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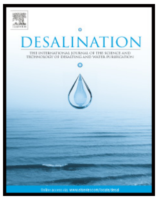

Promoted water transport across graphene oxide–poly(amide) thin film composite membranes and their antibacterial activity

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HIGHLIGHTS

- Graphene oxide was successfully incorporated into poly(amide) composite membrane.
- The membrane surface energy can be tuned by varying the amount of graphene oxide.
- GO sheets enhanced the water permeation properties of the fabricated PA membranes.
- Salt selectivity did not significantly decrease with graphene content increase.
- The novel composite membranes exhibited superior anti-microbial activity.

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ABSTRACT

Hybrid composite membranes have great potential for desalination applications since water transport can be favorably promoted by selective diffusion at the interface between matrix and reinforcement materials. In this paper, graphene oxide nano-sheets were successfully incorporated across 200 nm thick poly(amide) films by interfacial polymerization to form novel thin-film composite membranes. The impact of the graphene oxide on the morphology, chemistry, and surface charge of the ultra-thin poly(amide) layer, and the ability to desalinate seawater was investigated. The graphene oxide nano-sheets were found to be well dispersed across the composite membranes, leading to a lower membrane surface energy and an enhanced hydrophilicity. The iso-electric point of the samples, key to surface charge repulsion during desalination, was found to be consistently shifted to higher pH values with an increasing graphene oxide content. Compared to a pristine poly(amide) membrane, the pure water flux across the composite membranes with 0.12 wt.% of graphene oxide was also found to increase by up to 80% from 0.122 to 0.219 $L \cdot \mu m \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ without significantly affecting salt selectivity. Furthermore, the inhibitory effects of the composite membrane on microbial growth were evaluated and the novel composite membranes exhibited superior anti-microbial activity and may act as a potential anti-fouling membrane material.

1. Introduction

Membrane technologies are recognized as the most cost-effective processes for liquid purification and water desalination [1]. Nanofiltration (NF) and reverse osmosis (RO) are pressure driven desalination processes and offer an integrated solution to selective removal of salt and small contaminants from water. The membrane market reached $2.6 billion in 2013 and is expected to reach $3.7 billion by the end of 2014 [2]. The thin film composite (TFC) membranes used in NF or RO typically consist of an ultra-thin selective layer supported on a thick, porous and non-selective macro-porous layer [3]. Permeation across the TFC membranes occurs through interconnected sub-nanometer pores between the macro-molecular chains of the polymer matrix whose density will largely depend on the degree of cross-linking and the free volume between the macromolecular chains [4]. The performance of commercial TFC membranes is therefore limited due to the operational trade-off between maximizing water permeability and salt rejection across the selective layer [5] and membrane fouling [6]. Recently, routes to increase water permeability without compromising selectivity by modifying the chemistry or morphology of the active layer of TFC membranes were investigated. This led to the reduction of energy footprint, improvement in performance and the design of next generation pressure driven desalination membranes [4].

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The incorporation of inorganic nano-particles across NF or RO semi-permeable membranes was previously demonstrated to improve water permeation due to an increased hydrophobicity, changes of free volumes across the materials preventing diffusion of hydrated ions [7,8], and an increase in thermal stability, solvent resistance, lifetime, and antibacterial activity. The selectivity across the active layer of TFC membranes is directly related to the amount of free volumes across the thin active layer of the membrane [1,9] and the interactions between nano-additives and the polymer matrix should be investigated to understand how the liquid permeation can be enhanced and the salt diffusion across the membranes be prevented. Graphene has been studied as a possible separation material applicable to both gas and liquid media [10–15], and it is also known to be toxic to a wide variety of organisms including bacteria [16]. The use of graphene oxide (GO), a cheaper graphene source material, was also recently investigated through the formation of submicron thick membranes [15] by vacuum filtration of GO suspensions in water. Thin film graphene materials can be efficiently formed by vacuum filtration of well-dispersed graphene nano-sheet suspensions [14]. These membranes were shown to be impermeable to low molecular weight gases but to allow unimpeded permeation of water vapor due to a low-friction flow of a monolayer of water through two-dimensional capillaries formed by closely spaced GO sheets [15]. The presence of carboxyl, hydroxyl or epoxy groups on the surface of the GO sheets rendered the materials highly hydrophilic, therefore allowing for facilitated transport of water vapor between the graphene sheets upon wetting [15,17]. Recently, GO and its composites have been used for capacity deionization [18–20] and GO was also immobilized on the surface of TFC membranes in order to improve the resistance of membranes to fouling and chorine [21,22]. The development of high salt rejection composite graphene TFC membranes has however not been reported to date due to difficulties in the prevention of aggregation of individual GO nano-sheets during the fabrication of composite membranes, ultimately reducing selectivity by creating macro-defects [23].

One route that has been used to fabricate graphene based membranes from chemically converted graphene has shown potential application for nano-filtration where water molecules may permeate between graphene sheets across the polymeric matrix [14]. The water permeation rate of this new type of nano-filtration membrane is achieved by controlled corrugation of the graphene sheets through hydrothermal treatment of the chemically converted graphene suspension prior to vacuum filtration [14]. The chemical interactions between graphene nano-materials, primarily relying on van der Walls interactions render GO and pure graphene based assemblies relatively fragile and sensitive to swelling by hydration [24,25]. These disadvantages may be overcome by intercalating well-dispersed graphene nano-sheets across a polymeric matrix to promote water transport and improve membrane performance [25–30]. Such an approach was demonstrated for a number of membrane structures, including porous ultra-filtration membranes [30,31], semi-permeable nano-filtration [25,26, 32], pervaporation [32] and gas separation [33] applications. These new membranes exhibited improved pore structure, increased hydrophilicity and higher water permeation, opening the route to the design of advanced graphene reinforced membranes for pressure driven separation [2].

In this paper, the influence of blended GO sheets on the performance of poly(amide) TFC membranes has been investigated for the first time. GO nano-sheets were incorporated across poly(amide) thin films during interfacial polymerization to form novel nano-composite membranes. The GO poly(amide) composite membranes offer much improved liquid permeation during pressure driven operation compared to pure poly(amide) materials due to promoted water transport at the GO surface suspended across the poly(amide) player. The structure and properties of the nano-composite membranes will be discussed and correlated to their desalination performance and specific transport mechanisms. The inhibitory effects of the composite membrane on microbial growth will also be evaluated.

2. Experimental

2.1. Materials

Natural graphite (particle size < 45 μm), m-phenylenediamine (MPD), trimesoyl chloride (TMC), n-hexane (95%), H_2SO_4 (purity 98%), $KMnO_4$ (purity 99%) H_2O_2 (30% aqueous solution) and NaCl were purchased from Sigma-Aldrich and used as it is. Ultrafiltration (UF) poly(sulfone) supporting membranes (GE Osmonics Poly(sulfone) UF ER Membrane) with 30,000 molecular weight cut-off (MWCO) were purchased from Sterlitech (US) and used as backing materials for the fabrication of nano-composite membranes. Ultrapure Milli-Q® water was used in all filtration experiments.

2.2. GO synthesis

GO nano-sheets were synthesized from natural graphite by a modified Hummers method [34]. In brief, GO was prepared by the oxidation of graphite using $KMnO_4$ as an oxidizing agent. 30 mL of H_2SO_4, 0.5 g of $NaNO_3$ and 1 g of natural graphite were placed in a flask and vigorously stirred for 1 h at 0 °C. 5 g of $KMnO_4$ was then slowly added to the suspension, while maintaining the temperature below 20 °C throughout the addition and then kept under vigorous stirring for 1 h. The temperature of the suspension was then slowly raised to 38 °C and held for 12 h. This step was followed by the slow addition of 100 mL of water to the reaction vessel. Then the temperature was raised to 98 °C until the formation of a light brown color solution, characteristic of GO suspensions. At this point, the mixture was stirred at 98 °C for 15 min to finalize the exfoliation prior to adding 6 mL of hydrogen peroxide (30 wt.% in water) in order to initiate the oxidation which changed the color of the suspension from brown to dark yellow. The reaction mixture was then thoroughly washed 5 times with 100 ml of HCL solution at 10 wt.% and eventually ultra-sonicated for 30 min to fully exfoliate the remaining macro-particles into dingle GO sheets. The suspension of GO was further diluted in water and centrifuged at 3000 rpm for 20 min 3 times to remove any remaining graphite particulates. The as-synthesized GO suspension was then dialyzed to remove remaining salt and acid residues from the synthesis process. The GO was then suspended in water at a concentration of 120 g/L.

2.3. Fabrication of GO/poly(amide) TFC membranes

The poly(amide) TFC membranes were prepared by interfacial polymerization (IP) of a GO–poly(amide) composite layer on the surface of ultra-filtration (UF) poly(sulfone) (PSf) supporting membranes [35]. The PSf supporting membranes were immersed into an aqueous solution of MPD (2 wt.% in water) and allowed to soak for 1 h. The soaked PSf membranes were then removed from the MPD solution and their top surface rolled with a soft rubber to eliminate excessive solution resulting from soaking. Excessive solution was evaporated in air at room temperature for 5 min. Then, the soaked PSf membranes were clamped between two Teflon frames and the TMC solution (0.15 wt.% in hexane) was poured onto the top surface of the supporting membrane and allowed to be in contact for 1 min, which resulted in the formation of an ultrathin film over the PSf membrane. Excessive organic solution was removed from the surface through 5 successive surface rinsing with hexane, and the membrane, maintained within the frame, was heat cured at 70 °C for 10 min to ensure complete polymerization. Finally, the resulting membrane was sequentially washed with deionized (DI) water and stored in DI water. The amount of GO within the aqueous MPD solution was controlled and varied between 0.005 and 0.3 wt.% prior to soaking the PSf supporting membrane. The solutions containing the GO nano-sheets in MPD were ultra-sonicated prior to contacting the PSf supporting membrane in a bath sonicator (SONICLEAN, South Australia) for 20 min at 240 W in order to ensure homogeneous sheet suspension. The membranes will be designated