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REVIEW

Recent developments of nano-enhanced composite membranes designed for water/wastewater purification—a review

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Abstract

In this review, the latest advances on nano-enhanced composite membranes (NECMs, which contain nanostructured filler-like materials and nanoscale barrier polymeric substrates), comprising basic conceptions, working mechanisms, selection of active materials, structural designs, desirable effects, existing challenges, and potential applications for water/wastewater purification, were summarized and discussed in detail. This review paper will propose a comprehensive overview of NECMs designed for water/wastewater purification to understand the recent developments among active materials, strategies, or challenges regarding technical and innovative approaches. Several researchers have successfully proven the main capacities regarding adsorption and separation to remove various pollutants from water or wastewater. Herein, the NECMs designed by combining nanostructured filler-like materials and nanoscale barrier polymeric substrates have high performances of adsorption and separation; thus, these NECMs have attracted considerable attention in recent years. Given their nanostructured filler-like materials, NECMs can address fouling-related limitations by tailoring their surface features, particularly the structural design and desirable effect of NECMs; concomitantly, their performance might be enhanced through the use of a specific composition and structure of nanomaterials. Hence, a comprehensive guide of the advanced NECMs for water/wastewater purification, which are constructed on nanostructured filler-like materials, will be provided in detail. Therefore, this paper can provide a comprehensive understanding of NECMs that are designed for water/wastewater purification correspondingly and effectively.

Keywords Water purification · Nanomaterials · Nano-enhanced composite membranes · Adsorption · Separation

1 Introduction

Water is an essential demand to human and ecosystem lives. Nonetheless, water pollution caused by various pathways, including industries such as food, textile, pharmacy, plants/varnishing, and households (Fig. 1), has become a serious problem significantly impacting human health and aquatic organisms, in which the pollutants comprise heavy metals, organic dyes, harmful ions, and other toxic compounds. Thus, searching for quality water sources to promote the growth of modern societies is necessary. At present, several strategies have been effectively and suitably developed for removing pollutants from water, including chemical precipitation, ion exchange, electrodialysis, reverse osmosis, coagulation, adsorption, and filtration [1–3]. In particular, the development of technologies in water/wastewater purification is a trending topic to produce clean and drinkable water. In addition, cost-efficient and effective technologies have been greatly explored in recent years to overcome the limitations relating to the conventional methods. Among them, membrane technology has been greatly used in water/wastewater purification because of its availability, cost-effectiveness, and good scalability [1], and it can well remove diverse contaminants inducing human health and aquatic life, particularly its capacities in the adsorption and separation of pollutants from water.

Compared with other membranes, nano-enhanced composite membranes (NECMs) containing nanostructured filler-like materials and nanoscale barrier polymeric

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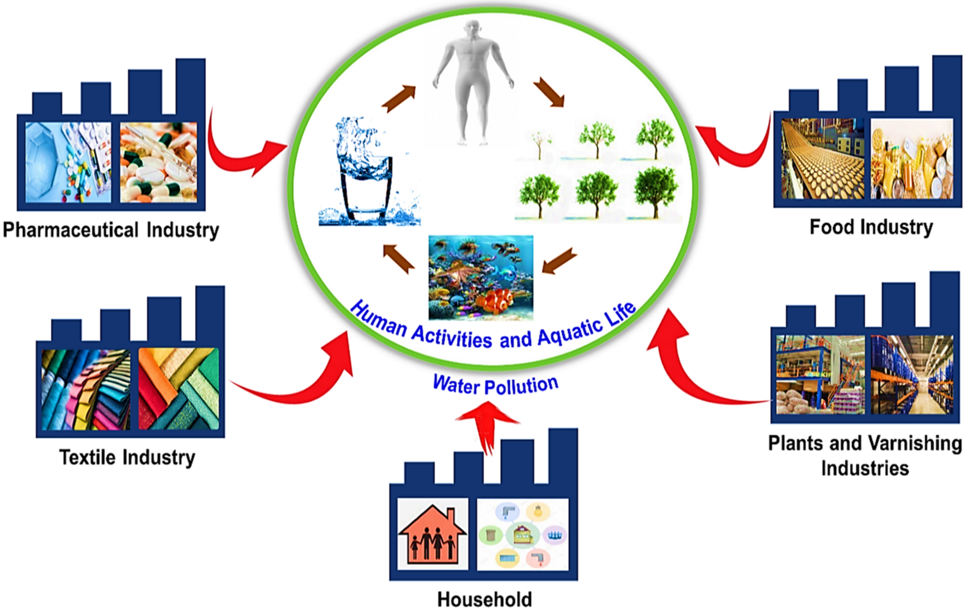

Fig. 1 Schematic diagram of the sources and pathways causing water pollution

substrates represent a type of recent-emerging membrane in water/wastewater purification, which exhibit high permeability, selectivity, and removal ability because of the specific groups and functional layer in the whole NECM structure [4, 5]. Through physical or chemical interactions between NECMs and pollutants, the use of nanostructured filler-like materials in nanoscale barrier polymeric substrates has become an important strategy for the adsorption and separation of toxic pollutants from water, which may be due to their effectiveness and versatility. The adsorption performance of NECMs is characterized with a special adsorptive function [1], while their separation performance is attributed to the pores found in the membranes [6]. However, some challenges and difficulties in the technical approaches of these membrane technologies are still encountered. With the incorporation of nanostructured active fillers in the membranes, several NECM-related studies have shown the excellent advantages of nanostructured materials in the enhancement of NECMs designed for water/wastewater purification, particularly the role of the structural and physicochemical characteristics of nanostructured active fillers. The performance of NECMs is remarkably affected by the composition and structure of selected active materials (i.e., polymeric substrates and functional nanofillers) for enhancing the adsorption and separation abilities of the membranes, particularly the compositional control and structural design of NECMs.

In this review, an entire overview is necessary to summarize and discuss comprehensively the latest progresses and trends of NECMs designed for water/wastewater purification, comprising basic conceptions and working mechanisms, selection of active materials, structural designs, desirable effects, existing challenges, and potential applications. Furthermore, novel NECMs and future outlooks are presented. Therefore, this paper can provide a comprehensive understanding of NECMs that are designed for water/wastewater purification correspondingly and effectively, particularly the current status of NECMs, and may open new perspectives toward the growth of NECMs that can adsorb and separate pollutants from water, as well as their significantly improved performance.

2 Conceptions of water/wastewater purification

Water is the universal solvent and most essential thing for lives on earth. From the tiniest creature to human beings, all cannot live without water. The conservation for purified water has been a global concern. Therefore, in obtaining a certified quantity of water, many research and technologies have been developed. Water/wastewater purification is the process of making water for drinking, pharmaceutical, medical, industrial, and chemical applications. It may involve a series of processes to remove diverse impurities and contaminants from water to be able to use for desired applications. Different treatments ranging from chemical or physical treatments can be utilized for water purification, and more technologies have been explored for more feasible and efficient applications for the future enhancement of water purification. Therefore, the membrane principle and key parameters for water/wastewater purification are discussed in the following sections for further understanding.

2.1 Membrane principle for water/wastewater purification

Many technologies have been developed to meet the demand of water, including distillation, freezing, desalination, solvent extraction, precipitation, chlorine disinfection of water, ion exchange purification, magnetic assistance purification, and absorption-based purification [7–13]. Solar-powered and wave-powered desalination technologies have also been used for energy and environmental conservations [14]. Apart from the abovementioned methods, emerging electrochemical methods are also proposed for electrochemical development and global water needs. Filtration for water purification involving UV irradiation is also innovative for its effectiveness against microorganisms, which are not visible to the human naked eye. Chlorination and ozonation are also alternative methods for the disinfection of water resource, for the treatment of water taste and odor problems, and for eliminating microbes.

There are some key features that the materials for water purification must have. Such materials must have compact modular construction, low chemical sludge effluent, and excellent separation efficiency [15]. In addressing all these requirements, the researchers have been developing techniques that meet the demand for the process. Absorption-based water purification technologies are among the widely used techniques because of their reliability, low cost, and process simplicity. Therefore, carbon-based materials such as carbon nanotubes (CNTs), carbon nanofibers, and graphene derivatives have also been widely used as absorbents as they are easy to modify, and such materials have high chemical stability, low density, and reusability. Distillation is also a promising technology for water purification (i.e., desalination). This process is primarily driven by the temperature gradient of the feed solution and distillate, which gives fresh water as the product. Distillation has been regarded as an efficient membrane technology for desalination as 100% solute rejection can be achieved theoretically [16, 17].

Membranes are proven to have advantages in water purification because of their ease of modification, simple fabrication techniques, diverse selectivity, and separation efficiency. Many studies have also been developed for the advancement in modification and membrane performance [18–20]. A membrane is a thin interface that is tailored to allow specific species to pass through. The feed solution with impurities is allowed to pass through the membrane, and the impurities are eliminated in the membrane system resulting in the purified filtrate. Modifications can be made during membrane fabrication to select the targeted materials [1, 21]. In particular, the development in membrane technologies is made to cover these factors: the development of high-efficiency cross-flow of the elements, creating the system with controllable capabilities to separate the target components, tailoring the morphology of the membrane for controlling microscopic control phenomena, and the economic and reliable fabrication of membrane materials.

Membranes have been applied to various membrane technologies, among which pressure-driven membrane technologies such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and RO have been applied for water/wastewater purification [22, 23]. They can filter out the contaminants in the water source in a limited size range as the name described [22]. The size range selectivity of the abovementioned membranes is described in Table 1. Membrane distillation is also another popular purification technology utilizing membranes. Other water purification technologies that utilize membranes include dialysis, electrodialysis, and electrodeionization.

MF, UF, NF, and RO are all pressure-driven processes [22–24]. Based on the selectivity in the elimination of impurity size ranges, MF membranes can remove bacteria and turbidity. UF membranes can remove viruses, fine collides, and biological impurities such as pyrogen endotoxin. NF and RO membranes can filter out salt ions, metal ions, and low molecular weight organic species. MF, UF, and NF pores can be measured by electron microscopy, while RO membranes could be non-porous, which can be read by positron annihilation lifetime spectroscopy. Meanwhile, MF and UF membranes should eliminate impurities while trapping the essential resource materials in water. Therefore, membranes must have selectivity in filtering out and processing high water flux. Another factor that the membranes should have is rousting over a wide pH range and insensitivity to oxidizing agents. Membranes should also establish balanced hydrophilicity and hydrophobicity to achieve the full performance of the membrane, including tunable and sensitive properties such as pore size, surface charge, and morphology to prevent the “fouling” of the membrane [25, 26]. While embracing all these properties, membranes with low cost must be fabricated to provide sufficient water for the growing global population.

In addition, membrane distillation is a temperature-driven membrane process involving the pressure difference between the heated feed and cool permeate, which results in purified pure water [16, 27]. It is also a promising technology for water purification as it can be used for the production of

Table 1 Types of filtrations and their selective sizes for filtering out impurities

Type of filtration	Abbreviation	Filtration range
Microfiltration	MF	0.05–10.0 μm
Ultrafiltration	UF	0.005–0.5 μm
Nanofiltration	NF	0.0005–0.01 μm
Reverse osmosis	RO	0.0001–0.001 μm

Table 2 Characteristics and requirements for an efficient distillation membrane

Characteristics	Requirements
– Hydrophobicity	– High (high hydrophobicity allows liquid retention)
– Chemical resistance	– High (for membrane stability)
– Thermal conductivity	– Low (high conductivity lowers the water flux)
– Pore size	– 100 Å–1 µm
– Thickness	– 30–60 µm
– Mechanical strength	– High (for membrane stability)
– Tortuosity	– Low (high tortuosity lowers the flux)

high-purity water by eliminating impurities such as ionic, colloid, or other volatile organic compounds. In the distillation membrane, pore wetting of the membrane must be avoided, and the hydrophobic properties of the membrane must be maintained, while the best performance of the distillation membrane is due to the super-hydrophobicity [16, 17]. The characteristics of the membrane distillation are summarized in Table 2.

Based on the membrane principle, the membranes can be grouped into two types, that is, anisotropic membranes and composite membranes, consisting of thin film, coated films, and self-assembled structures. In anisotropic membranes, the chemical composition is homogeneous, but the pore size and porosity over the membrane may vary. By contrast, composite membranes are heterogeneous in the chemical composition of the membrane and structure shape. Normally, the thin surface layer is supported by a thick porous layer, and the structures can be tailored by polymeric membranes depending on the target need. The commonly used polymeric materials for membranes include cellulose, polyacrylonitrile (PAN), polyetherimides, polyethersulfones, polyamide (PA), polycarbonates, cross-lined polyether, polypropylene (PP), and polyvinylidene fluoride [28, 29]. Moreover, nanocomposite materials have been widely used in different fields, and they have become an essential material source for water/wastewater purification applications. They contribute to the pore formation, large number of functional groups, and low-cost fabrication and modification. Therefore, nanoparticles and nanocomposites are implanted to the membrane to be used in water purification.

2.2 Key parameters

2.2.1 Water flux

Flux or water flux is typically expressed as volume per area per unit of time, meaning that the flux is concerned to express the rate at which water permeates a reverse osmosis membrane. More specifically, water flux was measured through a cross-flow membrane module, which is often determined from Eq. (1) (Table 3), at where the existence of nanofillers in the membrane can enhance hydrophilicity and reduce the cross-linking of NECMs, thereby reaching a high performance of water flux through the membrane. The increase in the water flux of membranes can depend on the active nanofillers' structure integrated in the polymeric

Table 3 Details of several equations used in water/wastewater purification

Name	Equation	Details of parameters
Water flux	$J = \frac{V}{A \times t}$ (1)	– Water flux of membrane (J, L·m^{-2}·h^{-1}) – Liquid volume (V, L) – Area of membrane (A, m^{2}) – Specific time (t, h)
Pollutant rejection	$R(\%) = \frac{C_\mathrm{f} - C_\mathrm{p}}{C_\mathrm{f}} \times 100$ (2)	– Rejection rate (R, %) – Permeated concentration (C_p) – Fed concentration (C_f)
Amount of pollutant adsorption	$q_\mathrm{e} = \frac{(C_\mathrm{o} - C_\mathrm{e}) \times V}{m}$ (3)	– Amount of pollutants adsorbed at equilibrium (q_e, mg·g^{-1}) – Initial concentration (C_o, mg·L^{-1}) – Concentration at equilibrium (C_e, mg·L^{-1}) – Liquid volume (V, L) – Mass of membrane (m, g)
Pollutant removal efficiency	Removal (%) $= \frac{(C_\mathrm{o} - C_\mathrm{t})}{C_\mathrm{o}} \times 100$ (4)	– Removal efficiency (%) – Initial concentration (C_o, mg·L^{-1}) – Concentration at time t (C_t, mg·L^{-1})

substrates/matrix. For example, porous silica nanoparticles, that is, MCM-41 (i.e., Mobil Composition of Matter No. 41, which is a mesoporous material with a hierarchical structure from a family of silicate and aluminosilicate solids), could serve as short pathways for favorably crossing water molecules through the nanoparticles' pores found in NECMs [30], which is similar to hydrophobic porous nanoparticles [31]. In addition, functional nanofillers with high surface porosity can decrease the formation of macro-voids and improve the rejection capacity of pollutants from water effectively. Active nanofillers such as channels, for example, CNTs, have a high performance of water flux [32], indicating that the water molecules could be partially sealed in the multi-walled CNT, instead of using a polymeric substrate alone. In addition, these functional nanofillers could aggregate together to form an interconnected network with other pores in NECMs and subsequently reach a greater increase in water flux.

2.2.2 Pollutant rejection

Pollutant rejection is able to be referred to molecular sieving effect during water/wastewater purification, which is often calculated using Eq. (2) (Table 3). It is also a transport of ions with various valences through nanochannels containing negatively charged functional groups, in which the ion exclusion depends on electrostatic interactions more than steric hindrance [33]. For example, NECMs reached a decrease in surface roughness with increasing loading content of reduced graphene oxide/titanium dioxide (reduced GO/TiO_2) hybrid fillers in the polymeric substrate [32], particularly the increase in intermolecular hydrogen bonds (H-bonds) between the polymeric layer and hydrophilic hybrid nanofillers. In addition, the increase in the content of hybrid nanofillers can reduce the water contact angle of NECMs correspondingly, particularly the membrane's hydrophilicity, the increase of surface charge density, and pure water flux.

2.2.3 Selectivity versus permeability

Selectivity and permeability are considered the main performances for membrane technology. Besides, it has to be considered that the salt rejection and the reverse solute flux have to be controlled in thin-film composite membranes and the hydrophilization of the porous support layer alone will reduce the separation efficiency. Thus, it is important to modify these membranes in terms of high selectivity and high water flux, simultaneously [34]. The use of functional nanofillers in polymeric substrates/matrix could change NECMs' physicochemical properties, particularly charge density, cross-linkage, and hydrophilicity, which provides specific water pathways with high performance permeability and selectivity [32]. The use of hydrophilic nanofillers in polymeric substrates/matrix can decrease the water contact angle of NECMs, which is favorable for improving their surface hydrophilicity. For example, surface hydrophilicity can be improved when the hydrolysis of acyl chloride occurred to form carboxylic acid functional groups in NECMs [35]; moreover, the existence of integrated hydrophilic nanofillers on NECMs' surface can provide a large number of hydrophilic functional groups to the surface.

Apart from the abovementioned hydrophilicity, the cross-linkage condition and thickness of the active layer are the main features for investigating the water permeability and selectivity of NECMs [35]. The molecular sieving effect also plays an important role in the performance. Hydrophilic molecular sieving nanoparticles can provide flow paths for water molecules, for example, highly ordered hexagonal pore-shaped mesoporous silica nanoparticles exhibited high permeability [30], whereas non-porous silica nanoparticles with cross-linking networks could increase permeability. An interfacial surface of dialysis cellulose has been well modified via molecular interactions of the GO/chitosan (GO/CTS) hybrid network without cross-linkers, which possessed high performance of organic dye fluxes and rejections. The organic dye separation performance of this polymer–composite membrane related to the existing physical channels, the molecular sieving effects, and the specific functional groups indicates its ability to trap and adsorb organic dye molecules selectively [18]. Therefore, it should meet some requirements in optimizing the internal structure, surface, and size characterization, as well as in ensuring appropriate interfacial interactions with polymeric substrates/matrix.

2.2.4 Adsorption performance

According to the adsorption approach, the adsorption ability is determined on the basis of the amount of pollutants adsorbed at equilibrium [Eq. (3)], at where it is calculated on statuses between adsorbents and adsorbates used during adsorption (Table 3) [1]. The adsorption performance can also be investigated on the basis of the removal efficiency of pollutants from water, as presented in Eq. (4) (Table 3) [1]. In addition, models regarding adsorption isotherms and kinetics are calculated and fitted to investigate the adsorption process and manner for removing pollutants from water using membranes (Table 4) [1]. These models are determined on non-linearized and linearized forms to explain in detail the adsorption mechanism of adsorbents correspondingly. In general, adsorption kinetics is established from plots of the adsorbed quantity versus a time function to reveal possible features of adsorption kinetic processes. Meanwhile, adsorption isotherms are obtained from changes in the concentration of pollutant solution, at where other

Table 4 Common adsorption isotherm and kinetic models

Adsorption isotherm	Details	Nonlinear	Linear	Plot	Constant
Langmuir	It is used to describe the equilibrium between the adsorbate and adsorbent system, where the adsorbate adsorption is limited to one molecular layer at or before a relative pressure of unity is reached	$q_e = \frac{q_m K_L C_e}{1+K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$	$\frac{C_e}{q_e}$ vs C_e	q_m and K_L
Freundlich	It refers that the surface of the adsorbent is heterogeneous, and the force of bonds decreases with an increase in the appropriation of sites	$q_e = K_F C_e^{\frac{1}{n}}$	$\log q_e = \log K_F + \frac{1}{n}\log C_e$	$\log q_e$ vs $\log C_e$	K_F and *n*
BET	It aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of materials	$q_e = \frac{K_B C_e q_m}{(C_s - C_e)[1+(K_B-1)(\frac{C_e}{C_s})]}$	$\frac{C_e}{q_e(C_s-C_e)} = (\frac{1}{K_B q_m}) + (\frac{K_B-1}{K_B q_m})(\frac{C_e}{C_s})$	$\frac{C_e}{q_e(C_s-C_e)}$ vs $(\frac{C_e}{C_s})$	K_B and q_m
Temkin	It assumes that the adsorption heat of all molecules decreases linearly with the increase in coverage of the adsorbent surface and that adsorption is characterized by a uniform distribution of binding energies, up to a maximum binding energy	$q_e = \frac{R.T.}{b}\ln(A_T C_e)$	$q_e = \frac{R.T.}{b}\ln A_T + \frac{R.T.}{b}\ln C_e$	q_e vs $\ln C_e$	A_T and *b*
Dubinin–Radushkevich	It is derived from the statistical thermodynamics of adsorption and is based on the assumption that adsorption occurs through a series of independent and equivalent sites on the adsorbent surface	$q_e = q_s e^{-K_{D.R.}\varepsilon^2}$	$\ln q_e = \ln q_s - K_{D.R.}\varepsilon^2$ $\varepsilon = RT\ln(1 + \frac{1}{C_e})$	$\ln q_e$ vs ε^2	$K_{D.R.}$ and q_s
Toth	It was derived and has been widely used for the inhomogeneous solid surfaces. The three-parameter isotherm incorporates the effect of the interaction between the adsorbed substances as well	$q_e = \frac{K_T C_e}{\sqrt[t]{(a_T + C_e^t)}}$	$\log q_e = 2\log K_T - \frac{1}{t}\log a_T + \left(2 - \frac{1}{t}\right)\log C_e$	$\log q_e$ vs $\log C_e$	K_T and a_T
Redlich–Peterson	It is a mix of the Langmuir and Freundlich isotherms, which is an exponential constant reflecting the heterogeneity of the adsorbent varying between 0.0 and 1.0 and K RP (L/g)	$q_e = \frac{A.C._e}{1+BC_e^{\beta}}$	$1n\frac{C_e}{q_e} = \beta 1nC_e - lnA$	$\ln\frac{C_e}{q_e}$ vs $\ln C_e$	A and β

Table 4 (continued)

Adsorption kinetic	Details	Linear	Plot	Constant
Pseudo-first-order	It assumes that physisorption limits the adsorption rate of the particles onto the adsorbent	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$\ln(q_e - q_t)$ vs.t	k_1
Pseudo-second-order	It considers chemisorption as the rate-limiting mechanism of the process	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	$\frac{t}{q_t}$ vs $\frac{t}{q_e}$	k_2
Elovich	It assumes that the rate of adsorption of solute decreases exponentially as the amount of adsorbed solute increase	$q_t = \frac{1}{\beta}\ln\alpha\beta + \frac{1}{\beta}\ln t$	q_t vs lnt	α and β
Intra-particle diffusion	It is known as the solution to the problem of free diffusion of a solute from a batch adsorber of constant concentration into a sphere that does not possess adsorption sites	$q_t = k_t t^{0.5} + l$	q_t vs $t^{0.5}$	k_t and l

parameters are constants corresponding to adsorption times, pH, temperatures, and stirring speeds.

2.2.5 Others

Antifouling and fouling abilities Apart from the abovementioned key parameters, the use of functional nanofillers in NECMs can decrease membranes' fouling ability, thereby enhancing the long-term duration of NECMs. That is, the antifouling and fouling abilities depend on several features, such as the negative charge, hydrophilicity, and smoothness of NECMs [33]. In addition, the integration of hydrophilic nanofillers into the polymeric structure can enhance the surface's hydrophilicity and decrease surface fouling, for example, the use of silica particles demonstrated the long-term fouling ability of NECMs with a lower flux reduction compared with polymer membranes [36]. This antifouling performance can be evaluated through filtration using NECMs. First, the membrane is closely packed using distilled water to obtain a constant permeate flux, regarding the extent of fouling. Afterward, a protein solution (bovine serum albumin) is poured into the reservoir to investigate membranes' permeability with a specific time period. Finally, membranes' fouling ability is measured through the decline in the flux based on the time investigated [33]. Besides, fouling ability can be divided into two approaches: (i) reversible fouling is formed on the membrane surface, at which it can be removed by a physical cleaning approach; and (ii) irreversible fouling relates to internal fouling in the membrane pores and can be removed only by chemical-cleaning approach [37]. In general, the membrane fouling exhibits the adsorption and deposition of constituents on a membrane surface or in the membrane pores; thus, the fouling ability probably induces a reduction in membrane permeability [37].

Chlorine resistance The good resistance of NECMs is primarily related to the consecutive exposure of oxidizing agents. In particular, chlorine, which is a disinfectant, is a strong oxidizing agent, in which removal of chlorine is an undesired option using NECMs because this approach can increase the number of processing steps and total cost during water/wastewater purification. However, PA-based membranes cannot be effectively used to treat chlorine-contained water; consequently, the modification of these membranes is necessary for efficiently treating chlorine from water, which is similar to the development of bio-membranes, particularly chlorine resistance. This performance is well subjected for a short time to free a high concentration of chlorine, which is similar to membranes' exposure to a low concentration of free chlorine for a long time [33], at where the water flux and pollutant rejection are determined during chlorination using the required membranes and prepared chlorinate solution [33].

3 Scientific keys of NECMs for water/wastewater purification

In general, the membranes used for water/wastewater purification are divided into three typical types, namely, inorganic membranes, polymeric membranes, and composite membranes (Fig. 2) [1]. Inorganic membranes consist of inorganic

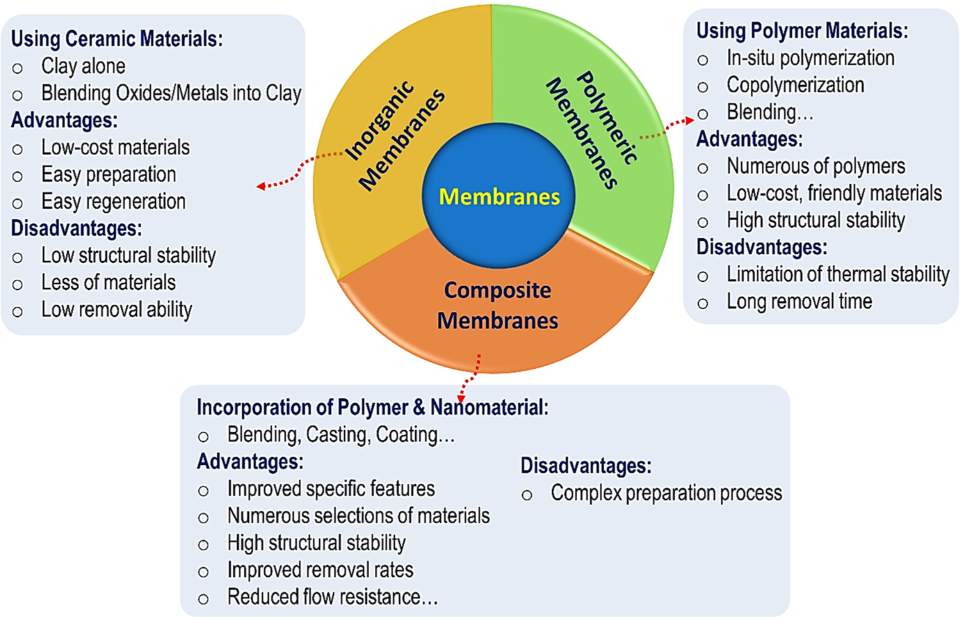

Fig. 2 Typical membranes utilized for water/wastewater purification

materials, such as clay, metals, or ceramics alone, or the combination of clay and metals/metal oxides. Their considerable advantages include low-cost materials, high mechanical and thermal strength, and easy preparation and regeneration compared with polymeric membranes. However, inorganic membranes still have some disadvantages that maybe related to a number of selectable materials, and their removal ability and structural stability are almost low compared with the two abovementioned membranes [1]. Therefore, they can reach a high selectivity; however, their permeability is almost limited, making them unsuitable for diverse applications, particularly for water/wastewater purification. For adsorption and separation in water/wastewater purification, silica microporous-based inorganic membranes are greatly utilized in molecular sieving. However, such silica microporous-based inorganic membranes require a pore size in nanometer range. Therefore, zeolite-based inorganic membranes are known as an alternate candidate in this challenge, which are applied at a molecular scale compared with others. Concomitantly, such membranes have hydrophilicity and high thermal stability [38].

Meanwhile, polymer materials are primarily used to form polymeric membranes containing one or more compounds, in which they are generated via in situ polymerization, copolymerization, blending, etc. There are numerous selections of active, inexpensive, and friendly materials, and their mechanical strength, structural stability, and selective transfer of chemical species are also remarkable. However, the thermal stability of polymer materials has a limitation compared with inorganic membranes; in addition, such materials require a long time to remove pollutants from water [1]. Common polymeric membranes include CTS, poly(vinyl alcohol) (PVA), polyethersulfone (PES), PAN, poly(vinyl chloride), polyimide (PI), polyethylene (PE), PP, cellulose acetate (CA), PA, poly(vinylidene fluoride) (PVDF), etc. [1, 39]. Given their special functional groups, that is, sulfonic acid, carboxyl, and amine on the polymer, polymeric membranes can be significantly effective for adsorbing organic dyes and heavy metal ions from water/wastewater [1]. To date, homogeneously organic membranes are usually fabricated by blending/mixing, copolymerization, or grafting/bonding methods [40].

Apart from the abovementioned membranes, several potential incorporations among polymers and nanomaterials might have been constructed successfully, which provide promising results in recent years, serving as composite membranes [1]. To date, many researchers have successfully fabricated various composite membranes toward water/wastewater purification. In particular, the technical approach for manufacturing composite membranes is diverse, such as blending, mixing, dry/drop/wet casting, and coating, indicating a diversity of the fabricated composite membranes. However, the manufacturing process of the composite membranes is quite complicated compared with that of the inorganic and polymeric membranes. Moreover, these composite membranes have numerous advantages, such as numerous selections of active materials, significantly improving and enhancing functional characteristics; high removal ability and structural stability; and reduced flow resistance.

Among the abovementioned membranes, composite membranes, particularly for NECMs containing nanostructured filler-like materials and nanoscale barrier polymeric substrates, are known as emerging membranes that are utilized for water/wastewater purification because of their high water permeability, low-pressure requirement, efficient adsorption and separation processes, and enhanced performance [1].

Therefore, NECMs can enhance the performance of the membrane by increasing the functional adsorption sites reasonably. In addition, the use of hydrophilic nanostructured active fillers to add into/onto the membranes can enhance the clean-treated water flux efficiently [41]. Nevertheless, the use of these active nanofillers should not be added overly to avoid damaging the membrane's structure and limiting its performance, which is often proposed with < 6 wt% of the nanofillers in the membrane matrix [41], as well as to prevent strong interactions among the used nanofillers and polymeric substrates. Moreover, the selection of polymeric substrate is considered an important factor enhancing the performance and structural stability of the membrane. Furthermore, the working mechanism and ideas of NECMs, as well as the selection of active materials for NECMs, are discussed in the following sections.

3.1 Working mechanisms and ideas of NECMs

In general, the selective removal of pollutants from water by using NECMs comprises two working mechanisms, namely, adsorption and separation (Fig. 3), which are considered recent efficient approaches. First, the NECMs are modified to contain potential functional groups (i.e., $-NH_2$, $-OH$, $-C=O$, and $-COOH$) that could interact well with the target pollutants from water [1]. The membranes based on the adsorption technology for water treatment has been reported in the 1980s [42]. In particular, such membranes allow the target pollutants to be selectively adsorbed by these potential groups because of the functional groups onto the membranes' surface and pore wall (Fig. 3A). This finding indicates the adsorption capacity of the membrane when the polluted water flows across the membrane; in addition, the high performance of the membrane can be achieved because of the short contact distance among the pollutants, and the adsorbed active binding site of the membranes was observed at a submicron-scale level [1]. Therefore, the chemical characteristics of active compounds in the designed membrane play an important role in the manufacture of suitable NECMs and their adsorption capacity.

Meanwhile, the separation capacity of the membrane is based on its permeability and physical pores, which can selectively separate pollutants from water and achieve a high separation performance during the exudation of wastewater across the membrane (Fig. 3B). This characteristic is attributed to the structural morphology of the membrane, which may lead to slow rate-limiting mass transport. In addition, the membranes should meet some requirements for large surface areas, and intra-particle diffusion results in short residence times, low backpressure, and large volumetric capacity in a large scale. In particular, their morphological characteristics are considered an important factor affecting their potential performance in water/wastewater purification.

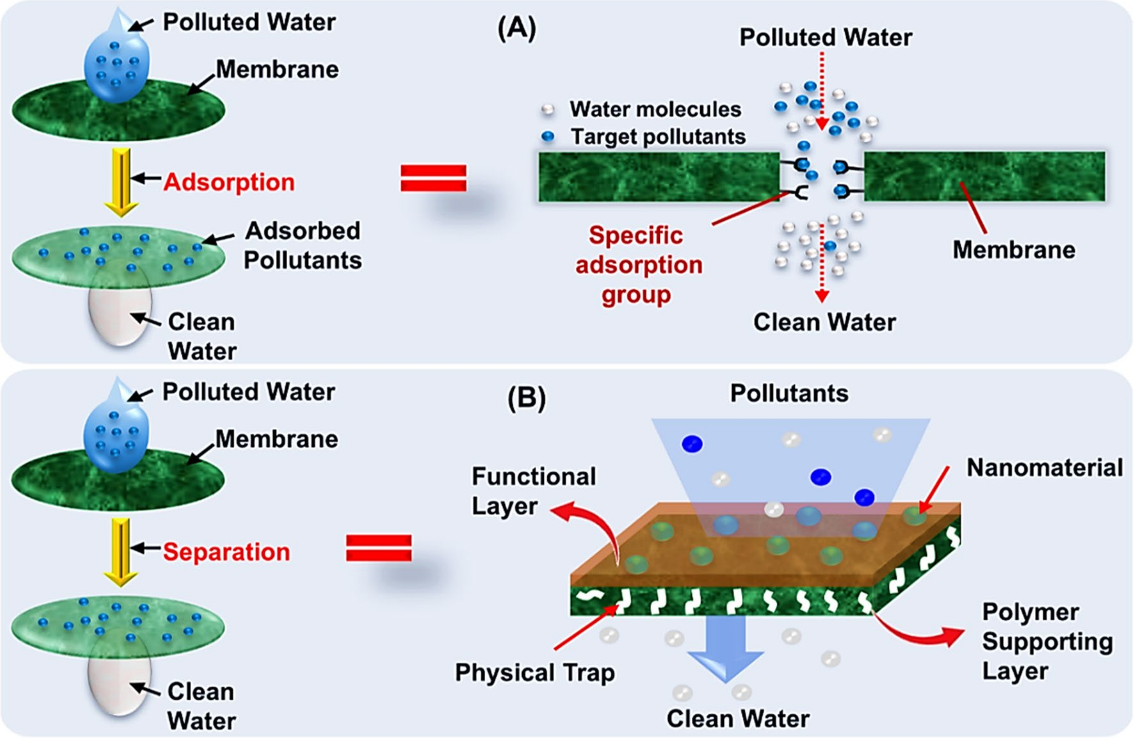

Fig. 3 Schematic illustration of the working mechanism of NECMs in water/wastewater purification consisting of adsorption (**A**) and separation (**B**) approaches

The target pollutants can contact the functional groups (i.e., existing on an active layer's surface) of the membrane to be adsorbed and removed from the water, and pollutants that have higher sizes than the membrane's pore will be rejected by molecular sieving. Meanwhile, the size of pollutants is smaller than the membrane's pore, which will cross the functional layer and arrive to a polymer-supporting layer that is considered adsorption microspheres (i.e., physical traps). Afterward, these molecules can be attached, reacted, and tightly sealed by NECMs, which produce a permeation of filtered water from NECMs, as clean water [41]. Such ideas should satisfy some requirements for the selection of active materials and design of NECMs to be applied for water/wastewater purification.

3.2 Selection of active materials for NECMs

A composite material is a combination of two active materials with various physical and chemical characteristics to improve and enhance their properties, which can be applied to many situations. Hence, NECMs are known as a recent-emerging composite membrane that contains nanostructured filler-like materials and nanoscale barrier polymeric substrates. A NECM is designed for water/wastewater purification that comprises a polymer supporting layer (bottom) and a functional layer (upper) in whole of its structure (Fig. 4). The incorporation of polymers and nanomaterials will be proposed to produce an appropriate NECM for water/wastewater purification, in which the polymeric materials often include CTS, cellulose, PVDF, PA, and PES [1, 21]. Apart from their good membrane-formed capacity, such an incorporation exhibits flexible, chemically stable, and low-cost materials, with good mechanical strength and high selectivity, to create membrane-based products [1, 21, 22]. Apart from their functional groups, they should meet the requirement of pore sizes to explore their application appropriately and effectively. Meanwhile, nanofiller-like materials can be divided into carbonaceous (i.e., GO and CNT), metals/oxide metals (i.e., TiO_2 and silver (Ag)), silica (i.e., zeolite and silica nanospheres), and crystalline organic (i.e., covalent organic frameworks (COFs) and porous organic frameworks) nanomaterials. In the following sections, the functions and potentials of each material will be presented in detail to obtain a comprehensive understanding.

3.2.1 Polymer substrates or matrixes

Natural and bio-polymers Natural or bio-polymers are typical adsorbent-like materials for removing various pollutants from water, including organic dyes and heavy metal ions. They are usually produced from biodegradable and renewable materials, indicating the existence of oxygen and nitrogen in their chemical structure [43, 44]. CTS is a polysaccharide biopolymer containing abundant hydroxyl and amine groups, which is greatly used in membrane's application for water/wastewater purification (Fig. 5) [1, 45]. Its physicochemical and biological properties are shown in Table 5 [46, 47]. CTS are derived from chitin, as a natural biopolymer in crustaceans' shell. The physicochemical properties of CTS and chitin depend on molecular chain orientation and regular packing. In the case of CTS, the number of hydroxyl and amino groups and *N*-acetyl content (i.e., deacetylation degree) with a strong interaction regarding intra- and intermolecular H-bonds are high, resulting in the formation of linear aggregates and rigid crystalline domains. In addition, the crystallinity of CTS is less than that of chitin, inducing CTS being more reachable to reagents and more soluble (i.e.,

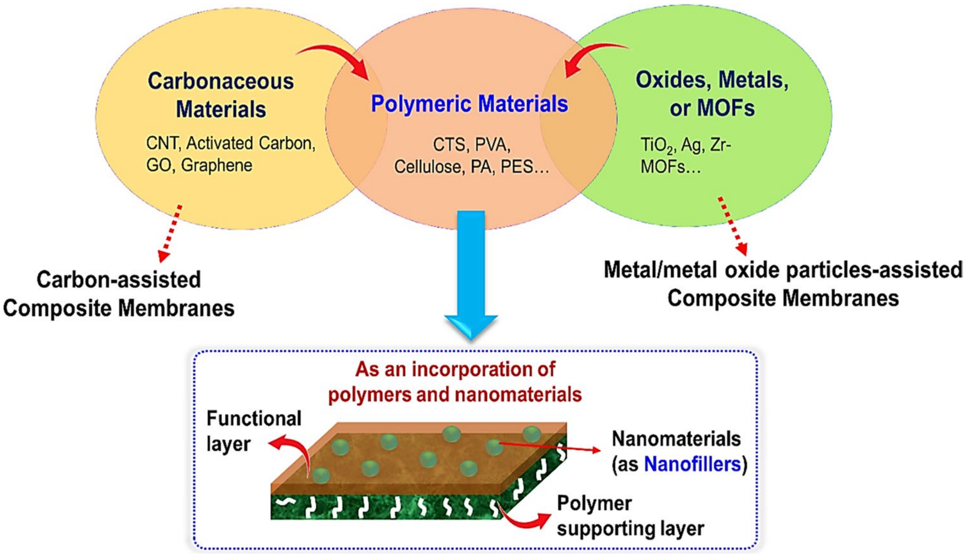

Fig. 4 Schematic illustration of NECMs by proposing the incorporation of polymers and nanomaterials

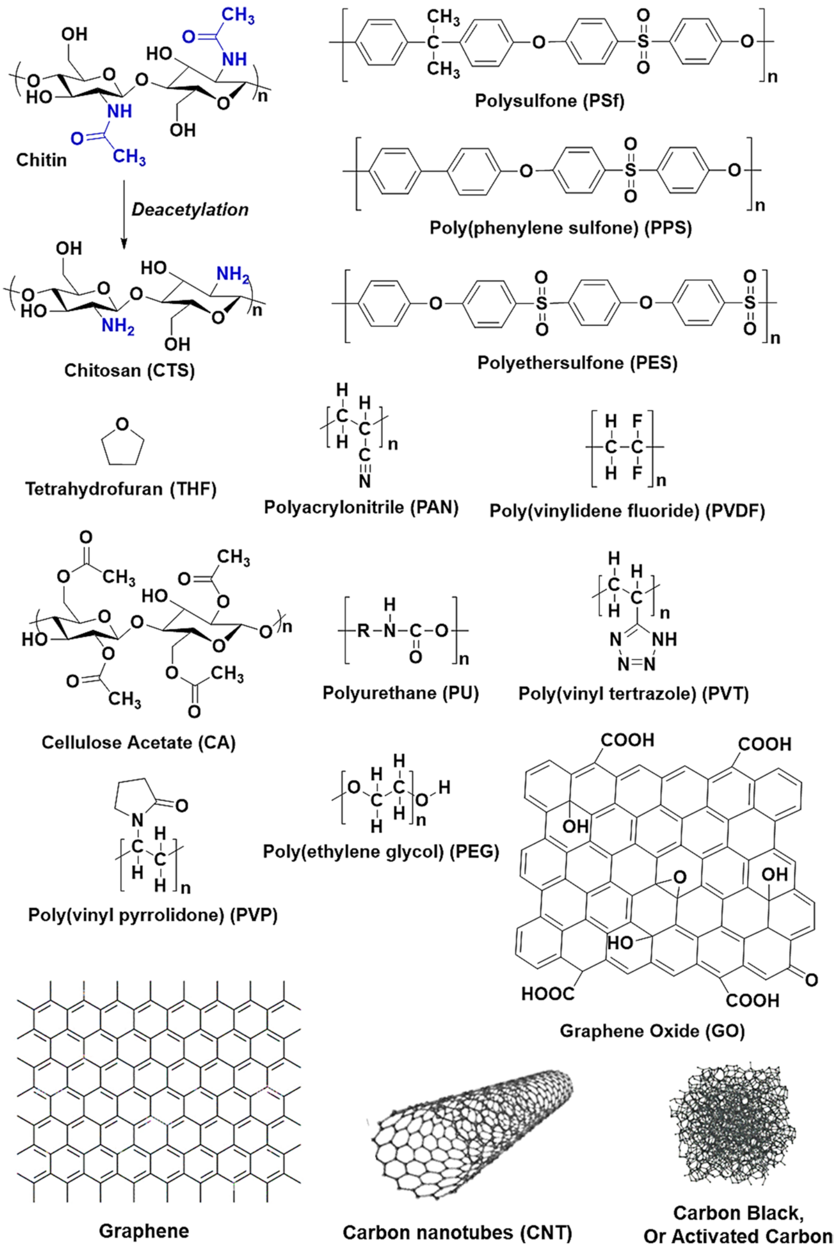

Fig. 5 Chemical structures of some active materials used in the construction of NECMs for water/wastewater purification

Table 5 Physicochemical and biological properties of CTS

Physicochemical properties	Biological properties
– Linear amino-polysaccharide: abundant nitrogen content	– Non-toxic
– Cationic biopolymer: a high charge density	– Bio-activity/adhesivity/degradability
– Numerous functional groups for chemical and cross-linking reactions	– Adsorbing capacity
– Ionic conductive and flocculating agent	– Antimicrobial and hypolipidemic activities
– Chelating, complexing, and adsorption properties	– Anti-acid, antiulcer, and antitumoral properties
– $pK_a = 6.5–6.7$	– Blood anticoagulants
– Creating intermolecular H-bonds	

weak acid media with pH less than 6.5) [46, 47]. Therefore, the protonation of amino groups in the acidic environment greatly occurred along the CTS chain that might produce numerous cationic sites, thereby increasing its solubility with the increase of polarity. Given this unique characteristic, the potential application of CTS can be expanded more than those of chitin because of its promising ability to adsorb various pollutants. For example, its amine groups can strongly interact with heavy metal ions contained in water media because of the presence of an electron pair in nitrogen atoms, which has chelating and complexing abilities [1]. Meanwhile, the protonation of amine groups can attract to anionic pollutants in water media (i.e., electrostatic attraction), comprising anionic dyes and halogens [7, 18, 19]. Furthermore, the existence of $–NH_2$ and –OH active groups enables the adsorption of other pollutants, particularly H-bonds and van der Walls. As CTS is well soluble in an aquatic medium (i.e., pH of < 6.5), several cross-linker agents, such as epichlorohydrin, formaldehyde, and glutaraldehyde, are proposed to avert any solubility issues and intensify its mechanical property with sorbents.

Among its physicochemical properties, including crystalline, mechanical, swelling, and thermally degradable properties, such cross-linker agents have been revealed to interdepend with the distribution of acetyl groups (i.e., deacetylation degree) along the CTS chain [48]. For CTS-based membranes, a deacetylation degree of 87% exhibited lower crystalline and mechanical properties, but its swelling ability could reach 75% or 96% [49]. When the deacetylation degree increases, its charge density will rise and make the CTS chain more flexible, thereby producing a random coil containing numerous inter- and intramolecular H-bonds in the CTS chain. For the proposed improvement of the mechanical properties of CTS flat membranes, CTS can be used to embed into compatible nano-biomaterials, or it can be used as a good supporting material in thin-film composites [50]. However, the use of a CTS component has disadvantages, such as the incomplete or nonuniform coating of the membrane. In addressing these issues, CTS is often combined with other polymers that can effectively enhance the mechanical property and chemical stability [1].

In addition, eggshell-inspired attractive substrates are known as low-cost natural and bio-resources; these eggshell-based polymers provide many advantages because of their porous entangled structures and unique chemical and mechanical properties [51]. Nonetheless, eggshell-based neat polymeric substrates have also some drawbacks such as a stereotypical microstructure and side effects, thereby limiting their potential applications and hindering their commercialization. Thus, these factors can affect the design and construction of eggshell-based functional membranes for water/wastewater purification, and their current limitations can be addressed through surface modification or integration of active nanomaterials that can maintain their advantages and correspondingly enhance the membrane performance [52, 53].

Synthetic polymers In addition to natural and bio-polymers, synthetic polymers are greatly explored for manufacturing membranes used in water/wastewater purification. Among them, PES is a polysulfone (consisting of para-linked aromatics, sulfonyl ether, and alkyl groups, such as polysulfone (PSf), poly(phenylene sulfone) (PPS), and PES) of high performance thermoplastics that is greatly utilized as a commercial material in various separation processes (Fig. 5). PES is often fabricated via phase inversion, and the final membrane product depends on additives, solvent, concentration, coagulation bath, and temperature [54]. The PES membrane has several advantages, including outstanding thermal, mechanical, hydrolytic, and oxidative stabilities, particularly its applicability in a wide pH range of 2–12. However, it also has several drawbacks, such as its fouling-related issues caused by the adsorption of nonpolar pollutants, bacteria, or hydrophobic particles, which shortens the membrane's lifetime. Therefore, membrane fouling is attributed to the inherent hydrophobicity of polysulfones, which significantly reduces the performance and working lifetime of the membrane, thereby limiting its application [55]. Similarly, other drawbacks can be due to biocompatibility, which is related to aggregation, as well as the inert state in water media. Thus, final product-related modifications of the membrane are usually proposed to common polymers/membranes for manufacturing adsorption and separation membranes, thereby addressing such limitations [56]. To date, considerable effort has been exerted to improve the hydrophilicity, adsorption, and separation properties of the membrane through corresponding modifications. For example, another hydrophilic polymer, that is, poly(vinyl pyrrolidone) or poly(ethylene glycol) (PEG), is added into the PES membrane casting solution (Fig. 5). These hydrophilic polymers can contribute to the formation of active pores in the polymeric membrane and intensify their permeation features correspondingly [57]. The PSf membrane could also be modified by using tetrahydrofuran (Fig. 5) and water pressure (8 bars) to separate sodium alginate from water, resulting in the high water flux (259 L/m^2) and sodium alginate rejection (98.8%) of the modified PSf [58].

Apart from the PSf and PES membranes, PAN (Fig. 5) is also a versatile synthetic polymer used for manufacturing membranes because of its outstanding solvent stability, cost-effectivity, and great mechanical properties. In addition, PAN fibers are considered a chemical precursor of high-quality carbon fibers. For manufacturing approaches, PAN could be used to successfully produce a membrane with a high adsorption and separation performance from synthesized poly(vinyl tetrazole)-*co*-PAN (PVT-*co*-PAN) by using a non-solvent-induced phase separation technique [59]. The use of PVT (Fig. 5) can change the pore size, hydrophilicity, and charge in the membranes; thus, this polymer enables the membranes to become more hydrophilic and negatively charged [60]. Concomitantly, PVDF (Fig. 5) is also widely used to produce the polymeric membrane because of its good thermal, chemical, and mechanical stabilities [61].

CA (Fig. 5) often refers to any acetate ester of cellulose, that is, cellulose diacetate, which is also known as a common filtration membrane because of its cost-efficiency, hydrophilic nature, and good antifouling characteristic [62]. Nevertheless, CA-based membranes have low thermal, chemical, and mechanical stabilities. At present, these disadvantages can be improved by using polyurethane (PU) with CA in blended membranes (Fig. 5), which is considered a heterogeneous matrix, including soft and hard sections arranged alternately in the polymer chain. The hard segments are not soluble in water media, but the soft ones are more flexible and soluble in water (i.e., polyether polyols) [63]. In addition, this membrane has a spongy structure because of its different pores on the surface, thereby facilitating the water flux rate [64]. Thus, the PU-CA membrane revealed an effective and cost-efficient approach to remove pollutants from water, such as chromium (Cr^{6+}) [63]. Furthermore, the surface modification of a CA-based membrane could be performed using chitin nanocrystals via surface coating [65]. Consequently, the modified CA-based membrane exhibited a significant decrease in water contact angle from 132° to 0°, serving as a super-hydrophilic membrane, and the high flux and rejection of bovine serum albumin and humic acid were also observed on this membrane. In addition, cellulose triacetate has been utilized as a common polymeric membrane in dialysis and reverse/forward osmosis membranes because of its good desalting ability, high biocompatibility, appropriate toughness, high hydrophilicity, enhanced fouling mitigation, and cost-effectiveness [66]. Several potential polymers could be used as polymer matrix, polymeric substrates, or functional layers in NECMs for effective water/wastewater purification. Nonetheless, the membrane performance still depends on the selection and modification of active materials.

3.2.2 Functional nanofillers

Apart from polymeric substrates, functional nanofiller-based materials are important components to enhance the performance of NECMs in water/wastewater purification, which can be divided to inorganic (i.e., carbon, silica, metals, and metal oxides), organic (i.e., non-porous and porous organics), and hybrid (i.e., inorganic–inorganic and inorganic–organic hybrids) nanomaterials. Such nanomaterials will be discussed in detail in the following sections.

Inorganic nanomaterials Typically, inorganic nanomaterials are commonly used as active components in the growth of composite membranes, in which they are considered inorganic fillers to be effectively added in/on the polymer matrix/substrate, improving the performance of NECMs in water/wastewater purification. Moreover, these nanofillers are often attached to the support materials through van der Waals forces, H-bonds, or covalent bonds, which are made via various technical processes (i.e., sol–gel, thermal plasma, ion sputtering, and electrodeposition).

(a) Carbon-based materials

Carbon-based inorganic nanomaterials are prevalently used in the manufacture of NECMs, such as graphene, GO, CNT, and carbon black (Fig. 5) [67–69]. For example, based on previous reports, GO could significantly enhance membrane performances, including permeability, anti-swelling/fouling, and mechanical strength [18, 70–73]. Given its abundant chemical groups and hydrophilicity, GO can well interact with pollutants via electrostatic attractions, π-stacking, or H-bonds, promoting adsorption and separation efficiency. For example, GO layers were added on hollow fiber membranes [i.e., poly(amide imide) (PAI) or poly(ether imide) (PEI)] to remove salt and divalent ions from water, and their fabrication process was based on a dip-coating technique [74]. The GO layers were used with PES membranes serving as nanoplates to remove dyes with a rejection of 99% [75]; it was also directly casted on dialysis cellulose membranes via molecular interactions to adsorb cationic and anionic dyes from water with rejections of 85.07% (methylene blue) and 80.03% (Congo red) [18]. Therefore, the outstanding advantages of these GO-based NECMs used in water/wastewater purification improve adsorption capacity, selectivity, flux, rejection, and deterring membrane fouling [76]. In addition, this high efficiency is attributed to the improved hydrophilicity, regarding the acidic groups (i.e., hydroxyl and carboxylic acid) that are attached on the membranes' surface through the addition of GO nanosheets to the support materials [76]. Meanwhile, CNT and carbon black are hydrophobic; consequently, corresponding modifications are proposed on these materials to become hydrophilic before coupling them into an active layer for water/wastewater purification.

To date, quantum dot-based nanomaterials with a general size range of < 20 nm, such as carbon, graphene, and GO quantum dots (C-QDs, G-QDs, and GO-QDs), have attracted considerable attention and possessed encouraging advantages in NECM separation [77, 78], which is attributed to their high specific surface area and superior chemical stability. Notably, their high hydrophilicity, good dispersing ability, and abundant active groups can enhance the membranes' separation and adsorption efficiencies. Moreover, the chemical stability and surface groups of quantum dots can reinforce other corresponding characteristics in solvent resistance and the anti-oxidation/fouling ability of the membranes [79–82].

(b) Silica-based materials

Apart from carbonaceous nanomaterials, silica-based ones have also shown application potential in enhancing NECMs' performance. Their negative charge and super-hydrophilic (i.e., abundance of hydroxyl groups) features can provide the membranes' surface with stronger negative charges and better wettability, resulting in a significantly enhanced separation performance. The use of porous and non-porous silica nanoparticles into the PA layer can also improve the membrane performance in adsorption and separation selectivity from various pollutants. In addition, other silica-based nanomaterials, such as zeolitic and non-zeolitic inorganic ones, were effectively used as nanofillers to produce membranes by dispersing them into the organic phase [83, 84]. For example, an incorporation of zeolitic imidazolate framework-302 (ZIF-302) and CA has been performed to generate a nanocomposite membrane via phase inversion, which was well applied for osmosis-driven membrane process [85]; moreover, glassy and rubbery polymers were used as a polymer matrix for manufacturing zeolitic NECMs [84].

(c) Others

Apart from the abovementioned inorganic nanomaterials, metal and metal oxides (i.e., Ag, Cu, Al_2O_3, and TiO_2) have been also greatly used for designing NECMs [86, 87]. In general, these active materials serve as hydrophilic bactericides to improve membranes' antifouling property; however, such materials can also support other performances of the membranes during water/wastewater purification. Among them, Ag nanoparticles have been used as an efficient candidate for membrane surface modification because of their anti-pollution capacity, antibacterial ability, and chemical stability [88]. Copper (Cu) nanoparticles are also known as an excellent antibacterial agent, and the fouling control of the membranes improves with the immobilization of Cu nanoparticles via in situ formation [89]. Meanwhile, the introduction of zinc oxide (ZnO) nanoparticles in PES, PSf, and PVDF matrix/substrates shows a significant improvement in hydrophilicity, porosity, rejection capacity, high permeability, and antifouling ability. For example, ZnO nanoparticles have been used in PES membranes to improve dye rejection from 47.5 to 82.3% [90], whereas ZnO/PVDF nanocomposite membranes exhibited 100% recovery and two times increase in water flux because of their internal hydrophilicity [91]. Zirconium dioxide (ZrO_2) with a band gap of 5.0 eV can be used as a heterogeneous catalyst (i.e., a photocatalytic agent) [92], which is used as an inorganic nanomaterial in membrane fabrication because of its high physical, hydrophilic, chemical, and thermal stability [93]. Meanwhile, a TiO_2 nanomaterial is also known as an outstanding candidate for the fabrication of NECMs, and its hydrophilic and photocatalytic (a band gap = ~ 3.2 eV) natures are favorable for degrading various organic dyes from water (dye removal performance of > 90%) [94, 95]. This inorganic nanomaterial is also greatly used to enhance the antifouling ability and stability of NECMs [94, 95].

Recently, several alternative inorganic nanofillers with numerous desired features have emerged, such as montmorillonite, bentonite, double-layered hydroxides, and metal–organic frameworks (MOFs), and such nanofillers have been greatly utilized for constructing NECMs [84, 96–98]. Moreover, new 2D materials, such as MXenes, are successfully explored and prepared through etching layered $M_{n+1}AX_n$ phases using hydrofluoric acid [99]. Given their high hydrophilicity, excellent chemical stability, negative charges, and environment-friendly features, they effectively exhibited the membranes' separation performance [100, 101] and enhanced membranes' anti-biofouling performance [102]. In addition, other 2D nanomaterials, such as boron nitride nanosheets (BN) [103, 104], carbon nitride (C_3N_4) [105–107], and molybdenum/tungsten disulfide (MoS_2/WS_2) [108–110], have been applied to construct NECMs correspondingly and effectively. Given their outstanding characteristics, such as hydrophilicity, and their negative (BN, and MoS_2/WS_2) and positive (C_3N_4) charges, the use of these 2D nanomaterials in the composite membranes can provide permeability, selectivity, and anti-organic fouling properties.

Organic nanomaterials Apart from inorganic nanomaterials, organic-based ones with porous/non-porous structures, versatile functions, and intrinsic polymeric characteristics have been considered potential candidates for designing advanced NECMs. Their flexible and diverse components as well as compatible organic composition can correspondingly enhance the membrane performance.

(a) Cellulose nanocrystal-based non-porous organic materials

Non-porous organic nanomaterials with hydrophilicity and electronegativity can well interact with the polymer matrix to improve membranes' adsorption and separation performance. In particular, cellulose nanocrystals (CNCs) are known as natural rod-like particles produced from acid hydrolysis of various sources containing cellulose (i.e., cotton, bamboo, wood, and straw), which are green, renewable, low cost, and biodegradable materials. Moreover, CNCs have a high negative zeta potential, hydrophilic surface, good mechanical properties, and flexible surface modification because of the abundance of hydroxyl and carboxyl groups [111]. These benefits enable the CNCs to be flexibly used for improving membranes' performance in water/wastewater purification, such as permeability and antifouling properties, and the functional groups on their surface can also endow the chemical and structure stabilities of the membranes [111, 112].

For example, a new CNC-based reverse osmosis NECM was well fabricated by Asempour et al. [112]. As a result, the highest performance NECM with 0.1 w/v% loading fraction of CNCs doubled water flux with salt rejection of 97.8%, indicating that the membrane hydrophilicity and surface area improved and enlarged effectively for permeation. On the contrary, the highest CNC loading of 0.2 w/v% induced decreased the water flux of the membrane because of the undesirable blockage of water pathways caused by waterproof CNCs. Simultaneously, its salt rejection dramatically decreased because of the possible defects in the PA layer caused by agglomerated CNCs. In addition, the permeability and monovalent salt rejection of CNC-based nanofiltration NECMs have significantly increased, whereas divalent salt rejection remained unchanged based on the increase of CNC loading because of the enhanced electronegativity, hydrophilicity, and cross-linking extent, as well as the reduced pore size [111]. Concomitantly, the CNC-based RO and nanofiltration NECMs indicated an improved fouling resistance. However, comprehensive understanding of the interaction of CNC nanofillers and PA matrix should be further studied, similarly for the influence of the optimal content of used components on the separation performance and long-term stability of the membranes.

In another work, carboxylated cellulose nanocrystals (C-CNCs) have been used to exhibit dispersibility, electronegativity, and hydrophilicity greater than those of CNCs because of the carboxyl groups on their surface [113]. Consequently, permeate flux, salt rejection, and mechanical strength improved significantly after the prepared C-CNCs were coupled into the active layer of the membranes. This result provided insights into constructing and designing CNC-based NECMs, which serve as environment-friendly nanomaterials in the polymer substrate/matrix for water/wastewater purification. In addition, 2,2,6,6-tetramethylpiperidine-1-oxyl-oxidized cellulose nanocrystals (TO-CNCs) were prepared via interfacial polymerization and then used to create RO NECMs [114]. Consequently, the carboxyl groups existed on the TO-CNC surface enabled the salt rejection and water flux of the membranes because of the enhanced H-bonds between TO-CNCs and the PA matrix. Moreover, the increase in salt rejection (98.98%) and water flux (260%) is related to the attained nanochannels, that is, the size of nanochannels and strength of the nanocrystal/polymer interface, enabling a fast water transport. Furthermore, the water flux and salt rejection can be optimized through attaching other surface-functionalized CNCs into the PA matrix [114]. Therefore, controlling nanomaterial/polymer interfaces is considered a promising strategy in adjusting molecular selectivity and transport of NECMs.

(b) Porous organic materials

The most important characteristic of porous organic nanomaterials is associated with the molecular sieving effect regarding their well-organized inner pore structures, passing on the flow paths for water molecules and eliminating the target pollutants. Hence, the use of NECMs containing porous organic nanofillers, such as porous organic polymers (POPs), COFs, and MOFs, might have greater potentials in water/wastewater purification.

POPs are known as cross-linked organic nanofillers that are usually constructed via covalent bonds, and these nanofillers are flexible because of their amorphous characteristic. Numerous selections of monomer can be used to synthesize POPs correspondingly and effectively. Moreover, POP-based nanospheres (i.e., hollow polymer nanocapsules, meso- or microporous polymer nanospheres) can be used to construct NECMs for water/wastewater purification, which may be attributed to their outstanding compatibility with the polymer matrix, good hydrophilicity, abundant surface groups, and their water selective and permeable inner nanochannels [115]. For example, amino-functional mesoporous polymer nanospheres (N-MPS) have been synthesized and added into a PA active layer to produce RO NECMs with high efficiency desalination [116]. The synthesized N-MPS showed excellent physicochemical properties of interconnected mesopores of ~ 5.6 nm, which provided flow paths favorable for water transport, and strong interactions of nanofillers containing abundant amino groups and the PA matrix via H-bonds and covalent bonds. Consequently, these RO NECMs containing N-MPS reached a high performance with the increase of water flux (62%) and a high NaCl rejection of 98.7%. Therefore, POPs are considered encouraging organic candidates to produce high performance NECMs for water/wastewater purification. Moreover, the performance of NECMs can be optimized by accurately adjusting and controlling the porosity, size, and morphology of POP nanofillers. Nonetheless, the long-term durability of these membranes should be considered and studied further for their better practical applications.

For crystalline porous organic materials, COFs are known as a new class, which are usually constructed from organic building blocks via strong covalent bonds [117]. COFs have numerous advantages, such as highly ordered nanochannel, high porosity, easily tuning functionalities, and flexible building of covalent bonds, serving as promising candidates for constructing adsorption and separation NECMs. Therefore, COFs can well disperse into the selective layer during the fabrication of NECMs because of their organic composition, high hydrophilicity, charge property, good affinity, and abundant surface active groups, which indicate their good stability and compatibility among other components [118]. Furthermore, the pore size of COFs is often reported in a range of 0.5–4.7 nm, which is favorable for removing pollutants from water consisting of organic dyes, divalent salts, and others, thereby enhancing NECMs' performance with regard to adsorption, permeability, and selectivity [117]. For example, COFs with secondary amine groups (i.e., SNW-1) were well incorporated with the PA layer [119], thereby improving its pure water flux up to 92.5% and Na_2SO_4 rejection up to > 80%. These results might be attributed to the appropriate pore size, high hydrophilicity, and porosity of synthesized SNW-1, and it could be covalently linked with the PA matrix based on the strong interaction of –COCl groups and –NH– groups that showed excellent stability of the prepared membranes. Meanwhile, SNW-1-based NECMs exhibited an increased rejection of Rhodamine B (99.4%), high permeability of ethanol (46.7%), and long-term stability in both processes of consecutive cross-flow filtration and static immersion. These results were attributed to the improved hydrophilicity, rough surface, and thin skin layer of the prepared NECMs [120]. In addition, the use of COFs into the NECMs for desalination has been investigated, for example, carboxyl-functionalized COFs (COF-COOH) were well synthesized and then incorporated into the PA layer [121]. Consequently, the as-designed membranes enhanced the water flux (64.2 Lm^{-2} h^{-1}) and the reverse flux selectivity (10.0 L/g), which is attributed to their ultrahigh hydrophilicity, small mean pore size, extra water channels, and negative charge property. In general, the inner pores and external surface of COFs can be modified to reach effective COFs and rationally tailor their physiochemical features [122]; moreover, their economic and facile fabrication strategies should be developed to perform mass production of COF-based membranes.

Apart from the aforementioned nanomaterials, MOFs are fabricated by organic linkers and metal ions or clusters, serving as hybrid organic–inorganic solid components [123]. At present, MOFs are considered an ideal candidate for producing NECMs used in the application of organic separation/adsorption and water/wastewater purification because of their flexible advantages in high surface area, flexible structure, tunable chemical composition, controlled porosity, and good affinity for organic polymers [124, 125]. For example, two new MOFs [ZIF-8, MIL-53 (Al), NH_2-MIL-53 (Al), and MIL-101 (Cr); MIL-101 (Cr), MIL-68 (Al), and ZIF-11] [126] have been successfully synthesized to become MOF-based NECMs for water purification. MIL-101(Cr) and ZIF-11 have been concomitantly integrated in the PA layer to produce high performance membranes [127]; Zr-MOFs have also exhibited good thermal and chemical stabilities that were ideal for nanofillers to enhance their molecular separations [128] and Cu^{2+} adsorption (988.2 mg/g) [129]. Notably, UiO-66-NH_2 was used to improve MOFs' dispersibility in nonpolar solvents and interfacial compatibility between MOFs and polymer matrix [130]. Consequently, the membranes reached high performances, with methanol permeability of 20 Lm^{-2} h^{-1}/bar and tetracycline rejection of 99%. Furthermore, UiO-66 is a promising adsorbent that can strongly interact with boric acid, indicating that the pore effect of the adsorbed boron could be narrowed on the sub-nanometer pores of UiO-66, thereby significantly reducing the pore size and increasing boron rejection [131]. In general, MOFs have diverse advantages such as highly porous structure, tailorable chemical functionality, mild synthesis conditions, molecular sieving property, and favorable polymer affinity, which indicate their potential applications in advanced NECMs and, thus, need more intensive research in the future. Moreover, a balanceable establishment of the loading amount among the active components should be further investigated in detail, similarly to MOFs' dispersibility and adsorption/separation performance, indicating that optimizing the MOF loading' approach and reasonable modifications of their surface and multi-functionality are favorable evaluation methods. Simultaneously, the long-term durability and stability of MOF-based NECMs should be also studied under practical conditions, and idea designs are suggested to obtain cost-effectiveness toward their industrial applications.

(c) Others

In addition, solid organic nanomaterials are effectively utilized in NECMs for the removal of pollutants from water, which is attributed to their good compatibility with polymer matrix as well as their diverse functionalities and structures. With regard to membranes' antifouling property, zwitterionic nanomaterials were also considered promising nanofillers because of their special water-binding ability and good antifouling property [132]. Their free surface carboxyl and hydroxyl groups can link to PA chains to form a dense and stable selective layer on the NECMs, and they can limit the adsorption/deposition of hydrophobic pollutants on their surface because of their anionic and cationic groups, thereby maintaining a high separation performance and extended lifetime [133].

In another type of porous organic nanomaterials, aquaporins (AQPs) have been used for desalination, which are known as the natural water channel proteins with superior selectivity and high water permeability, indicating that these channels may enable water transport when rejecting pollutants from water, and each channel can pass up to ~ 109 water molecules per second [134–136]. For example, a hollow fiber membrane has been effectively extended by embedding AQP-incorporated proteoliposomes into the PA layer [135], resulting in the ultrahigh performance of the membranes with high salt rejection and improved water flux. In addition, AQP-based membranes could be efficient chemical-cleaning agents that contain sodium hydroxide, ethylenediaminetetraacetic acid, and citric acid, and they could be sensitive to temperature and pressure. The chemically cleaned AQP-based membrane has reached a high salt rejection (> 98%), and it is well maintained; however, its water flux significantly increased probably because of the changes in membrane structure and enhanced hydrophilicity close to the aquaporin [136]. Therefore, further research must be conducted to demonstrate the durability and stability of AQP-based membranes in more detailed operation conditions. Similarly, their mass production and non-defected membranes should also be considered to reduce the manufacture costs.

Furthermore, calix[n]arene is considered closed-loop size-selective macrocyclic molecules, in which some units of phenolic blocks are repeated, reaching a hollow cup-like structure. For example, sulfocalix[4]arene and sulfothiacalix[4]arene have been explored and integrated into the PA network [137]. Consequently, the membranes significantly enhanced the free volume, decreased the selective layer's thickness, doubling-enhanced ethanol flux, and ensured high rejection because of their molecular tunability/sieving effects. Therefore, calix[n]arene can be used in the NECMs to improve selectivity and permeability for desalination, water/wastewater purification, and solvent reclamation.

At present, soft organic nanomaterials were designed and functionalized as active nanofillers to fabricate NECMs for water/wastewater purification [138, 139], for example, organic resorcinol–formaldehyde nanobowls (ORFBs) were well prepared and dispersed in monomer solution with non-agglomeration before interfacial polymerization process [140] that was due to their excellent hydrophilicity. Moreover, the ORFBs were tightly attached into the PA matrix, indicating a highly stable separation, because of the strong chemical reactions between monomers and surface groups (i.e., hydroxyl and amino groups). Therefore, RFBs are potential candidates for charges in the surface and groups of the membranes appropriately, providing an enhanced alkaline resistance and rejection.

Using the approaches of various functional nanomaterials in NECMs, serving as active nanofillers, their potentials are significantly attributed to their stability in water/wastewater purification. Therefore, the stability of various active nanofillers under different conditions depends on water, acid/base, chemical, other solvents, and mechanical property (Fig. 6). Moreover, several active nanofillers can be easily hydrolyzed when they are exposed to a solute medium or water vapor, inducing possible collapses of the original structure. Concomitantly, at an applied pressure on NECM processing, these nanofillers should achieve mechanical stability; hence, these functional nanomaterials should be stable at the applied pressure, as well as their long-term durability/stability must be ensured. In general, carbonaceous nanomaterials, crystalline organic nanomaterials, and inorganic–organic hybrid nanocomposites are highly stable in various aqueous solutions. Meanwhile, nanomaterials based on metal, metal oxides, silica, and inorganic–inorganic hybrid are not stable in an acid/base environment, which is similar to the case of amorphous organic ones in chemical and other solvent media.

Hybrid nanocomposites Apart from inorganic or organic nanomaterials using a single component, hybrid nanocomposites, which are proposed to combine the advantages of distinct nanomaterials to rationally tune material functions for ideal designs of NECMs, can also enhance the adsorption and separation performance of NECMs, which indicates that the distinct functions of each component can be preserved at the very least. Therefore, membrane limitations and membrane performance can be appropriately and effectively improved when the active compositions are combined.

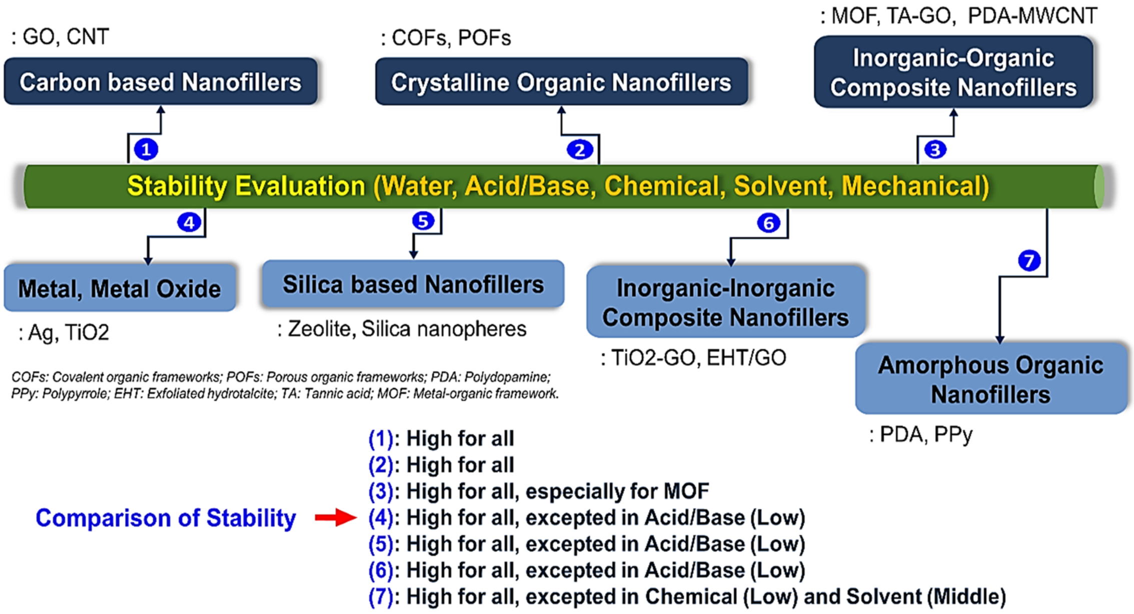

Fig. 6 Schematic illustration of the stability evaluation of various nanostructured active fillers, regarding water, acid/base, solvent, chemical, and mechanical property

Among the membrane restrictions, granular nanomaterials may agglomerate during the manufacture of membranes, for example, the use of GO lamellar nanosheets can reduce the unexpected agglomeration by in situ hydrothermal growth [141]. In addition, the interspace of GO can be adjusted by adding nanoparticles, which are preferable for membrane selectivity and permeability. Moreover, instead of using only GO or TiO_2 integrated into the polymer matrix or substrates, they could be combined to form TiO_2–GO hybrid composites as the synergistic effects of rationally incorporated segments, and they could be used to produce high performance NECMs, indicating their great anti-oxidation and antifouling abilities [32]. In addition, the incorporation of TiO_2-SiO_2 hybrid composites was more effective than a distinct component because of the suppressed agglomeration, high hydrophilicity, and tailorable composition [142]. Moreover, the interlayer distances of GO can contain an exfoliated hydrotalcite (EHT) to tailor the layer gap correspondingly, which provides several transport pathways and changes the surface charge of the modified membrane [143]. Therefore, the incorporation of hydrophilic EHT/GO composite nanosheets into the membrane achieved a superior salt rejection and flux. ZIF-8 containing Zn^{2+} was also coordinated with the carboxyl groups of GO nanosheets to create ZIF-8/GO hybrid nanocomposites by in situ growth and then wrapped and stacked into the membranes, serving as an antimicrobial agent [144]. Consequently, the ZIF-8/GO nanocomposites not only enhanced the separation performance of the membrane comprising well-maintained selectivity and improved permeability but also improved the lifetime of the membrane, which were attributed to their effective antimicrobial ability, regarding the oxidative stress of GO nanosheets and the release of Zn^{2+} of ZIF-8.

Recently, a proposed strategy to enhance the compatibility of active nanomaterials is the addition of chemical groups or soft organic units [145, 146]. For example, dopamine (DA) and *N*-aminoethyl piperazine propane sulfonate (AEPPS) are deposited onto the multi-wall CNT (MWCNT), and DA-AEPPS@MWCNT hybrid composites are generated, leading to good compatibility with the polymer matrix because of the added organic segments [147], which promoted stable and highly permeable membranes. In addition, tannic acid-Fe(III) (TA-Fe) was used to modify MWCNT, resulting in improved compatibility, better dispersion in aqueous solution [148], and enhanced anti-oxidation performance. Similarly, TA-coated GO nanosheets could significantly improve its compatibility with the polymer matrix and become hydrophilic, providing these hybrid nanocomposite-based nanofillers with a radical cleaning ability [149]. Furthermore, polyhedral oligomeric silsesquioxane (POSS) is another potential hybrid nanocomposite for constructing NECMs in water/wastewater purification, which is known as a coordination of an inorganic cage-shaped core and organic compositions [150, 151]. The POSS has high hydrophilicity, good compatibility, and improved surface charge of the membranes, resulting in significantly enhanced antifouling and separation capacities [152]. Concomitantly, metal-induced ordered microporous polymer (MMP) was also incorporated into an active polymer layer of the separation membranes, thereby significantly improving the water flux and chlorine resistance [153]. Therefore, the –Cl and –COOH groups of MMP could protect amidic –N from being pounced by chlorine because of their electron-withdrawing and steric hindrance effects [154]. These advantages could improve the chlorine resistance of membranes, particularly under alkaline conditions.

The composition of functional nanomaterials as nanofillers and their integration into the polymer matrix/substrates should meet some requirements to ensure a balance of the permeability and selectivity of NECMs as well as the stability of the used nanofillers for long-term adsorption and separation. Therefore, organic nanofillers or nanofillers containing organic segments/chemical groups are more profitable because they can limit the appearance of unexpected interfacial defects between the organic nanofillers and polymer matrix/substrates. In addition, their other functions comprising bactericidal activity, anti-adhesion, and anti-oxidation capacity are important to ensure the multifunction of NECMs during adsorption and separation.

4 Common approaches in structural designs for NECMs

4.1 Surface-modified NECMs

In surface-modified NECMs, the functional layer is fixed on the polymer support surface, which can contact directly with water/wastewater, indicating their adsorption and separation capacities. Their surface can be fabricated by various methods, including depositing, coating, grafting, bonding and assembling, and molecular imprinting (Fig. 7A–E).

4.1.1 Surface deposition

Surface deposition is also a simple method to produce NECMs (Fig. 7A), in which it can be conducted using various technical approaches, such as vacuum filtration, immersion, dipping, spin/dry coating, and dry casting, which are often performed on one step, and the final membrane products are air-dried at room temperature after surface deposition. For example, surface-deposited NECMs could be produced by filtration deposition, which are used as a highly ordered GO nanosheet-contained NECM [155]. In addition, a β-cyclodextrin-modified GO nanocomposite membrane

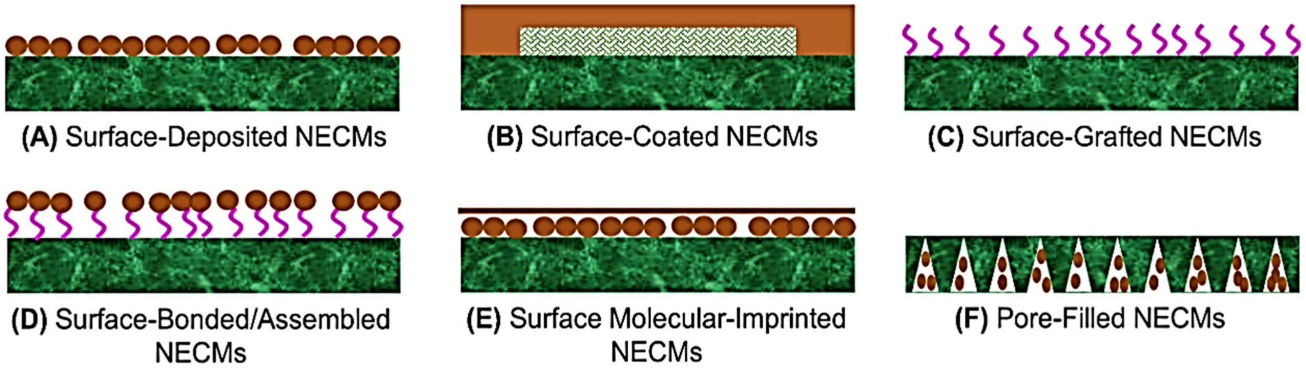

Fig. 7 Schematic illustrations of NECMs' structural designs: **A** surface deposition, **B** surface coating, **C** surface grafting, **D** surface bonding/assembling, **E** surface molecular imprinting, and **F** pore-filled NECMs

has been fabricated by stacking and wrapping this hybrid nanocomposite on porous substrates through vacuum filtration [156]. Moreover, hydroxylated/carboxylated CNT was blended with Cu nanoparticles to produce a hybrid nanocomposite and then directly deposited onto polymeric platforms to achieve NECMs; consequently, the maximum adsorption capacity of arsenic [As(III)] pollutants reached up to 6.77 mg/g of the prepared NECMs [157]. The mixture of GO/CTS hybrid composites was also directly casted on flat dialysis cellulose and glass fibers membranes, indicating that the surface modification of interfacial dialysis cellulose and glass fibers was conducted on the basis of the molecular interaction of the GO–CTS hybrid network without any external cross-linkers, serving as new NECMs for organic dye removal application [18, 19]. Moreover, the pre-treated PVDF substrates could be directly immersed into ZnO suspension [158]. The ZnO nanoparticles were mixed with the PVDF matrix before film casting [158]. Similarly, CA was blended in ZIF-302 solution before casting films [159]. Furthermore, spin coating (only one step) was greatly concerned to uniformly deposit the graphene component onto the fiber surface of the eggshell membrane [52, 73], which obtained graphene-based NECMs after they have been air-dried and stored at room temperature.

4.1.2 Surface coating

Compared with the surface deposition, surface-coated NECMs (Fig. 7B) are often fabricated through two steps: (i) the active nanomaterials are deposited or stacked on the membrane surface by coating, dipping, immersing, casting and filtering; (ii) subsequently, they are coated by the polymer layer with cross-linking (interfacial polymerization) [160]. This method can provide adsorption capacity and removal efficiency of pollutants better than the commercial membranes. At present, this fabrication approach of NECMs is known as the sandwich structure [161]. For example, spin coating has been used to uniformly stack the GO nanosheets on the fiber surface of the eggshell membrane, and the final membrane product was obtained after interfacial polymerization; consequently, the GO/eggshell membrane (ESM) was used as a nanocomposite membrane for osmotically driven water flux [69]. In addition, other sandwich-type NECMs were developed [162, 163], in which the active layer would be among the surface layer and the support layer. Given this specially constructed structure, the surface layer's polymer solution can penetrate into the substrate layer' micro-pores, thereby enhancing their stability and strength, and the asymmetric structure of the surface layer can avoid membrane's blockages caused by small particles. In other works, sandwich-type NECMs, such as PES-sulfonated PES/amino-MIL-53(Al)/polytetrafluoroethylene [163] and PES-sulfonated PES/polystyrene-polydivinyl benzene/polytetrafluoroethylene [161], were produced through simultaneous filtration and immersion precipitation. These sandwich-type membranes can effectively absorb *p*-nitrophenol (297.8 mg/g) [163] and 4-nitrotoluene (3.372 mg/g) [161] from water. In addition, the membrane's support layer was modified by using Fe_3O_4 microspheres to form the Fe_3O_4-contained sandwich structure [41], in which these metal oxide microspheres were filtrated onto the support layer. Subsequently, the DA agent was used as a surface layer to seal them. Consequently, the prepared NECM possessed a greater adsorption capacity (277.9 mg/g) for organic pollutants with a comparable water flux.

4.1.3 Surface grafting

Surface grafting is a common method of attaching the organic groups onto the membrane surface (Fig. 7C), in which various techniques can be well exploited such as radiation, chemical initiation, and UV irradiation [164, 165]. Therefore, surface-grafted NECMs can be produced by a photoinduced technique, namely, post-synthetic polymerization, which occurred on the contact surface of the membrane, thereby fixing the active materials on the membrane surface through covalent bonds. This method has efficient benefits in enhancing the physical and chemical interface interactions between the active nanomaterials and the polymer matrix/substrates. For example, the acrylamide groups were grafted on the high-density PE substrate by using a radiation technique. Afterward, Cu(II) particles were loaded onto the acrylamide-grafted PE membranes through the chelating reaction (pH 8, ~ 3.5 h). Consequently, the modified membrane was effectively applied to remove phosphate ions (100 mg/g) [166]. In another work, the ethylenediaminetetraacetic acid (EDTA) was used to graft on the bacterial cellulose membrane through the amidation-related reaction; the result showed that the adsorption capacity of Sr^{2+} reached 44.86 mg/g using the obtained membranes probably because of the carboxylate and tertiary amines of the grafted EDTA [167]. Moreover, the surface-grafted membranes were well applied for the removal of Cr(VI) from water as it improved the interaction between metal–organic framework particles and the polymer chains in the membrane [168]. However, the application of such membranes is hindered by complications in the process and harsh reaction conditions [169].

4.1.4 Surface bonding and assembling

Surface bonding (Fig. 7D) is utilized for the manufacture of affinity membranes; therefore, the surface-bonded membrane comprises the capacities of membrane and affinity separations. Moreover, these membranes will be more specific and efficient to capture the target biomolecules because of their affinity ligands, revealing the high selectivity, wide processing capacity, and high scale of these membranes. Thus, the coupling of affinity ligands, design/construction of affinity modules and kinetics, and potential applications have been greatly developed [170]. In another approach, surface-assembled NECMs are obtained on the basis of electrostatic interactions (as assembled polyelectrolytes). This method depends on electrostatic attractions between polycations and polyanions (as polyelectrolytes), which occurred onto porous substrates through a layer-by-layer approach [171]. Moreover, the polyelectrolyte multilayer containing poly(allylamine hydrochloride) and poly(acrylic acid) was used to modify the PES substrate via varying depositions [171]. Nonetheless, these polyelectrolytes of the membrane can be separated from the assembled layers during working periods, which is considered a limitation of the surface-assembled NECMs [169]. Thus, surface bonding is often proposed to enhance the strength and stability of the membranes. For example, the PVA-co-PE membrane was an excellent candidate because of its good mechanical strength and stable properties. In addition, the existence of abundant hydroxyl groups could combine affinity ligands and biomolecules on this membrane. This membrane has been activated by NaOH and functionalized by various amine compounds (i.e., diethylenetriamine, hexamethylenediamine, 1,3-propane diamine) for bilirubin removal (110 mg/g) [172].

4.1.5 Surface molecular imprinting

Surface molecular-imprinted membranes (Fig. 7E) contain structural pores that have been specifically recognized on the target molecules by the potential binding effects, using molecularly imprinted technology. These membranes reveal membrane separation and permeation characteristics because of their constructed template [173]. Moreover, they can be fabricated by three steps: (i) template molecules are used to interact with functional monomers (i.e., electrostatic attraction, H-bonds, van der Waals); (ii) a cross-linker agent is added into the abovementioned solution to perform polymerization; (iii) the template molecules are removed at certain conditions, and then the molecularly imprinted membrane is formed, such as the 3D template, with the same size, shape, and functional groups. For example, a porous NECM containing Cr(III)-PVA/sodium alginate has been constructed through ionic imprinting, and the final product has been applied for adsorbing Cr(III) ions from water (59.9 mg/g) [174]; however, it possessed a low flux that is considered a main obstacle. Therefore, future studies on this technical approach must be conducted, which must have a long route based on industrial applications.

4.2 Pore-filled NECMs

In addition to the aforementioned surface-modified NECMs, pore-filled ones (Fig. 7F) can be used to address the drawbacks of NECMs with mixed/blended functional components. These membranes are obtained by trapping/filling the active nanomaterials into the polymer substrates' pores (i.e., physical caves or traps), instead of blending/mixing the nanomaterials into the polymer matrix. Given this special structure of functions in rejection and adsorption capacities, it can meet the requirements for the simultaneous removal of several pollutants from water. For example, Fe_3O_4 microspheres were used to fill into the PES substrate's pores via reverse filtration and polymerization (using DA) [41]. Consequently, As(V) pollutants were completely removed by this modified NECM because of its functional groups and magnetic properties, indicating that small As(V) pollutants crossed the separation layer and reacted with Fe_3O_4 microspheres by chemical adsorption to generate a strong spherical complex [41]. In another work, trapping $Zr(OH)_x$ nanospheres into the PES substrate's finger-like pores has also been well proposed and protected by polydopamine (PDA) coating [175], which exhibited an effective adsorption capacity for lead (Pb^{2+}) ions and a good removal of colloidal gold (Au) and PEG, and its reusability and regeneration were also significantly effective [175].

The use of active nanomaterials into polymer matrix/substrates is considered a potential technology for the removal of pollutants from water because of their low molecular weight, high surface area, abundant adsorption sites, and fast kinetics [60]. However, the application, reusability, and regeneration of these nanomaterials can be limited because of their small fine powders, high cost, strong agglomeration, and potential toxicity [176]. Combining the advantages of nanomaterials and polymer matrix/substrates and overcoming their drawbacks in water/wastewater purification should meet some requirements to develop a membrane fabrication technology effectively and appropriately; therefore, further investigations must be conducted to promote their application in water/wastewater purification.

5 Desired effects and existing challenges of NECMs

5.1 Structural morphology

For NECMs, several requirements of intra-particle diffusion and large surface area resulted in low backpressure, short residence time, and large volumetric ability, indicating that the structural morphology of NECMs is an important factor [177, 178], which significantly affects the removal efficiency of pollutants from water/wastewater. In obtaining the morphological features of active nanofillers and NECMs, scanning (SEM) and transmission (TEM) electron microscopy are commonly used to determine features regarding morphology, thickness, shape, size distribution, and size of the functional nanofillers and membrane surface.

5.1.1 Shape and size

The shape of functional nanofillers indicates a significant effect on the membrane performance. For example, NECMs' performance has been dramatically improved through the potential integration of differently shaped silica and ZnO nanofillers in the polymeric substrate/matrix. Among them, spherical nanofillers have better membrane performance than those with a cubic, rod-like, and flower-like shape (Fig. 8A) because the dimension of spherical nanofillers is low, inducing a corresponding decrease in their aggregation compared with others, which results in a higher performance of water flux with favorable salt rejection [179]. Therefore, a rational design is necessary for the shape of active nanofillers, and the suitable option of functional nanofillers with a specific shape can maximize the advantages of NECMs.

Substantively, the NECMs' performance is determined by the structure, size, and composition of the nanofillers incorporated in polymeric substrates/matrix, for example, a new asymmetric organic nanofiller, such as resorcinol–formaldehyde nanobowls (Fig. 8B), was integrated into the PA—a selective layer through interfacial polymerization [180]. Consequently, the membrane's NF performance was significantly enhanced, that is, higher water fluxes and well-maintained salt rejections, because of the potential features of the incorporated nanobowl-shaped organic nanofillers, that is, their asymmetric structure, concave cavity, and chemical groups. Therefore, silica nanospheres with different sizes, such as 50, 200, and 500 nm, were added into the PA layer (Fig. 8C) [181], which exhibited higher transport resistances of the membrane. The thickness of the selective layer was effective in a range of 50–200 nm, which is being limited by the nanofillers' size of 200 nm. Similarly, UiO-66 nanoparticles with various sizes of 30, 100, and 500 nm were also incorporated into the PA layer (Fig. 8D), showing that the membranes' water flux reduced with the increasing size of UiO-66 nanoparticles [182]. Therefore, the oversized active nanofillers can be weakly coupled with PA chains, separating partially or totally from the membranes' surface during filtration, which results in low separation performance and more pollution. Similarly, these oversized nanofillers might have less contribution to membrane performance compared with the smaller ones because of their insufficient utilizations [183]. Meanwhile, small nanofillers can easily agglomerate and limit their active sites to the membranes' surface, reaching a suboptimal contribution to membrane performance. Therefore, nanofillers' sizes must be further studied to determine their effective roles in NECMs' fabrication and application in water/wastewater purification; concomitantly, theoretical models should also be established and investigated to optimize the key parameters of active nanofillers.

5.1.2 Porosity or pore size

Among NECMs' structural morphologies, the porosity of active nanofillers has an important effect on NECMs' pore size distribution. The use of porous nanofillers in NECMs can flexibly change membranes' pore size; evidently, pore size increased with the increase of nanofillers' porosity, thereby improving membranes' permeability [184]. In addition, porous nanofillers are more desirable compared with the solid ones because pore channels can provide more mass transport pathways for the selective layer in NECMs. In particular, the pore size of common porous nanofillers often ranges from 0.5 to 5 nm for producing thin-film nanocomposite membranes, whereas the membranes will obtain more free spaces when nanofillers with a large pore size are integrated into the selective layer, which dramatically decrease mass transport resistance, reaching a higher permeability.

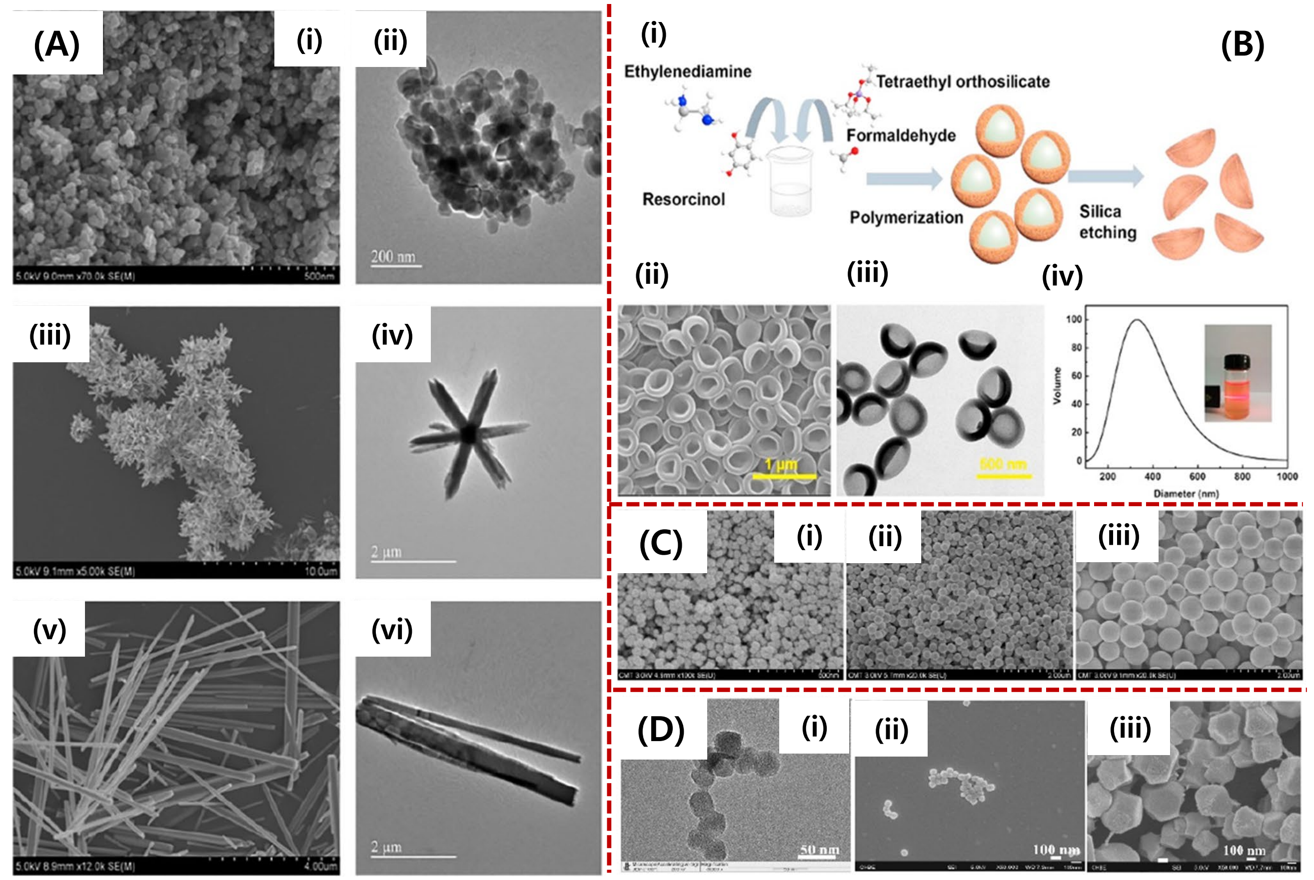

Fig. 8 SEM and TEM images of functional nanofillers: **A** ZnO nanostructures: (i, ii) spherical, (iii, iv) nanoflowers, and (v, vi) nanorods [179]; **B** resorcinol–formaldehyde nanobowls: (i) fabrication, (ii) SEM capture, (iii) TEM capture and DLS graph of resorcinol–formaldehyde nanobowls [180]; **C** silica particles with various diameters of (i) 47.54 ± 7.11 nm, (ii) 228.52 ± 16.91 nm, and (iii) 578.95 ± 86.47 nm [181]; and **D** UiO-66 particles with sizes of (i) 30 nm by TEM capture and (ii) 100 nm and (iii) 500 nm by SEM captures [182]

Therefore, nanofillers with a small pore size (< 0.5 nm) can further supply favorable transport pathways and good sieving effects to the membrane. For example, the pore size of UiO-66 nanofillers was 0.51 nm, which was fixed among water molecules and hydrated ion sizes [185]; thus, the use of UiO-66 nanofillers has enhanced the NECMs' permeability and selectivity.

In addition, the long-term operational stability of NECMs is important during water/wastewater purification, indicating the structural morphology. For example, ZnO nanofillers have been well embedded in PES membranes through strong adhesion and interactions of the active nanofillers and the porous PES substrate (Fig. 9A) [179]. Consequently, these membranes possessed high performance with stable long-term water flux, salt rejection, and good antibacterial activity. Therefore, the incorporation of ZnO spherical nanoparticles in the selective layer dramatically improved the membrane water permeability, as well as antibacterial and antifouling abilities. In another work, UiO-66 nanoparticles were incorporated into the selective layer to produce thin-film nanocomposite membranes for the removal of selenium (Se) and arsenic (As) from water; consequently, the membranes reached a high performance of pure water permeability and rejection for both pollutants (Fig. 9B) [182]. These results were attributed to the small pore size and high hydrophilicity of the incorporated UiO-66 nanoparticles, and the membranes showed a long-term durability because of their stable morphology. Meanwhile, the active mixture of GO/CTS composites was effectively incorporated into various substrates, that is, flat dialysis cellulose (Fig. 9C) and glass fibers (Fig. 9D), via molecular interactions among the active materials, producing new 3D porous NECMs containing specific groups and physical traps for efficiently removing organic dyes from water [18, 19]. Under these circumstances, the prepared hybrid nanocomposites were observed as active nanosheets, which strongly adhere and interact with the substrates. Furthermore, these membranes exhibited a long-term stability during the recycling process. Therefore, the rational selection of active nanofillers should be considered to provide appropriate matches among the

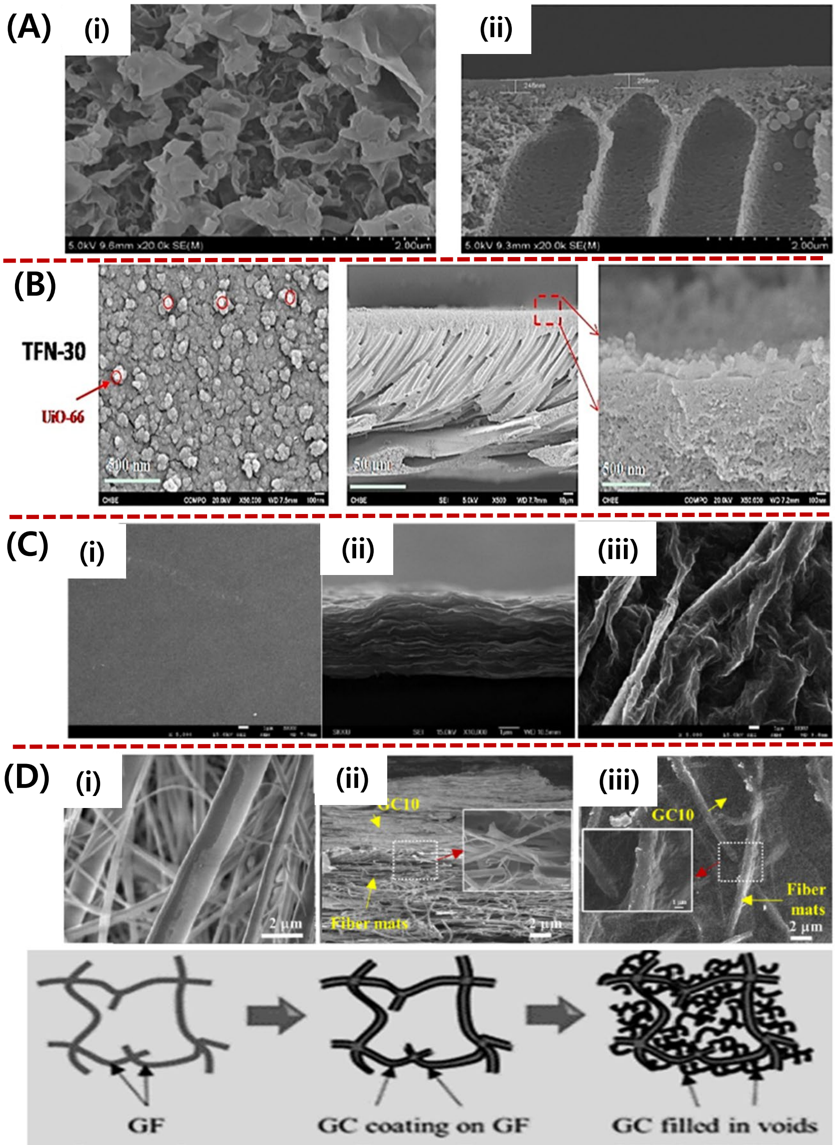

Fig. 9 SEM images of different NECMs: **A** ZnO-contained PSf membrane at the (i) top surface and (ii) cross-section [179]; **B** UiO-66-contained PES membrane [182]; **C** GO/CTS hybrid network-contained dialysis cellulose membrane at the (i) top surface of flat dialysis cellulose, (ii) cross-section, and (iii) and top surface of NECMs [18]; **D** GO/CTS hybrid network-contained glass fiber membrane at the (i) glass fibers, (ii) cross-section, and (iii) and top surface of NECMs [19]

nanofillers' pore size, the targeted contaminants' molecular size, and the membranes' stable morphology.

5.2 Chemical characteristics

Apart from the aforementioned structural morphology of NECMs, chemical characteristics also play an important role in achieving the high performance NECMs for water/wastewater purification [177, 178]. In particular, incorporating active nanomaterials into polymer matrix/substrates can further enhance and improve membrane performance; in addition, the efficient integration of these functional materials can be achieved because of the chemical feature of each material [1, 21, 22]. Organic-based nanomaterials are added in the polymer layer to increase membrane flux without affecting solute rejection, and their potentials can improve the separation performance of the membranes particularly rejection and permeability. At present, many successful studies have developed NECMs containing organic nanomaterials and have addressed challenges such as compromised selectivity, low permeability, and fouling tendency to correct the defects induced by rigid inorganic nanoparticles, such as interfacial defects between nanofillers and polymer matrix/substrates. Furthermore, different porous and solid organic nanomaterials are used to produce NECMs for water/wastewater purification, which are often based on interfacial polymerization through dispersing them in aqueous or organic phase. In particular, MOFs are inorganic–organic hybrid porous nanomaterials that have received considerable attention in the manufacture of NECMs for water/wastewater purification. The incorporation of various active nanomaterials in the selective polymer layer not only provides additional nanochannels and surface roughness (i.e., morphological features) for better solvent transport and good solute rejection but also efficiently changes the membrane properties, such as zeta potential, charge property, hydrophilicity/hydrophobicity, and cross-linking degree (i.e., chemical features), which are also favorable for conspicuously determining the adsorption and separation performance for membranes. The chemical characteristics will be discussed in detail in the following parts.

5.2.1 Hydrophilicity or hydrophobicity (contact angle)

For water/wastewater purification of NECMs, it should meet a requirement of hydrophilic/hydrophobic surface, which is known as an important factor affecting membrane performance, particularly liquid separation. The hydrophilic surface of the membranes has a greater wettability, a better diffusion rate of liquid molecules, and increased anti-organic fouling ability; consequently, the suitable selection of hydrophilic nanomaterials integrated in polymer matrix/substrates will significantly enhance membranes' hydrophilicity, resulting in an elevated permeability. The hydrophobicity/hydrophilicity of active nanomaterials also depends on their surface groups, for example, their hydrophilic functional groups often refer to the amino, hydroxyl, sulfonic, and carboxyl ones. In addition, their hydrophobicity is attributed to post-modification and intrinsic properties with hydrophobic segments. In general, in determining the hydrophobicity/hydrophilicity of membranes, the contact angle is utilized to indicate an interfacial tension between water droplets laid out on the membrane surface. In the contact angle measurement, the contact angle of the water droplet on the membrane surface is less than 90°, which results in a hydrophilic membrane. This contact angle also shows an opposite trend to hydrophobicity, that is, > 90°. Furthermore, the contact angle is used to reveal the antifouling behavior of the membrane.

For example, titanium (Ti) and zirconium (Zr)-integrated PES membranes have a water contact angle of 48°, indicating their hydrophilicity [186]. The use of various nanoparticles to coat the hydrophilic layer on PVDF membranes could reduce the fouling ability of the modified membranes as a surface modification based on cross-linking or physical adsorption [187]. Moreover, another modified PVDF membrane, that is, PVDF/γ-Al_2O_3, has exhibited greater separation performance [188]. The use of TiO_2 nanoparticles to integrate into PVDF membranes showed improved fouling resistance [189]. The hydrophilic nanoparticles of polymers of intrinsic micro-porosity (PIM) hybrid nanocomposite containing numerous hydroxyl groups were added to the aqueous phase for the fabrication of NECMs [190]. Consequently, the membrane surface becomes more hydrophilic with increasing dose of PIM hybrid nanocomposites, thereby reaching a high water permeability, good antibiotic and comparable salt rejection, and low water contact angle of the membrane. Therefore, the dispersion of active nanomaterials in aqueous solution will be improved through the selection of hydrophilic nanomaterials, thereby preventing the formation of defects from the heterogeneous solution [144].

In addition to the hydrophilic nanomaterials, several hydrophobic ones are also used to integrate into polymer matrix/substrates for liquid separation. In particular, the water molecules will pass smoothly through the hydrophobic pores because of the existence of adsorption and friction forces between the water molecules and the hydrophobic wall [191]. Moreover, the hydrophobic nanomaterials are often well dispersed in an organic solution instead of an aqueous one, for example, a hydrophobic methyltrichlorosilane ($MeSiCl_3$) nanomaterial was well introduced into the organic phase to produce a $MeSiCl_3$-contained NECM [192], resulting in the dramatic increase of water flux with the decrease of hydrophilicity, particularly the significant promotion of hydrophobic nanomaterials. Nevertheless, a hydrophobic membrane with an enhanced permeability often shows an opposite trend to the good antifouling properties. At present, three hydrophobic nanomaterials, namely, ZIF-8 [191], $MeSiCl_3$ [192], and fluorinated silica [193], have been applied to improve membrane performance. The use of hydrophobic nanomaterials to enhance membrane performances is necessary. Thus, further studies must be investigated in detail.

5.2.2 Charge property (zeta potential)

The membrane performance is also closely related to its surface charge (i.e., electron-donating or coordinating chemical groups). Normally, the charge on the membrane surface is measured and named zeta potential, which greatly affects the membrane performance, reveals the fouling ability, and checks the stability [194, 195]. A greater zeta potential shows less possibility of fouling because electrostatic repulsions are higher than negative charges, such as the membrane surface and hydrophobic pollutants (i.e., proteins and humic acid). On the contrary, the membrane is more stable when the value of zeta potential is greater, and a lower zeta potential shows less stability of the membrane.

Concomitantly, the surface charge of membranes also plays a role in rejection. The strong negative/positive charge on the membrane surface significantly contributes to the efficient removal of pollutants with an identical charge based on electrostatic repulsions. For example, an ethylenediamine-grafted MIL-101(Cr) hybrid nanocomposite has been successfully designed, and it has constructed a membrane containing positive charges inside the nanochannels and negative charges on the membrane surface [196]. Therefore, inner-positive and outer-negative charges can repulse positively and negatively charged species because of their electrostatic forces among these charges. Consequently, an outstanding removal performance for various charged pollutants has been observed on the obtained membrane. Furthermore, the use of charged nanomaterials greatly improves the antifouling capacity of the membranes. Therefore, the membrane surface with a high charge density is more favorable for strongly interacting with water molecules by electrostatic interactions and then generating a protectively hydrophilic water layer [197], which may limit the deposition of hydrophobic organic pollutants occurring on the membrane surface with a hydrophilic water layer. As a result, such a surface charge not only rejects the solutes from the membrane but also refuses the attachment of identical charged pollutants. The addition of properly charged nanomaterials can bring outstanding advantageous for the selectivity, antifouling ability, and stability of NECMs.

5.2.3 Adsorption and multi-functionality

Adsorption is known as a surface phenomenon, which is defined as the increase in the concentration of adsorbates at the surface of adsorbents, particularly physical or chemical adsorption, at which adsorption ability is significantly impacted by contact time, pH, temperature, adsorbent dose, adsorbate concentration, and nature of adsorbent and adsorbate. In general, functional groups, such as the amino, hydroxyl, sulfonic, carboxyl, and other electron-donating ones, are important factors that should be considered to obtain an efficient adsorption performance of the membrane. Hence, designing and constructing the chemical structure of membranes is necessary to meet the requirements of adsorbing pollutants from water (i.e., organic dyes and heavy metal ion). In particular, a membrane comprises separation and adsorption that will concomitantly occur during one process. Therefore, the adsorptive sites of the membrane (as adsorbents) will capture the target pollutants (as adsorbates) from water with a rapid adsorption rate and a high adsorption capacity when a liquid flows crossing the membrane, which may be due to the short contact distance (i.e., submicron-scale sizes) between the membrane's active binding sites and the pollutants [1, 7, 18, 45]. These pollutants will be absorbed rather than trapped by the membrane, indicating that the chemical and surface characteristics of the membranes play important roles in the adsorption process. In general, adsorbents based on a polymer matrix/substrate exhibit a longer equilibrium time and a lower adsorption capacity [169, 198]. Thus, the integration of active nanomaterials into the polymer matrix/substrates can greatly improve the adsorption capacity and contact time among the modified membranes as well as the target pollutants. For example, zeolite nanoparticles (i.e., inorganic nanomaterials) were effectively used and integrated onto the PSf membrane through a hydrothermal process [199], indicating that the resultant membrane well-removed lead (Pb^{2+}) and nickel (Ni^{2+}) cations from water. Hence, NECMs are based on the integration of inorganic or organic or hybrid nanomaterials that serve as adsorbents to the polymer matrix/substrates by certain methods.

In general, the multi-functionality of the active nanomaterials is considered a valuable bonus for the potential application of NECMs. In addition, the high removal performance of boron is difficult to reach by a RO membrane with a low feed concentration because of its small molecular size and electroneutrality. Hence, the use of active nanomaterials with high adsorption capacity to boron is effectively suggested to achieve a higher removal performance, for example, the incorporation of UiO-66 in a polymer matrix can remove boron molecules via chemisorption (~ 11% higher boron removal efficiency) because of its outstanding adsorption capacity [131]. Apart from adsorption, the degradation ability of nanomaterials is favorable for NECMs' application, particularly for catalytic degradation. Their catalytic behavior can reduce the adsorption and fouling propensities on the membrane surface caused by biological and organic matters on the feed side [200]. For example, Ag-contained MOFs were added into the PA layer to enhance a catalytic effect [201], indicating that the modified membrane had an outstanding capacity of separating pollutants and degrading chemicals concomitantly. In addition to the biocidal nature of Ag_2O nanoparticles, the use of Ag_2O nanoparticles in polymer matrix/substrates significantly improves the desalination performance of the modified membrane [202], for example, Ag nanoparticles were incorporated in CA and PSf matrixes to improve biofouling resistance [203, 204]. Meanwhile, TiO_2, which is considered a photocatalytic agent, has been effectively applied for water splitting, self-cleaning, and water treatment, indicating its multi-functionality [205]. Moreover, UV-irradiated TiO_2/PES membranes have a greater flux and improved fouling resistance because of their high hydrophilicity and photocatalysis, which dramatically improved under UV irradiation [206].

5.3 Stability and recyclability

For potential membrane materials, it should meet an important requirement of membrane stability during long-term adsorption and selectivity [1, 21]. However, several nanomaterials incorporated in NECMs still have weak stability, which are easily degraded under working conditions, inducing a significant decrease in membrane performance. Therefore, further research must be conducted to track the membrane stability in long-term periods, that is, recyclability in consecutive adsorption/desorption cycles, solvent and fouling resistance, antimicrobial activity, chlorine resistance in desalination, and pH tolerance. Almost all organic nanomaterials exhibit a good affinity with polymer matrix/substrates, but they can be separated from the membranes into permeate streams during the working process because of their nano-sizes or weak interactions. This unexpected issue can dramatically impact environmental and drinking water safety rules because of the leaching of toxic nanomaterials. Therefore, strongly anchoring the nanomaterials into the polymeric layer should be proposed on the basis of the construction of strong interactions and chemical bonds among the used components or exploitation of biocompatible, bioinspired, environment-friendly, and green nanomaterials. Furthermore, in maintaining the membrane performance during the repeated regeneration and reuse of the membranes for water/wastewater purification, the selection of washing and desorbing solvents is necessary to achieve long-term stability and durability of the membranes during recycling; this strategy depends on each research purpose to maintain the high performance of the regenerated membranes.

5.4 Others

5.4.1 Further optimization in membrane performance

To date, the manufacture of optimized NECMs without defects is considered an important challenge for researchers, particularly the compatibility of nanomaterials and polymer matrix/substrates as well as the dispersity of functional nanomaterials in the selective layer [207, 208]. Organic nanomaterials have better affinity with polymer matrix/substrates than inorganic nanoparticles, which can reject unexpected interfacial defects in the NECM structure. However, unexpected agglomeration still occurs in the monomer phase and heterogeneous locals inside the polymeric layer, thereby generating defects in the NECM structure that maybe related to their high surface energy and inter-particle interactions. Furthermore, the membrane performance regarding rejection dramatically reduces at a high added amount of nanofillers, whereas the resultant flux variation of the membrane is inconsistent with reported related studies. In particular, the membrane flux can enhance with solvent passing the defects because of the solvent resistance induced by the wrapped nanomaterials, when their loading amount surpasses the optimal condition; thus, the total membrane performance can progressively worsen. Nonetheless, the use of a small loading fraction of nanomaterials into polymer matrix/substrates can restrict their potential effectiveness on promoting the membrane performance and result in a considerable loss of nanomaterials' worth. In ensuring the homogeneous, strong, and sufficient interactions of active nanofillers into the polymeric layer, the surface of these nanomaterials can be modified correspondingly to improve the incorporation approach and membrane performance. Based on the main purpose of research, the modification and incorporation among the functional materials will be proposed appropriately and effectively.

5.4.2 Scalable production process

In addition to membrane stability, it also should meet an important requirement of the scalable fabrication of membrane materials. The manufacture of membranes requires the use of active nanofillers to the polymer matrix/substrates to promote the membrane performance, such as reducing fouling and increasing hydrophilicity. Thus, these active nanofillers should be selected appropriately and effectively to avoid cost-related drawbacks or complexity in the production and to enhance the membrane's properties. In addition, the selection of polymer matrix/substrates plays an important role in membrane performance. In the scalable fabrication of the membranes, such selections of functional materials are performed on the basis of their size, performance, cost, complexity in manufacturing, etc.

In general, the organic nanomaterials selected for manufacturing NECMs are often related to complex synthesis processes, that is, chemical synthesis and polymerization with numerous steps, delicate and difficult synthesis routes, and greater time and cost consumption. These factors will increase the total cost of membrane manufacture to a certain extent. Therefore, the cost-effectiveness of the selected functional nanomaterials should be greater than the cost of membrane growth and fabrication. In addition, functional nanomaterials must be used effectively to eliminate the loss of expensive ones. Thus, the production of NECMs can be conducted conveniently and cost-effectively for their application in water/wastewater purification. Moreover, strategies related to the manufacture of green and sustainable nanomaterials must be consistent with the demands for a more scalable production of NECMs. Furthermore, other properties, such as long-term stability and selectivity, antibacterial activity, antifouling ability, and chlorine resistance of NECMs, are important factors that must be further explored by researchers.

6 Recent applications of NECMs in water/wastewater purification

NECMs developed using various types of nanofillers with diverse functionality are becoming increasingly applicable to a variety of water/wastewater applications. NECMs have been developed to address the challenges of water purification and have been applied to many sectors for global water conservation. The purification of water/wastewater using the membrane technology has advantages over other conventional methods because of its high efficiency at a low operating cost. Moreover, NECMs can remove contaminants over the nanoscale. Thus, they have been widely applied to water/wastewater purifications based on adsorption and separation approaches, such as NF, desalination, and removal of organic dyes and toxic heavy metals.

Nanofiltration using the medium of the nanostructured membrane is a simple method that ensures water quality, in which the materials that are used for surface enhancement include traditional nanomaterials such as TiO_2, SiO_2, CNT, and MOFs. Such materials are generally produced by layer-by-layer self-assembly and interfacial polymerization. Surface modification could be achieved by chemical/physical interaction and electrostatic interaction of the membrane bed and nanomaterials that would be used for functional enhancement integrated on the modified surface. The surface-enhanced NECMs are proven to have better performance for NF applications. For example, Wang et al. have developed a novel thin-film nanocomposite membrane, in which TiO_2 nanoparticles were introduced between the GO nanosheets to form a TiO_2@GO/PA membrane with dilated and stable nanochannels (Fig. 10A) [141]. The fabricated TiO_2@GO nanocomposite incorporated on the polymeric membrane was used as the antifouling NF membrane, which showed remarkable filtration performance, that is, water flux of 22.43 L.m^{-2}.h^{-1} at 0.4 MPa and salt rejection of 98.8%.

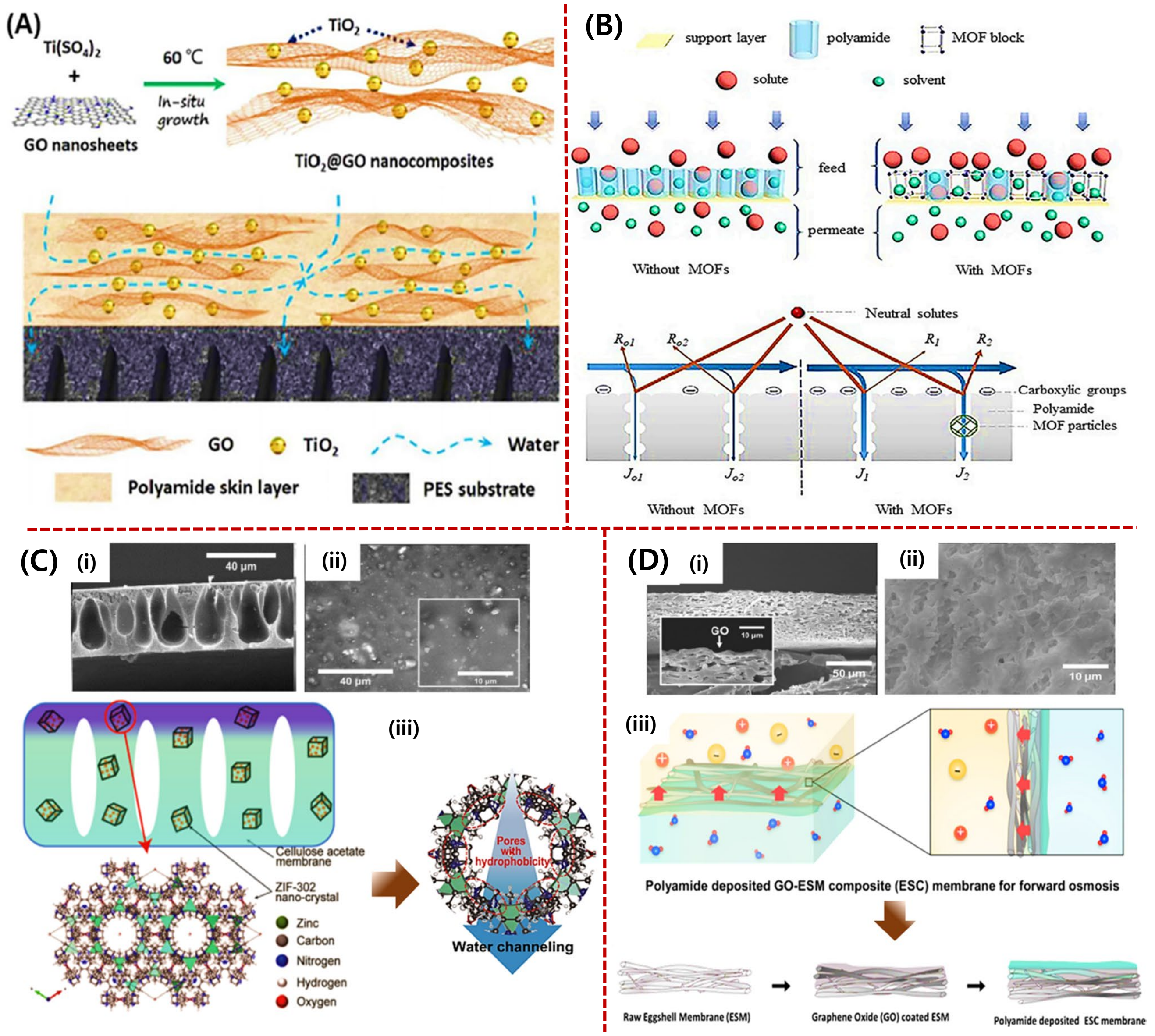

Fig. 10 Schemes of the fabrication of TiO_2@GO nanocomposites integrated into the PA membrane used as a NECM for nanofiltration (**A**) [141]. Schematic illustration of thin-film NECMs without and with the use of various MOFs (**B**) [209]. SEM images and schemes of nano-enhanced ZIF-302/CA membranes, serving as an NECM for an osmosis-driven technique (**C**) [159]. SEM images and schematic of the GO/ESM membrane used as a bio-composite FO membrane (**D**) [69]

These results indicated an improvement in permeate flux, which is two times higher than the pristine membrane and five times greater than the GO-modified membrane, with a slight difference in the solute rejection. In another work conducted by Zhao et al., the use of MOFs (i.e., a type of hybrid organic–inorganic materials) allowed the PA layer to produce thin-film nanocomposite membranes (Fig. 10B) [209], in which various hydro-stable MOFs consisted of MIL-53(Al), NH_2-UiO-66, and ZIF-8 that were used to fabricate NF membranes via blending and preloading interfacial polymerization methods. The results indicated that the incorporation of MOFs on the PA membrane was favorable for enhancing the water permeability of the obtained NECMs. In addition, the integration of MOFs played a role in regulating membrane performance and promoting the molecular design of MOF-incorporated NECMs through precise control of MOF–polymer interactions. Another type of MOF, namely, ZIF-302 nanoparticles, was used to embed NECMs into the CA membrane using a phase inversion method proposed by Kim et al. (Fig. 10C) [159]. Consequently, the obtained NECM was considered a high performance osmosis-driven membrane. Concomitantly, Kim et al. also developed a thin-film bio-composite membrane supported by the ESM that is an abundant waste material (Fig. 10D) [69]. This bio-composite FO membrane was deposited by interfacial polymerization and surface coating using GO nanosheets, serving as a NECM for exhibiting osmotically driven water flux. Using the ESM supporting substrate, which is a waste agricultural product, instead of synthetic polymers as the supporting membrane could reduce chemical waste and the development of expensive products, as well as the strong interaction between the functional GO nanosheets and the ESM substrate.

In addition, industrial waste sources are discarded into the water, which has been a threat to the portal and drinking water resources. The concern arises as this waste includes toxic heavy metals that can cause a severe risk to living things, including human beings and the environment [210]. For example, heavy metals, including arsenic, chromium, copper, and zinc ions, exposed to industries are carcinogenic. Therefore, the removal of heavy metals becomes a vital challenge in water/wastewater purification studies. Nanomaterials have shown excellent performances in the removal of heavy metals. For example, Au, Ag, Cu, Fe_3O_4, GO, and zeolite are the commonly used active nanomaterials for heavy metal removal. NECMs could enhance these inorganic nanoparticles more than the membrane, indicating their applicability in water/wastewater purification. In addition, NECMs can eliminate heavy metals via ion exchange with the metal ion. Zeolite-functionalized NECMs with a well-defined pore structure caused by the filler zeolite have been widely used in water softening and heavy metal removal [211]. Yuan et al. have also fabricated a ZIF-300-assisted membrane for removing heavy metal ions from wastewater (Fig. 11A) [212]. With the good size discrimination property and water stability of the ZIF-300 membrane, it exhibited high water permeance (39.2 $L.m^{-2}.h^{-1}.bar^{-1}$) and enhanced rejection (99.21%) for $CuSO_4$. This research also confirmed the availability of MOF-functionalized membranes as a potential candidate for wastewater treatment particularly in heavy metal removal. In the case of GO-assisted NECMs, they have various oxygenated functional groups such as carbonyl and carboxylic acid, epoxy, and hydroxyl groups, indicating their excellent adsorptive properties for heavy metal removal from wastewater [1]. Meanwhile, new adsorption membranes were constructed by decorating the walls of membrane internal pores with PDA nanoparticles for the removal of Pb^{2+}, Cd^{2+}, and Cu^{2+} ions, indicating that self-polymerized DA solution could be penetrated throughout the PES substrate, using a special method of circulatory filtration, which formed a PDA nanoparticle to be coated around the walls of finger-like pores (Fig. 11B) [213]. Consequently, the fabricated NECM based on the integration of PDA nanoparticles on the internal pore walls enhanced the UF performance and adsorption capacity of heavy metal ions, with a maintainable pure water flux of 166 $L.m^{-2}.h^{-1}$; high rejection of bovine serum albumin (92.9%); and high adsorption capacities for Pb^{2+} (20.23 mg/g), Cd^{2+} (17.01 mg/g), and Cu^{2+} (10.42 mg/g). In addition, NECMs assisted with Fe_2O_3 nanoparticles showed excellent biocompatibility, biodegradation, and good thermal and mechanical properties. Zhang et al. developed a new adsorptive membrane by modifying the support layer with Fe_3O_4 nanoparticles to remove As^{5+} ions (Fig. 11C) [41]. This new NECM was prepared by modifying the porous support layer of a phase-inversion-formed membrane. The Fe_3O_4 microspheres were immobilized in the support layer of the PES membrane by reverse filtration, followed by DA polymerization. Consequently, the membrane of 1 m^2 could treat over 7 tons of water to the drinking water standard with regard to As^{5+} concentration during three regeneration cycles. Bio-originated materials such as CTS could also be used for the removal of heavy metals [1]. CTS-assisted NECMs can be used in heavy metal removal because of the presence of hydroxyl and amine on their surface.

Aside from the heavy metal impurities in water resources, organic dye impurities are also found in the water source. Organic dyes are due to waste from pharmaceutical and personal care products and leather and textile industries. They are difficult to decompose, and they exist as structurally resistant pollutants. Therefore, organic dyes inhibit serious side effects on the aquatic lives and living organisms that are living off the purified water source. Thus, eliminating organic dye impurities using safe, efficient, and environment-friendly purification techniques is necessary. The removal of organic dyes from water/wastewater using the

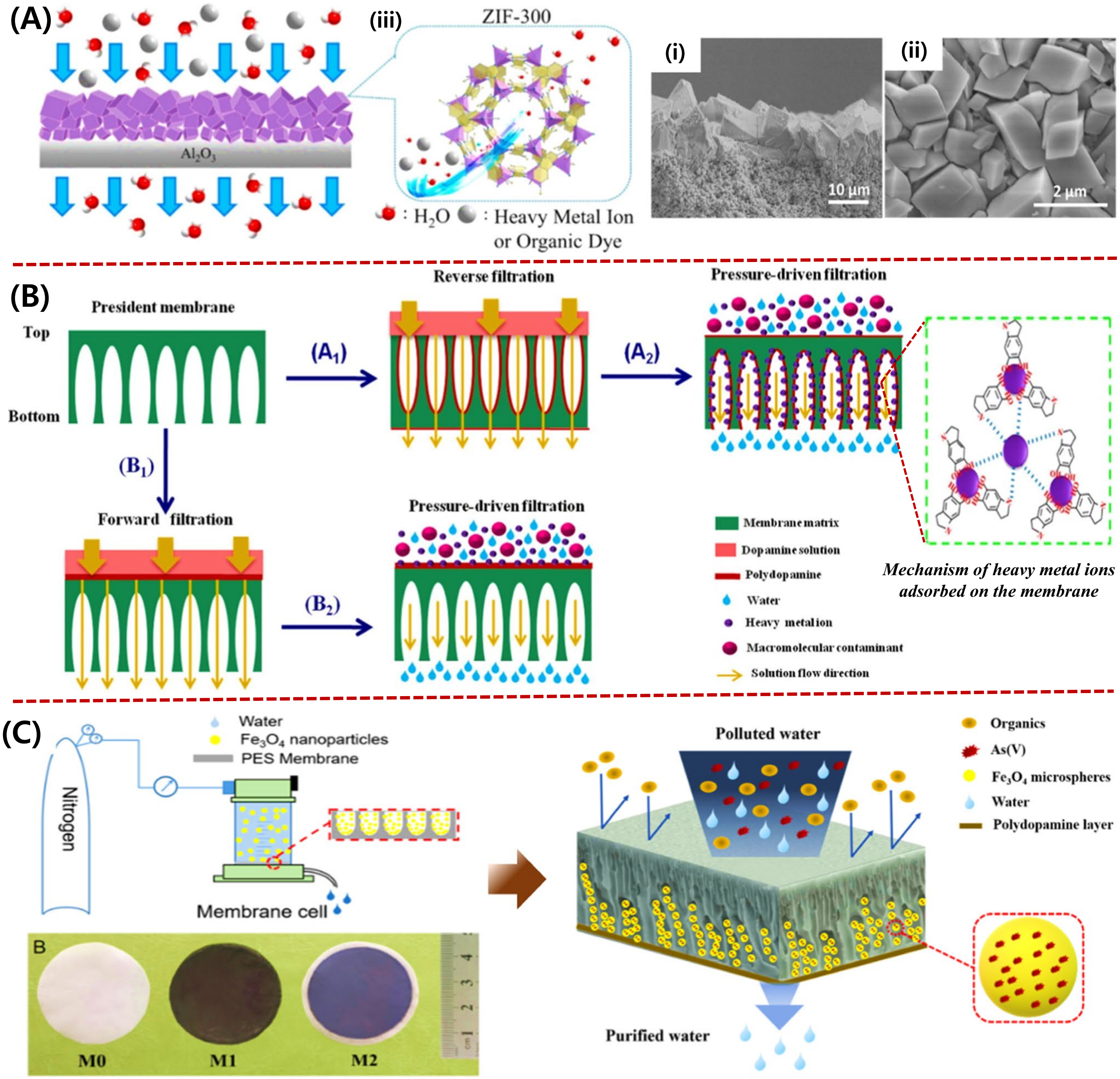

Fig. 11 SEM images and schematic of removing heavy metal ion from water on a novel asymmetric ZIF-300 membrane (**A**) [212]. Scheme illustrations of the preparation of PES/PDA membranes and the process of macromolecular contaminant separation and heavy metal ion adsorption (**B**) [213]. Digital captures and scheme for the adsorptive membrane with different membranes (M0, pristine PES membrane; M1, Fe_3O_4 blended membrane; and M2, Fe_3O_4 loaded membrane) (**C**) [41]

membrane purification technique is considered cost-effective and energy-efficient among all alternative techniques for organic dye removal. The membranes used for organic dye removal contain nanofiller modifiers to enhance the physiochemical properties of the membrane such as hydrophobicity, pore size, selectivity, and surface change to select and reject the target organic dyes during filtration. The nanomaterials that are used for NECMs include carbon-based nanomaterials such as CNTs, CNFs, and graphene oxides; inorganic nanomaterials such as MXene, MoS_2, and hexagonal boron nitride; and cellulose nanomaterials such as chitin nanocrystal. NECMs fabricated from GO/CNT nanomaterials on the PTFE substrate have removed methylene blue and Congo red pollutants, whereas NECMs enhanced with chitin nanocrystals have eliminated methylene blue and Congo red pollutants from the water source. Vo et al. have demonstrated that the GO–CTS active network on a dialysis cellulose substrate can efficiently remove various organic dyes from aqueous solution [18], in which the modification of the interfacial dialysis cellulose surface was based on the molecular interaction of an active GO–CTS composite hydrogel network without the use of an external cross-linker, by using a simple casting method and low-cost adsorption technique. The membrane exhibited an excellent performance in removing cationic and anionic dyes from aqueous solution (methylene blue, 93.98%; Rhodamine B, 80.97%; methyl orange, 82.68%; and Congo red, 90.08%) and a long-term stability in recycling performances (six desorption–adsorption cycles). Concomitantly, Vo et al. also used these active GO–CTS hybrid networks to integrate into glass fibers, producing a new NECM-based adsorptive membrane (Fig. 12A) [19]. The adsorption performance of removing various organic dyes was excellent on the fabricated adsorptive membrane (methylene blue, 552.7 mg/g; Rhodamine B, 416.1 mg/g; methyl orange, 383.7 mg/g; and Congo red, 476.6 mg/g), and it reached superb recycling performance compared with other adsorptive membranes (four desorption–adsorption cycles). Evidently, the adsorptive membranes based on the NECMs, that is, GO/CTS/dialysis cellulose and GO/CTS/glass fibers, were potential adsorbents containing functional adsorption sites and physical sieving effects to remove various pollutants from water/wastewater because of their simple manufacturing process, eco-friendly characteristics, structural stability, and high performance.

In addition, desalination is a process of eliminating mineral components and salts from water. Saline water causes problems in agriculture causing the limitation in human consumption. Desalinating salt water to get fresh water is expensive because of energy consumption [3]. However, using desalination with the membrane is an alternative method to solve the aforementioned problem. Nanofiller-assisted membranes could be applied to water desalination for the removal of salts and metal ions from contaminated water. The salt rejection rate and performance efficiency depend on the type of nanofillers used in the membrane. Based on previous reports, the CNT-assisted membranes showed a good performance in desalinating contaminated water [215]. CNTs have always been an excellent material for the elimination of toxic substances, heavy metals, and fluoride from water. Therefore, CNT nanoparticles can be combined with the membrane, and the required functional groups can be injected to the membrane surface, which can undergo desalination of the target water source. Moreover, titania nanotubes could be used as surface enhancement nanomaterials for desalination purposes, for example, Khoo et al. demonstrated acrylic acid/titania nanotube–PA membranes to improve desalination and antifouling properties (Fig. 12B) [214]. An eco-friendly surface modification technique based on plasma-enhanced chemical vapor deposition was used to deposit hydrophilic acrylic acid onto the titania

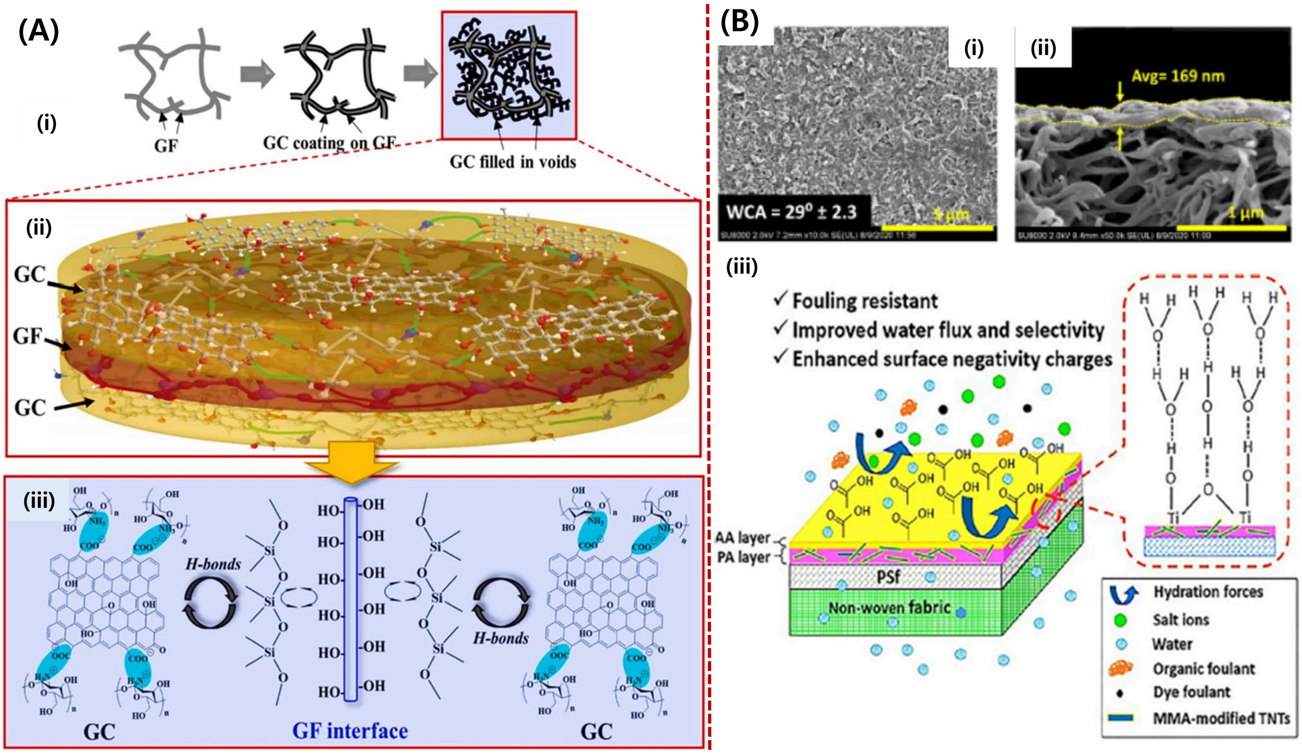

Fig. 12 Schematic illustration of the GO/CTS/glass fiber membrane and molecular interactions among GO, CTS, and glass fibers (**A**) [19]. SEM images and schematic of acrylic acid/titania nanotube–PA membrane used as a thin-film NECM (**B**) [214]

nanotube–PA surface of thin-film NECMs to simultaneously minimize PA surface defects caused by nanomaterial incorporation and improve membrane surface hydrophilicity. The results showed that the desalination rate of plasma-modified thin-film NECMs was improved with the reduction of salt passage from 2.43 to 1.50% without significantly altering pure water flux. The acrylic acid–modified membrane also possessed a remarkably enhanced antifouling property over 12-h filtration. In addition, the use of nanoparticles assisted into the membrane for desalination contains 2D nanosheets, such as GO, MOF, boron nitride (h-BN), and MXene [216]. These 2D nanosheets exhibit a high specific area, huge amount of eliminated salts, and fast absorption properties. In particular, MXene-assisted NECMs showed a significantly high surface area, strong adhesion properties, and excellent thermal and mechanical properties giving a new class of desalting nanocomposite membranes. Moreover, the membranes incorporated with metallic oxide nanomaterials such as silver, zeolite, silica, ZnO, and $Mg(OH)_2$ inhibit high water flux, membrane hydrophilicity, good mechanical stability, and selectivity, which are considered good candidates for desalination.

In general, photocatalytic applications are defined as the performance of the photoreaction in the presence of a catalyst, in which the photocatalytic activity can be appealed by the material's high degradation efficiency to the target, non-selectivity of the material, stability, and low cost. Given its high performance over its low cost, photocatalysis has been widely used for the degradation of contaminants in the water source [15, 217, 218]. Impurities in water such as pharmaceutical impurities, organic dyes, and pesticides could be degraded by photocatalysis. Common photocatalysis is known to TiO_2, ZnO_2, tungsten oxide, and cadmium sulfide; of these, TiO_2 has been widely used. TiO_2 has been used for the removal of phenol, pesticides, and antibiotics from the target material. Therefore, TiO_2 nanoparticle-assisted membranes can show high photocatalytic activity and chemical stability with low-cost modification. They are efficiently used for the disinfection of water by removing *Escherichia coli* and toxic organic pollutants, including humic acid, benzene derivatives, and organic dyes. NECMs with good photocatalytic activities have positive impacts on water resource conservation and remediation.

Meanwhile, failure to eliminate biological impurities could be one drawback of the membrane technology. NECMs modified with carbon nanomaterials have been widely used for the removal of biological contaminants (bacteria and viruses), toxic dyes, heavy materials and ions, phenols, and pharmaceutical impurities [219]. They show cost-effectiveness, robustness, fast water transport, and reduction of membrane fouling. Considering environmental conservation, bio-based membrane materials have also been developed. Cellulose materials based on chitin and CTS, which can be recycled from waste materials, have also been widely used as bio-filters for environmental applications. However, such biological impurities can often clog the membrane's pores causing a decrease in performance. In addition, biofoulings could affect the operational cost and prolongation effort. Therefore, the membranes must have antimicrobial activity. Metal oxides such as nickel oxide and titanium oxide with antibacterial properties are implanted in the membrane for the removal of biological impurities without getting affected by biofouling. Nanoparticles such as gold, titanium, chromium, and copper are also widely used to fabricate membranes for antimicrobial applications. These materials in the membranes eliminate biological impurities without delivering toxic effects on human health, indicating their antibacterial and biological applications of the membrane.

7 Conclusions and outlooks

The use of NECMs in waste/wastewater purification applications is considered an encouraging approach that effectively combines the advantages of adsorption and separation techniques to remove various pollutants from water. The types and functional materials used in the manufacture of membranes promote the application of NECM. However, NECMs still have many limitations that are associated with their production, safety to humans and the environment, and industrial applications. Future research should address these challenges to be able to utilize NECMs in water treatment fields efficiently. To date, numerous efforts have been well succeeded on the production and development of NECMs for water/wastewater purification, such as the exploitation of new nanomaterials, flexible integration of inorganic or organic nanomaterials into polymer matrix/substrates, and incorporation of various nanomaterials to the polymeric layer. Moreover, research on comprehensive mechanism with advanced analytic techniques should be proposed to demonstrate the key role of the used functional materials, which will significantly contribute to the suitable construction of NECMs for potential applications. Concomitantly, approaches to an economic, facile, and sustainable modification/synthesis of inorganic and organic nanomaterials, as well as potential strategies of attaching/wrapping active nanofillers with a small loading amount and a good dispersing ability, should be further explored to minimize the cost and efforts regarding the manufacture of NECMs. Further research on the long-term durability and stability, environmental concerns, and commercial potential of various nanomaterial-incorporated NECMs should also be conducted.

Author contribution Thi Sinh Vo: conceptualization, design, data curation, formal analysis, writing—original draft, and writing—review and editing; Khin Moe Lwin: writing—original draft; and Kyunghoon Kim: writing—review and editing, supervision, and funding acquisition.

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Data availability The data are available from the corresponding author upon reasonable request.

Declarations

Competing interests The authors declare no competing interests.

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