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Polyamide-crosslinked graphene oxide membrane for forward osmosis

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ABSTRACT

A novel polyamide-graphene oxide (PA-GO) membrane was synthesized on a polyethersulfone support by first intra-crosslinking GO aggregates via m-xylylenediamine (MXDA) and then inter-crosslinking GO aggregates via trimethyle chloride (TMC). This method allows for the use of hydrophilic, more porous supports in forward osmosis (FO) membranes, thereby lending much flexibility to membrane synthesis and also potentially reducing internal concentration polarization in FO. The elemental composition, morphology, and hydrophilicity of the synthesized PA-GO membrane were characterized to confirm intra- and inter-crosslinking reactions and understand membrane properties. It was found that the mixing temperature of MXDA and GO should be controlled below 20 °C to avoid the formation of large GO aggregates and hence reduce membrane heterogeneity and defects. The performance of the PA-GO membrane was compared with that of a commercial FO membrane using trisodium citrate (TSC), Na_2SO_4, and $MgCl_2$, respectively, as draw solutes. Under the same osmotic pressure, the water flux of the PA-GO membrane was the highest with TSC as draw solute, moderate with Na_2SO_4, and almost zero with $MgCl_2$, while the ranking of solute fluxes followed a reverse order, revealing that an effective solute barrier plays an important role in making FO membranes with high water flux and low solute flux.

1. Introduction

Membrane processes are among the most effective technologies to remove contaminants from water and thus address the global water shortage. Over the past decades, extensive research efforts have been made to advance the membrane technology with many important applications in desalination [1], water purification [2], and wastewater reuse [3]. In particular, the emerging nanotechnology has opened up new opportunities for innovation in membrane materials. As one of the most promising nanomaterials, the two-dimensional (2D) graphene oxide (GO) nanosheets can be used to make novel membranes via simple, scalable layer-stacking techniques, providing great flexibility to control the interlayer spacing (equivalent to the cylindrical pores in conventional polymeric membranes), charge, and functionality of the resulting GO membrane for improved separation capability and filtration efficiency [4–10]. Besides, the thickness of the GO membrane can be easily adjusted by using a different number of GO layers [11], thereby conveniently tailoring the membrane performance [12]. In the meantime, many of the biological and physicochemical properties of GO, such as photocatalytic, antibacterial, and highly hydrophilic properties, potentially enable the multifunctionality of the GO membrane toward enhanced contaminant removal and fouling control [13–18]. Equally important, because GO nanosheets can be mass-produced by oxidizing and exfoliating graphite as an inexpensive raw material, the scaled-up fabrication of GO membranes is expected to be both facile and economical.

GO membranes have demonstrated excellent separation performance in nanofiltration (NF) [6] and forward osmosis (FO) processes [7]. Unlike the hydraulic pressure-driven NF process, FO is a membrane process driven by the osmotic pressure gradient across a semipermeable membrane. Due to many of its advantages, including low fouling potential [19–21] and capability of using low-grade heat as the major energy source [22], FO has found various applications in wastewater treatment, membrane bioreactors, sustainable power generation, desalination, and food processing [23]. Compared with the performance (e.g., water flux and selectivity) of an NF membrane primarily determined by its active layer, the performance of an FO membrane is significantly affected by its support layer as well due to the internal concentration polarization [24,25], which hinders the diffusion of solutes within the porous structure of the support layer and decreases the effective osmotic driving force for water flux. Therefore, in order to develop high-performance (e.g., high selectivity and high water flux) FO membranes, it is extremely critical to manipulate the structure of the membrane support layer so that its resistance to solute transport can be minimized [26–28]. Typical strategies include decreasing the tortuosity, increasing the porosity, and improving the hydrophilicity of the

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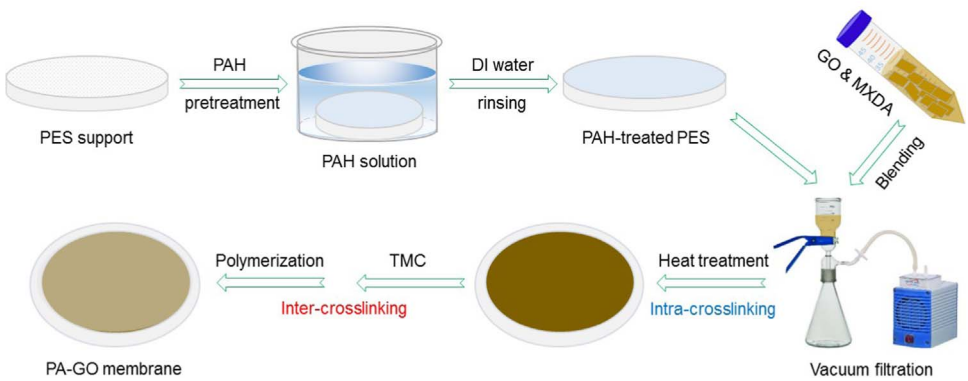

Fig. 1. Schematic diagram for the synthesis of the PA-GO membrane on a polyethersulfone (PES) support by first intra-crosslinking GO aggregates via m-xylylenediamine (MXDA) and then inter-crosslinking GO aggregates via trimesoyl chloride (TMC).

support layer [29].

So far, research on the use of GO to optimize the structure of FO membranes for enhanced performance, in particular reduced internal concentration polarization, has been rather limited. Recently, an FO membrane was synthesized by layer-by-layer assembly of GO and polyelectrolyte on both sides of a support layer [7]. The resulting membrane achieved separation from both sides and thus reduced the internal concentration polarization within its support layer. Note that such a "double-skin" approach was also proven in other studies to be effective in achieving water flux an order-of-magnitude higher than that of commercial FO membranes [30,31]. However, the corresponding ionic solute flux of the double-skinned GO membrane was also much higher due to the swelling (i.e., enlargement of interlayer spacing) of the GO membrane soaked in aqueous solutions. Therefore, GO nanosheets, the building blocks forming a GO membrane, must be appropriately treated (e.g., chemically crosslinked) in order to mitigate membrane swelling and thus decrease solute flux.

In view of polyamide (PA) membrane as a gold standard for today's aqueous phase separation due to its well-balanced selectivity and permeability [32], the integration of PA and GO during membrane synthesis may offer a viable route for reducing the solute flux of a GO membrane. So far, a common strategy for integrating PA and GO has been the incorporation of GO into the polymer matrix of either the active layer or support layer of a PA membrane. It was found that blending GO into the PA active layer during interfacial polymerization not only improved the water flux in FO mode [33] but also enhanced the natural organic matter removal and antifouling properties [34]. Similarly, embedding GO into the polysulfone (PSf) support layer during phase inversion resulted in a composite PA membrane that exhibited a water flux three times that of a membrane with a pristine PSf support [35].

Despite the fruitful development of GO-enhanced PA membranes for FO applications, a fundamental issue remains to be addressed. That is, synthesis of high-performance PA-based FO membranes ideally demands that a support layer be highly hydrophilic, thin, and structurally open in order to minimize the internal concentration polarization [36,37]. However, it is very challenging to fabricate a PA active layer with satisfactory membrane integrity via interfacial polymerization on such an ideal type of support [37], thus often ending up with the use of a hydrophobic PSf support layer that has a sponge-like internal structure with surface pore sizes in a range of 10–20 nm. To circumvent this issue, it is highly desirable to seek alternative strategies for synthesizing PA-GO membranes with separation performance not so much restricted by the support layer properties.

In the present study, we developed a novel membrane synthesis method that aims to take full advantage of the appealing properties of GO and PA while lessening the typical reliance of PA membrane performance on support layer properties. The PA-GO membrane was synthesized on a highly porous polyethersulfone (PES) support via both intra- and inter-crosslinking of GO aggregates. The elemental composition, morphology, and hydrophilicity of the synthesized PA-GO membranes were characterized, and their water and solute flux performances were systematically tested in an FO system and critically compared with those of a commercial FO membrane.

2. Materials and methods

2.1. Chemicals

The PES ultrafiltration membrane (PES00347100, Sterlitech, Kent, WA), with a nominal pore size of 30 nm, was used as a support layer for GO deposition and crosslinking. Analytical reagent grade m-xylylenediamine (MXDA) monomer was purchased from Aladdin Industrial Corporation (Nashville, TN). Poly-allylamine-hydrochloride (PAH), trimethyl chloride (TMC), phenol, and hexane were obtained from Sigma-Aldrich (St. Louis, MO). Deionized (DI) water was used for solution preparation and experimental washing.

2.2. Membrane synthesis by intra and inter-crosslinking

The procedure for PA-GO membrane synthesis is schematically illustrated in Fig. 1. In the first step, the PES membrane support was pretreated by soaking it in PAH solution (1 g/L) for 30 min on a shaking table to deposit a layer of positively charged PAH on the PES surface. A suspension of MXDA-intra-crosslinked GO aggregates was prepared in parallel. To do so, an aqueous suspension of GO (1 g/L, pH 4) was prepared by a modified Hummers' method with the detailed procedure described in our previous work [6], and 15 mg MXDA monomer was dissolved in 100 mL DI water with 1 g/L phenol via vortex mixing. The resulting MXDA solution was added dropwise to the GO suspension with a volume ratio of 1:1 in an ice bath under vigorous stirring. As the second step, the fresh MXDA-GO suspension was filtered through the PAH-treated PES membrane using vacuum filtration at room temperature (25 °C) and under an absolute pressure of −0.7 bar to form an MXDA-GO thin film on top of the PES membrane, which was then heated in an oven at 80 °C for 2 h to enhance the intra-crosslinking of GO by MXDA. In the third step, the MXDA-GO membrane was contacted with TMC dissolved in hexane for 90 s at room temperature to allow the PA chemistry-based inter-crosslinking to seal the large gaps between GO aggregates in the membrane. The PA-crosslinked GO (PA-GO) membrane was then heated in an oven at 60 °C for 15 min to end the reaction and remove residual solvent. As the last step, the membrane was cleaned at least three times by soaking it in DI water and then stored in a 4 °C refrigerator until use. Note that, by varying the loading (1, 2, and 3 mL, respectively) of MXDA-GO suspension used in the second step, membranes with different active layer thicknesses were obtained and designated as PA-GO1, PA-GO2 and PA-GO3, respectively. Considering the density of a GO film falls in the range of 1–1.5 g/cm^3 [38], the 1-mL loading led to an active layer thickness of 400–600 nm for the PA-GO1 membrane, and the thickness doubled and tripled for