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Engineering nanocomposite membranes: addressing current challenges and future opportunities

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Abstract

The engineering of novel membranes through fabrication and modification using engineered nanoscale materials (ENMs) presents tremendous opportunity within desalination and water treatment. In this paper, we present an overview of applications of ENMs to organic polymeric membranes and desalination. The review will examine the motivation for introducing ENMs into polymeric membranes identifying how the characteristics of the ENMs, such as high surface area to volume ratio and mechanical strength, can be used to optimise and tailor membranes for particular applications. The overview will include ENMs classification, incorporation strategies and how their properties impact on the surface characteristics, robustness, functionality, morphologies and antifouling properties of polymeric membranes. The review will also feature discussion on the current issues facing the development and commercialization of nanocomposite membrane that harness the benefits of ENMs.

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1. Introduction

There is currently a wealth of research activity developing novel nanocomposite materials that harness the benefits of engineered nanoscale materials (ENMs). Indeed, one of the legacies of nanotechnology has been improved design and control of nanoparticles and ultimately nanocomposite materials. This has gone hand in hand with improvements in technologies, such as atomic force microscopy (AFM), that enable characterisation of materials at the nanoscale and so optimisation of the nanoscale materials as they are developed. Thus, many tools and processes are now available to optimise the engineering of nanocomposite materials. This offers great potential for the fabrication of novel membranes for desalination and water treatment and this review showcases the flourishing research community that has been established and is now meeting the opportunities and challenges presented by ENMs.

Much effort in the last decade has been focussed on fabricating synthetic membranes for particular applications with desired characteristics such as selectivity, permeability, structure, chemical and physical properties. To achieve this goal, several techniques have been implemented such as phase inversion, stretching, track-etching, sintering, interfacial polymerization and electrospinning [1]. Membranes used in water treatment applications can be made from a wide variety of inorganic and organic materials; inorganic material include ceramics, metals and glass; organic materials include polymers, composite materials or mixed matrixes [2]. Inorganic membrane fabrication has recently gained attention due to their high mechanical strength and chemical resistance, however their applicability for water treatment purposes is restricted due to the high fabrication costs and preparation difficulties [3]. In contrast, polymeric membranes are more preferable in industrial applications. Their selectivity, variety of membrane structures and properties, ease of preparation and pore formation control and the inexpensiveness of polymers have meant that they dominate in membrane applications [4] Some of these polymers are listed in Table 1.

Table 1: Commonly used polymers and membrane fabrication techniques in water treatment processes [4].

Water treatment processes	Polymers used for membranes fabrication	Fabrication techniques
Reverse osmosis	Cellulose acetate/triacetate Aromatic polyamide Polypiperazine Polybenzimidazoline	Phase inversion Interfacial polymerization
Nanofiltration		Interfacial polymerization

	Polyamide Polysulfone Polyol Polyphenol	Phase inversion
Ultrafiltration	Polyacrylonitrile Polyethersulfone Polysulfone Poly(phthalazineone ether sulfone ketone) Poly(vinyl butyral) Polyvinylidene fluoride	Phase inversion
Microfiltration	Polyvinylidene fluoride Poly(tetrafluorethylene) Polypropylene Polyethylene Polyethersulfone Polyetheretherketone	Phase inversion Stretching Track-etching
Membrane distillation	Poly(tetrafluorethylene) Polyvinylidene fluoride	Phase inversion Stretching Electrospinning

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2   Despite the relatively advanced state of the membrane industry, there are still some issues

3 that need to be tackled for large scale applications. The primary issue is membrane fouling

4 which is the main limiting factor in industrial membrane applications [5]. Membrane fouling

5 occurs due to the accumulation of various solutes on the membrane surface and/or interior

6 structure of the membrane, forming an additional barrier at the membrane surface or blocking

7 the internal pores. This hinders the solvent from passing through the membrane, reducing

8 permeation, and raising the trans-membrane pressure required to maintain the same

9 productivity. Thus, ultimately shortening the membrane lifespan. Moreover, fouled membranes

10 may consume a massive amount of cleaning chemicals, which may also impact on the

11 membrane surface and lead to membrane replacement in severe cases. The consequence of all

12 these issues is to increase the operation and the maintenance costs of the water treatment unit

13 [6-8]. The good selection of membrane materials available, operating design, pretreatment

14 processes and conditions could mitigate the fouling phenomena to some extent, however

15 membrane sustainability is still problematical at the industrial scale and represents a

16 challenging issue due to its complexity and variety [9, 10]. For several decades, membrane

17 fouling phenomena have been widely addressed from many angles in attempts to minimize

their consequences, for instance understanding fouling mechanisms, incidence, types and factors affecting fouling growth [11].

Membrane modification is a method by which the hydrophilicity of the membrane can be tailored to reduce the fouling from the components of the process fluid. Indeed, some argue that membrane modification can be defined as the process of incorporation of a hydrophilic functional group at the surface of a membrane, aiming to enhance the free surface energy and thereby reducing fouling since the interactions of most foulants with membranes are hydrophobic in nature [12, 13]. In fact, membrane separation processes are surface dependent, where the membrane's active layer (skin) controls the separation process and the membrane-foulant interactions. Introducing a hydrophilic functional group to that surface is believed to improve the separation performance of the membrane and to reduce/control the undesired adhesion and/or adsorption interactions between foulants and that active layer [14, 15]. For achieving this an assortment of methods have been suggested which could be used individually or in combination [16, 17], These surface modifications include grafting [18], surface chemical reaction [19], blending [20-22], plasma treatment [23], dip coating [24] and ion implantation [25]. A variety of polymeric, organic and inorganic compounds, and nanoscale materials can be utilized via these techniques to improve polymeric membrane hydrophilicity.

Recently, the incorporation of ENMs into a polymeric membrane matrix has gained significant attention for water and wastewater treatment applications [26]. The fabrication of nanocomposite membranes that conserve the advantages of polymeric membranes yet overcome their disadvantages by incorporation of ENMs is a highly desired outcome for membrane development. Nanocomposite membranes, are a new class of membranes, consisting of both organic polymers and inorganic nanoscale materials, which are believed to exhibit enhanced performance in comparison to standard membranes [27-29]. The membrane that merges the beneficial properties of both organic and inorganic materials to create a new membrane with enhanced hydrophilicity, permeability, thermal and chemical stability, porosity and mechanical properties has been sought by many research groups [30, 31]. However, many processes and environmental disruptive issues can arise from incorporation of ENMs into polymeric membranes, such as disruption of membrane morphology and particulate leaching, these will impact on process effiiency, Choosing application-specific nanomaterials with an optimum composition is essential to overcome limitations in polymeric membrane applications [3].

There are a large number of studies that have used different ENMs in the development of novel composite polymer membranes for water treatment applications. The materials that have been studied include, graphene oxide (GO) [32, 33], carbon nanotubes (CNTs) [34-36], Silver (Ag) [37, 38], Titanium (TiO_2) [39-41], Aluminium (Al_2O_3) [42], Silicon (SiO_2) [22], Iron (Fe_3O_4) [43], Zirconium (ZrO_2) [44] and Zinc (ZnO) [45], Clay nanoparticles [46] and Zeolite (NaX) [47, 48]. However, the focus of this review is mainly on the modification of polymeric membranes using the diverse range of ENMs, this includes the features of ENMs, strategies of incorporation, influence of ENMs on polymeric membranes surface characteristics and antifouling properties and issues associated from incorporation of ENMs. The review sheds light on findings have not been covered in previous reviews. It gives an overview on wide range of nanoscale materials (metal/metal oxide nanomaterials, carbon based, and for the first time, cellulose nanoscale materials). In addition to addressing the advantages and main issues associated with incorporating these nanomaterials (environmental and cost issues) and presents the recent attempts to improve the compatibility with polymeric membranes to overcome these issues.

2. Special features of ENMs

During the last two decades, materials and structures, manifesting geometric dimensions below 100 nm, have inspired the scientific world [49]. Different nanomaterials synthesized by various techniques have been applied in many fields, including medical supplies, pigments, cosmetics production, catalysts, toner and ink [50]. Nanomaterials are classified under different criteria, depending on the applications, materials, and fields concerned. However, a widely accepted definition of nanoparticles is that they are particles with a diameter less than 10-20nm; a size with a surface area to volume ratio where a drastic change in the physical behaviour of the materials occurs. Moreover, in many cases, particles with size ranging from 1-100 nm are also referred to as nanoparticles [51]. In a narrower scene, based on their dimensionality, nanoscale materials are divided into four broad categories: zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D). 0D nanoscale materials include uniform particles arrays, heterogeneous particle arrays, core–shell quantum dots, onion-like layered particles, nanolenses and hollow spheres, Fig.1. 1D include nanorods, nanowires, nanobelts, nanotubes and hierarchical nanostructures, Fig.2. 2D compose nanoplates, nanosheets,
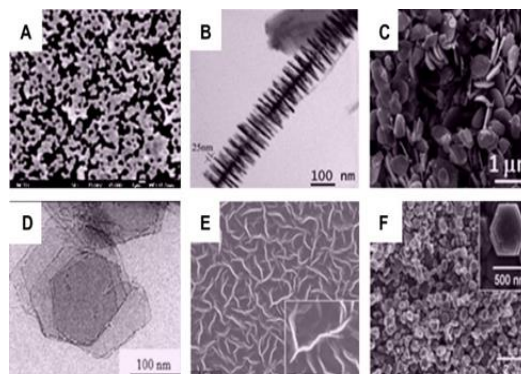
1 branched structures, nanoprisms, nanowalls and nanodisks, Fig.3. Lastly, 3D nanostructure

2 includes nanocones, nanocoils, nanopillers and nanoflowers [52], Fig.4.
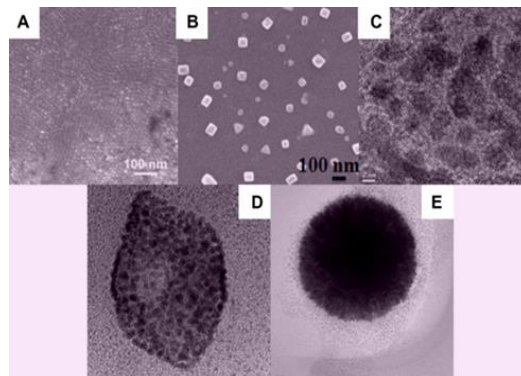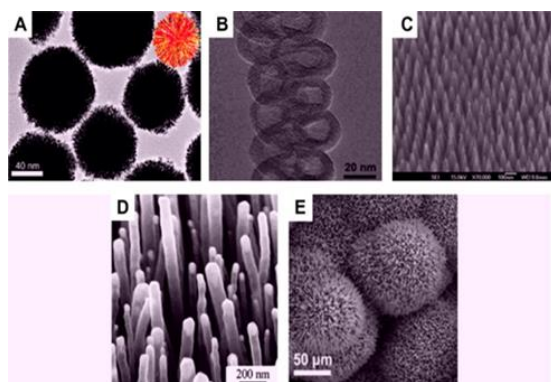

3 Fig 1: SEM and TEM images for various zero-dimensional (0D) ENMs. (A) Quantum dots, (B)
4 nanoparticles arrays, (C) core–shell nanoparticles, (D) hollow cubes and (E) nanospheres. Adopted
5 from [52].
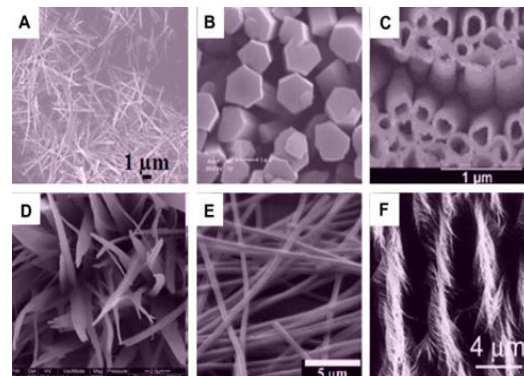
6 Fig 2: SEM and TEM images for various one-dimensional (1D) ENMs. (A) Nanowires, (B) nanorods,
7 (C) nanotubes, (D) nanobelts, (E) nanoribbons, and (F)hierarchical nanostructures. Adopted from [52].

8 Fig 3: SEM and TEM images for various two-dimensional (2D) ENMs (A) Junctions (continuous
9 islands), (B) branched structures, (C) nanoplates, (D) nanosheets, (E) nanowalls, and (F) nanodisks
10 Adopted from [52].

Fig 4: SEM and TEM images for various three-dimensional (3D) ENMs. (A) Nanoballs, (B) nanocoils, (C) nanocones, (D) nanopillers and, (E) nanoflowers. Adopted from [52].

As material is distributed as smaller particles within a system (and the surface area to volume ratio of particles increases) the proportion of surface atoms increases resulting in a higher active surface area, e.g. 5 nm particles compose only a few 10^3 of atoms or unit cells, and possess about 40% of the atoms at the surface. While 0.1 µm particles compose 10^7 atoms or unit cells and possess only 1% of the atoms on the surface [49]. The increase in the number of the interfacial atoms of material distributed within a system as nanoparticles means that their behaviour at the interface will dominate the behaviour of the bulk material within the system. This behaviour is manifest for nanoparticles as differences in optical, magnetic, thermodynamic, thermomechanical, electronic and structural properties. Consequently, the desired properties of the aimed nanocomposite might show enhanced electrical, thermal, mechanical, and rheological properties depending on the size, shape, composition of these nanomaterials and their interactions with the host polymeric matrix [27].

3. Strategies for incorporating ENMs into polymeric membranes

In general, two strategies have been adopted to prepare nanocomposite membranes, thin film nanocomposite membranes, where ENMs have been deposited on the surface of a polymeric membrane, and mixed matrix nanocomposite membranes fabricated through the direct entrapment of ENMs within the polymeric matrix [53]. A combination of both techniques has also been examined [38]. However, to enable the fabrication of novel multifunctional nanocomposite membranes avoiding complex processes, both coating/deposition and blending can be used to achieve a broad range of membranes with diverse properties that can be bespoke for the desired application.

Coating/deposition is the process of forming a layer of ENMs on the active surface layer of a membrane, aiming to control the hydrophilicity of the membrane surface through altering the chemical groups that are displayed at the surface [13]. The most straightforward and economic technique is by introducing ENMs to the membrane surface by self-assembly. Self-assembly is based on immersion of a membrane or its active layer in a diluted-colloidal solution of ENMs. There is a spontaneous association of ENMs with the membrane material. The thickness of the fabricated layer depends on the exposure time and ENMs concentration used during the modification process. However, the self-assembly process is only applicable for certain ENMs that have sufficiently strong interaction with polymeric materials [41, 54]. Li et al. [40] prepared a novel TiO_2 nanocomposite membranes via electrostatic self-assembly, based on an ultrahigh molecular weight poly (styrene-alt-maleic anhydride)/poly (vinylidene fluoride) (SMA/PVDF) blend membrane. The SMA/PVDF blend membranes prepared by the phase inversion method were immersed in a TiO_2 nanoparticle solution for a week to produce the TiO_2 self-assembly membranes. An extension of this method used in coating membrane surfaces with ENMs is the layer by layer technique (LBL) which has shown great potential in the fabrication of nanocomposite membranes since it was introduced to prevent destruction of self-assembled layer [4]. LBL assembled layers can introduce further binding sites for ENMs and create membrane surface multi-functionalization [55]. A further method, grafting has also shown promising results. Trejo and Frey [56] conducted a comparative research study that immobilized carboxylic acid coated Fe_2O_3 nanoparticles on the surface of Nylon 6 membrane via three techniques; (1) simultaneous electrospinning/electrospraying, (2) LBL, and (3) chemical grafting. These researchers only found uniform dispersion of the nanoparticles with electrospraying and grafting even though good bonding interaction control between ENMs was observed for all of the membranes, Fig 5. In another study, Mauter et al. [57] applied biocidal Ag nanoparticles via a post-fabrication grafting technique. The authors claimed that grafting can maximize the density of ENMs at the surface and provide efficient routes for fabricating reactive nanocomposite membranes.
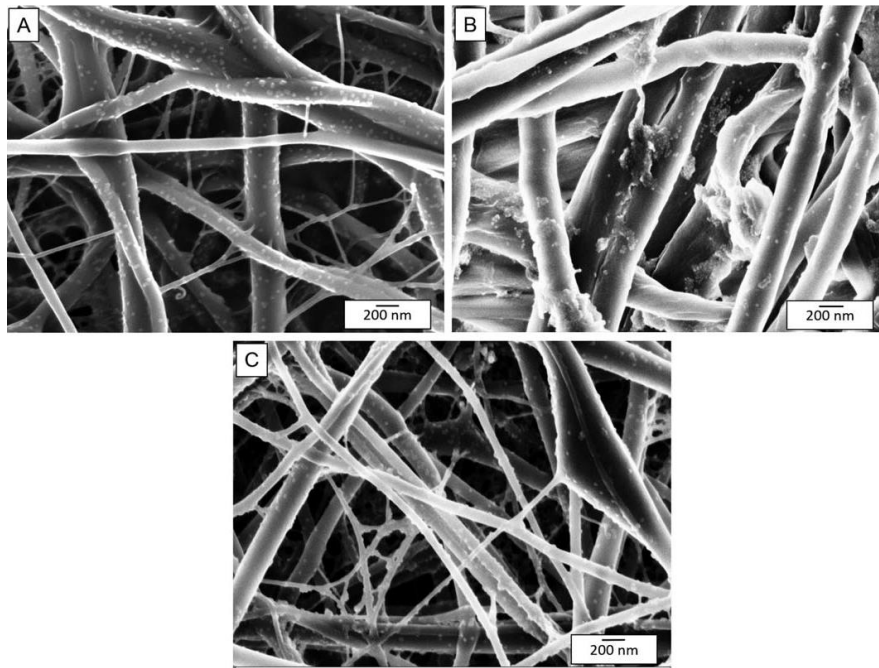
Fig 5: Comparison of FE-SEM images (A) simultaneous electrospin/electrospray, (B) LBL, and (C) grafting [56].

In contrast to the previously discussed techniques, ENMs blending or bulk addition can be achieved during membrane synthesis processes based on phase inversion. This results in ENMs that are impregnated within the inner structure of the membranes other than concentrated on the surface. Therefore, their functionalities and influence on the separation processes are partially exploited due to the shielding of ENMs by the embedding polymer matrix [54]. However, these ENMs could influence the skin (pore size and pore size distribution) and the support layer morphologies for the asymmetric porous nanocomposite membranes. Membrane selectivity, permeability and compaction behavior, and change in membrane morphology is reported to be a function of ENMs type, loading density and their method of incorporation [58]. Various membrane surface and inner morphologies can be tailored as desired by finely tuning these parameters, as will be seen in the next section.

## 4. Influence of various ENMs on morphological and antifouling properties of polymeric membranes.

There are numerous ENMs that are available for the incorporation into polymeric membranes to create innovative solutions that mitigate fouling, achieve high sustainable fluxes and improve the chemical and physical response of the membrane material. This review now

9

1 focuses on the most promising and investigated ENMs that have been used for fabrication of

2 composite membranes for application in water treatment.

3 **4.1 Nanocomposite membranes based on Metal/metal oxides nanoparticles**

4 **4.1.1 Silver (Ag-NPs) based nanocomposite membranes**

5 Silver nanoparticles (Ag-NPs) have gained a special interest due to their unique characteristics

6 that include, antimicrobial, optical, and electrical properties [59] (Fig 6). So far, a wide variety

7 of physical [60], chemical [61, 62], and biological [63, 64], techniques have been introduced

8 to synthesize Ag-NPs with a range of characteristics. Ag-NPs have a broad range of

9 applications which include electronics, biosensing, clothing, food industry, paints, sunscreens,

10 cosmetics and medical devices [65].

S4800 30.0kV 7.7mm x180k TE   300nm S4800 30.0kV 8.9mm x200k TE   200nm
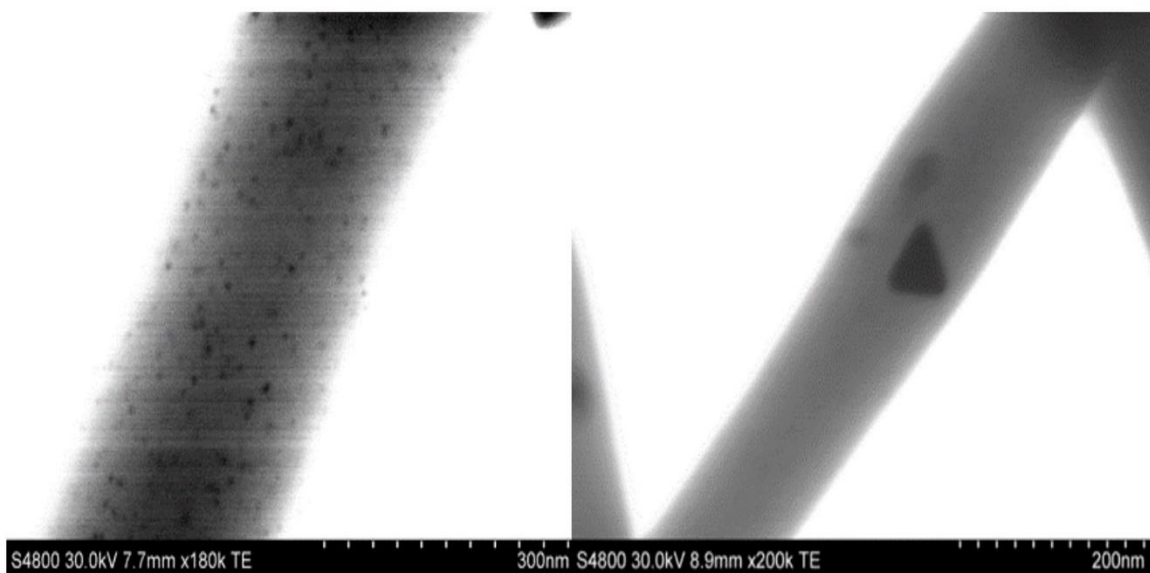
11   Fig 6: SEM images of silver nanoparticles incorporated into electrospun membrane filters (PEO). The
12 right hand image demonstrates the incorporation of triangular silver nanoparticles

13

14 A key feature of Ag-NPs is their antibacterial activity, which is a highly desirable trait that they

15 could bestow on a membrane. This is a major challenge in water treatment applications, which

16 require alternative disinfection technologies, without forming harmful disinfection by-products

17 an issue for many of the conventional costly chemicals that currently dominate the industry

18 [66]. From this point of view and growing experience within nanotechnology and improved

19 capabilities in the fabrication of ENMs with biocidal activity, new opportunities exist for the

development of novel antimicrobial membranes. This is particularly pertinent to the development of composite membranes as Ag-NPs are considered to be the most prevalent bactericide of ENMs [67].

The antimicrobial effects of silver ions (Ag$^+$) or salts are well recognized, but the effects of Ag-NPs on microorganisms and the antimicrobial mechanisms are not comprehensively understood [68]. The major obstruction now is deciphering whether the biocidal activity is attributed to the direct exposure to Ag-NPs, or to dissolved silver ions (Ag$^+$) released from Ag-NPs in an aqueous environment, or likely, a combination of both mechanisms may also be responsible [69-71]. Navarro et al. [72] tested the toxicity of Ag-NPs against algae, the research concluded that Ag-NPs functioned as a source of Ag$^+$, while only minimal toxicity was attributed to the Ag-NPs alone. Similarly, Ag$^+$ was found to be the main source for *Escherichia. coli* inactivation [73]. Mauter et al. [74] linked the bactericidal efficiency of Ag-NPs to the release of silver ions and their residual concentration. In contrast, Fabriga et al. [75] reported poor antibacterial activity for Ag+ and thus, the toxicity was mostly attributed to the direct contact with Ag-NPs. Sotiriou et al.[76] and Foldbjerg et al. [77] claimed that both Ag-NPs and Ag$^+$ ions could have antibacterial and cytotoxicity affects, respectively. Li et al. [66] suggested that the antimicrobial mechanism of Ag-NPs was due to the disruption of the cell membrane functions and electron transport chains as well as damage to proteins and DNA. Yin et al. [78] reported that Ag-NPs could inhibit the growth of microbes through multiple pathways: (i) release of Ag$^+$ ions to interact with disulfide or thiol groups of enzymes or DNA, then disrupt the microbes metabolic processes, generate reactive oxygen species (ROS) or interrupt replication of DNA (ii) affect the cell integrity and metabolism by direct interaction with cell membranes of microbe species (iii) Ag-NPs having size below 10 nm could penetrate inside bacteria and cause further damage through interacting with DNA. Another investigation claimed that Ag-NPs might behave as a "Trojan horse" by penetrating the cell membrane, then releasing Ag$^+$ to cause cytotoxicity [79]. In addition, a number of studies have linked the antimicrobial activity of Ag-NPs to their physiochemical properties. Pal et al. [80] claimed that the Ag-NPs activity is shape dependent, where truncated triangular Ag-NPs showed better antibacterial effects than rod-shaped and spherical nanoparticles against the gram-negative bacterium *E.coli*. Whereas, Ag- NPs size are found to be the basic determinant for their toxicity, smaller Ag-NPs appeared to have a greater antimicrobial activity than bigger Ag-NPs due to the greater contact surface area of the material with the bacteria [81]. Also Xiu et al. [82] found

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that smaller nanoparticles (8 nm) exhibited better bactericidal effects than larger nanoparticles (11-23) nm against *E*. coli. Similar observations have been reported in other studies [69, 76]

Ag-NPs have been widely used to prepare novel nanocomposite membranes with enhanced pure water flux, antifouling and self-cleaning properties with imperceptible or no effect on the membranes selectivity. According to Zodrow et al. [83], Ag-NPs impregnated into UF/PS membrane showed significant bactericidal effects to two species of bacteria; *Pseudomonas mendocino* and *E. coli*. The antimicrobial activity was mostly attributed to Ag^+ release. Moreover, the nanocomposite membrane restrained the bacterial attachment to the surface and inhibited biofilm growth. In addition, incorporation Ag-NPs enhanced the membrane surface hydrophilicity, water flux and mitigated other types of fouling. Similarly, Zhang et al. [84] prepared mixed matrix PES membrane using biogenic silver nanoparticles (bio Ag^0) as additives. The surface of the nanocomposite membrane was tested to evaluate the attachment of *E. coli* and *P.aeruginosa*, (as pure cultures) and activated sludge (as a mixed culture). Results demonstrated that bio Ag^0 addition showed excellent antibacterial activity, prevented bacterial attachment and reduced the biofilm formation on the membrane surface during nine weeks of monitoring, whereas the control membrane was heavily fouled. Furthermore, a slight improvement in hydrophilicity was reported. Kim et al. [38] entrapped Ag-NPs in a thin film via interfacial polymerization on a polyethersulfone PES substrate containing acid modified MWCNTs, high antibacterial activities were achieved and low adhesion of *P. aeruginosa* (PA01) to the membrane surface was observed. Moreover, the thin-film nanocomposite (n-TFN) had better hydrophilicity and permeability compared to the original unmodified membrane while no change in roughness and rejection values for Nacl and Na_2SO_4 were observed before or after Ag-NPs addition. This suggests that Ag-NPs did not effectively influence the membrane surface characteristics; pore size and pore distribution.

4.1.2   Copper based nanocomposite membranes (Cu-NPs)

Antimicrobial activity is not limited to silver nanoparticles, the anti-biofouling properties of copper-based nanoparticles (Cu-NPs) are also well known. In addition to their antibacterial/ antifungal applications, Cu-NPs exhibit superior antioxidant, optical, catalytic and electrical properties that make them attractive for a broad range of applications [85, 86]. This includes; antimicrobial agents in coating/paints [87, 88], healthcare [89], energy storage [90], chemical sensors [91], catalysts [92], and so on. Similar to Ag-NPs, the exact antimicrobial mechanism by which Cu-NPs exhibit its biocidal effects is still unclear [89]. Ruparelia et al. [93] speculated

that they have a similar mechanism as Ag-NPs. Bagchi et al. [94] suggested that various mechanisms such as; membrane disruption, complex formation with proteins, DNA damage and blocking of biochemical pathways were responsible for the antibacterial action of Cu-NPs. Ramyadevi et al. [95] claimed high inhibitory activity of copper nanoparticles against a diverse range of bacteria including *Staphylococcus aureus, Klebsiella pneumoniae, E. coli, P. aeruginosa* and *Micrococcus luteus*, and fungi including *Candida albicans, Aspergillus flavus*, and *Aspergillus niger*. However, incorporation of Cu in the synthesis and application of nanocomposite membranes has rarely been addressed.

Recently, Isloor et al. [96] conducted novel research to immobilize atomic copper onto PS/modified poly isobutylene-alt-maleic anhydride blend membrane surface by a physical vapor deposition technique. The copper coated membranes exhibited slightly higher (96%) salt rejection and surface roughness with only a slight decrease in pure water flux. Further characterization to test the antimicrobial resistance of the coated membrane was investigated using the food poisoning organism *Bacillus. cereus*. Good inhibition was observed against bacterial growth indicating that copper deposition could be an effective technique for the fabrication of antimicrobial membranes. Akar et al. [85] studied two types of nanoparticles; Selenium (nSe) and copper (nCu). nSe were prepared by the reduction of aqueous sodium selenite solution with freshly prepared glucose solution, while nCu were prepared by sonochemical reduction of copper(II) hydrazine carboxylate Cu–$(N_2H_3COO)_2$ $2H_2O$ complex in an aqueous medium. The synthesized nanoparticles were incorporated, at (0.002, 0.010, 0.030, and 0.050 wt.%), into UF/PES membrane via the classical phase inversion technique. The resultant nanocomposites were characterized with activated sludge as a biological suspension and bovine serum albumin (BSA) as a protein foulant model. The findings indicated good membrane antifouling properties against both of activated sludge and BSA. Moreover, the morphology, hydrophilicity and permeability of the nanocomposites were dependent on ENMs composition in the blend.

4.1.3 Iron oxides based nanocomposite membranes (Fe-NPs)

Iron is one of the most abundant metals in the earth's crust. Similar to other metals at the nanoscale level, iron nanoparticles, as a pure metal, are extremely reactive, which has made them difficult to study and restricted their practical applications [3]. For instance, zero valent iron (nZVI) nanoparticles possess high reactivity, and easily oxidized to Fe^{+2} and/or Fe^{+3} ions when exposed to water [97]. However, iron compounds are relatively stable when present at

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the nanoscale level. Their crystallographic structures provide high surface area/volume ratio and superparamagnetic properties that offer a high reactivity. In addition to their excellent magnetic and reactivity, they have low toxicity, high surface modifiability, great biocompatibility and are chemically inert [98, 99]. The unique features of iron oxide based nanoparticles (Fe-NPs), mainly magnetite (Fe_3O_4) and maghemite (γFe_2O_3), have encouraged many researchers to investigate these engineered magnetic nanoparticles in remediation and water treatments. Depending on the oxidation state of the iron, these magnetic nanoparticles possess different chemical properties. Indeed, they offer distinct capabilities and reactivity for contaminants removal [97]. Based on the aforementioned unique characteristics, the addition of Fe-NPs is believed to impart great potential to the fabrication of organo-mineral nanocomposite membrane with novel process control properties.

Impregnation of Fe-NPs into polymeric membranes is believed to introduce innovative solutions for many of the problems associated with polymeric membrane applications. In a recent study, Homayoonfal et al. [100] investigated the influence of iron oxide (Fe_3O_4) nanoparticles immobilised in PSF membranes. The nanocomposites were synthesized via three techniques; deposition by interfacial polymerization, deposition by photopolymerization and by blending into the polymeric matrix. These researchers concluded that the presence of Fe_3O_4 nanoparticles significantly enhanced membranes surface roughness, pure water flux, and surface hydrophilicity. The blending method performed better in terms of structural properties while deposition was better for dye separation yield. In another recent study, Rambabu et al. [101] studied the influence of Fe-NPs concentration on the resultant membrane composites. 0, 1, 2, 3 and 4 wt.% of the NPs were blended with PES through the classical phase inversion method to fabricate Fe/PES-UF nanocomposite membrane. The results indicated that up to certain Fe-NPs concentration, synthesized membranes exhibited higher flux, thermal stability, and hydrophilicity than the original unmodified PES membrane. In addition, heavy metal ion (Cu^{+2} and Zn^{+2}) rejection was slightly decreased due to the increased pore size and porosity induced by the nanoparticles addition. Ghaemi et al. [102] studied the influence of surface modified Fe_3O_4 nanoparticles on NF membranes used for heavy metal removal. Fe-NPs modification was achieved by immobilization of metformine, silica, and amine. Thereafter, modified Fe-NPs were blended in a PES/NF membrane matrix at various compositions. Similar to the previously mentioned studies, results indicated that Fe-modified nanoparticles influenced the morphology of the membranes with higher porosity and larger pore size found in all nanocomposites except that contained amine modified NPs. In addition, a further increase

14

in surface roughness parameters, pure water flux and hydrophilicity were reported. However, the nanocomposite membrane prepared with 0.1 wt.% metformine exhibited a higher rejection for copper ions (92%) and higher membrane reusability due to the large number of N atoms around each particle which offered active adsorption sites through their lone electron pairs. In contrast to Ghaemi findings, Daraei et al. [103] reported a decrease in pure water flux at all the different loadings of 0.01, 0.1 and 1wt% of Fe-NPs and an increase in Cu(II) removal. Alam et al [43] prepared Fe_3O_4/PES nanocomposite membrane for desalination applications. Their results showed higher rejection values (68% and 82%) for NaCl and $MgSO_4$ respectively at 10 % Fe- NPs loading. Furthermore, lower contact angle and smoother surfaces were obtained that showed promise for lower fouling properties.

4.1.4   Aluminium oxide based nanocomposite membranes (Al_2O_3-NPs)

Similarly to other metal/metal oxide nanoparticles, Al_2O_3 has also attracted interest for many applications that include surface protective coating, catalysis, fire retardation and composite materials [104]. However, due to their high adsorption capacity, resistance to chemical agents, and excellent catalytic performance for many reactions [105, 106] Al_2O_3-NPs have gained the attention of membrane technologists for the development of new nanocomposite membranes with novel properties.

Mehrnia et al [107] investigated the influence of alumina NPs on the morphology and performance of PSf nanocomposite membrane. Al_2O_3-NPs (70 nm) were blended into PSf membrane via a classical phase inversion method at a concentration ranging from 0-0.52 wt.%. The NPs loading threshold was found to be 0.39 wt.%. Nanocomposite prepared at the loading threshold was further evaluated, and the characteristics of the resultant nanocomposite were compared up to and below the loading threshold by rheometric analysis, contact angle measurements and SEM images. By adding the NPs, rheological features of the casting solution changed from a Newtonian fluid to a non-Newtonian one. Hydrophilicity of the nanocomposites was enhanced by increasing the loading weight even after the threshold. Raising the concentration of NPs up to 0.39 Wt.% resulted in porosity development, flux enhancement, and separation percentage reduction, while after this point, porosity diminished due to further increase in solution viscosity. In a similar study , Homayoonfal et al. [108] prepared Al_2O_3/PES nanocomposite membrane blend for membrane bioreactor applications. Two compositions were used (0.02 and 0.03 wt. %) in the preparation. The results suggested that the presence of alumina nanoparticles up to 0.03 wt. % in the mixed matrix membrane

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could hinder biofilm formation and provide a 75% reduction in cake layer resistance and up to 83% reduction in irreversible resistance. Thus, enhanced antifouling properties that was further confirmed by the reduced contact angle from 73 to 51. Furthermore, the pure water flux was more than four times that of the original PES membrane. Ghaemi et al. [109] investigated the ability of alumina NPs to improve adsorption of heavy metals and the removal efficiency of copper by PES membranes. Different amounts of alumina NPs (0.01, 0.1 and 1%) were blended to prepare the mixed matrix membrane. All membranes exhibited higher water permeability up to NPs loading ≤ 1 wt.% due to the enhanced porosity and hydrophilicity of the nanocomposites. In addition, larger microvoids in the support layer and thinner skin layer were also observed. Furthermore, copper removal efficiency was also improved. However, any further increase in Al_2O_3-NPs wt.% did not show any change in the characteristics and performance of the nanocomposites. The authors suggested that the adsorption was the dominant separation mechanism in the nanocomposite membranes. In another study, a similar influence for alumina NPs on PES membrane morphology was observed, Arsuaga et al.[42] compared the influence of three different metal oxide nanoparticles, TiO_2, ZrO_2 and Al_2O_3, on PES membrane. The nanocomposites fouling behaviour was characterised by using BSA and humic acid as model organic foulants. Their research demonstrated that Al_2O_3/PES nanocomposite membrane had higher pure water flux, higher rejection, long-term stability and lower flux decline for both model foulants in comparison to the other nanocomposites and original membranes. This behaviour was attributed to the fact that Al_2O_3 nanocomposite membrane has introduced more hydrophilic centers in the vicinity of the membrane surface, which reduced the possible adsorption of foulants. For MBR applications, Maximous et al [110] prepared Al_2O_3 entrapped PES/UF membranes to characterize their fouling characteristics through activated sludge filtration. Nanocomposite membranes exhibited lower flux decline compared to nascent membrane. In addition to a greater fouling mitigation with increasing Al_2O_3 content. In contrary with the previously mention literatures, Yan et al [111] found that the addition of Al_2O_3 NP did not show any influence on pore size and porosity of the nanocomposite membranes, while a noticeable enhancement was observed on surface hydrophilicity, permeation, antifouling and mechanical characteristic of the nanocomposites.

4.1.5   Titanium dioxide based nanocomposite membranes (TiO₂-NPs)

Titanium dioxide (TiO_2) is one of the most common materials in our daily life [112]. It is estimated that of all the nanoparticles in consumer products, TiO_2 nanoparticles (TiO_2-NPs)

currently have the highest degree of commercialization [113]. However, TiO_2-NPs excellent hydrophilic and photocatalytic properties have led to attention in environmental purification applications [112]. Under UV irradiation, TiO_2-NPs show a superior capability to deactivate microorganisms and to decompose organic compounds [114, 115]. Materials with photocatalytic properties could offer the possibility to introduce such functionalities when incorporated into polymeric membranes [116].

According to Madaeni & Ghaemi [24], UV irradiation of TiO_2 nanocomposite membranes could impart two functionalities to the membranes; photocatalytic and ultra-hydrophilicity. As a consequence of photocatalysis, groups of active oxidant reagents appear on the surface of the membrane which leads to decomposition and removal of the membrane foulants. While, ultra-hydrophilicity could impart a self-cleaning property and increase the nanocomposite's water permeability as well. Kim et al. [117] prepared TiO_2-NPs/TFC hybrid membrane via a self-assembly technique. The new nanocomposite membrane provided a substantial photo-bactericidal effect on *E coli* under UV light irradiation. In another study, Rahimpour et al.[41] investigated the impact of incorporating TiO_2-NPs on the antifouling properties of PES/UF membranes for application in the dairy industry. Three sets of membranes were fabricated; TiO_2-bended membranes, UV-irradiated TiO_2-blended membranes, and UV-irradiated TiO_2-deposited membranes. TiO_2 entrapped membranes showed lower milk water permeation and initial pure water flux in comparison to the original membrane. In contrast however, flux stability and fouling resistance were better in the long term. On the other hand, UV irradiation of TiO_2-blended membranes added further enhancement to the flux and antifouling properties whereas coating exhibited superior affects, compared to the other membranes, to mitigate membrane fouling and to overcome PES hydrophobicity. In another piece of research, Li et al. [40] prepared a novel TiO_2 self-assembly nanocomposite membrane by immersing a blend membrane of poly (styrene-alt-maleic anhydride)/polyvinylidene fluoride (SMA/PVDF) in a suspension of TiO_2. Their results demonstrated that permeability and antifouling properties against BSA were significantly improved when compared to the (SMA/PVDF) blend membrane. In another study, TiO_2 NPs were used to fabricate a novel polyamide-titanium oxide (PA-TiO_2) nanocomposite membrane via *in-situ* interfacial polymerization [118]. Results demonstrated higher flux and hydrophilicity at 5 wt.% TiO_2, with high and stable rejection to $MgSO_4$ (> 95%). In another study, Vatanpour et al. [119] investigated the impact of nano-TiO_2 type and size on the morphology, performance and antifouling properties of mixed matrix PES/NF membranes. Various types of TiO_2 nanoparticles (PC500, PC105, and PC25) were

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used in the preparation. Pure water flux and hydrophilicity, for all the blended membranes, were higher compared to that of the original PES membrane. However, after a particular concentration of TiO_2, nanoparticles aggregation occurred. This aggregation was more severe in the case of PC105 and PC500 membranes and the increased concentration clogged the pores and reduced the pure water flux. Furthermore, the biofouling resulting from whey filtration tended to decrease with the smaller nanofiller size. More flux recovery was achieved due to the higher surface area and water adsorption affinity.

4.2   Carbon-based nanomaterials

4.2.1   Carbon nanotubes (CNTs)

Since the discovery of carbon nanotubes (CNTs) in 1991, CNTs have become an established material in commercial products [120] (Fig. 7). A lot of interest and research endeavour has focused on CNTs due to their tuneable electrical and thermal characteristics, novel optical properties and superlative strength. Most of their applications to date have been focussed within electronics, energy and composites sectors [121]. CNTs have been described as seamless cylinders derived from the honeycomb lattice of a graphite sheet (single atomic layer of crystalline graphite) [122]. They exist in three basic structures namely; single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs are made from a single atom thick sheet of graphene rolled up into a cylinder while DWCNTs have another graphene sheet around the central SWCNT. Likewise, MWCNTs are a series of concentric SWCNTs [123],(Fig 78). Due to their outstanding features, CNTs have been widely studied as a nanofiller for modification of polymeric membranes, mainly using MWCNTs and SWCNTs [124].
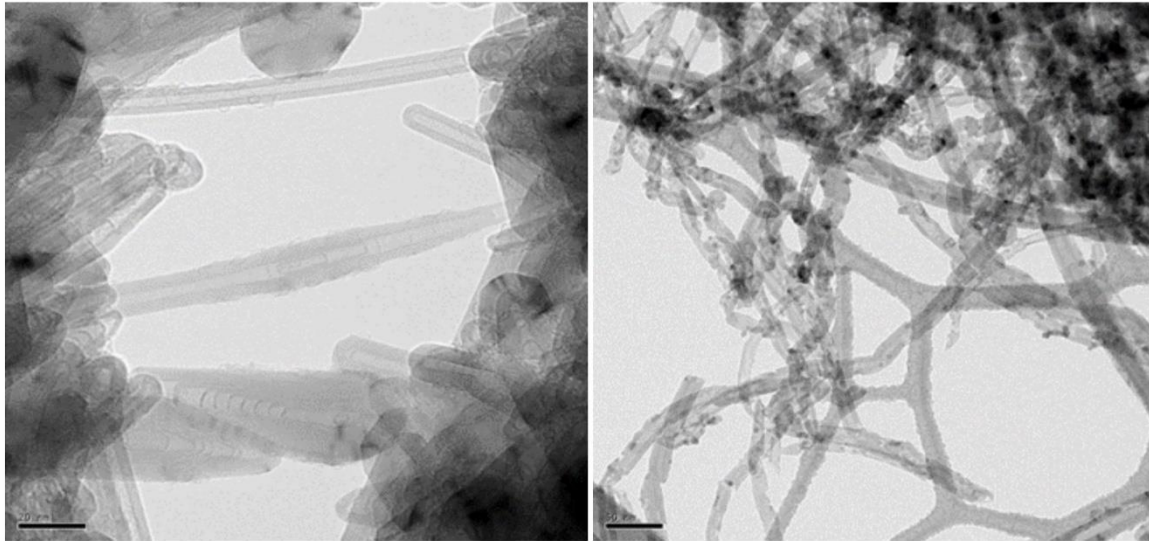
3

4   The exact magnitude of CNTs properties relies mainly on the chirality, length and

5   diameter of the nanotubes themselves and whether they are MWCNTs, DWCNTs or SWCNTs

6   [125, 126]. In a recent work, Wang et al. [127] compared the performance of PES/NF mixed

7   matrix membranes (MMMs) using two different diameters (20 and 40 nm) of MWCNTs. Both

8   MMMs showed higher salt rejection and water flux than the original PES membrane while

9   MMMs embedded with thinner CNTs obtained better filtration performances than MMMs with

10   thicker CNTs at 0.1 wt.%. CNTs may act as water channels when impregnated in the membrane

11   matrix. MWCNTs have been found to have great influence on permeation properties and the

12   morphology of the membranes depending on the CNTs content [34]. In addition, MWCNTs

13   can enhance the wettability of membrane materials and the electrostatic repulsion between the

14   polymeric membranes and foulants (e.g. proteins) [36]. Celik et al. [128] reported that

15   MWCNTs/PES membrane had lower tendency to foul and smaller irreversible fouling ratio in

16   comparison to the control PES membrane when using BSA and ovalbumin (OVA) for the

17   fouling assessment. Furthermore, the fouled membranes could be more effectively treated by

18   a water backwash cleaning process. In another study, Shen et al.[35] exploited MWCNs-grafted

19   by poly(methyl methacrylate) (PMMA) to synthesize polyamide thin film composite (PA-TFC)

20   membrane via interfacial polymerization, the results demonstrated higher rejection for Na_2SO_4

21   (99%) and the water flux was about 62% increased to that of the unmodified TFC membrane.

22   In another study, Kang et al. [129] observed a superior antimicrobial activity for SWCNTs,

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much higher than their MWCNTs counterparts., cell membrane damage is the most likely mechanism causing bacterial cell death on direct contact with SWCNTs

CNTs are well known for their mechanical strength and they are the materials of choice for composites reinforcement [130]. Shawky et al. [131] claimed that the tensile strength and Young's modulus of the nanocomposite membrane could be increased with MWCNTs content addition. Similar findings were observed by Chen et al. [132] when (0-0.15 wt.%) carboxyl functionalized MWCNTs were blended with PVDF/PVA UF membrane. At 0.12 wt.% MWCNTs content in the matrix, the break strength, elongation at break, and Young's modulus were enhanced by 60%, 215.5%, and 56.7%, respectively in comparison to the original membrane.
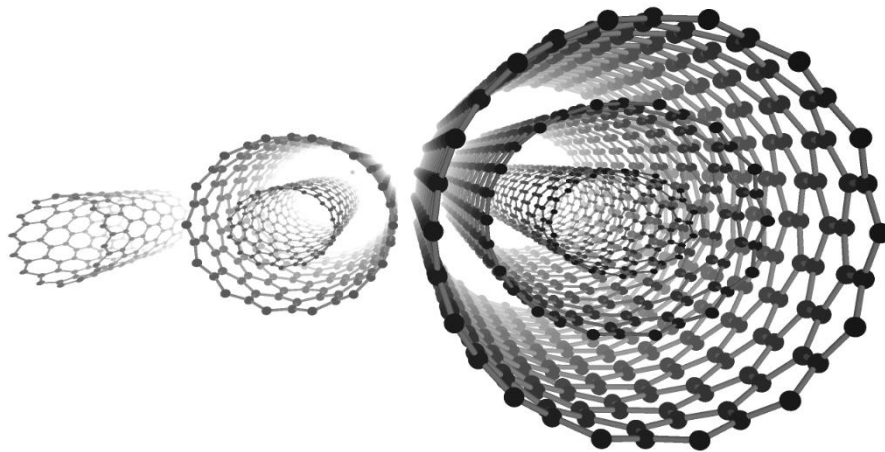
Fig 8: Arrangement of graphene sheets to produce SWCNTs, DWCNTs and MWCNTs respectively (from left to right).

4.2.2 Graphene (G) and Graphene Oxide (GO)

Graphene (G), has emerged as the 'wonder' material of the 21st century. With two-dimensional monoatomic thick building blocks of a carbon allotrope, graphene has better thermal, electrical and mechanical characteristics, higher aspect ratio and surface area than other materials including CNTs, Kevlar and carbon fibers [133], as shown in (Table 2). The significant potential of graphene has attracted enormous interest in applications for nanocomposites [134]. The anticipated physicochemical properties of graphene-based polymer nanocomposites depend mainly on the interfacial bonding between the polymer matrix and graphene layers, in addition to the distribution level of graphene layers inside the polymer matrix. On the other hand, it should be noted that pristine graphene does not form homogeneous composites due to

its incompatibility with organic polymers; this may create inferior composite properties [135, 136]. To overcome the polymer incompatibility issues of pristine graphene, oxidation of graphene has been suggested to introduce highly hydrophilic and stable colloidal dispersions [137]. Graphene oxide (GO) is a highly chemically modified form of graphene that consists of a variety of functional groups, such as carboxylic acid at the edges and hydroxyl and epoxide groups on the basal plane. These functional groups can control the van der Waals forces and improve the compatibility with organic polymers to achieve better dispersion [138]., In recent years, incorporation of GO into polymeric membranes has gained more and more attraction. Various nanocomposite membranes have been fabricated to impart the exceptional characteristics of graphene into these membranes, like; PSF-GO [139, 140], PES-GO [141] and PVDF-GO [33].

According to Chang et al.[142], graphene oxide has demonstrated high hydrophilicity and anti-fouling properties against BSA when incorporated within PVDF/UF membrane, this is attributed to the electrostatic repulsion of GO, which acts as a barrier to prevent BSA adsorption on the nanocomposite membrane surface. Zinadini et al.[143] reported that carboxylic acid, hydroxyl and other functional groups of GO surfaces are migrated to the surface of the membrane during the phase separation fabrication process and thus enhanced the surface properties and hydrophilicity of the nanocomposite membrane. Similarly, these enhanced interactions and hydrophilicity were also reported in membrane bioreactor (MBR) applications using GO-PSF MMMs [144]. In addition, GO was also found to have antibacterial activities [145]. The presence of functional groups ensures high negative zeta potential and impedes attachment of biofouling and subsequent accumulation on the membrane surface [146]. Hu et al. [147] reported high toxicity to *Staphylococcus aureus* and *E. coli*, which was mainly attributed to the mechanical damage of the bacterial cell membrane caused by the sharp edges of GO as revealed by study using transmission electron microscopy TEM. In another study Yu et al. [141] found superior anti-biofouling properties for GO nanosheets modified by hyper branched polyethyleneimine (HPEI) when blended with PES/UF membrane.

From the mechanical performance perspective, in pressure-driven membrane processes, high tensile strength and elongation at break values mean better toughness and sustained integrity of membranes, which will assure a comprehensive performance and provide good abilities for repeated use, and long-term membrane separation applications [148]. Graphene and its derivatives have been widely used for composite reinforcement purposes as graphene

is the stiffest and strongest material known [149]. It has been reported that the enhancement in the mechanical properties of graphene-polymer composites is much higher than that of clay or other carbon based polymer nanocomposites [150]. The enhancements of graphene-based nanocomposites can be achieved at very low filler content in the polymer matrix [151]. A comparative study was carried out by Zhang et al. [152], who studied the impact of blending OMWCNTs, GO, and OMWCNTs-GO on the mechanical properties of PVDF ultrafiltration membrane fabricated via a phase inversion technique. These researchers reported superior enhancement in tensile strength, 12.86% and 43.94%, and elongation at break ,31.50% and 39.24%, for the OMWCNTs and GO synthesized composite membranes, respectively. Slightly less mechanical performance was shown for the MWCNTs-GO/PVDF membrane due to the bigger pore size that stemmed from the synergetic effect for the oxidized low-dimensional carbon nanomaterials. Xu et al. [33] studied the influence of GO functionalization with 3-aminopropyltriethoxysilane (APTS) on the mechanical properties of PVDF/UF membrane. The tensile strength measurement of the f-GO/PVDF membrane was improved by 69% while the elongation at break was 48% more in comparison to GO/PVDF. Thus, GO could be a promising solution to fabricate hybrid membranes with excellent reinforced, antifouling and permeation properties.

Table 2: Properties of graphene, CNT, nano-sized steel and polymers [134].

Materials	Tensile strength	Thermal conductivity (W/mk) at room temperature	Electrical conductivity (S/m)
Graphene	130±10 GPa	$(4.84\pm0.44)\times10^3$ to $(5.30\pm0.48)\times10^3$	7200
CNT	60–150 GPa	3500	3000–4000
Nano-sized steel	1769 MPa	5–6	1.35×10^6
Plastic (HDPE)	18–20 MPa	0.46–0.52	Insulator
Rubber (natural rubber)	20–30 MPa	0.13–0.142	Insulator
Fiber (Kevlar)	3620 MPa	0.04	Insulator

4.3 Cellulose based nanoscale materials.

Recent interest has been applied to produce so-called green or eco-composite materials. Such eco-composites include nanocellulose based materials, which have been widely used as reinforcement materials due to their sustainability, green and environmentally friendly specifications,[153-155]. Nanocellulose applications to hybrid composite materials (Fig 9) have shown promising results for the three categories of nanocellulose that are nanofibrillated cellulose (NFC), cellulose nanocrystal (CNC) and bacterial nanocellulose (BNC) [156]. Interestingly, these materials not only possess the properties of natural cellulose, which include hydrophilicity, biodegradability, and renewability but also has the characteristics of nanomaterials , for instance; high mechanical strength, high tensile modulus and high specific surface area [157]. However, there are only a few examples of nanocomposite membrane applications.
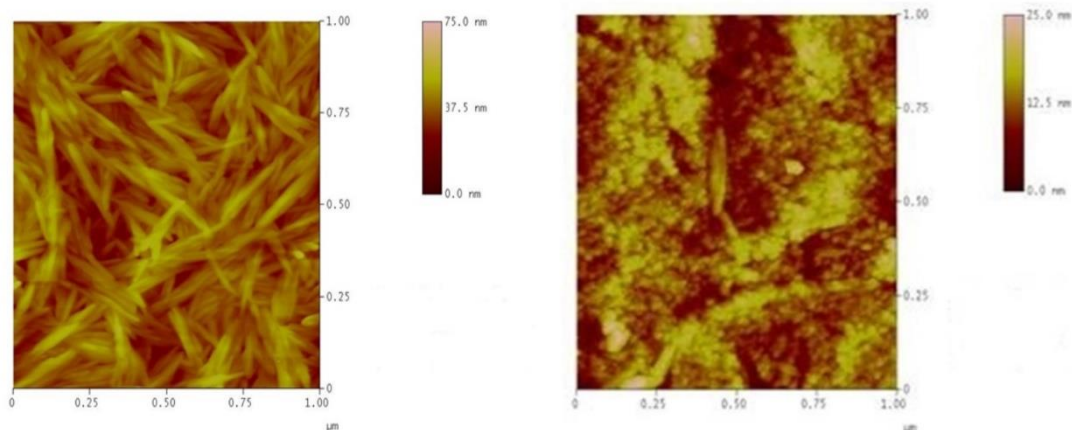
Fig 9: AFM images of dried cellulose nanocrystals (left) fabricated membrane impregnated with 4% cellulose nanocrystals (right)

Bai et al. [158] prepared CNC/PVDF mixed matrix membrane to investigate the influence of CNC composition (0.05-0.25 wt.%) on the nanocomposite performance. Their results demonstrated that CNC has great influence on the surface characteristics and morphology of the nanocomposites. For CNC content up to 0.1 %, pure water flux, porosity and mean pore size increased without significant change in BSA rejection. In addition, both elongation-at-break and the tensile strength of the nanocomposite improved as well, (from 84 to 150%) and (from 4.3 to 6.3 MPa) respectively. Similarly, Al malek [159] blended higher concentrations (2, 4, 6 wt.%) of CNC into PES membrane. Increasing the CNC content in the casting solution

was found to increase pore size, pore size distribution and pure water flux of the nanocomposites, while no impact was observed on surface roughness parameters. Moreover, the nanocomposite membrane with 2 wt. % CNC exhibited higher strength (8.843 MPa) with elongation of 6% in comparison to the control membrane (4.186 MPa), this was attributed to the structural changes in the membranes in the presence of CNC that changed the macrovoids to a more homogeneous and narrow form. However, the further increase in CNC content decreased the strength of the membrane to 8.047 and 4.63 MPa for the 4 and 6 wt.% respectively, which are still higher than that of the unmodified membrane. In another work, NFC/PES nanocomposites were prepared at different NFC loading weights. In comparison with pure PES membrane, the mean pore size, porosity, Pure water flux, mechanical strength, and elongation at break of nanocomposites were the highest at 1 wt.%. However, further increase resulted in a decrease in all characteristics [160]. These findings suggest a threshold content of cellulose-based materials in composites, where optimum exploitation can be achieved.

Based on the previously mentioned sections, a conclusion can be drawn that ENMs could have distinguish influence on polymeric membranes depending on their dimension and type, as summarised in Table 3 below.

Table 3: Influence of various types of ENMs on polymeric membranes

Type of membrane	Foulant	Type of ENMs	Influence on modified membranes	Ref.
UF/PS	-*Pseudomonas Mendocino* (KR1) -*E. coli*(K12) -*Virus*	Ag NP	-Improved hydrophilicity -No effect on membranes surface charge and morphology -Slight increase in pure water permeability -Enhance antibacterial and virus removal, inhabited biofilm growth	[83]
NF/PES	-*P. aeruginosa* (PA01)	Ag NP	-Enhanced antibacterial, hydrophilicity and permeability -No effect on surface roughness, and salt rejection	[38]
UF/PES	-Activated sludge -BSA	Cu NP	-Decreased permeability -Increased hydrophilicity and protein rejection	[85]
UF/PES	-Dye	Fe_2O_3	-Improved hydrophilicity, surface roughness, dye removal and permeability	[100]
UF/PES	-Heavy metals (Cu^{+2} and Zn^{+2})	Fe_3O_4	-Enhanced hydrophilicity, water permeability, thermal stability -Slight decrease in heavy metals rejection -Increased pore size and porosity	[101, 102]

UF/PES	-BSA -Humic acid	Al_2O_3	-Higher water permeability, hydrophilicity, rejection and long term stability -Lower flux decline compared to neat membrane	[42]
NF/PES	-Whey	TiO_2	-Improved permeability and hydrophilicity -Improved antifouling characteristics and flux recovery	[119]
RO/PVA	-Whey	TiO_2	-Enhanced water permeability and self-cleaning property (reduced fouling and increased whey flux) -Enhanced hydrophilicity and photocatalytic characteristics.	[24]
RO/PA	-Ca(HCO$_3$)$_2$ - BSA	MWCNTs	-Enhance membrane surface charge. -Affected the morphology. -Increased water flux and slight decrease in rejection. -Better antifouling and antioxidative properties.	[161]
UF/PVDF	-BSA	GO	-Improved mechanical strength of modified membrane. -Enhance, hydrophilicity, antifouling and permeation properties.	[33]

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5. Issues arising from the incorporation of ENMs into polymeric membranes.

Despite the huge attention and funding devoted so far to the applications of ENMs in membrane technologies, the commercialization of ENMs-membrane composites has yet to be achieved. In fact, with the marked demand of nanomaterials in the marketplace, there is a growing public debate whether the social and environmental cost of nanomaterials outweigh their benefits [162]. Apart from this debate, ENMs durability under various operation conditions as well as their degradability at the end of their service life represents the main challenges that have not yet been fully addressed [31, 54]. In polymeric membrane applications, incorporation of ENMs also has some obstacles. Predominantly, their limited dispersion in the casting solutions, especially for nanomaterials having a diameter less than 100 nm [3]. Poor dispersion results in nanomaterial agglomeration and uneven distribution in the polymeric matrix. This agglomeration may give rise to undesired changes in the nanocomposite membrane characteristics such as free surface energy, pore size, hydrophilicity, roughness and antifouling properties [163]. Weak interfacial interaction/adhesion between ENMs and the polymeric structure will end up in the leaching of these ENMs out of nanocomposite membranes, causing a gradual deterioration in the nanocomposite membrane over time, reducing performance

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stability and potentially raising many environmental issues [164]. These weak interactions have been mainly attributed to poor polymer–inorganic incompatibility, poor polymer–particle adhesion, the different thermal expansion coefficients for the ENMs and the polymer, and solvent evaporation during nanocomposite formation [9]. In addition, agglomeration could be induced from incorporating a high content of ENMs during the fabrication [165]. From an environmental point of view, there is a growing concern regarding the potential hazards of ENMs release into ecosystems. This is compounded by the lack of quantitative data available from monitoring their release, or knowledge as to which form they have been released into the environment [166]. For instance, De Kwaadsteniet et al. [88] reported that Ag-NPs can form a composite colloid with some organics leading to entirely different toxicity from that of pure Ag nanoparticles. Therefore, the environmental studies should not only quantify the released nanoparticles but also assess the toxicity of released nanoparticle composites. Very little is known regarding the transport and fate of ENMs in environmental waters since the bulk of the current nanotoxicological research are laboratory scale studies focusing on single species in a simple media [167]. Thus, ensuring the reliability of nanocomposites through minimizing their toxicity in biotic and abiotic environments could offer new prospects regarding their industrialization.

6. Future improvements for ENMs incorporation into polymeric membranes.

One of the pragmatic approaches used to improve the interactions between the inorganic ENMs and the organic polymer chains is by revising the surface characteristics of ENMs. Several methods have been suggested for alteration of these characteristics through introducing a specific functional group at their surfaces. This research strategy is required to achieve improved interactions and more homogenous distribution for the ENMs within the polymeric matrix. Such methods include chemical treatments, grafting of synthetic polymers, ligand exchange techniques and adsorption of polymeric dispersants [27]. Among these techniques, surface functionalization/modification by chemical treatment is currently an intensive research focus in nanocomposite membrane applications.

Surface functionalization/ modification increase the stability of ENMs in their host materials, and various functional groups can be used to achieve this, such as carboxylic acid, phosphoric acid, silane coupling agents, and dopamine (Fig 10) [168]. Silanes, have been recently applied as coupling agents to modify ENMs surfaces and promote adhesion in the fabrication of nanocomposite membranes. Silanes are bifunctional molecules that possess dual reactivity, that

enables them to act as intermediate materials to link two dissimilar materials [169, 170]. Polysiloxane has been used as a saline coupling agent, to chemically functionalize SiO_2 nanoparticles and then to immobilize PEG molecules on their surface [171]. The modified nanoparticles were then dispersed in a casting solution to prepare modified SiO_2/ PVDF nanocomposite membranes. The stability of the chemically modified SiO_2 nanoparticles in the membrane matrix was significantly improved during membrane filtration processes and membrane cleaning, enabling the long-term usage of the blend membrane. A similar study, reported good dispersion for chemically modified TiO_2 in PES nanocomposite membrane when TiO_2 particles were first modified using Aminopropyltriethoxysilane (APTES) as a silane coupling agent [163]. In a similar study, a novel PA/TFN nanofiltration membrane was prepared by dispersing aminosilanized TiO_2 nanoparticles into a diamine monomer solution followed by polymerization [172]. The silane coupling agent was grafted onto the surface of TiO_2 to avoid agglomeration encouraged during the TFN preparation and to obtain a greater interfacial adhesion between the polymer matrix and TiO_2 nanoparticles. Functionalized graphene oxide (f-GO) nanosheets with 3-aminopropyltriethoxysilane (APTS) were found to have better dispersion in organic solvents that non-functionalized GO [33]. Polydopamine (PDA), also known as "bio-glue", has been recently used as an excellent coupling ligand in nanocomposite membranes. Zhang et al. [173] conducted research to robustly bind TiO_2 nanoparticles on the surface of TFC membrane using PDA. PDA can be self- polymerized on TiO_2 and membrane surfaces forming a firm connection between them [174]. Similarly, TiO_2 nanoparticles have been strongly bound and homogeneously distributed into PVDF ultrafiltration membrane by exploiting PDA. Zhao et al.[175] uniformly embedded PDA modified MWCNTs (PDA-MWCNTs) in polyamide (PA) thin-film composite membranes. Their results demonstrated a fine dispersion for the coated MWCNTs in polyethyleneimine aqueous solutions, which was interracially polymerized with trimesoylchloride n-hexane solutions to fabricate nanocomposite membranes. The improved compatibility/interactions between the modified MWCNTs and PA matrix were attributed to the PDA coating layer on the nanotubes surface. In another study, Khalid et al. [176] prepared functionalized MWCNTs with dodecylamine (DDA) that were then used to fabricate PS nanocomposite membrane for desalination applications. The long alkyl chains of DDA functionalized MWNTs were found to improve the interfacial interactions/adhesion and compatibility between inorganic nanotubes and polymeric matrix.

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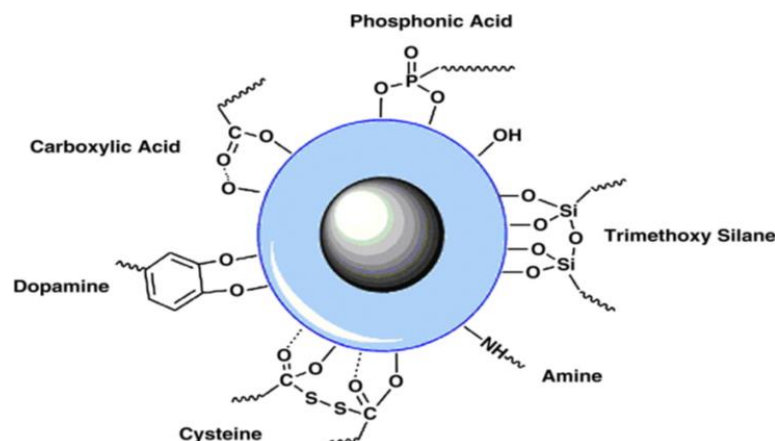
Fig 10: Different functional groups attached to iron oxide NPs surface [168].

7. Conclusion

The diverse and often unique properties of ENMs provide the membrane technologist with an extended toolbox for the bespoke fabrication of nanocomposite membranes with properties ideally suited for a particular process. ENMs have the potential for the creation of membranes that are optimised to meet all the challenges of desalination and waste water treatment including fouling and biofouling while extending the life time of the membrane by enhancing their mechanical robustness and resistance to cleaning regimes. All of this with no impact on selectivity. An impressive list indeed of the benefits for membrane processes but arguably highly achievable. We have witnessed tremendous advances in all aspects of life as a result of our improved capabilities in the monitoring, control and fabrication of materials at the nanoscale, these advances are beginning to impact on the quality and functionality of membrane materials used in water treatment. The dissemination of nanotechnological experience is set to continue and will inevitability impact positively on the engineering of membrane processes. However, in the short term enhancing the interfacial interactions between organic polymers and ENMs is essential in order to establish these highly dependable nanocomposite materials as the next generation of membranes. As with all nanomaterials more effort needs to be devoted to monitor the long term stability of these nanocomposites within real processes, and to evaluate the ecological issues of use and potential release of ENMs. Further research is required before their commercialisation to ensure that the benefits of ENM-membrane nanocomposites outweigh their fabrication and environmental costs.

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Acronyms	Description
0D	Zero Dimension
1D	One Dimension
2D	Two Dimension
3D	Three Dimension
AFM	Atomic Force Microscopy
Ag	Silver
Ag^+	Silver ions
Ag-NPs	Silver nanoparticles
Al_2O_3	Aluminum oxide
APTES	Aminopropyltriethoxysilane
APTS	3-aminopropyltriethoxysilane
bio Ag^0	Biogenic silver nanoparticles
BNC	Bacterial nanocellulose
BSA	Bovine Serum Albumin
CNC	Cellulose Nanocrystal
CNTs	Carbon Nanotubes
Cu	Copper
CuO-NPs	Copper oxide nanoparticles
DDA	Dodecylamine
DNA	Deoxyribonucleic acid
DWCNTs	Double-Walled Carbon Nanotubes
ENMs	Engineered Nanoscale Materials
Fe^{+2}	Iron(II)
Fe^{+3}	Iron(III)
Fe_3O_4	Magnetite
Fe-NPs	Iron nanoparticles
FE-SEM	Field Emission Scanning Electron Microscopy
f-GO	Functionalized Graphene Oxide
G	Graphene
γFe_2O_3	Maghemite
GO	Graphene Oxide
HPEI	Hyper branched polyethyleneimine
LBL	Layer By Layer
MBR	Membrane bioreactor
$MgSO_4$	Magnesium sulfate
MMMs	Mixed matrix membranes
MWCNTs	Multi- Walled Carbon Nanotubes
Na_2SO_4	Sodium sulfate
Nacl	Sodium chloride
NaX	Zeolite
NF	Nanofiltration
NFC	nanofibrillated cellulose

nSe	Selenium nanoparticles
n-TFN	Thin-Film Nanocomposite
nZVI	Zero Valent Iron nanoparticles
OVA	Ovalbumin
PA	Polyamide
PDA	Polydopamine
PEG	Polyethylene glycol
PES	Polyethersulfone
PMMA	Poly (methyl methacrylate)
PSF	Polysulfone
PVA	Polyvinyl alcohol
PVDF	Polyvinylidene fluoride
ROS	Generate reactive oxygen species
SEM	Scanning Electron Microscopy
SiO_2	Silicon oxide
SMA	Styrene-alt-maleic anhydride
SWCNTs	Single-Walled Carbon Nanotubes
TEM	Transmission Electron Microscopy
TiO_2	Titanium dioxide
TiO_2-NPs	Titanium dioxide nanoparticles
UF	Ultrafiltration
UV	Ultraviolet
ZnO	Zinc oxide
ZrO_2	Zirconium oxide

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