Nanohybrid Polymeric Membranes for Water Purification and Separation

P. V. Chai, C. Y. Jong, S. F. Chua, and W. L. Ang

Abstract Nanohybrid based polymeric membranes technology for water purification and separation have grown over the years associated to its advancement in the past decades and remarkable impact to the membrane characteristics and performance is encouraging. In this chapter, the progress of the nanohybrid based polymeric membranes for water-based application was divided into two major sections namely membrane technology and nanohybrid polymeric membranes. The membrane technology discussed on the pressure driven membrane process, membrane configuration, membrane fabrication, membrane materials and types of membranes while the latter part discussed on graphene oxide based and non-graphene nanohybrid based polymeric membrane for water purification and separation.

Keywords Nanohybrid · Polymeric membrane · Water purification and separation · Graphene

1 Introduction

A membrane is defined as a thin sheet, film, or layer, which acts as a selective barrier between two phases and controls the passage of matter between the phases adjacent to it [1]. Membrane technologies are the processes that utilize membranes to obtain separation goals. Although membrane technologies became commercially available more than several decades ago, they are currently one of the fastest growing separation technologies for a wide range of applications.

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In water and wastewater industries, membrane processes have been deployed to remove impurities and hazardous pollutants for the production of clean drinking water, prevention of environmental pollution from industrial effluent, and reclamation and recovery of treated water as sustainable water resource [2–4]. Tapping on its molecular-separation capability, the membrane has also been applied to control the outdoor and indoor air pollution by preventing the gaseous pollutants from being released to the atmosphere [5, 6]. Membrane technology is also widely employed in the food, pharmaceutical, and biotechnology industries, where it can separate the valuable compounds from undesired components to obtain high-purity products [7, 8]. Driven by the increasingly cost-effective membranes, with increasingly improved performance and characteristics, the applications of membranes in the industries are expected to experience rapid growth and development.

1.1 Pressure-Driven Membrane Processes

There are many different types of membrane processes available but this book chapter will focus on membrane processes related to water purification. In the water industry, pressure-driven membrane processes hold the dominant share in the market due to its maturity and ease of operation. Generally, a pressure is exerted on the solution at the feed side of the membrane to serve as a driving force to separate the stream into permeate and retentate as shown in Fig. 1 [9]. The permeate is the filtered water free from impurities or pollutants, whereas the retentate is a concentrated solution laden with rejected impurities that must be disposed of or treated by other methods. In another case, particularly for microfiltration (MF) and ultrafiltration (UF) membranes, the driving force for the membrane processes is vacuum-driven instead
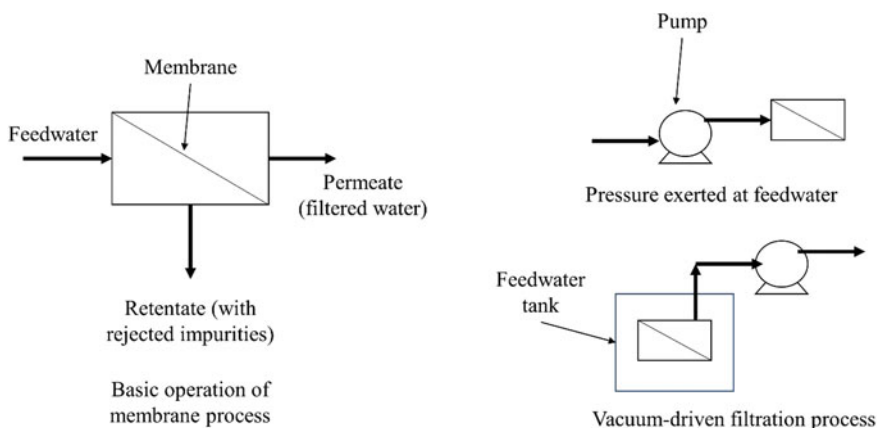

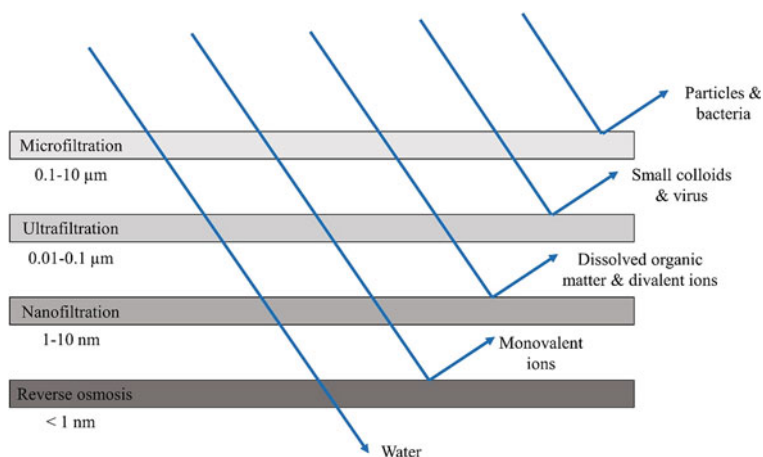**Fig. 1** Pressure-driven membrane processes

Fig. 2 Separation capability of pressure-driven membranes

of pressurized feedwater. A partial vacuum in the filtrate flow stream is created by a filtrate pump or gravity siphon, which extracts the water from the feedwater tank.

The pressure-driven membrane processes are categorized according to the membrane types, namely MF, UF, nanofiltration (NF), and reverse osmosis (RO). These membranes are permeable to water but not to components that are rejected and removed, depending on the characteristics of membranes, particularly membrane pore size [10]. As shown in Fig. 2, MF membranes possess the largest pore size and are capable of rejecting larger impurities such as particulate matter and bacteria. UF membranes with smaller pore size in between 0.01 and 0.1 µm could remove small colloids and viruses in water. The removal of dissolved organic matter and divalent ions (e.g., Ca^{2+} and Mg^{2+}) is normally conducted with NF membranes. RO membranes have the tightest and dense surface that could remove even the smallest size of monovalent species (e.g., Na^+ and Cl^-).

The selection of membrane processes relies on the quality of feed water to be treated and the desirable quality of treated water to be obtained. For instance, RO should be used for desalination of seawater since the monovalent ions could only be removed by RO membranes [11]. On the other hand, UF membranes will be used for surface water treatment since viruses and small colloids in surface water are the typical impurities to be removed [12]. The removal capability of membranes is affected by the membrane characteristics. MF and UF membranes reject the impurities through sieving action, which mainly relies on the size difference between the membrane pores and impurities size. On the other hand, NF and RO membranes possess a thin and dense permselective layer on top of the membrane surface, which separates solutes by diffusion and sieving action [13]. This also reflects that higher feed pressure is required for NF and RO processes to overcome the resistance from the permselective layer.

1.2 Membrane Configuration

Most pressure-driven membrane processes for water industry appear in the form of spiral-wound or hollow fiber configuration or, to a much lesser extent, a tubular or plate-and-frame form. Hollow fiber membranes are fibers of 0.1–1 mm diameter with a hollow space inside. Feed water is supplied either inside or outside of the membrane and the permeate passes through the fiber wall to the other side of the fiber [14]. Hollow fiber membrane module is frequently used for MF and UF membranes due to its high surface/volume ratio that could filter and produce more water in a much smaller footprint. For instance, hollow fiber UF membranes have been successfully deployed for drinking water treatment plants in China, where the membranes were capable of showing excellent rejection of particles and organic matter [15]. Nonetheless, advancement of membrane sciences has enabled the production of fiber strong enough to withstand high operating pressure. This can be seen from the reported articles on the fabrication of hollow fiber NF and RO membranes [16].

On the other hand, commercial NF and RO are normally sold in spiral-wound configurations, where flat-sheet membranes are assembled into spiral-wound elements. The spiral-wound module is particularly suitable for NF and RO membrane processes due to several features such as high-pressure durability, compactness, minimum concentration polarization, and minimum pressure drop in the permeate channel. For example, membrane desalination plants around the world deployed spiral-wound RO membranes to convert the salty water to drinkable water [17].

1.3 Membrane Fabrications

There are several methods to fabricate membranes. The synthesis conditions play a key role in altering the membrane structures and properties. Hence, understanding the membrane fabrication methods will help to control the synthesis conditions to produce membranes with desired properties. In general, the typical fabrication methods employed for the synthesis of commercial membranes are phase inversion (PI), interfacial polymerization (IP), and hollow fiber spinning.

1.3.1 Phase Inversion

PI is a process mainly used for the preparation of MF and UF membranes. It can be described as a demixing process in which the initially homogeneous polymer solution (polymer dissolved in solvent) is transformed in a controlled way from a liquid to a solid phase [18]. There are four basic techniques used to fabricate PI membranes: precipitation from vapour phase, precipitation by controlled evaporation, thermally induced phase separation, and immersion precipitation [19–21]. Out of these techniques, immersion precipitation is the most widely used method to prepare polymeric

MF and UF membranes. The polymers will be dissolved in solvent and casted on a proper supporting layer before submerged in a coagulation bath containing nonsolvent. The solvent and nonsolvent exchange will lead to the precipitation of polymers, which eventually end up as polymeric membranes [22].

1.3.2 Interfacial Polymerization

IP is the fabrication technique that revolutionises the membrane field with the production of thin film composite (TFC) RO membrane. IP involves the cross linking between two types of monomers deposited on a support layer to form a dense yet thin permselective layer. The monomers used are aqueous solution of m-phenylenediamine or piperazine and organic solution of trimesoyl chloride. The cross linking between these monomers results in the formation of polyamide layers that are responsible for the high rejection capability of NF and RO membranes towards dissolved mineral ions [23].

1.3.3 Hollow Fiber Spinning

Hollow fiber spinning is a fabrication process used to produce hollow fiber membranes. The concept is based on PIyet the polymer solution is extruded through a spinneret to form a hollow fiber shape before solidified to membrane in coagulation bath (usually water). The properties of the membranes can be altered by manipulating the dimensions of the spinneret, temperature and composition of dope (polymer) and bore (solvent) solutions, and temperature and composition of the coagulation bath [24, 25].

1.4 Membrane Materials

Intensive research has been conducted to improve the characteristics of membranes as the properties will directly affect the filtration efficiency and production of treated water. The most straightforward method to tune the membrane properties is to alter the formulation of membrane solution before casted to membrane. Generally, membranes can be synthesised from two material sources: organic and inorganic. Organic membranes are fabricated from various types of polymers such as polyethersulfone (PES), polyvinlyidenedifluoride (PVDF), polytetrafluoroethylene (PTFE), polyamide-imide, cellulose, and polyacrylonitrile (PAN) [26, 27]. Majority of the commercialised membranes (polymeric membranes) are produced from these materials due to the lower cost and ease of synthesis.

The second group of membrane materials belong to the inorganic class that includes metallic membranes, ceramic membranes, and zeolite membranes. Though

the cost of inorganic membranes is higher than polymeric membranes, it outperforms the latter at other aspects such as better chemical, mechanical, and thermal resistance, which enables it to be used in harsh environments such as corrosive and high temperature environments [28, 29].

Regardless of the materials used to synthesize membranes, researchers have been actively working on studies to incorporate nanomaterials during the membrane synthesis process to further improve the characteristics and performance of the membrane.

1.5 Types of Nanocomposite Membrane

Nanocomposite membranes are membranes that could be fabricated by incorporation of nanoparticles. The techniques of nanoparticles incorporation can be divided into two main groups, which includes modification done on polymer matrix and surface modification [30]. By incorporation of nanoparticles, such as zeolite nanoparticles, carbon or nanocarbon, silica nanoparticles and zirconium dioxide, besides creating pore channel, the nanoparticles have also enhanced the membrane surface hydrophilicity and surface area at the same time showing stable performance [2, 3].

Mixed matrix membrane (MMM) is membrane prepared via polymer matrix modification. The surface modification membrane on the other hand can be divided into four main groups, which are TFC membrane, thin-film nanocomposite (TFN) membrane, TFC membrane with nanocomposite substrate and surface located nanocomposite membrane. Table 1 shows some review papers and articles regarding the advancement of different types of nanocomposite membranes in recent years.

1.5.1 Mixed Matrix Membrane (MMM)

MMM is membrane with the incorporation of a solid phase or inorganic materials into the continuous polymer matrix as shown in Fig. 3 [41]. In order to fabricate MMM, PI is one of the most commonly used method in which the nanoparticles will be blended into the dope solution before the casting and PI procedure. Besides enhancing the membrane properties and performance, the incorporation of nanoparticles such as silver (Ag) and titanium dioxide (TiO_2) nanoparticles also enable membranes to behave as multifunctional membrane by having additional functions such as antibacterial and photocatalytic properties [5–7].

1.5.2 Conventional Thin-Film Composite (TFC) Membrane

The conventional TFC membranes are thin-film membrane that could be fabricated even without the addition of nanoparticles. By referring to Fig. 4, TFC consists of a support or substrate layer and a selective layer. The substrate layer is often the

Table 1 Recent advancement of nanocomposite membrane

Title	Type of modification	Year	References
Surface modified nanocomposite membrane	Surface modification	2018	Lakhotia et al. [30]
Critical review of montmorillonite/polymer mixed-matrix filtration membranes: Possibilities and challenges	Polymer matrix modification	2018	Dlamini et al. [31]
Carbon nanotube membranes for water purification: Developments, challenges, and prospects for the future	Polymer matrix & surface modification	2018	Ihsanullah [32]
Recent advances in thin film composites membranes for brackish groundwater treatment with critical focus on Saskatchewan water sources	Surface modification	2019	Mollahosseini and Abdelrasoul [33]
Metal–organic framework membranes for wastewater treatment and water regeneration	Polymer matrix and surface modification	2019	Li et al. [34]
Challenges and opportunities in functional carbon nanotubes for membrane-based water treatment and desalination	Polymer matrix and surface modification	2019	Ali et al. [35]
Recent development of graphene oxide based forward osmosis membrane for water treatment: a critical review	Polymer matrix and surface modification	2020	Wu et al. [36]
Recent development in modification of polysulfone membrane for water treatment application	Polymer matrix and surface modification	2020	Mamah et al. [37]

Table 1 (continued)

Title	Type of modification	Year	References
Mussel-inspired polydopamine modification of polymeric membranes for the application of water and wastewater treatment: a review	Polymer matrix and surface modification	2020	Yan et al. [38]
Layered double hydroxide-modified membranes for water treatment: recent advances and prospects	Polymer matrix and surface modification	2021	Sajid et al. [39]
Incorporation of graphene oxide-based nanocomposite in the polymeric membrane for water and wastewater treatment: a review on recent development	Polymer matrix and surface modification	2021	Ng et al. [40]

Fig. 3 Mixed matrix membrane incorporated with nanoparticles (represented by red dots)
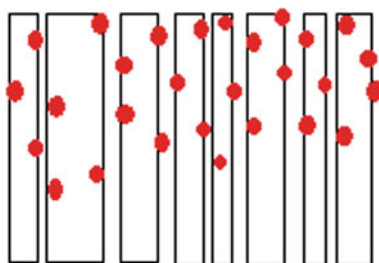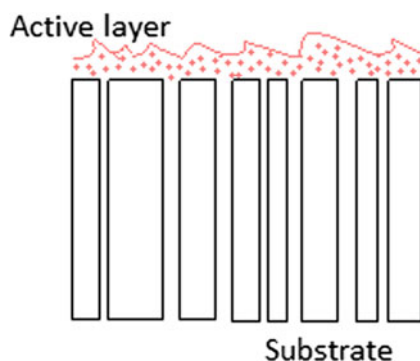

Fig. 4 TFC membrane without addition of nanoparticles

polymeric porous layer that are made of materials such as polysulfone (PSF) and PESwhich could be prepared via PI technique. On the other hand, the selective layer which also known as the active layer is a polyamide layer deposited on top of the substrate layer by using IP method. The active layer is formed by crosslinking of the aqueous and organic monomers. These thin-film membranes are mainly being utilized in NF, RO and FO process [42]. However, trade-off effect in between water permeability and solution rejection often occurs in TFC membrane. Hence, the incorporation of nanoparticles is to enhance the hydrophilicity and water permeability, without sacrificing or reducing the solute rejection.

1.5.3 Thin-Film Nanocomposite (TFN) Membrane

As shown in Fig. 5, TFN membrane has emerged from TFC membrane by the incorporation of nanoparticles. The nanoparticles could be added as nanofillers either into the aqueous or organic phase monomers. Hydrophilic nanofillers, such as the carbon-based or nanocarbon-based materials, TiO_2 and nanohybrid layered double hydroxide (LDH) are usually added into aqueous monomers phase. This is because the hydrophilic nanofillers cannot dispersed well in organic solution [43]. However, the surface of the nanofillers could be modified in order to enhance its dispersion ability in organic or non-polar solvent. Surface modification could be done on nanoparticles by using organic compound or silane compound in order to provide

Fig. 5 TFN membrane
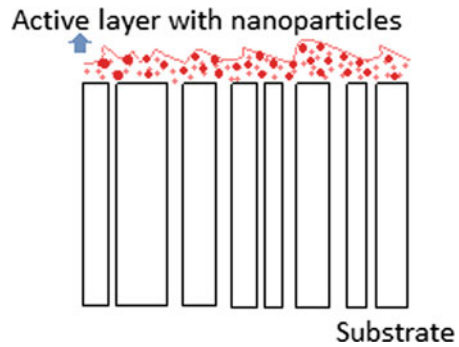
hydrophobic functional chains to the nanoparticles [10, 11]. These nanofillers has found to increase the hydrophilicity and reduce the fouling propensity [44].

1.5.4 TFC Membrane with Nanocomposite Substrate

For TFC membrane with substrate that is incorporated with nanoparticles (Fig. 6), the structure is of similar as TFN membrane and MMM. The difference is the position of adding the nanoparticles, in TFN nanoparticles are added to the selective layer (either aqueous or organic phase monomers), whereas for this TFC membrane, the nanoparticles are incorporated in the substrate layer. This substrate layer has structure which is similar to MMM but on top of the substrate layer, there will be a selective layer which mainly made by crosslinking or aqueous and organic monomer. This TFC membrane with nanocomposite substrate has found to have high porosity support layer and also improving hydrophilicity of TFC membrane as well as lower the internal concentration polarization which often a major issue for FO [12, 13].

**Fig. 6** TFC membrane with nanocomposite substrate
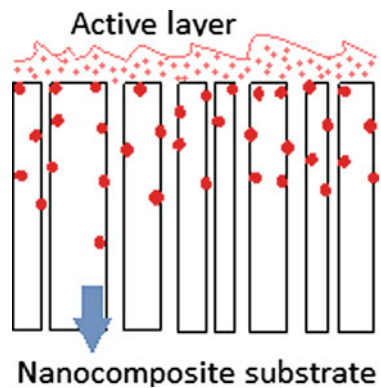
1.5.5   Surface Located Nanocomposite Membrane

Figure 7 shows the surface located nanocomposite membrane. For this type of membrane, membrane surface modification is usually done by depositing nanoparticles on membrane via self-assembly method, chemical grafting, layer-by-layer assembly and coating method. Both self-assembly and coating are simpler methods. In self-assembly method, membrane is soaked completely into solution that contains nanoparticles or by allowing the nanoparticles solution to sit on the membrane surface then follow by drying and solvent evaporation. For coating method, the deposition of nanoparticles is done via filtration or dipping method. However, the nanoparticles are weakly attached to the membrane surface and leaching often occurs during filtration process [45]. Different from coating and self-assembly method, nanoparticles are deposited on the surface of the membrane either via weak Van Der Waals force or electrostatic force in chemical grafting method. Layer-by-layer method on the other hand involved multiple layers of nanoparticles attached to the membrane surface through different interaction, such as chemical bonding, electrostatic force and also hydrogen bonding [30]. Due to these membranes have the minimal effect on membrane intrinsic structure, it has seen to be one of the potential techniques to be implemented in enhancing the membrane surface properties [26].

2   Nanohybrid Polymeric Membranes

In the recent years, there are a number of works have been devoted in designing nanohybrid based polymeric membrane for water purification. One of the approaches is to adopt nanohybrid materials as itcould offer various possibilitiesduring the design of the membrane. Nanohybrid materials is simply defined as a combination of at least two nanomaterials by means of chemical or physical bonding to obtain synergistic effect [46–48]. Up to date, there are a lot of available nanohybrid polymeric membrane for water purification application available in theonline database. This section will discuss two major types of nanohybrid materials that wasused namely graphene oxide (GO) and non-graphene oxide based nanohybrids materials.

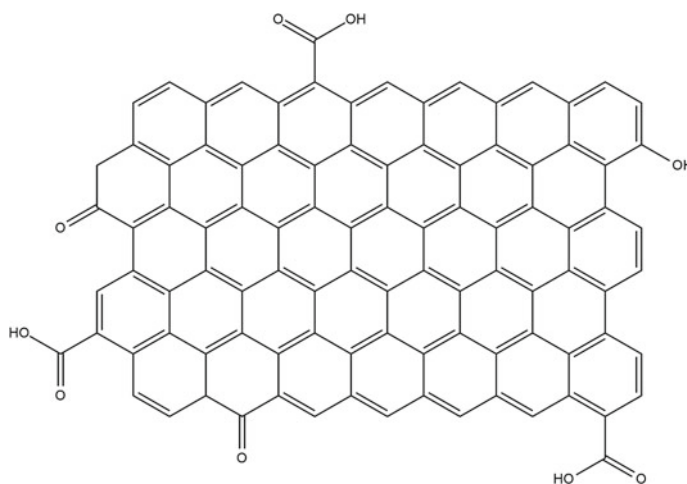**Fig. 7**   Surface located nanocomposite membrane
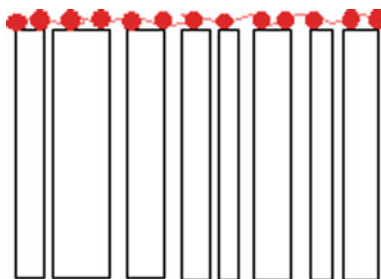
Fig. 8 Graphene oxide structure

2.1 Graphene Oxide

Over the last decades, GO has shown its capability as a unique nanomaterial in designing polymeric based membrane attributed to its good mechanical and physical strength, high flexibility, and abundance in oxygenated functional groups namely carboxyl, hydroxyl and other hydrophilic functional group as shown in Fig. 8. The presence of these functionals group provides GO with good hydrophilicity and tuneable properties that favour the synthesis of polymeric membrane especially in water treatment and purification related process [49]. The positive impact of GO in membrane fabrication process has received tremendous interest from the researchers globally and there are lots of available review papers discussing on the encouraging performance of GO in membrane technology [50–58]. These review papers discussed on the recent development of GO based membrane, morphology and structural properties, modification and performance strategies, applications and preparation of GO based membrane. In view of these, the interest of this paper will outline the recent GO and non-GO nanohybrid polymeric based membrane for water treatment and purification application.

2.1.1 Silicon Dioxide Graphene Oxide Nanohybrid

Silicon dioxide (SiO_2) or known as silica is one of the attractive materials to be embedded into polymer matrices owing to its structural flexibility, excellent physical and thermal properties, and hydrophilicity property that helps to improve permeability. Together with GO, the formed nanohybrid present a stronger hydrophilicity, higher surface area as well as good mechanical-thermo stability. For instance, Wu

et al. [46] is one of the earliest researchers attempt of usage of SiO_2-GO nanohybrid in PSF membrane via phase inversion. The findings reveal that by using 0.3 wt% of SiO_2-GO nanohybrid, the pure water flux improved nearly twice as compared to the neat PSF membrane associated with the improved hydrophilicity as seen in the drop of contact angle measurement from approximately 72°–64°. The addition of hydrophilic SiO_2-GO nanohybrid also accelerate the solvent and nonsolvent exchange rate and thus forming a larger pore size that allowed more water molecules to permeate through the membrane barrier. Although the pore size increased, the egg albumin rejections remain high (>98%) and comparable to the neat membrane attributed to the good dispersion and compatibility of SiO_2-GO nanohybrid with the polymer matrices. The author further concludes that the addition of SiO_2-GO nanohybrid help to enhance the antifouling property of the membrane to the highest degree and it was evident through when the flux recovery ratio improved from approximately 61% to 70% [46]. Others reported SiO_2-GO nanohybrid polymeric based membranes for dye wastewater and oily wastewater treatment were also seen in the literatures [59–62].

2.1.2 Titanium Oxide Graphene Oxide Nanohybrid

Among the wide range of materials used for membrane modification process, TiO_2 is one of the nanomaterials that has gained numerous attentions in the field of membrane research attributed to its photocatalytic properties. By coupling it with GO, the TiO_2-GO nanohybrid can produce membrane with synergistic photocatalytic antifouling properties. With this concept, Xu et al. [63], prepared photocatalytic antifouling TiO_2-GO PVDF membrane displayed superior photodegradation efficiency (improved about 50–70%), enhanced photodegradation kinetics (1.0–1.5 times faster) toward the BSA pollutants. During the antifouling test, the subsequent water flux decreased after the BSA filtration due to the occurrence of BSA fouling on the membrane surface. In this case, the presence of the photocatalyst property from the TiO_2-GO nanohybrid equip the modified membrane with self-cleaning property that can effectivelyremove strongly bound BSA. In terms of flux, it recorded more than 2 times improvement from about 150 LMH to 487 LMH while keeping the BSA rejection (>90%). This is as expected as the hydrophilicity of the membrane increased about 20% and this wasdue to the presence of oxygen based functional group in GO/TiO_2 nanohybrid. The supplementation of the nanohybrid caused the formation of larger porous structure due to the acceleration in the exchange rate. This was evidence as the porosity for the modified membrane was seen to expand from 69.6 to 83.1% [63]. To date, there have been numerous efforts seen in the introduction of TiO_2-GO nanohybrid in the membrane research for water treatment and purification as documented in the literatures [64–68].

2.1.3 Silver Graphene Oxide Nanohybrid

Ag has been continuously explored due to its strong antibacterial property that favourable in producing membrane with antibiofouling properties which can effectively prevent formation of microorganisms [27]. GO on the other hand also possessed antimicrobial property and the combination of both these nanomaterials serve as a great auxiliary in forming a desirable membrane [69]. For instance, Mahmoudi et al. [70] prepared an Ag-GO PSF membrane for BSA application and the addition of Ag-GO nanohybrid showed obvious improvement to the membrane antibacterial property. The FESEM images shown that membrane with the presence of Ag-GO nanohybrid prevent the formation of *E-coli* bacteria while PSF neat membrane showed high number of bacteria colony growth. Apart from that, at 0.5 wt% of Ag-GO nanohybrid, the membrane showed twofold fluximprovement as compared to neat membrane this probably associated with the enhanced hydrophilicity property as seen in the significant drop in water contact angle from 83.3° to about 58°. The membrane enjoyed a higher hydrophilicity owing the presence of oxygenated functional groups from GO nanomaterials [70]. Subsequently, the authors continue to apply the Ag-GO nanohybrid in nylon-6,6 membrane and membrane bioreactor applications [71, 72]. Apart from conventional types of MMM, the adoption Ag-GO nanohybrid could also been seen in one interesting work by Ko et al. 2018 whereby the authors coated the Ag-GO nanohybrid on the surface of PVDF membrane via pressurized filtration process. The coating process was performed through filtration of Ag-GO nanohybrid suspensions using batch dead end filtration cell. Through this method the contact angle measurement reduced from 89.45° to 81.55° which indicating the improvement in the membrane hydrophilicity. This improvement facilitates more water uptake across membrane as the permeability increased by 53% and it also showing a comparable bacterial cell removal. The Ag-GO PVDF membrane also demonstrated strong antibiofouling properties as the membrane show low cell viability which is less for 50% for modified membrane and approximate 100% for neat membrane [73]. Other than that, the usage of Ag-GO nanohybrid in hollow fibre and FO membrane for protein, NOM and desalination application was also reported somewhere else [74, 75].

2.1.4 Zinc Oxide Graphene Oxide Nanohybrid

Like Ag nanomaterials, zinc oxide (ZnO) nanomaterials also had been widely adopted in the preparation of polymeric membrane due to its multifunctional properties such as antibacterial property, great hydrophilic property, high surface area, non-toxic and chemically stable [76–78]. To date, works that involved ZnO-GO in polymeric membrane has grown over the years. For instance, Chung et al. 2017 prepared ZnO-GO PSF membrane via PI technique to investigate the antibacterial and the antifouling properties of ZnO-GO nanohybrid. The authors claimed that the usage of ZnO-GO nanohybrid has greatly enhanced the properties of the fabricated membrane in terms of hydrophilicity where the contact angle measurement drops from about

68° (ZnO-GO membrane) to 40° (neat membrane). Associated with the improved hydrophilicity, the permeability showed positive enhancement from 0.89 LMH to 5.11 LMH while the antifouling properties of ZnO-GO membrane recorded more than 90% of FRR as compared to neat membrane at approximately 80%. The better permeability can be correlated with the addition of hydrophilic ZnO-GO nanohybrid and through this addition, it greatly reduces the viscosity of the dope solution and thus enhanced the diffusion rate to produce highly permeable membrane. It is also evident through the morphological study as the addition of ZnO-GO nanohybrid helps to create more finger like channels and macro voids that favour the transportation of water molecules. On the other hand, the ZnO-GO membrane showed outstanding antibacterial properties as compared to the neat membrane as there are no bacterial colonies was seen [79]. Others study that adopted different types of polymers (PVDF and PES), different experiment conditions (concentration of polymers, ZnO-GO nanohybrid concentration, and so forth) and different application such as pharmaceutical wastewater treatment, activated sludge treatment, wastewater reclamation and water desalination were also seen in the literatures [80–83].

2.1.5 Iron Oxide Graphene Oxide Nanohybrid

Iron oxide (Fe_3O_4) nanomaterials is gaining tremendous attention in the wastewater treatment field because of its chemical and thermal stability, low toxicity and possessed hydrophilic property. The presence of these property allowed Fe_3O_4 to be used in membrane fabrication field for water treatment and purification purposes. Combining Fe_3O_4 with GO, this nanohybrid offered a better enhancement towards the membrane performances. For instances, Chai et al. 2019 carried out a performance comparison study of Fe_3O_4 based membrane and Fe_3O_4-GO based membrane with PSF neat membrane and the finding reveals that by adopting Fe_3O_4-GO nanohybrids, it helps to improve the flux from 51.82 LMH to 112.47 LMH while the adoption of single Fe_3O_4 based membrane does not show much positive enhancement on the water flux. The increased of the flux can be related to the improved hydrophilicity as shown in the contact angle measurement for neat membrane drops from 78.80° to 69.97° for the Fe_3O_4-GO based membrane. On the other hand, the lower flux obtained by Fe_3O_4 based membrane was probably due to the fact of aggregation and this provide an insight that with presence of GO, ithelps to minimize the aggregation of the single nanomaterials Fe_3O_4 [84]. On his subsequent works, the authors also continue to study effect of the nanohybrid concentrations and optimal iron to GO molar ratio that provides the optimum flux, rejection and flux recovery ratio in various applications [85–87]. In his recent study, at 0.6 wt% of Fe_3O_4-GO nanohybrid, the fabricated MMM membrane showed a better performance as compared to neat membrane. The flux improved by 67.91%, Congo red rejection improved by 12.64% while the FRR improved 32.11%. Such improvement is related to the improvement of the hydrophilicity properties of the membrane by 11.42% and highly negative charge membrane (from about −3 to −30 mV) that induced by the presence

of Fe_3O_4-GO nanohybrid [87]. Others relevant Fe_3O_4-GO nanohybrid based polymeric membrane for various application such as heavy metal removal and different anionic dyes also available in the literatures [88, 89].

Another interesting study was carried out by Huang et al. 2016 wherein the authors utilize magnetic property of Fe_3O_4-GO nanohybrid and altering the movement of the Fe_3O_4-GO nanohybridthrough the presence of external magnetic field. The advantages of this method allowed the nanohybrid to be orderly arrangedand anchored on the porous substrate and the proposed behaviour of the Fe_3O_4-GO nanohybrid during the fabrication process is illustrated in Fig. 9. The migration behaviour of the Fe_3O_4-GO nanohybrid was supported by various analyses in terms of the Fe_3O_4-GO nanohybrid movement recorded by micrograph images, SEM cross sectional images and EDS mapping, and surface roughness. In terms of performance indicator, the membrane prepared in the presence of magnetic field showed enhancement of highwater flux from about 310 LMH to 484 LMH with comparable BSA rejection (>75%). This improvement is strongly related to the migration of the Fe_3O_4-GO nanohybrid to the surface thus induced a more hydrophilic membrane (improved approximately by 20%) and the slight improvement in the porosity that caused by the quick exchange between solvent and non-solvent phase. These two criteria help to facilitate more water transportation across the membrane. Apart from that, the FRR also improved from 43 to 83% which further justify the advantage of Fe_3O_4-GO nanohybrid migration behaviour to the surface [90]. Another similar study that utilizes the external magnetic field at different experimental condition for BSA application could also be seen somewhere else [91].
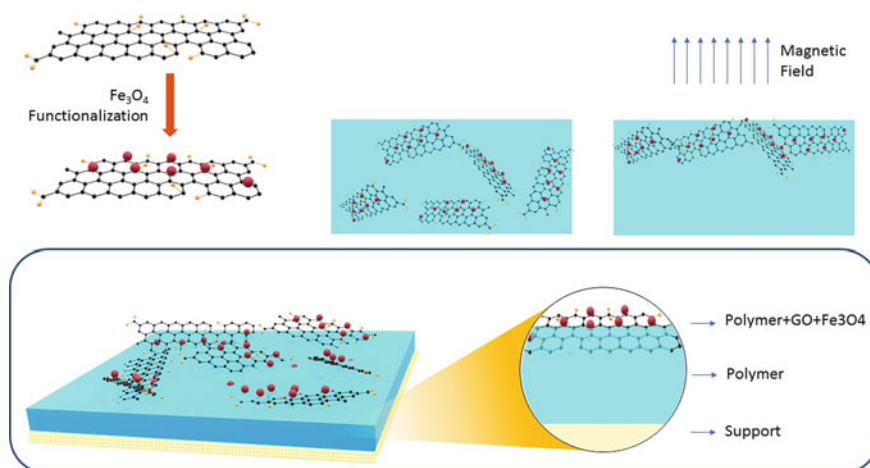

Fig. 9 Fabrication of Fe_3O_4/GO PVDF Membrane under the Magnetic Field

2.1.6 Carbon Nanotubes Graphene Oxide Nanohybrid

Carbon nanotubes (CNTs) is another carbon derivatives family that showed great support while designing a membrane due to its inherent characteristics in terms of resistance, mechanical and chemical properties, high surface area, remarkable water transport property and membrane performance. In particular, CNTs includes single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs) and oxidized multi-walled carbon nanotubes (OMWCNTs) received a very high attention during the design of membrane for water treatment applications [92–94]. Herein, we report the synergy effect of OWCNTs GO nanohybrid in polymer membrane for water purification application. For example, Yuan et al. 2019, prepared a CNT-GO PVDF membrane for BSA pollutant application. The presence of OWCNTs-GO nanohybrid help to membrane to enjoy high water flux that increased from 75.5 LMH to 125.6 LMH while producing a comparable BSA rejection. This increased of flux was associated with the increased hydrophilicity as shown in the reduction of water contact angle from 79.6° to 62.1°. Also, the synergy effect of the OWCNTs-GO nanohybrid showed better enhancement as compared to single MWCNTs nanomaterials as the wettability measurement reduce from 69.5° to 62.1° which can be explained by the large number of oxidized functionals groups. From the improved hydrophilicity, it further accelerates the PI process thus formed an interconnected finger-like pores that is desirable in promoting water transport [95]. Other relevant CNTs GO based nanohybrid used during preparation of polymeric membrane for BSA, palm oil mill effluent (POME) and desalination are also reported somewhere else [96–98].

2.1.7 Other Graphene Oxide Nanohybrid

The previous section highlights specific types of nanohybrid to be used in membrane research. There are also other interesting studies related with the combination of other GO based nanohybrid in polymeric membrane for water purification. For instance, a study that adopts GO based nanohybrid could also be seen by Du et al. 2020. The authors combine zinc sulfide (ZnS) with GO into PVDF polymer to improve the antifouling property of the membrane. With the incorporation of the nanohybrids, the modified membrane reached 431.9 LMH which is approximately two times higher than neat membrane (227.4 LMH) while maintaining similar BSA rejection rate. On the other hand, the modified membrane also showed enhanced FRR at about 10.2% andboth improvement of flux and antifouling property was largely associated with the enhanced hydrophilicity as observed in the modified membrane. From the water contact angle measurement, it drops from 77.5° to 61.7° and this could be closely related to the presence of the hydrophilic nature of GO. Apart from that, the presence of ZnS in the membrane also helped in adding a self-cleaning effect under UV irradiation and the results under the UV irradiation showed greater FRRcompared to sample without irradiation. Under the UV irradiation, the modified membrane FRR showed notable improvement from 66.7% (without UV) to 84.6% (with UV) while

for the neat membrane, the FRR is very close (with and without UV), and this prove the presence of ZnS help to facilitate self-cleaning that able to reduce the tendency of fouling [99].

2.1.8   Non-Graphene Oxide Based Nanohybrid

The growth and demandfor GO nanohybrids polymeric based membrane for water purification and separation has received well and positive response from the researchers. Besides GO based nanohybrids, there are others non-GO based polymeric membrane that worth to be discuss. For instance, Nguyen et al. 2014 deposited Ag and TiO_2 onto the cellulose acetate (CA) forward osmosis membrane. TiO_2 is broadly known as photocatalyst which utilizes the low band gap energy to initiate radicals for organic matter decomposition. On the other hand, negative surface charge, good hydrophilicity and antibacterial properties made Ag nanoparticles a famous component in wastewater treatment research. This surface modification resulted in a greater roughness compared to virgin membrane, reducing the contact angle from 48° to 44°. The membrane with Ag nanoparticle alone did significantly killed bacteria. From adenosine triphosphate (ATP) bioluminescence assay, it is shown to have reduction of bacterial growth from 23.5 µg/L to 6.0 µg/L with Ag nanoparticles coated membrane. However, the antibacterial property of nanocomposite can be even better than Ag nanoparticles alone. Growth was dropped further to 2.0 µg/L possibly due to antifouling property of TiO_2, which increased the interaction between Ag nanoparticles and bacteria. The inhibition of biofouling was further confirmed with the observation of delaying water-flux inhibition by 47% after 3 h of filtration experiment [100].

In another study, Li et al. 2019 alsoimmobilized Ag and TiO_2 coupled with polyethylenimine (PEI) glued with polydopamine (PDA) onto PAN membrane. Comparing with control cases, the decoration of PDA, PEI and TiO_2 decreased water contact angle by ~50% owing to their hydrophilic properties. TiO_2 deposition also reduced surface roughness, promote hydrophilicity. However, the presence of Ag layer increased water contact angle slightly, but the antibacterial advantage outweighs its hydrophobicity. In filtration performance wise, the complex surface modification did not increase dye rejection significantly, but the permeation flux improved about twofold compared to PEI/PAN membrane. It was hypothesized that the incorporation of TiO_2 contributes to looser membrane structure and more voids to increase water penetration. Plate counting method suggested the pristine membrane can kill e. coli at bacteriostasis rate of 20%. This merit arisen from the presence of cationic groups which impede bacteria through intense electrostatic interaction. Significant improvement can be seen with modified membrane case, where incorporation of Ag and TiO_2 achieved bacteriostatic rate of 99.7%, manifesting enhanced antibacterial feature [101]. Another similar work has been developed by Chen et al. [102] to produce TiO_2-AgNP nanocomposite PSF membrane. Interestingly, they worked with rejection test against the pollutant called antibiotic rejection genes (ARG). This

is alarming as the uncontrolled usage of antibiotics in livestock has led to rapid development of ARG, suppressing the medication effect. This research team developed the membrane with filtration and antimicrobial to treat ARB contaminated sewage water. The nanoparticles, TiO_2 and Ag were mixed with dopamine and fabricated to obtain the hybrid membrane. Dopamine functioned to reduce Ag ions and immobilize the product, Ag nanoparticles. AgNP has been hypothesized to form schottky barrier with the presence of TiO_2, lowering the possibility for electron-hole recombinant. This hybrid property can increase the availability of reactive oxygen species for rapid photocatalytic effect. The hydrophilicity increased water contact angle analysis, manifested about 20% reduction with the incorporation of Ag and TiO_2. The study observed significant crack on bacterial cell surface in SEM image, proving the antibacterial ability of hybrid membrane. It was proposed that Ag ions released killed bacteria by suppressing RNA polymerase transcriptional ability [102].

Membrane bioreactor often bothered with the extracellular polymeric substances resulted from the microorganisms inhibited inside. These sludge flocs arisen from abundant availability of organic substance and oxygen content in bioreactor, promoted the growth of microorganisms. Therefore, antifouling issue is the hot topic to ensure long term operation of membrane. Ahsani et al. 2020 synthesized Ag-SiO_2PVDF and the presence of Ag-SiO_2 nanoparticles reduce the hydrophobicity of PVDF and thus reduce the cake formation on membrane surface. At the same time, the antibacterial effect of Ag nanoparticles inhibited deposited bacteria growth on membrane surface thereby prevented clogging of membrane pores. There were 87% and 92% less of *E. coli* and *s. aureus* respectively compared to the control sample. To prolong and stabilize the antibacterial operation of Ag nanoparticles, SiO_2 nanoparticles was used as a support to immobilize Ag nanoparticles. This innovative solution helped in preventing Ag nanoparticle agglomeration and this maximizing the effective surface area. In addition to function as the support, silica nanoparticle also acted as physical cross linker thus improving the mechanical strength of the membrane. Under microscopy observation, the foreign nanoparticles changed the surface morphology by increasing surface pore quantity and larger internal void. In this regard, flux has increased, and water diffused at greater rate. At steady filtration state, the modified membrane maintained 59% more permeate flux compared to pristine PVDF membrane. Chemical oxygen demand was reduced to 90% while ammonium removal achieved over 95%. Biofilm formation was controlled in 55% less compared to pristine sample [103].

Besides that, a recent type of nanomaterials namely quantum dots found its interest in membrane fabrication. For instance, Heng et al. [104] modified membrane with nitrogen doped carbon quantum dots (NCQD) and TiO_2 on PES to reject methylene blue pollutants. Interestingly, the process of making CQD was green method as it was sourced from oil palm frond. It also served as electron reservoir during TiO_2 photocatalysis process. The incorporation of nanoparticles into the membrane is in self-assembly mode onto the PES membrane. Therefore, PES must be surface activated and grafted to enable possible interactions for nanoparticles immobilization. The surface activation method started with irradiation where UV broke the polymer bond and then the cleaved bond promoted the polymerization of acrylic acid. Hence,

the surface is grafted and coated with a layer of PAA. PAA contributed carboxyl groups site, serves to bond covalently with titanium cations. The functionalization of nanoparticles reduced the water contact angle from ~70 to ~30. This is attributed to the nature of hydrophilic nature of carboxyl and hydroxyl groups in nanocomposite. The enhanced hydrophilicity hindered the attachment of hydrophobic pollutant, aid in membrane rejection. Pristine membrane rejected at 46.6% of methylene blue while modified one can reject up to 90.9%. The addition of TiO_2 showed a positive effect in antifouling property. Modified membrane reached to steady filtration rate at shorter duration by four-fold, testifying minor attachment of foulants. Most of the pores were safe from clogging owing to surface tension provided by nanocomposite. Moreover, the TiO_2 lengthened the operational efficiency by improving the reusability of membrane. Self-cleaning is anticipated and performed 10% better on flux recovery compared to conventional washing method [104].

Another similar report was also reported by Koe et al. [105] co-doped nitrogen and sulphur to the CQD and mixed with TiO_2 before incorporated to PSF membrane. Doping of N and S is necessary to reduce the band gap energy and inhibit recombination of charges and holes, promoting more photocatalysis. Interestingly, the source of nitrogen was from green material, egg yolks with hydrothermal treatment. While sulphur was from mixture of hydrochloric acid and sulfuric acid. The up converted photoluminescence (UPCL) nature of CQD converts morelight into shorter wavelength useful for the excitation of TiO_2 nanoparticles. In another words, long wavelength light is unable to activate the photocatalysis of TiO_2 and thus addition of CQD can capture more light energy. This was verified by photocatalysis under UV light and visible light. The visible light activated the TIO_2 and performed better as broader light wavelength can be absorbed for pollutant degradation. Although CQD catalyzes reaction, overloaded CQD may covered up the active sites of TIO_2, doing more harm than good. In hydrophilicity test, greater amount of hydroxyl groups presented on membrane test after the modification led to reduction in contact angle. The hydrophilicity played an important role in improving the porosity where the functional groups speeded up the mass transfer in PI process. However, excessive CQD caused aggregation of nanoparticles. In this case, membrane became rougher and hydrophilicity reduced. Moreover, viscous membrane suspension hindered the formation of pores thereby reduced the effective working area and water permeation rate. CQD is hypothesized to function as electron acceptor to hold electrons temporary. This merited photocatalysis through hindering of electron-hole recombination. The hybrid membrane has brought 59% removal efficiency for diclofenac compared to pristine TiO_2 membrane [105].

Apart from TiO_2-CQD based nanohybrid, other CQD based nanohybrid also seen in the literature. For example, extracted pulp-free lemon juice has been used by Gan et al. [106] with hydrothermal treatment to produce CQD. The obtained CQD was mixed with Ag precursor and reduced to form nanohybrid solution. Associated with the involvement of the nanohybrid, the fabricated modifiedmembrane is causing 10% increment in water contact angleto presence of hydrophilic functional group. In pore size analysis, the incorporation of nanoparticles improved the pore diameter, implying the rapid mass transfer between solvent and water bath. However, at

very high composition of nanoparticles incorporation, the pore size decreased. High viscosity during the fabrication stage may impede the mass transfer and unable to produce large pore structure. With the effect of hydrogen bonding, the movement of water molecules across the membrane was enhanced and improved the permeability. Tartrazine, a negatively charge pollutant was ejected with electrostatic force by Ag-CQD nanocomposite PSF membrane. The pollutant was rejected at 92% improvement with the use of modified membrane compared to the virgin PSF membrane. Notably, the lowest loading of nanoparticles in PSF membrane has resulted in poorest rejection among all cases. This is due to the formation of big pore diameter and insufficient electronegativity of membrane, led to undesired passage of pollutant molecule through the pore structure. As mentioned, modified membrane has higher electronegativity. This feature builds up repulsive force, prevents the foulant from staying stagnant on membrane surface. In this way, fouling layer formation can be reduced. Thus, the electronegativity improved the reusability of membrane by reducing foulant accumulation [106].

Incorporated Ag doped $ZnO/Fe_3O_4/MWCNTS$ to polyacrylic acid (PAA) modified polyamide disc to remove amoxicillin. ZnO can act as photocatalyst only excitation with light wavelength greater than 400 nm. This reduces the efficiency of light irradiated utilization. Moreover, the photo-generated electron-hole pairs are susceptible for recombination and reduce photocatalyst efficiency. Thus, the plasmonic-metal Ag nanoparticles and MWCNTS can widen the ZnO absorption spectrum range at the same time form Schottky barrier to reduce electron-hole recombinant. These nanoparticles are impregnated over Fe_3O_4 to enable easy separation during the operation. However, the deposition of these nanocomposite onto polyamide disc require grafting with PAA. The PAA reduced the hydrophobicity of polyamide disc, reducing the foulant attachment. Other than that, the carboxyl functional groups of PAA rendered as the site to anchor nanocomposite via covalent bonds. Nitrogen adsorption desorption isotherm test manifested about two-fold increase in specific area and 60% increase in pore volume. The nanocomposite created more active area for membrane. Ionized carboxylic groups presented in both membrane surface and internal structure repel the attachment of pollutant. Incorporation of nanocomposites has inevitable disadvantage in reducing the flux. However, the modified membrane can function better with xenon lamp irradiation. This may be attributed to the photo-wetting effect generated by the functional groups [107].

3   Conclusion and Future Prospects

Over the past years, we have seen a huge amount of effort and research showing positive impacts to the polymeric membrane design in water treatment application. The adoption of nanohybrids in membrane science is definitely a great option to the membrane science. In spite of the advancement of membrane science, more research is still required to address challenges in terms commercialization and sustainability.

In terms of commercialization, to the best of the author's knowledge the nanohybrid incorporated polymer membrane for water treatment are currently not available. Several areas of improvement in terms of nanohybrid stabilities, performance stabilities, life span of the membrane shall be addressed before the point of commercialization can be reached. On the hand, in terms of sustainability, adoption of green materials, biopolymers, green solvent, compatibility of nanohybrid with the polymer should also be considered as during this era of sustainability.

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