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## Polymer-matrix nanocomposite membranes for water treatment

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## ABSTRACT

One of the grand challenges to sustain the modern society is to secure adequate water resources of desirable quality for various designated uses. To address this challenge, membrane water treatment is expected to play an increasingly important role in areas such as drinking water treatment, brackish and seawater desalination, and wastewater treatment and reuse. Existing membranes for water treatment, typically polymeric in nature, are still restricted by several challenges including the trade-off relationship between permeability and selectivity (also called Robeson upper boundary in membrane gas separation), and low resistance to fouling. Nanocomposite membranes, a new class of membranes fabricated by combining polymeric materials with nanomaterials, are emerging as a promising solution to these challenges. The advanced nanocomposite membranes could be designed to meet specific water treatment applications by tuning their structure and physicochemical properties (e.g. hydrophilicity, porosity, charge density, and thermal and mechanical stability) and introducing unique functionalities (e.g. antibacterial, photocatalytic or adsorptive capabilities). This review is to summarize the recent scientific and technological advances in the development of nanocomposite membranes for water treatment. The nanocomposite membranes were classified into (1) conventional nanocomposite, (2) thin-film nanocomposite (TFN), (3) thin-film composite (TFC) with nanocomposite substrate, and (4) surface located nanocomposite, based on the membrane structure and location of nanomaterial. Challenges and future research directions in developing high performance nanocomposite membranes were also discussed.

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**Abbreviations:** AgNPs, Silver nanoparticles; BPPO, Brominated polyphenylene oxide; BSA, Bovine serum albumin; CA, Cellulose acetate; CNTs, Carbon nanotubes; Da, Dalton; DBPs, Disinfection by-products; EDCs, Endocrine disrupting compounds; EVAL, Ethylene vinyl alcohol; FMBO, Fe–Mn binary oxide; FO, Forward osmosis; FT-IR, Fourier transform infrared spectroscopy; GO, Graphene oxide; HFMs, Hollow fiber membranes; HMO, Hydrous manganese dioxide; H-OMCs, Hydrophilized ordered mesoporous carbons; HPAAE, Hyperbranched poly(amine-ester); ICP, Internal concentration polarization; iGO, Isocyanate-treated GO; iLSMM, In-situ hydrophilic surface modifying macromolecules; IP, Interfacial polymerization; MBR, Membrane bioreactor; MF, Microfiltration; MMM, Mixed matrix membrane; MPD, M-phenylenediamine; MWNTs, Multi-walled carbon nanotubes; NF, Nanofiltration; NMP, 1-methyl-2-pyrrolidinone; NPs, Nanoparticles; OD, Outside diameter; OMC, Ordered mesoporous carbon; OSN, Organic solvent nanofiltration; PA, Polyamide; PAA, Polyacrylic acid; PAH, Poly(allylamine hydrochloride); PAN, Polyacrylonitrile; PANI, Polyaniline; PAI, Polyamide-imide; PCL, Polycaprolactone; PEG, Polyethylene glycol; PEI, Polyetherimide; PEMFCs, Proton exchange membrane fuel cells; PEO, Poly(ethylene oxide); PES, Polyethersulfone; PI, Phase inversion; PMA, Polymethylacrylate; PMMA, Poly(methyl methacrylate); PMR, Photocatalytic membrane reactor; PPESK, Poly(phthalazine ether sulfone ketone); PRO, Pressure-retarded osmosis; PSU, Polysulfone; PU, Polyurethane; PV, Pervaporation; PVDF, Polyvinylidene fluoride; PVA, Polyvinyl alcohol; PVB, Polyvinyl butyral; PVC, Polyvinyl chloride; PVDC, Poly(vinylidene chloride); PVP, Polyvinylpyrrolidone; RO, Reverse osmosis; S, Structural parameter; SCH, Silver citrate hydrate; SL, Silver lactate; SN, Silver nitrate; SPES, Sulfonated polyethersulfone; SWNTs, Single-walled carbon nanotubes; TAP, 2,4,6-triamino pyrimidine; TFC, Thin-film composite; TFN, Thin-film nanocomposite; TMC, Trimesoyl chloride; TMP, Trans-membrane pressure; UF, Ultrafiltration; UV, Ultraviolet; XPS, X-ray photoelectron spectroscopy

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## 1. Introduction

Water is the foundation of life. However, due to the rapid growth of world population, abuse of water resources, and water pollution, water shortage problem becomes more and more serious. World-wide, around 780 million people still lack access to improved drinking water sources (WHO, Progress on Drinking Water and Sanitation, 2012). Hence, cost-effective technologies must be developed to extend water resources and solve water pollution problems. Membrane water treatment is expected to play an increasingly important role in areas such as drinking water treatment, brackish and seawater desalination, and wastewater treatment and reuse, because it is simple in concept and operation, does not involve phase changes or chemical additives, and can be made modular for easy scale up [1,2].

Polymeric membrane is currently the most widely used membrane type for water treatment due to its straightforward pore forming mechanism, higher flexibility, smaller footprints required for installation and relatively low costs compared to inorganic membrane equivalents [3]. However, it is still restricted by several challenges such as trade-off relationship between permeability and selectivity (also called Robeson upper boundary in membrane gas separation), and low resistance to fouling. The development of membranes with high permeability and rejection, and good antifouling property is much needed for water purification under the context of energy efficiency and cost effectiveness.

Polymer-matrix nanocomposite membranes are advanced membranes with nanomaterials dispersed in their polymer matrices. They could be used for gas–gas, liquid–liquid, and liquid–solid separations. The concept of making nanocomposite membranes was originally developed to overcome the Robeson upper boundary in the field of gas separation in the 1990s [4,5], where highly selective zeolites were incorporated into polymers to improve both permeability and selectivity [6,7]. Besides gas separation [8–10], many other applications have been examined by using nanocomposite membranes, such as direct methanol fuel cells [11,12], proton exchange membrane fuel cells (PEMFCs) [13], sensor applications [14,15], lithium ion battery [16,17], pervaporation (PV) [18–20], organic solvent nanofiltration (OSN) [21,22], and water treatment. Due to its promise of overcoming the trade-off relationship between permeability and selectivity as well as mitigating membrane fouling problem during water

treatment applications, it has gained considerable attention and is considered as the cutting edge of creating the next generation of high performance membranes.

The aim of this review is to summarize the recent scientific and technological advances in the development of nanocomposite membranes for water treatment. Challenges and future research directions will also be discussed. Readers interested in gas separation are referred to two excellent reviews recently published on nanocomposite gas separation membranes [5,8].

According to membrane structure and location of nanomaterials, nanocomposite membranes can be classified into four categories: (1) conventional nanocomposite; (2) thin-film nanocomposite (TFN); (3) thin-film composite (TFC) with nanocomposite substrate; and (4) surface located nanocomposite. The typical structures of these membranes are illustrated in Fig. 1. It is worth noting that the red spheres used in the figure not only stand for nanoparticles (NPs), but also could represent nanotubes, nanofibers or nanosheets. The publication numbers related to each type of the nanocomposite membranes for water treatment are also depicted in Fig. 1, where the data are obtained based on searching and screening using the key words “nanocomposite and membrane” or “mixed matrix and membrane” in the database, Scopus.

## 2. Conventional nanocomposite

In the conventional nanocomposite membranes, nanofillers fall into one of the four categories: 1) inorganic material; 2) organic material; 3) biomaterial, and 4) hybrid material with two or more material types. Fabrication of nanocomposite membranes is mostly based on phase inversion (PI) method in which nanofillers are dispersed in polymer solution prior to the PI process, and can be prepared in either flat sheet or hollow fiber configurations (Fig. 2). This type of membrane is mainly used in microfiltration (MF) or ultrafiltration (UF) processes due to its typical porous structure.

Representative publications on the development and use of nanocomposite membranes in each category are summarized in Table 1, along with filler and polymer types, fabrication methods, and main advantages of the filler materials.

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