometimes inclusion of NPs reduces the mechanical strength, which is associated with high concentration of NPs (Figure 4b). High concentration of NPs favors the formation of macrovoids in membrane matrix resulting in decreased mechanical strength [39]. Therefore, it can be concluded that an appropriate concentration of NPs should be used that do not produce agglomerates in dope solution and macrovoids in membrane matrix, and results in strengthening of the membrane.

3.1.6. Effect on surface roughness

The relationship of surface roughness to membrane fouling has been described earlier but the impact of NPs incorporation into polymer membrane is contradictory. Some reports found that the surface roughness of the membrane decreased by incorporation of NPs while some stated that the surface roughness increased by introducing NPs into the membrane matrix. In both cases, either surface roughness decreases or increases after incorporation of NPs, the antifouling potential of the membrane was increased. Consequently, it remains challenging to relate the surface roughness with membrane fouling and impact of NPs on surface roughness. As observed by Zhang et al. [39] that incorporation of TiO₂ NPs constantly increased surface roughness of the membrane. Irrespective of increase in surface roughness, all

the membranes showed improved fouling resistance (Figures 5a,b). On contrary, Razmjou et al. [48] found that addition of TiO₂ NPs decreased the surface roughness of the membrane, thus the membrane fouling is reduced. They recorded a minute difference between surface roughness of PES membrane and PES-TiO₂ NPs nanocomposite membrane: from 50.76 nm to 39.77 nm, (Figure 5c). Likewise, Song et al. [17] also reported the impact of TiO₂ NPs towards reduced surface roughness of PVDF membrane, but the degree of difference was so minute (4 nm) to be considered effective in mitigating membrane fouling (Figure 5d).

3.2. Thin film nanocomposite membrane

With the development of thin film composite membrane over the past decade, the integration of nanoparticles in various fields have also drawn the attention of the researchers to modify the TFC membranes into thin film nanocomposite membranes. TFC membranes are majorly RO and NF membranes with the potential to remove salts through desalination of sea water and brackish water, emerging organic pollutant including pharmaceuticals and pesticides, and heavy metals. TFC membranes for high solute separation with high fluxes that is managed by optimized support layer of the membranes.

The preparation of TFN membranes is based on the same procedures as of TFC membrane with the difference of incorporation of NPs in the surfaces and support layer. During the fabrication step of the TFN membranes, NPs of various particle sizes are introduced in surface and sublayer that make the membrane more hydrophilic and/or alter the surface charge density of the membrane without compromising the membrane selectivity. TFN membranes can also be used for RO, FO, and NF for the removal of said foulants and also including organic solvents. The most commonly used procedures for the preparation of TFN membranes include in situ interfacial polymerization of polyamide and dip coating. Table 2 summarizes various types of TFN membranes, NPs modifications, and the obtained properties after modification.

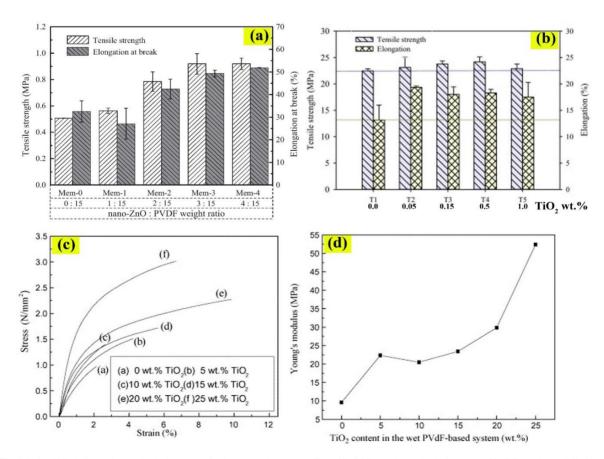


Fig. 4. Role of NPs in improving mechanical strength of polymer membranes, (a) effect of ZnO NPs on the mechanical strength of PVDF membrane [23]; (b) effect of TiO₂ NPs concentration on the mechanical strength and elongation at break of PVDF membrane [39]; (c) (d) stress vs. strain curves for the $PVdF/LiClO_4/TiO_2$ membranes, variation of Young's modulus with the TiO₂ content for $PVdF/LiClO_4/TiO_2$ membranes, respectively [51].

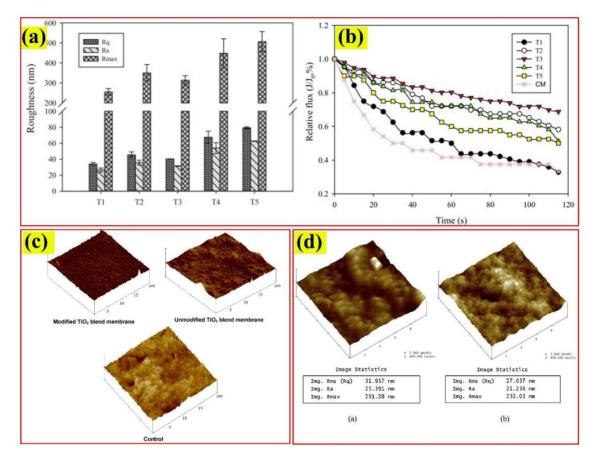


Fig. 5. Effect of NPs addition to the membrane surface roughness, and its relation to the fouling of the membrane. (a, b) surface roughness parameters of TiO₂-PVDF nanocomposite membrane, and its relationship to the fouling of the membrane, the concentration of TiO₂ NPs increased from T1 to T5 [39]; (c) surface roughness (detected using AFM) of the PES membranes by addition of TiO2 NPs and modified TiO2 NPs [48]; (d) surface roughness parameters (measured by AFM) of (a) PVDF-PEG membrane and (b) PVDF-PEG-TiO₂ NPs composite membrane [17].

Table 2

Types of nanomaterial used to fabricate TFN membrane and changes in membrane properties acquired after modification.

Membrane	Modifier	Modification Technique	Application/ foulant	Membrane properties and performance evaluation
PSf	GO	IP of PA	RO/ 2000 ppm NaCl	High flux, antibacterial activity, chlorine resistance [52]
PSf	GO nanosheets	IP of PA		Antimicrobial activity [53]
PSf	Al ₂ O ₃	IP	NF	Excellent molecular separation properties [54]
Arylene sulfide sulfone O-PASS	SiO ₂ and ZIF8	Filtration of OPASS solution	UF	Dye rejection [55]
PSf	Ag NPs	IP of PA	UF	Increased salt rejection of NaCl and MgSO ₄ , antimicrobial properties [56]
polyhedral oligomeric silsesquioxane (POSS)	TiO ₂ -SiO ₂	IP of PA	RO	Seawater desalination [57]
PES	CNT	IP of PA	UF	Improved separation efficiency [58]
	UiO-66	IP of PA	RO	boron rejection by $\sim 11\%$ [59]
PA(TFC)	ZnO	IP of PA	RO	Improved water flux and salt rejection [60]
PA-TFN	graphene quantum dots (GODs)	IP of PA	FO	Improved surface hydrophilicity, antimicrobial activity [61]
TFC	(ZIF-8)/chitosan layer	chitosan layer coated on PVDF	UF	NaCl rejection of >99.5 [62]
PSS-TFN	ZIF-8	IP of PA	FO	Better swelling resistance [63]
PES	SAPO-34	IP of PA	UF	Dye removal methyl violet 6B, reactive blue 4 and acid blue 193) from water [64]
PSf	Functionalized MWCNTs	IP of PA	FO	High water permeability and acceptable salt rejection [65]
PSf	Modified SiO ₂	Piperazine-TMC	NF	Anti-fouling ability, long-term stability [66]

3.2.1. Interfacial polymerization

The most common TFN membrane is polyamide (PA) membrane, where PA layer is formed on the surface of the porous support membrane. The process of IP initiated by depositing the reactive diamine monomer on the surface of the porous support membrane. Mostly, the membrane is dipped in the monomer solution of m-phenylenediamine (MDP), followed by immersion into organic solution of second reactive monomer, usually di/triacid chloride (trimesoyl chloride (TMC)). The highly reactive monomers start polymerization as soon as they come into contact and form a highly crosslinked thin layer of PA on the surface of the porous support membrane, which remains attached on the membrane. The polymerization process also prevents further diffusion of TMC into DMP that terminates the polymerization leaving a thin layer (up to 500 nm) of PA on the membrane. The chemical properties of the monomers play an important role in determining the thickness of the film, roughness, hydrophilicity and surface charge. Based on the chemical properties of the monomer, the membrane can be optimized for solute rejection for example zwitterion-based polymers possess strong antifouling and anti-biofouling potential for TFC membranes due to their high hydrophilicity, durability, and environmental stability [67]. The zwitterionic polymers contains both anionic and cationic groups within the same monomer unit, that strongly interact with surrounding water molecules via the electrostatic forces and form a tighten hydro-layer over the membrane [67-69]. It is also found that the zwitterionic polymer brushes extend the surface carboxylic groups that provide significant antifouling and anti-biofouling potential during water purification e.g., FO. [67, 68].

As mentioned previously that TiO₂ NPs have gained much attention in various fields including water filtration because of its numerous characteristics, TiO₂ NPs have also been applied for the preparation of TFN membranes. Lee et al. [70] introduced a new method where aqueous solution of MDP and organic solution of TMC containing substantial amount (about 5%) of TiO₂ were in situ polymerized and the resulting PA layer was enriched in TiO2 NPs. The resultant NF membrane rejected more than 95% of MgSO4 salt with stable performance due to the presence of TiO₂. Emadzadeh et al. [71-73] prepared a modified porous substrate by dispersing TiO₂ NPs in PSf and the PA thin film layer was established on the surface of PSf-TiO₂ membrane by first pouring 1,3-phenylendiamine (MDP) onto the substrate for 2 min, removed the excess MDP, and then pouring 1,3,5-benzenetricarbonyl trichloride on the MDP anchored substrate. The resultant TFN membrane showed 120% higher flux while 10 mM NaCl feed solution was used for FO process. Moreover, the internal concentration polarization (ICP) was also reduced several folds due to the modified porous substrate used to prepare TFN membrane

SiO₂ NPs also showed the improve membrane morphology and performance of TFN membranes due to their strong surface energy, small size, thermal resistant and the most important is environmentally inert behavior that makes them applicable in a wide range of industries. Niksefat et al. [74] dispersed the SiO₂ NPs in the aqueous solution of MDP. The prepared porous support of PSf was immersed in aqueous solution of SiO₂ NPs and MDP for some time and later the amine functionalized substrate membrane was soaked into organic solution of TMC for IP process. The resultant TFN membrane showed flux of 36 ± 2 LMH that was nearly twice the flux of TFC membrane. Moreover, the salt rejection was also more than 90% with 10 mM NaCl as feed solution and 2 mM NaCl as draw solution. Yin et al. [75] used porous MCM-41 (~100 nm) and non-porous spherical silica NPs (~100 nm) to fabricate the TFN membrane at concentrations ranging from 0 to 0.1 wt%, and reported that the MCM-41 NPs dispersed well in PA thin-film layer and suggested that the internal pores of MCM-41 NPs contributed significantly to the increase of water permeability. Where the permeate water flux increased from 28.5±1.0 to 46.6±1.1 L/m² h without compromising the salt rejection with the incorporation of MCM-41 NPs.

Recently, GO and carbon nanotubes (CNT) have been used for the preparation of several kinds of membranes including RO, FO, and NF membranes: GO is used due to its numerous hydrophilic functional groups [52], CNTs due to the similarity between their fluid transport properties and those of water transport channels in membranes [76-78]. The application of both GO and CNTs has been reported to improve various properties of the membrane s including modulus and tensile strength, water flux and permeability, and rejection. Chae et al. [52] reported that a TFN membrane with GO embedded in its PA layer exhibited high water permeability, antibiofouling property, and chlorine resistance without loss of salt rejection. The water permeability and anti-biofouling property of the GO-TFC membrane were enhanced by approximately 80% and 98%, respectively, as compared to TFC membrane only. Amini et al. [65] prepared TFN FO membranes by applying amine functionalized multi walled CNTs (MWCNTs) into PA thin film prepared by IP process. The performance of the prepared FO membrane was evaluated by using NaCl as feed (10 mM) and draw (2 mM) solutions.

The TFN membranes exhibited 95.7 L/m^2 h flux with 0.1 wt% functionalized MWCNTs that was nearly 160% higher than TFC membrane. The high water flux with higher MWCNTs loading was attributed to the increase in hydrophilicity of the membrane that was evaluated with decrease in the CA.

3.3. Surface located nanocomposite

It has been previously seen that incorporation of NPs into membrane matrix improve the membrane intrinsic properties e.g. membrane porosity, membrane morphology, membrane internal resistance, membrane pore size, membrane mechanical strength, and membrane charge. In both types of the membranes stated above (nanocomposite and thin-film nanocomposite), NPs remain partially covered by the polymer. It is widely reported that blending of NPs with polymer solution allows polymer to encase large amount of NPs, which prohibits the NPs to reveal their actual properties [28, 38, 79]. Therefore, huge efforts are allocated to develop membranes with maximum exposure of NPs and different procedures have been developed and adopted to attain NPs exposure and their stability on membrane surface. The major characteristics possessed by surface located NPs membranes are: decreased fouling tendency of the membranes, maximum hydrophilicity depending on the type of NPs, and reduced intrinsic resistance of membrane. Below, some of the commonly practiced techniques to incorporate NPs on the surface of the membrane are discussed.

3.3.1. Self-assembly

Self-assembly is a technique where NPs get assembled on the membrane surface without an external aid. This process is widely used to immobilize different NPs on the membrane. In self-assembly, membranes are functionalized with different groups that are capable to produce hydrogen bonding with NPs. Some of the functional groups include –COOH, -SO $_3$ H⁺, and sulfone groups. If the membranes do not have any functional group, membrane is pretreated to induce active functional group that can develop hydrogen bonding with NPs. The TiO2 NPs can be self-assembled on PSf based membrane (with PA thin-layer) by dipping the membrane in colloidal solution of TiO2, which allows self-attachment of TiO2 with -COO group of polymer [80]. The possible assembly schemes of TiO2 on membranes are given in Figure 6a, and schematic of self-assembled TiO₂ on membrane is shown in Figure 6e. Similar kind of interaction is also shown in the Figure 6b: between TiO₂ and PES film, and TiO₂ and DEA modified surface of PI [81]. Bae and Tak [82, 83] successfully immobilized TiO₂ NPs on a commercially available PES MF membrane, where the membrane was immersed into 20% H₂SO₄ for different time durations (soaking for more time generated more sulfonic acid groups at the membrane surface) followed by immersion of membranes in laboratory made transparent TiO2 colloidal suspension. It was seen that the membrane soaked for more time in H₂SO₄ contained more TiO₂ NPs on its surface (Figure 6d), which was ascribed to the formation of more sulfonic groups on the membrane as a factor of dipping time. The membranes with self-assembled NPs also exhibit self-cleaning potential and photocatalytic degradation of organics; only partial membrane surface possesses such properties that is covered by NPs, rest of the membrane surface shows fouling and inability of self-cleaning [35, 84, 85].

3.3.2. Coating/deposition

Coating/deposition is the simplest technique used to immobilize NPs on the membrane surface. Either a membrane is dipped into NPs solution and pulled back with a constant slow rate [dip coating (Figure 7a)] or NPs solution is filtered through the membrane so as to force NPs to stay on the membrane: deposition [86, 87] (Figure 7b). Fan et al. [88] prepared hydrophilic PSf membrane by filtering polyaniline nanofiber aqueous dispersion and found a sharp increase in water flux and huge decline in contact angle i.e. 64° and 27° for simple PSf membrane and PANI nanofiber deposited membrane, respectively. Gao et al. [89] deposited NPs on cellulose acetate (CA) membrane by filtering 200 mg GO-TiO₂, P25 TiO₂, and TiO₂ microsphere NPs solution through CA membrane followed by 30 sec N₂ gas treatment. A deposition procedure usually results in a sharp decline of membrane water flux due to pore blocking and pore plugging by NPs. As shown in Figure 7c, the membrane with P25 TiO₂ NPs deposition showed the least flux that was attributed to the very small size of P25 plugging the pores. Irrespective of the low flux, membranes with different kinds of NPs deposited on the surface demonstrated TOC degradation in feed solution under UV light (Figure 7d), which was maximum with GO-TiO₂ deposited membrane that was in accordance to the high photocatalytic oxidation potential of GO-TiO₂ NPs as compared to other NPs.

Although membrane performance improves initially by depositing NPs on the membrane, NPs leach as a factor of time and membrane efficiency decreases [38, 86]. This simple method seemed to be largely scalable but nonaffirmative behavior of NPs on the membrane prohibited coating/deposition of NPs to be largely practiced.

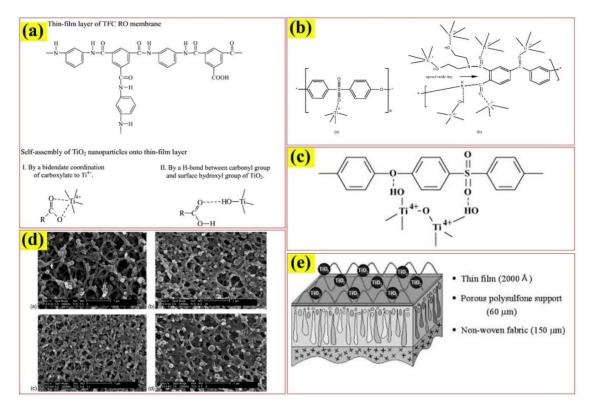


Fig. 6. Self-assembly mechanism of different NPs on different polymer based membranes: (a) mechanism of self-assembly of TiO_2 nanoparticles [35, 80]; (b) mechanism of self-assembly of TiO_2 nanoparticles: (a) on PES surface (b) on DEA-modified surface of PI [84]; (c) chemical bond structure model of the PES/TiO₂ composites: [81]; (d) SEM photographs of the surface of neat and composite membranes (×20,000). (a) Neat membrane, (b) composite-1, (c) composite-2 and (d) composite-3 (composite 1-3 refers to the time for which membrane was soaked in sulfonic acid 0, 1, 2, 4 h) [82]; (e) schematic drawing of hybrid membrane self-assembled by TiO₂ NPs [80].

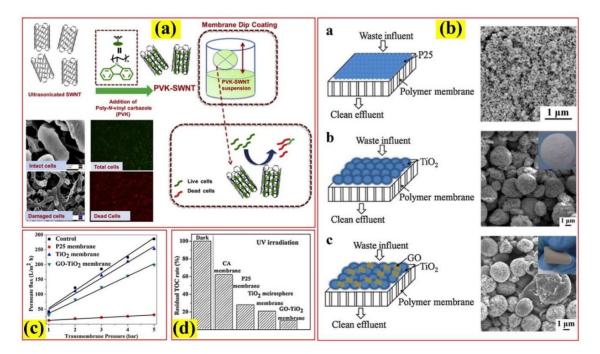


Fig. 7. (a) A schematic of dip-coating procedure and antimicrobial property of membranes [86]; (b) filtration deposition of different NPs on the membranes: [(a) schematic diagram of P25 membrane (left side) and FESEM image of P25 membrane surface (right side), (b) schematic diagram of TiO₂ microsphere membrane (left side) and FESEM image of TiO₂ microsphere membrane surface (right side (inset: digital photo of TiO₂ microsphere membrane)], (c) schematic diagram of GO–TiO₂ membrane surface (right side (inset: digital photo of GO–TiO₂ membrane)], (c) schematic diagram of GO–TiO₂ membrane surface (right side (inset: digital photo of GO–TiO₂ membrane)], (c) schematic diagram of GO–TiO₂ membrane surface (right side (inset: digital photo of GO–TiO₂ membrane)], (c) schematic diagram of GO–TiO₂ membrane surface (right side (inset: digital photo of GO–TiO₂ membrane)], (c) schematic diagram of GO–TiO₂ membrane surface (right side (inset: digital photo of GO–TiO₂ membrane)], (c) schematic diagram of GO–TiO₂ membrane surface (right side (inset: digital photo of GO–TiO₂ membrane)], (c) schematic diagram of GO–TiO₂ membrane surface (right side (inset: digital photo of GO–TiO₂ membrane)], (c) schematic diagram of GO–TiO₂ membrane surface (right side (inset: digital photo of GO–TiO₂ membrane)], (c) schematic diagram of GO–TiO₂ membrane surface (right side (inset: digital photo of GO–TiO₂ membrane)], (c) schematic diagram of GO–TiO₂ membrane surface (right side (inset: digital photo of GO–TiO₂ membrane)], (c) schematic diagram of GO–TiO₂ membrane surface (right side (inset: digital photo of GO–TiO₂ membrane)], (c) schematic diagram of GO–TiO₂ membrane surface (right side (inset: digital photo of GO–TiO₂ membrane)], (c) schematic diagram of GO–TiO₂ membrane surface (right side (inset: digital photo of GO–TiO₂ membrane)], (c) schematic diagram surface (right side (inset: digital photo of GO–TiO₂ membrane)], (c) schematic diagram surface (right side (inset: digital photo

3.3.3. Electrostatic attraction

Electrostatic attraction is the process in which two differently charged molecules are bounded through physical attraction: electrostatic bonding. To attain electrostatic bonding, molecules must possess opposite charges. Usually, it is seen that most of the polymers are negatively charged. Therefore, NPs are tailored with a positively charged group that can interact with the polymer to successfully bound to the membrane through electrostatic attraction. Ben-Sasoon et al. [90] used PEI to charge Cu NPs (amine groups of PEI attracted with cupric ion to bind strongly with Cu NPs), as a result amine group of PEI produced electrostatic attraction with COO group of membrane. The membranes prepared with electrostatic interactions performed well as antibacterial membranes (due to presence of antibacterial Cu NPs) but leaching of active antibacterial species (Cu2+ or Cu NPs) suggested insignificant use of such membranes for long time and wide range applications. A high amount (30%) of Cu⁺² and Cu NPs were detached from the membrane in first two days. Therefore, to sustain antibacterial activity of such membranes, Cu NPs or Ag NPs are required to be continuously recharged on the membrane surface [90].

3.3.4. Layer-by-layer assembly

In layer-by-layer assembly, several layers of materials are coated on the

membrane by any or multiple procedures described earlier. During this procedure, several layers of NPs are deposited on the membrane. Park et al. [91] prepared the membrane with LBL deposition of MWCNTs. Initially, a PSf membrane was negatively charged under treatment of 0.5M H₂SO₄, the negatively charged PSf membrane was alternatively dipped into cationic poly(allylamine hydrochloride) and anionic MWCNTs/poly(acrylic acid) solutions. Finally, a thermal annealing was done at 180 °C to induce crosslinking of MWCNTs and PE (Figure 8a). The resultant membranes exhibited high flux and high ion rejection. Wang et al. [92] prepared a PAN UF membrane with LBL deposition of modified GO NPs. At first, they hydrolyzed the PAN UF membrane by immersing in 2M NaOH solution at 65 °C for 30 min. Meanwhile, 0.25 wt.% PEI and 0.05 wt.% PAA solutions were prepared. In PEI solution, required amount of GO was dispersed to prepare modified GO i.e. PEI/GO. The hydrolyzed membrane was rinsed with pure water. The PEI-GO solution was filtered through hydrolyzed membrane followed by PAA solution filtration, and the filtration process with both solutions was repeated according to required deposition layer thickness. The membrane was rinsed gently, and dried at 50 °C for 2 h. Then the membrane was immersed in PVA solution at 75 °C for 30 min. Finally, the membrane was cross-linked with 3% glutaraldehyde solution (Figure 8b). The resultant membrane showed high level of selectivity for dye and monovalent ions and produced very high flux.

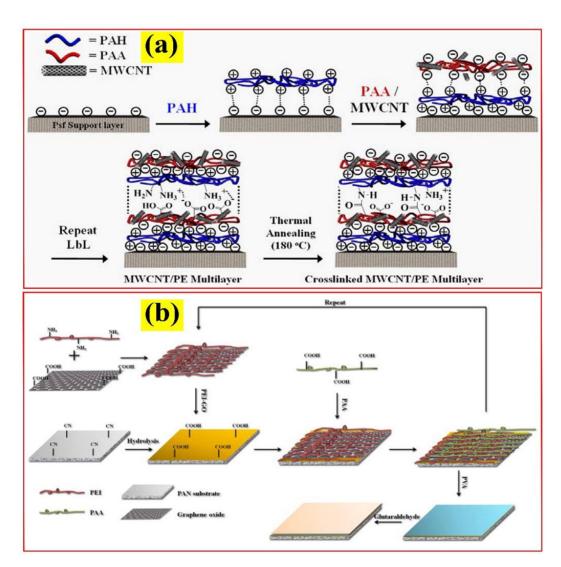


Fig. 8. Layer-by-layer assembly of NPs on the membrane surface: (a) schematic illustration of the fabrication of nanocomposite (MWCNT-PAA/PAH)n multilayers via layer-by-layer assembly on PSf substrate [91]; (b) schematic illustration of the preparation of GO and polyelectrolyte complex nanohybrid membranes [92].

3.3.5. Chemical grafting

The main challenge with the surface immobilized NPs is the leaching of NPs over a long duration of use. The leaching of the NPs could cause potential threat to the biological system of the water that should be avoided. Suitably, chemical grafting produces strong association of NPs with the membrane surface and resolves the leaching issue of NPs to a greater extent. However, the leaching of ionic species from NPs remains inevitable: leaching of usually Ag and Cu ions. The chemical grafting method is partly related to the self-assembly or electrostatic attraction method. But in chemical grafting, both membrane and NPs are chemically modified with strongly opposite charged groups, which produces a strong chemical bond at contact. Ling et al. [21] recently introduced a series of steps to immobilize SiO₂ NPs on PVDF membrane. First, a PVDF membrane was plasma treated to obtain -OOH groups on the membrane surface. Then, methacrylic acid (MAA) was chemically associated with -OOH group, and finally, amine group modified SiO₂ NPs solution was prepared. The MAA modified membrane was dip coated into NH₃-SiO₂ NPs solution (Figure 9a). The final membrane was antifouling with high flux recovery by hydraulic flushing, and had a low attraction between organic foulant and membrane surface. Likewise, PEI modified Ag NPs were coated on the surface of PSf UF membrane that improved membrane selectivity and membrane flux with antibacterial properties [93]. In detail, oxygen plasma activates the PSf membrane skin layer with the addition of active and/or charged functional groups. The activated membrane is subsequently incubated with charged or functionalized NPs that generates electrostatic and covalent bonds to form a persistent coating of reactive NPs on the membrane (Figure 9b).

4. Challenges and future perspectives

An overall comparison among different membrane modification methods is presented in Table 3, which is our interpretation of the reported studies in the above-mentioned literature. Please note that it is not always straightforward to interpret and compare results, because many parameters may be influenced simultaneously by one modification method; here we only attempt to give a general impression. All the modification techniques improve the membrane performance; sometimes more fouling is reported but the absolute flux value increase by modification and occasionally less fouling is reported without any significant effect on the water permeation level. Mostly, nanocomposite membranes show completely different behavior than membranes with surface located NPs. At times, surface located membranes show more advantages than nanocomposite membranes and sometimes it shows more disadvantages. It is important to note that the advantages and limitations mentioned in Table 3 regarding surface located NPs are described based on the limited number of techniques which are widely practiced out of many different reported techniques. Overall, two most important factors considered for modification include stability of NPs in membrane system and exposure of NPs to the feed/foulant solution. In a larger picture, nanocomposite membranes provide excellent stability of NPs in the

membrane system because NPs are completely embedded in the polymer but less exposure of the NPs is experienced, and surface located NPs membranes express complete exposure of the NPs but less stability of NPs in the membrane system. It is expected that membrane properties can be tuned for specific applications through the discussed methods, although they still need to be developed further in such a way that they allow even better and more environmentally friendly control over modification.

The nanocomposite membranes have been targeted as a dominant future technology for the purification of water using filtration techniques. However, to meet the future demands of safe potable water and to meet the stringent potential regulations, the fabrication of robust, durable and economically viable nanocomposite membranes with high water permeability and high selectivity deemed necessary for various kinds of water treatment. The permeability and selectivity of the membrane is highly dependent on membrane structure that is controlled by the polymer and NPs to be used along with the fabrication process. Thus, optimized polymer concentration and NPs loading plays a vital role in improving the membrane performance, which can be attained by understanding the deep phenomenon and to optimize the fabrication methods.

It is also important to assess the leaching of nanomaterials from the nanocomposite membranes and their toxicity to the environment during water purification. At first, health issues regarding the production of nanomaterials should be considered with great concerns that include from the exposure of labor in the industry at large scale nanomaterials production and the fate and impact of leached nanomaterials from the nanocomposite membrane. Moreover, nanomaterials itself are very expensive that possess major contribution in the cost of nanocomposite membrane. Thus, the leaching of the nanomaterials from the nanocomposite membranes would directly increase the cost of nanocomposite membrane and the potentially attained benefits from the nanomaterials would be outweighed due to the high cost of the nanocomposite membrane [94]. Also, the cost of environment by the leaching of the nanomaterials should be completely determined by keeping in view several previous cases such as Dichlorodiphenyltrichloroethane (DDT), that showed promising results against the insects and largely used in the agriculture but later it became the Achille's heel. It has been reported about several kinds of NPs that they were leached out of the nanocomposite membrane during different steps of the filtration and lack the durability inside membrane matrix. Under normal conditions, the NPs show stability but under high pressure, high temperature, and chemical cleaning process the NPs are washed out of the membranes. Therefore, there is an urgent need for in-depth studies and advancement in the fabrication methods for the durable nanocomposite membranes that allow the long-term operational cycles of the membrane including filtration and cleaning without leaching of NPs. For durability of nanomaterials in nanocomposite membranes, the compatibility of polymer and nanocomposite could play an important role. The tightly bound nanomaterials with polymer could prevent the leaching of nanomaterials from the nanocomposite membrane and reduces the environmental foot-prints.

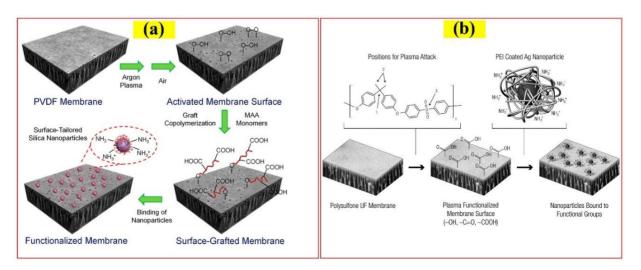


Fig. 9. Chemical grafting of NPs to the polymeric membrane surface: (a) schematic protocal of PVDF membrane functionalization, illustrating Argon plasma treatment, graft copolymerization, and NPs binding [21]; (b) post-synthesis grafting process for the fabrication of reactive membranes [93].

Table 3

Comparison of different modification techniques after application of NPs.

Modification method	Advantages	Limitations
Nanocomposite/mixed matrix	 A simple technique Large amount of NPs can be loaded in the membrane. Different kind of polymers can be used for membrane preparation. Different kind of NPs can be applied to the membrane. NPs remain highly stable in the membrane. Environmentally safe technique because NPs do not leach out of the membrane. Cost-effective. 	 Agglomeration of NPs is largely experienced. Huge number of NPs is masked by the polymer. Alteration in pore size, porosity, and void structure is inevitable and uncontrollable. Uneven distribution of NPs in the membrane matrix. Instability in reproducibility because the level of agglomeration of NPs remains largely uncontrollable. Active sites of NPs may interact with polymer and not exposed.
Thin film nanocomposite	 The voids structure of the membranes is not affected. Agglomeration of nanomaterials could be reduced by well dispersion in aqueous MDP. The resultant membrane exhibits increased tensile strength. 	 Nanomaterials are masked by the IP of PA. Loading of nanomaterials is limited due to interruption in IP process.
Surface located NPs	 NPs remain unmasked by any of the membrane material. The loading of NPs is controllable. Pore size and porosity can be altered based on the treatment adopted (plasma treatment, radiation treatment). Some techniques are environmentally secure as NPs are not leached easily (chemical grafting). Active sites of NPs are completely exposed. Highly reproducible (e.g. chemical grafting, LBL assembly, deposition). 	 The stability of NPs on the membrane is weak. In some techniques (coating/deposition) pores are plugged and blocked by NPs (coating/deposition, LBL assembly). Most of the techniques possess potential hazards for environment (coating/deposition) because of NPs leaching. Most of the techniques are economically ineffective because of number of chemicals used and the requirement of special equipment.

The energy consumption is an important factor for nanocomposite membranes during separation process especially with high pressure filtration processes. For example, RO and NF both require large amount of energy that increase the operational cost for the application of the membranes. Therefore, developing new methods for fabrication of high permeability nanocomposite membranes in addition to energy harvesting devices and low-carbon foot prints processes is also the need of the time. With high permeability, less pressure is required to exert on the membrane for water to pass through across the membrane that consumes less energy. Moreover, under low pressure less foulants accumulate on the membrane and fouling is reduced that enhances the life time of the membrane and reduces the usage of chemicals for the cleaning of the membrane. Thus, by deep consideration of only one factor, permeability, overall energy consumption and running cost of the system decrease, which could help in the widespread application of the RO and NF membranes. Therefore, the optimal design of the installation system and selection of polymer materials and nano-materials for nanocomposite membrane by consideration the specific properties that influence the permeability and strength (pore size and porosity, thickness, tensile strength etc.) could help to achieve the low energy consuming membranes.

The influential factors in the fabrication of nanocomposite membrane includes type of nanomaterials used with specific physicochemical properties namely surface charge, surface area, size, compatibility with polymer and type of polymer itself. The nanocomposite membranes have proven to be promising membranes with showing significant performances regarding high water permeation and high solute rejections in various water treatments such as desalination, removal of organic pollutants, and removal of bacteria with high flux recovery potential. Nevertheless, still there is a need to conduct deep research and to develop high throughput nanocomposite membranes in wide range of applications including heavy metal removal, dye removal, and persistent and emerging organic contaminants removal from water and wastewater.

Acknowledgements

The authors would like to express their appreciation for the financial support of the National Key R&D Program of China (2017YFC0403702), the National Natural Science Foundation of China (Grant No. 21606125), and the Priority Academic Program Development of Jiangsu Higher Education Institution (PAPD).

References

- M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Mariñas, A.M. Mayes, Science and technology for water purification in the coming decades, Nature 452 (2008) 301-310.10.1038/nature06599
- [2] H. Bouwer, Integrated water management: emerging issues and challenges, Agri. Water Manage. 45 (2000) 217-228

- [3] F.R. Rijsberman, Water scarcity: Fact or fiction?, Agri. Water Manage. 80 (2006) 5-22.10.1016/j.agwat.2005.07.001
- [4] M. Qadir, B.R. Sharma, A. Bruggeman, R. Choukr-Allah, F. Karajeh, Nonconventional water resources and opportunities for water augmentation to achieve food security in water scarce countries, Agri. Water Manage. 87 (2007) 2-22.10.1016/j.agwat.2006.03.018
- [5] L.S. Pereira, T. Oweis, A. Zairi, Irrigation management under water scarcity, Agri. Water Manage. 57 (2002) 175-206
- [6] J. Eliasson, The rising pressure of global water shortages, Nature 517 (2015) 6-6.10.1038/517006a
- [7] R. Zhang, Y. Liu, M. He, Y. Su, X. Zhao, M. Elimelech, Z. Jiang, Antifouling membranes for sustainable water purification: strategies and mechanisms, Chem. Soc. Rev. 45 (2016) 5888-5924.10.1039/C5CS00579E
- [8] L.V. Dijk, G.C.G. Roncken, Membrane bioreactors for wastewater treatment: the state of the art and new development, Water Sci. Technol. 35 (1997) 35-41
- [9] J.H. Jhaveri, Z.V.P. Murthy, A comprehensive review on anti-fouling nanocomposite membranes for pressure driven membrane separation processes, Desalination 379 (2016) 137-154.https://doi.org/10.1016/j.desal.2015.11.009
- [10] M. Cheryan, N. Rajagopalan, Membrane processing of oily streams. Wastewater treatment and waste reduction, J. Membr. Sci. 151 (1998) 13-28
- [11] G. Zeng, Y. He, Z. Yu, Y. Zhan, L. Ma, L. Zhang, Preparation and characterization of a novel PVDF ultrafiltration membrane by blending with TiO₂-HNTs nanocomposites, Appl. Surf. Sci. 371 (2016) 624-632.10.1016/j.apsusc.2016.02.211
- [12] B.P. Tripathi, N.C. Dubey, R. Subair, S. Choudhury, M. Stamm, Enhanced hydrophilic and antifouling polyacrylonitrile membrane with polydopamine modified silica nanoparticles, RSC Adv. 6 (2016) 4448-4457.10.1039/c5ra22160a
- [13] S.-D. Jiang, A.Y.K. Koh, K.H. Chong, S. Zhang, Opening organic solvent pathways by molybdenum disulfide in mixed matrix membranes for molecular separation, J. Membr. Sci. 585 (2019) 60-66.https://doi.org/10.1016/j.memsci.2019.05.021
- [14] Y. Jiang, Q. Zeng, P. Biswas, J.D. Fortner, Graphene oxides as nanofillers in polysulfone ultrafiltration membranes: Shape matters, J. Membr. Sci. 581 (2019) 453-461.https://doi.org/10.1016/j.memsci.2019.03.056
- [15] H. Younas, J. Shao, Y. He, G. Fatima, S.T.A. Jaffar, Z.U.R. Afridi, Fouling-free ultrafiltration for humic acid removal, RSC Adv. 8 (2018) 24961-24969.10.1039/c8ra03810d
- [16] H. Younas, H. Bai, J. Shao, Q. Han, Y. Ling, Y. He, Super-hydrophilic and fouling resistant PVDF ultrafiltration membranes based on a facile prefabricated surface, J. Membr. Sci. 541 (2017) 529-540.10.1016/j.memsci.2017.07.035
- [17] H. Song, J. Shao, Y. He, B. Liu, X. Zhong, Natural organic matter removal and flux decline with PEG-TiO₂-doped PVDF membranes by integration of ultrafiltration with photocatalysis, J. Membr. Sci. 405-406 (2012) 48-56.10.1016/j.memsci.2012.02.063
- [18] S. Kasemset, A. Lee, D.J. Miller, B.D. Freeman, M.M. Sharma, Effect of polydopamine deposition conditions on fouling resistance, physical properties, and permeation properties of reverse osmosis membranes in oil/water separation, J. Membr. Sci. 425-426 (2013) 208-216.10.1016/j.memsci.2012.08.049
- [19] X.-S. Shao, J.-H. Li, Q. Zhou, J. Miao, Q.-Q. Zhang, Amphiphilic poly(vinyl chloride)-g-poly[poly(ethylene glycol) methylether methacrylate] copolymer for the surface hydrophilicity modification of poly(vinylidene fluoride) membrane, J. Appl. Polym. Sci. 129 (2013) 2472-2478.10.1002/app.3889110.1002/APP.38891

- [20] X. Shen, Y. Zhao, L. Chen, The construction of a zwitterionic PVDF membrane surface to improve biofouling resistance, Biofouling 29 (2013) 991-1003.10.1080/08927014.2013.823484
- [21] S. Liang, Y. Kang, A. Tiraferri, E.P. Giannelis, X. Huang, M. Elimelech, Highly Hydrophilic Polyvinylidene Fluoride (PVDF) Ultrafiltration Membranes via Postfabrication Grafting of Surface-Tailored Silica Nanoparticles, ACS Appl. Mater. Interfaces 5 (2013) 6694-6703.10.1021/am401462e
- [22] J. Zhang, Z. Xu, M. Shan, B. Zhou, Y. Li, B. Li, J. Niu, X. Qian, Synergetic effects of oxidized carbon nanotubes and graphene oxide on fouling control and antifouling mechanism of polyvinylidene fluoride ultrafiltration membranes, J. Membr. Sci. 448 (2013) 81-92.10.1016/j.memsci.2013.07.064
- [23] S. Liang, K. Xiao, Y. Mo, X. Huang, A novel ZnO nanoparticle blended polyvinylidene fluoride membrane for anti-irreversible fouling, J. Membr. Sci. 394-395 (2012) 184-192.10.1016/j.memsci.2011.12.040
- [24] S.J. Oh, N. Kim, Y.T. Lee, Preparation and characterization of PVDF/TiO₂ organic– inorganic composite membranes for fouling resistance improvement, J. Membr. Sci. 345 (2009) 13-20.10.1016/j.memsci.2009.08.003
- [25] L. Yan, S. Hong, M.L. Li, Y.S. Li, Application of the Al2O3–PVDF nanocomposite tubular ultrafiltration (UF) membrane for oily wastewater treatment and its antifouling research, Sep. Purif. Technol. 66 (2009) 347-352.10.1016/j.seppur.2008.12.015
- [26] A. Cui, Z. Liu, C. Xiao, Y. Zhang, Effect of micro-sized SiO₂-particle on the performance of PVDF blend membranes via TIPS, J. Membr. Sci. 360 (2010) 259-264.10.1016/j.memsci.2010.05.023
- [27] H.P. Ngang, B.S. Ooi, A.L. Ahmad, S.O. Lai, Preparation of PVDF–TiO₂ mixedmatrix membrane and its evaluation on dye adsorption and UV-cleaning properties, Chem. Eng. J. 197 (2012) 359-367.10.1016/j.cej.2012.05.050
- [28] H. Younas, J. Shao, H. Bai, L. Liu, Y. He, Inherent porous structure modified by titanium dioxide nanoparticle incorporation and effect on the fouling behavior of hybrid poly(vinylidene fluoride) membranes, J. Appl. Polym. Sci. 133 (2016) 43265-432616.10.1002/app.43265
- [29] M. Kumar, Z. Gholamvand, A. Morrissey, K. Nolan, M. Ulbricht, J. Lawler, Preparation and characterization of low fouling novel hybrid ultrafiltration membranes based on the blends of GO–TiO₂ nanocomposite and polysulfone for humic acid removal, J. Membr. Sci. 506 (2016) 38-49.10.1016/j.memsci.2016.02.005
- [30] M. Hossein Razzaghi, A. Safekordi, M. Tavakolmoghadam, F. Rekabdar, M. Hemmati, Morphological and separation performance study of PVDF/CA blend membranes, J. Membr. Sci. 470 (2014) 547-557.10.1016/j.memsci.2014.07.026
- [31] 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) 9084-9092.10.1039/c3cp50955a
- [32] B. Rajaeian, A. Heitz, M.O. Tade, S. Liu, Improved separation and antifouling performance of PVA thin film nanocomposite membranes incorporated with carboxylated TiO₂ nanoparticles, J. Membr. Sci. 485 (2015) 48-59.10.1016/j.memsci.2015.03.009
- [33] N. Li, J. Zhang, Y. Tian, J. Zhao, J. Zhang, W. Zuo, Anti-fouling potential evaluation of PVDF membranes modified with ZnO against polysaccharide, Chem. Eng. J. 304 (2016) 165-174.10.1016/j.cej.2016.06.088
- [34] A. Rahimpour, S.S. Madaeni, S. Zereshki, Y. Mansourpanah, Preparation and characterization of modified nano-porous PVDF membrane with high antifouling property using UV photo-grafting, Appl. Surf. Sci. 255 (2009) 7455-7461.10.1016/j.apsusc.2009.04.021
- [35] J.-H. Li, Y.-Y. Xu, L.-P. Zhu, J.-H. Wang, C.-H. Du, Fabrication and characterization of a novel TiO₂ nanoparticle self-assembly membrane with improved fouling resistance, J. Membr. Sci. 326 (2009) 659-666.10.1016/j.memsci.2008.10.049
- [36] F. Li, L. Li, X. Liao, Y. Wang, Precise pore size tuning and surface modifications of polymeric membranes using the atomic layer deposition technique, J. Membr. Sci. 385-386 (2011) 1-9.10.1016/j.memsci.2011.06.042
- [37] F. Liu, N.A. Hashim, Y. Liu, M.R.M. Abed, K. Li, Progress in the production and modification of PVDF membranes, J. Membr. Sci. 375 (2011) 1-27.10.1016/j.memsci.2011.03.014
- [38] S. Leong, A. Razmjou, K. Wang, K. Hapgood, X. Zhang, H. Wang, TiO₂ based photocatalytic membranes: A review, J. Membr. Sci. 472 (2014) 167-184.10.1016/j.memsci.2014.08.016
- [39] J. Zhang, Z. Wang, X. Zhang, X. Zheng, Z. Wu, Enhanced antifouling behaviours of polyvinylidene fluoride membrane modified through blending with nano-TiO₂/polyethylene glycol mixture, Appl. Surf. Sci. 345 (2015) 418-427.10.1016/j.apsusc.2015.03.193
- [40] L.-x. Dong, H.-w. Yang, S.-t. Liu, X.-m. Wang, Y.F. Xie, Fabrication and antibiofouling properties of alumina and zeolite nanoparticle embedded ultrafiltration membranes, Desalination 365 (2015) 70-78.10.1016/j.desal.2015.02.023
- [41] A. Alpatova, M. Meshref, K.N. McPhedran, M. Gamal El-Din, Composite polyvinylidene fluoride (PVDF) membrane impregnated with Fe₂O₃ nanoparticles and multiwalled carbon nanotubes for catalytic degradation of organic contaminants, J. Membr. Sci. 490 (2015) 227-235.10.1016/j.memsci.2015.05.001
- [42] M. Baghbanzadeh, D. Rana, T. Matsuura, C.Q. Lan, Effects of hydrophilic CuO nanoparticles on properties and performance of PVDF VMD membranes, Desalination 369 (2015) 75-84.10.1016/j.desal.2015.04.032

- [43] S. Han, L. Mao, T. Wu, H. Wang, Homogeneous polyethersulfone hybrid membranes prepared with in-suit synthesized magnesium hydroxide nanoparticles by phase inversion method, J. Membr. Sci. 516 (2016) 47-55.10.1016/j.memsci.2016.05.040
- [44] A. Sotto, A. Boromand, S. Balta, J. Kim, B. Van der Bruggen, Doping of polyethersulfone nanofiltration membranes: antifouling effect observed at ultralow concentrations of TiO2 nanoparticles, J. Mater. Chem. 21 (2011) 10311.10.1039/c1jm11040c
- [45] S. Zhang, R. Wang, S. Zhang, G. Li, Y. Zhang, Treatment of wastewater containing oil using phosphorylated silica nanotubes (PSNTs)/polyvinylidene fluoride (PVDF) composite membrane, Desalination 332 (2014) 109-116.10.1016/j.desal.2013.11.008
- [46] H. Song, J. Shao, J. Wang, X. Zhong, The removal of natural organic matter with LiCl-TiO₂-doped PVDF membranes by integration of ultrafiltration with photocatalysis, Desalination 344 (2014) 412-421.10.1016/j.desal.2014.04.012
- [47] J. Huang, H. Wang, K. Zhang, Modification of PES membrane with Ag–SiO₂: Reduction of biofouling and improvement of filtration performance, Desalination 336 (2014) 8-17.10.1016/j.desal.2013.12.032
- [48] A. Razmjou, J. Mansouri, V. Chen, The effects of mechanical and chemical modification of TiO₂ nanoparticles on the surface chemistry, structure and fouling performance of PES ultrafiltration membranes, J. Membr. Sci. 378 (2011) 73-84.10.1016/j.memsci.2010.10.019
- [49] Y. Yang, H. Zhang, P. Wang, Q. Zheng, J. Li, The influence of nano-sized TiO₂ fillers on the morphologies and properties of PSF UF membrane, J. Membr. Sci. 288 (2007) 231-238.10.1016/j.memsci.2006.11.019
- [50] Z.-H. Wang, Y.-L. Lu, J. Liu, Z.-M. Dang, L.-Q. Zhang, W. Wang, Preparation of nanoalumina/EPDM composites with good performance in thermal conductivity and mechanical properties, Polym. Advan. Technol. 22 (2011) 2302-2310.10.1002/pat.1761
- [51] Y.-J. Wang, D. Kim, Crystallinity, morphology, mechanical properties and conductivity study of in situ formed PVdF/LiClO₄/TiO₂ nanocomposite polymer electrolytes, Electrochim. Acta 52 (2007) 3181-3189.10.1016/j.electacta.2006.09.070
- [52] H.-R. Chae, J. Lee, C.-H. Lee, I.-C. Kim, P.-K. Park, Graphene oxide-embedded thin-film composite reverse osmosis membrane with high flux, anti-biofouling, and chlorine resistance, J. Membr. Sci. 483 (2015) 128-135.https://doi.org/10.1016/j.memsci.2015.02.045
- [53] F. Perreault, M.E. Tousley, M. Elimelech, Thin-Film Composite Polyamide Membranes Functionalized with Biocidal Graphene Oxide Nanosheets, Environ. Sci. Technol. Let. 1 (2014) 71-76.10.1021/ez4001356
- [54] W. Ogieglo, T. Puspasari, M.K. Hota, N. Wehbe, H.N. Alshareef, I. Pinnau, Nanohybrid thin-film composite carbon molecular sieve membranes, Mater. Today Nano 9 (2020) 100065.https://doi.org/10.1016/j.mtnano.2019.100065
- [55] S. Yuan, J. Zhu, J. Li, A. Volodine, J. Yang, P. Van Puyvelde, B. Van der Bruggen, Nano/microstructure decorated thin film composite poly (arylene sulfide sulfone) membrane constructed by induced fouling in organic solvent ultrafiltration, Chem. Eng. J. 348 (2018) 180-190.https://doi.org/10.1016/j.cej.2018.04.183
- [56] Z. Yang, Y. Wu, H. Guo, X.-H. Ma, C.-E. Lin, Y. Zhou, B. Cao, B.-K. Zhu, K. Shih, C.Y. Tang, A novel thin-film nano-templated composite membrane with in situ silver nanoparticles loading: Separation performance enhancement and implications, J. Membr. Sci. 544 (2017) 351-358.https://doi.org/10.1016/j.memsci.2017.09.046
- [57] V. Dalvi, Y.P. Tang, C. Staudt, T.S. Chung, Influential effects of nanoparticles, solvent and surfactant treatments on thin film nanocomposite (TFN) membranes for seawater desalination, Desalination 420 (2017) 216-225.https://doi.org/10.1016/j.desal.2017.07.016
- [58] X. Zhao, J. Li, C. Liu, A novel TFC-type FO membrane with inserted sublayer of carbon nanotube networks exhibiting the improved separation performance, Desalination 413 (2017) 176-183.https://doi.org/10.1016/j.desal.2017.03.021
- [59] L. Liu, X. Xie, S. Qi, R. Li, X. Zhang, X. Song, C. Gao, Thin film nanocomposite reverse osmosis membrane incorporated with UiO-66 nanoparticles for enhanced boron removal, J. Membr. Sci. 580 (2019) 101-109.https://doi.org/10.1016/j.memsci.2019.02.072
- [60] M.B. El-Arnaouty, A.M. Abdel Ghaffar, M. Eid, M.E. Aboulfotouh, N.H. Taher, E.-S. Soliman, Nano-modification of polyamide thin film composite reverse osmosis membranes by radiation grafting, J. Radiat. Res. Appl. Sci. 11 (2018) 204-216.https://doi.org/10.1016/j.jrras.2018.01.005
- [61] S.F. Seyedpour, A. Rahimpour, A.A. Shamsabadi, M. Soroush, Improved performance and antifouling properties of thin-film composite polyamide membranes modified with nano-sized bactericidal graphene quantum dots for forward osmosis, Chem. Eng. Res. Des. 139 (2018) 321-334.https://doi.org/10.1016/j.cherd.2018.09.041
- [62] M.R.S. Kebria, A. Rahimpour, G. Bakeri, R. Abedini, Experimental and theoretical investigation of thin ZIF-8/chitosan coated layer on air gap membrane distillation performance of PVDF membrane, Desalination 450 (2019) 21-32.https://doi.org/10.1016/j.desal.2018.10.023
- [63] J.J. Beh, B.S. Ooi, J.K. Lim, E.P. Ng, H. Mustapa, Development of high water permeability and chemically stable thin film nanocomposite (TFN) forward osmosis (FO) membrane with poly(sodium 4-styrenesulfonate) (PSS)-coated zeolitic imidazolate framework-8 (ZIF-8) for produced water treatment, J. Water Process Eng. 33 (2020) 101031.https://doi.org/10.1016/j.jwpe.2019.101031
- [64] N. Ghaemi, P. Safari, Nano-porous SAPO-34 enhanced thin-film nanocomposite polymeric membrane: Simultaneously high water permeation and complete removal

of cationic/anionic dyes from water, J. Hazard. Mater. 358 (2018) 376-388.https://doi.org/10.1016/j.jhazmat.2018.07.017

- [65] M. Amini, M. Jahanshahi, A. Rahimpour, Synthesis of novel thin film nanocomposite (TFN) forward osmosis membranes using functionalized multiwalled carbon nanotubes, J. Membr. Sci. 435 (2013) 233-241.https://doi.org/10.1016/j.memsci.2013.01.041
- [66] H. Wu, B. Tang, P. Wu, Optimizing polyamide thin film composite membrane covalently bonded with modified mesoporous silica nanoparticles, J. Membr. Sci. 428 (2013) 341-348.https://doi.org/10.1016/j.memsci.2012.10.053
- [67] C. Liu, J. Lee, J. Ma, M. Elimelech, Antifouling Thin-Film Composite Membranes by Controlled Architecture of Zwitterionic Polymer Brush Layer, Environ. Sci. Technol. 51 (2017) 2161-2169.10.1021/acs.est.6b05992
- [68] C. Liu, J. Lee, C. Small, J. Ma, M. Elimelech, Comparison of organic fouling resistance of thin-film composite membranes modified by hydrophilic silica nanoparticles and zwitterionic polymer brushes, J. Membr. Sci. 544 (2017) 135-142.https://doi.org/10.1016/j.memsci.2017.09.017
- [69] Y.-L. Ji, Q.-F. An, X.-D. Weng, W.-S. Hung, K.-R. Lee, C.-J. Gao, Microstructure and performance of zwitterionic polymeric nanoparticle/polyamide thin-film nanocomposite membranes for salts/organics separation, J. Membr. Sci. 548 (2018) 559-571.https://doi.org/10.1016/j.memsci.2017.11.057
- [70] 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.https://doi.org/10.1016/j.desal.2007.06.003
- [71] D. Emadzadeh, W.J. Lau, A.F. Ismail, Synthesis of thin film nanocomposite forward osmosis membrane with enhancement in water flux without sacrificing salt rejection, Desalination 330 (2013) 90-99.https://doi.org/10.1016/j.desal.2013.10.003
- [72] D. Emadzadeh, W.J. Lau, T. Matsuura, A.F. Ismail, M. Rahbari-Sisakht, Synthesis and characterization of thin film nanocomposite forward osmosis membrane with hydrophilic nanocomposite support to reduce internal concentration polarization, J. Membr. Sci. 449 (2014) 74-85.10.1016/j.memsci.2013.08.014
- [73] D. Emadzadeh, W.J. Lau, T. Matsuura, M. Rahbari-Sisakht, A.F. Ismail, A novel thin film composite forward osmosis membrane prepared from PSf–TiO₂ nanocomposite substrate for water desalination, Chem. Eng. J. 237 (2014) 70-80.10.1016/j.cej.2013.09.081
- [74] N. Niksefat, M. Jahanshahi, A. Rahimpour, The effect of SiO2 nanoparticles on morphology and performance of thin film composite membranes for forward osmosis application, Desalination 343 (2014) 140-146.https://doi.org/10.1016/j.desal.2014.03.031
- [75] J. Yin, E.-S. Kim, J. Yang, B. Deng, Fabrication of a novel thin-film nanocomposite (TFN) membrane containing MCM-41 silica nanoparticles (NPs) for water purification, J. Membr. Sci. 423-424 (2012) 238-246.https://doi.org/10.1016/j.memsci.2012.08.020
- [76] E.-S. Kim, G. Hwang, M. Gamal El-Din, Y. Liu, Development of nanosilver and multi-walled carbon nanotubes thin-film nanocomposite membrane for enhanced water treatment, J. Membr. Sci. 394-395 (2012) 37-48.10.1016/j.memsci.2011.11.041
- [77] H. Zarrabi, M.E. Yekavalangi, V. Vatanpour, A. Shockravi, M. Safarpour, Improvement in desalination performance of thin film nanocomposite nanofiltration membrane using amine-functionalized multiwalled carbon nanotube, Desalination 394 (2016) 83-90.https://doi.org/10.1016/j.desal.2016.05.002
- [78] H. Wu, B. Tang, P. Wu, Optimization, characterization and nanofiltration properties test of MWNTs/polyester thin film nanocomposite membrane, J. Membr. Sci. 428 (2013) 425-433.https://doi.org/10.1016/j.memsci.2012.10.042
- [79] S. Liang, G. Qi, K. Xiao, J. Sun, E.P. Giannelis, X. Huang, M. Elimelech, Organic fouling behavior of superhydrophilic polyvinylidene fluoride (PVDF) ultrafiltration membranes functionalized with surface-tailored nanoparticles: Implications for organic fouling in membrane bioreactors, J. Membr. Sci. 463 (2014) 94-101.10.1016/j.memsci.2014.03.037
- [80] S.H. Kim, S.-Y. Kwak, B.-H. Sohn, T.H. Park, Design of TiO₂ nanoparticle selfassembled aromatic polyamide thin-film-composite (TFC) membrane as an approach to solve biofouling problem, J. Membr. Sci. 211 (2003) 157-165
- [81] M.-I. Luo, W. Tang, J.-q. Zhao, C.-s. Pu, Hydrophilic modification of poly(ether sulfone) used TiO₂ nanoparticles by a sol-gel process, J. Mater. Process. Technol. 172 (2006) 431-436.10.1016/j.jmatprotec.2005.11.004
- [82] T. Bae, T. Tak, Preparation of TiO₂ self-assembled polymeric nanocomposite membranes and examination of their fouling mitigation effects in a membrane bioreactor system, J. Membr. Sci. 266 (2005) 1-5.10.1016/j.memsci.2005.08.014
- [83] T.-H. Bae, I.-C. Kim, T.-M. Tak, Preparation and characterization of foulingresistant TiO₂ self-assembled nanocomposite membranes, J. Membr. Sci. 275 (2006) 1-5.10.1016/j.memsci.2006.01.023
- [84] Y. Mansourpanah, S.S. Madaeni, A. Rahimpour, A. Farhadian, A.H. Taheri, Formation of appropriate sites on nanofiltration membrane surface for binding TiO₂ photo-catalyst: Performance, characterization and fouling-resistant capability, J. Membr. Sci. 330 (2009) 297-306.10.1016/j.memsci.2009.01.001
- [85] S.S. Madaeni, N. Ghaemi, Characterization of self-cleaning RO membranes coated with TiO₂ particles under UV irradiation, J. Membr. Sci. 303 (2007) 221-233.10.1016/j.memsci.2007.07.017
- [86] F. Ahmed, C.M. Santos, J. Mangadlao, R. Advincula, D.F. Rodrigues, Antimicrobial PVK:SWNT nanocomposite coated membrane for water purification: performance and toxicity testing, Water Res. 47 (2013) 3966-3975.10.1016/j.watres.2012.10.055

- [87] S.S. Madaeni, N. Ghaemi, A. Alizadeh, M. Joshaghani, Influence of photo-induced superhydrophilicity of titanium dioxide nanoparticles on the anti-fouling performance of ultrafiltration membranes, Appl. Surf. Sci. 257 (2011) 6175-6180.10.1016/j.apsusc.2011.02.026
- [88] Z. Fan, Z. Wang, M. Duan, J. Wang, S. Wang, Preparation and characterization of polyaniline/polysulfone nanocomposite ultrafiltration membrane, J. Membr. Sci. 310 (2008) 402-408.10.1016/j.memsci.2007.11.012
- [89] P. Gao, Z. Liu, M. Tai, D.D. Sun, W. Ng, Multifunctional graphene oxide-TiO₂ microsphere hierarchical membrane for clean water production, Appl. Catal. B: Environ. 138-139 (2013) 17-25.10.1016/j.apcatb.2013.01.014
- [90] M. Ben-Sasson, K.R. Zodrow, Q. Genggeng, Y. Kang, E.P. Giannelis, M. Elimelech, Surface functionalization of thin-film composite membranes with copper nanoparticles for antimicrobial surface properties, Environ. Sci. Technol. 48 (2014) 384-393.10.1021/es404232s
- [91] J. Park, W. Choi, J. Cho, B.H. Chun, S.H. Kim, K.B. Lee, J. Bang, Carbon nanotube-based nanocomposite desalination membranes from layer-by-layer assembly, Desalin. Water Treat. 15 (2012) 76-83.10.5004/dwt.2010.1670
- [92] N. Wang, S. Ji, G. Zhang, J. Li, L. Wang, Self-assembly of graphene oxide and polyelectrolyte complex nanohybrid membranes for nanofiltration and pervaporation, Chem. Eng. J. 213 (2012) 318-329.10.1016/j.cej.2012.09.080
- [93] M.S. Mauter, Y. Wang, K.C. Okemgbo, C.O. Osuji, E.P. Giannelis, M. Elimelech, Antifouling ultrafiltration membranes via post-fabrication grafting of biocidal nanomaterials, ACS Appl. Mater. Interfaces 3 (2011) 2861-2868.10.1021/am200522v
- [94] M.R. Esfahani, S.A. Aktij, Z. Dabaghian, M.D. Firouzjaei, A. Rahimpour, J. Eke, I.C. Escobar, M. Abolhassani, L.F. Greenlee, A.R. Esfahani, A. Sadmani, N. Koutahzadeh, Nanocomposite membranes for water separation and purification: Fabrication, modification, and applications, Sep. Purif. Technol. 213 (2019) 465-499.https://doi.org/10.1016/j.seppur.2018.12.050