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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.

**Keywords:** Polymeric membranes, nanomaterials, nanoparticles, membranes fouling, Nanocomposite membrane.

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1 **1. Introduction**

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

12 Much effort in the last decade has been focussed on fabricating synthetic membranes  
 13 for particular applications with desired characteristics such as selectivity, permeability,  
 14 structure, chemical and physical properties. To achieve this goal, several techniques have been  
 15 implemented such as phase inversion, stretching, track-etching, sintering, interfacial  
 16 polymerization and electrospinning [1]. Membranes used in water treatment applications can  
 17 be made from a wide variety of inorganic and organic materials; inorganic material include  
 18 ceramics, metals and glass; organic materials include polymers, composite materials or mixed  
 19 matrixes [2]. Inorganic membrane fabrication has recently gained attention due to their high  
 20 mechanical strength and chemical resistance, however their applicability for water treatment  
 21 purposes is restricted due to the high fabrication costs and preparation difficulties [3]. In  
 22 contrast, polymeric membranes are more preferable in industrial applications. Their selectivity,  
 23 variety of membrane structures and properties, ease of preparation and pore formation control  
 24 and the inexpensiveness of polymers have meant that they dominate in membrane applications  
 25 [4] Some of these polymers are listed in Table 1.

26 Table 1: Commonly used polymers and membrane fabrication techniques in water treatment processes  
 27 [4].

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

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

1

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

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

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

18 Recently, the incorporation of ENMs into a polymeric membrane matrix has gained significant  
19 attention for water and wastewater treatment applications [26]. The fabrication of  
20 nanocomposite membranes that conserve the advantages of polymeric membranes yet  
21 overcome their disadvantages by incorporation of ENMs is a highly desired outcome for  
22 membrane development. Nanocomposite membranes, are a new class of membranes,  
23 consisting of both organic polymers and inorganic nanoscale materials, which are believed to  
24 exhibit enhanced performance in comparison to standard membranes [27-29]. The membrane  
25 that merges the beneficial properties of both organic and inorganic materials to create a new  
26 membrane with enhanced hydrophilicity, permeability, thermal and chemical stability, porosity  
27 and mechanical properties has been sought by many research groups [30, 31]. However, many  
28 processes and environmental disruptive issues can arise from incorporation of ENMs into  
29 polymeric membranes, such as disruption of membrane morphology and particulate leaching,  
30 these will impact on process efficiency, Choosing application-specific nanomaterials with an  
31 optimum composition is essential to overcome limitations in polymeric membrane applications  
32 [3].

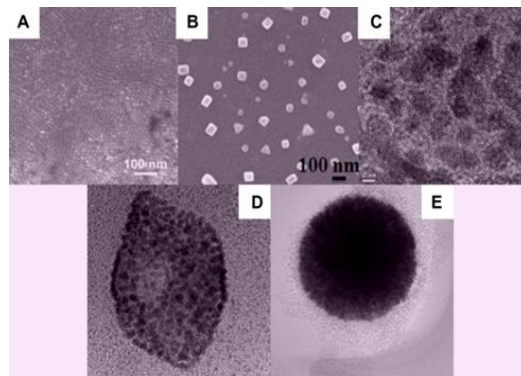
1           There are a large number of studies that have used different ENMs in the development of  
2 novel composite polymer membranes for water treatment applications. The materials that have  
3 been studied include, graphene oxide (GO) [32, 33], carbon nanotubes (CNTs) [34-36], Silver  
4 (Ag) [37, 38], Titanium (TiO<sub>2</sub>) [39-41], Aluminium (Al<sub>2</sub>O<sub>3</sub>) [42], Silicon (SiO<sub>2</sub>) [22], Iron  
5 (Fe<sub>3</sub>O<sub>4</sub>) [43], Zirconium (ZrO<sub>2</sub>) [44] and Zinc (ZnO) [45], Clay nanoparticles [46] and Zeolite  
6 (NaX) [47, 48]. However, the focus of this review is mainly on the modification of polymeric  
7 membranes using the diverse range of ENMs, this includes the features of ENMs, strategies of  
8 incorporation, influence of ENMs on polymeric membranes surface characteristics and  
9 antifouling properties and issues associated from incorporation of ENMs. The review sheds  
10 light on findings have not been covered in previous reviews. It gives an overview on wide range  
11 of nanoscale materials (metal/metal oxide nanomaterials, carbon based, and for the first time,  
12 cellulose nanoscale materials). In addition to addressing the advantages and main issues  
13 associated with incorporating these nanomaterials (environmental and cost issues) and presents  
14 the recent attempts to improve the compatibility with polymeric membranes to overcome these  
15 issues.

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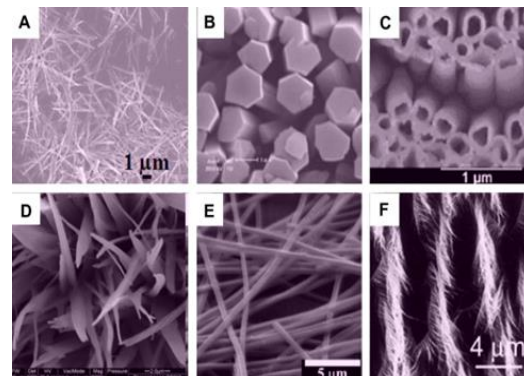
## 17 **2. Special features of ENMs**

18 During the last two decades, materials and structures, manifesting geometric dimensions below  
19 100 nm, have inspired the scientific world [49]. Different nanomaterials synthesized by various  
20 techniques have been applied in many fields, including medical supplies, pigments, cosmetics  
21 production, catalysts, toner and ink [50]. Nanomaterials are classified under different criteria,  
22 depending on the applications, materials, and fields concerned. However, a widely accepted  
23 definition of nanoparticles is that they are particles with a diameter less than 10-20nm; a size  
24 with a surface area to volume ratio where a drastic change in the physical behaviour of the  
25 materials occurs. Moreover, in many cases, particles with size ranging from 1-100 nm are also  
26 referred to as nanoparticles [51]. In a narrower scene, based on their dimensionality, nanoscale  
27 materials are divided into four broad categories: zero-dimensional (0D), one-dimensional (1D),  
28 two-dimensional (2D), and three-dimensional (3D). 0D nanoscale materials include uniform  
29 particles arrays, heterogeneous particle arrays, core-shell quantum dots, onion-like layered  
30 particles, nanolenses and hollow spheres, Fig.1. 1D include nanorods, nanowires, nanobelts,  
31 nanotubes and hierarchical nanostructures, Fig.2. 2D compose nanoplates, nanosheets,

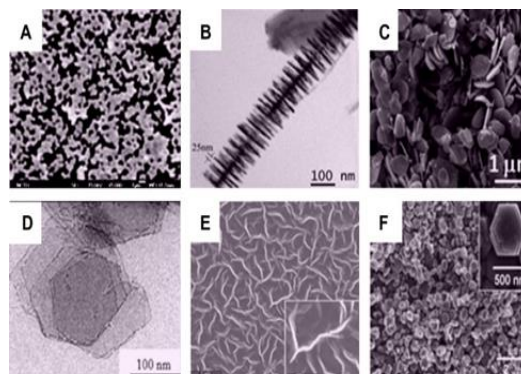
1 branched structures, nanoprisms, nanowalls and nanodisks, Fig.3. Lastly, 3D nanostructure  
 2 includes nanocones, nanocoils, nanopillars and nanoflowers [52], Fig.4.



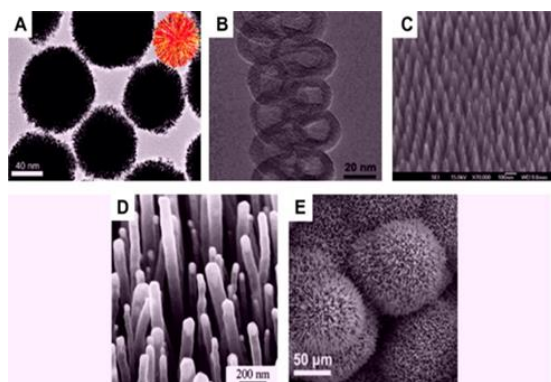
3 Fig 1: SEM and TEM images for various zero-dimensional (0D) ENMs. (A) Quantum dots, (B)  
 4 nanoparticles arrays, (C) core-shell nanoparticles, (D) hollow cubes and (E) nanospheres. Adopted  
 5 from [52].



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].



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

3

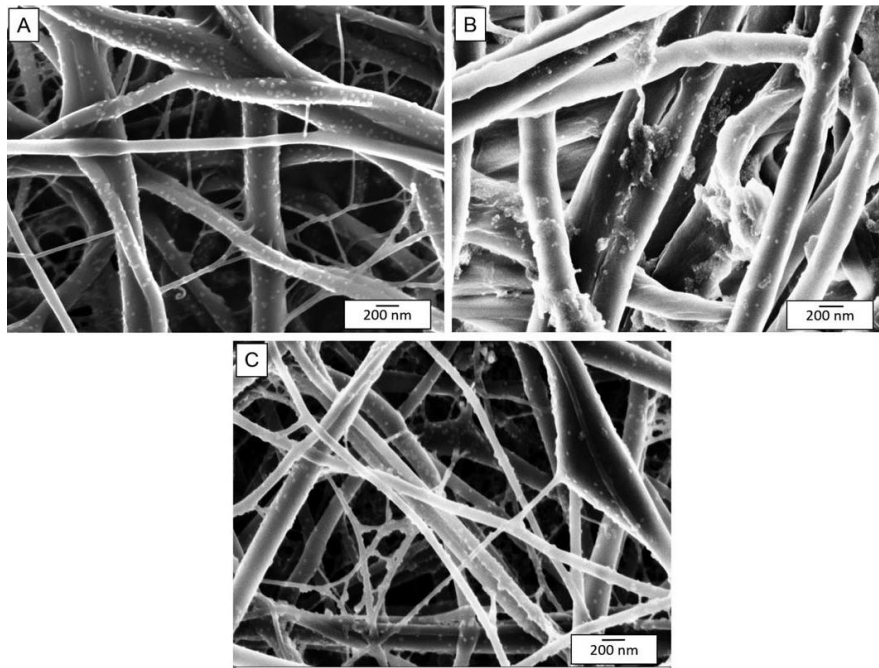
4 As material is distributed as smaller particles within a system (and the surface area to  
 5 volume ratio of particles increases) the proportion of surface atoms increases resulting in a  
 6 higher active surface area, e.g. 5 nm particles compose only a few  $10^3$  of atoms or unit cells,  
 7 and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

### 16 3. Strategies for incorporating ENMs into polymeric membranes

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



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



1 Fig 5: Comparison of FE-SEM images (A) simultaneous electrospin/electrospray, (B) LBL, and (C)  
 2 grafting [56].

3

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

15 **4. Influence of various ENMs on morphological and antifouling properties of**  
 16 **polymeric membranes.**

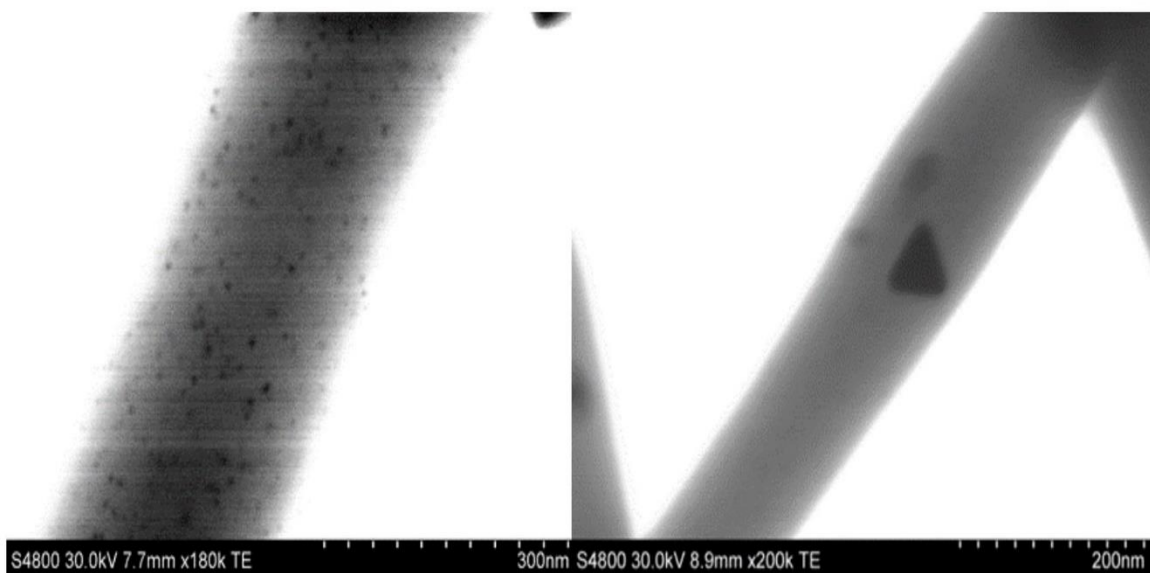
17 There are numerous ENMs that are available for the incorporation into polymeric membranes  
 18 to create innovative solutions that mitigate fouling, achieve high sustainable fluxes and  
 19 improve the chemical and physical response of the membrane material. This review now

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].



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

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

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

1 that smaller nanoparticles (8 nm) exhibited better bactericidal effects than larger nanoparticles  
2 (11-23) nm against *E. coli*. Similar observations have been reported in other studies [69, 76]

3 Ag-NPs have been widely used to prepare novel nanocomposite membranes with enhanced  
4 pure water flux, antifouling and self-cleaning properties with imperceptible or no effect on the  
5 membranes selectivity. According to Zodrow et al. [83], Ag-NPs impregnated into UF/PS  
6 membrane showed significant bactericidal effects to two species of bacteria; *Pseudomonas*  
7 *mendocino* and *E. coli*. The antimicrobial activity was mostly attributed to Ag<sup>+</sup> release.  
8 Moreover, the nanocomposite membrane restrained the bacterial attachment to the surface and  
9 inhibited biofilm growth. In addition, incorporation Ag-NPs enhanced the membrane surface  
10 hydrophilicity, water flux and mitigated other types of fouling. Similarly, Zhang et al. [84]  
11 prepared mixed matrix PES membrane using biogenic silver nanoparticles (bio Ag<sup>0</sup>) as  
12 additives. The surface of the nanocomposite membrane was tested to evaluate the attachment  
13 of *E. coli* and *P.aeruginosa*, (as pure cultures) and activated sludge (as a mixed culture). Results  
14 demonstrated that bio Ag<sup>0</sup> addition showed excellent antibacterial activity, prevented bacterial  
15 attachment and reduced the biofilm formation on the membrane surface during nine weeks of  
16 monitoring, whereas the control membrane was heavily fouled. Furthermore, a slight  
17 improvement in hydrophilicity was reported. Kim et al. [38] entrapped Ag-NPs in a thin film  
18 via interfacial polymerization on a polyethersulfone PES substrate containing acid modified  
19 MWCNTs, high antibacterial activities were achieved and low adhesion of *P. aeruginosa*  
20 (PA01) to the membrane surface was observed. Moreover, the thin-film nanocomposite (n-  
21 TFN) had better hydrophilicity and permeability compared to the original unmodified  
22 membrane while no change in roughness and rejection values for NaCl and Na<sub>2</sub>SO<sub>4</sub> were  
23 observed before or after Ag-NPs addition. This suggests that Ag-NPs did not effectively  
24 influence the membrane surface characteristics; pore size and pore distribution.

#### 25 **4.1.2 Copper based nanocomposite membranes (Cu-NPs)**

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

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

9 Recently, Isloor et al. [96] conducted novel research to immobilize atomic copper onto  
10 PS/modified poly isobutylene-alt-maleic anhydride blend membrane surface by a physical  
11 vapor deposition technique. The copper coated membranes exhibited slightly higher (96%) salt  
12 rejection and surface roughness with only a slight decrease in pure water flux. Further  
13 characterization to test the antimicrobial resistance of the coated membrane was investigated  
14 using the food poisoning organism *Bacillus. cereus*. Good inhibition was observed against  
15 bacterial growth indicating that copper deposition could be an effective technique for the  
16 fabrication of antimicrobial membranes. Akar et al. [85] studied two types of nanoparticles;  
17 Selenium (nSe) and copper (nCu). nSe were prepared by the reduction of aqueous sodium  
18 selenite solution with freshly prepared glucose solution, while nCu were prepared by  
19 sonochemical reduction of copper(II) hydrazine carboxylate  $\text{Cu}-(\text{N}_2\text{H}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  complex  
20 in an aqueous medium. The synthesized nanoparticles were incorporated, at (0.002, 0.010,  
21 0.030, and 0.050 wt.%), into UF/PES membrane via the classical phase inversion technique.  
22 The resultant nanocomposites were characterized with activated sludge as a biological  
23 suspension and bovine serum albumin (BSA) as a protein foulant model. The findings indicated  
24 good membrane antifouling properties against both of activated sludge and BSA. Moreover,  
25 the morphology, hydrophilicity and permeability of the nanocomposites were dependent on  
26 ENMs composition in the blend.

### 27 **4.1.3 Iron oxides based nanocomposite membranes (Fe-NPs)**

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

1 the nanoscale level. Their crystallographic structures provide high surface area/volume ratio  
2 and superparamagnetic properties that offer a high reactivity. In addition to their excellent  
3 magnetic and reactivity, they have low toxicity, high surface modifiability, great  
4 biocompatibility and are chemically inert [98, 99]. The unique features of iron oxide based  
5 nanoparticles (Fe-NPs), mainly magnetite ( $\text{Fe}_3\text{O}_4$ ) and maghemite ( $\gamma\text{Fe}_2\text{O}_3$ ), have encouraged  
6 many researchers to investigate these engineered magnetic nanoparticles in remediation and  
7 water treatments. Depending on the oxidation state of the iron, these magnetic nanoparticles  
8 possess different chemical properties. Indeed, they offer distinct capabilities and reactivity for  
9 contaminants removal [97]. Based on the aforementioned unique characteristics, the addition  
10 of Fe-NPs is believed to impart great potential to the fabrication of organo-mineral  
11 nanocomposite membrane with novel process control properties.

12 Impregnation of Fe-NPs into polymeric membranes is believed to introduce innovative  
13 solutions for many of the problems associated with polymeric membrane applications. In a  
14 recent study, Homayoonfal et al. [100] investigated the influence of iron oxide ( $\text{Fe}_3\text{O}_4$ )  
15 nanoparticles immobilised in PSF membranes. The nanocomposites were synthesized via three  
16 techniques; deposition by interfacial polymerization, deposition by photopolymerization and  
17 by blending into the polymeric matrix. These researchers concluded that the presence of  $\text{Fe}_3\text{O}_4$   
18 nanoparticles significantly enhanced membranes surface roughness, pure water flux, and  
19 surface hydrophilicity. The blending method performed better in terms of structural properties  
20 while deposition was better for dye separation yield. In another recent study, Rambabu et al.  
21 [101] studied the influence of Fe-NPs concentration on the resultant membrane composites. 0,  
22 1, 2, 3 and 4 wt.% of the NPs were blended with PES through the classical phase inversion  
23 method to fabricate Fe/PES-UF nanocomposite membrane. The results indicated that up to  
24 certain Fe-NPs concentration, synthesized membranes exhibited higher flux, thermal stability,  
25 and hydrophilicity than the original unmodified PES membrane. In addition, heavy metal ion  
26 ( $\text{Cu}^{+2}$  and  $\text{Zn}^{+2}$ ) rejection was slightly decreased due to the increased pore size and porosity  
27 induced by the nanoparticles addition. Ghaemi et al. [102] studied the influence of surface  
28 modified  $\text{Fe}_3\text{O}_4$  nanoparticles on NF membranes used for heavy metal removal. Fe-NPs  
29 modification was achieved by immobilization of metformine, silica, and amine. Thereafter,  
30 modified Fe-NPs were blended in a PES/NF membrane matrix at various compositions. Similar  
31 to the previously mentioned studies, results indicated that Fe-modified nanoparticles  
32 influenced the morphology of the membranes with higher porosity and larger pore size found  
33 in all nanocomposites except that contained amine modified NPs. In addition, a further increase

1 in surface roughness parameters, pure water flux and hydrophilicity were reported. However,  
2 the nanocomposite membrane prepared with 0.1 wt.% metformine exhibited a higher rejection  
3 for copper ions (92%) and higher membrane reusability due to the large number of N atoms  
4 around each particle which offered active adsorption sites through their lone electron pairs. In  
5 contrast to Ghaemi findings, Daraei et al. [103] reported a decrease in pure water flux at all the  
6 different loadings of 0.01, 0.1 and 1wt% of Fe-NPs and an increase in Cu(II) removal. Alam et  
7 al [43] prepared Fe<sub>3</sub>O<sub>4</sub>/PES nanocomposite membrane for desalination applications. Their  
8 results showed higher rejection values (68% and 82%) for NaCl and MgSO<sub>4</sub> respectively at 10  
9 % Fe- NPs loading. Furthermore, lower contact angle and smoother surfaces were obtained  
10 that showed promise for lower fouling properties.

#### 11 **4.1.4 Aluminium oxide based nanocomposite membranes (Al<sub>2</sub>O<sub>3</sub>-NPs)**

12 Similarly to other metal/metal oxide nanoparticles, Al<sub>2</sub>O<sub>3</sub> has also attracted interest for many  
13 applications that include surface protective coating, catalysis, fire retardation and composite  
14 materials [104]. However, due to their high adsorption capacity, resistance to chemical agents,  
15 and excellent catalytic performance for many reactions [105, 106] Al<sub>2</sub>O<sub>3</sub>-NPs have gained the  
16 attention of membrane technologists for the development of new nanocomposite membranes  
17 with novel properties.

18 Mehrnia et al [107] investigated the influence of alumina NPs on the morphology and  
19 performance of PSf nanocomposite membrane. Al<sub>2</sub>O<sub>3</sub>-NPs (70 nm) were blended into PSf  
20 membrane via a classical phase inversion method at a concentration ranging from 0-0.52 wt.%.  
21 The NPs loading threshold was found to be 0.39 wt.%. Nanocomposite prepared at the loading  
22 threshold was further evaluated, and the characteristics of the resultant nanocomposite were  
23 compared up to and below the loading threshold by rheometric analysis, contact angle  
24 measurements and SEM images. By adding the NPs, rheological features of the casting solution  
25 changed from a Newtonian fluid to a non-Newtonian one. Hydrophilicity of the  
26 nanocomposites was enhanced by increasing the loading weight even after the threshold.  
27 Raising the concentration of NPs up to 0.39 Wt.% resulted in porosity development, flux  
28 enhancement, and separation percentage reduction, while after this point, porosity diminished  
29 due to further increase in solution viscosity. In a similar study , Homayoonfal et al. [108]  
30 prepared Al<sub>2</sub>O<sub>3</sub>/PES nanocomposite membrane blend for membrane bioreactor applications.  
31 Two compositions were used (0.02 and 0.03 wt. %) in the preparation. The results suggested  
32 that the presence of alumina nanoparticles up to 0.03 wt. % in the mixed matrix membrane



1 could hinder biofilm formation and provide a 75% reduction in cake layer resistance and up to  
2 83% reduction in irreversible resistance. Thus, enhanced antifouling properties that was further  
3 confirmed by the reduced contact angle from 73 to 51. Furthermore, the pure water flux was  
4 more than four times that of the original PES membrane. Ghaemi et al. [109] investigated the  
5 ability of alumina NPs to improve adsorption of heavy metals and the removal efficiency of  
6 copper by PES membranes. Different amounts of alumina NPs (0.01, 0.1 and 1%) were blended  
7 to prepare the mixed matrix membrane. All membranes exhibited higher water permeability up  
8 to NPs loading  $\leq 1$  wt.% due to the enhanced porosity and hydrophilicity of the nanocomposites.  
9 In addition, larger microvoids in the support layer and thinner skin layer were also observed.  
10 Furthermore, copper removal efficiency was also improved. However, any further increase in  
11  $\text{Al}_2\text{O}_3$ -NPs wt.% did not show any change in the characteristics and performance of the  
12 nanocomposites. The authors suggested that the adsorption was the dominant separation  
13 mechanism in the nanocomposite membranes. In another study, a similar influence for alumina  
14 NPs on PES membrane morphology was observed, Arsuaga et al.[42] compared the influence  
15 of three different metal oxide nanoparticles,  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{Al}_2\text{O}_3$ , on PES membrane. The  
16 nanocomposites fouling behaviour was characterised by using BSA and humic acid as model  
17 organic foulants. Their research demonstrated that  $\text{Al}_2\text{O}_3$ /PES nanocomposite membrane had  
18 higher pure water flux, higher rejection, long-term stability and lower flux decline for both  
19 model foulants in comparison to the other nanocomposites and original membranes. This  
20 behaviour was attributed to the fact that  $\text{Al}_2\text{O}_3$  nanocomposite membrane has introduced more  
21 hydrophilic centers in the vicinity of the membrane surface, which reduced the possible  
22 adsorption of foulants. For MBR applications, Maximous et al [110] prepared  $\text{Al}_2\text{O}_3$  entrapped  
23 PES/UF membranes to characterize their fouling characteristics through activated sludge  
24 filtration. Nanocomposite membranes exhibited lower flux decline compared to nascent  
25 membrane. In addition to a greater fouling mitigation with increasing  $\text{Al}_2\text{O}_3$  content. In  
26 contrary with the previously mention literatures, Yan et al [111] found that the addition of  
27  $\text{Al}_2\text{O}_3$  NP did not show any influence on pore size and porosity of the nanocomposite  
28 membranes, while a noticeable enhancement was observed on surface hydrophilicity,  
29 permeation, antifouling and mechanical characteristic of the nanocomposites.

#### 30 **4.1.5 Titanium dioxide based nanocomposite membranes ( $\text{TiO}_2$ -NPs)**

31 Titanium dioxide ( $\text{TiO}_2$ ) is one of the most common materials in our daily life [112]. It is  
32 estimated that of all the nanoparticles in consumer products,  $\text{TiO}_2$  nanoparticles ( $\text{TiO}_2$ -NPs)

1 currently have the highest degree of commercialization [113]. However, TiO<sub>2</sub>-NPs excellent  
2 hydrophilic and photocatalytic properties have led to attention in environmental purification  
3 applications [112]. Under UV irradiation, TiO<sub>2</sub>-NPs show a superior capability to deactivate  
4 microorganisms and to decompose organic compounds [114, 115]. Materials with  
5 photocatalytic properties could offer the possibility to introduce such functionalities when  
6 incorporated into polymeric membranes [116].

7 According to Madaeni & Ghaemi [24], UV irradiation of TiO<sub>2</sub> nanocomposite membranes  
8 could impart two functionalities to the membranes; photocatalytic and ultra-hydrophilicity. As  
9 a consequence of photocatalysis, groups of active oxidant reagents appear on the surface of the  
10 membrane which leads to decomposition and removal of the membrane foulants. While, ultra-  
11 hydrophilicity could impart a self-cleaning property and increase the nanocomposite's water  
12 permeability as well. Kim et al. [117] prepared TiO<sub>2</sub>-NPs/TFC hybrid membrane via a self-  
13 assembly technique. The new nanocomposite membrane provided a substantial photo-  
14 bactericidal effect on *E coli* under UV light irradiation. In another study, Rahimpour et al.[41]  
15 investigated the impact of incorporating TiO<sub>2</sub>-NPs on the antifouling properties of PES/UF  
16 membranes for application in the dairy industry. Three sets of membranes were fabricated;  
17 TiO<sub>2</sub>-bended membranes, UV-irradiated TiO<sub>2</sub>-blended membranes, and UV-irradiated TiO<sub>2</sub>-  
18 deposited membranes. TiO<sub>2</sub> entrapped membranes showed lower milk water permeation and  
19 initial pure water flux in comparison to the original membrane. In contrast however, flux  
20 stability and fouling resistance were better in the long term. On the other hand, UV irradiation  
21 of TiO<sub>2</sub>-blended membranes added further enhancement to the flux and antifouling properties  
22 whereas coating exhibited superior affects, compared to the other membranes, to mitigate  
23 membrane fouling and to overcome PES hydrophobicity. In another piece of research, Li et al.  
24 [40] prepared a novel TiO<sub>2</sub> self-assembly nanocomposite membrane by immersing a blend  
25 membrane of poly (styrene-alt-maleic anhydride)/polyvinylidene fluoride (SMA/PVDF) in a  
26 suspension of TiO<sub>2</sub>. Their results demonstrated that permeability and antifouling properties  
27 against BSA were significantly improved when compared to the (SMA/PVDF) blend  
28 membrane. In another study, TiO<sub>2</sub> NPs were used to fabricate a novel polyamide-titanium oxide  
29 (PA-TiO<sub>2</sub>) nanocomposite membrane via *in-situ* interfacial polymerization [118]. Results  
30 demonstrated higher flux and hydrophilicity at 5 wt.% TiO<sub>2</sub>, with high and stable rejection to  
31 MgSO<sub>4</sub> (> 95%). In another study, Vatanpour et al. [119] investigated the impact of nano-TiO<sub>2</sub>  
32 type and size on the morphology, performance and antifouling properties of mixed matrix  
33 PES/NF membranes. Various types of TiO<sub>2</sub> nanoparticles (PC500, PC105, and PC25) were

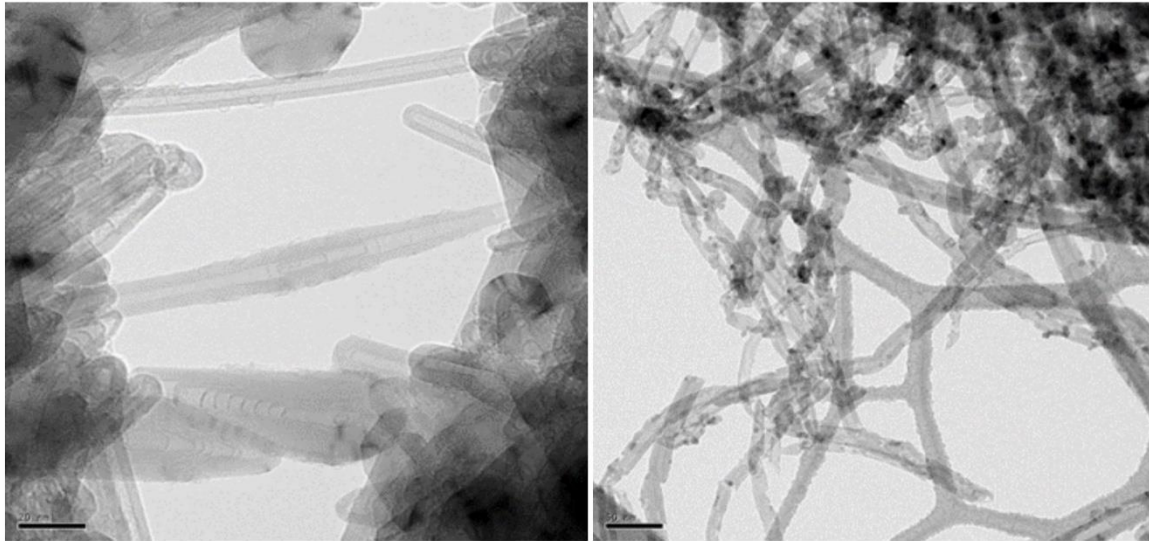
1 used in the preparation. Pure water flux and hydrophilicity, for all the blended membranes,  
2 were higher compared to that of the original PES membrane. However, after a particular  
3 concentration of TiO<sub>2</sub>, nanoparticles aggregation occurred. This aggregation was more severe  
4 in the case of PC105 and PC500 membranes and the increased concentration clogged the pores  
5 and reduced the pure water flux. Furthermore, the biofouling resulting from whey filtration  
6 tended to decrease with the smaller nanofiller size. More flux recovery was achieved due to the  
7 higher surface area and water adsorption affinity.

## 8 **4.2 Carbon-based nanomaterials**

### 9 **4.2.1 Carbon nanotubes (CNTs)**

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

23



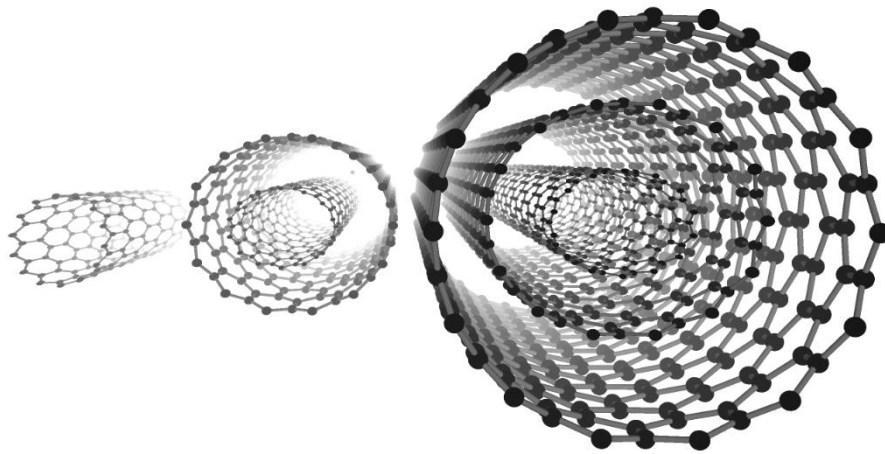
1 Fig 7: SEM images of CNTs. The left image presents CNTs (scale bar 20nm), the right image presents  
2 Fe-CNTs (scale bar 50nm).

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 MWCNTs-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  $\text{Na}_2\text{SO}_4$   
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,

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

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



11 Fig 8: Arrangement of graphene sheets to produce SWCNTs, DWCNTs and MWCNTs  
12 respectively (from left to right).

13

#### 14 4.2.2 Graphene (G) and Graphene Oxide (GO)

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

1 its incompatibility with organic polymers; this may create inferior composite properties [135,  
2 136]. To overcome the polymer incompatibility issues of pristine graphene, oxidation of  
3 graphene has been suggested to introduce highly hydrophilic and stable colloidal dispersions  
4 [137]. Graphene oxide (GO) is a highly chemically modified form of graphene that consists of  
5 a variety of functional groups, such as carboxylic acid at the edges and hydroxyl and epoxide  
6 groups on the basal plane. These functional groups can control the van der Waals forces and  
7 improve the compatibility with organic polymers to achieve better dispersion [138]., In recent  
8 years, incorporation of GO into polymeric membranes has gained more and more attraction.  
9 Various nanocomposite membranes have been fabricated to impart the exceptional  
10 characteristics of graphene into these membranes, like; PSF-GO [139, 140], PES-GO [141] and  
11 PVDF-GO [33].

12 According to Chang et al.[142], graphene oxide has demonstrated high hydrophilicity and  
13 anti-fouling properties against BSA when incorporated within PVDF/UF membrane, this is  
14 attributed to the electrostatic repulsion of GO, which acts as a barrier to prevent BSA adsorption  
15 on the nanocomposite membrane surface. Zinadini et al.[143] reported that carboxylic acid,  
16 hydroxyl and other functional groups of GO surfaces are migrated to the surface of the  
17 membrane during the phase separation fabrication process and thus enhanced the surface  
18 properties and hydrophilicity of the nanocomposite membrane. Similarly, these enhanced  
19 interactions and hydrophilicity were also reported in membrane bioreactor (MBR) applications  
20 using GO-PSF MMMs [144]. In addition, GO was also found to have antibacterial activities  
21 [145]. The presence of functional groups ensures high negative zeta potential and impedes  
22 attachment of biofouling and subsequent accumulation on the membrane surface [146]. Hu et  
23 al. [147] reported high toxicity to *Staphylococcus aureus* and *E. coli*, which was mainly  
24 attributed to the mechanical damage of the bacterial cell membrane caused by the sharp edges  
25 of GO as revealed by study using transmission electron microscopy TEM. In another study Yu  
26 et al. [141] found superior anti-biofouling properties for GO nanosheets modified by hyper  
27 branched polyethyleneimine (HPEI) when blended with PES/UF membrane.

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

1 is the stiffest and strongest material known [149]. It has been reported that the enhancement in  
 2 the mechanical properties of graphene-polymer composites is much higher than that of clay or  
 3 other carbon based polymer nanocomposites [150]. The enhancements of graphene-based  
 4 nanocomposites can be achieved at very low filler content in the polymer matrix [151]. A  
 5 comparative study was carried out by Zhang et al. [152], who studied the impact of blending  
 6 OMWCNTs, GO, and OMWCNTs-GO on the mechanical properties of PVDF ultrafiltration  
 7 membrane fabricated via a phase inversion technique. These researchers reported superior  
 8 enhancement in tensile strength, 12.86% and 43.94%, and elongation at break ,31.50% and  
 9 39.24%, for the OMWCNTs and GO synthesized composite membranes, respectively. Slightly  
 10 less mechanical performance was shown for the MWCNTs-GO/PVDF membrane due to the  
 11 bigger pore size that stemmed from the synergetic effect for the oxidized low-dimensional  
 12 carbon nanomaterials. Xu et al. [33] studied the influence of GO functionalization with 3-  
 13 aminopropyltriethoxysilane (APTS) on the mechanical properties of PVDF/UF membrane. The  
 14 tensile strength measurement of the f-GO/PVDF membrane was improved by 69% while the  
 15 elongation at break was 48% more in comparison to GO/PVDF. Thus, GO could be a promising  
 16 solution to fabricate hybrid membranes with excellent reinforced, antifouling and permeation  
 17 properties.

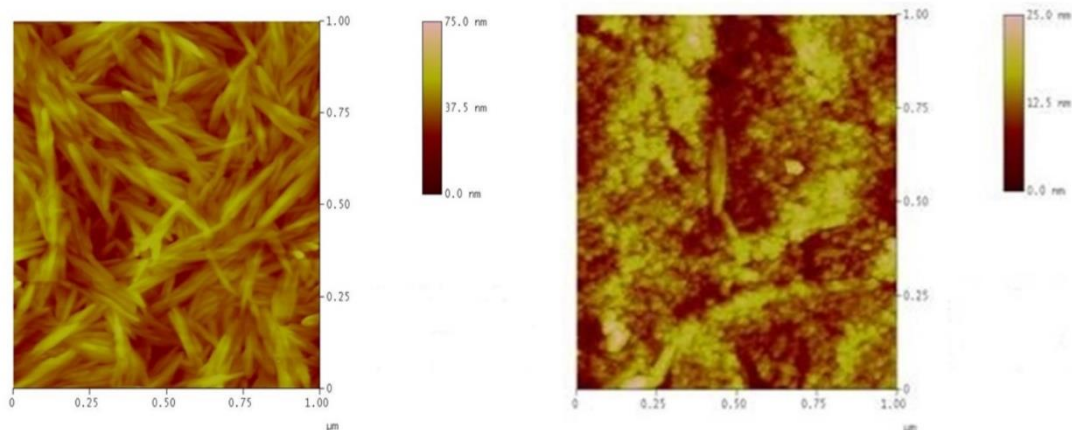
18

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

| <b>Materials</b>        | <b>Tensile strength</b> | <b>Thermal conductivity (W/mk) at room temperature</b>     | <b>Electrical conductivity (S/m)</b> |
|-------------------------|-------------------------|--|--------------------------------------|
| Graphene                | 130±10 GPa              | (4.84±0.44)×10 <sup>3</sup> to (5.30±0.48)×10 <sup>3</sup> | 7200                                 |
| CNT                     | 60–150 GPa              | 3500   | 3000–4000                            |
| Nano-sized steel        | 1769 MPa                | 5–6  | 1.35×10 <sup>6</sup>                 |
| 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                            |

### 1 4.3 Cellulose based nanoscale materials.

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



13 Fig 9: AFM images of dried cellulose nanocrystals (left) fabricated membrane impregnated with 4%  
14 cellulose nanocrystals (right)

15

16 Bai et al. [158] prepared CNC/PVDF mixed matrix membrane to investigate the influence  
17 of CNC composition (0.05-0.25 wt.%) on the nanocomposite performance. Their results  
18 demonstrated that CNC has great influence on the surface characteristics and morphology of  
19 the nanocomposites. For CNC content up to 0.1 %, pure water flux, porosity and mean pore  
20 size increased without significant change in BSA rejection. In addition, both elongation-at-  
21 break and the tensile strength of the nanocomposite improved as well, (from 84 to 150%) and  
22 (from 4.3 to 6.3 MPa) respectively. Similarly, Al malek [159] blended higher concentrations  
23 (2, 4, 6 wt.%) of CNC into PES membrane. Increasing the CNC content in the casting solution



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

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

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

| Type of membrane | Foulant  | Type of ENMs                   | Influence on modified membranes  | Ref.       |
|------------------|--|--------------------------------|--|------------|
| UF/PES           | - <i>Pseudomonas Mendocino</i> (KR1)<br>- <i>E. coli</i> (K12)<br>- <i>Virus</i> | Ag NP                          | -Improved hydrophilicity<br>-No effect on membranes surface charge and morphology<br>-Slight increase in pure water permeability<br>-Enhance antibacterial and virus removal, inhabited biofilm growth | [83]       |
| NF/PES           | - <i>P. aeruginosa</i> (PA01)  | Ag NP                          | -Enhanced antibacterial, hydrophilicity and permeability<br>-No effect on surface roughness, and salt rejection  | [38]       |
| UF/PES           | -Activated sludge<br>-BSA  | Cu NP                          | -Decreased permeability<br>-Increased hydrophilicity and protein rejection   | [85]       |
| UF/PES           | -Dye   | Fe <sub>2</sub> O <sub>3</sub> | -Improved hydrophilicity, surface roughness, dye removal and permeability  | [100]      |
| UF/PES           | -Heavy metals (Cu <sup>+2</sup> and Zn <sup>+2</sup> )                           | Fe <sub>3</sub> O <sub>4</sub> | -Enhanced hydrophilicity, water permeability, thermal stability<br>-Slight decrease in heavy metals rejection<br>-Increased pore size and porosity   | [101, 102] |

|         |  |                                |  |       |
|---------|--|--------------------------------|--|-------|
| UF/PES  | -BSA<br>-Humic acid                          | Al <sub>2</sub> O <sub>3</sub> | -Higher water permeability, hydrophilicity, rejection and long term stability<br>-Lower flux decline compared to neat membrane   | [42]  |
| NF/PES  | -Whey  | TiO <sub>2</sub>               | -Improved permeability and hydrophilicity<br>-Improved antifouling characteristics and flux recovery   | [119] |
| RO/PVA  | -Whey  | TiO <sub>2</sub>               | -Enhanced water permeability and self-cleaning property (reduced fouling and increased whey flux)<br>-Enhanced hydrophilicity and photocatalytic characteristics.              | [24]  |
| RO/PA   | -Ca(HCO <sub>3</sub> ) <sub>2</sub><br>- BSA | MWCNTs                         | -Enhance membrane surface charge.<br>-Affected the morphology.<br>-Increased water flux and slight decrease in rejection.<br>-Better antifouling and antioxidative properties. | [161] |
| UF/PVDF | -BSA   | GO                             | -Improved mechanical strength of modified membrane.<br>-Enhance, hydrophilicity, antifouling and permeation properties.  | [33]  |

1

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

3 Despite the huge attention and funding devoted so far to the applications of ENMs in membrane  
4 technologies, the commercialization of ENMs-membrane composites has yet to be achieved.  
5 In fact, with the marked demand of nanomaterials in the marketplace, there is a growing public  
6 debate whether the social and environmental cost of nanomaterials outweigh their benefits  
7 [162]. Apart from this debate, ENMs durability under various operation conditions as well as  
8 their degradability at the end of their service life represents the main challenges that have not  
9 yet been fully addressed [31, 54]. In polymeric membrane applications, incorporation of ENMs  
10 also has some obstacles. Predominantly, their limited dispersion in the casting solutions,  
11 especially for nanomaterials having a diameter less than 100 nm [3]. Poor dispersion results in  
12 nanomaterial agglomeration and uneven distribution in the polymeric matrix. This  
13 agglomeration may give rise to undesired changes in the nanocomposite membrane  
14 characteristics such as free surface energy, pore size, hydrophilicity, roughness and antifouling  
15 properties [163]. Weak interfacial interaction/adhesion between ENMs and the polymeric  
16 structure will end up in the leaching of these ENMs out of nanocomposite membranes, causing  
17 a gradual deterioration in the nanocomposite membrane over time, reducing performance

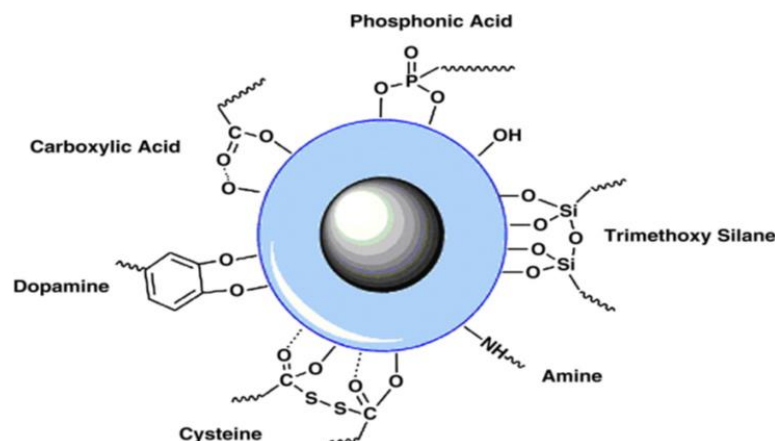
1 stability and potentially raising many environmental issues [164]. These weak interactions have  
2 been mainly attributed to poor polymer–inorganic incompatibility, poor polymer–particle  
3 adhesion, the different thermal expansion coefficients for the ENMs and the polymer, and  
4 solvent evaporation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

## 18 **6. Future improvements for ENMs incorporation into polymeric membranes.**

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

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

1 enables them to act as intermediate materials to link two dissimilar materials [169, 170].  
2 Polysiloxane has been used as a silane coupling agent, to chemically functionalize SiO<sub>2</sub>  
3 nanoparticles and then to immobilize PEG molecules on their surface [171]. The modified  
4 nanoparticles were then dispersed in a casting solution to prepare modified SiO<sub>2</sub>/ PVDF  
5 nanocomposite membranes. The stability of the chemically modified SiO<sub>2</sub> nanoparticles in the  
6 membrane matrix was significantly improved during membrane filtration processes and  
7 membrane cleaning, enabling the long-term usage of the blend membrane. A similar study,  
8 reported good dispersion for chemically modified TiO<sub>2</sub> in PES nanocomposite membrane when  
9 TiO<sub>2</sub> particles were first modified using Aminopropyltriethoxysilane (APTES) as a silane  
10 coupling agent [163]. In a similar study, a novel PA/TFN nanofiltration membrane was  
11 prepared by dispersing aminosilanized TiO<sub>2</sub> nanoparticles into a diamine monomer solution  
12 followed by polymerization [172]. The silane coupling agent was grafted onto the surface of  
13 TiO<sub>2</sub> to avoid agglomeration encouraged during the TFN preparation and to obtain a greater  
14 interfacial adhesion between the polymer matrix and TiO<sub>2</sub> nanoparticles. Functionalized  
15 graphene oxide (f-GO) nanosheets with 3-aminopropyltriethoxysilane (APTS) were found to  
16 have better dispersion in organic solvents than non-functionalized GO [33]. Polydopamine  
17 (PDA), also known as “bio-glue”, has been recently used as an excellent coupling ligand in  
18 nanocomposite membranes. Zhang et al. [173] conducted research to robustly bind TiO<sub>2</sub>  
19 nanoparticles on the surface of TFC membrane using PDA. PDA can be self- polymerized on  
20 TiO<sub>2</sub> and membrane surfaces forming a firm connection between them [174]. Similarly, TiO<sub>2</sub>  
21 nanoparticles have been strongly bound and homogeneously distributed into PVDF  
22 ultrafiltration membrane by exploiting PDA. Zhao et al.[175] uniformly embedded PDA  
23 modified MWCNTs (PDA-MWCNTs) in polyamide (PA) thin-film composite membranes.  
24 Their results demonstrated a fine dispersion for the coated MWCNTs in polyethyleneimine  
25 aqueous solutions, which was interfacially polymerized with trimesoylchloride n-hexane  
26 solutions to fabricate nanocomposite membranes. The improved compatibility/interactions  
27 between the modified MWCNTs and PA matrix were attributed to the PDA coating layer on  
28 the nanotubes surface. In another study, Khalid et al. [176] prepared functionalized MWCNTs  
29 with dodecylamine (DDA) that were then used to fabricate PS nanocomposite membrane for  
30 desalination applications. The long alkyl chains of DDA functionalized MWNTs were found  
31 to improve the interfacial interactions/adhesion and compatibility between inorganic nanotubes  
32 and polymeric matrix.



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

2

### 3 7. Conclusion

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

23

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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 <sup>+</sup>                 | Silver ions                                 |
| Ag-NPs                          | Silver nanoparticles                        |
| Al <sub>2</sub> O <sub>3</sub>  | Aluminum oxide                              |
| APTES                           | Aminopropyltriethoxysilane                  |
| APTS                            | 3-aminopropyltriethoxysilane                |
| bio Ag <sup>0</sup>             | 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 <sup>+2</sup>                | Iron(II)                                    |
| Fe <sup>+3</sup>                | Iron(III)                                   |
| Fe <sub>3</sub> O <sub>4</sub>  | Magnetite                                   |
| Fe-NPs                          | Iron nanoparticles                          |
| FE-SEM                          | Field Emission Scanning Electron Microscopy |
| f-GO                            | Functionalized Graphene Oxide               |
| G                               | Graphene                                    |
| γFe <sub>2</sub> O <sub>3</sub> | Maghemite                                   |
| GO                              | Graphene Oxide                              |
| HPEI                            | Hyper branched polyethyleneimine            |
| LBL                             | Layer By Layer                              |
| MBR                             | Membrane bioreactor                         |
| MgSO <sub>4</sub>               | Magnesium sulfate                           |
| MMMs                            | Mixed matrix membranes                      |
| MWCNTs                          | Multi- Walled Carbon Nanotubes              |
| Na <sub>2</sub> SO <sub>4</sub> | 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 <sub>2</sub>      | Silicon oxide                    |
| SMA                   | Styrene-alt-maleic anhydride     |
| SWCNTs                | Single-Walled Carbon Nanotubes   |
| TEM                   | Transmission Electron Microscopy |
| TiO <sub>2</sub>      | Titanium dioxide                 |
| TiO <sub>2</sub> -NPs | Titanium dioxide nanoparticles   |
| UF                    | Ultrafiltration                  |
| UV                    | Ultraviolet                      |
| ZnO                   | Zinc oxide                       |
| ZrO <sub>2</sub>      | Zirconium oxide                  |

1

2

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