



# Synthesis and characterization of silica gel–polyacrylonitrile mixed matrix forward osmosis membranes based on layer-by-layer assembly



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## ARTICLE INFO

### Article history:

Received 5 September 2013

Received in revised form 13 January 2014

Accepted 17 January 2014

Available online 28 January 2014

### Keywords:

Silica gel (SG)

Mixed matrix membrane (MMM)

Forward osmosis (FO)

Phase inversion

Crosslinked layer-by-layer (xLbL) assembly

Internal concentration polarization

## ABSTRACT

Silica gel (SG)–polyacrylonitrile (PAN) composite forward osmosis (FO) membranes have been synthesized and characterized in the present work. The incorporation of SG particles into the PAN support layer significantly changed its water permeability and salt rejection rate. In the range of 0.25–1.0 wt.% SG loading, water permeability of membranes were enhanced after the embedment of SG, most likely due to the both porous nature of SG and the enhanced substrate porosity. However, a reduction in both water permeability and salt rejection was observed if further increase in SG loading (2.0 wt.%), possibly as a result of the agglomeration of SG. The most permeable SG–PAN FO membrane (M1.00, with 1.0 wt.% SG loading) had a significantly higher water permeability compared to the control pure PAN FO membrane (M0.00). This membrane achieved high FO water fluxes of >100 L/m<sup>2</sup> h was achieved by using the 1 M MgCl<sub>2</sub> as the draw solution (DS) and 0–10 mM NaCl as the feed solution (FS). To the best knowledge of the authors, this is the first study reporting the development and application of SG–PAN mixed matrix FO membranes (MMMs) based on layer-by-layer assembly.

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## 1. Introduction

By using the osmotic pressure difference between a low concentration feed solution (FS) and a high concentration draw solution (DS) as the driving force to move water through a semi-permeable membrane, forward osmosis (FO) can potentially reduce the energy consumption of current technologies by up to thirty percent [1,2]. Compared to high pressure-driven reverse osmosis (RO) and nanofiltration (NF) membrane processes, FO process has been reported to have several advantages including (1) low energy consumption and higher fouling resistance, (2) high rejection of a variety of solutes, and (3) low operating cost because of the utilization of high osmotic pressure difference instead of the high pressure difference across the membranes as the driving force [3–5]. Hence, FO process has been employed in a wide range of applications such as wastewater treatment [4,6–8], seawater desalination [5,9,10], food processing [11,12], and valuable product concentration [12,13].

Comprehensive reviews of FO technology have been provided by Cath et al. [1], Zhao et al. [2], and Chung et al. [14]. Existing commercial FO membranes are based on triacetate (CTA) chemistry [15]. These membranes have relatively low water permeability and are prone to hydrolysis and biodegradation. Therefore, one of the highest priorities in the research area of FO is to develop high performance FO membranes [15–26]. Generally, FO membranes are synthesized by phase inversion method [27,28] followed by either interfacial polymerization [15,17,19,23,24,26] or layer-by-layer (LbL) [20–22,25], with a dense rejection layer on top of a porous support layer. One of the major limitations for these asymmetric composite FO membranes is the internal concentration polarization (ICP), a specific and serious problem in FO process [1,29–32]. In reality, the actual effective osmotic concentration difference will be significantly lower than the theoretical bulk osmotic concentration difference across the rejection layer [31]. Concentrative ICP occurred when the active layer faces the draw solution (AL-DS), the solutes were concentrated in the membrane porous substrate. Alternatively, dilutive ICP occurred when the active layers faces the feed solution (AL-FS), the draw solution was diluted in the support layer. In general, a smaller structural parameter *S*, which means thinner membrane, smaller tortuosity, and

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higher porosity of membrane) can reduce the severity of ICP during the FO process.

Recently, mixed matrix membrane (MMM) is an emerging topic under membrane development area. Several membrane properties, such as permeability, selectivity, thermal and mechanical stability, can be potentially enhanced by incorporating nanomaterials such as zeolite [33–38], silica nanoparticle [39–41], titanium oxide nanoparticle [42], and silver nanoparticle [43–45]. For example, silica nanoparticle, which has a variety of advantages such as high thermal and chemical stability, inexpensive and commercially viable, tunable particle and pore size [46,47], has been reported to increase gas permeability without significantly decrease the selectivity of mixed matrix membranes [48–50]. The performance enhancement was believed due to the good compatibility between the polymer and the silica nanoparticle and they could be potentially used to fabricate not only gas separation, but also ultrafiltration and reverse osmosis MMM for industrial application. Unlike pressure driven membranes, FO water flux is strongly affected by ICP. The mixed matrix approach can be potentially effective in enhancing the mass transfer efficiency of membrane substrate and thus in controlling ICP. Nevertheless, the utilization of silica gel (SG) as the filler for the preparation of mixed matrix FO membranes has not been reported in the open literature.

The objective of current study is to improve FO performance by using SG-based mixed matrix substrate. SG was embedded into polyacrylonitrile (PAN) to cast MMMs with various SG loadings. The morphology, structure and performance of these SG–PAN MMMs were systematically characterized. To the best knowledge of all the authors, this is the first report systematically studying the synthesis and characterization of SG–PAN MMM based membranes for FO application based on layer-by-layer assembly.

## 2. Experimental

### 2.1. Materials and chemicals

All chemicals and reagents were used as received unless otherwise stated. PAN (Sigma–Aldrich,  $M_w \sim 150,000$ , Lot# MKBD6325V) was used for polymer dope solution preparation. PAN is used in the current study for its ease of processing, good chemical resistance, mechanical strength, and thermal stability [22,51]. *N,N*-dimethylformamide (DMF, purity  $\geq 99.8\%$ , Merck) was used as solvent while lithium chloride (anhydrous LiCl, Merck) was added as the pore former, respectively. Sodium hydroxide (anhydrous NaOH, purity  $\geq 98\%$ , Merck) was used to prepare alkali solution for base treatment of PAN substrate to enhance hydrophilicity. Silica gel (SiliaFlash® Irregular Silica Gels – F60 Silica, SiliCycle, Lot# 070612) were used for MMMs preparation due to its high surface area, neutral pH, low trace metal content, tight particle size distribution, and well characterized properties [52]. According to the product characteristics provided by the company, the particle size and pore size of silica gel ranged from 40 to 63  $\mu\text{m}$  and 55 to 65 Å respectively.

Poly(allylamine hydrochloride) (PAH,  $M_w \sim 112,000$ –200,000, Polyscience, Lot# 639458) was used as polycation and poly(sodium 4-styrene-sulfonate) (PSS,  $M_w \sim 70,000$ , 30 wt.% in  $\text{H}_2\text{O}$ , Sigma–Aldrich, Batch# 09622HH) was used as polyanion for LbL self-assembly. The ionic strength of both PAH and PSS was adjusted by sodium chloride (NaCl, 99%, Merck). The LbL rejection layers were crosslinked by using glutaraldehyde (GA, 25% in water, Sigma–Aldrich). Previous studies [20–22,53] have shown that xLbL FO membranes have relatively high FO water flux and good rejection to divalent ions and may have potential applications in biomass concentration, food processing, etc.

### 2.2. Fabrication of PAN nanocomposite substrates

To achieve good dispersion of the particles, different amounts (0.0 wt.%, 0.25 wt.%, 0.5 wt.%, 1.0 wt.% and 2.0 wt.% based on the dope solution) of dry silica gel particles were added into DMF followed by ultrasonicated the solution for 1 h. PAN (18 wt.%) and LiCl (2 wt.%) were then added into the DMF solution followed by stirring for at least 24 h at 60 °C until a homogeneous solution was obtained. The polymer solution was then cooled down to room temperature overnight without stirring to completely remove any gas bubbles. A casting knife was set at a gate height of 150  $\mu\text{m}$  (Elcometer Pte. Ltd., Asia) was used to cast the polymer solution onto a clean glass plate. The polymer film was then solidified in the tap water bath at room temperature. The PAN substrate was then immersed into the 1.5 M NaOH solution at 45 °C for 1.5 h to partially hydrolyze the PAN substrate surface.

### 2.3. Layer by layer assembly and crosslinking

The details procedure for LbL rejection layer preparation can be found elsewhere [20–22,25]. Briefly, the rejection layer was formed by alternatively soaking the PAN substrate into the PAH and PSS solution for 15 min followed by soaking the substrate into the DI water after each polyelectrolyte soaking step. Based on the optimization performed in our prior studies [21,22], the PAH/PSS treatment was repeated three times to prepare membranes rejection layer with suitable rejection properties for FO applications. LbL FO membranes were cross-linked by soaking the membranes in a 0.1 wt.% GA solution for 30 min followed by soaking with DI water for 5 min to remove excess GA and the resulting membrane was designated as (M0.00, M0.25, M0.50, M1.00, and M2.00). Table 1 shows the compositions of polymer dope solution and active layer.

### 2.4. Membrane characterization

The surface and cross section morphological structures of the prepared PAN membranes were characterized by field emission scanning electron microscope (FESEM, JSM-7600F, USA) [25]. A freeze-dryer was used to dry all the membranes samples at room temperature for at least 12 h followed by coated with a uniform platinum layer before observation. Element mapping was detected with the FESEM microscope equipped with energy-dispersive X-ray spectroscopy (EDX) [37]. The surface roughness of the membrane samples were tested by atomic force microscope (AFM, Park Systems XE-100, Korea). Micromeritics ASAP 2020 instrument (USA) was used to obtain the nitrogen sorption isotherm at  $-196$  °C [39]. The sample was degassed in a vacuum oven for 6 h at 200 °C to remove the gases and vapors absorbed on the sample surface before the measurement. By plotting the volume of nitrogen adsorption against the relative pressure, the specific surface area, pore diameter, and pore volume of silica gel was calculated using multiple point Brunauer–Emmett–Teller (BET) equation.

$$\frac{1}{[V_a(\frac{P_0}{P} - 1)]} = \frac{C - 1}{V_m C} \times \frac{P}{P_0} + \frac{1}{V_m C}$$

where  $V_a$  is volume of gas absorbed at standard temperature and pressure and  $V_m$  is volume of gas absorbed at standard temperature and pressure to produce an apparent monolayer on the sample surface.  $P$  is partial vapor pressure of adsorbed gas in equilibrium with the surface at 77.4 K and  $P_0$  is saturated pressure of adsorbed gas.  $C$  is dimensionless constant that is related to the enthalpy of adsorption of the adsorbed gas on the powder sample.

By measuring the dry mass ( $m_{dry}$ ) and wet mass ( $m_{wet}$ ) of membrane samples, the membrane porosity ( $\epsilon$ ) can be calculated according to following equation [15,54]:

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