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Engineering nanocomposite membranes: Addressing current challenges and future opportunities

Saif Al Aani [a], Chris J. Wright [b], Muataz Ali Atieh [c], Nidal Hilal [a,*]

[a] Centre for Water Advanced Technologies and Environmental Research (CWATER), College of Engineering, Swansea University, Fabian Way, Swansea SA1 8EN, UK
[b] Biomaterials, Biofouling and Biofilms Engineering Laboratory (B^3EL), The Systems and Process Engineering Centre (SPEC), College of Engineering, Swansea University, Fabian Way, Swansea SA1 8EN, UK
[c] Qatar Environment and Energy Research Institute, Qatar Foundation, PO Box 5825, Doha, Qatar

HIGHLIGHTS

- A comprehensive review of the engineered nanoscale materials (ENMs) used in the development of desalination and water treatment membranes.
- Discussion and analysis of the methods used to engineer nanocomposite membranes by incorporating ENMs in polymeric materials.
- Identification of the benefits of incorporating particular ENMs into polymeric membranes.
- Discussion of the problems associated with incorporating ENMs into polymeric membranes and the strategies adopted to overcome these.
- Future prospects for the development of nanocomposite membranes.

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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 the 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 ENM's 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.

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

* Corresponding author.
E-mail address: N.Hilal@swansea.ac.uk (N. Hilal).

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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.

Despite the relatively advanced state of the membrane industry, there are still some issues that need to be tackled for large-scale applications. The primary issue is membrane fouling, which is the main limiting factor in industrial membrane applications [5]. Membrane fouling occurs due to the accumulation of various solutes on the membrane surface and/or interior structure of the membrane, forming an additional barrier at the membrane surface or blocking the internal pores. This hinders the solvent from passing through the membrane, reducing permeation and raising the transmembrane pressure required to maintain the same productivity. Thus, ultimately shortening the membrane's lifespan. Moreover, fouled membranes may consume a massive amount of cleaning chemicals, which may also impact on the membrane surface and lead to membrane replacement in severe cases. The consequence of all these issues is to increase the operation and the maintenance costs of the water treatment unit [6–8]. The good selection of membrane materials available, operating design, pretreatment processes and conditions could mitigate the fouling phenomena to some extent; however, membrane sustainability is still problematical at the industrial scale and represents a challenging issue due to its complexity and variety [9,10]. For several decades, membrane 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.

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	Polyamide Polysulfone Polyol Polyphenol	Interfacial polymerization 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

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 environmentally 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 $<$10–20 nm; 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 to 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 includes nanorods, nanowires, nanobelts, nanotubes and hierarchical