

Perspectives on Surface Functionalization of Polymeric Membranes with Metal and Metal-Oxide Nanoparticles for Water/Wastewater Treatment

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ABSTRACT. Membrane filtration technology has been extensively applied in water/wastewater treatment to help address the issue of water shortage, in which polymeric membranes are most commonly used. However, the hydrophobic nature of polymeric membranes would contribute to membrane damage caused by accumulation of organic/inorganic fouling during filtration processes. The strategy of membrane surface functionalization with nanoparticles (NPs) has been investigated and utilized to effectively improve membrane performance. Herein, recent research efforts on surface functionalization of polymeric membranes with a variety of NPs for water/wastewater treatment were concisely reviewed, focusing on metal and metal-oxide NPs. Methods for the immobilization of NPs on membrane surface and their influences on membrane properties and performances were overviewed. Results and contributions achieved in the improvement of membrane performances through surface functionalization with NPs were summarized, and emphasis was given to membrane hydrophilicity, stability, as well as antifouling and antibacterial property. Furthermore, perspectives on the current challenges and future research needs in the development and application of surface functionalized polymeric membranes were discussed.

Keywords: water/wastewater treatment, polymeric membranes, metal and metal-oxide NPs, surface functionalization

1. Introduction

Water shortage is a global challenge with growing concern because of population growth, industrial development, environmental pollution, and climate change. Worldwide, around 1.8 billion people would live in areas with severe water scarcity, and 2/3 of the population would suffer from water shortage by 2025 (UN-Water, 2020). Facing this challenge, researchers keep developing reliable, efficient, and sustainable technologies for water and wastewater treatment. Among various water and wastewater treatment technologies, membrane filtration technology has been regarded as one of the most efficient and cost-effective ways to retain water resources (Sri Abirami Saraswathi et al., 2019; Li et al., 2021b; Li et al., 2021c; Zhang et al., 2022). It offers excellent separation efficiency of pollutants with distinct advantages in easy maintenance, low chemical consumption, and small environmental footprint (Kang and Cao, 2014). Many kinds of materials have been used for membrane fabrication, including organic and/or polymeric materials, inorganic and/or ceramic, and even metallic materials (Bettmoussoul et al., 2016). In the choice of membrane materials, important considerations include mechanical property, easy pro-

cessing, thermal stability, and chemical resistance. Thus, polymers, such as poly(vinylidene fluoride) (PVDF), poly(ether sulfone) (PES), polysulfone (PSf), polypropylene (PP), poly(acrylonitrile) (PAN), cellulose acetate (CA), and polyamides (PA), which have appropriate properties with irreplaceable advantages in low cost, rich category, and high processing, are the most commonly used membrane materials (Kochkodan et al., 2014). Usually, the fabrication of polymeric membranes requires organic solvents, which makes the polymeric membranes relatively hydrophobic (Miller et al., 2017). Such hydrophobicity would contribute to membrane damage caused by organic/inorganic fouling and biofouling during filtration processes, which reduces membrane service life and increases system operational cost.

Generally, fouling is undesirable accumulation of foulants on membrane surface and/or pores, which include different forms of organic, inorganic, and biological substances (Sri Abirami Saraswathi et al., 2019). Most of these foulants have higher propensities for adhesion to surfaces of hydrophobic membranes compared to hydrophilic membranes. Besides hydrophobicity, other properties include surface roughness and surface charge also have significant effects on membrane fouling (Zhao et al., 2018). Fouling may intensify on rougher membrane surfaces since foulants may accumulate in valleys, especially when the characteristic dimensions of surface features and pollutants are similar (Rana and Matsuura, 2010). Surface charge affects the fouling formation through electrostatic interactions between charged surface and foulants (Koehler et al.,

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1997). Various techniques have been employed to mitigate membrane fouling during filtration process (Goh et al., 2018), such as, feed water pretreatment (Li et al., 2014a), operation parameter optimization (Sassi and Mujtaba, 2011), module design characteristics (Abid et al., 2017), as well as physical and chemical cleaning approaches (Lin et al., 2010). However, these techniques may suffer from low efficiency and/or high cost for fouling mitigation with possible secondary pollution. To reduce the frequency of using these techniques, membrane modification to alter the surface properties for enhancing fouling resistance has been considered as a promising alternative (Remanan et al., 2018).

In recent years, applications of nanoparticles (NPs) for membrane modification to improve membrane performance have been reported extensively (Pendergast and Hoek, 2011; Dlamini et al., 2019). Typically, approaches of membrane modification with NPs can be divided into two main categories: blending NPs into casting solutions to obtain mixed matrix membranes, and immobilizing NPs on membrane surfaces to obtain surface modified membranes (Kang and Cao, 2014). A variety of mixed matrix membranes have been developed using diverse compositions of NPs/polymers and applied in a range of waste treatment with improved separation, physicochemical, and antifouling properties (Zhao et al., 2011; Ng et al., 2013; Sri Abirami Saraswathi et al., 2019). However, one of the biggest problems of the blending approach is the aggregation phenomena of NPs. Aggregation causes the instability of casting solution and non-uniform distribution of NPs in the membrane matrixes. This will lead to changes of membrane surface morphology and section cross microstructure, thus resulting in potential reductions in filtration performance and antifouling ability (Kang and Cao, 2014). The aggregation behavior control in incorporating NPs is very difficult, since NPs have small size (less than 100 nm) and high surface energy, which lead to their bad compatibility with hydrophobic polymer bulk due to surface interactions (Dlamini et al., 2019). Currently, the attempt to disperse NPs for preparing mixed matrix membranes is mainly undertaken through strong mechanical stirring or sonication. Nevertheless, the effectiveness would be limited if the NPs concentration is relatively high (Kang and Cao, 2014).

In comparison, the other approach of membrane modification, which is immobilization of NPs on surfaces of existing polymeric membranes, is also frequently used and could be more effective in performance improvement (Asadollahi et al., 2017). Generally, the goal of surface modification with NPs is to form a functional coating on the existing membrane surface without damaging the original membrane. In this way, most of NPs can disperse on the coating to maximally improve membrane performances. This coating can avoid the directly contact between membrane surface and foulants (Kochkodan et al., 2014), and endow special properties to the membrane surface (i.e., hydrophilicity, antibacterial property, catalytic activity), thus reducing membrane fouling and improving filtration performance. These NPs can be organic or inorganic materials and can effectively act as hydrophilic modifiers for membranes. Various NPs also have excellent antifouling property, in particular against microorganisms. The modification and develop-

ment of polymeric membranes with NPs coating is an emerging and promising research field, altering membrane surface properties in a favorable way. Membrane surface modification and functionalization with organic nanomaterials (e.g., carbon-based nanomaterials) has been extensively studied and reviewed elsewhere (Hegab et al., 2015; Al-anzi and Siang, 2017; Li et al., 2021a). However, carbon-based nanomaterials, such as nano graphene oxide and carbon nanotubes, are generally expensive. Thus, many researchers have turned their attentions to inorganic nanomaterials, such as metal and metal-oxide based NPs, to develop cost-effective and problem-free membranes. Herein, a comprehensive review on surface functionalization of polymeric membranes with metal and metal-oxide nanoparticles for water/wastewater treatment will be presented.

2. Immobilization of Metal and Metal-Oxide NPs

Metal and metal-oxide NPs are pure metals and metallic oxides with nanoscale sizes (usually between 1 and 100 nm). So far, many kinds of metal and metal-oxide NPs have been engineered, and their chemical and physical properties have also been well documented. They are attractive nominees from various scientific and technological perspectives due to their unique properties in nano size as compared to their bulk particles. Generally, metal and metal-oxide NPs exhibit fascinating optical, magnetic, electronic, and catalytic properties, thus they have been widely produced and utilized in industry, agriculture, consumer products, and household goods. For example, four metal and metal-oxide NPs (i.e., cerium oxide (CeO₂), silver (Ag), zinc oxide (ZnO), and titanium dioxide (TiO₂) NPs) have been regarded as high interest because of their widespread use and commercial importance (OECD, 2009; Baker et al., 2014). CeO₂ NPs are broadly used as glass polishers and in heat-resistant coatings (EPA, 2009). Ag NPs are found in over hundreds of consumer products as antibacterial agents, and are especially effective against *E. coli* (McQuillan et al., 2012; Baker et al., 2014). TiO₂ NPs and ZnO NPs are commonly incorporated in sunscreens where they can protect against cell damage through blocking UV light due to their light absorption and photocatalytic properties (Osmond and McCall, 2010; Baker et al., 2014). Table S1 summarizes the productions and typical usages of common metal and metal-oxide NPs. Recent years, many kinds of metal and metal-oxide NPs have also been extensively applied in the field of environmental research (Khin et al., 2012), such as environmental remediation, pollution control, antimicrobial agent, etc. One of latest applications of these NPs includes the immobilization of them on polymeric membrane surfaces to increase the membrane performances for water and wastewater treatment, such as hydrophilicity, selectivity, antibacterial and catalytic activities.

The most important bottleneck affecting the immobilization of NPs into any membrane surface is achieving a uniform distribution and reliable stability to avoid pore blocking and NP leaching. To improve the durability of NP coatings, one popular strategy is to introduce appropriate functional groups or polymer coatings on membrane surfaces as binding agents to adsorb NPs or their precursors. NPs can then be immobilized

on membrane surfaces though secondary interactions (van der Waals or electrostatic interactions) or covalent bonding or their combinations, or be generated on membrane surfaces through in-situ formation.

Polymeric membrane surfaces may be activated to have functional groups through chemical treatment. The surface-active agent could be acid, alkali, or oxidizer solution with suitable concentration. The formation of polymer coatings can be achieved through simple adsorption or covalent coupling. These coatings may consist of materials that can be simply fixed to membrane surfaces through secondary interactions, or materials that are cured (cross-linking) on membrane surfaces with enhanced stability. The strength of secondary interactions would depend on the polymer surface nature and the modifier characteristics. Membrane surface coated with polyelectrolytes through layer-by-layer (LBL) deposition due to electrostatic adsorption has been reported as an effective way (Gao et al., 2018). The resulted coatings exhibit robust adhesion due to the large number of charged groups on polyelectrolytes. This method is not sensitive to small imperfections on membrane surface, nevertheless, deposition of too many layers may affect the membrane permeability.

Covalent coupling, such as cross-linking, is usually attained through a curing step, thus the obtained coating could have mechanical integrity. Many techniques can be applied to accomplish cross-linking on membrane surface. The commonly used techniques may include, chemically induced polymerization by adding initiator or chemically induced small molecule coupling by chemical surface treatment, UV-induced polymerization in the presence of photo-initiator, plasma polymerization or plasma-induced graft polymerization, corona discharge-induced polymerization. Table S2 presents the outline information of these techniques (Miller et al., 2017). For example, plasma activation can induce the graft polymerization of vinyl monomers to polymeric membrane surfaces (Ulbricht and Belfort, 1996). Peroxides can be formed on membrane surface through plasma treatment, which can then generate radicals to trigger polymerization reactions through thermolysis (Ulbricht and Belfort, 1996). Figure 1 shows a typical approach of membrane surface modification with NPs, which begins with plasma treatment, followed by graft polymerization and subsequent NP immobilization.

The other strategy to improve the durability of NP coating on membrane surface is to disperse NPs on solution of polymeric monomer, followed by co-polymerization which can be induced by the techniques in Table 2. It is noteworthy that the treatment conditions of most mentioned polymerization techniques should be optimized to avoid permeability reduction due to unreasonable coating and membrane damage due to aggressive treatment.

3. Membrane Surface Functionalization with NPs

3.1. Titanium Dioxide-Based NPs

Titanium dioxide nanoparticles (TiO_2 NPs) are hydrophilic inorganic nanomaterials commonly employed in the surface functionalization of polymeric membranes due to their high stability, low cost, strong hydrophilicity and photocatalytic activity. Performances of polymeric membranes before and after surface functionalization with TiO_2 NPs are shown in Tables 1 and 2. It was reported by Luo et al. (2005) and Moghimifar et al. (2014) that the immobilization of TiO_2 NPs on PES UF membrane surfaces could effectively increase the permeation of the resultant membranes due to the enhancement of surface hydrophilicity (Luo et al., 2005; Moghimifar et al., 2014). Surface wettability and water permeability of polypropylene (PP) membranes were remarkably enhanced through surface modification with TiO_2 NPs, which were demonstrated by remarkably decreased water contact angle and increased water flux (Saffar et al., 2014; Pi et al., 2016). Significant improvement in the hydrophilicity of PVDF membrane surface was also obtained by Chen et al. (2019b) for oily wastewater treatment. After surface modification with TiO_2 NPs, the water contact angle was decreased from 83.5° to 9.1° , and the permeation flux was increased by 4 times without compromising oil rejection rate. The effects of the nano- TiO_2 immobilization at different concentrations on filtration performance of a PES membrane were investigated by Pourjafar et al. (2012). It was found that the increase in TiO_2 concentration could highly affect the surface morphology (rougher surface) and permeation (lower flux) of coated membranes.

In recent years, a number of researchers have studied the deposition of TiO_2 NPs on membrane surfaces to enhance anti-fouling properties, since TiO_2 NPs have a tendency to decline

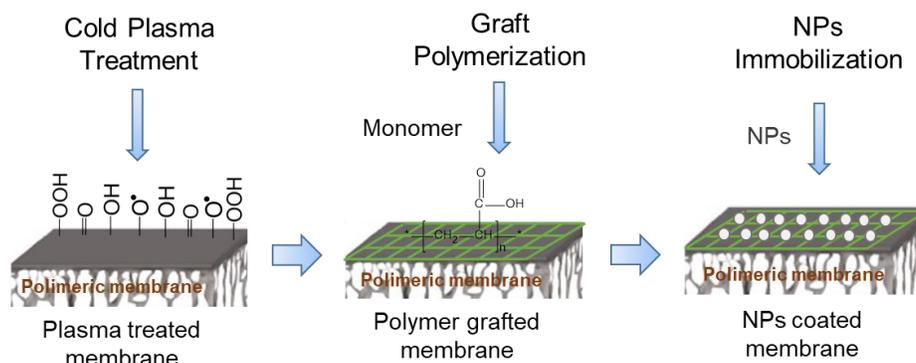


Figure 1. Typical approach of membrane surface modification through plasma induced graft polymerization followed by NP immobilization.

the adhesions of organic foulants and microorganisms on membrane surfaces due to their super hydrophilicity (Bet-moushoul et al., 2016). Li et al. (2009) fabricated an antifouling SMA/PVDF membrane via electrostatic self-assembly between anatase TiO₂ NPs and carboxyl groups of styrene-alt-maleic anhydride (SMA) on the membrane surface. In comparison to the membrane without TiO₂ NPs, the permeability and antifouling ability of modified membranes were significantly improved. The permeate flux was much higher during the filtration of BSA solution, and flux recovery ratio (FRR) was increased from 28.2 to 80.5% through the introduction of TiO₂ NPs on the membrane surface. Due to the high specific surface area of TiO₂ NPs, membrane surface coated with nano-TiO₂ may have capability to help remove metal ions through adsorption during filtration process. Zhang et al. (2012) evaluated the adsorption behavior of Cu²⁺ on a nano-TiO₂ entrapped PVDF membrane which was obtained by cetyltrimethyl ammonium bromide (CTAB) treatment and TiO₂ NPs self-assembly. It was found that the entrapped TiO₂ NPs increased the adsorption rate of Cu²⁺ from 53.84 to 68.8%, while improved the membrane surface hydrophilicity, permeability, and BSA resistance.

The self-assembly of TiO₂ NPs on polymeric membrane surfaces following graft polymerization for enhancing the membrane performances such as permeance and fouling resistance, have been successfully demonstrated in many studies (You et al., 2012; Zhang et al., 2013a; Saffar et al., 2014; Shi et al., 2016; Chen et al., 2019b). Tremendously enhanced antifouling effects were observed in the modified membranes, which were reflected by relatively better flux recovery and lower flux reduction. These favorable effects could be attributed to the hydrophilicity of the self-assembled TiO₂ NPs. It was reported that nano-TiO₂ coatings could improve the membrane hydrophilicity and also form a hydrophilic layer near the membrane surface. This layer could prevent the direct contact of foulants with the membrane surface, and thus improve the antifouling properties (Kang and Cao, 2014). However, during self-assembly process, TiO₂ NPs may be randomly attached to the functional groups of the grafted layer, part of NPs may become detached during cross-flow filtration, leading to discounts in antifouling properties. Madaeni et al. (2011b) compared filtration performances of two PVDF membranes whose surfaces were modified through the nano-TiO₂ self-assembly method on grafted PAA layer and in situ immobilization of AA monomer-functionalized TiO₂ NPs, respectively. The results of antifouling tested showed that the second method was better in terms of nano-TiO₂ durability in the modified membrane surface. To further improve the durability of nano-TiO₂ coating, Shi et al. (2016) anchored TiO₂ NPs on the surface of a commercial PVDF MF membrane through PDA/TiO₂ co-polymerization method with the help of a silane coupling agent KH550. The obtained membrane was superhydrophilic and had an ultrahigh efficiency (nearly 99%) for the separation of surfactant stabilized oil/water emulsions. The immobilized TiO₂ NPs were reported to be firmly embedded on the membrane surface even after immersed in water with strong shear flow for 30 days. This made the modified membrane durable in oil resistance and antifouling performance. Xiong et al. (2017) dec-

orated TiO₂ NPs with hydrophilic copolymer through hydrolysis, condensation, and crosslinking, and then immobilized TiO₂ NPs on PVDF membrane surfaces using spin coating. The prepared membranes showed robust superwetting property (water contact angle in air dropped to 0° within 1 s), and excellent durability in long-term separation of both stabilized water/oil and oil/water emulsion with few NPs loss. Wang et al. (2021) developed a cellulose-based NF membrane (CS/DA-TiO₂-NFM) through casting of both chitosan (CS) and (DA-TiO₂) on cellulose membrane surface. The irreversible recovery ratio of the resultant membrane was only 23.25% of the control during the antifouling test against BSA. Also, significant improvement in the rejection performances of the modified membranes were observed. Li et al. (2014b) modified PVDF hollow fiber membranes through PVA/TiO₂ co-polymerization. The optimal membrane presented $92.7 \pm 2.20\%$ of Congo red (CR) rejection rate, which was much higher than that of the original membrane ($54.5 \pm 6.1\%$). However, the permeate flux was severely declined due to the PVA cross linking. Qin et al. (2015) fabricated a hydrophilic PVDF membrane via chemically binding TiO₂ NPs followed by poly(vinyl alcohol) (PVA) coating on the membrane surface. During filtration tests with BSA solution, besides the FRR was significantly increased from 20.0 to 80.5% after modification, the BSA rejection rate was increased from 44.7 to 86.5%.

Using the photocatalytic properties of TiO₂ NPs, membrane performances can be further improved. For example, Mansourpanah et al. (2009) examined the performance of PES/PI membrane modified through diethanolamine (DEA) coating and TiO₂ self-assembly followed by ultraviolet (UV) irradiation. It was found that -OH groups originated excellent adhesion of TiO₂ NPs on the membrane surface, increased reversible deposition and diminished irreversible fouling. Later, this research group directly deposited TiO₂ NPs on a cellulose UF membrane surface through coordinance bonds with native -OH groups, and then irradiated the coated membrane using UV light (Madaeni et al., 2011a). The modified membrane flux was increased to a large extent compared to the virgin membrane. The deposited TiO₂ NPs could be revived through UV irradiation, thus improving the antifouling performance. Ngo et al. (2016) modified a commercial TFC-PA membrane for dye removal through dip-coating of TiO₂ NPs with subsequent UV irradiation. The permeate flux was increased by about 60% and the dye rejection rate was improved from 92 to 99%. The antifouling property of the modified membrane was also enhanced with a higher maintained flux ratio and a lower irreversible fouling factor compared with the pristine membrane. TiO₂ NPs were also applied to membrane self-cleaning and pollution degradation through photocatalysis. You et al. (2012) evaluated the antifouling and photocatalytic properties of PVDF plasma-grafted PAA membranes with self-assembled TiO₂ NPs. Besides tremendous improvement in hydrophilicity, the membrane's original performance could be recovered after 30 min of cumulative UV irradiation. The TiO₂-modified membranes could also remove 30 ~ 42% of Reactive Black 5 (RB5) dye (50 mg/L in solution) under UV light (254 nm, 15 W) within 120 min. Fischer et al. (2015; 2017) in-situ synthesized TiO₂

Table 1. Summary of the Performance of Polymeric Membranes before and after Surface Modification with TiO₂ NPs (Part 1: Hydrophilicity)

Membrane	Filtration Category	Material	Modification method	Contact angle		Permeate flux		Rejection rate		TMP	Application	Reference
				Before	After	Before	After	Before	After			
PES membrane	UF	Na ₂ CO ₃ , TiO ₂	Self-assembly	39.6°	19.2°	70.2 L/m ² h	102.9 L/m ² h	-	-	0.2 Mpa	PEG-5000 rejection	Luo et al., 2005
PES/PI membrane	NF	DEA, TiO ₂	Self-assembly	61°	53°	13 L/m ² h bar	17 L/m ² h bar	15%	65%	0.7 MPa	BSA filtration	Mansourpanah et al., 2009
SMA/PVDF membrane	MF	Poly(styrene-alt-maleic anhydride) (SMA), TiO ₂	Self-assembly	85°	54.1°	150 L/m ² h	550 L/m ² h	98.6 ± 2.3%	92.5 ± 1.4%	100 kPa	BSA rejection	Li et al., 2009
PVDF membrane	MF	PAA, TiO ₂ (P25)	In situ polymerization	-	-	6 L/m ² h bar	6.5 L/m ² h bar	70%	90%	2 atm	Protein filtration	Madaeni et al., 2011
Cellulose membrane	UF (MWCO: 10,000 Da)	TiO ₂ (P25)	Self-assembly followed by UV light irradiation	48°	12°	4 L/m ² h	6 L/m ² h	-	-	3 bar	Protein filtration	Madaeni et al., 2011
PES/PVA/TiO ₂ composite membranes	NF	PVA, TiO ₂	Chemical cross-linking followed by dip-coating (self-assembly)	55.3°	39°	7 L/m ² h	24 L/m ² h	28%	41%	5 bar	NaCl rejection	Pourjafar et al., 2012
PVDF-g-PAA-TiO ₂ membrane	MF (pore size: 0.45 um)	PAA, TiO ₂ (P25)	Plasma-induced polymerization followed by self-assembly	116.4°	23°	20 L/m ² h	30 L/m ² h	-	-	98 kPa	BSA filtration	You et al., 2012
PVDF membrane	MF (pore size: 2 um)	Cetyltrimethyl ammonium bromide (CTAB), TiO ₂	Self-assembly	104.3°	56.6°	630 L/m ² h	1,485 L/m ² h	53.8%	68.8%	150 kPa	Adsorption of Cu ²⁺	Zhang et al., 2012
TFC membrane	-	Polydopamine (PDA)	Self-polymerized PDA followed by TiO ₂ self-assembly	32°	27.7°	1.41 L/m ² h bar	1.18 L/m ² h bar	80.3%	87.8%	-	Salt rejection (MgSO ₄)	Zhang et al., 2013
PVDF membrane	MF (pore size: 0.4 um)	PVA, TiO ₂ , glutaraldehyde (GA), H ₂ SO ₄	PVA/TiO ₂ co-polymerization	87°	55°	89.20 ± 13.60 L/m ² h	5.10 ± 2.00 L/m ² h	54.5 ± 6.1%	92.2 ± 2.2%	0.3 MPa	CR rejection	Li et al., 2014
PES membrane	UF (pore size: 14 nm)	TiO ₂	Corona air plasma treatment followed by dip coating	65°	5°	2.54 kg/m ² h	16.45 kg/m ² h	94%	99%	1.5 bar	Oil rejection	Moghimifar et al., 2014
PP membrane	MF	PAA, TiO ₂	Self-assembly	90°	40°	-	-	-	-	-	-	Saffar et al., 2014
PVDF membrane	MF (pore size: 0.22 um)	Titanium isopropoxide	Hydrolysis crystallization	73°	76°	-	Increase 25%	-	-	2 bar	BSA filtration	Fischer et al., 2015

Continued

Membrane	Filtration Category	Material	Modification method	Contact angle		Permeate flux		Rejection rate		TMP	Application	Reference
				Before	After	Before	After	Before	After			
PVDF/TiO ₂ /PVA membrane	UF	TBAF, NaHSO ₃ , trimesoyl chloride, PVA, TiO ₂	Chemically binding TiO ₂ followed by PVA cross-linking	84°	24°	390 L/m ² h	430 L/m ² h	44.7%	86.5%	0.1 MPa	BSA filtration	Qin et al., 2015
TiO ₂ coated TFC-PA membrane	NF	TiO ₂	UV-irradiated TiO ₂ -coating	50°	7°	-	Increase 60%	92%	99%	15 bar	Dye removal	Ngo et al., 2016
TiO ₂ NPs on the PDA/PEI-deposited PP membrane	MF	DA, PEI, Ti-BALDH, NH ₃ H ₂ O	PDA/PEI co-deposition method followed by sol-gel process	135°	20°	605 ± 26 L/m ² h	5,720 ± 207 L/m ² h	-	-	0.10 MPa	BSA filtration	Pi et al., 2016
TiO ₂ decorated PVDF membrane	MF (pore size: 0.22 μm)	DA, TiO ₂ , (3-aminopropyl) triethoxy-silan (KH550)	PDA/TiO ₂ co-polymerization	123.8°	26.9°	50 L/m ² h	785 L/m ² h	-	99%	0.09 MPa	Surfactant stabilized oil-in-water emulsion	Shi et al., 2016
PES membrane	MF (pore size: 0.22 μm)	Titanium (IV) isopropoxide (TTIP), hydrochloric acid	In-situ formation	55°	15°	28 mL/min cm ² bar	30 mL/min cm ² bar	21%	39%	1 bar	MB photocatalytic degradation	Fischer et al., 2017
PVA/PAA/GO-COOH-TiO ₂ nanofiber membrane	-	PVA, PAA, GO, TiO ₂	Heat-induced crosslinking followed by self-assembly	-	-	-	-	-	30.45 mg/g	-	MB photocatalytic degradation	Hou et al., 2017
PVDF-PAA-TiO ₂ membrane	MF (pore size: 0.1 μm)	PAA, TiO ₂ (P25)	Plasma induced PAA grafting followed by self-assembly	83°	9°	15 L/m ² min	64 L/m ² min	91.8%	92.1%	0.3 MPa	COD removal in oil/water emulsion	Chen et al., 2019

NPs at the surfaces of PVDF and PES membranes through hydrolysis crystallization, and investigated their photocatalytic activities for removal of dyes and drugs. For instance, after 120 min of UV irradiation, TiO₂/PVDF and TiO₂/PES membranes could degrade 100 and 70% of methylene blue (3.2 mg/L), 68 and 55% of diclofenac (25 mg/L), respectively (Fischer et al., 2015). Hou et al. (2017) prepared a photoactive PVA/PAA/GO-COOH-TiO₂ electrospun membrane for dye degradation. The as-prepared membrane demonstrated 30.45 mg dye/g membrane of degradation capacity at equilibrium state under mercury lamp illumination (20 W, 365 nm), which was attributed to the large specific surface area of the electrospun membrane and the photoactivity of TiO₂ NPs.

In addition to the mentioned properties above, the disinfection performance and antibacterial activity of nano-TiO₂ functionalized membranes have also been investigated due to their high efficiency in generating active reactive oxygen species (ROS) under UV irradiation (Leong et al., 2014; Laxma Reddy et al., 2017). When subjected to light irradiation, the generation of energy occurs due to the excitation of electrons in TiO₂ NPs as photocatalyst, especially under UV irradiation

(Leong et al., 2014; Xu et al., 2020). This results in the creation of positively charged electron holes and negatively charged free electrons, which react with atmospheric oxygen and water, forming ROS (e.g., hydroxyl radicals, superoxide radicals, hydrogen peroxide, etc.) (Laxma Reddy et al., 2017; Sri Abirami Saraswathi et al., 2019). Hydroxyl radicals are primarily responsible for the disinfection activity, especially against bacteria; other ROS (such as hydrogen peroxide) play pivotal roles in cell damage, such as oxidation of cellular components and membrane leakage of the microbial cell (Laxma Reddy et al., 2017). Thus, the polymeric membranes functionalized with TiO₂ NPs exhibit anti-biofouling properties. Immobilization of TiO₂ NPs on TFC-PA membrane surfaces were carried out to solve biofouling problem as an approach (Kwak et al., 2001; Kim et al., 2003). The modified TFC-PA membranes were showed to possess dramatic photo bactericidal effects on *E. coli* under UV light illumination, and displayed less loss of RO permeability. Rahimpour et al. (2012) modified a PVDF/sulfonated polyethersulfone (SPES) blend membrane through TiO₂ NPs deposition followed by UV irradiation. After modification, the resultant membrane showed lower tendency to BSA fouling

Table 2. Summary of the Performance of Polymeric Membranes before and after Surface Modification with TiO₂ NPs (Part 2: Antibacterial Activity)

Membrane	Filtration type	Material	Modification method	Contact angle		Permeate flux		Surface charge		Rejection rate		TMP	Antibacterial performance	Applica-tion	Refer-ence
				Before	After	Before	After	Before	After	Before	After				
TFC	RO	Na ₂ CO ₃ , TiO ₂	Self-assembly	-	-	55.4 gfd	66.1 gfd	-	-	94.7%	96%	225 psi	100% after 4 h UV	NaCl rejection	Kim et al., 2008
TiO ₂ deposited PVDF/SPES membrane	MF	Sulfonated polyether-sulfone (SPES), TiO ₂	Self-assembly followed by UV light irradiation	74.4 ± 1.7°	25.2 ± 1.0°	130 L/m ² h	140 L/m ² h	-	-	70%	93%	1 bar	Clear inhibition zone	BSA rejection	Rahim-pour et al., 2012
Ag/TiO ₂ -coated cellulose triacetate (CTA) membrane	FO	AgNO ₃ , TiO ₂	UV photo-induced Ag NPs growth followed by charge-driven self-assembly of TiO ₂ NPs	48°	44°	6 L/m ² h	8 L/m ² h	-40 mV	-25 mV	-	-	-	The ATP concentration decreased from 23.5 to 2.0 µg/L	-	Nguye n et al., 2014
TiO ₂ -modified PVDF membrane	UF (MWCO: 100 kDa)	Dopamine, TiO ₂ (P25)	Polydopa-mine (PDA)-deposition followed by self-assembly	80°	60°	1225 L/m ² h	1925 L/m ² h	-	-	98.9%	99.9%	1.4 bar	-	Retention of total bacteria	Ren et al., 2018
PEI-TiO ₂ /Ag modified PAN membrane	UF (MWCO: 200 kDa)	PEI-TiO ₂ , AgNO ₃ , PDA	Vacuum filtration followed by Ag in site reduction	49°	20°	1211 L/m ² h	588 L/m ² h	-20.4 mV	10.4 mV	5%	48%	2 bar	High bacterio-static rate of 99.7%	Na ₂ SO ₄	Li et al., 2019

and higher antibacterial property, with moderate increase in BSA retention efficiency. A clear inhibition ring on the modified membrane was the evidence of the antibacterial effect against *E. coli*. Ren et al. (2018) loaded TiO₂ NPs on a PVDF UF membrane surface to improve the removal efficiencies of antibiotic resistant bacteria (ARB) and antibiotic resistance genes (ARGs) from secondary wastewater effluent. Compared to the unmodified PVDF membrane, the TiO₂-modified membrane provided complete retention of ARB with a much higher permeate flux, and it could effectively degraded of ARGs and integrons which accumulated on membrane surface under UV irradiation.

It is a well-established fact that silver (Ag) has strong antimicrobial property to a variety of bacteria through the release of Ag⁺ ions. Hence, more intense disinfection/antibacterial activity can be acquired through the combination of Ag and TiO₂ NPs (Laxma Reddy et al., 2017). Nguyen et al. (2014) deposited Ag NPs on the surface of a cellulose triacetate (CTA) forward osmosis (FO) membrane by using UV-induced growth approach, followed by nano-TiO₂ self-assembly on the layer of Ag NPs. The bacterial growth on the Ag/TiO₂-coated CTA membrane surface was almost 11 times less than that on the virgin membrane. They reported that this was primarily due to the antibacterial activities of the Ag NPs, while the TiO₂ NPs

played an effective role in regenerating the Ag NPs through decomposing organic matters which covered the Ag NPs. The coated membrane thus achieved much higher recovery of initial water flux (67 ~ 72%) compared to the virgin membrane (33%) after cleaning. In turn, Li et al. (2019) loaded Ag NPs onto a TiO₂-coated PAN UF membrane surface through in-situ formation. The nano-TiO₂ coating notably enhanced the water permeability during the process of dye removal, and the Ag NPs loading enabled the membrane with a high antibacterial activity. The optimal membrane had a water permeability of 40.6 L/m² h bar and CR removal rate of > 98%, with 99.7% of bacteriostatic rate on membrane surface.

3.2. Zinc Oxide-Based NPs

Zinc oxide nanoparticles (ZnO NPs) have emerged as an efficient and promising candidate in environmental research field because of their outstanding characteristics, such as wide band gap in the near-UV spectral region, strong thermal stability, excellent photocatalytic property, and large free-exciton binding energy (Lee et al., 2016). Besides as a semiconductor oxide, ZnO NPs also have great hydrophilicity and antibacterial property. ZnO NPs thus have been used as a replacement for TiO₂ NPs since they have similar characteristics. In addition, compared with TiO₂ NPs, the crystal form of ZnO NPs is easier

to be controlled and the production cost is lower up to 75% (Liang et al., 2012; Ong et al., 2018). Hence, ZnO and ZnO-based NPs have attracted an increasing amount of interest in surface modification for polymeric membranes. Table 3 presents the performances of polymeric membranes before and after surface modification with ZnO-based NPs.

It has been reported that nano-ZnO coating has a great influence on improving the water permeation of base membranes through enhancing their surface hydrophilicity. This is because ZnO NPs can easily become hydrophilic through the quick absorption of hydrophilic -OH groups (Javdaneh et al., 2016). The influence of ZnO NPs in enhancing the surface hydrophilicity of a PVDF membrane for produced water treatment was studied by Chen et al. (2019a). A PAA-ZnO coating was formed on membrane surface via cold plasma-induced PAA polymerization followed by nano-ZnO self-assembly. This decreased the water contact angle from 101.1° to 18.7°, thus bringing about significantly improvement of membrane performances in both water permeation flux and oil rejection rate. Due to its photocatalytic property, ZnO NPs were employed for membrane self-cleaning through photocatalysis. Laohaprapanon et al. (2017) loaded ZnO NPs on a PVDF MF membrane surface and studied the self-cleaning property of the resulted membrane. After severely fouled on the filtration of alginate (1 wt%), the ZnO-coated membrane could fully recover the original flux through UV irradiation for 30 min. The modified membrane also exhibited excellent photocatalytic activity, achieving 86% of remazol black B decolourization under UV irradiation for 5 h.

Nano-ZnO was also employed to protect polymeric membranes from biofouling since it exhibits a higher level of toxicity compared to nano-TiO₂ (Huang et al., 2020). The antibacterial activity of ZnO NPs can be attributed to the generation of hydrogen peroxide at its surface (Sirelkhatim et al., 2015). Isawi et al. (2016) developed a nano-ZnO modified PMAA-g-PA (TFC) membrane for groundwater desalination through incorporating ZnO NPs into MAA grafting solution. After exposure to UV light for 90 min, almost no survival *E. coli* cells was observed on the modified membrane surface, while 12% of survival *E. coli* cells was found on the pure PA(TFC) membrane surface. The nano-ZnO modified membrane also showed 99 and 98% of rejection rates for dissolved bivalent ions (Ca²⁺, SO₄²⁻ and Mg²⁺) and mono valent ions constituents (Cl⁻ and Na⁺), respectively. Jo et al. (2016) studied the functionalization of PES UF membrane surface with ZnO NPs by reaction of amine groups in PES-NH₂ with thionyl chloride-terminated ZnO NPs. The antibacterial rates for *E. coli* and *S. aureus* were increased from 38.0 and 35.2% on the pristine membrane surface to both over 99% on the functionalized membrane surface. Due to the high specific surface area, nano-ZnO coating on membrane surface was used to remove copper ions through adsorption during filtration process, while the membrane performances were also improved (Zhang et al., 2014). Chen et al. (2018) fabricated an omniphobic membrane for membrane distillation (MD) by depositing ZnO NPs on a glass fiber (GF) membrane to form hierarchical re-entrant structures through chemical bath deposition, followed by surface fluorination and

polymer coating to lower the membrane surface energy. Compared to the hydrophobic GF membrane without ZnO NP deposition, the omniphobic membrane showed a much higher wetting resistance to feed solution with low surface tension (SDS solution) in direct MD with more than 99.99% of salt rejection rate (1 M NaCl).

3.3. Silver and Silver-Based NPs

In recent decades, silver nanoparticles (Ag NPs) have received high attention because of their broad spectrum antibacterial activity (Liu et al., 2017). It is generally recognized that the toxicity of Ag NPs is mainly driven by the release of Ag⁺ ions (Cao et al., 2010; de Lima et al., 2012; Zhang et al., 2016a). The released Ag⁺ ions inactivate the membrane protein of bacterial cell, and then bind with bacterial DNA to disrupt DNA replication, thus leading to inactivation of the cytochrome b and bacterial cell (Chudobova et al., 2013; Ong et al., 2016). Owing to the antimicrobial features of Ag-based compounds, Ag and Ag-based NPs have been widely employed to improve the biofouling resistance of polymeric membrane surfaces. Table S3 summarizes the performances of polymeric membranes before and after surface modification with silver and silver-based NPs.

Efforts have been devoted to directly immobilize Ag NPs on membrane surfaces to prevent membrane biofouling caused by Gram-negative and Gram-positive bacteria such as *E. coli* and *B. subtilis*, respectively. Yang et al. (2009) reported better performances of Ag-coated TFC RO membrane in terms of much better stability in permeate flux and total dissolved solids (TDS) removal rate compared to the unmodified membrane, since much less viable bacteria could adhere to the modified membrane surface during cross-flow filtration test. Ben-Sasson et al. (2014a) loaded Ag NPs on a TFC RO membrane surface through in site reduction of silver salt. This method resulted in uniform coverage and irreversible bond of Ag NPs on the membrane surface, thus Ag NPs did not impact the original membrane properties but endowed strong antibacterial activity to the membrane. The amount of live bacteria attached to the membrane surface was reduced more than 75%, and biofilm formation was significantly suppressed with 41% reduction in total biovolume, though water permeability was slight declined (up to 17%). Mecha and Pillay (2014) explored combining a woven fabric MF membrane with Ag NPs which were directly deposited on membrane surface by chemical reduction of AgNO₃. With controlled amount of Ag NPs, the membrane morphology was not significant changed, while higher water permeability and bacteria removal efficiency were obtained for potable water treatment.

Since the toxicity of Ag-modified membranes largely depends on the durability of Ag NPs, researchers made many efforts to improve the particle durability and reactivity of Ag NPs on membrane surfaces (Sharma, 2013; Prince et al., 2014; Liu et al., 2015a). To reduce Ag leaching from membrane surface during filtration process, Yin et al. (2013) applied cysteamine as a bridging agent to attach Ag NPs on TFC-PA membrane surface via covalent bonding. Similar approach for attaching

Table 3. Summary of the Performance of Polymeric Membranes before and after Surface Modification with ZnO NPs

Membrane	Filtration type	Material	Modification method	Contact angle		Permeate flux		Rejection rate		Antibacterial performance	TMP	Application	Reference
				Before	After	Before	After	Before	After				
PVDF/ZnO hybrid membrane	MF (pore size: 1.1 μm)	KMnO ₄ , NaHSO ₃ , CTAB, ZnO NPs	Chemical treatment followed by self-assembly	62°	52°	285 L/m ² h	465 L/m ² h	9.83 ug/cm ²	87.4 ug/cm ²	-	150 kPa	Cu ²⁺ adsorption	Zhang et al., 2014
ZnO NPs modified PMAA-g-PA(TFC) membrane	RO	K ₂ S ₂ O ₈ , Na ₂ S ₂ O ₅ , MAA, ZnO NPs	Redox grafting PMAA polymerization followed by self-assembly	71 ± 2.8°	50 ± 3°	31 L/m ² h	35 L/m ² h	96.6%	98%	No live cell on surface after 90 min of UV light exposure	15 bar	NaCl rejection	Isawi et al., 2016
PES/PES-NH ₂ /ZnO membrane	UF	Na ₂ S ₂ O ₄ , APTES, SOCl ₂	Chemical treatment followed by self-assembly	-	-	2 L/m ² h	12 L/m ² h	95%	90%	> 99% on membrane surface	-	C16E8 nonionic surfactant removal	Jo et al., 2016
PVDF-g-PAA/ZnO-3% membrane	MF (pore size: 0.45 μm)	AA, ZnO NPs	Plasma induced PAA grafting followed by self-assembly	126.3°	11.7°	283 L/m ² h	295 L/m ² h	24%	86% under UV of 5 h	-	-	Remazol black B decolorization	Laohapapanon et al., 2017
Glass fiber (GF) membrane	MF (pore size: 0.4 μm)	KMnO ₄ , Zn(NO ₃) ₂ , FAS17, PVDF	Chemical bath deposition followed by polymer coating	0°	150°	-	11.4 ± 0.9 kg/m ² h	-	99.99%	-	-	Removal of sodium dodecyl sulfate (SDS) solution with 1 M NaCl	Chen et al., 2018
PVDF-PAA-ZnO membrane	MF (pore size: 0.1 μm)	PAA, ZnO NPs	Plasma induced PAA grafting followed by self-assembly	101.1°	18.7°	68.5 L/m ² ·m in	1400 L/m ² ·min	89%	93%	-	3 bar	COD removal from oily wastewater	Chen et al., 2019

Ag NPs was used by Reis et al. (2015) who selected 1-vinyl imidazole (VIm) as a binding agent for nano-Ag immobilization. Sawada et al. (2012) coated acrylamide on a PES UF membrane using UV-induced graft polymerization. This coating was applied to adsorb AgNO₃ for in site reduction of Ag NPs on the membrane surface. Thus, the membrane hydrophilicity was improved by acrylamide grafting (from 90° to 40°), and the loaded Ag NPs killed more than 99.999% of *E. coli* attached on membrane surface. Similar improvements were also reported on a research about Ag/PVDF-g-PAA composite membrane (Li et al., 2013). Zhang et al. (2013b) grafted poly(ethylene glycol) methyl ether acrylate (PEGMEA) on TFC membrane surface to adsorb AgNO₃ followed by light-induced formation of Ag NPs. Significant reduction of *E. coli* and BSA attachments on membrane surface were obtained due to remarkable decrease in adhesion forces, which could be attributed to hydrophilicity improvement (from 68° to 50°) and surface charge increase (from -70 to +120 mV). AgNO₃ was also adsorbed by a PVA coating, which led to the formation of Ag NPs with 10 ~ 20 nm in diameter on a TFC NF membrane surface through thermal reduction (Zhang et al., 2016b). The PVA coating acted as a reducing agent to reduce Ag⁺ into Ag NPs, and played an important role in stabilizing Ag NPs on the membrane surface by the interaction between PVA and Ag NPs. Liu et al. (2015b) successfully synthesized biogenic Ag

NPs (BioAg) with 6 nm of averaged diameter and grafted them on a TFC PA NF membrane surface with the help of H₂N-(CH₂)₂-SH ethanol. The modified membrane showed effective antibacterial ability to constrain the growth of both *P. aeruginosa* and *E. coli*. Besides, the grafted BioAg had long-lasting stability on the membrane, 95% of Ag remained on the membrane surface after soaked in pure water for 50 days. Dong et al. (2017) deposited an ultrathin precursor layer which consisted of tannic acid-ferric ion-polyethylenimine (TA-Fe-PEI) complex onto a TFC RO membrane surface. Ag NPs were then in-situ formed on the membrane surface due to the strong reducibility of TA. This modification increased the bacteria mortalities on membrane surface by about 85% after contacting with *E. coli* and *Bacillus subtilis* for 1.5 h, while slightly improving water flux and salt rejection.

The ability to simultaneously improve membrane hydrophilicity and reduce Ag⁺ to Ag NPs has been also found on polydopamine (PDA) which is a hydrophilic material due to its abundant catechol, quinine, and amine groups. PDA formation can be achieved on most of substrates to generate a thin and conformal coating under mild, aqueous conditions without requirement of special reaction (Miller et al., 2017; Qi et al., 2018). Due to such nonspecific nature of PDA deposition, many kinds of polymeric membranes, such as TFC-PA, PSf, CA, and PES have been rendered hydrophilic (Miller et al., 2017). The

hydrophilic PDA coating could be applied as a platform for the secondary conjugation of Ag NPs (Yang et al., 2021). For example, to mitigate membrane biofouling, Tang et al. and Huang et al. modified PSf membranes with PDA films followed by in-situ formation of Ag NPs. The catechol groups in PDA adsorbed and reduced Ag⁺ ions, thus the Ag NPs were generated and firmly immobilized on the membrane surface via metal coordination. The PDA film significantly improved membrane hydrophilicity, leading to enhanced membrane antiadhesive property. Ag NPs imparted strong antimicrobial properties to the membrane, resulting in > 99% inactivation of bacteria attached to the surface. Besides, the release of Ag⁺ ions was stable and slow during the filtrate operation. Tang et al. (2015b) reported that the concentration of Ag⁺ ion released was 2 to 3 orders of magnitude lower than the established standard level for drinking water, and Huang et al. (2016) tested little release of silver in water for 12 days. Similarly, in-situ regeneration of Ag NPs on the PDA modified TFC FO membrane was achieved by Liu and Hu (2016) for NaCl rejection. After modification, the water contact angle was decreased from $68.4 \pm 1.9^\circ$ to $28.5 \pm 4.6^\circ$, and the number of live *E. coli* attached on membrane surface was reduced by $94.4 \pm 2.3\%$. Sri Abirami Saraswathi et al. (2019b) also reported effective modification of CA UF membranes through bioinspired PAD coating followed by in-situ deposition of Ag NPs. The water contact angle (55.8°), pure water flux ($113.1 \text{ L/m}^2 \text{ h}$), and biofouling resistance (clear inhibition zones) of the modified CA membrane confirmed significant enhancements in membrane hydrophilicity, permeability, antifouling and antibiofouling properties, compared to the pristine membrane with 76.4° of water contact angle and $24.7 \text{ L/m}^2 \text{ h}$ of pure water flux.

Recently, significant attention has also been dedicated to surface modification using zwitterionic polymers which contain negatively and positively charged residues at the same monomer unit. They have been applied to delay or prevent microbial attachment to membrane surfaces due to their hydrophilicity. Thus, combining application of highly hydrophilic zwitterionic polymers and biocidal Ag NPs on membrane surfaces has been investigated to reduce the adhesion of foulants and enhance the inactivation of bacteria through optimization of surface chemistry (Liu et al., 2017). For example, poly(sulfobetaine methacrylate) (PSBMA) which is regarded as a promising class of zwitterionic polymers for antifouling applications, has been popularly employed to combine Ag NPs for membrane surface functionalization. The functionalized membranes with simultaneous antiadhesive and bactericidal capabilities have been demonstrated in several research (He et al., 2017; Liu et al., 2017; Xie et al., 2017; Xie et al., 2018; Zhang et al., 2018). Besides, Yi et al. (2019) employed two different zwitterions (SO³⁻-based and COO⁻-based) to modify TFC PA NF membranes followed by in-situ formation of Ag NPs. The presence of both zwitterions helped increase Ag content, resulting in significant improvements of antimicrobial and antifouling properties for membranes. The COO⁻-based zwitterion polymer was found to be more favorable toward Ag NP immobilization compared to the SO³⁻-based zwitterion polymer.

Besides using unmodified Ag NPs, researchers also func-

tionalized/modified Ag NPs before immobilization to membrane surfaces. Mauter et al. (2011) synthesized PEI coated Ag NPs and then fixed them on an oxygen plasma modified PSf UF membrane surface. The nucleophilic primary amines of the PEI could react with the electrophilic carboxyl groups on the PSf membrane surface, forming electrostatic and covalent bonds. This led to an irreversible modification process that significantly improved the antibacterial activity to the membrane surface. The bacterial inactivation rate could be over 94% within 1 h of contacting time; however, the permeate flux was decreased from 75 to 30 L/m² h bar. Both organic and biological fouling was reduced on a PES MF membrane whose surface was functionalized with citrate-stabilized Ag NPs using polyelectrolyte multilayer modification method with poly(styrenesulfonate) (PSS) (Diagne et al., 2012). Zirehpour et al. (2017) investigated the use of an Ag-based metal-organic framework (MOF) for mitigating biofouling in TFC FO membranes. This immobilization improved the membrane hydrophilicity and transport property without adversely affecting the selectivity. The number of live bacteria attached to the modified membrane surface was 90% less than that of control membranes, and this biocidal activity could last for 6 months. Sprick et al. (2018) chemically loaded casein-coated Ag NPs on cellulose acetate (CA) UF membranes with the help of cysteamine via the affinity of Ag to the thiol groups. This immobilization chemistry effectively prevented the leaching of Ag NPs during cross-flow studies.

The development and application of Ag-based nanocomposites is also a research trend since nanocomposites perform even better than pure Ag NPs. Researchers have proposed many Ag-based nanocomposites for membrane surface functionalization to improve membrane performances (Rusen et al., 2014; Ilyas et al., 2019; Yu et al., 2021). Gunawan et al. (2011) coated Ag NPs on PEG-grafted multiwalled carbon nanotubes (MWNTs) to obtain Ag/MWNT nanocomposites. The Ag/MWNTs were then covalently coated on the external surface of an ethylene diamine (EDA) modified PAN hollow fiber UF membrane as a disinfection barrier. The nanoscale diameter and one-dimensional morphology of MWNTs allowed an open network structure on the membrane surface to minimize the water flux reduction and also to facilitate the contact of Ag NPs with pathogens. Thus, the presence of the Ag/MWNT disinfection layer effectively inhibited the bacteria growth during filtration process and prevented the biofilm formation on the membrane surface. Under a continuous filtration mode using *E. coli* (10^6 cfu/ml) feed water, the flux of Ag/MWNTs modified PAN membrane dropped 6% and kept stable at $193 \text{ L/m}^2 \text{ h}$ bar during 20 h of filtration, whereas the flux of the pristine membrane dropped 55% and remained at $117 \text{ L/m}^2 \text{ h}$ bar. Soroush et al. (2015) synthesized GO/Ag nanocomposites and then immobilized them onto a TFC-PA FO membrane surface through an amide forming condensation reaction using cysteamine. In this research, Ag NPs were formed in-situ on the surface of GO nanosheets by a wet chemical reduction of AgNO₃. The resultant membranes exhibited highly hydrophilic properties (contact angles < 25°) and strong *E. coli* inactivation (> 95% within 1 h) on the surfaces without damaging the mem-

brane transport properties. Likewise, the synthesis and characterization of another TFC-PA FO membrane functionalized with GO-Ag nanocomposite was reported by Faria et al. (2017) using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) as cross-links. About 80% of inactivation rate against *P. aeruginosa* cells attached on membrane surface was achieved in this work. Also, Ko et al. (2018) coated Ag-GO nanocomposites on a PVDF membrane MF membrane via pressurized filtration process. During the compaction study, the number of attached live *E. coli* on membrane surface was decreased by > 94.7% after filtration test due to increased hydrophilicity and smoother membrane surface. More recently, PEG functionalized GO-Ag nanocomposites were developed and used to enhance the hydrophilicity, permeability, and antifouling resistance of PVDF membrane (Ilyas et al., 2019; Yu et al., 2021). Besides, the effects of inorganic Ag-based nanocomposites on antifouling and antibacterial behaviors of membranes were explored. Pan et al. (2017) synthesized and immobilized Ag/SiO₂ nanocomposites onto a PVDF UF membrane surface, and found that the pure water flux was notably increased by 4 times. The potential of Ag-zeolite nanocomposite coating to provide long-lasting antimicrobial activity was demonstrated by Wu et al. (2017) on a TFC membrane which surface inactivation rate could be ~70% for *P. aeruginosa* after 17 days. Feng et al. (2021) modified PES membranes through coating AgNPs@ZIF-8 hybrid crystals which simultaneously improves the membrane water permeability and antifouling property.

Further membrane modification with grafting of polymer brushes was used to modify the membrane/water interface through creating a thin and stable coating upon Ag NPs, thus limited the adhesion and viability of the biofilm. Rahaman et al. (2014) synthesized PEI coated Ag NPs and then immobilized them on a TFC membrane surface via polyelectrolyte LBL self-assembly. The membrane was further modified by grafting polymer brushes using hydrophilic poly(sulfobetaine). The composite coating significantly increased the hydrophilicity and reduce irreversible bacterial cell adhesion to the membrane surface, while achieved > 95% inactivation of attached bacteria. Tang et al. (2015a) assembled polyelectrolyte multilayers which composed of poly(allylamine hydrochloride) and PAA on Ag NP deposited PSf MF membrane surface using LBL adsorption technique. In comparison to the unmodified PSf membrane, the kinetics of bacterial deposition on the modified membrane were reduced by ca. 50%, and the bacterial removal efficiency was increased from about 0% to more than 90% during all three-cycle filtration and rinsing experiments.

However, Liu et al. (2017) observed that the improvement of antibacterial activity may be limited because the coverage of Ag NPs by polymer brush layer could hinder direct contact between bacteria cells and Ag NPs. To deal with the concern of long-term efficiency caused by the dissolution property of Ag NPs, the regenerative capability of Ag NPs was studied during the design of Ag-modified membranes for biofouling mitigation. Liu and Hu (2016) investigated the rechargeability of Ag NPs on a PDA coated TFC FO membrane surface. In their work, the membrane deposited with Ag NPs was dipped in a

3.5% HNO₃ solution for 48 h to deplete the Ag NPs. Then, the membrane was placed in a 50 mM AgNO₃ solution and incubated for 24 h at room temperature to regenerate Ag NPs. All membranes with regenerated Ag NPs for two cycles and three cycles still exhibited outstanding antibacterial properties (100% bactericidal efficacy after 2 h of contacting time). Liu et al. (2017) resynthesized Ag NPs on a PSBMA coated TFC membrane surface through in-situ reduction of AgNO₃ by NaBH₄ after leaching test. The Ag-regenerated membrane showed a comparable toxicity to *P. aeruginosa* without affecting its antiadhesive property. Qiu and He (2018) used a similar approach with Liu et al. to regenerate Ag NPs on a 1,4-Bis(3-aminopropyl)-piperazine propane carboxylate (DAPPC) coated TFC FO membrane surface to maintain the long-term anti-biofouling property of the membrane.

3.4. Copper and Copper-Based NPs

Like Ag NPs, copper nanoparticles (Cu NPs) also exhibit a broad-spectrum of biocidal activity and can effectively inhibit the growth of microorganisms, such as bacteria, fungi, viruses, and algae (Rubilar et al., 2013; Ingle et al., 2014). Compared to nano-Ag, nano-Cu is much cheaper and more easily available (Ingle et al., 2014), though its biocidal activity is relatively weaker (Zain et al., 2014). In addition, copper and copper oxides in nano sizes can easily mix with polymers or macromolecules and are relatively stable both chemical and physical properties (Rubilar et al., 2013). Thus, Cu NPs are considered as a cheap substitute for Ag NPs, and have been applied in membrane surface modification to improve antimicrobial property and mitigate biofouling in recent years. Table 4 shows the performance of polymeric membranes before and after surface modification with Cu and Cu-based NPs.

The influence of Cu NPs in enhancing the antibacterial properties of TFC-PA membranes for RO desalination was studied by Ben-Sasson et al. (2014b; 2016). The resultant membranes exhibited strong antibacterial activity, leading to 80 ~ 95% reduction of live bacteria that attached on membrane surfaces, without significant effect on the original membrane transport performances. To improve the efficiency of nano-Cu coating, Ma et al. (2016) developed a spray and spin-assisted LBL method to functionalize the TFC-PA RO membrane with controllable loading of Cu NPs. Static bacterial inactivation tests demonstrated that Cu NPs could decrease > 94% of live bacteria on membrane surface within 1 h of contact time. During cross-flow filtration tests, multi-layer coating of Cu NPs effectively mitigated the permeate flux reduction caused by bacterial deposition on the membrane surface, while did not weaken the salt rejection ability, though water permeation flux was reduced 13.3%. Zhang et al. (2017) loaded Cu NPs on a carboxylated chitosan (CCTS) coated TFC membrane. With the help of CCTS, the modified TFC membrane showed efficient and long-lasting antibacterial property for 90 days, since Cu²⁺ was released in a slow and sustainable way because of chelating effect between CCTS and Cu²⁺.

Similar to TFC membranes, improved antibacterial properties and decreased permeate fluxes were observed on PVDF membranes after surface functionalization with Cu NPs (Li et

Table 4. Summary of the Performance of Polymeric Membranes before and after Surface Modification with Cu-based NPs

Membrane	Filtration type	Material	Modification method	Contact angle		Permeate flux		Surface charge		Rejection rate		Antibacterial performance	TMP	Applica-tion	Refer-ence
				Before	After	Before	After	Before	After	Before	After				
TFC	RO	Cu NPs	Self-assembly	52.6 ± 5.3°	45.6 ± 8.4°	2.41 ± 0.14	2.54 ± 0.19	-8 mV	10 mV	98.86 ± 0.26%	98.6 ± 0.27%	Decrease 87 ± 0.2% of viable bacteria with 1 h contact	400 psi	NaCl rejection	Ben- Sasson et al., 2013
TFC	RO	CuSO ₄ , NaBH ₄	In-situ grafting	50°	60°	-	-	-8 mV	-9 mV	-	-	Decreased 89.6 ± 8.2% of live bacteria on surface	-	Desalina- tion	Ben- Sasson et al., 2016
TFC	RO	PEI- coated Cu NPs, PAA	Spray- and spin-assisted LBL coating	53°	60°	1.54 ± 0.18	1.38 ± 0.14	-18 mV	-20 mV	-	-	Decreased > 94 % of live bacteria on surface in 1 h	400 psi	-	Ma et al., 2016
PAN membrane	NF	PDA, PEI- modified Cu NPs.	Co- deposition by using PDA and Cu NPs.	60°	35.5°	300 L/m ² h	120.3 L/m ² h	-45 mV	-10 mV	52.9%	98.5%	Decreased > 97% of live bacteria on surface in 1 h	8 bar	Reactive blue 2 rejection	Zhu et al., 2016
Cu- metalized PVDF membrane	MF (pore size: 0.1 um)	Copper target	Vacuum magnetron sputtering	-	-	80 L/m ² h	40 L/m ² h	-	-	55%	80%	Decreased > 99 % of live bacteria on surface after 18 h	-	BSA rejection	Li et al., 2017
PA- CCTS-Cu TFC membrane	RO	Carboxyl- ated chitosan (CCTS), CuCl ₂	Thermal induced cross linking followed by in-situ reduction	41.6 ± 2.1°	27.4 ± 1.1°	58 L/m ² h	45 L/m ² h	-	-	99.7%	99.3%	> 99% antibacterial efficiency after 90 days' in water	1.5 MPa	NaCl rejection	Zhang et al., 2017

al., 2017). The decrease in water flux could be mainly due to the increase in membrane resistance caused by nano-Cu coating, and Cu NPs could not significantly improve the membrane hydrophilicity to offset the resistance increase. Nevertheless, Zhu et al. (2016) used PDA to immobilize PEI-modified Cu NPs onto a porous PAN membrane surface, bridging the surface cavities from UF to loose NF. The surface charge was significantly increased, which promoted an excellent salt permeation (82% Na₂SO₄ and 98% NaCl). The functionalized membrane also displayed distinct antibacterial activity with a reduction of 93.7% in the number of live *E. coli*.

3.5. Iron and Iron Oxides NPs

Applications of engineered Fe NPs in environmental cleanup came about after it was found that Fe NPs could rapidly transform a group of recalcitrant groundwater pollutants (i.e., trichloroethylene (TCE) and polychlorinated biphenyls (PCBs)) (Wang and Zhang, 1997; Yan et al., 2013). In recent years, Fe NPs have been involved into the most active sub-field of environmental nanotechnology with a series of incredible advances, which were seen in the areas of fundamental understanding of nano-Fe reactivity with environmental pollutants,

surface engineering, as well as pilot and full-scale field implementation (Yan et al., 2013). Research work has taken advantages of Fe NPs to pursue better performances of polymeric membranes in separation processes. Immobilizing Fe NPs on membrane surfaces can enhance particle dispersion and enable applications of Fe NPs in continuous flow systems. Table 5 shows of the performances of polymeric membranes before and after immobilizing Fe/Fe₂O₃-based NPs on membrane surfaces.

PVDF membranes have been regarded as the most popular support of Fe NPs because of its excellent chemical resistance and thermal stability. Ma et al. (2015) deposited Fe NPs onto a PVDF UF membrane surface through suction filtration for HA fouling reduction. Increased loading amount of Fe NPs on the membrane surface increased the fouling resistance while slightly reducing the water permeability. However, the Fe NP agglomeration reduces its surface area and reactivity, which hampers the practical application of Fe NPs. By using stabilizers such as thiols, carboxylic acids, surfactants, and polymers, Fe NPs could be strongly attached on membrane surfaces without serious agglomeration. These stabilizers contain carboxylic, hydroxylic, or amine groups which can act as chelating sites for Fe NPs or precursors to enhance particle dispersion and im-

Table 5. Summary of the Performance of Polymeric Membranes before and after Surface Modification with Fe/Fe₂O₃-based NPs

Membrane	Filtration type	Material	Modification method	Contact angle		Permeate flux		Rejection rate		TMP	Application	Reference
				Before	After	Before	After	Before	After			
Pd/Fe NPs immobilized PVDF membrane	MF	PAA, EG, FeSO ₄ ·7H ₂ O, NaBH ₄ , palladium acetate	In-situ reduction	-	-	-	-	-	75% within 30 min	-	Dechlorination of trichloroacetic acid	Wang et al., 2008
Ni/Fe NPs immobilized nylon 66 membrane	MF	FeSO ₄ ·7H ₂ O, PEG, NaBH ₄ , NiCl ₂ ·6H ₂ O	In-situ reduction	-	-	-	-	-	100% within 25 min	-	Dechlorination of tri-chloroethylene	Parshetti et al., 2009
PAA-Fe/Pd-modified PVDF membrane	MF	PAA, FeCl ₂ , NaBH ₄ , K ₂ PdCl ₄	In-situ reduction	-	-	4824 × 10 ⁻⁴ cm ³ /cm ² s bar	9.9 × 10 ⁻⁴ cm ³ /cm ² s bar	-	-	-	Dechlorination of 2, 2'dichlorobiphenyl	Smuleac et al., 2010
Pd/Fe NPs immobilized PAA/PVDF·Al ₂ O ₃ membrane	UF (pore size: 60 nm)	PAA, ferrous solution, KBH ₄ , palladium acetate	PAA grafting followed by in-situ reduction	58.4°	39.5°	-	-	10%	95% within 30 min	-	Dechlorination of mono-chloroacetic acid	Meng et al., 2011
Pd/Fe-based PVDF composite membrane	MF	PAA	In-situ reduction	78°	49°	-	-	-	95%	-	Dechlorination of trichloroacetic acid	Wang et al., 2013
Fe ₃ O ₄ /polysulfone nanocomposite PSf membranes	-	PAA, Fe ₃ O ₄ NPs	UV-induced copolymerization	85°	50°	1700 L/m ² h	2300 L/m ² h	40%	85%	300 kPa	Dye separation	Homa-yoonfal et al., 2014
PAA/PVDF-NZVI hybrid membrane	MF (pore size: 0.65 μm)	PAA	PAA thermal grafting followed by in-situ reduction	-	-	-	-	70%	98% within 120 min	-	Metronidazole removal	Yang et al., 2014
PVDF membrane	UF (MWCO: 100 kDa)	NZVI NPs	Deposition by suction filtration	-	-	79% flux decline	32% flux decline	19.92%	98.52%	0.1 MPa	HA removal	Ma et al., 2015
Pd/Fe NPs immobilized PVDF/Al ₂ O ₃ membrane	-	PAA, ferrous solutin, KBH ₄ , palladium acetate	PAA thermal grafting followed by in-situ reduction	58.4°	39.5°	-	-	-	97.71% within 90 min	-	Dechlorination of trichloroacetic acid	Zhang et al., 2015
AM-0.4NP polyethylene membrane	-	PPO, Fe ₂ O ₃	Chemical cross linking	100.1 ± 3.2°	65.8 ± 0.9°	-	-	-	Improved 45% of fouling resistance	-	Rejection of 0.1 mol/L NaCl and 0.0018 mol/L SDS	Fernandez-Gonzalez et al., 2017
Fe/Pd-PAA-PVDF membrane	UF (pore size: 49.8 ± 24.1 nm)	PAA	Thermal induced PAA grafting followed by in-situ reduction	81.3 ± 1.9°	52.5 ± 3.9°	-	-	-	96% within 15 s of residence time	2.76 bar	3,3',4,4',5-pentachlorobiphenyl (PCB 126) degradation	Wan et al., 2017
FeOCl/PVDF membrane	UF (pore size: 33.5 nm)	FeCl ₃ ·6H ₂ O	Dip coating followed by thermal treatment	86.5°	58.2°	70% flux decline	30% flux decline	74%	96%	0.7 bar	BSA rejection	Sun et al., 2018

Continued

Membrane	Filtration type	Material	Modification method	Contact angle		Permeate flux		Rejection rate		TMP	Application	Reference
				Before	After	Before	After	Before	After			
Fe-HP-PVDF membrane	MF (pore size: 175 nm)	PDA/PEI, FeCl ₂ , NaBH ₄	Co-deposition followed by in-situ reduction	103.5°	43.4°	~257 L/m ² h	578 L/m ² h	~12%	~31%	0.1 MPa	BSA rejection	He et al., 2020
TA-Fe ³⁺ /PAN composite membrane	NF	Tannic acid (TA), FeCl ₃ ·6H ₂ O	Layer-by-layer self-assembly	56°	8°	198.5 L/m ² h	40.9 L/m ² h	9.6%	93.9%	2 bar	IR dye separation	Xiao et al., 2020
PES	UF	Hydrous Fe ₂ O ₃ , PDA	Dip coating followed by UV irradiation	70°	30°	-	20% flux decline	-	> 90%	1 bar	Oil/water separation	Abdi et al., 2021

prove its longevity (Cushing et al., 2004). Yang et al. (2014) and Silva et al. (2021) encapsulated Fe NPs on PAA grafted PVDF membrane surface for the degradation of organic contaminants. The resultant membranes had high reactivity, excellent stability, and reusability during the reaction process. He et al. (2020) developed a hierarchical active PVDF membrane with PDA/PEI co-supported Fe NPs. The developed membrane showed advanced oxidation activity with high flux recovery rate (~85% with BSA and ~95% with HA solutions). It was especially reported that highly exposed active sites with a trace amount of H₂O₂ flowing were observed over the membrane surface. Thus, unwanted foulants could be removed from the membrane interface, allowing multi-cycle use of the membrane after backwashing with H₂O₂ (0.33 wt %).

Nevertheless, the reactivity of Fe NPs could reduce over time due to the formation of a passivation layer on the particle surface. Compared with Fe NPs, bimetallic NPs such as Pd/Fe, Ni/Fe, and Cu/Fe NPs were found to have higher efficiencies for the dechlorination of organic contaminants (Parshetti and Doong, 2009). For example, in Pd/Fe bimetallic system, the corrosion of Fe leads to the emerging of hydrogen, and Pd has the ability to absorb hydrogen into its lattice and then acts as catalyst to accelerate hydro-dechlorination (Korte et al., 2000). Wang et al. (2008) prepared and immobilized Pd/Fe NPs on a PAA/PVDF blend membrane surface in which a hydrophilic layer composed of PVA, glutaraldehyde, and PEG was coated. The obtained membrane exhibited high reactivity in trichloroacetic acid (TCAA) dechlorination, achieving 75% of dechlorination rate within 30 min. They also reported that the hydrophilization process facilitated the even dispersion of Pd/Fe NPs inside the membrane pores, leading to 6.8 times greater catalytic dechlorination rate of TCAA compared with unhydrophilized PVDF membrane (Wang et al., 2013). Smuleac et al. (2010) loaded Pd/Fe NPs on PAA grafted PVDF membrane surface for degradations of dichlorobiphenyl and TCE, and investigated the recovery of reactivity. Using convective flow (flux in the range of $2.4 \times 10^{-4} \sim 3.9 \times 10^{-4}$ cm³/cm² s) could substantially reduce the degradation time, for instance, 43% of dichlorobiphenyl was converted to biphenyl in less than 40 s. The regeneration and reuse of Fe/Pd modified PVDF membrane could be realized by washing with NaBH₄ solution, and the initial reactivity in the membrane domain could be sustained even after 3 months of multiple use (Smuleac et al.,

2011). This Fe/Pd NPs-PVDF membrane system also showed excellent performance in the degradation of 3,3',4,4',5-pentachlorobiphenyl (PCB 126), over 96% degradation rate was achieved within 15 s of residence time in convective flow mode (0.171 L/m² h) (Wan et al., 2017). In addition, Pd/Fe NPs were immobilized in the PAA grafted PVDF/Al₂O₃ blend membrane surfaces by Meng et al. (2011) and Zhang et al. (2015). The obtained membranes demonstrated high efficiency and stability for dechlorinations of monochloroacetic acid (MCAA) and dichloroacetic acid (DCAA).

Besides pure Fe and bimetallic NPs, other kinds of iron compound NPs were applied to improve filtration performances of polymeric membranes. Homayoonfal et al. (2014) fixed Fe₃O₄ NPs on a PSf membrane surface using UV-induced PAA co-polymerization. The permeate flux was increased from 1,700 to 2,300 L/m² h, and the rejection rate was raised from 40 to 85% for dye separation after modification. Higher hydrophilicity and enhanced fouling resistance were observed on polyethylene (PE) anion exchange membranes after immobilization of sulfonated Fe₂O₃ NPs on membrane surfaces (Fernandez-Gonzalez et al., 2017). Lately, Sun et al. (2018) fabricated a reactive, self-cleaning, and antifouling PVDF UF membrane with nano-FeOCl coating for the separation and degradation of organic contaminants. The functional PVDF membrane fouled by BSA could achieve about 100% of water flux recovery rate through H₂O₂ (340 mg/L) cleaning process. The reactive membrane had ability to in-situ produce active hydroxyl radicals, and thus could completely degrade bisphenol A when H₂O₂ was added in the feed solution under neutral pH condition. Abdi et al. (2021) modified PES membranes through both adding hydrous Fe₂O₃ NPs into membrane matrix and coating such NPs on membrane surface with the help of dopamine and UV irradiation. The optimal membrane was synthesized with 5 and 0.5 wt % of hydrous Fe₂O₃ NPs in the membrane matrix and surface, respectively. This membrane rendered more than 80% of FRR and 95% of oil rejection rate for oil/water separation.

3.6. Other Metal and Metal Oxide NPs

In addition to the metal and metal oxide NPs reviewed above, noble metal NPs have also been investigated for functionalization of water treatment membranes due to their special properties (Table 6). For example, Pd NPs are good catalysts

for various hydrogenation reactions because of their unique affinity to hydrogen. Several studies loaded Pd NPs onto PAA and poly(ionic liquid) grafted PES membrane surfaces through in-situ chemical reduction for catalytic reactions (Emin et al., 2014; Gu et al., 2015; López-Viveros et al., 2021). However, the catalytic activity of Pd nanoparticles may be reduced due to the coverage of biofoulants like proteins and polysaccharides during filtration process (Cheng et al., 2016). Cheng et al. (2016) introduced 1,2,3-triazole as an antibacterial agent to protect Pd NP coated PSf membrane from antifouling in membrane bioreactors.

Like Pd NPs, Au NPs were also immobilized on polymeric membrane surfaces to obtain membrane catalytic reactors with long-term catalytic stability (Niu et al., 2014). Subair et al. (2016) modified poly(ethylene terephthalate) (PET) track-etched membrane surfaces by PDA polymerization and further grafted PEI for in-situ nano-Au formation. It was reported that Au NPs were generated through self-reduction of $[\text{AuCl}_4]^-$ ions adsorbed on PDA coating. The catalytically active membranes were used for continuous flow catalysis in membrane reactors to degrade p-nitrophenol (PNP) and dyes. About 99% of reduction rate for PNP to p-aminophenol (PAP) was obtained at $\sim 40 \text{ L/m}^2 \text{ h}$ of permeation rate, and the reduction rates for Congo red and MB were $\sim 95\%$ and 98% at 947 and $473 \text{ L/m}^2 \text{ h}$, respectively. These catalytic activities could maintain 11 cycles of dye degradation. Wu et al. (2016) reported self-assembly of Au NPs on a PDA coated PVDF MF membrane surface. The resultant membrane was superhydrophilic and could degraded more than 90% of PNP in 5 minutes with a kinetic reaction rate constant of $47.84 \times 10^{-2} \text{ min}^{-1}$ over 6 cycles. A membrane catalytic reactor with this modified membrane could be designed to continuously degrade PNP under a kinetic reaction rate constant of $7 \times 10^{-2} \text{ min}^{-1}$.

MnO_2 NPs have superior adsorption performance due to their large surface areas and polymorphic structures. Li et al. (2016) reported an affinity membrane for removal of heavy metals under MF operation. The membrane was developed by modifying RGO-PVDF blend membrane surface with nano- MnO_2 coating. The developed membrane showed a high removal rate (87.4%) of Ni^{2+} in dynamic adsorption, and the membrane could be regenerated through dipping in 0.1 M HNO_3 solution. Besides, the application of nano- MnO_2 coating on membrane surface was found to be beneficial for fouling resistance. Yu et al. (2016) assessed the effectiveness of combining a PVDF UF membrane and MnO_2 NP coating for the treatment of river water. With the help of pre-treatment using low dose ozone, there was much less fouling on the nano- MnO_2 coated membrane surface (0.5 kPa for 70 days), but the uncoated membrane suffered from both reversible and irreversible fouling. This could be attributed to the increase in membrane hydrophilicity because of the nano- MnO_2 coating, and catalytic reactions between the ozone and MnO_2 NPs which enhanced the degradation of organic foulants.

Al_2O_3 NPs and ZrO_2 NPs have been extensively applied to develop and manufacture ceramic membranes due to their excellent thermal inertness, surface reactivity, and mechanical strength (Goh and Ismail, 2018; Samaei et al., 2018; Chen et

al., 2022). Several researchers also immobilized them on polymeric membrane surfaces to obtain desirable performances. Garcia-Ivars et al. (2014) deposited Al_2O_3 NPs on a PES UF membrane surface via UV-induced co-polymerization with PEG. The hydraulic permeability and fouling resistance were significantly improved with the optimized PEG/ Al_2O_3 coating. Chen et al. (2020) modified a commercial PVDF UF membrane with PAA- ZrO_2 coating to treat high-concentration TBBPA wastewater. Compared to the original membrane, the modified PVDF membrane exhibited 4 times of permeate flux ($200 \text{ L/m}^2 \cdot \text{min}$) without reducing TBBPA rejection rate.

Recently, metal-organic frameworks (MOFs) that contain both organic and inorganic moieties have been paid attention as novel nanomaterials due to their tunable pore structure, compatibility with polymers, and large surface area (Li et al., 2015; Cao et al., 2018; Deng et al., 2021). However, most of MOFs are not stable in water environment for a long time, which restricts their application in water treatment. Researchers have tried to develop new MOFs or MOF-based materials with water stability and hydrophilicity, and applied them to water treatment membranes. Gao et al. (2018) synthesized UiO66-NH_2 -PAA and loaded the MOFs on mixed cellulose ester (MCE) MF membrane surface through vacuum-assisted self-assembly process. The resultant membrane showed high hydrophilicity and underwater super-oleophobicity due to the high-water absorption ability and surface roughness of MOF coating. Accordingly, the membrane exhibited high separation efficiency for oil/water emulsion (rejection $> 99.9\%$), and the FRR after 3 cycles could maintain over 80%. Zheng et al. (2021) successfully synthesized a kind of Cu-MOF-74 and coated it on PVDF membrane surfaces to improve membrane anti-biofouling performance. The antibacterial efficiency of the modified membrane could be 97.7% at 4 h due to the generation of Cu^{2+} from MOF coating.

4. Conclusions and Discussions

Over the past few decades, polymeric membrane-based separation technologies have been commonly utilized for practical water and wastewater treatment. However, polymeric membranes are usually hydrophobic and electrically charged, which leads to undesirable phenomena such as fouling tendency and low water permeability. Many surfaces modification techniques that aim to endow desirable surface properties have been developed. More recently, surface functionalization/modification with NPs to boost overall membrane performances for water treatment has attracted attention from researchers. In this regard, various NPs have been synthesized and immobilized onto polymeric membrane surfaces using different techniques. In general, these efforts try to improve the hydrophilicity, anti-fouling properties, and pollutant separation efficiencies of polymeric membranes. Herein, the roles of metal and metal-oxide based NPs (TiO_2 , Ag, ZnO, Cu, Fe/ Fe_3O_4 , etc.) are particularly investigated in enhancing the performances of polymeric membranes for water and wastewater treatment. Undoubtedly, these NPs have significant effects on the improvements of the desired characteristics of membranes due to their unique properties,

Table 6. Summary of the Performance of Polymeric Membranes before and after Surface Modification with Other NPs

NPs	Membrane	Filtration type	Material	Modification method	Contact angle		Permeate flux		Rejection rate		TMP	Application	Reference
					Before	After	Before	After	Before	After			
Palladium (Pd) NPs	PES membrane	MF (pore size: 0.2 μm)	PAA, Pd(NH ₃) ₄ Cl ₂ , H ₂ O, NaBH ₄	UV photo-grafting PAA polymerization followed by in-situ reduction	-	-	-	-	58%	90% under UV	-	Catalytic conversion of p-nitrophenol	Emin et al., 2014
Al ₂ O ₃ NPs	PSf membrane	UF (pore size: 14.3 nm)	PEG, Al ₂ O ₃ NPs	UV photo-grafting	72.9 \pm 1.5°	51.9 \pm 1.6°	2.352 L/m ² h kPa	387.85 L/m ² h kPa	-	-	200 kPa	PEG rejection	Garcia-Ivars et al., 2014
Pd NPs	PES membrane	MF (pore size: 0.2 μm)	Poly(Ionic liquid) (PIL)	UV photo-grafting PIL polymerization followed by in-situ reduction	-	-	-	-	-	-	-	Suzuki-Miyaura cross-coupling reaction	Gu et al., 2015
Pd NPs	PSf membrane	MF	N,N-dimethylacetamide (DMAc)	In-situ reduction	69.60 \pm 0.75°	47.72 \pm 1.34°	-	-	95%	95%	10 kPa	COD removal	Cheng et al., 2016
MnO ₂ NPs	PVDF/RGO membrane	-	KMnO ₄	Cicrowave induced in-situ formation	78.5 \pm 0.8°	76.7 \pm 1.9°	4.5 L/m ² h	10 L/m ² h	75%	80%	0.1 MPa	BSA solution	Li et al., 2016
Au NPs	Poly (ethylene terephthalate) (PET) membrane	MF (pore size: 0.4 μm)	Dopamine, PEI, HAuCl ₄ , NaBH ₄	Self-polymerization of PDA and PEI followed by Au in-situ reduction	-	-	789.2 L/m ² h	473.5 L/m ² h	-	98%	0.2 bar	Methylene blue degradation	Subair et al., 2016
Au NPs	Au-PDA-PVDF membrane	MF	DA, Au NPs	PDA self-polymerization followed by Au self-assembly	27.7°	19.1°	7,000 L/m ² h	8,000 L/m ² h	-	90% in 30 min	-	Degradation of p-nitrophenol	Wu et al., 2016
MnO ₂ NPs	PVDF membrane	UF (pore size: 0.03 μm)	-	Dip-coating (self-assembly)	-	-	-	-	-	Small foul-ing for 70 days	0.5 kPa	MBR, drinking water treatment	Yu et al., 2016
UiO-66	UiO-66-NH ₂ -PAA mixed cellulose ester (MCE) membrane	MF (pore size: 0.22 μm)	PAA	Vacuum-assisted self-assembly	60.8°	11.9°	-	-	99.9%	99.9%	-	Oil removal from oil/water emulsion	Gao et al., 2018
Metal-Nano GO frameworks	Metal-NGO frameworks modified PPS membrane	-	GO NPs, HCl, divalent metal cations	Vacuum-assisted self-assembly	50.4°	36°	446.2 L/m ² h MPa	3109.5 L/m ² h MPa	-	99.9%	0.03 MPa	RB rejection	Gao et al., 2019
ZrO ₂ NPs	PVDF10-PAA-ZrO ₂ membrane	UF (MWCO: 10 kDa)	PAA, ZrO ₂	Plasma induced PAA grafting followed by self-assembly	75.52°	34.5°	41.0 L/m ² min	210 L/m ² min	73.6%	78%	8 bar	TBBPA removal	Chen et al., 2020

Continued

NPs	Membrane	Filtration type	Material	Modification method	Contact angle		Permeate flux		Rejection rate		TMP	Application	Reference
					Before	After	Before	After	Before	After			
Cu-MOF-74	Cu-MOF-74/PDA-PVDF	MF (pore size: 0.45 μm)	DA, Cu-MOF-74	PDA self-polymerization followed by MOF self-assembly	70°	15°	-	-	-	97.7%	4.5	Anti-biofouling	Zheng et al., 2021
ZrO ₂ NPs	PES-PAA-ZrO ₂ membrane	NF	PAA, ZrO ₂	Plasma induced PAA grafting followed by self-assembly	49.7°	8.6°	87.4 L/m ² min	436.9 L/m ² min	73.6%	78%	4.5 MPa	PAH removal	Chen et al., 2022

such as high hydrophilicity, large surface area, or/and excellent antibacterial activity.

So far, surface functionalization/modification of polymeric membranes with Ag and TiO₂ based NPs have been exploited well. TiO₂ based NPs are the most commonly choice to improve membrane hydrophilicity, and Ag NPs are mostly involved in reducing the biofouling. ZnO and Cu based NPs are paid increasing attention to act as alternatives of TiO₂ and Ag based NPs, respectively, due to their lower cost. Nevertheless, the chemical stability of nano-ZnO is not as good as that of nano-TiO₂, and the bactericidal activity of nano-Cu is not as strong as that of nano-Ag. These limit their application in membrane surface functionalization to a certain extent, and can be considered in future research. For pure Fe and noble metal NPs, they have been proved to be useful for degradation of organic pollutants in membrane catalytic reactors, whereas their high reactivity and cost are not favorite in practical applications. They may be more suitable to be applied as doping materials to decorate other kinds of nanomaterials, forming nanocomposites with superior properties. Applications of emerging NPs such as nanocomposites and MOFs would be a trend in the field of membrane surface functionalization if their syntheses can be well addressed with reasonable costs.

However, the biggest challenge/risk to overcome in using these NPs is their releases from membrane surfaces into the environment during filtration processes, which may cause serious health risks due to their accumulation in the environment. Thus, the effective adhesion of NPs on membrane surfaces should be achieved in membrane modification processes to ensure the high stability of NPs during filtration applications. Currently, some methods of NP immobilization are too complicated, leading to difficulties in large scale application, even if the resultant NP coatings are stable enough. In the future, efforts should be continued to realize minimal leaching of the immobilized NPs from the concerned membrane surface with facile strategy.

In addition, in most of the research on membrane fabrication and modification, the developed membranes are characterized by traditional techniques mentioned above. In some cases, the mechanism of membrane fabrication and modification cannot be clearly revealed. With the development of synchrotron radiation techniques, the application of synchrotron-based techniques can be promising in this research field. Combined use of synchrotron-based and conventional techniques can not only

comprehensively characterize the modified membranes, but also collect more information from different angles for synergistically analyzing the relevant mechanism of membrane modification and filtration.

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References

- Abdi, S., Nasiri, M., Yuan, S., Zhu, J. and Van der Bruggen, B. (2021). Fabrication of PES-based super-hydrophilic ultrafiltration membranes by combining hydrous ferric oxide particles and UV irradiation. *Separation and Purification Technology*, 259, 118132. <https://doi.org/10.1016/j.seppur.2020.118132>
- Abid, H.S., Johnson, D.J., Hashaiekh, R. and Hilal, N. (2017). A review of efforts to reduce membrane fouling by control of feed spacer characteristics. *Desalination*, 420, 384-402. <https://doi.org/10.1016/j.desal.2017.07.019>
- Al-anzi, B.S. and Siang, O.C. (2017). Recent developments of carbon based nanomaterials and membranes for oily wastewater treatment. *RSC Advances*, 7(34), 20981-20994. <https://doi.org/10.1039/C7RA02501G>
- Asadollahi, M., Bastani, D. and Musavi, S.A. (2017). Enhancement of surface properties and performance of reverse osmosis membranes after surface modification: A review. *Desalination*, 420, 330-383. <https://doi.org/10.1016/j.desal.2017.05.027>
- Baker, T.J., Tyler, C.R. and Galloway, T.S. (2014). Impacts of metal and metal oxide nanoparticles on marine organisms. *Environmental Pollution*, 186, 257-271. <https://doi.org/10.1016/j.envpol.2013.11.014>
- Ben-Sasson, M., Lu, X., Bar-Zeev, E., Zodrow, K.R., Nejati, S., Qi, G., Giannelis, E.P. and Elimelech, M. (2014a). In situ formation of silver nanoparticles on thin-film composite reverse osmosis membranes for biofouling mitigation. *Water Research*, 62, 260-270. <https://doi.org/10.1016/j.watres.2014.05.049>
- Ben-Sasson, M., Lu, X., Nejati, S., Jaramillo, H. and Elimelech, M. (2016). In situ surface functionalization of reverse osmosis membranes with biocidal copper nanoparticles. *Desalination*, 388, 1-8. <https://doi.org/10.1016/j.desal.2016.03.005>
- Ben-Sasson, M., Zodrow, K.R., Genggen, Q., Kang, Y., Giannelis, E.P. and Elimelech, M. (2014b). Surface functionalization of thin-film composite membranes with copper nanoparticles for antimicrobial surface properties. *Environmental Science & Technology*, 48(1), 384-393. <https://doi.org/10.1021/es404232s>
- Bet-moushoul, E., Mansourpanah, Y., Farhadi, K. and Tabatabaei, M. (2016). TiO₂ nanocomposite based polymeric membranes: A review on performance improvement for various applications in che-

- mical engineering processes. *Chemical Engineering Journal*, 283, 29-46. <https://doi.org/10.1016/j.cej.2015.06.124>
- Cao, J., Su, Y., Liu, Y., Guan, J., He, M., Zhang, R. and Jiang, Z. (2018). Self-assembled MOF membranes with underwater superoleophobicity for oil/water separation. *Journal of Membrane Science*, 566, 268-277. <https://doi.org/10.1016/j.memsci.2018.08.068>
- Cao, X., Tang, M., Liu, F., Nie, Y. and Zhao, C. (2010). Immobilization of silver nanoparticles onto sulfonated polyethersulfone membranes as antibacterial materials. *Colloids and Surfaces B: Biointerfaces*, 81(2), 555-562. <https://doi.org/10.1016/j.colsurfb.2010.07.057>
- Chen, L.H., Huang, A., Chen, Y.R., Chen, C.H., Hsu, C.C., Tsai, F.Y. and Tung, K.L. (2018). Omniphobic membranes for direct contact membrane distillation: Effective deposition of zinc oxide nanoparticles. *Desalination*, 428, 255-263. <https://doi.org/10.1016/j.desal.2017.11.029>
- Chen, X., Huang, G., An, C., Feng, R., Wu, Y. and Huang, C. (2019a). 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. *Journal of Membrane Science*, 582, 70-82. <https://doi.org/10.1016/j.memsci.2019.03.091>
- Chen, X., Huang, G., An, C., Feng, R., Wu, Y. and Huang, C. (2022). Superwetting polyethersulfone membrane functionalized with ZrO₂ nanoparticles for polycyclic aromatic hydrocarbon removal. *Journal of Materials Science & Technology*, 98, 14-25. <https://doi.org/10.1016/j.jmst.2021.01.063>
- Chen, X., Huang, G., An, C., Feng, R., Yao, Y., Zhao, S., Huang, C. and Wu, Y. (2019b). Plasma-induced poly(acrylic acid)-TiO₂ coated polyvinylidene fluoride membrane for produced water treatment: Synchrotron X-Ray, optimization, and insight studies. *Journal of Cleaner Production*, 227, 772-783. <https://doi.org/10.1016/j.jclepro.2019.04.226>
- Chen, X., Huang, G., Li, Y., An, C., Feng, R., Wu, Y. and Shen, J. (2020). Functional PVDF ultrafiltration membrane for Tetrabromobisphenol-A (TBBPA) removal with high water recovery. *Water Research*, 115952. <https://doi.org/10.1016/j.watres.2020.115952>
- Cheng, H., Xie, Y., Villalobos, L.F., Song, L., Peinemann, K.V., Nunes, S. and Hong, P.Y. (2016). Antibiofilm effect enhanced by modification of 1,2,3-triazole and palladium nanoparticles on polysulfone membranes. *Scientific Reports*, 6(1), 24289. <https://doi.org/10.1038/srep24289>
- Chudobova, D., Nejd, L., Gumulec, J., Krystofova, O., Rodrigo, M.A.M., Kynicky, J., Ruttkay-Nedecky, B., Kopel, P., Babula, P. and Adam, V. (2013). Complexes of silver (I) ions and silver phosphate nanoparticles with hyaluronic acid and/or chitosan as promising antimicrobial agents for vascular grafts. *International Journal of Molecular Sciences*, 14(7), 13592-13614. <https://doi.org/10.3390/ijms140713592>
- Cushing, B.L., Kolesnichenko, V.L. and O'Connor, C.J. (2004). Recent advances in the liquid-phase syntheses of inorganic nanoparticles. *Chemical Reviews*, 104(9), 3893-3946. <https://doi.org/10.1021/cr030027b>
- de Lima, R., Seabra, A.B. and Durán, N. (2012). Silver nanoparticles: A brief review of cytotoxicity and genotoxicity of chemically and biogenically synthesized nanoparticles. *Journal of Applied Toxicology*, 32(11), 867-879. <https://doi.org/10.1002/jat.2780>
- Deng, Y., Wu, Y., Chen, G., Zheng, X., Dai, M. and Peng, C. (2021). Metal-organic framework membranes: Recent development in the synthesis strategies and their application in oil-water separation. *Chemical Engineering Journal*, 405, 127004. <https://doi.org/10.1016/j.cej.2020.127004>
- Diagne, F., Malaisamy, R., Boddie, V., Holbrook, R.D., Eribo, B. and Jones, K.L. (2012). Polyelectrolyte and silver nanoparticle modification of microfiltration membranes to mitigate organic and bacterial fouling. *Environmental Science & Technology*, 46(7), 4025-4033. <https://doi.org/10.1021/es203945v>
- Dlamini, D.S., Mamba, B.B. and Li, J. (2019). The role of nanoparticles in the performance of nano-enabled composite membranes – A critical scientific perspective. *Science of The Total Environment*, 656, 723-731. <https://doi.org/10.1016/j.scitotenv.2018.11.421>
- Dong, C., Wang, Z., Wu, J., Wang, Y., Wang, J. and Wang, S. (2017). A green strategy to immobilize silver nanoparticles onto reverse osmosis membrane for enhanced anti-biofouling property. *Desalination*, 401, 32-41. <https://doi.org/10.1016/j.desal.2016.06.034>
- Emin, C., Remigy, J.C. and Lahitte, J.F. (2014). Influence of UV grafting conditions and gel formation on the loading and stabilization of palladium nanoparticles in photografted polyethersulfone membrane for catalytic reactions. *Journal of Membrane Science*, 455, 55-63. <https://doi.org/10.1016/j.memsci.2013.12.049>
- EPA, U.S. (2009). *Toxicological Review of Cerium Oxide and Cerium Compounds*. EPA/635/R-08/002F.
- Faria, A.F., Liu, C., Xie, M., Perreault, F., Nghiem, L.D., Ma, J. and Elimelech, M. (2017). Thin-film composite forward osmosis membranes functionalized with graphene oxide-silver nanocomposites for biofouling control. *Journal of Membrane Science*, 525, 146-156. <https://doi.org/10.1016/j.memsci.2016.10.040>
- Feng, Y., Guo, N., Ren, S., Xie, X., Xu, J. and Wang, Y. (2021). AgNPs@ZIF-8 hybrid material-modified polyethersulfone microfiltration membranes for antibiofouling property and permeability improvement. *Chemical Engineering & Technology*, 44(2), 265-272. <https://doi.org/10.1002/ceat.202000417>
- Fernandez-Gonzalez, C., Zhang, B., Dominguez-Ramos, A., Ibañez, R., Irabien, A. and Chen, Y. (2017). Enhancing fouling resistance of polyethylene anion exchange membranes using carbon nanotubes and iron oxide nanoparticles. *Desalination*, 411, 19-27. <https://doi.org/10.1016/j.desal.2017.02.007>
- Fischer, K., Gawel, A., Rosen, D., Krause, M., Abdul Latif, A., Griebel, J., Prager, A. and Schulze, A. (2017). Low-temperature synthesis of anatase/rutile/brookite TiO₂ nanoparticles on a polymer membrane for photocatalysis. *Catalysts*, 7(7), 209. <https://doi.org/10.3390/cata7070209>
- Fischer, K., Grimm, M., Meyers, J., Dietrich, C., Gläser, R. and Schulze, A. (2015). Photoactive microfiltration membranes via directed synthesis of TiO₂ nanoparticles on the polymer surface for removal of drugs from water. *Journal of Membrane Science*, 478, 49-57. <https://doi.org/10.1016/j.memsci.2015.01.009>
- Gao, S., Zhu, Y., Wang, J., Zhang, F., Li, J. and Jin, J. (2018). Layer-by-layer construction of Cu²⁺/alginate multilayer modified ultrafiltration membrane with bioinspired superwetting property for high-efficient crude-oil-in-water emulsion separation. *Advanced Functional Materials*, 28(49), 1801944. <https://doi.org/10.1002/adfm.201801944>
- Garcia-Ivars, J., Iborra-Clar, M.I., Alcaina-Miranda, M.I., Mendoza-Roca, J.A. and Pastor-Alcañiz, L. (2014). Development of fouling-resistant polyethersulfone ultrafiltration membranes via surface UV photografting with polyethylene glycol/aluminum oxide nanoparticles. *Separation and Purification Technology*, 135, 88-99. <https://doi.org/10.1016/j.seppur.2014.07.056>
- Goh, P.S., Lau, W.J., Othman, M.H.D. and Ismail, A.H. (2018). Membrane fouling in desalination and its mitigation strategies. *Desalination*, 425, 130-155. <https://doi.org/10.1016/j.desal.2017.10.018>
- Goh, P.S. and Ismail, A.F. (2018). A review on inorganic membranes for desalination and wastewater treatment. *Desalination*, 434, 60-80. <https://doi.org/10.1016/j.desal.2017.07.023>
- Gu, Y., Favier, I., Pradel, C., Gin, D.L., Lahitte, J.F., Noble, R.D., Gómez, M. and Remigy, J.C. (2015). High catalytic efficiency of palladium nanoparticles immobilized in a polymer membrane containing poly(ionic liquid) in Suzuki-Miyaura cross-coupling reaction. *Journal of Membrane Science*, 492, 331-339. <https://doi.org/10.1016/j.memsci.2015.05.051>
- Gunawan, P., Guan, C., Song, X., Zhang, Q., Leong, S.S.J., Tang, C.,

- Chen, Y., Chan-Park, M.B., Chang, M.W., Wang, K. and Xu, R. (2011). Hollow fiber membrane decorated with Ag/MWNTs: toward effective water disinfection and biofouling control. *ACS Nano*, 5(12), 10033-10040. <https://doi.org/10.1021/nn2038725>
- He, M., Wang, Q., Wang, R., Xie, Y., Zhao, W. and Zhao, C. (2017). Design of antibacterial poly (ether sulfone) membranes via covalently attaching hydrogel thin layers loaded with Ag nanoparticles. *ACS Applied Materials & Interfaces*, 9(19), 15962-15974. <https://doi.org/10.1021/acsami.7b03176>
- He, Z., Mahmud, S., Zhao, S., Yang, Y., Zhu, L., Zhao, Y., Zeng, Q., Xiong, Z. and Hu, C. (2020). Hierarchically active poly(vinylidene fluoride) membrane fabricated by in-situ generated zero-valent iron for fouling reduction. *ACS Applied Materials & Interfaces*, 12(9), 10993-11004. <https://doi.org/10.1021/acsami.9b22147>
- Hegab, H.M., Wimalasiri, Y., Ginic-Markovic, M. and Zou, L. (2015). Improving the fouling resistance of brackish water membranes via surface modification with graphene oxide functionalized chitosan. *Desalination*, 365, 99-107. <https://doi.org/10.1016/j.desal.2015.02.029>
- Homayoonfal, M., Mehrnia, M.R., Shariaty-Niassar, M., Akbari, A., Ismail, A.F. and Matsuura, T. (2014). A comparison between blending and surface deposition methods for the preparation of iron oxide/polysulfone nanocomposite membranes. *Desalination*, 354, 125-142. <https://doi.org/10.1016/j.desal.2014.09.031>
- Hou, C., Jiao, T., Xing, R., Chen, Y., Zhou, J. and Zhang, L. (2017). Preparation of TiO₂ nanoparticles modified electrospun nanocomposite membranes toward efficient dye degradation for wastewater treatment. *Journal of the Taiwan Institute of Chemical Engineers*, 78, 118-126. <https://doi.org/10.1016/j.jtice.2017.04.033>
- Huang, J., Huang, G., An, C., Xin, X., Chen, X., Zhao, Y., Feng, R. and Xiong, W. (2020). Exploring the use of ceramic disk filter coated with Ag/ZnO nanocomposites as an innovative approach for removing *Escherichia coli* from household drinking water. *Chemosphere*, 245, 125545. <https://doi.org/10.1016/j.chemosphere.2019.125545>
- Huang, L., Zhao, S., Wang, Z., Wu, J., Wang, J. and Wang, S. (2016). In situ immobilization of silver nanoparticles for improving permeability, antifouling and anti-bacterial properties of ultrafiltration membrane. *Journal of Membrane Science*, 499, 269-281. <https://doi.org/10.1016/j.memsci.2015.10.055>
- Ilyas, H., Shawuti, S., Siddiq, M., Niazi, J.H. and Qureshi, A. (2019). PEG functionalized graphene oxide-silver nano-additive for enhanced hydrophilicity, permeability and fouling resistance properties of PVDF-co-HFP membranes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 579, 123646. <https://doi.org/10.1016/j.colsurfa.2019.123646>
- Ingle, A.P., Duran, N. and Rai, M. (2014). Bioactivity, mechanism of action, and cytotoxicity of copper-based nanoparticles: A review. *Applied Microbiology and Biotechnology*, 98(3), 1001-1009. <https://doi.org/10.1007/s00253-013-5422-8>
- Isawi, H., El-Sayed, M.H., Feng, X., Shawky, H. and Abdel Mottaleb, M.S. (2016). Surface nanostructuring of thin film composite membranes via grafting polymerization and incorporation of ZnO nanoparticles. *Applied Surface Science*, 385, 268-281. <https://doi.org/10.1016/j.apsusc.2016.05.141>
- Javdaneh, S., Mehrnia, M.R. and Homayoonfal, M. (2016). Fabrication of polysulfone/zinc oxide nanocomposite membrane: Investigation of pore forming agent on fouling behavior. *Korean Journal of Chemical Engineering*, 33(11), 3184-3193. <https://doi.org/10.1007/s11814-016-0178-3>
- Jo, Y.J., Choi, E.Y., Kim, S.W. and Kim, C.K. (2016). Fabrication and characterization of a novel polyethersulfone/aminated polyethersulfone ultrafiltration membrane assembled with zinc oxide nanoparticles. *Polymer*, 87, 290-299. <https://doi.org/10.1016/j.polymer.2016.02.017>
- Joo, S.H. and Zhao, D. (2017). Environmental dynamics of metal oxide nanoparticles in heterogeneous systems: A review. *Journal of Hazardous Materials*, 322, 29-47. <https://doi.org/10.1016/j.jhazmat.2016.02.068>
- Kang, G.D. and Cao, Y.M. (2014). Application and modification of poly (vinylidene fluoride) (PVDF) membranes – A review. *Journal of Membrane Science*, 463, 145-165. <https://doi.org/10.1016/j.memsci.2014.03.055>
- Khin, M.M., Nair, A.S., Babu, V.J., Murugan, R. and Ramakrishna, S. (2012). A review on nanomaterials for environmental remediation. *Energy & Environmental Science*, 5(8), 8075-8109. <https://doi.org/10.1039/c2ee21818f>
- Kim, S.H., Kwak, S.Y., Sohn, B.H. and Park, T.H. (2003). Design of TiO₂ nanoparticle self-assembled aromatic polyamide thin-film-composite (TFC) membrane as an approach to solve biofouling problem. *Journal of Membrane Science*, 211(1), 157-165. [https://doi.org/10.1016/S0376-7388\(02\)00418-0](https://doi.org/10.1016/S0376-7388(02)00418-0)
- Ko, K., Yu, Y., Kim, M.J., Kweon, J. and Chung, H. (2018). Improvement in fouling resistance of silver-graphene oxide coated polyvinylidene fluoride membrane prepared by pressurized filtration. *Separation and Purification Technology*, 194, 161-169. <https://doi.org/10.1016/j.seppur.2017.11.016>
- Kochkodan, V., Johnson, D.J. and Hilal, N. (2014). Polymeric membranes: Surface modification for minimizing (bio)colloidal fouling. *Advances in Colloid and Interface Science*, 206, 116-140. <https://doi.org/10.1016/j.cis.2013.05.005>
- Koehler, J.A., Ulbricht, M. and Belfort, G. (1997). Intermolecular forces between proteins and polymer films with relevance to filtration. *Langmuir*, 13(15), 4162-4171. <https://doi.org/10.1021/la970010m>
- Korte, N.E., Zutman, J.L., Schlosser, R.M., Liang, L., Gu, B. and Fernando, Q. (2000). Field application of palladized iron for the dechlorination of trichloroethene. *Waste Management*, 20(8), 687-694. [https://doi.org/10.1016/S0956-053X\(00\)00037-4](https://doi.org/10.1016/S0956-053X(00)00037-4)
- Kwak, S.Y., Kim, S.H. and Kim, S.S. (2001). Hybrid organic/inorganic reverse osmosis (RO) membrane for bactericidal anti-fouling. 1. Preparation and characterization of TiO₂ nanoparticle self-assembled aromatic polyamide thin-film-composite (TFC) membrane. *Environmental Science & Technology*, 35(11), 2388-2394. <https://doi.org/10.1021/es0017099>
- Laohaprapanon, S., Vanderlipe, A.D., Doma Jr, B.T. and You, S.J. (2017). Self-cleaning and antifouling properties of plasma-grafted poly(vinylidene fluoride) membrane coated with ZnO for water treatment. *Journal of the Taiwan Institute of Chemical Engineers*, 70, 15-22. <https://doi.org/10.1016/j.jtice.2016.10.019>
- Laxma Reddy, P.V., Kavitha, B., Reddy, P.A.K. and Kim, K.H. (2017). TiO₂-based photocatalytic disinfection of microbes in aqueous media: A review. *Environmental Research*, 154, 296-303. <https://doi.org/10.1016/j.envres.2017.01.018>
- Lee, K.M., Lai, C.W., Ngai, K.S. and Juan, J.C. (2016). Recent developments of zinc oxide based photocatalyst in water treatment technology: A review. *Water Research*, 88, 428-448. <https://doi.org/10.1016/j.watres.2015.09.045>
- Leong, S., Razmjou, A., Wang, K., Hapgood, K., Zhang, X. and Wang, H. (2014). TiO₂ based photocatalytic membranes: A review. *Journal of Membrane Science*, 472, 167-184. <https://doi.org/10.1016/j.memsci.2014.08.016>
- Li, C., Yang, J., Zhang, L., Li, S., Yuan, Y., Xiao, X., Fan, X. and Song, C. (2021a). Carbon-based membrane materials and applications in water and wastewater treatment: A review. *Environmental Chemistry Letters*, 19(2), 1457-1475. <https://doi.org/10.1007/s10311020-01112-8>
- Li, J.H., Shao, X.S., Zhou, Q., Li, M.Z. and Zhang, Q.Q. (2013). The double effects of silver nanoparticles on the PVDF membrane: Surface hydrophilicity and antifouling performance. *Applied Surface Science*, 265, 663-670. <https://doi.org/10.1016/j.apsusc.2012.11.072>
- Li, J.H., Xu, Y.Y., Zhu, L.P., Wang, J.H. and Du, C.H. (2009). Fabrication and characterization of a novel TiO₂ nanoparticle self-assembled

- bly membrane with improved fouling resistance. *Journal of Membrane Science*, 326(2), 659-666. <https://doi.org/10.1016/j.memsci.2008.10.049>
- Li, J., Yuan, S., Zhu, J. and Van der Bruggen, B. (2019). High-flux, antibacterial composite membranes via polydopamine-assisted PEI-TiO₂/Ag modification for dye removal. *Chemical Engineering Journal*, 373, 275-284. <https://doi.org/10.1016/j.cej.2019.05.048>
- Li, K., Liang, H., Qu, F., Shao, S., Yu, H., Han, Z.S., Du, X. and Li, G. (2014a). Control of natural organic matter fouling of ultrafiltration membrane by adsorption pretreatment: Comparison of mesoporous adsorbent resin and powdered activated carbon. *Journal of Membrane Science*, 471, 94-102. <https://doi.org/10.1016/j.memsci.2014.08.006>
- Li, M.N., Chen, X.J., Wan, Z.H., Wang, S.G. and Sun, X.F. (2021b). Forward osmosis membranes for high-efficiency desalination with Nano-MoS₂ composite substrates. *Chemosphere*, 278, 130341. <https://doi.org/10.1016/j.chemosphere.2021.130341>
- Li, N., Fu, Y., Lu, Q. and Xiao, C. (2017). Microstructure and performance of a porous polymer membrane with a copper nano-layer using vapor-induced phase separation combined with magnetron sputtering. *Polymers*, 9(10), 524. <https://doi.org/10.3390/polym9100524>
- Li, R., Liu, L., Zhang, Y. and Yang, F. (2016). Preparation of a nano-MnO₂ surface-modified reduced graphene oxide/PVDF flat sheet membrane for adsorptive removal of aqueous Ni(II). *RSC Advances*, 6(25), 20542-20550. <https://doi.org/10.1039/c5ra20776b>
- Li, W., Zhang, Y., Li, Q. and Zhang, G. (2015). Metal-organic framework composite membranes: Synthesis and separation applications. *Chemical Engineering Science*, 135, 232-257. <https://doi.org/10.1016/j.ces.2015.04.011>
- Li, X., Chen, Y., Hu, X., Zhang, Y. and Hu, L. (2014b). Desalination of dye solution utilizing PVA/PVDF hollow fiber composite membrane modified with TiO₂ nanoparticles. *Journal of Membrane Science*, 471, 118-129. <https://doi.org/10.1016/j.memsci.2014.08.018>
- Li, X., Huang, G., Chen, X., Huang, J., Li, M., Yin, J., Liang, Y., Yao, Y. and Li, Y. (2021c). A review on graphitic carbon nitride (g-C₃N₄) based hybrid membranes for water and wastewater treatment. *Science of The Total Environment*, 792, 148462. <https://doi.org/10.1016/j.scitotenv.2021.148462>
- Liang, S., Xiao, K., Mo, Y. and Huang, X. (2012). A novel ZnO nanoparticle blended polyvinylidene fluoride membrane for anti-irreversible fouling. *Journal of Membrane Science*, 394-395, 184-192. <https://doi.org/10.1016/j.memsci.2011.12.040>
- Lin, J.C.T., Lee, D.J. and Huang, C. (2010). Membrane fouling mitigation: Membrane cleaning. *Separation Science and Technology*, 45(7), 858-872. <https://doi.org/10.1080/01496391003666940>
- Liu, C., Faria, A.F., Ma, J. and Elimelech, M. (2017). Mitigation of biofilm development on thin-film composite membranes functionalized with zwitterionic polymers and silver nanoparticles. *Environmental Science & Technology*, 51(1), 182-191. <https://doi.org/10.1021/acs.est.6b03795>
- Liu, Q., Zhou, Z., Qiu, G., Li, J., Xie, J. and Lee, J.Y. (2015a). Surface reaction route to increase the loading of antimicrobial Ag nanoparticles in forward osmosis membranes. *ACS Sustainable Chemistry & Engineering*, 3(11), 2959-2966. <https://doi.org/10.1021/acssuschemeng.5b00931>
- Liu, S., Fang, F., Wu, J. and Zhang, K. (2015b). The anti-biofouling properties of thin-film composite nanofiltration membranes grafted with biogenic silver nanoparticles. *Desalination*, 375, 121-128. <https://doi.org/10.1016/j.desal.2015.08.007>
- Liu, Z. and Hu, Y. (2016). Sustainable antibiofouling properties of thin film composite forward osmosis membrane with rechargeable silver nanoparticles loading. *ACS Applied Materials & Interfaces*, 8(33), 21666-21673. <https://doi.org/10.1021/acami.6b06727>
- López-Viveros, M., Favier, I., Gómez, M., Lahitte, J.F. and Remigy, J.C. (2021). Remarkable catalytic activity of polymeric membranes containing gel-trapped palladium nanoparticles for hydrogenation reactions. *Catalysis Today*, 364, 263-269. <https://doi.org/10.1016/j.cattod.2020.04.027>
- Luo, M.L., Zhao, J.Q., Tang, W. and Pu, C.S. (2005). Hydrophilic modification of poly(ether sulfone) ultrafiltration membrane surface by self-assembly of TiO₂ nanoparticles. *Applied Surface Science*, 249(1), 76-84. <https://doi.org/10.1016/j.apsusc.2004.11.054>
- Ma, B., Yu, W., Jefferson, W.A., Liu, H. and Qu, J. (2015). Modification of ultrafiltration membrane with nanoscale zerovalent iron layers for humic acid fouling reduction. *Water Research*, 71, 140-149. <https://doi.org/10.1016/j.watres.2014.12.034>
- Ma, W., Soroush, A., Van Anh Luong, T., Brennan, G., Rahaman, M. S., Asadishad, B. and Tufenkji, N. (2016). Spray- and spin-assisted layer-by-layer assembly of copper nanoparticles on thin-film composite reverse osmosis membrane for biofouling mitigation. *Water Research*, 99, 188-199. <https://doi.org/10.1016/j.watres.2016.04.042>
- Madaeni, S.S., Ghaemi, N., Alizadeh, A. and Joshaghani, M. (2011a). Influence of photo-induced superhydrophilicity of titanium dioxide nanoparticles on the anti-fouling performance of ultrafiltration membranes. *Applied Surface Science*, 257(14), 6175-6180. <https://doi.org/10.1016/j.apsusc.2011.02.026>
- Madaeni, S.S., Zinadini, S. and Vatanpour, V. (2011b). A new approach to improve antifouling property of PVDF membrane using in situ polymerization of PAA functionalized TiO₂ nanoparticles. *Journal of Membrane Science*, 380(1), 155-162. <https://doi.org/10.1016/j.memsci.2011.07.006>
- Mansourpanah, Y., Madaeni, S.S., Rahimpour, A., Farhadian, A. and Taheri, A.H. (2009). Formation of appropriate sites on nanofiltration membrane surface for binding TiO₂ photo-catalyst: Performance, characterization and fouling-resistant capability. *Journal of Membrane Science*, 330(1), 297-306. <https://doi.org/10.1016/j.memsci.2009.01.001>
- Mauter, M.S., Wang, Y., Okemgbo, K.C., Osuji, C.O., Giannelis, E.P. and Elimelech, M. (2011). Antifouling ultrafiltration membranes via post-fabrication grafting of biocidal nanomaterials. *ACS Applied Materials & Interfaces*, 3(8), 2861-2868. <https://doi.org/10.1021/am200522v>
- McQuillan, J.S., Infante, H.G., Stokes, E. and Shaw, A.M. (2012). Silver nanoparticle enhanced silver ion stress response in Escherichia coli K12. *Nanotoxicology*, 6(8), 857-866. <https://doi.org/10.3109/17435390.2011.626532>
- Mecha, C.A. and Pillay, V.L. (2014). Development and evaluation of woven fabric microfiltration membranes impregnated with silver nanoparticles for potable water treatment. *Journal of Membrane Science*, 458, 149-156. <https://doi.org/10.1016/j.memsci.2014.02.001>
- Meng, Z., Liu, H., Liu, Y., Zhang, J., Yu, S., Cui, F., Ren, N. and Ma, J. (2011). Preparation and characterization of Pd/Fe bimetallic nanoparticles immobilized in PVDF-Al₂O₃ membrane for dechlorination of monochloroacetic acid. *Journal of Membrane Science*, 372(1), 165-171. <https://doi.org/10.1016/j.memsci.2011.01.064>
- Miller, D.J., Dreyer, D.R., Bielawski, C.W., Paul, D.R. and Freeman, B.D. (2017). Surface modification of water purification membranes. *Angewandte Chemie International Edition*, 56(17), 4662-4711. <https://doi.org/10.1002/anie.201601509>
- Moghimi, V., Raisi, A. and Aroujalian, A. (2014). Surface modification of polyethersulfone ultrafiltration membranes by corona plasma-assisted coating TiO₂ nanoparticles. *Journal of Membrane Science*, 461, 69-80. <https://doi.org/10.1016/j.memsci.2014.02.012>
- Ng, L.Y., Mohammad, A.W., Leo, C.P. and Hilal, N. (2013). Polymeric membranes incorporated with metal/metal oxide nanoparticles: A comprehensive review. *Desalination*, 308, 15-33. <https://doi.org/10.1016/j.desal.2010.11.033>
- Ngo, T.H.A., Nguyen, D.T., Do, K.D., Nguyen, T.T.M., Mori, S. and Tran, D.T. (2016). Surface modification of polyamide thin film composite membrane by coating of titanium dioxide nanoparticles.

- Journal of Science: Advanced Materials and Devices*, 1(4), 468-475. <https://doi.org/10.1016/j.jsamd.2016.10.002>
- Nguyen, A., Zou, L. and Priest, C. (2014). Evaluating the antifouling effects of silver nanoparticles regenerated by TiO₂ on forward osmosis membrane. *Journal of Membrane Science*, 454, 264-271. <https://doi.org/10.1016/j.memsci.2013.12.024>
- Niu, T., Xu, J., Xiao, W. and Huang, J. (2014). Cellulose-based catalytic membranes fabricated by deposition of gold nanoparticles on natural cellulose nanofibres. *RSC Advances*, 4(10), 4901-4904. <https://doi.org/10.1039/c3ra44622k>
- OECD (2009). *Nanotechnology: An Overview Based on Indicators and Statistics*. <https://doi.org/10.1787/223147043844>
- Ong, C.B., Ng, L.Y. and Mohammad, A.W. (2018). A review of ZnO nanoparticles as solar photocatalysts: Synthesis, mechanisms and applications. *Renewable and Sustainable Energy Reviews*, 81, 536-551. <https://doi.org/10.1016/j.rser.2017.08.020>
- Ong, C.S., Goh, P.S., Lau, W.J., Misdan, N. and Ismail, A.F. (2016). Nanomaterials for biofouling and scaling mitigation of thin film composite membrane: A review. *Desalination*, 393, 2-15. <https://doi.org/10.1016/j.desal.2016.01.007>
- Osmond, M.J. and Mccall, M.J. (2010). Zinc oxide nanoparticles in modern sunscreens: An analysis of potential exposure and hazard. *Nanotoxicology*, 4(1), 15-41. <https://doi.org/10.3109/17435390903502028>
- Pan, Y., Yu, Z., Shi, H., Chen, Q., Zeng, G., Di, H., Ren, X. and He, Y. (2017). A novel antifouling and antibacterial surface-functionalized PVDF ultrafiltration membrane via binding Ag/SiO₂ nanocomposites. *Journal of Chemical Technology & Biotechnology*, 92(3), 562-572. <https://doi.org/10.1002/jctb.5034>
- Parshetti, G.K. and Doong, R.A. (2009). Dechlorination of trichloroethylene by Ni/Fe nanoparticles immobilized in PEG/PVDF and PEG/nylon 66 membranes. *Water Research*, 43(12), 3086-3094. <https://doi.org/10.1016/j.watres.2009.04.037>
- Pendergast, M.M. and Hoek, E.M.V. (2011). A review of water treatment membrane nanotechnologies. *Energy & Environmental Science*, 4(6), 1946-1971. <https://doi.org/10.1039/c0ee00541j>
- Pi, J.K., Yang, H.C., Wan, L.S., Wu, J. and Xu, Z.K. (2016). Polypropylene microfiltration membranes modified with TiO₂ nanoparticles for surface wettability and antifouling property. *Journal of Membrane Science*, 500, 8-15. <https://doi.org/10.1016/j.memsci.2015.11.014>
- Pourjafar, S., Rahimpour, A. and Jahanshahi, M. (2012). Synthesis and characterization of PVA/PES thin film composite nanofiltration membrane modified with TiO₂ nanoparticles for better performance and surface properties. *Journal of Industrial and Engineering Chemistry*, 18(4), 1398-1405. <https://doi.org/10.1016/j.jiec.2012.01.041>
- Prince, J.A., Bhuvana, S., Boodhoo, K.V.K., Anbharasi, V. and Singh, G. (2014). Synthesis and characterization of PEG-Ag immobilized PES hollow fiber ultrafiltration membranes with long lasting antifouling properties. *Journal of Membrane Science*, 454, 538-548. <https://doi.org/10.1016/j.memsci.2013.12.050>
- Qi, L., Liu, Z., Wang, N. and Hu, Y. (2018). Facile and efficient in situ synthesis of silver nanoparticles on diverse filtration membrane surfaces for antimicrobial performance. *Applied Surface Science*, 456, 95-103. <https://doi.org/10.1016/j.apsusc.2018.06.066>
- Qin, A., Li, X., Zhao, X., Liu, D. and He, C. (2015). Engineering a highly hydrophilic PVDF membrane via binding TiO₂ nanoparticles and a PVA layer onto a membrane surface. *ACS Applied Materials & Interfaces*, 7(16), 8427-8436. <https://doi.org/10.1021/acsami.5b00978>
- Qiu, M. and He, C. (2018). Novel zwitterion-silver nanocomposite modified thin-film composite forward osmosis membrane with simultaneous improved water flux and biofouling resistance property. *Applied Surface Science*, 455, 492-501. <https://doi.org/10.1016/j.apsusc.2018.06.020>
- Rahaman, M.S., Thérien-Aubin, H., Ben-Sasson, M., Ober, C.K., Nielsen, M. and Elimelech, M. (2014). Control of biofouling on reverse osmosis polyamide membranes modified with biocidal nanoparticles and antifouling polymer brushes. *Journal of Materials Chemistry B*, 2(12), 1724-1732. <https://doi.org/10.1039/C3TB21681K>
- Rahimpour, A., Jahanshahi, M., Mollahosseini, A. and Rajaeian, B. (2012). Structural and performance properties of UV-assisted TiO₂ deposited nano-composite PVDF/SPES membranes. *Desalination*, 285, 31-38. <https://doi.org/10.1016/j.desal.2011.09.026>
- Rana, D. and Matsuura, T. (2010). Surface modifications for antifouling membranes. *Chemical reviews*, 110(4), 2448-2471. <https://doi.org/10.1021/cr800208y>
- Reis, R., Dumée, L.F., He, L., She, F., Orbell, J.D., Winther-Jensen, B. and Duke, M.C. (2015). Amine enrichment of thin-film composite membranes via low pressure plasma polymerization for antimicrobial adhesion. *ACS Applied Materials & Interfaces*, 7(27), 14644-14653. <https://doi.org/10.1021/acsami.5b01603>
- Remanan, S., Sharma, M., Bose, S. and Das, N.C. (2018). Recent advances in preparation of porous polymeric membranes by unique techniques and mitigation of fouling through surface modification. *ChemistrySelect*, 3(2), 609-633. <https://doi.org/10.1002/slct.201702503>
- Ren, S., Boo, C., Guo, N., Wang, S., Elimelech, M. and Wang, Y. (2018). Photocatalytic reactive ultrafiltration membrane for removal of antibiotic resistant bacteria and antibiotic resistance genes from wastewater effluent. *Environmental Science & Technology*, 52(15), 8666-8673. <https://doi.org/10.1021/acs.est.8b01888>
- Rubilar, O., Rai, M., Tortella, G., Diez, M.C., Seabra, A.B. and Durán, N. (2013). Biogenic nanoparticles: Copper, copper oxides, copper sulphides, complex copper nanostructures and their applications. *Biotechnology Letters*, 35(9), 1365-1375. <https://doi.org/10.1007/s10529-013-1239-x>
- Rusen, E., Mocanu, A., Nistor, L.C., Dinescu, A., Călinescu, I., Muștătea, G., Voicu, Ș.I., Andronescu, C. and Diacon, A. (2014). Design of antimicrobial membrane based on polymer colloids/multi-wall carbon nanotubes hybrid material with silver nanoparticles. *ACS Applied Materials & Interfaces*, 6(20), 17384-17393. <https://doi.org/10.1021/am505024p>
- Saffar, A., Carreau, P.J., Kamal, M.R. and Ajjji, A. (2014). Hydrophilic modification of polypropylene microporous membranes by grafting TiO₂ nanoparticles with acrylic acid groups on the surface. *Polymer*, 55(23), 6069-6075. <https://doi.org/10.1016/j.polymer.2014.09.069>
- Samaei, S.M., Gato-Trinidad, S. and Altaee, A. (2018). The application of pressure-driven ceramic membrane technology for the treatment of industrial wastewaters – A review. *Separation and Purification Technology*, 200, 198-220. <https://doi.org/10.1016/j.seppur.2018.02.041>
- Sassi, K.M. and Mujtaba, I.M. (2011). Optimal design and operation of reverse osmosis desalination process with membrane fouling. *Chemical Engineering Journal*, 171(2), 582-593. <https://doi.org/10.1016/j.cej.2011.04.034>
- Sawada, I., Fachrul, R., Ito, T., Ohmukai, Y., Maruyama, T. and Matsuyama, H. (2012). Development of a hydrophilic polymer membrane containing silver nanoparticles with both organic antifouling and antibacterial properties. *Journal of Membrane Science*, 387-388, 1-6. <https://doi.org/10.1016/j.memsci.2011.06.020>
- Sharma, V.K. (2013). Stability and toxicity of silver nanoparticles in aquatic environment: A review. *Sustainable Nanotechnology and the Environment: Advances and Achievements*, American Chemical Society, pp 165-179. <https://doi.org/10.1021/bk-2013-1124.ch010>
- Shi, H., He, Y., Pan, Y., Di, H., Zeng, G., Zhang, L. and Zhang, C. (2016). A modified mussel-inspired method to fabricate TiO₂ decorated superhydrophilic PVDF membrane for oil/water separation. *Journal of Membrane Science*, 506, 60-70. <https://doi.org/10.1016/j.memsci.2016.01.053>
- Silva, L.L.S., Abdelraheem, W., Nadagouda, M.N., Rocco, A.M., Dionysiou, D.D., Fonseca, F.V. and Borges, C.P. (2021). Novel micro-

- wave-driven synthesis of hydrophilic polyvinylidene fluoride/polyacrylic acid (PVDF/PAA) membranes and decoration with nano zero-valent-iron (nZVI) for water treatment applications. *Journal of Membrane Science*, 620, 118817. <https://doi.org/10.1016/j.memsci.2020.118817>
- Sirelkhatim, A., Mahmud, S., Seeni, A., Kaus, N.H.M., Ann, L.C., Bakthori, S.K.M., Hasan, H. and Mohamad, D. (2015). Review on zinc oxide nanoparticles: Antibacterial activity and toxicity mechanism. *Nano-Micro Letters*, 7(3), 219-242. <https://doi.org/10.1007/s40820-015-0040-x>
- Smuleac, V., Bachas, L. and Bhattacharyya, D. (2010). Aqueous-phase synthesis of PAA in PVDF membrane pores for nanoparticle synthesis and dichlorobiphenyl degradation. *Journal of Membrane Science*, 346(2), 310-317. <https://doi.org/10.1016/j.memsci.2009.09.052>
- Smuleac, V., Varma, R., Sikdar, S. and Bhattacharyya, D. (2011). Green synthesis of Fe and Fe/Pd bimetallic nanoparticles in membranes for reductive degradation of chlorinated organics. *Journal of Membrane Science*, 379(1), 131-137. <https://doi.org/10.1016/j.memsci.2011.05.054>
- Soroush, A., Ma, W., Silvino, Y. and Rahaman, M.S. (2015). Surface modification of thin film composite forward osmosis membrane by silver-decorated graphene-oxide nanosheets. *Environmental Science: Nano*, 2(4), 395-405. <https://doi.org/10.1039/C5EN00086F>
- Sprick, C., Chede, S., Oyanedel-Craver, V. and Escobar, I.C. (2018). Bio-inspired immobilization of casein-coated silver nanoparticles on cellulose acetate membranes for biofouling control. *Journal of Environmental Chemical Engineering*, 6(2), 2480-2491. <https://doi.org/10.1016/j.jece.2018.03.044>
- Sri Abirami Saraswathi, M.S., Nagendran, A. and Rana, D. (2019a). Tailored polymer nanocomposite membranes based on carbon, metal oxide and silicon nanomaterials: A review. *Journal of Materials Chemistry A*, 7(15), 8723-8745. <https://doi.org/10.1039/C8TA11460A>
- Sri Abirami Saraswathi, M.S., Rana, D., Alwarappan, S., Gowrishankar, S., Kanimozhi, P. and Nagendran, A. (2019b). Cellulose acetate ultrafiltration membranes customized with bio-inspired polydopamine coating and in situ immobilization of silver nanoparticles. *New Journal of Chemistry*, 43(10), 4216-4225. <https://doi.org/10.1039/C8NJ04511A>
- Subair, R., Tripathi, B.P., Formanek, P., Simon, F., Uhlmann, P. and Stamm, M. (2016). Polydopamine modified membranes with in situ synthesized gold nanoparticles for catalytic and environmental applications. *Chemical Engineering Journal*, 295, 358-369. <https://doi.org/10.1016/j.cej.2016.02.105>
- Sun, M., Zucker, I., Davenport, D.M., Zhou, X., Qu, J. and Elimelech, M. (2018). Reactive, self-cleaning ultrafiltration membrane functionalized with iron oxochloride nanocatalysts. *Environmental Science & Technology*, 52(15), 8674-8683. <https://doi.org/10.1021/acs.est.8b01916>
- Tang, L., Huynh, K.A., Fleming, M.L., Larronde-Larretche, M. and Chen, K.L. (2015a). Imparting antimicrobial and anti-adhesive properties to polysulfone membranes through modification with silver nanoparticles and polyelectrolyte multilayers. *Journal of Colloid and Interface Science*, 451, 125-133. <https://doi.org/10.1016/j.jcis.2015.03.051>
- Tang, L., Livi, K.J.T. and Chen, K.L. (2015b). Polysulfone membranes modified with bioinspired polydopamine and silver nanoparticles formed in situ to mitigate biofouling. *Environmental Science & Technology Letters*, 2(3), 59-65. <https://doi.org/10.1021/acs.estlett.5b00008>
- Ulbricht, M. and Belfort, G. (1996). Surface modification of ultrafiltration membranes by low temperature plasma II. Graft polymerization onto polyacrylonitrile and polysulfone. *Journal of Membrane Science*, 111(2), 193-215. [https://doi.org/10.1016/0376-7388\(95\)00207-3](https://doi.org/10.1016/0376-7388(95)00207-3)
- UN-Water. Water scarcity. <https://www.unwater.org/water-facts/scarcity/#>. (accessed May 30, 2020).
- Wan, H., Briot, N.J., Saad, A., Ormsbee, L. and Bhattacharyya, D. (2017). Pore functionalized PVDF membranes with in-situ synthesized metal nanoparticles: Material characterization, and toxic organic degradation. *Journal of Membrane Science*, 530, 147-157. <https://doi.org/10.1016/j.memsci.2017.02.021>
- Wang, C.B. and Zhang, W.X. (1997). Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs. *Environmental Science & Technology*, 31(7), 2154-2156. <https://doi.org/10.1021/es970039c>
- Wang, D., Lin, J., Huang, J., Zhang, H., Lin, S., Chen, L., Ni, Y. and Huang, L. (2021). A chitosan/dopamine-TiO₂ composite nanofiltration membrane for antifouling in water purification. *Cellulose*, 28(8), 4959-4973. <https://doi.org/10.1007/s10570-021-03845-3>
- Wang, X., Chen, C., Liu, H. and Ma, J. (2008). Preparation and characterization of PAA/PVDF membrane-immobilized Pd/Fe nanoparticles for dechlorination of trichloroacetic acid. *Water Research*, 42(18), 4656-4664. <https://doi.org/10.1016/j.watres.2008.08.005>
- Wang, X., Yang, J., Zhu, M. and Li, F. (2013). Characterization and regeneration of Pd/Fe nanoparticles immobilized in modified PVDF membrane. *Journal of the Taiwan Institute of Chemical Engineers*, 44(3), 386-392. <https://doi.org/10.1016/j.jtice.2012.12.007>
- Wu, J., Yu, C. and Li, Q. (2017). Novel regenerable antimicrobial nanocomposite membranes: Effect of silver loading and valence state. *Journal of Membrane Science*, 531, 68-76. <https://doi.org/10.1016/j.memsci.2017.02.047>
- Wu, Z., Lin, H., Wang, Y., Yu, X., Li, J., Xiong, Z., Wang, Y., Huang, Y., Chen, T. and Liu, F. (2016). Enhanced catalytic degradation of 4-NP using a superhydrophilic PVDF membrane decorated with Au nanoparticles. *RSC Advances*, 6(67), 62302-62309. <https://doi.org/10.1039/C6RA11380J>
- Xie, Y., Chen, L., Zhang, X., Chen, S., Zhang, M., Zhao, W., Sun, S. and Zhao, C. (2018). Integrating zwitterionic polymer and Ag nanoparticles on polymeric membrane surface to prepare antifouling and bactericidal surface via Schiff-based layer-by-layer assembly. *Journal of Colloid and Interface Science*, 510, 308-317. <https://doi.org/10.1016/j.jcis.2017.09.071>
- Xie, Y., Tang, C., Wang, Z., Xu, Y., Zhao, W., Sun, S. and Zhao, C. (2017). Co-deposition towards mussel-inspired antifouling and antibacterial membranes by using zwitterionic polymers and silver nanoparticles. *Journal of Materials Chemistry B*, 5(34), 7186-7193. <https://doi.org/10.1039/C7TB01516J>
- Xiong, Z., Lin, H., Liu, F., Xiao, P., Wu, Z., Li, T. and Li, D. (2017). Flexible PVDF membranes with exceptional robust superwetting surface for continuous separation of oil/water emulsions. *Scientific Report*, 7(1), 14099. <https://doi.org/10.1038/s41598-017-14429-2>
- Xu, Z., Huang, G., An, C., Huang, J., Chen, X., Xin, X., Song, P., Feng, R. and Li, Y. (2020). Low-cost microbiological purification using a new ceramic disk filter functionalized by chitosan/TiO₂ nanocomposites. *Separation and Purification Technology*, 116984. <https://doi.org/10.1016/j.seppur.2020.116984>
- Yan, W., Lien, H.L., Koel, B.E. and Zhang, W.X. (2013). Iron nanoparticles for environmental clean-up: Recent developments and future outlook. *Environmental Science: Processes & Impacts*, 15(1), 63-77. <https://doi.org/10.1039/c2em30691c>
- Yang, H.L., Lin, J.C.T. and Huang, C. (2009). Application of nanosilver surface modification to RO membrane and spacer for mitigating biofouling in seawater desalination. *Water Research*, 43(15), 3777-3786. <https://doi.org/10.1016/j.watres.2009.06.002>
- Yang, J., Wang, X., Zhu, M., Liu, H. and Ma, J. (2014). Investigation of PAA/PVDF-nZVI hybrids for metronidazole removal: Synthesis, characterization, and reactivity characteristics. *Journal of Hazardous Materials*, 264, 269-277. <https://doi.org/10.1016/j.jhazmat.2013.11.037>
- Yang, Z., Takagi, R., Zhang, X., Yasui, T., Zhang, L. and Matsuyama, H. (2021). Engineering a dual-functional sulfonated polyelectrolyte-

- silver nanoparticle complex on a polyamide reverse osmosis membrane for robust biofouling mitigation. *Journal of Membrane Science*, 618, 118757. <https://doi.org/10.1016/j.memsci.2020.118757>
- Yi, M., Lau, C.H., Xiong, S., Wei, W., Liao, R., Shen, L., Lu, A. and Wang, Y. (2019). Zwitterion–Ag complexes that simultaneously enhance biofouling resistance and silver binding capability of thin film composite membranes. *ACS Applied Materials & Interfaces*, 11(17), 15698-15708. <https://doi.org/10.1021/acsami.9b02983>
- Yin, J., Yang, Y., Hu, Z. and Deng, B. (2013). Attachment of silver nanoparticles (AgNPs) onto thin-film composite (TFC) membranes through covalent bonding to reduce membrane biofouling. *Journal of Membrane Science*, 441, 73-82. <https://doi.org/10.1016/j.memsci.2013.03.060>
- You, S.J., Semblante, G.U., Lu, S.C., Damodar, R.A. and Wei, T.C. (2012). Evaluation of the antifouling and photocatalytic properties of poly(vinylidene fluoride) plasma-grafted poly(acrylic acid) membrane with self-assembled TiO₂. *Journal Hazardous Materials*, 237-238, 10-19. <https://doi.org/10.1016/j.jhazmat.2012.07.071>
- Yu, W., Brown, M. and Graham, N.J.D. (2016). Prevention of PVDF ultrafiltration membrane fouling by coating MnO₂ nanoparticles with ozonation. *Scientific Reports*, 6(1), 30144. <https://doi.org/10.1038/srep30144>
- Yu, Y., Yang, Y., Yu, L., Koh, K.Y. and Chen, J.P. (2021). Modification of polyvinylidene fluoride membrane by silver nanoparticles-graphene oxide hybrid nanosheet for effective membrane biofouling mitigation. *Chemosphere*, 268, 129187. <https://doi.org/10.1016/j.chemosphere.2020.129187>
- Zain, N.M., Stapley, A.G.F. and Shama, G. (2014). Green synthesis of silver and copper nanoparticles using ascorbic acid and chitosan for antimicrobial applications. *Carbohydrate Polymers*, 112, 195-202. <https://doi.org/10.1016/j.carbpol.2014.05.081>
- Zhang, A., Zhang, Y., Pan, G., Xu, J., Yan, H. and Liu, Y. (2017). In situ formation of copper nanoparticles in carboxylated chitosan layer: Preparation and characterization of surface modified TFC membrane with protein fouling resistance and long-lasting antibacterial properties. *Separation and Purification Technology*, 176, 164-172. <https://doi.org/10.1016/j.seppur.2016.12.006>
- Zhang, C., Hu, Z. and Deng, B. (2016a). Silver nanoparticles in aquatic environments: Physicochemical behavior and antimicrobial mechanisms. *Water Research*, 88, 403-427. <https://doi.org/10.1016/j.watres.2015.10.025>
- Zhang, D.Y., Hao, Q., Liu, J., Shi, Y.S., Zhu, J., Su, L. and Wang, Y. (2018). Antifouling polyimide membrane with grafted silver nanoparticles and zwitterion. *Separation and Purification Technology*, 192, 230-239. <https://doi.org/10.1016/j.seppur.2017.10.018>
- Zhang, L., Meng, Z. and Zang, S. (2015). Preparation and characterization of Pd/Fe bimetallic nanoparticles immobilized on Al₂O₃/PVDF membrane: Parameter optimization and dechlorination of dichloroacetic acid. *Journal of Environmental Sciences*, 31, 194-202. <https://doi.org/10.1016/j.jes.2014.12.009>
- Zhang, R.X., Braeken, L., Luis, P., Wang, X.L. and Van der Bruggen, B. (2013a). Novel binding procedure of TiO₂ nanoparticles to thin film composite membranes via self-polymerized polydopamine. *Journal of Membrane Science*, 437, 179-188. <https://doi.org/10.1016/j.memsci.2013.02.059>
- Zhang, S., Qiu, G., Ting, Y.P. and Chung, T.S. (2013b). Silver–PEGylated dendrimer nanocomposite coating for anti-fouling thin film composite membranes for water treatment. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 436, 207-214. <https://doi.org/10.1016/j.colsurfa.2013.06.027>
- Zhang, X., Wang, Y., Liu, Y., Xu, J., Han, Y. and Xu, X. (2014). Preparation, performances of PVDF/ZnO hybrid membranes and their applications in the removal of copper ions. *Applied Surface Science*, 316, 333-340. <https://doi.org/10.1016/j.apsusc.2014.08.004>
- Zhang, X., Wang, Y., You, Y., Meng, H., Zhang, J. and Xu, X. (2012). Preparation, performance and adsorption activity of TiO₂ nanoparticles entrapped PVDF hybrid membranes. *Applied Surface Science*, 263, 660-665. <https://doi.org/10.1016/j.apsusc.2012.09.131>
- Zhang, Y., Wan, Y., Shi, Y., Pan, G., Yan, H., Xu, J., Guo, M., Qin, L. and Liu, Y. (2016b). Facile modification of thin-film composite nanofiltration membrane with silver nanoparticles for anti-biofouling. *Journal of Polymer Research*, 23(5), 105. <https://doi.org/10.1007/s10965-016-0992-7>
- Zhang, Z., Huang, G., Li, Y., Chen, X., Yao, Y., Ren, S., Li, M., Wu, Y. and An, C. (2022). Electrically conductive inorganic membranes: A review on principles, characteristics and applications. *Chemical Engineering Journal*, 427, 131987. <https://doi.org/10.1016/j.cej.2021.131987>
- Zhao, X., Lv, L., Pan, B., Zhang, W., Zhang, S. and Zhang, Q. (2011). Polymer-supported nanocomposites for environmental application: a review. *Chemical Engineering Journal*, 170(2-3), 381-394. <https://doi.org/10.1016/j.cej.2011.02.071>
- Zhao, X., Zhang, R., Liu, Y., He, M., Su, Y., Gao, C. and Jiang, Z. (2018). Antifouling membrane surface construction: Chemistry plays a critical role. *Journal of Membrane Science*, 551, 145-171. <https://doi.org/10.1016/j.memsci.2018.01.039>
- Zheng, H., Wang, D., Sun, X., Jiang, S., Liu, Y., Zhang, D. and Zhang, L. (2021). Surface modified by green synthetic of Cu-MOF-74 to improve the anti-biofouling properties of PVDF membranes. *Chemical Engineering Journal*, 411, 128524. <https://doi.org/10.1016/j.cej.2021.128524>
- Zhu, J., Uliana, A., Wang, J., Yuan, S., Li, J., Tian, M., Simoens, K., Volodin, A., Lin, J., Bernaerts, K., Zhang, Y. and Van der Bruggen, B. (2016). Elevated salt transport of antimicrobial loose nanofiltration membranes enabled by copper nanoparticles via fast bioinspired deposition. *Journal of Materials Chemistry A*, 4(34), 13211-13222. <https://doi.org/10.1039/C6TA05661J>
- Zirehpour, A., Rahimpour, A., Arabi Shamsabadi, A., Sharifian Gh, M. and Soroush, M. (2017). Mitigation of thin-film composite membrane biofouling via immobilizing nano-Sized biocidal reservoirs in the membrane active layer. *Environmental Science & Technology*, 51(10), 5511-5522. <https://doi.org/10.1021/acs.est.7b00782>