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# Graphene oxide incorporated thin-film composite membranes for forward osmosis applications

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## H I G H L I G H T S

- TFC FO membranes are fabricated with GO incorporated PA layer.
- GO nanosheets are covalently bonded to the polyamide chains.
- GO-incorporated TFC membranes exhibit enhanced hydrophilicity and water flux.
- GO-incorporated TFC membranes also exhibit low fouling propensity.
- The optimized GO loading in the PA layer is about 400–600 ppm.

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## A B S T R A C T

In this work, graphene oxide (GO) nanosheets are synthesized and incorporated into the polyamide (PA) selective layer to develop a novel thin-film composite (TFC) membrane for forward osmosis (FO) application. The chemical structure and morphology of the synthesized GO and GO-incorporated TFC membranes are studied by various characterization techniques. Compared with the control TFC membrane, GO-incorporated TFC membranes exhibit higher water flux and reasonable draw solute rejection. The effects of the GO loading on the membrane morphology and FO performance of the GO-incorporated TFC membranes are investigated systematically in terms of various characterizations and intrinsic separation performance. The influence of the draw solution concentration is also studied. The GO-incorporated TFC membranes also possess lower fouling propensity in FO test than that without embedded GO.

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**Abbreviations:** CaCl<sub>2</sub>, calcium chloride; CNT, carbon nano-tube; DMF, N,N-dimethylformamide; DI, deionized; FESEM, field emission scanning electron microscope; FTIR, Fourier transform infrared; FO, forward osmosis; GO, graphene oxide; IP, interfacial polymerization; HCl, hydrochloric acid; H<sub>2</sub>O<sub>2</sub>, hydrogen peroxide; HPAN, hydrolyzed polyacrylonitrile; H<sub>2</sub>SO<sub>4</sub>, sulfuric acid; KH<sub>2</sub>PO<sub>4</sub>, potassium dihydrogen phosphate; KMnO<sub>4</sub>, potassium permanganate; LBL, layer-by-layer; LiCl, lithium chloride; MgSO<sub>4</sub>, magnesium sulfate; MMM, mixed matrix membrane; MnO<sub>2</sub>, manganese dioxide; MPD, m-phenylenediamine; NaCl, sodium chloride; NaHCO<sub>3</sub>, sodium bicarbonate; NaNO<sub>3</sub>, sodium nitrate; NaOH, sodium hydroxide; NF, nanofiltration; NH<sub>4</sub>Cl, ammonium chloride; ODMP, osmotic driven membrane process; PA, polyamide; PAN, polyacrylonitrile; PDMP, pressure driven membrane process; RO, reverse osmosis; SA, sodium alginate; SEM, scanning electron microscopy; TEM, transmission electron microscopy; TFC, thin-film composite; TMC, 1,3,5-trimesoyl chloride; XRD, X-ray diffractometer; ZIF, zeolitic imidazolate framework

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## 1. Introduction

Nowadays, the scarcity of fresh water has terribly constrained the sustainable development of public health, ecosystem, economy, and so on. To solve this global water scarcity problem, extensive researches have been devoted to explore novel technologies for desalination and wastewater reclamation within acceptable cost. Although various techniques including the solvent extraction, distillation and pressure driven membrane processes for water treatment have achieved lots of achievements, high energy consumption of above processes restricts their further development. Alternatively, forward osmosis (FO), an osmotically driven membrane process (ODMP) which utilizes the osmotic pressure difference across the permeable membranes for driving force, has drawn more and more attention in past decades. Since there is low or no hydraulic pressures required, the FO technology exhibits many potential advantages, such as relative low energy

consumption (McGinnis and Elimelech, 2007), high water recovery (Martinetti et al., 2009) and low fouling propensity (Achilli et al., 2009; Mi and Elimelech, 2010) compared to these pressure driven membrane process (PDMP) like reverse osmosis, nanofiltration, microfiltration and ultrafiltration.

FO membrane is the heart of a successful FO technology with a good separation performance. A desirable FO membrane should own high water permeability, high solute rejection, superior anti-fouling property and good stability. In past years, membrane scientists have developed various FO membranes towards this target, including cellulosic membranes (Ong and Chung, 2012; Su et al., 2010; Zhang et al., 2011), thin film composite (TFC) membranes (Liu et al., 2015a; Sukitpaneenit and Chung, 2012; Wang et al., 2015; Wang and Xu, 2015), layer-by-layer (LBL) self-assembled membranes (Qi et al., 2012; Saren et al., 2011), and so on. Among them, TFC membranes, fabricated by the formation of the polyamide layer on the substrate via interfacial polymerization (IP), have gained much attention for water treatment applications because of the excellent separation performance over a wide operation temperature and pH ranges.

However, conventional TFC membranes also face problems of low water flux and fouling propensity ascribed to their relative hydrophobic surfaces formed by TMC and MPD monomers (Rana and Matsuura, 2010). Many efforts have been devoted to solve these issues by appropriate modification approaches, such as using additives or surfactants in the monomer solutions (Cui et al., 2014), immersing the nascent PA membrane into active solvent (Li et al., 2013; Zhang et al., 2013), and grafting the hydrophilic polymer chains (Bernstein et al., 2011; Lu et al., 2013), zwitterions (Azari and Zou, 2012; Mi et al., 2015; Yu et al., 2014) or nanoparticles (Tiraferri et al., 2012) on the membrane surface of the PA layer. Recently, various nano-structured materials have been widely employed to be incorporated into the PA selective layer of the TFC membrane to improve the membrane performance in membrane separation processes and shown a great performance enhancement with a reasonable particle loading, including inorganic salt (Emadzadeh et al., 2015; Ghanbari et al., 2015), zeolite (Dong et al., 2015; Huang et al., 2013; Liu et al., 2015b), zeolitic imidazolate framework (ZIF) (Duan et al., 2015; Sorribas et al., 2013), carbon nano-tubes (CNT) (Amini et al., 2013; Shen et al., 2013), graphene oxide (Safarpour et al., 2015), etc.

Among them, graphene oxide, a novel and promising two-dimensional carbon nanomaterial, has attracted great attention in the field of material research. Its excellent physical properties coupled with flexibility in chemical functionalization ascribed to the abundant oxygen-containing functional groups, make GO a good candidate for various applications (Han et al., 2013; Sun et al., 2011; Wang et al., 2011). Recently, the eccentric water permeability of a graphene oxide membrane (Huang et al., 2014; Joshi et al., 2014; Nair et al., 2012) was reported in the membrane separation field. Later, incorporating GO into the polymer matrix to form mixed matrix membranes (MMMs) has been reported to enhance the membrane hydrophilicity and anti-fouling property (Chang et al., 2014; Xu et al., 2014). But the anti-microbial effect becomes unavailable when GO was buried within the bulk polymer matrix compared to that being incorporated onto the membrane surface (Liu et al., 2011; Tu et al., 2013). Previous researches have incorporated GO in the membrane in the selective layer by layer-by-layer self-assembling (Choi et al., 2013; Kim et al., 2013) or chemical crosslinking (Perreault et al., 2013), and achieved improved separation performance with enhanced water permeability, chlorine resistance, or anti-fouling property. However, those membranes prepared by above methods may suffer the water permeability decline with time since the GO coating layer may interfere with water permeation (Chae et al., 2015).

In this study, novel TFC membranes for FO applications are fabricated with GO-incorporated into the PA selective layer by interfacial polymerization, using an aqueous mixture of *m*-phenylenediamine (MPD)–GO solutions. Similar works have been demonstrated in previous works for RO (Chae et al., 2015) and NF (Bano et al., 2015) applications with different GO loadings, but no any work has been reported for FO applications so far. This works studies the structure, morphology and fundamental properties of the synthesized GO and the GO-incorporated PA layer with detailed characterizations. Effects of GO loading on the membrane morphology, intrinsic separation performance, FO performance and antifouling performance of the resultant TFC membranes are also investigated systematically.

## 2. Materials and methods

### 2.1. Materials

Natural flake graphite (average particle diameter of 40 mm, 99.95% purity) was purchased from Qingdao Hengsheng graphite Co. Ltd. (China). Polyacrylonitrile (PAN) powder (Mn: 250,000 Da) was purchased from Chushengwei Chemistry Co. Ltd. (Hubei, China), and dried in the vacuum oven at 80 °C for overnight before use. The *m*-phenylenediamine (MPD, 99.5%) and 1,3,5-benzenetricarbonyl trichloride (TMC, 98%) were obtained from Aladdin and kept in refrigerator before use. Concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, ≥ 70%), potassium permanganate (KMnO<sub>4</sub>, 99.5%), sodium nitrate (NaNO<sub>3</sub>, ≥ 99%), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%), concentrated hydrochloric acid (HCl, 16–18%), lithium chloride (LiCl, 97%), *N,N*-dimethylformamide (DMF, anhydrous, ≥ 99.5%) and ethanol (≥ 99.7%, anhydrous), sodium hydroxide (NaOH, ≥ 96%), *n*-hexane (≥ 97%, anhydrous), sodium chloride (NaCl, ≥ 99.5%), sodium alginate (SA, Mw: 98.11), potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>, 99.5%), magnesium sulfate (MgSO<sub>4</sub>, 99%), sodium bicarbonate (NaHCO<sub>3</sub>, 99.5%), calcium chloride (CaCl<sub>2</sub>, 96%) and ammonium chloride (NH<sub>4</sub>Cl, 99.5%) were all purchased from China National Medicine Corporation.

### 2.2. Synthesis and characterization of graphene oxide (GO)

Graphene oxide (GO) was synthesized from graphite powder by the modified Hummer's method (Jiang et al., 2014). The reaction mechanism is shown in Fig. S-1 in the Supplementary information. In brief, 2 g graphite and 2.5 g NaNO<sub>3</sub> were added into a 500 ml three-necked flask with 150 ml concentrated sulfuric acid solution, and then stirred under an ice bath. After that, 15 g KMnO<sub>4</sub> was slowly added under vigorous stir with the temperature maintained below 20 °C, to allow the mixture to react under stir for overnight at room temperature. Then 180 ml DI water was slowly added, and the reaction was continued for 24 h with the temperature raised to 98 °C. Next, 80 ml 35 wt% H<sub>2</sub>O<sub>2</sub> aqueous solution was added to reduce the residual KMnO<sub>4</sub> and MnO<sub>2</sub>. The obtained mixture was rinsed repeatedly with 10 wt% HCl aqueous solution to remove metal ions. Subsequently, the mixture was dialyzed by the dialysis bag with MWCO of 3500 Da for one week. Finally, the obtained product was freeze-dried for two days to obtain the sheet-like graphite oxide.

The fractionated GO was characterized by Fourier transform infrared (FTIR) (Tensor 27, Bruker, USA), with the wavenumber range of 4000–400 cm<sup>-1</sup> and a resolution of 2 cm<sup>-1</sup>, and an average of 16 scans was taken. Its morphology was observed using a scan electron microscopy (SEM, VEGA3, TESCAN, Czech) and an atomic force microscope (SPM9700, Shimadzu, Japan). The SEM sample was prepared by attaching the graphite oxide powder onto the conducting tape, and being coated with gold using a sputter

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