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High water permeable free-standing cellulose triacetate/graphene oxide membrane with enhanced antibiofouling and mechanical properties for forward osmosis

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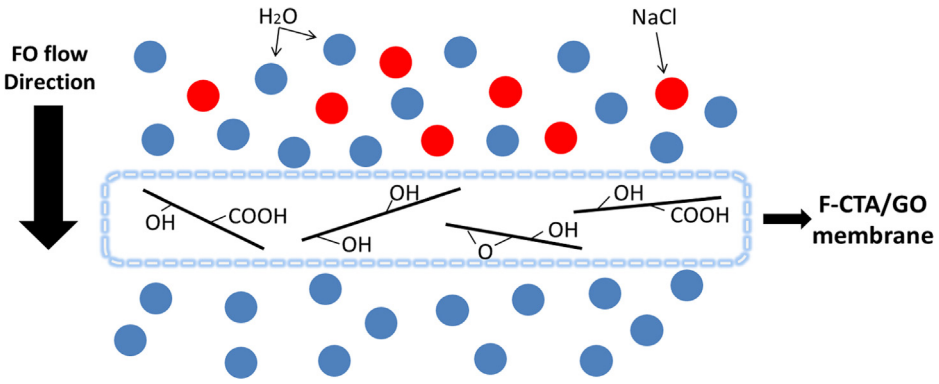
HIGHLIGHTS

- Free-standing cellulose triacetate (F-CTA)/graphene oxide (GO) membranes without substrate support layer were prepared.
- Free-standing structure effectively reduced the water resistance and effect of internal concentration polarization.
- Incorporation of GO enhanced water flux and salt rejection of the F-CTA membrane.
- F-CTA/GO exhibited remarkable resistance to biofouling.
- F-CTA/GO showed high tensile strength and modulus, ensuring excellent mechanical stability of the free-standing membranes.

GRAPHICAL ABSTRACT



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ABSTRACT

Free-standing cellulose triacetate (F-CTA)/graphene oxide (GO) membranes for forward osmosis were fabricated by means of phase inversion. The membranes exhibited low water resistance and degree of internal concentration polarization (ICP). The improvement was attributed to the absence of support layer in the free standing membranes. Moreover, incorporation of GO further increased the hydrophilicity of the F-CTA membrane. The water flux significantly increased to 18.43 L per square meter per hour (LMH) when deionized (DI) water was feed solution (FS) and 0.5 M NaCl was draw solution (DS). Meanwhile, the specific salt flux was 0.22 g/L. According to the microorganism attachment test, F-CTA/GO membranes exhibited remarkable resistance to biofouling. The anti-biofouling capability increased with the increase of GO content. The thickness of the biofilm formed on the pristine F-CTA membrane was 18.5 μm. It finally decreased to 4 μm on the surface of the F-CTA/GO membrane. Tensile test revealed that strength and Young's modulus of the F-CTA/GO membrane substantially increased to 42.8 MPa and 1.18 GPa, corresponding to ~84% and ~136% increase, respectively, compared with the pristine F-CTA. The presence of GO enabled excellent mechanical stability of the free standing membranes.

1. Introduction

Forward osmosis (FO), an emerging desalination process, has attracted increasing attention in both scientific research and indus-

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trial development in the last decade [1–3]. Unlike traditional pressure driven membrane processes that require external pressure to facilitate osmosis, FO is an osmotically driven process occurs naturally across the semi-permeable membrane [4]. The driving force results from the osmotic pressure gradient between the feed solution and the draw solution with high chemical potential. Therefore, FO possesses advantages such as low energy consumption, low fouling propensity, and high water recovery [1,5–7]. Its potential applications including wastewater treatment [8,9], seawater desalination [10,11], power generation [12,13] and food processing [14,15] have been reported. However, severe ICP in the support layer has been one of the major drawbacks of FO that limits the osmotic properties. Besides, membrane fouling always obstructs the separation and purification processes. Although FO has shown reduced fouling propensity and simple cleaning compared with the external pressure driven osmosis, the anti-fouling behavior is still not satisfactory. Mechanical and chemical limitations are also to be overcome [2,16]. They are the main issues in the development of high performance FO system. Desired FO membrane for use should have a thin, porous and hydrophilic support layer with mechanical stability, in order to minimize the effect of ICP. The membrane exhibits a high affinity for water or hydrophilicity for reduced fouling propensity [1,17].

Recently, structure and surface of membranes have been modified to improve the FO performances [18,19]. For instance, by means of introducing improved support layer structure such as finger-like structure [17], scaffold structure [20] and interpenetrating network structure [21], the adverse effect of ICP is effectively mitigated. The fouling resistance of membranes has been increased through surface modification by either coating or grafting anti-fouling polymers [22] and/or anti-microbial polymers [23] /biocidal inorganic particles [24]. However, preparation of high performance FO membrane with excellent combined properties is still challenging. Very recently, various nanoparticles including zeolite [25], silica [26], titanium dioxide (TiO_2) [27] and carbon nanotubes (CNTs) [28] have been employed to be incorporated into the FO membranes. The hybrid membranes show high permeability, selectivity and antifouling property with a low particle loading [29–31]. Compared with traditional particles, the nanoparticles are more efficient in enhancing membrane performance, owing to the high surface to volume ratio and/or high aspect ratio.

Graphene is a promising nanoparticle that possesses an atomically thick, two-dimensional structure. It has extraordinarily high surface area, aspect ratio, Young's modulus, tensile strength, chemical stability and resistance to microbe [32–34]. Since it was achieved in 2004, it has intensively attracted tremendous interest in exploring its applications. The superior properties of graphene also reflected in the polymer/graphene nanocomposites [35]. Oxidation of graphene is a common approach that improves its dispersion quality in polymer matrix and optimizes their interfacial adhesion, which is critical in graphene reinforcement [36–38]. The functional groups of GO offer strong hydrophilicity that could promote high water permeation and impede biofouling [39]. Latest studies have used GO as filler for the preparation of thin film composite (TFC) FO membranes. Yin et al. [40] modified the polyamide active layer of TFC membrane by adding low amount of GO. At optimal GO loading, the water flux of the membrane increased by 52%, compared with pristine TFC membrane. But the salt rejection was slightly decreased. Park et al. [41] synthesized TFC FO membranes with GO-modified support layer. The water permeability was significantly improved. However, reverse salt flux increased, which implied reduced salt rejection. Also, tensile strength of the membrane decreased. The mechanical property was sacrificed.

CTA is another widely used material to prepare commercial FO membranes. It has relatively high hydrophilicity, wide availability, good mechanical strength and excellent resistance to chlorine and other oxidants [42,43]. To our best knowledge, the potential of GO to improve the properties of CTA membrane has not yet been explored. In this study, the F-CTA/GO membrane is reported for the first time. We intend to improve the water permeation of the membrane by removing the substrate support layer and improving the hydrophilicity of the membrane. The mechanical support of the free-standing membrane is achieved from the successful transfer of the mechanical properties from GO to the polymeric matrix. Compared with traditional CTA membrane with polyester mesh or non-woven fabrics support layer, the free standing membrane is efficient to mitigate the effect of ICP and reduces water resistant, owing to the absence of a substrate support layer. It also simplifies the processing routine of FO membranes. The hydrophilicity of GO contributes to the improvement on the water permeation and anti-biofouling behavior of the membrane. The F-CTA/GO membrane possesses a combination of excellent osmotic, antifouling and mechanical properties, in comparison to the current FO membranes.

2. Experimental

2.1. Materials

CTA granules were provided by Acros Organics, the Acetyl content was 43–44 wt%. Ultra-fine graphite flakes were purchased from Qingdao Graphite Company. Methanol, lactic acid, 1,4-dioxane and sodium chloride was purchased from Chengdu Kelong Chemical Co., Ltd. Acetone was obtained from Chongqing Chuandong Chemical Co., Ltd. DI water with a resistivity of 18.25 MΩ cm was produced from an ultrapure water system (Molecular ΣH2O®, China).

2.2. Preparation of F-CTA/GO FO membrane

GO was synthesized from graphite by Hummer's method [44]. The dispersion of GO in acetone was achieved by means of ultrasonication for 30 min (300 W) at room temperature. The dispersion was mixed with calculated amount of methanol, lactic acid, 1,4-dioxane and dried CTA granules. Casting solution was prepared by stirring the mixture at 70 °C for 3 h, followed by de-bubbling at room temperature for 2 days. The solution drop was then cast on to a grass plate, by using a casting knife at room temperature. After evaporation of the solvent for 60s, the plate was immersed into a DI water bath for 2 h, instigating phase inversion reaction. The membrane was formed and peeled off from the glass plate. Then, it was washed by DI water, in order to remove the residual solvent. The membrane was further treated at 60 °C for 15 min in water bath. The thickness of all membranes was 50 ± 10 μm.

2.3. Characterization of GO

A Malvern Instruments Mastersizer was used to measure the particle size distribution of GO. The beam length was 2.4 mm and the stirrer speed was 900 rpm. A Fourier transform infrared (FTIR) spectrum of the GO sheets was recorded from 4000 to 600 cm^{-1} by a Shimadzu FTIR 8400 s spectrophotometer with a resolution of 2 cm^{-1} over 64 scans. The GO sheets were observed by a transmission electron microscopy, TEM (JEOL 2100 FX instrument). The layered structure of GO sheets was observed by a Philips Tecnai F20 high-resolution transmission electron microscopy (HRTEM). The GO sheets were firstly dispersed in acetone, and casted on copper grid for observation. The accelerating voltage was 200 kV.