Nanostructured Membranes for Water Purification

Xin Li, Gomotsegang Fred Molelekwa, Meryem Khellouf and Bart Van der Bruggen

Abstract Membrane based processes enjoy numerous industrial applications and have greatly enhanced our capabilities to restructure production processes, protect the environment and public health, and provide new technologies for water purification. The scope of membrane technology is still extending, stimulated by the developments of novel membrane materials and membranes with better properties, as well as by the decrease of capital and operation costs. Recent advances in nanomaterials empower next-generation multifunctional membrane processes with exceptional catalytic, adsorptive, optical and/or antibacterial abilities that enhance treatment cost-efficiency. This chapter reviews emerging opportunities and sustainable approaches for the design of nanostructured membranes for water purification. Potential development and implementation barriers are discussed along with research needs to overcome them for enhancing water purification.

Keywords Nanomaterials · Membrane · Water purification · Wastewater treatment

1 Introduction

Water is the lifeblood of ecosystems, vital to human health and well-being and a precondition for economic prosperity. For this reason, it is at the very core of the 2030

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Agenda for Sustainable Development [1]. Although encouraging progress has been achieved in the field of water treatment in the 20th century, water scarcity is more than ever before the main challenge to provide clean, fresh water for the world's inhabitants. As estimated by the World Water Council (WWC), 3.9 billion people in the world will live in water-scarce regions by 2030 (WWC, Urban Urgency, Water Caucus Summary, 2007). In addition, water-associated vector-borne diseases continue to be a major public health problem in many countries. 2.1 billion people lack a safely managed drinking-water supply, and more than half of the 842,000 water-related die attributed to unsafe drinking-water (World Health Organization, Water, Sanitation and Hygiene strategy 2018–2025, 2018). Therefore, water resources, quality and treatment have become major topics of public and government.

Consolidated and emerging water purification strategies are pressingly acclaimed to offer compelling solutions to the water pollution issues and indeed, increasingly available approaches have surfaced. Initially, activated carbon was employed for wastewater purification, but has been replaced recently by more cost-effective membrane technologies [2]. Based on a range of synthetic membranes with various functions, membrane technologies offer the best options to 'drought proof' mankind on an increasingly thirsty planet by purifying seawater or wastewater [3]. Reverse osmosis (RO), which involves pushing water through a semipermeable membrane that blocks dissolved salts, is now considered the heart of conventional desalination plants. Other membrane processes, microfiltration (MF) and ultrafiltration (UF), have become major technologies for water treatment from non-saline sources, pretreatment for RO processes and in wastewater treatment in membrane bioreactors. Nanofiltration (NF) finds application in water softening and color removal, industrial wastewater treatment, water reuse, and desalination. Additionally, as emerging technology, forward osmosis (FO) has shown great promise in water supply, because it requires much less energy to induce a net flow of water across the membrane compared to traditional pressure-driven membrane processes such as RO. However, FO as a stand-alone process has to be integrated in an overall process scheme to be used as a desalination process. Although commercially available membranes perform well in water purification and desalination, current materials and fabrication methods for membranes are largely based on empirical approaches and lack molecular-level design [4]. The drive to protect existing water resources and produce new water resources demands membranes with improved productivity, selectivity, fouling resistance, and stability at lower cost and with fewer manufacturing defects.

The recent development of nanotechnology offers leapfrogging opportunities for developing innovative technologies for more efficient water purification and wastewater treatment processes. It is now a popular belief that many of the solutions to the existing and even future water-based challenges are most likely to come from nanotechnology and especially novel nanomaterials with increased affinity, capacity, and selectivity for water contaminants [5]. Particularly, the incorporation of these novel nanomaterials into the chemical composition of membranes for water purification has been the focus in this field, as illustrated by the number of publications and related citations (Fig. 1). The obtained nanostructured membranes can alter the membrane properties such as permeability, selectivity, mechanical resistance and

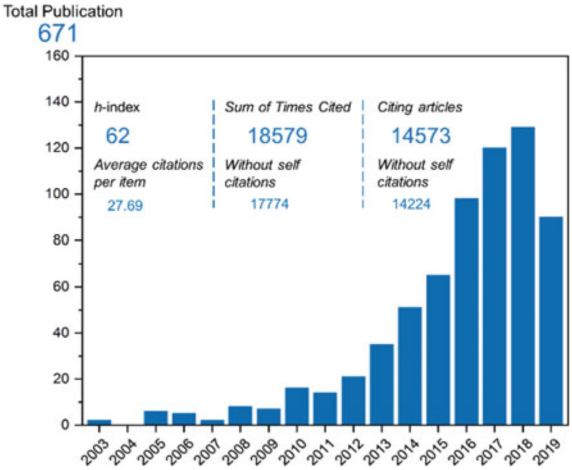

Fig. 1 The number of journal papers on nanostructured membrane for water purification since 2003. Data were obtained from Web of Science on July 2019. Search topics were 'membrane, nanoparticles and water purification'

hydrophilicity as compared to virgin polymers [6]. Nanomaterial properties desirable for nanostructured membranes also include a high surface area for adsorption, a high activity for (photo)catalysis and degradation, antibacterial properties for disinfection and biofouling control, and other unique optical and electronic properties that find use in novel treatment processes in water purification [7–9]. Since the use of nanostructured membranes in water purification is considered an achievement of high importance, they should be designed to maintain the surface reactivity, effective contact and uptake capacity. For this reason, the class of applied nanomaterials, and fabrication strategies of nanostructured membranes combining the respective advantages should be preferred for water purification.

This chapter presents promising nanostructured membranes and provides a broad view on how they could transform our water purification and wastewater treatment systems. The extraordinary properties of prevalent nanomaterials in nanostructured membranes, such as high surface area, photosensitivity, catalytic and antibacterial activity, and electrochemical, were introduced. The fabrication strategies and relevant applications of nanostructured membranes in water purification were critically reviewed based on their functions in unit operation processes. The potential impact of nanostructured membranes on ecosystems and economics as well as their technological capacity were also discussed.

2 Prevalent Nanomaterials for Nanostructured Membrane

Most of the prevalent nanomaterials used in nanostructured membranes are either metal or metal oxide, with some recently emerging materials like metal organic frameworks (MOFs) [10], covalent organic frameworks (COFs) [11], and two-dimensional (2D) nanomaterials [12]. Each of these nanomaterials can be incorporated with most of polymeric materials available to produce nanostructured membranes with specific characteristics, as a result of the synergistic properties between synthetic membranes and advanced nanomaterials. The unique properties of nanomaterials mentioned above will be discussed in the following sections. The focus will be placed on how these properties contribute to water purification in membrane processes.

2.1 Metal Nanoparticles

The challenge to achieve appropriate disinfection without forming harmful disinfection byproducts in point-of-use water treatment calls for new technologies for efficient disinfection and microbial control. Several natural and engineered nanomaterials have demonstrated strong antibacterial properties through diverse mechanisms. Among them, Ag nanoparticles have drawn special attention due to their excellent antibacterial and antifungal activity [13]. It is now well accepted that the antibacterial activity of Ag nanoparticles stems from the release of Ag^+, which can bind to thiol groups in vital proteins, resulting enzyme damage [7]. It has also been reported that Ag^+ can prevent DNA replication and induce structural changes in the cell envelope [14] (Fig. 2a). With these advantages, significant progress has been made in the development of Ag nanoparticles-based membranes for water purification. For example, Ag nanoparticles were impregnated in a polysulfone matrix to improve biofouling resistance and virus removal [15]. Biogenic Ag nanoparticles were also incorporated in polyethersulfone (PES) membranes for enhancing their antibiofouling capability in a membrane bioreactor [16]. Besides, Ag nanoparticles were embedded into woven fabric MF membranes. Such designed membranes were more hydrophilic, showing a higher water permeability and 100% removal of bacterial load from drinking water [17].

One challenge with the Ag nanoparticles inside the membrane matrices is their weak resistance to washing, as they can be released either as nanoparticles or dissolved ions form [18], so the antibacterial ability of membrane would be attenuated with time. A more advanced in situ reduction coating procedure is introduced to address this issue: Ag ions are firstly dissolved in the polymer/polyelectrolyte solution, followed by coating the mixtures and in situ synthesizing Ag nanoparticles onto a membrane for stable attachment. With this strategy, polydopamine (PDA) has been proposed to improve the long-term antibacterial efficiency of Ag nanoparticles-based membranes [19]. Huang et al. successfully immobilized Ag nanoparticles on

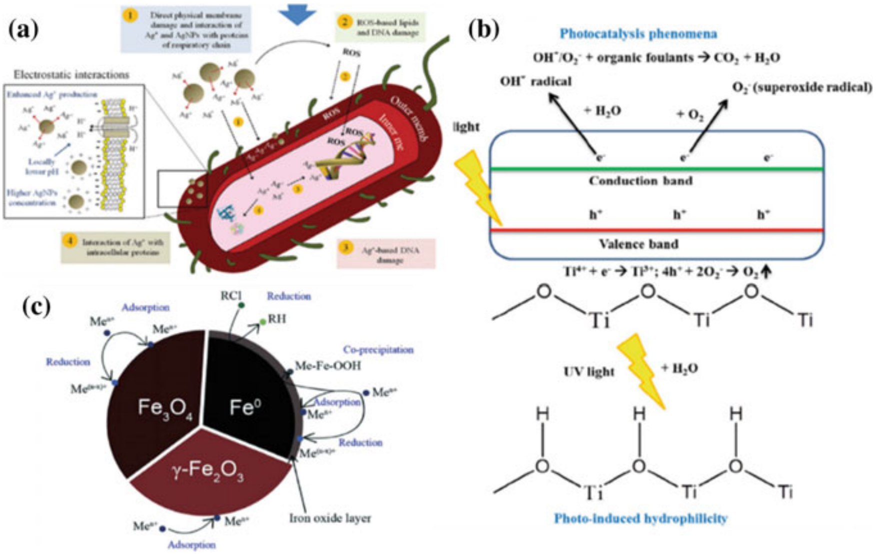

Fig. 2 **a** Proposed mechanism of Ag nanoparticles-related toxicity. Reprinted with the permission from Ref. [25]. Copyright 2014 The Royal Society of Chemistry. **b** Photocatalysis and photo-induced ultrahydrophilicity mechanism of TiO_2 nanoparticles. Reprinted with the permission from Ref. [26]. Copyright 2015 Elsevier. **c** Schematic model of magnetic nanoparticles. Reprinted with the permission from Ref. [27]. Copyright 2013 Elsevier

a PES UF membrane by PDA mediated in situ reduction of $Ag(NH_3)_2OH$. The static immersion test of the membrane exhibited a slight release of Ag^+ ions even after 12 days [20]. The inhibition zone study showed a clear halo, confirming its tremendous disinfection properties against *E. coli* and *B. subtilis*. Meanwhile, compared with a control membrane, the pure water flux of optimized membrane was increased from 248 to 336 L/m^{2}h. Similarly, tannic acid (TA) also has been used to enhance the stability of Ag nanoparticles due to its metal chelating and adhesive ability. Based on this strategy, an ultrathin precursor layer of TA-Fe-PEI complexes was deposited onto the membrane surface, followed by in situ reduction of Ag nanoparticles in the presence of polyvinylpyrrolidone. After contacting with *E. coli* and *B. subtilis* for 1.5 h, the bactericidal efficiency of TA-Fe-PEI/Ag-modified membrane could reach 100% [21]. Moreover, constructing nanocomposites by immobilizing Ag nanoparticles onto a larger-scale support can also tackle the instability problem. Promising carriers for Ag nanoparticles include carbon nanotubes (CNTs) [22], graphene oxide (GO) [23], and TiO_2 [24]. These carriers are either antibacterial agents themselves or possess the advantages of hydrophilic, antifouling, and photocatalytic properties, which can even lead to a higher antibacterial capability than that of pure Ag nanoparticles due to a synergistic enhancement effect.

Due to their considerably lower cost than silver, Cu nanoparticles were also explored in term of their antibacterial activity against various bacterial species. Although the exact antibacterial mechanisms remain elusive, substantial efforts have been devoted to designing Cu-based antibacterial membranes [28–30]. Similar with Ag nanoparticles, mitigating the release of Cu nanoparticles has been the focus of research in this area. An improvement of the pure water flux for Cu nanoparticles based membranes with the increase of Cu content was observed [28].

Beside bacteria or fungus, toxic organic compounds such as chlorinated aliphatic and aromatic molecules are another common class of contaminants in natural water, which were implicated with several diseases, chronic damages and carcinogenicity [31]. Due to the low cost and broad availability, zero-valent iron nanoparticles have drawn more attention in the detoxification of these compounds by electron transfer reactions [32]. Particularly, bimetals such as Pd/Fe, Ni/Fe, Cu/Fe are found to have higher efficiency for dichlorination of chlorinated organic compounds (COCs). For example, in the Pd/Fe bimetallic system, the corrosion of iron leads to the emergence of hydrogen. Pd is known to have the unique ability to absorb hydrogen into its lattice and acts as a catalyst to accelerate hydrodechlorination [33]. During the past years, many theoretical and experimental studies focused on designing Fe-based catalytic membranes for COCs dichlorination [33, 34]. In parallel, a continuous effort to enhance the stability of bimetals nanoparticles in membrane structures and to evaluate the degradation efficiency of target COCs is still under progress. The preservation and regeneration of Fe-based catalytic membranes are also an important issue for their prolonged applications.

2.2 Metal Oxide Based Nanomaterials

Metal oxides nanomaterials are widely explored as highly efficient adsorbents and catalysts for contaminants removal from water/wastewater, due to their easy and well-developed synthesis method, cost effectiveness and functionalization to nanostructured membranes. There has been bountiful literature published on the application of TiO_2 nanoparticles in membranes for water purification [35]. This could be attributed to two main reasons—its excellent photocatalysis that decomposes/disintegrates organic foulants and microbes, and photo-induced ultrahydrophilicity that repels hydrophobic foulants and forms hydration layer of water on the membrane surface, thereby enhancing fouling control [36, 37] (Fig. 2b). TiO_2 based photocatalytic membranes exhibit a more obvious effect on dye degradation [38], humic substances removal [39], and oil-water emulsion separation [40], as compared with virgin membranes. In particular, TiO_2 free-standing membranes have been reported, providing higher photocatalytic surface area and mass transfer rate than TiO_2 nanoparticles coated and blended membranes. For example, TiO_2 nanotube membranes shown a satisfying permeability and antifouling performance due to the rejection and photodegradation of foulants on the surface of membrane under UV irradiation [41]. Despite of these advantages, UV-responsive TiO_2 based membranes still face challenges. TiO_2 based catalysts suffer from the limited photocatalytic performance due to fast recombination of the photogenerated charges, and exhibit poor photoactivity in the visible light region [42]. Moreover, the membrane structure may suffer from severe destruction by both UV light and reactive oxygen species [43]. Recently, modification of TiO_2, by metal or nonmetal doping, co-doping, coupling with another semiconductor or developing composites with carbon materials, has led to a significant enhancement of its photocatalytic performance under visible light irradiation. With this progress, the attempt to extend the modified TiO_2 photocatalysts into the design of visible-light responsive membranes has become a topic of great interest. A timely review by Shi et al. discussed the development of these novel TiO_2 based membranes for water purification [44].

The presence of heavy metals in aqueous systems is considered a major worldwide problem related to many harmful effects on the health of humans and other life forms. Iron-based nanoparticles are the widely applied materials for the uptake of heavy metals in water [45]. During the water treatment, zero-valent iron is oxidized forming in situ oxy-hydroxides and oxides with enhanced surface area, charge density and reactivity (Fig. 2c). Iron oxide nanoparticles may surpass the drawback of soluble iron release. In addition, the magnetic behavior of Fe_3O_4 and γ-Fe_2O_3 facilitates their recovery after application. Cr (VI) removal is the early studies case of iron oxide nanoparticles based membranes application in water purification, based on the electrostatic adsorption and redox reaction [46, 47]. Similarly, the adsorptive removal of Cu (II) was remarkably improved using an Fe_3O_4 nanoparticles embedded PES membrane [48]. Recently, for improving stability and controlling aggregation, a metformin/GO/Fe_3O_4 hybrid was introduced into nanofiltration for effective removal of dye and Cu (II) [49].

Several metal oxide nanoparticles, namely CuO and ZnO were also studied for inclusion in antibacterial membranes. CuO nanoparticles presented enhanced bactericidal behavior against *E. coli* and *P. aeruginosa* [50]. The proposed antibacterial mechanism of ZnO nanoparticles is closely correlated with the photocatalytic formation of reactive oxygen species or the release of Zn^{2+} ions, both of which can effectively inhibit the bacteria. A recent work reported the development of CuO or ZnO decorated polyacrylonitrile (PAN) nanofibers membranes for drinking water purification [51]. The hybrid membranes exhibited an excellent antibacterial potential against both *E. coli* and *S. aureus*. The developments and breakthroughs on antibacterial membranes with metal oxide nanoparticles for water treatment have been well described by Zhu et al. [18]. Besides, ZnO nanoparticles have shown more obvious advantages related to membrane fouling control based on their hydrophilic nature. The reduced flux drop, extended operational lifespan or higher flux recovery rate for ZnO nanoparticles based membranes have been experimentally/theoretically confirmed when tested with model foulants (e.g., oleic acid solution [52], sodium alginate solution [53]) and river water [54]. More recently, surface modified ZnO nanoparticles were also immobilized on the polyvinylidene difluoride (PVDF) membrane surface for oily wastewater treatment [55].

In the same direction, SiO_2, ZrO_2, and Al_2O_3 nanoparticles have been proven efficient for designing antifouling membranes in water purification. The addition of these nanoparticles to membranes enhanced the surface hydrophilicity, water permeability, or fouling resistance, along with the mechanical and thermal stability [7]. In the light of molecular-level design, in situ preparation, permitting the in situ generation of nanoparticles into/on the membrane matrix, has pushed the design of metal oxide based nanostructured membranes to the next stage [56]. With the in situ formation process (i.e., the formation of SiO_2, ZrO_2, and Al species via sol-gel process), the deposition of nanoparticles can be preciously controlled on the membrane surface or around membrane pores, which triggers the maximum exposure of hydrogen accepter groups. Research has been undertaken to compare the influence of in situ and ex situ created SiO_2 nanoparticles on the structure and performance of PES membranes [57]. In recent research PVDF MF/UF membranes were modified via in situ biomimetic silicification for oily emulsion and protein wastewater treatment [58] (Fig. 3a). Similarly, a successful design was achieved with ultrathin ZrO_2 film as selective layer to prepare a novel NF membrane using hydrolysis of zirconium sulfate [59] (Fig. 3b). By this stage, researchers realized that the chemistry and the functions of metal oxide nanoparticles could be deliberately pre-designed for specific water treatment purposes, while integrating with a suitable membrane formation process.

2.3 Metal Organic Framework/Covalent Organic Framework

The development of crystalline materials extended their applications for designing next-generation nanostructured membranes in water purification. Among these materials, porous inorganic solids are highly attractive due to their porous structure and high surface area, which can increase the overall porosity and separation ability of membranes. MOFs/COFs have emerged as porous solids of superior new types [60]. These solids have a regular and highly tunable pore structure, along with an enormous variability in secondary building units connected by multitopic organic ligands and linker topology, connectivity, and chemical functionality, which are preferred over conventional porous materials such as zeolites and carbon based materials. Both continuous MOFs/COFs and MOFs/COFs based composite membranes have been developed as multifunctional materials for membrane separation beyond the traditional uses for dye removal and fouling-resistance, and even contribute to catalytic degradation, heavy metal adsorption, and oil/water separation. For example, trace nickel (II) (ppm level) could be effectively removed from high-salinity wastewater ($[Na^+] = 15{,}000$ mg/L) with a ZIF-8 modified PVDF UF membrane under the protection of a polyacrylic acid layer [61]. The hybrid membrane could be regenerated by a HCl-NaCl solution ($pH = 5$) for repeated use. Recently, COFs based mixed matrix membranes with much higher permselectivities were obtained by embedding carboxyl-functionalized COFs in PAN UF membrane [62]. The best performing membrane displayed a relatively high pure water flux of 940 L/m^2 h bar and an enhanced fouling resistance, maintaining a 99.4% rejection of γ-globulin. Furthermore, novel composites, such as UiO-66-$(COOH)_2$/prGO [63] and TpBD@Fe_3O_4 [64], were introduced into membrane for water treatment, which represented the latest trends for MOFs/COFs based membranes. The recent progress of MOFs/COFs based membranes for water purification has been discussed in published reviews [10, 11].

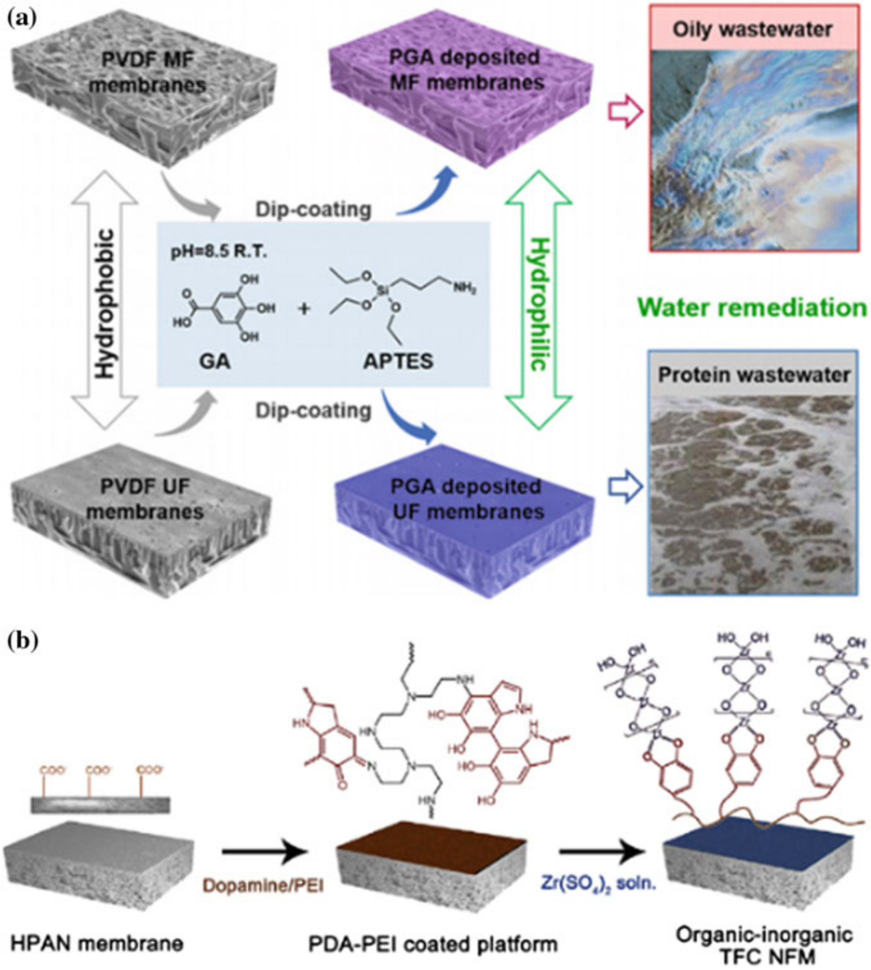

Fig. 3 Scheme of (**a**) co-deposition of gallic acid (GA) and γ-aminopropyltriethoxysilane (APTES) on the PVDF MF/UF membranes for application in water remediation on oily and protein wastewater. PGA refers to the abbreviation of the hydrophilic hybrid network derived from polymerization of GA and APTES-derived polysiloxane. Reprinted with the permission from Ref. [58]. Copyright 2018 American Chemical Society. **b** Preparation process and mechanism for the organic–inorganic TFC membranes with ultrathin ZrO_2 film as the selective layer on the PDA-PEI coated PAN membranes. Reprinted with the permission from Ref. [59]. Copyright 2015 Elsevier

2.4 *Two-Dimensional Materials*

With the development in materials science, the dimension has become a significant parameter of materials classification. 2D nanomaterials, such as graphene and GO [65], exfoliated nanosheets of MOFs [66], zeolite nanosheets [67], transition metal dichalcogenides (TMDs) [68], and 2D MXene nanosheets [69], have attracted increasing attention owing to their outstanding mechanical properties, excellent thermal stability, and superior flexibility that surpass their 3D counterparts. With these advantages, 2D nanomaterials are rapidly emerging in the development of nanostructured membranes with high performance in desalination and wastewater treatment. The introduction of 2D nanomaterials manipulates the morphology, stability, surface hydrophilicity, charge, and roughness of a membrane [12]. Meanwhile, the obtained membranes have the potential to balance the trade-off between thermal and physicochemical stability, permeability and selectivity, while mitigating membrane fouling, which has been the bottleneck of membrane processes. In this part, three main families of 2D materials widely used in nanostructured membranes will be discussed.

2.4.1 Graphene Derivative Nanomaterials

Graphene is a 2D single-layered nanomaterial consisting of sp^2-related carbon atoms arranged in a hexagonal honeycomb lattice structure. Since its discovery in 2004, several synthesis methods have been proposed, which were mainly classified into two routes, i.e., top-down methods (such as micromechanical cleavage [70] and liquid exfoliation [71]) or bottom-up methods (such as chemical vapor deposition (CVD) [72] and wet-chemical synthesis [73]).

Graphene finds its application in nanostructured membranes due to its better properties compared to other materials. For instance, compared with polyamide for preparing thin film membrane, graphene is thinner with better selectivity and higher porosity, and a better mechanical, and chemical resistance [74]. Despite these advantages, the application of graphene in membrane separation is constrained by the limited potential for large scale production. Carbon nanosheets of GO and reduced graphene oxide (rGO) have received increasing attention due to their potentials for enhancing membrane performances and easy scale-up [75]. Besides the basic structure of graphene, GO contains a large variety of functional groups created during the synthesis process, such as hydroxyl and epoxy on the basal plane and carboxyl groups at the edges [76]. These functional groups facilitate the adjustment of the adjacent interlayer distance of the stacked GO sheets by different methods so that the stability, the interaction with the charged particles or the channels size of the laminated GO membrane were modified. Moreover, the oxygen groups of a GO nanosheet ensure the interlayers hydrogen bonding interactions that play an important role in assembling laminated GO membranes [77].

Figure 4 illustrates the investigations about tuning interlayer spacing GO sheets to create laminates GO and change the surface charge of modified GO based membranes [78]. By intercalating various nanoparticles, such as TiO_2, SiO_2 and Si_3N_4, GO based composite nanomaterials have been developed to design novel GO based nanostructured membranes with high rejection against specific water pollutant and desired water flux. For example, an intercalated GO base membrane with Si_3N_4 nanoparticles provided approximatively a doubled water flux compared with a pristine membrane, while maintaining a high rejection of methylene blue and methyl

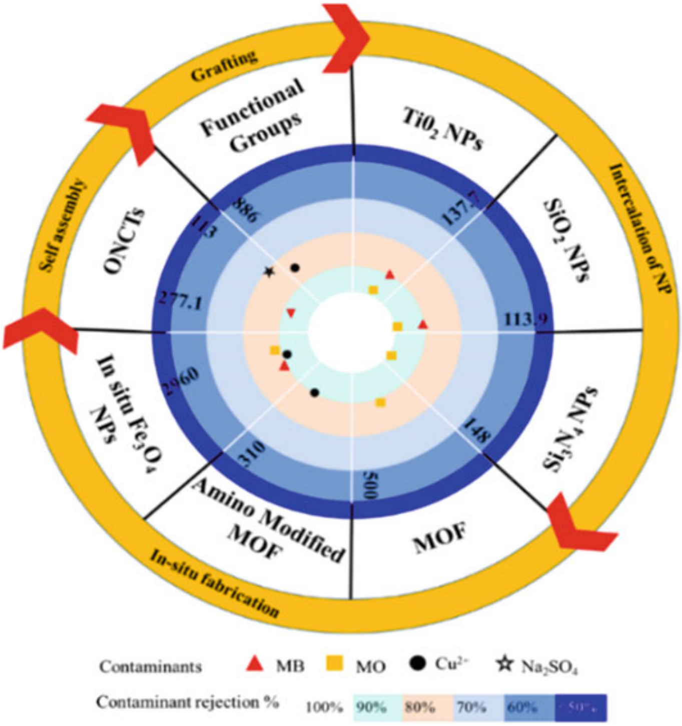

Fig. 4 Effect of GO intercalation with different nanoparticles and grafting of functional groups on membrane's performances (contaminant rejection % and water flux L/m^2 h MPa)

orange of 88.9% and 99.3%, respectively [79]. Moreover, rGO nanosheets were doped with oxidized CNTs to enlarge the GO interlayer spacing using layer-by-layer self-assembly technique, which instantly increased the water permeability to 5.65 L/m^2 h bar with a Na_2SO_4 rejection of 80.0% [80].

2.4.2 TMDs Materials

2D nanomaterials with semiconducting character, such as TMDs, were also received extraordinary research attention due to their electrical, physicochemical, mechanical, and biological properties [68], which make them promising candidates to fabricate TMDs based membranes in water purification.

TMDs are a kind of 2D nanoporous materials of three-atom thickness with the formula MX_2, where M is a transition metal atom (like Mo or W) and X is the chalcogen atom (mainly S, Se or Te); showing a 'sandwich' structure with two chalcogen atomic layers separated by a transition metal atomic layer [68]. Molybdenum disulfide (MoS_2) is one of the most extensively studied TMDs materials in membrane separation. Although there exist few in-plane nanopores within a single

MoS_2 nanosheet, it has a high potential in water desalination assuming that in-plan nanopores with controllable shape, size and functionality could be drilled in a large scale [81]. Heiranian et al. studied the desalination ability of a single layered MoS_2 membrane using molecular dynamics simulation [82]. Similarly, Hirunpinyopas et al. prepared a functionalized laminar MoS_2 membrane that delivered water flux of 40 $\times$ 10^{-3} L/m^2 h bar for a 3 μm-thick membrane and 11.6 $\times$ 10^{-3} L/m^2 h bar, with a salt rejection ratio up to 97% [83]. The obtained MoS_2 nanoporous membranes demonstrated excellent water permeation which was 2–5 times higher than that of GO based membranes as comparable thickness, while maintaining the rejection ratio (89%) for Evans blue. The high water flux can be attributed to the low hydraulic resistance of smooth channel surface, since MoS_2 nanosheets do not have any functional groups. In comparison, GO contains many oxygenated functional groups sticking out from its carbon plane, generating hydraulic resistance to water flow. Meanwhile, the smooth MoS_2 channel also allows the continuous transport of light organic vapors, to which a GO membrane is impermeable because of the blocked pathway by its oxygenated groups [84]. The water permeance of a layer stacked MoS_2 membrane can be increased by templating ultrathin nanowires between MoS_2 layers, a strategy that has been demonstrated in an analogue MoS_2 made membrane [85]. A study by Sun et al. found that water molecules could not pass through the MoS_2 nanopores with a diameter smaller than 0.23 nm, while freely circulating throw the nanopores with a diameter of 0.44 nm [86]. Unfortunately, salt molecules can pass through at this pore size, resulting in ineffective salt rejection. Thus, in order to balance the water flux and salt rejection, the size of MoS_2 nanopores should be maintained in the range of 0.23 nm.

2.4.3 2D MXene Nanosheets

MAX phases are a new class of ternary nanolayered, hexagonal ceramics with the general formula $M_{n+1}AX_n$, where: M is an early transition metal, A is a group of element mainly Al, Ga, In, Tl, Si, Ge, Sn and Pb, X is carbon or nitrogen with $n = 1$–3. These materials are attracting increasing scientific attention as candidate materials for diverse applications [87]. They have a unique combination of metallic and ceramic properties, which has advantages in low density, good machinability, high strength and high Young's modulus with excellent thermal and chemical resistance [88]. The excitement about the mass production of 2D materials from 3D layered one using exfoliation and sonication, was shared by the finding of a new family derived from MAX phases called MXene with the general formula $M_{n+1}X_nT_z$ (T is the functional group edging the surface, such as O^{2-}, OH^-, F^-, NH_3, NH^{4+}). Till now, over 70 compounds of MXene were reported in both experimental syntheses and numerical simulation, which has been shown in Fig. 5 [89].

Due to its excellent exfoliation capability, $Ti_3C_2T_x$ is the most reported MXene material for designing nanostructured membranes. Gogotsi et al. prepared $Ti_3C_2T_x$ MXene based membranes via assembling freestanding or supported membranes for

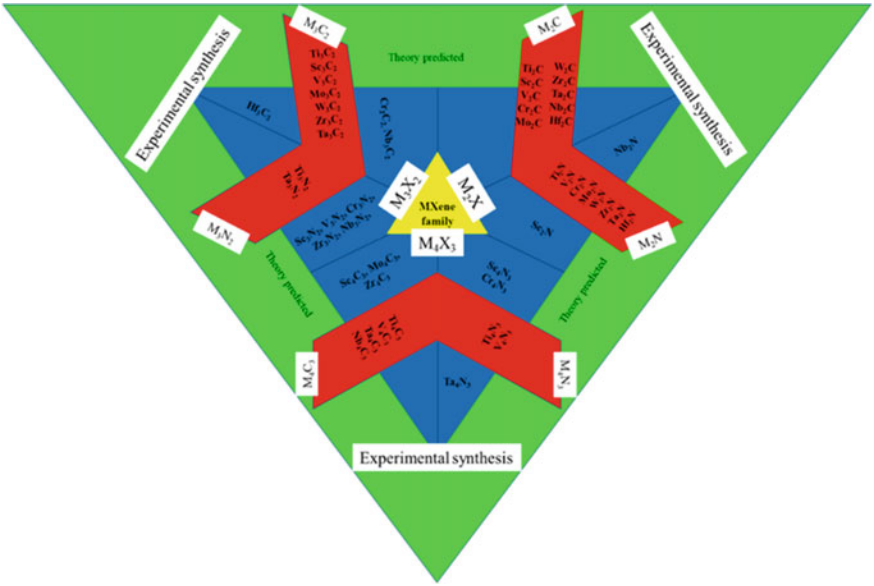

Fig. 5 Schematic classification of MXene compounds with examples

the charge- and size-selective rejection [90]. The micrometer-thick MXene membranes was found to have an ultrafast water flux, which was attributed to the hydrophilic nature and the presence of H_2O molecule layers between the wet $Ti_3C_2T_x$ layers. It also showed a high selectivity towards metal and dye cations with different charge and size. Another nano-sized MXene sheets based membrane was prepared by Wang et al. who intercalated Fe_3O_4 nanoparticles followed by mild acid etching as pillars to achieve larger interlayer distance and create more nanochannels [91]. These nanochannels exhibited a water flux of over 10,000 L/m^2 h MPa while achieving a 90% rejection rate for particles larger than 2.5 nm.

Recently, for further improving the performance of MXene based membranes, composite MXene based nanomaterials, such as $Ti_3C_2T_x$-GO [92] and $Ti_3C_2T_x$-PEI [93], were introduced to overcome defects in the structure and selectivity of nanochannels for pure MXene membranes. The post-modification of MXene materials was also explored, by grafting multiple functional groups including $–NH_2$ and –COOR [94]. Moreover, improving the hydrophilicity of MXene based nanomaterials may extend their applications in water treatment.

2.5 Environmental Effects of Nanomaterials

The fate of nanoparticles in the environment relies on the synergistic effects of their physicochemical properties and interactions with pollutants. The sources of nanoparticles in the environment include, but are not limited to, various natural activities (e.g., volcanic activities, veld fires, soil erosion, weathering, clay minerals, and dust storms); anthropogenic activities (e.g., burning fossil fuels, mining, construction, production of nanoparticles and waste materials) [95]. After reaching the environment, nanoparticles accumulate in different environmental media (e.g., air, water, soil and sediments) and harm the health of humans and animals [96]. The health effects associated with the release of nanoparticles to the environment include damaging of cell and DNA, inflammatory and immune responses, oxidative stress, lipid peroxidation, genotoxicity, lung diseases, inflammation, pulmonary pathological changes [97]. Furthermore, the transfer of certain nanoparticles such as TiO_2 was also found to cause a genotoxic effect (at low dose of 0.25 mM), and to damage DNA (at higher concentrations) of the plants.

Given the benefits as well as the environmental and health impacts of nanoparticles, there is a need to develop and implement strategies to manage the production and use of nanoparticles in a manner that would prevent or reduce their impact on human health and the environment. To this effect, Patil et al. suggested the use of innovative greener routes for nanoparticle synthesis; advanced engineering ways for manufacturing smarter and more degradable nanoparticles; and governing local and international legislation to monitor nanoparticles released into the environment [98].

3 Rational Design Strategies

3.1 Blending

Blending is the classical membrane elaboration method which was mainly applied in fabricating nanomaterials based mixed matrix membranes (MMMs), using either organic or organic-inorganic materials. A large number of studies has been dedicated to investigating the effect of blending polymeric materials with mineral nanoparticles including silica, ZrO_2 and TiO_2 etc. [26], which have been considered as convenient operation with mild conditions and stable performances. Besides, blending newly emerging nanomaterials, such as GO, MOFs, COFs, and 2D materials, into membrane matrix were also intensively investigated [10–12, 75]. The major inconvenience of the blending method was the absence of evenly dispersed inorganic interconnected networks compared with other methods such as the sol-gel process. In the area of nanostructured membranes, the blending procedure is assisted by phase inversion. Typically, nanomaterials were directly dispersed into a polymer dope (e.g., PSF, PES, PVDF) or in situ formed within the dope in the presence of solvent [26]. The blending procedure in presence of solvent conventionally involves in three main steps, (i) mixing the nanomaterials and the polymer with a solvent, (ii) casting the mixed solution on a porous support, (iii) drying and thermal treatment to eliminate the solvent.

The blended nanomaterials influence the pore size and pore size distribution of MMMs. Meanwhile, the performances of MMMs depend upon the size and loading rate of blended nanomaterials, as well as their interaction with the polymer matrix. It has been reported that nanomaterials blended UF membrane display a higher permeability and hydrophilicity, improved photocatalytic activity, antifouling and antimicrobial properties, and lower compaction under pressure [26].

3.2 Interfacial Polymerization

The interfacial polymerization process is a classical method, where two monomers react on the surface of the porous support. The developed membranes to date are integrally composed of an ultrathin polyamide (PA) layer containing functional nanomaterials and a porous polymer support [99]. The addition of these nanomaterials to the barrier layer endows the membranes with various attractive properties such as high permeability, increased mechanical strength, desirable contaminant selectivity, and antibacterial ability etc. Taking silica as an example, a representative fabrication step for silica nanoparticles based thin film RO membrane was reported by Peyki et al. [100]. The substrate was dipped in an aqueous amine solution containing different contents of silica nanoparticles. Then the membrane was immersed into the hexane solution of acid chloride, which formed a PA thin film with silica nanoparticles. In another study, NF membrane active layers of polyimine COF were synthesized via the interfacial polymerization of terephthalaldehyde and tris (4-aminophenyl) benzene monomers on top of a PES UF membrane support [101]. The rejection efficiencies of the COF NF membrane for a model organic compound, Rhodamine WT, and a background electrolyte, NaCl, were higher than those of the PES support without the COF film. The changes in properties of nanocomposite membranes are strongly influenced by the chemical properties, type, size and concentration of the nanomaterial used. Based on rational design strategies, intentionally selected nanomaterials were employed to modify PA thin film composite (TFC) membranes for enhancing forward osmosis performances. A comprehensive review summarized the recent advances of nanostructured TFC membrane in this area [102].

The control of the molecular and structural characteristics of the PA layer are of great importance in improving the permeance and selectivity. Porous nanomaterials can be ideal fillers embedded in the PA layer for preparing TFN membranes, which behave like water channels to facilitate water permeability while blocking hydrated cations, leading to an enhanced permeance without adversely affecting the selectivity. However, a significant change of water transport properties in the PA-based active layers is difficult to achieve because water transport is heavily restricted by the highly cross-linked polymer chains in a tortuous manner. Recently, Wang et al. fabricated a TFC NF membrane with a crumpled PA layer, which provided a simple avenue to overcome this challenge [103]. Interfacial polymerization was performed in a single-walled carbon nanotubes/polyether sulfone composited support loaded with ZIF-8 as a sacrificial templating material. ZIF-8 can be removed by water dissolution, which facilitates the formation of a rough PA active layer with crumpled nanostructure. The resultant membrane exhibits an unprecedented permeance up to 53.2 L/m^2 h bar while maintaining a high rejection of 95.2% for Na_2SO_4.

3.3 *In Situ Preparation*

In situ preparation has been considered a promising strategy to fabricate next-generation nanostructured membranes with rational design. Under this in situ design platform, the functionalized elaboration for nanomaterials and sophisticated modification for membrane matrix/surface with nanomaterials can be judiciously merged, which farthest exploits the advantages of nanomaterials in disinfection, adsorption and catalytic degradation for water treatment. Based on the general preparation process for membranes, in situ formation of nanomaterials takes place (i) within the casting solution, (ii) during the solidification of casting solution, or (iii) after the solidification of the casting solution [56].

In the past two decades, two kinds of main in situ design strategies have been developed: (i) sol-gel process. Through the controlled hydrolysis and polycondensation reaction of the inorganic precursors, accompanying the polymer solidification, a nanostructured membrane is obtained during the in situ generation of metal oxide nanoparticles on/within the membrane matrix. For example, the classical in situ preparation of TiO_2 based nanostructured membranes is moderately controlling the synchronous formation of TiO_2 nanoparticles (derived from the sol-gel process of titanium (IV) butoxide [104] or titanium tetraisopropoxide [105]) and a polymeric membrane. Furthermore, SiO_2 [106] and ZnO [107] nanoparticles were also introduced into membrane via the in situ sol-gel process for water treatment. Recently, biomimetic mineralization opens a new avenue to design nanostructured membranes with complex structures [108]. The mineralization inducers act as catalysts to promote the in situ nucleation and growth of inorganics within the confined spaces among polymer chains, which favor the uniform dispersion of inorganics in a molecule level. (ii) In situ reduction. Inorganic precursors are reduced by a reducing agent; metal nanoparticles are in situ synthesized in the casting solution or on the membrane surface/pore. The fabrication strategy was attractive particularly for preparing membranes functionalized with Ag [109], Fe [34], Cu [30] nanoparticles. Two methods have been reported to fabricate nanostructured membranes via in situ reduction [56]. The classical method is the 'generating before' method, in which the precursor is in situ reduced in the casting solution before the formation of the membrane matrix. The 'generating after' method allows the in situ reduction and localized loading of nanoparticles on the membrane exterior surface or membrane pore.

3.4 Surface Modification

It is well known that surfaces/interfaces play a crucial role in the fabrication and application of nanostructured membranes in water purification owing to its simplicity and sustainability [110]. Compared with blending, surface modification minimized the effects of nanomaterials on the internal structure of membranes, which offers opportunities for modification of commercial membranes. In addition, the functionality of nanomaterials could be fully utilized.

A simple method is to modify the membrane surface with active moieties to ‘capture’ nanomaterials from suspension via physical interactions. Some researchers grafted hydroxyl or sulfonic acid groups onto the membrane surfaces to capture TiO_2 nanoparticles [111, 112]. To further improve the nanomaterials coverage and their stability on the membrane surface, strong interactions, such as electrostatic interaction, hydrogen bonding, coordination, or covalent bonding, were applied between the membrane and nanomaterials. For example, Choi et al. attempted to modify the TFC membrane surface by depositing multilayers of oppositely charged GO and aminated GO nanosheets using layer-by-layer technique [113]. Similarly, to develop a low-fouling antibacterial membrane, azide-functionalized GO was covalently anchored onto commercial flat sheet membrane surfaces via azide photochemistry [23]. Alternatively, in another development, a commercial RO membrane was functionalized by a spray- and spin-assisted layer-by-layer (SSLbL) method through the alternate coating of polyethyleneimine modified Cu nanoparticles and poly(acrylic) acid [29]. Cu nanoparticles can be potentially regenerated on the membrane surface via the same SSLbL method. Besides, as introduced in Sect. 3.3, biomimetic mineralization, defined as a mineral formation process regulated by bio-macromolecules, was also involved for sophisticated surface modification of membranes. The mineralized membranes are composed of three major layers: polymer membrane (as the skeleton), intermediate layer (as the connection, e.g., polydopamine/polyethyleneimine intermediate layer) and mineral coating (e.g., $CaCO_3$, SiO_2, ZrO_2 nanoparticles). The relevant progress on fabrications of nanostructured membrane for water purification have been extensively reviewed by other researchers [9].

Polymer/nanomaterials composites were considered as promising candidate for membrane surface modification in the past few years. Especially in the field of membrane fouling, these composites imparted synergistic effects of nanoparticles and polymers to membrane surfaces, where nanoparticles and polymers provide microbial and fouling resistant properties, respectively. Recently, a hybrid of GO-poly L-lysine (GO/PLL-H) was covalently bonded to the PA layer of TFC FO membranes [114]. The membrane surface grafted with GO/PLL-H had improved surface morphology, smoothness, antibacterial and hydrophilic properties.

3.5 3D Printing

Three-dimensional (3D) printing or additive manufacturing is a game changer in manufacturing space due to its capability to design complex customized products. Specifically, this technology presented the capability to design advanced materials, such as nanocomposites by introducing nanoparticles into the matrix [115]. It is different from conventional manufacturing in that it is the closest to the 'bottom up' manufacturing where a structure can be built into its designed shape using a 'layer-by-layer' approach rather than casting or forming by forging or machining. 3D printing is versatile, flexible, highly customizable and, as such, can suit most sectors of industrial production. Again, a wide range of raw materials can be used, including metallic, ceramic and polymeric materials along with combinations in the form of composites, hybrid, or functionally graded materials [116]. Generally, all the 3D printing methods follow a basic process of additive manufacturing [115]: (1) 3D modeling through CAD software, 3D scanner, or a photogrammetry procedure; (2) digitalization of the 3D model by converting it into a STL file; (3) converting the STL file data into a G-code file which contains the geometrical information of each 2D layer slicing from the 3D model; (4) printing the materials in a layer-by-layer manner.

3D printing has been applied in various fields, including membranes. For instance, 3D printing was used by Thomas et al. to create different feed channel spacer designs aimed at enhancing the spacer performance specifically for membrane distillation (MD) application [117]. The triply periodic minimal surfaces (TPMS) were used as feed spacers. The best performing TPMS spacer topology exhibited 60% higher water flux and 63% higher overall film heat transfer coefficient than the commercial spacer. Al-Shimmery et al. fabricated 3D printed composite membranes by depositing a thin PES selective layer onto ABS-like 3D printed flat and wavy structured supports [118]. The resultant flat and wavy composite membranes were tested in terms of permeance, rejection, and cleanability by filtering oil-in-water emulsions. Results showed that the pure water permeance through a wavy membrane is 30% higher than of a flat membrane. The wavy 3D printed membrane had a 52% higher permeance recovery ratio compared to the flat one after the first filtration cycle, with both membranes having an oil rejection of 96% ± 3% [118]. Besides, Tsai et al. designed three turbulence promoters with different configurations (circular, diamond and elliptic) using 3D printing technology for cross-flow MF [119]. The elliptic type of promoter with a hydraulic angle of 90° displays the flux enhancement by approximately 30–64% under 20 kPa compared to the normal type of MF, whereas the diamond type of promoter with a hydraulic angle of 60° shows a lower flux enhancement by approximately 7–16%.

Although the applications of 3D printing in membrane technology are increasing, some challenges still need attention, including void formation, poor adhesion of fillers and matrix, blockage due to filler inclusion, increased curing time, and limited resolution [120], production of high performance membranes (e.g., highly permselective membranes). These could be addressed by conducting extensive research using both experimental and simulation approaches.

4 Applications of Nanostructured Membrane for Water Purification

4.1 Desalination

Desalination has been touted as one of the promising technologies that could provide a solution for global water crisis. It offers effective removal of minerals and salts from brackish or seawater to achieve pure water for industrial, domestic, agriculture and human consumption [121]. The Global Water Intelligence and International Desalination Association revealed that the installed desalination plants around the world have the capacity to produce more than 74.8 billion liter freshwater per day and there is an increase in demand for membrane-based desalination market throughout the globe due its advantage and advancement in the production of low-cost pure water.

With the progress of membranes in desalination, nanostructured membranes have been an area of interest for many researchers to further improve the desalination performances. For instance, Shi et al. prepared GO-cellulose acetate (CA) nanocomposite membranes for high-flux desalination [122]. The GO-CA membrane with 0.01 wt.% GO showed the optimal water flux (16.82 L/m^2 h) due to its best hydrophilicity and highly porous structure. Similarly, the effect of the loading rate of candle soot (CS) nanoparticles on the desalination process using CA/polyethylene glycol (PEG) membranes was investigated [123]. The results indicated that CS nanoparticles contributed in improving the NaCl rejection with a slight reduction in the water permeability. Perera et al. fabricated a novel TFN membrane by interfacial polymerization to enhance FO membrane desalination performance [124]. They incorporated fullerenol ($C_{60}(OH)_n$, $n = 24$–28) nanomaterials into the active layer. The TFN membrane with a fullerenol loading of 400 ppm exhibited a water flux of 26.1 L/m^2 h, which is 83.03% higher than that of TFC membrane with a specific reverse salt flux of 0.18 g/L using 1 M NaCl draw solution against deionized water in FO mode. The incorporation of fullerenol also contributed to a decreased fouling propensity. Besides, Nemati et al. examined the desalination and heavy metal removal abilities using $NiFe_2O_4$/hydrogel based on 2-acrylamido-2-methyl propane sulfonic acid (HAMPS) nanocomposite modified ion exchange membrane [125].

Given their unique structural and morphological features, nanomaterials have gained considerable attention for their applications in membrane desalination. The progress in enhancing water flux and salt rejection for desalination has been witnessed and well-reviewed [126, 127]. Future studies should be directed at more long-term performance data using real feed solutions.

4.2 Contaminant Removal

In the last two decades, the advancement in membrane technology permitted the development of a variety of nanostructured membranes to effectively remove multiple water contaminants ranging in size and nature from yeast and virus to humic acids and salts. Table 1 gives some examples on recently reported nanostructured membranes (mainly in NF and RO process) elaborated for contaminants removal. Contaminants can be classified in four main classes: (i) emergent contaminants and pharmaceutical compounds that can be eliminated by TFC membrane, (ii) textile dyes, (iii) metal ions, and (iv) salts. Overall, the ability of nanostructured membranes for the removal of contaminants has been well confirmed.

Table 1 Nanomaterial based membrane preparation methods and their contaminant/solute removal efficiency

Nanomaterial	Preparation method	Applied process	Contaminant	Efficiency (%)	Ref.
Polyamide thin-film composite	Commercial	RO	Caffeine, theobromine, theophylline, amoxicillin, and penicillin G	100	[128]
PVDF/APTES-functionalized halloysites	Blending	NF	Dye, Cr (VI)	94.9, 52.3	[129]
Ultrathin GO framework	Layer-by-layer self-assembly	NF	Pb (II)	95	[130]
SAPO-34 nanoparticles	Wet phase inversion	NF	Methyl violet 6B, reactive blue 4, and acid blue 193	100	[131]
Multiple hierarchic structures on porous polypropylene	Surface modification	NF	Methylene blue, nano sized oil droplet	≤95, ≤99	[132]
rGO–CNT-AAO	Vacuum assisted filtration method, surface modification	NF	Na_2SO_4, NaCl	84, 42	[133]
$Ti_3C_2T_x$ (MXene)	Vacuum assisted filtration method	NF	MB+	~99	[92]
GO-TFC	IP	RO	NaCl	99	[134]

4.3 Fouling Mitigation

The main issue of membrane processes in water purification is its high-energy consumption derived from fouling in long term operation [26]. Membrane fouling occurs during an increase in trans membrane pressure to maintain a particular flux or during a decrease in flux when the system is operated at constant pressure. Membrane fouling can be classified as reversible fouling and irreversible fouling, which was mainly determined by pore size, surface charge, roughness, and hydrophilicity/hydrophobicity of membranes [135].

Because of the adverse effects that fouling has on membrane processes, the literature on developing nanostructured membranes in improving fouling resistance is vast, and readers are referred to comprehensive reviews [26, 136]. Incorporating metal oxide nanoparticles by blending or surface modification is one of the most promising and versatile antifouling strategies for nanostructured membranes. This favorable effect was attributed to the hydrophilic nature of most metal oxide nanoparticles. For example, the self-assembly of TiO_2 nanoparticles on a PES UF membrane via a synergistic analysis method for enhancing the antifouling behavior was demonstrated [137]. Li et al. studied the synthesis and incorporation of hollow mesoporous SiO_2 spheres (HMSS) to improve the antifouling property of PES membrane [138]. Especially, the irreversible fouling resistance was improved for a membrane with 1.5% HMSS compared with the pristine PES membrane using bovine serum albumin as the model foulant. In addition, a significant number of research papers indicates that membranes incorporated with GO show enhanced hydrophilic performance and improved water flux [139]. Lee et al. reported that a GO membrane had a high water permeability and antibiofouling capability due to its hydrophilicity and electrostatic repulsion characteristics [140]. Similarly, the negatively charged GO-incorporated nanocomposite membranes were responsible for a gradual decline in the adsorbed amount of humic acid [141].

Nanomaterials such as zeolite, multiwalled CNTs and TiO_2 nanoparticles have also been incorporated into the PA layer to enhance the membrane anti-scaling properties [142]. For instance, Zhao et al. incorporated multiwalled CNTs into PA polymer membrane [143]. The flux decline of the PA/multiwalled CNTs membrane was remarkably lower than that of neat PA membrane, demonstrating that the PA/MWNTs membrane could effectively reduce inorganic fouling. The improved antifouling property against $Ca(HCO_3)_2$ was mainly attributed to the enhanced electrostatic repulsion between charged membrane surface and the inorganic ions. The excitement and great benefits harnessing from the nanomaterials on antifouling ability of TFC membrane have spurred great interest in the desalination industry. Several key technical constraints ranging from economic feasibility to the synthesis process have to be addressed. Furthermore, research needs to continue to discover alternative means for fabricating such membranes on a large scale.

5 Technological Capacity and Economic Impact of Nanostructured Membranes

Figure 6 displays a graphic classification of the most used membrane technologies for aquatic depollution and water treatment based on pore size, operating pressure, contaminant rejection, and process cost investment. Meanwhile, the respective rate of nanocomposite membrane is illustrated. The nanostructured membrane applied in UF process represents 45% of total nanostructured membranes whereas their application on NF and RO processes represents 32% and 6%, respectively.

The incorporation of nanomaterials in membranes improved their water permeability and contaminant removal ability. The current state-of-the-art of hydrophilic commercial and hydrophobic laboratory membranes performances has been the research focus [144]. All reported data agree that commercial hydrophilic dense membranes were mainly applied in RO process with relatively low permeability ranging from 0.01 to 0.12 L/m^2 h bar, while exhibiting high selectivity toward pollutants. Conversely, laboratory-made nanostructured membranes showed an excellent permeability with relatively low contaminant rejection/selectivity.

Figure 7 compares the commercial and laboratory nanostructured membranes according to their technical capacities (pollutant removal rate and water permeability). Commercial nanostructured membranes from different manufacturers (e.g., DOW, Microdyn Nadir and Trisep) exhibited the highest pollutant removal ability (>99%) with relatively low water permeability [145]. Taking MXene nanomaterial as example, the laboratory made MXene based membranes presented an unpreceded

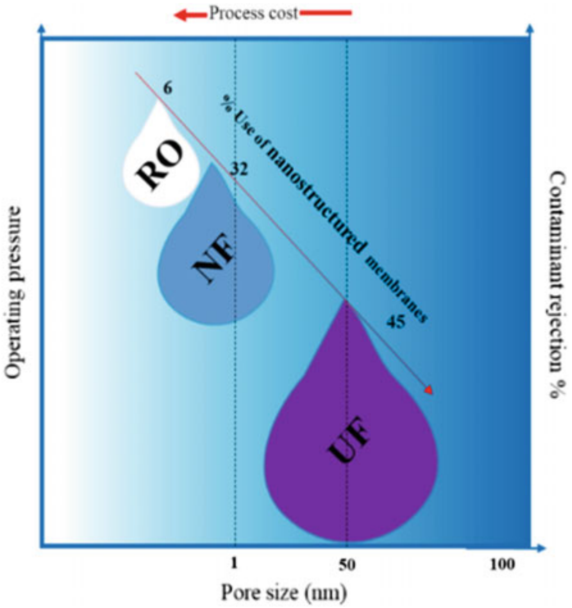

Fig. 6 Schematic classification of nanostructured membranes in water treatment

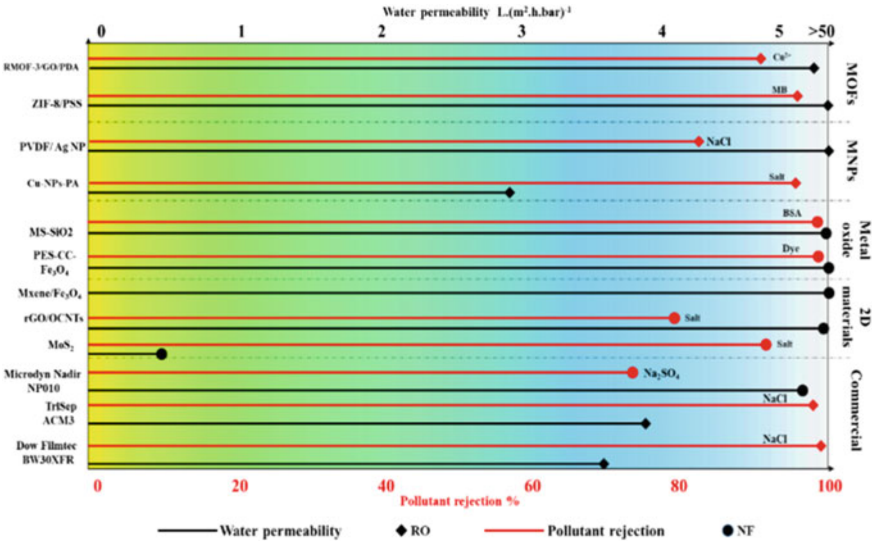

Fig. 7 Technical capacities of commercial and lab-made nanostructured membranes

ability for water permeation [91]. Correspondingly, metal/metal oxide nanoparticles based nanostructured membranes showed a limited improvement in water permeability and fouling resistance, owing to the lack of functional groups on their surface. In this issue, Li et al. reported the incorporation of carboxylated nanodiamonds into PVDF membrane during phase inversion [145]. Carboxylate group minimized the aggregation of nanomaterials compared with the raw nanodiamonds, at the same time improving the porosity and surface pore size, water permeability and hydrophilicity, and antifouling ability of obtained membrane.

For a membrane based configuration, three main parameters are considered to be crucial for an economic analysis, (i) cost investment of general installations (e.g., pumps, pipe, control and monitoring devices, energy consumption and efficiency), (ii) physical and chemical properties of the feed (i.e., salinity, pollutant concentration, feed flowrate, and target quality of treated water according to the final reuse purpose), (iii) membrane performances (e.g., water flux, pollutant hydraulic permeability, structural properties, and cost). Today, RO and NF membranes are the leading technologies for desalination installations and water treatment plants. However, current commercial membranes performances are less than optimal, resulting in inefficient and energy-intensive separation processes.

The economic impact and cost assessment of membrane based processes have been analyzed in many papers. They focused on those membrane based separation processes, especially NF and RO, which continue to be used worldwide for water treatment, industrial and municipal wastewater reuse, and desalination [146]. In 2017, BCC Research claimed that the global market for RO system components for water treatment reached nearly $6.6 billion in 2016 and it should reach over $11.0 billion by 2021, growing at a compound annual growth rate (CAGR) of 11% in this period. The report further indicated that US market of liquid separation membranes almost reached \$3.5 billion in 2018 and it is expected to reach \$5.0 billion in 2030, if the CAGR of 30% is maintained [147].

Additionally, to engineer solutions throughout process combination and intensification, research teams from all over the world developed nano-engineered, high permeance membrane materials, aiming to reduce energy consumption, thereby decreasing production cost in water treatment. To date, advances made in membrane nanomaterials could reduce the cost of wastewater treatment. This could be explained by the enhancement of water permeability and selectivity as well as the low operation pressure which reduces the energy consumption during the treatment. Moreover, the development of fouling mitigation property extends the life cycle of the process and decreases the operating and maintenance cost.

6 Conclusion and Future Perspectives

In the present chapter, various nanomaterials used to design nanostructured membrane for water purification are reviewed. 2D materials and MOFs/COFs with tunable surface chemistry are qualified to optimize membrane properties or add additional functionalities. A special emphasis has been given to the most adopted preparation techniques of nanostructured membranes, along with their applications in water purification. Specifically, 3D printing, expected to have a significant future impact on designing nanostructured membranes, is highlighted.

The toxicity of nanomaterials was also reviewed with a brief discussion of their economic impact on water purification. Nanostructured membranes have huge potential in developing next-generation membrane technology by removing microorganisms, heavy metal, salt ions, organic compounds, and emerging micropollutants. They would have leapfrogging potential for futurist multifunctional membranes. Nevertheless, several challenges for industrial application still exist, including (i) difficulty/cost for large scale (ii) recyclability/reusability of the membranes at the end of cycle, (iii) lack of comprehension on their behavior during the treatment of complex municipal and industrial effluents. Meanwhile, a continue working is necessary on understanding and improving the surface physicochemical properties of nanostructured membrane, such as hydrophilicity and surface charge, to gain wider social and economic acceptability.

References

1. Progress on Safe Treatment and Use of Wastewater: Piloting the Monitoring Methodology and Initial Findings for SDG Indicator 6.3.1. World Health Organization and UN-HABITAT, Geneva (2018)
2. Saraswathi, S.A., Sundaram, M., Nagendran, A., Rana, D.: Tailored polymer nanocomposite membranes based on carbon, metal oxide and silicon nanomaterials: a review. J. Mater. Chem. A **7**(15), 8723–8745 (2019)
3. Fane, A.G., Wang, R., Hu, M.X.: Synthetic membranes for water purification: status and future. Angew. Chem. Int. Ed. **54**(11), 3368–3386 (2015)
4. Werber, J.R., Osuji, C.O., Elimelech, M.: Materials for next-generation desalination and water purification membranes. Nat. Rev. Mater. 16018 (2016)
5. Alvarez, P.J., Chan, C.K., Elimelech, M., Halas, N.J., Villagrán, D.: Emerging opportunities for nanotechnology to enhance water security. Nat. Nanotechnol. **13**(8), 634 (2018)
6. Pendergast, M.M., Hoek, E.M.V.: A review of water treatment membrane nanotechnologies. Energy Environ. Sci. **4**(6), 1946–1971 (2011)
7. Qu, X., Alvarez, P.J.J., Li, Q.: Applications of nanotechnology in water and wastewater treatment. Water Res. **47**(12), 3931–3946 (2013)
8. Li, R., Zhang, L., Wang, P.: Rational design of nanomaterials for water treatment. Nanoscale **7**(41), 17167–17194 (2015)
9. Yang, H.-C., Hou, J., Chen, V., Xu, Z.-K.: Surface and interface engineering for organic-inorganic composite membranes. J. Mater. Chem. A **4**, 9716–9729 (2016)
10. Li, X., Liu, Y., Wang, J., Gascon, J., Li, J., Van der Bruggen, B.: Metal-organic frameworks based membranes for liquid separation. Chem. Soc. Rev. **46**(23), 7124–7144 (2017)
11. Yuan, S., Li, X., Zhu, J., Zhang, G., Van Puyvelde, P., Van der Bruggen, B.: Covalent organic frameworks for membrane separation. Chem. Soc. Rev. **48**(10), 2665–2681 (2019)
12. Zhu, J., Hou, J., Uliana, A., Zhang, Y., Tian, M., Van der Bruggen, B.: The rapid emergence of two-dimensional nanomaterials for high-performance separation membranes. J. Mater. Chem. A **6**(9), 3773–3792 (2018)
13. Chernousova, S., Epple, M.: Silver as antibacterial agent: ion, nanoparticle, and metal. Angew. Chem. Int. Ed. **52**(6), 1636–1653 (2013)
14. Wang, Z., Xia, T., Liu, S.: Mechanisms of nanosilver-induced toxicological effects: more attention should be paid to its sublethal effects. Nanoscale **7**(17), 7470–7481 (2015)
15. Zodrow, K., Brunet, L., Mahendra, S., Li, D., Zhang, A., Li, Q., Alvarez, P.J.J.: Polysulfone ultrafiltration membranes impregnated with silver nanoparticles show improved biofouling resistance and virus removal. Water Res. **43**(3), 715–723 (2009)
16. Zhang, M., Zhang, K., De Gusseme, B., Verstraete, W.: Biogenic silver nanoparticles (bio-Ag^0) decrease biofouling of bio-Ag^0/PES nanocomposite membranes. Water Res. **46**(7), 2077–2087 (2012)
17. Mecha, C., Pillay, V.L.: Development and evaluation of woven fabric microfiltration membranes impregnated with silver nanoparticles for potable water treatment. J. Membr. Sci. **458**, 149–156 (2014)
18. Zhu, J., Hou, J., Zhang, Y., Tian, M., He, T., Liu, J., Chen, V.: Polymeric antimicrobial membranes enabled by nanomaterials for water treatment. J. Membr. Sci. **550**, 173–197 (2018)
19. Mukherjee, M., De, S.: Antibacterial polymeric membranes: a short review. Environ Sci: Water Res. Technol. **4**(8), 1078–1104 (2018)
20. Huang, L., Zhao, S., Wang, Z., Wu, J., Wang, J., Wang, S.: In situ immobilization of silver nanoparticles for improving permeability, antifouling and anti-bacterial properties of ultrafiltration membrane. J. Membr. Sci. **499**, 269–281 (2016)
21. Dong, C., Wang, Z., Wu, J., Wang, Y., Wang, J., Wang, S.: A green strategy to immobilize silver nanoparticles onto reverse osmosis membrane for enhanced anti-biofouling property. Desalination **401**, 32–41 (2017)

22. Akhavan, O., Abdolahad, M., Abdi, Y., Mohajerzadeh, S.: Silver nanoparticles within vertically aligned multi-wall carbon nanotubes with open tips for antibacterial purposes. J. Mater. Chem. **21**(2), 387–393 (2011)
23. Huang, X., Marsh, K.L., McVerry, B.T., Hoek, E.M., Kaner, R.B.: Low-fouling antibacterial reverse osmosis membranes via surface grafting of graphene oxide. ACS Appl. Mater. Interface **8**(23), 14334–14338 (2016)
24. Habib, Z., Khan, S.J., Ahmad, N.M., Shahzad, H.M.A., Jamal, Y., Hashmi, I.: Antibacterial behavior of surface modified composite polyamide nanofiltration (NF) membrane by immobilizing Ag doped TiO_2 nanoparticles. Environ. Technol. 1–48 (2019, in press)
25. Rizzello, L., Pompa, P.P.: Nanosilver-based antibacterial drugs and devices: mechanisms, methodological drawbacks, and guidelines. Chem. Soc. Rev. **43**(5), 1501–1518 (2014)
26. Jhaveri, J.H., Murthy, Z.V.P.: A comprehensive review on anti-fouling nanocomposite membranes for pressure driven membrane separation processes. Desalination **379**, 137–154 (2016)
27. Tang, S.C., Lo, I.M.: Magnetic nanoparticles: essential factors for sustainable environmental applications. Water Res. **47**(8), 2613–2632 (2013)
28. Duan, L., Zhao, Q., Liu, J., Zhang, Y.: Antibacterial behavior of halloysite nanotubes decorated with copper nanoparticles in a novel mixed matrix membrane for water purification. Environ. Sci.: Water Res. Technol. **1**(6), 874–881 (2015)
29. Ma, W., Soroush, A., Luong, T.V.A., Brennan, G., Rahaman, M.S., Asadishad, B., Tufenkji, N.: Spray- and spin-assisted layer-by-layer assembly of copper nanoparticles on thin-film composite reverse osmosis membrane for biofouling mitigation. Water Res. **99**, 188–199 (2016)
30. Zhu, J., Wang, J., Uliana, A.A., Tian, M., Zhang, Y., Zhang, Y., Volodin, A., Simoens, K., Yuan, S., Li, J.: Mussel-inspired architecture of high-flux loose nanofiltration membrane functionalized with antibacterial reduced graphene oxide–copper nanocomposites. ACS Appl. Mater. Interface **9**(34), 28990–29001 (2017)
31. Simeonidis, K., Mourdikoudis, S., Kaprara, E., Mitrakas, M., Polavarapu, L.: Inorganic engineered nanoparticles in drinking water treatment: a critical review. Environ. Sci.: Water Res. Technol. **2**(1), 43–70 (2016)
32. Lowry, G.V., Johnson, K.M.: Congener-specific dechlorination of dissolved PCBs by microscale and nanoscale zerovalent iron in a water/methanol solution. Environ. Sci. Technol. **38**(19), 5208–5216 (2004)
33. Wang, X., Chen, C., Liu, H., Ma, J.: Preparation and characterization of PAA/PVDF membrane-immobilized Pd/Fe nanoparticles for dechlorination of trichloroacetic acid. Water Res. **42**(18), 4656–4664 (2008)
34. Wan, H., Briot, N.J., Saad, A., Ormsbee, L., Bhattacharyya, D.: Pore functionalized PVDF membranes with in-situ synthesized metal nanoparticles: material characterization, and toxic organic degradation. J. Membr. Sci. **530**, 147–157 (2017)
35. Bet-Moushoul, E., Mansourpanah, Y., Farhadi, K., Tabatabaei, M.: TiO_2 nanocomposite based polymeric membranes: a review on performance improvement for various applications in chemical engineering processes. Chem. Eng. J. **283**, 29–46 (2016)
36. Liu, K., Cao, M., Fujishima, A., Jiang, L.: Bio-inspired titanium dioxide materials with special wettability and their applications. Chem. Rev. **114**(19), 10044–10094 (2014)
37. Chen, X., Mao, S.S.: Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications. Chem. Rev. **107**(7), 2891–2959 (2007)
38. Ngang, H., Ooi, B., Ahmad, A., Lai, S.: Preparation of PVDF-TiO_2 mixed-matrix membrane and its evaluation on dye adsorption and UV-cleaning properties. Chem. Eng. J. **197**, 359–367 (2012)
39. Rajesh, S., Senthilkumar, S., Jayalakshmi, A., Nirmala, M., Ismail, A., Mohan, D.: Preparation and performance evaluation of poly (amide-imide) and TiO_2 nanoparticles impregnated polysulfone nanofiltration membranes in the removal of humic substances. Colloid Surf. A: Physicochem. Eng. Asp. **418**, 92–104 (2013)

40. Wang, Y., Li, Y., Yang, H., Xu, Z-l: Super-wetting, photoactive TiO_2 coating on amino-silane modified PAN nanofiber membranes for high efficient oil-water emulsion separation application. J. Membr. Sci. **580**, 40–48 (2019)
41. Zhang, X., Du, A.J., Lee, P., Sun, D.D., Leckie, J.O.: Grafted multifunctional titanium dioxide nanotube membrane: separation and photodegradation of aquatic pollutant. Appl. Catal. B: Environ. **84**(1–2), 262–267 (2008)
42. Kuvarega, A.T., Khumalo, N., Dlamini, D., Mamba, B.B.: Polysulfone/N, Pd co-doped TiO_2 composite membranes for photocatalytic dye degradation. Sep. Purif. Technol. **191**, 122–133 (2018)
43. Chin, S.S., Chiang, K., Fane, A.G.: The stability of polymeric membranes in a TiO_2 photocatalysis process. J. Membr. Sci. **275**(1–2), 202–211 (2006)
44. Shi, Y., Huang, J., Zeng, G., Cheng, W., Hu, J.: Photocatalytic membrane in water purification: is it stepping closer to be driven by visible light? J. Membr. Sci. **584**, 364–392 (2019)
45. Li, L., Fan, M., Brown, R.C., Van Leeuwen, J., Wang, J., Wang, W., Song, Y., Zhang, P.: Synthesis, properties, and environmental applications of nanoscale iron-based materials: a review. Crit. Rev. Environ. Sci. Technol. **36**(5), 405–431 (2006)
46. Xu, G.-R., Wang, J.-N., Li, C.-J.: Preparation of hierarchically nanofibrous membrane and its high adaptability in hexavalent chromium removal from water. Chem. Eng. J. **198**, 310–317 (2012)
47. Li, C.-J., Li, Y.-J., Wang, J.-N., Cheng, J.: PA6@FexOy nanofibrous membrane preparation and its strong Cr (VI)-removal performance. Chem. Eng. J. **220**, 294–301 (2013)
48. Daraei, P., Madaeni, S.S., Ghaemi, N., Salehi, E., Khadivi, M.A., Moradian, R., Astinchap, B.: Novel polyethersulfone nanocomposite membrane prepared by PANI/Fe_3O_4 nanoparticles with enhanced performance for Cu (II) removal from water. J. Membr. Sci. **415**, 250–259 (2012)
49. Abdi, G., Alizadeh, A., Zinadini, S., Moradi, G.: Removal of dye and heavy metal ion using a novel synthetic polyethersulfone nanofiltration membrane modified by magnetic graphene oxide/metformin hybrid. J. Membr. Sci. **552**, 326–335 (2018)
50. Das, D., Nath, B.C., Phukon, P., Dolui, S.K.: Synthesis and evaluation of antioxidant and antibacterial behavior of CuO nanoparticles. Colloids Surf. B **101**, 430–433 (2013)
51. Shalaby, T., Hamad, H., Ibrahim, E., Mahmoud, O., Al-Oufy, A.: Electrospun nanofibers hybrid composites membranes for highly efficient antibacterial activity. Ecotoxicol. Environ. Saf. **162**, 354–364 (2018)
52. Leo, C., Lee, W.C., Ahmad, A., Mohammad, A.W.: Polysulfone membranes blended with ZnO nanoparticles for reducing fouling by oleic acid. Sep. Purif. Technol. **89**, 51–56 (2012)
53. Li, N., Zhang, J., Tian, Y., Zhao, J., Zhang, J., Zuo, W.: Anti-fouling potential evaluation of PVDF membranes modified with ZnO against polysaccharide. Chem. Eng. J. **304**, 165–174 (2016)
54. Ahmad, A., Abdulkarim, A., Shafie, Z.M., Ooi, B.: Fouling evaluation of PES/ZnO mixed matrix hollow fiber membrane. Desalination **403**, 53–63 (2017)
55. Chen, X., Huang, G., An, C., Feng, R., Wu, Y., Huang, C.: Plasma-induced PAA-ZnO coated PVDF membrane for oily wastewater treatment: preparation, optimization, and characterization through Taguchi OA design and synchrotron-based X-ray analysis. J. Membr. Sci. **582**, 70–82 (2019)
56. Li, X., Sotto, A., Li, J., Van der Bruggen, B.: Progress and perspectives for synthesis of sustainable antifouling composite membranes containing in situ generated nanoparticles. J. Membr. Sci. **524**, 502–528 (2017)
57. Ananth, A., Arthanareeswaran, G., Mok, Y.S.: Effects of in situ and ex situ formations of silica nanoparticles on polyethersulfone membranes. Polym. Bull. **71**, 2851–2861 (2014)
58. Yang, X., Sun, H., Pal, A., Bai, Y., Shao, L.: Biomimetic silicification on membrane surface for highly efficient treatments of both oil-in-water emulsion and protein wastewater. ACS Appl. Mater. Interface **10**(35), 29982–29991 (2018)
59. Lv, Y., Yang, H.-C., Liang, H.-Q., Wan, L.-S., Xu, Z.-K.: Novel nanofiltration membrane with ultrathin zirconia film as selective layer. J. Membr. Sci. **500**, 265–271 (2016)

60. Slater, A.G., Cooper, A.I.: Function-led design of new porous materials. Science **348**(6238), 8075 (2015)
61. Li, T., Zhang, W., Zhai, S., Gao, G., Ding, J., Zhang, W., Liu, Y., Zhao, X., Pan, B., Lv, L.: Efficient removal of nickel (II) from high salinity wastewater by a novel PAA/ZIF-8/PVDF hybrid ultrafiltration membrane. Water Res. **143**, 87–98 (2018)
62. Duong, P.H., Kuehl, V.A., Mastorovich, B., Hoberg, J.O., Parkinson, B.A., Li-Oakey, K.D.: Carboxyl-functionalized covalent organic framework as a two-dimensional nanofiller for mixed-matrix ultrafiltration membranes. J. Membr. Sci. **574**, 338–348 (2019)
63. Zhang, P., Gong, J.-L., Zeng, G.-M., Song, B., Liu, H.-Y., Huan, S.-Y., Li, J.: Ultrathin reduced graphene oxide/MOF nanofiltration membrane with improved purification performance at low pressure. Chemosphere **204**, 378–389 (2018)
64. Yang, H., Cheng, X., Cheng, X., Pan, F., Wu, H., Liu, G., Song, Y., Cao, X., Jiang, Z.: Highly water-selective membranes based on hollow covalent organic frameworks with fast transport pathways. J. Membr. Sci. **565**, 331–341 (2018)
65. Shen, J., Liu, G., Huang, K., Jin, W., Lee, K.R., Xu, N.: Membranes with fast and selective gas-transport channels of laminar graphene oxide for efficient CO_2 capture. Angew. Chem. **127**(2), 588–592 (2015)
66. Liu, G., Cadiau, A., Liu, Y., Adil, K., Chernikova, V., Carja, I.D., Belmabkhout, Y., Karunakaran, M., Shekhah, O., Zhang, C.: Enabling fluorinated MOF-based membranes for simultaneous removal of H_2S and CO_2 from natural gas. Angew. Chem. Int. Ed. **57**(45), 14811–14816 (2018)
67. Varoon, K., Zhang, X., Elyassi, B., Brewer, D.D., Gettel, M., Kumar, S., Lee, J.A., Maheshwari, S., Mittal, A., Sung, C.-Y.: Dispersible exfoliated zeolite nanosheets and their application as a selective membrane. Science **334**(6052), 72–75 (2011)
68. Manzeli, S., Ovchinnikov, D., Pasquier, D., Yazyev, O.V., Kis, A.: 2D transition metal dichalcogenides. Nat. Rev. Mater. **2**(8), 17033 (2017)
69. Zheng, Z., Grünker, R., Feng, X.: Synthetic two-dimensional materials: a new paradigm of membranes for ultimate separation. Adv. Mater. **28**(31), 6529–6545 (2016)
70. Novoselov, K.S., Jiang, D., Schedin, F., Booth, T., Khotkevich, V., Morozov, S., Geim, A.K.: Two-dimensional atomic crystals. Proc. Natl. Acad. Sci. USA **102**(30), 10451–10453 (2005)
71. Edwards, R.S., Coleman, K.S.: Graphene synthesis: relationship to applications. Nanoscale **5**(1), 38–51 (2013)
72. Yu, J., Li, J., Zhang, W., Chang, H.: Synthesis of high quality two-dimensional materials via chemical vapor deposition. Chem. Sci. **6**(12), 6705–6716 (2015)
73. Tan, C., Zhang, H.: Wet-chemical synthesis and applications of non-layer structured two-dimensional nanomaterials. Nat. Commun. **6**, 7873 (2015)
74. Cohen-Tanugi, D., Grossman, J.C.: Nanoporous graphene as a reverse osmosis membrane: recent insights from theory and simulation. Desalination **366**, 59–70 (2015)
75. Song, N., Gao, X., Ma, Z., Wang, X., Wei, Y., Gao, C.: A review of graphene-based separation membrane: materials, characteristics, preparation and applications. Desalination **437**, 59–72 (2018)
76. Dreyer, D.R., Park, S., Bielawski, C.W., Ruoff, R.S.: The chemistry of graphene oxide. Chem. Soc. Rev. **39**(1), 228–240 (2010)
77. Sun, P., Wang, K., Zhu, H.: Recent developments in graphene-based membranes: structure, mass-transport mechanism and potential applications. Adv. Mater. **28**(12), 2287–2310 (2016)
78. Zhang, N., Qi, W., Huang, L., Jiang, E., Bao, J., Zhang, X., An, B., He, G.: Review on structural control and modification of graphene oxide-based membranes in water treatment: From separation performance to robust operation. Chinese J. Chem. Eng. (2019)
79. Chen, L., Li, N., Wen, Z., Zhang, L., Chen, Q., Chen, L., Si, P., Feng, J., Li, Y., Lou, J.: Graphene oxide based membrane intercalated by nanoparticles for high performance nanofiltration application. Chem. Eng. J. **347**, 12–18 (2018)
80. Zhang, H., Quan, X., Chen, S., Fan, X., Wei, G., Yu, H.: Combined effects of surface charge and pore size on co-enhanced permeability and ion selectivity through RGO-OCNT nanofiltration membranes. Environ. Sci. Technol. **52**(8), 4827–4834 (2018)

81. Azamat, J., Khataee, A.: Improving the performance of heavy metal separation from water using MoS_2 membrane: molecular dynamics simulation. Comput. Mater. Sci. **137**, 201–207 (2017)
82. Heiranian, M., Farimani, A.B., Aluru, N.R.: Water desalination with a single-layer MoS_2 nanopore. Nat. Commun. **6**, 8616 (2015)
83. Hirunpinyopas, W., Prestat, E., Worrall, S.D., Haigh, S.J., Dryfe, R.A., Bissett, M.A.: Desalination and nanofiltration through functionalized laminar MoS_2 membranes. ACS Nano **11**(11), 11082–11090 (2017)
84. Huang, L., Zhang, M., Li, C., Shi, G.: Graphene-based membranes for molecular separation. J. Phys. Chem. Lett. **6**(14), 2806–2815 (2015)
85. Deng, M., Kwac, K., Li, M., Jung, Y., Park, H.G.: Stability, molecular sieving, and ion diffusion selectivity of a lamellar membrane from two-dimensional molybdenum disulfide. Nano Lett. **17**(4), 2342–2348 (2017)
86. Sun, L., Ying, Y., Huang, H., Song, Z., Mao, Y., Xu, Z., Peng, X.: Ultrafast molecule separation through layered WS_2 nanosheet membranes. ACS Nano **8**(6), 6304–6311 (2014)
87. Low, I.M.: Advances in ceramic matrix composites: introduction. In: Advances in Ceramic Matrix Composites, pp. 1–7. Elsevier (2018)
88. Pang, W.K., Low, I.M.: Understanding and improving the thermal stability of layered ternary carbides in ceramic matrix composites. In: Advances in Ceramic Matrix Composites, pp. 340–368. Elsevier (2014)
89. Chakraborty, P., Das, T., Saha-Dasgupta, T.: MXene: a new trend in 2D materials science. Comprehensive Nanoscience and Nanotechnology, 2nd edn., pp. 319–330 (2018)
90. Ren, C.E., Hatzell, K.B., Alhabeb, M., Ling, Z., Mahmoud, K.A., Gogotsi, Y.: Charge-and size-selective ion sieving through $Ti_3C_2T_x$ MXene membranes. J. Phys. Chem. Lett. **6**(20), 4026–4031 (2015)
91. Ding, L., Wei, Y., Wang, Y., Chen, H., Caro, J., Wang, H.: A two-dimensional lamellar membrane: MXene nanosheet stacks. Angew. Chem. Int. Ed. **56**(7), 1825–1829 (2017)
92. Kang, K.M., Kim, D.W., Ren, C.E., Cho, K.M., Kim, S.J., Choi, J.H., Nam, Y.T., Gogotsi, Y., Jung, H.-T.: Selective molecular separation on $Ti_3C_2T_x$-graphene oxide membranes during pressure-driven filtration: comparison with graphene oxide and mXenes. ACS Appl. Mater. Interface **9**(51), 44687–44694 (2017)
93. Wu, X., Hao, L., Zhang, J., Zhang, X., Wang, J., Liu, J.: Polymer-$Ti_3C_2T_x$ composite membranes to overcome the trade-off in solvent resistant nanofiltration for alcohol-based system. J. Membr. Sci. **515**, 175–188 (2016)
94. Hao, L., Zhang, H., Wu, X., Zhang, J., Wang, J., Li, Y.: Novel thin-film nanocomposite membranes filled with multi-functional $Ti_3C_2T_x$ nanosheets for task-specific solvent transport. Compos. A: Appl. Sci. Manuf. **100**, 139–149 (2017)
95. Kabir, E., Kumar, V., Kim, K.-H., Yip, A.C.K., Sohn, J.R.: Environmental impacts of nanomaterials. J. Environ. Manag. **225**, 261–271 (2018)
96. Colvin, V.L.: The potential environmental impact of engineered nanomaterials. Nat. Biotechnol. **21**(10), 1166 (2003)
97. Lee, J., Mahendra, S., Alvarez, P.J.: Nanomaterials in the construction industry: a review of their applications and environmental health and safety considerations. ACS Nano **4**(7), 3580–3590 (2010)
98. Patil, S.S., Shedbalkar, U.U., Truskewycz, A., Chopade, B.A., Ball, A.S.: Nanoparticles for environmental clean-up: a review of potential risks and emerging solutions. Environ. Technol. Innov. **5**, 10–21 (2016)
99. Paul, M., Jons, S.D.: Chemistry and fabrication of polymeric nanofiltration membranes: a review. Polymer **103**, 417–456 (2016)
100. Peyki, A., Rahimpour, A., Jahanshahi, M.: Preparation and characterization of thin film composite reverse osmosis membranes incorporated with hydrophilic SiO_2 nanoparticles. Desalination **368**, 152–158 (2015)
101. Valentino, L., Matsumoto, M., Dichtel, W.R., Mariñas, B.J.: Development and performance characterization of a polyimine covalent organic framework thin-film composite nanofiltration membrane. Environ. Sci. Technol. **51**(24), 14352–14359 (2017)

102. Akther, N., Phuntsho, S., Chen, Y., Ghaffour, N., Shon, H.K.: Recent advances in nanomaterial-modified polyamide thin-film composite membranes for forward osmosis processes. J. Membr. Sci. **584**, 20–45 (2019)
103. Wang, Z., Wang, Z., Lin, S., Jin, H., Gao, S., Zhu, Y., Jin, J.: Nanoparticle-templated nanofiltration membranes for ultrahigh performance desalination. Nat. Chem. **9**(1), 2004 (2018)
104. Li, X., Fang, X., Pang, R., Li, J., Sun, X., Shen, J., Han, W., Wang, L.: Self-assembly of TiO_2 nanoparticles around the pores of PES ultrafiltration membrane for mitigating organic fouling. J. Membr. Sci. **467**, 226–235 (2014)
105. Fischer, K., Grimm, M., Meyers, J., Dietrich, C., Gläser, R., Schulze, A.: Photoactive microfiltration membranes via directed synthesis of TiO_2 nanoparticles on the polymer surface for removal of drugs from water. J. Membr. Sci. **478**, 49–57 (2015)
106. Hu, Y., Lü, Z., Wei, C., Yu, S., Liu, M., Gao, C.: Separation and antifouling properties of hydrolyzed PAN hybrid membranes prepared via in-situ sol-gel SiO_2 nanoparticles growth. J. Membr. Sci. **545**, 250–258 (2018)
107. Li, X., Li, J., Van der Bruggen, B., Sun, X., Shen, J., Han, W., Wang, L.: Fouling behavior of polyethersulfone ultrafiltration membranes functionalized with sol-gel formed ZnO nanoparticles. RSC Adv. **5**(63), 50711–50719 (2015)
108. Zhao, X., Jia, N., Cheng, L., Liu, L., Gao, C.: Dopamine-induced biomimetic mineralization for in situ developing antifouling hybrid membrane. J. Membr. Sci. **560**, 47–57 (2018)
109. Li, X., Pang, R., Li, J., Sun, X., Shen, J., Han, W., Wang, L.: In situ formation of Ag nanoparticles in PVDF ultrafiltration membrane to mitigate organic and bacterial fouling. Desalination **324**, 48–56 (2013)
110. Miller, D.J., Dreyer, D.R., Bielawski, C.W., Paul, D.R., Freeman, B.D.: Surface modification of water purification membranes. Angew. Chem. Int. Ed. **56**(17), 4662–4711 (2017)
111. Zhang, R.-X., Braeken, L., Luis, P., Wang, X.-L., Van der Bruggen, B.: Novel binding procedure of TiO_2 nanoparticles to thin film composite membranes via self-polymerized polydopamine. J. Membr. Sci. **437**, 179–188 (2013)
112. Ren, S., Boo, C., Guo, N., Wang, S., Elimelech, M., Wang, Y.: Photocatalytic reactive ultrafiltration membrane for removal of antibiotic resistant bacteria and antibiotic resistance genes from wastewater effluent. Environ. Sci. Technol. **52**(15), 8666–8673 (2018)
113. Choi, W., Choi, J., Bang, J., Lee, J.-H.: Layer-by-layer assembly of graphene oxide nanosheets on polyamide membranes for durable reverse-osmosis applications. ACS Appl. Mater. Interface **5**(23), 12510–12519 (2013)
114. Hegab, H.M., ElMekawy, A., Barclay, T.G., Michelmore, A., Zou, L., Saint, C.P., Ginic-Markovic, M.: Fine-tuning the surface of forward osmosis membranes via grafting graphene oxide: performance patterns and biofouling propensity. ACS Appl. Mater. Interface **7**(32), 18004–18016 (2015)
115. Guo, H., Lv, R., Bai, S.: Recent advances on 3D printing graphene-based composites. Nano Mater. Sci. **1**(2), 101–115 (2019)
116. Tofail, S.A., Koumoulos, E.P., Bandyopadhyay, A., Bose, S., O'Donoghue, L., Charitidis, C.: Additive manufacturing: scientific and technological challenges, market uptake and opportunities. Mater. Today **21**(1), 22–37 (2018)
117. Thomas, N., Sreedhar, N., Al-Ketan, O., Rowshan, R., Al-Rub, R.K.A., Arafat, H.: 3D printed triply periodic minimal surfaces as spacers for enhanced heat and mass transfer in membrane distillation. Desalination **443**, 256–271 (2018)
118. Al-Shimmery, A., Mazinani, S., Ji, J., Chew, Y.J., Mattia, D.: 3D printed composite membranes with enhanced anti-fouling behaviour. J. Membr. Sci. **574**, 76–85 (2019)
119. Tsai, H.-Y., Huang, A., Luo, Y.-L., Hsu, T.-Y., Chen, C.-H., Hwang, K.-J., Ho, C.-D., Tung, K.-L.: 3D printing design of turbulence promoters in a cross-flow microfiltration system for fine particles removal. J. Membr. Sci. **573**, 647–656 (2019)
120. Parandoush, P., Lin, D.: A review on additive manufacturing of polymer-fiber composites. Compos. Struct. **182**, 36–53 (2017)

121. Chandrashekara, M., Yadav, A.: Water desalination system using solar heat: a review. Renew. Sustain. Energy Rev. **67**, 1308–1330 (2017)
122. Shi, Y., Li, C., He, D., Shen, L., Bao, N.: Preparation of graphene oxide-cellulose acetate nanocomposite membrane for high-flux desalination. J. Membr. Sci. **52**(22), 13296–13306 (2017)
123. Abdelhamid, A.E., Khalil, A.M.: Polymeric membranes based on cellulose acetate loaded with candle soot nanoparticles for water desalination. J. Macromol. Sci. A **56**(2), 153–161 (2019)
124. Perera, M.G.N., Galagedara, Y.R., Ren, Y., Jayaweera, M., Zhao, Y., Weerasooriya, R.: Fabrication of fullerenol-incorporated thin-film nanocomposite forward osmosis membranes for improved desalination performances. J. Polym. Res. **25**(9), 199 (2018)
125. Nemati, M., Hosseini, S., Parvizian, F., Rafiei, N., Van der Bruggen, B.: Desalination and heavy metal ion removal from water by new ion exchange membrane modified by synthesized $NiFe_2O_4$/HAMPS nanocomposite. Ionics 1–11 (2019)
126. Daer, S., Kharraz, J., Giwa, A., Hasan, S.W.: Recent applications of nanomaterials in water desalination: a critical review and future opportunities. Desalination **367**, 37–48 (2015)
127. Teow, Y.H., Mohammad, A.W.: New generation nanomaterials for water desalination: a review. Desalination **451**, 2–17 (2019)
128. Lopera, A.E.-C., Ruiz, S.G., Alonso, J.M.Q.: Removal of emerging contaminants from wastewater using reverse osmosis for its subsequent reuse: pilot plant. J. Water Process. Eng. **29**, 100800 (2019)
129. Zeng, G., He, Y., Zhan, Y., Zhang, L., Pan, Y., Zhang, C., Yu, Z.: Novel polyvinylidene fluoride nanofiltration membrane blended with functionalized halloysite nanotubes for dye and heavy metal ions removal. J. Hazard. Mater. **317**, 60–72 (2016)
130. Zhang, Y., Zhang, S., Gao, J., Chung, T.-S.: Layer-by-layer construction of graphene oxide (GO) framework composite membranes for highly efficient heavy metal removal. J. Membr. Sci. **515**, 230–237 (2016)
131. Ghaemi, N., Safari, P.: 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**, 376–388 (2018)
132. Wang, Z., Ji, S., Zhang, J., He, F., Xu, Z., Peng, S., Li, Y.: Dual functional membrane with multiple hierarchical structures (MHS) for simultaneous and high-efficiency removal of dye and nano-sized oil droplets in water under high flux. J. Membr. Sci. **564**, 317–327 (2018)
133. Chen, X., Qiu, M., Ding, H., Fu, K., Fan, Y.: A reduced graphene oxide nanofiltration membrane intercalated by well-dispersed carbon nanotubes for drinking water purification. Nanoscale **8**(10), 5696–5705 (2016)
134. Chae, H.-R., Lee, J., Lee, C.-H., Kim, I.-C., Park, P.-K.: Graphene oxide-embedded thin-film composite reverse osmosis membrane with high flux, anti-biofouling, and chlorine resistance. J. Membr. Sci. **483**, 128–135 (2015)
135. Qu, F., Liang, H., Zhou, J., Nan, J., Shao, S., Zhang, J., Li, G.: Ultrafiltration membrane fouling caused by extracellular organic matter (EOM) from *Microcystis aeruginosa*: effects of membrane pore size and surface hydrophobicity. J. Membr. Sci. **449**, 58–66 (2014)
136. Kim, J., Van der Bruggen, B.: The use of nanoparticles in polymeric and ceramic membrane structures: review of manufacturing procedures and performance improvement for water treatment. Environ. Pollut. **158**(7), 2335–2349 (2010)
137. Li, X., Li, J., Fang, X., Bakzhan, K., Wang, L., Van der Bruggen, B.: A synergetic analysis method for antifouling behavior investigation on PES ultrafiltration membrane with self-assembled TiO_2 nanoparticles. J. Colloid Interface Sci. **469**, 164–176 (2016)
138. Li, Q., Pan, S., Li, X., Liu, C., Li, J., Sun, X., Shen, J., Han, W., Wang, L.: Hollow mesoporous silica spheres/polyethersulfone composite ultrafiltration membrane with enhanced antifouling property. Colloid Surf. A **487**, 180–189 (2015)
139. Jiang, Y., Biswas, P., Fortner, J.D.: A review of recent developments in graphene-enabled membranes for water treatment. Environ. Sci.: Water Res. Technol. **2**(6), 915–922 (2016)

140. Lee, J., Chae, H.-R., Won, Y.J., Lee, K., Lee, C.-H., Lee, H.H., Kim, I.-C., Lee, J-m: Graphene oxide nanoplatelets composite membrane with hydrophilic and antifouling properties for wastewater treatment. J. Membr. Sci. **448**, 223–230 (2013)
141. Shao, J., Hou, J., Song, H.: Comparison of humic acid rejection and flux decline during filtration with negatively charged and uncharged ultrafiltration membranes. Water Res. **45**(2), 473–482 (2011)
142. Ong, C., Goh, P., Lau, W., Misdan, N., Ismail, A.: Nanomaterials for biofouling and scaling mitigation of thin film composite membrane: a review. Desalination **393**, 2–15 (2016)
143. Zhao, H., Qiu, S., Wu, L., Zhang, L., Chen, H., Gao, C.: Improving the performance of polyamide reverse osmosis membrane by incorporation of modified multi-walled carbon nanotubes. J. Membr. Sci. **450**, 249–256 (2014)
144. Sterlitech (2019) https://www.sterlitech.com/flat-sheet-membranes.html
145. Li, Y., Huang, S., Zhou, S., Fane, A.G., Zhang, Y., Zhao, S.: Enhancing water permeability and fouling resistance of polyvinylidene fluoride membranes with carboxylated nanodiamonds. J. Membr. Sci. **556**, 154–163 (2018)
146. Osipi, S.R., Secchi, A.R., Borges, C.P.: Cost assessment and retro-techno-economic analysis of desalination technologies in onshore produced water treatment. Desalination **430**, 107–119 (2018)
147. BCC Research LLC MST041J Membrane Technology for Liquid and Gas Separations (2019). https://www.bccresearch.com/market-research/membrane-and-separation-technology/membrane-separation-technology-research-review.html