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# Nanoparticle-embedded nanofibers in highly permselective thin-film nanocomposite membranes for forward osmosis



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## ABSTRACT

Here we report a scalable approach to fabricate osmotic membranes with high permselectivity based on nanocomposite of mesoporous silica nanoparticles and nanofibers by electrospinning. Transmission electron microscopy (TEM) images provide visualization of dispersed and clustered nanoparticles embedding within or at the surface of nanofibers. Energy-dispersive X-ray (EDX) point analysis confirms the chemical identity of the nanocomposite structure. Brunauer-Emmett-Teller (BET) analyses show a 75-fold increase in specific surface area when 15% of silica nanoparticles were integrated into polyacrylonitrile nanofibrous mats. Mechanical strength tests show that even at high load of silica nanoparticles, e.g. 15 wt%, the mechanical integrity of the membranes was maintained. Incorporating nanoparticles into nanofibrous mats enhanced their water uptake up to two times. In osmotic transport studies, we observed an outstanding permselectivity of our membranes compared to ones reported in literature. Our membranes show a remarkable 7-fold and 3.5-fold enhancements in osmotic water permeability and water/sodium chloride selectivity, respectively, compared to standard commercial forward osmosis membranes. These results suggest a pathway to develop scalable, high performance osmotic membranes and to further study the predominant mechanism governing transport behaviors of water and solute across nanomaterials interfaces.

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## 1. Introduction

Forward osmosis (FO) has emerged as a versatile platform for sustainable water and energy production [1,2]. This technology exploits osmotic potential energy to drive water across a semi-permeable membrane from a low-salinity solution (feed) to a high-salinity one (draw). It offers hope for low-cost desalination and water reuse with less fouling propensity compared to conventional pressure driven membrane processes [3,4]. Osmosis can also be harnessed for power generation by capturing osmotic flow with a hydroturbine, essentially turning every salinity gradient, either naturally occurring or engineered, into a potential source of electricity (pressure retarded osmosis) [5–11]. FO has therefore inspired an increasing number of imaginative uses for both broad and niche applications. The key element to effectively implement this platform technology is a membrane with high permselectivity, mechanical stability and scalability.

Internal concentration polarization (ICP) is the prominent factor causing poor flux performance for any FO membrane [12,13]. ICP is mainly influenced by specific characteristics of this layer, such as the porosity, tortuosity, and thickness [14–16]. This structure's contribution to these resistances is often quantified using the structural parameter:

$$S = \frac{t^* \tau}{\varepsilon} \quad (1)$$

where  $t$  is the thickness,  $\tau$  is the tortuosity and  $\varepsilon$  is the porosity of the support layer. To tailor good membranes for FO,  $S$  must be minimized [9,17]. Accomplishing this requires the support layer be engineered to exhibit a high porosity, minimal thickness, low tortuosity, and hydrophilicity without greatly sacrificing strength or flexibility [14,17–19].

We previously proposed nanofiber nonwovens as a material that provides the necessary support of the polyamide layer yet exhibits the necessary properties to minimize structural parameter [20]. Nanofiber nonwovens can be made by electrospinning and have recently been used to fabricate thin-film composite (TFC) membranes for FO applications [9,10,17,21–24]. Possessing a high

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porosity, low tortuosity and an interconnected porous structure, nanofibrous mats exhibit exceptionally low structural parameters [9,17] and thus are promising for use as supports for FO membranes.

Furthermore, recent advances in spinning technology offer a promising commercial outlook for the roll-to-roll production of nanofiber materials. Moving collectors on conveyor belt can readily be integrated with multi-needle systems to mass produce fibers [25]. The emergence of needleless (free liquid surface) electrospinning, developed in the past decade [26], was a step-change nanofiber manufacturing. An early entrant into commercial was Elmarco Co. with their “Nanospider™” product line [27,28]. Other players in the space have emerged as well, including Finetex, eSpin Technologies, Donaldson, Dienes Apparatebau GmbH, SNS Nanofiber Technology, Ahlstrom and TopTec. On the market, filtration products that incorporate nanofibers include Ultra-Web™ from Donaldson, NanoWave™ from Hollingsworth & Vose, TechnoWeb™ from Finetex, ProTura™ from United Air Specialists (a Clarcor company) [29] and so on. As such, this membrane platform, if tuned appropriately to increase membranes permselectivity and mechanical integrity, can be an excellent candidate for the next generation of FO membranes.

With commercialization potential of nanofiber based membranes less in doubt, exploring the entire parameter space of nanofiber materials for membranes is increasing in importance. In the FO space in particular, finding ways to increase wettability, improve mechanical properties, and decrease structural parameter are of key interest, and the flexible and versatile nanofiber platform is still a unique and worthwhile material to explore. This work explores the novel area of mixed matrix TFC supports through the incorporation of nanoparticles into the nanofibers in order to enhance overall membrane performance. Specifically, mesoporous silica nanoparticles (SiNPs) were incorporated into nanofibers during electrospinning to make a nanocomposite nanofiber support for what we term thin-film nanocomposite (TFN) membranes. A particle size of ~200 nm with 4 nm-pore-size was selected to match the expected nanofiber diameter, thus, may create “through-wall” nanocomposite fibers with possible additional pathways for solute and water transports. These particles are stable and possess well-ordered mesoporous structures with a high specific surface area, large pore volume and loading capacity, and tunable nm-sized pore architecture [35]. Moreover, the controllable, scalable and cost-effective fabrication of SiNPs [31] is an important factor when considering the possibilities for scale up.

Incorporating SiNPs into PAN nanofibers offers a number of advantages for FO membranes. The pore network within and around the particles themselves further enhances the continuity of water and solute pathways [32]. While the larger pores enable high mass transfer due to convective flow, the high-surface-area mesopores could enable high water adsorption capacity [32–35]. This adsorption is likely in the presence of the silanol groups on and within the SiNPs and helps increase the support layer wettability [36,37] which is critical for reducing ICP [15,17]. Preferential sorption into the SiNPs may also reduce swelling of the nanofibers in the presence of water and help maintain the integrity of the nanocomposite structure [34,36]. Nanomaterials have also been considered as additives to the support layer to reduce compaction [38–41] that may lead to reduced structure parameter. These anticipated benefits should mean that by incorporating SiNPs into the nanofiber structure, ICP can be further reduced.

## 2. Experimental section

### 2.1. Materials and chemicals

Polyacrylonitrile (PAN,  $M_w = 150,000$  g/mol), mesoporous silica nanoparticles ( $\text{SiO}_2$ , 200 nm particles size, 4 nm pore size), *m*-phenylene diamine (MPD, >99%), 1,3,5-benzenetricarbonyl trichloride (TMC, 98%), *N,N*-dimethylformamide (DMF, anhydrous, 99.8%), and direct blue 71 (DB71) were purchased from Sigma Aldrich (St. Louis, MO). Sodium chloride (NaCl, crystalline, certified ACS) was obtained from Fisher Scientific (Pittsburgh, PA). ISOPAR-G, referred to hereafter as “isopar”, was supplied by Gallade Chemical, Inc. (Santa Ana, CA). Deionized water was achieved from a Millipore Integral 10 water system (Millipore, Billerica, MA). Commercial asymmetric cellulose triacetate forward osmosis membrane embedded with a nonwoven mesh (CA) was provided by Hydration Technology Innovation (HTI, Albany, OR) and used as controls. The structure of this membrane has been broadly studied and reported elsewhere [14,15]. Polyester nonwoven fabric sheet (PET, Novatexx 2442) was supplied by Freudenberg (Weinheim, Germany). Chemicals were used as-received.

### 2.2. Membrane fabrication

#### 2.2.1. Silica nanoparticles-embedded nanofiber formation via electrospinning

Solutions of 12 wt% polyacrylonitrile loading with 0, 5, 10 and 15 wt/wt% silica nanoparticles were continuously stirred at 60 °C for 12 h and then overnight at room temperature before electrospinning. Suspension of silica nanoparticles in DMF was first sonicated for 30 min before blending with PAN in DMF. A volume of 3 mL of as-prepared polymeric solutions were electrospun under a potential field of 28.5 kV.  $\text{SiO}_2$ /PAN nanofibrous mats were collected onto the PET nonwoven fabric. The flow rate was 1.0 mL/h and the tip-to-collector distance was 16 cm. The experiments were conducted in a 50% relative humidity atmosphere at ambient temperature. Silica nanoparticles were homogeneously suspended in PAN solutions during electrospinning, therefore their weight percent in the fiber mats are expected to be approximate to the initial loadings.

#### 2.2.2. Polyamide selective layer formation via interfacial polymerization

Polyamide was deposited onto the as-spun nanofibrous supports by *in-situ* interfacial polymerization between an aqueous solution of 1.0 wt% of *m*-phenylene diamine (MPD) and an organic solution of 0.15 wt% of 1,3,5-benzenetricarbonyl trichloride (TMC) in isopar [17]. The as-prepared TFN membrane was then dried in the ambient atmosphere for 4 min, dry-cured in the oven at 90–95 °C for 8 min and rinsed thoroughly with deionized (DI) water at room temperature and stored in DI water at 4 °C before testing.

### 2.3. Membrane characterization

#### 2.3.1. Characterization of structural and physical properties

Representative surface morphology of nanocomposite supports and selective layer of TFN membranes were observed with a cold cathode JSM-6335F field emission scanning electron microscope (FESEM). Chemical identity of the nanocomposite structure was confirmed with Energy-dispersive X-ray (EDX) point analysis. Structure of nanoparticle-embedded nanofiber was observed by transmission electron microscope (JEOL JEM-2010 FasTEM). Samples were first sputter coated with a thin layer of gold (Au) before imaging to obtain better contrast and to avoid charge accumulation. Mechanical properties of nanocomposite supports were

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