Nanoparticle-embedded Nanofibers in High Permselectivity Thin-film Nanocomposite Membranes for Forward Osmosis

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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 confirmed 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 path to develop scalable, high performance osmotic membranes and to further study the predominant mechanism governing transport behaviors of water and solute across nanomaterials interfaces.

Keywords: Mesoporous nanoparticles, nanofibers, thin-film nanocomposite, pressure-retarded osmosis, sustainable water and energy.

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 semipermeable 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 even 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, τ is the tortuosity and ε 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 [9,10,17,21,22-24]. Possessing a high 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 “NanospiderTM” 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-WebTM from Donaldson, NanoWaveTM from Hollingsworth & Vose, TechnoWebTM from Finetex, ProTuraTM 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 4nm-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 [30]. Moreover, the controllable, scalable and cost-effective fabrication of SiNPs [31] is an important factor when considering the possibilities for scaleup.

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 help to increase 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 [38,39-41] 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

EXPERIMENTAL SECTION

Materials and Chemicals: Polyacrylonitrile (PAN, $M_w = 150,000$ g/mol), mesoporous silica nanoparticles (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.

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 hours and then overnight at room temperature before electrospinning. Suspension of silica nanoparticles in DMF was first sonicated for 30 minutes 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. SiO₂/PAN nanofibrous mats were collected onto the PET nonwoven fabric. The flow rate was 1.0 ml/hr 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.

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 minutes, dry-cured in the oven at 90 - 95 °C for 8 minutes and rinsed thoroughly with deionized (DI) water at room temperature and stored in DI water at 4 °C before testing.

Membrane Characterization:

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 obtained from tensile tests with an Instron Microforce Tester connected to a universal TA instrument model 2980 DMA. Samples were first removed from the PET substrates and cut into 5 mm x 30 mm (W x L) rectangular strips. Thickness of these strips varied from 0.025 – 0.032 μm . The tests were conducted at 25 $^{\circ}\text{C}$ in air and the loading rate was 0.5 N/min. Each measurement represents an average of at least 6 samples. Specific surface area of as-received silica nanoparticles and as-spun SiO_2 -PAN nanofibrous mats were evaluated using Brunauer-Emmett-Teller (BET) analysis (ASAP 2020, Micromeritics, USA) after degassing samples at 90 $^{\circ}\text{C}$ for 12 hours.

Reverse Osmosis (RO) Test: A bench-scale crossflow RO testing unit was used to evaluate the intrinsic pure water permeability coefficient, A , and solute permeability, B of the TFN membranes at 20 ± 0.5 $^{\circ}\text{C}$. A was measured at pressures of 50, 75, 100, 125 and 150 psi. To determine B , a rejection test was conducted following the measurement of A at 125 psi with a fixed crossflow velocity of 26.36 cm/s ($\text{Re} \sim 1312$) using a 2000 ppm NaCl feed solution. No spacer was used. B was calculated based on the following equation:

$$B = \frac{(1-R)A(\Delta P - \Delta \pi)}{R} = \frac{(1-R)J_w}{R}$$

where R is the rejection which was determined based on the difference of the solute concentration of the feed and permeate solutions, ΔP is the transmembrane hydrostatic

pressure, $\Delta\pi$ is the transmembrane osmotic pressure and J_w is the water flux of the rejection test.

Evaluating the role of SiNPs in enhancing membrane – water affinity:

Water uptake measurement: To evaluate the intrinsic wettability of the open porous structure of nanofibrous mats with non-characterized rough surfaces, we conducted water uptake measurement using weight-gain method. As-spun nanofibrous mats were first dried at 40 °C under vacuum for 24 hours. Dried samples were weighted (m_{dry}), saturated with deionized water for 24 hours, removed the excess water with kimwipes, and weighted again (m_{wet}). The percentage of water uptake is calculated as follow: $100 \cdot (m_{wet} - m_{dry}) / m_{dry}$. Separate water-saturated samples were also prepared and imaged with a measuring microscope (Olympus STM6-F21-3). Furthermore, to *qualitatively* observe the possible transport channels introduced by SiNPs and their clusters, Pa-Si0 and Pa-Si15 nanofibers were selected for the dye solution uptake test.

Dye uptake test: Aqueous solution of 10 μ M direct blue 71 (DB71) was used for this test. Strips of Pa-0Si and Pa-Si15 were prepared with the same area (2 cm x 3 cm) and weight ($\sim$ 0.0045 g). These samples were first immersed in 10 mL of the dye solution for 10 hours. They were then dried off with kimwipe and soaked in 2 mL deionized water to extract any trace of the dye solution that may be stored in SiNPs and their clusters. The extractions were then characterized with UV-vis spectroscopy. Given the fact that DB71 is highly soluble in water, detected dye stored within the SiNPs and their clusters may show additional transport pathways introduced by these porous nanoparticles.

Osmotic Flux Tests and Structural Parameter Calculation: Osmotic water flux and reverse salt leakage through TFN membranes were characterized using a lab-scale cross-flow forward osmosis system. The experimental setup was described elsewhere [18]. The fluxes were measured in forward osmosis (FO) and pressure-retarded osmosis (PRO) modes at 20 ± 0.5 °C using DI water as the feed solution and 1.0 M NaCl as the draw solution. The hydraulic pressure was equal (1 psi) on both sides of the membrane. Note that there was no pressure difference across the membranes for both the FO and PRO modes. The crossflow velocity was maintained at 15.82 cm/s ($Re \sim 757$) for both the feed and draw solution. A polypropylene mesh with an opening size of 2.032 mm x 1.397 mm was used at two sides of the membranes as spacers.

RESULTS and DISCUSSION

Figure 1

Schematic diagrams of individual nanoparticles, clusters, and their dispersion in nanofiber is shown in Figure 1A. PAN nanofibers loading with 5, 10 and 15 wt% of SiO₂ nanoparticles were electrospun onto polyester nonwoven fabric (Figure 1C). The samples are referred to as Pa-Si5, Pa-Si10 and Pa-Si15, respectively, hereafter. All samples exhibited a mixture of dispersed and clusters of nanoparticles embedded within continuously long and cylindrical fiber structure (Figure 1D). The appearance of nanoparticles clusters were more pronounced at higher silica loadings. Figure 1E shows TEM images of the SiNPs embedded within PAN nanofibers. Both individual nanoparticles and their clusters are shown to be successfully embedded either within or at the surface of nanofibers. The chemical identity of the PAN-SiO₂ nanocomposite was confirmed with Energy-dispersive X-ray (EDX) point analysis (Figure 1F).

A polyamide selective layer was then formed onto these as-spun nanocomposite supports *via in-situ* interfacial polymerization. *m*-phenylene diamine (MPD) and 1,3,5-benzenetricarbonyl trichloride (TMC) were selected to generate a dense, three dimensional cross-linked polyamide selective layer. As representatively shown in Figure 1G, the polyamide generated on nanocomposite support possessed a typical ridge-and-valley morphology [30].

Figure 2

Mechanical properties of the nanocomposite nanofibers and thin-films are shown in Figure 2. The polyester backing layer was removed before all tests. Results show that after depositing polyamide selective layer onto the nanofibrous supports, tensile strength and modulus of TFN membranes increased two – three-fold, as similarly observed in our previous study [17]. Moreover, adding SiNPs into PAN nanofiber did not weaken the supports. The water permeance (A) and salt permeability (B) of the membranes were obtained from a bench-scale cross-flow reverse osmosis (RO) unit (Table 1). In general, water permeability of our TFN membranes are of ~2 – 4 times higher than that of commercial asymmetric cellulose triacetate membranes produced by Hydration Technology Innovation (HTI). Adding SiNPs increased both water and salt permeability coefficients A and B of TFN membranes. This is likely due to the increased wettability of the support layer which impacts the vigorosity of the polyamidation reaction and thus the polyamide selective layer properties (e.g. thickness, roughness, crosslinking degree, and so on). Typically, it is desired to maximize both A and A/B. However, it is true that A/B tends to decrease when modifications are made to increase A [42]. In this case, we were able to maintain similar values of A/B for our TFN

membranes while increasing A up to ~4 times compared with those of HTI membranes. Table 1 also tabulates empirical figure of merit, A^2/B , which combines into a single value both water flux and salt rejection [42]. Results show that the addition of SiNPs, in fact, enhanced the figures of merit for TFN membranes.

Table 1

Some of the attractive attributes of nanoparticles that determine their functionalities is their specific surface area (SSA) and porous structures. Specific surface area, while not an indicator of a substantial increased porosity, is suggestive of the number of possible transport pathways related to the exposed mesopores of the particle in nanocomposite fibers. N_2 adsorption measurements at 77 K were conducted on nanocomposite fibers to evaluate the degree of nanoparticles mesoporosity exposure. Figure 3 shows N_2 adsorption – desorption isotherms, BET specific surface areas and mesoporous structures of the nanocomposite materials compared to PAN nanofibers and SiNPs.

Figure 3

In this Figure, the type IV adsorption isotherm for SiNPs has similarities to the amorphous ordered mesoporous MCM-41 with the inflection characteristic of capillary condensation within the pores [31]. Interestingly, nanofibers loaded with SiNPs show similar adsorption – desorption behaviors as SiNPs. The SSA of as-received silica nanoparticles was of 672.7 m^2/g and pure PAN nanofibrous mats were of 0.6 m^2/g . Adding 5, 10 and 15 wt% of mesoporous silica nanoparticles increased the SSA of PAN nanofibrous supports from 14.3 to 27.6 and 45.2 m^2/g , respectively. Weighing the SSA between the two materials (i.e. PAN-SiNPs nanocomposite nanofibers and SiNPs)

would suggest that some of the surface area is indeed blocked by polymer. However the SSA does increase by a factor of ~25 to 75 when 5 to 15 wt% of SiNPs were used, respectively, suggesting that some of the channels are open to transport. Furthermore, polymer coating of the nanoparticles does not necessarily preclude the internal mesoporosity from acting as a transport pathway or favorable sorbent sites, especially when water and ions can readily diffuse through hydrated PAN. Note that the SSA of nanofibrous mats could partially increase due to the slightly reduced fiber diameter when SiNPs were added, however this attribution is insignificant [43-45] compared to the pronounced increase observed with SiNPs-incorporated nanofibers.

Figure 4

In osmosis, membrane wettability is the key factor determining membrane performance [15,17]. To evaluate the role of SiNPs in enhancing membrane – water affinity, water and aqueous dye solution uptake measurements were conducted. Table 1 shows that adding SiNPs increased the water uptake of the nanofibrous materials up to two times. Microscopic images (Figure 4) of water-saturated fibers confirm the high affinity of water to SiNPs-located domains. These images should be used as a complementary part for the water uptake test. They provide proper visualization for one to locate domains where water is preferably adsorbed onto nanoparticles and their clusters. Furthermore, dye uptake test shows that, unlike Pa-Si0 nanofibers, fibers loaded with 15 wt% SiO₂ (Pa-Si15) could store an observable amount of dye solution shown by the pronounced dye peak on its UV curve (Figure 4). Note that in this test, the dye was merely used as a trackable indicator to locate the adsorbed water. In fact, DB71 is negatively charged, therefore it tends not to adsorb onto the negatively charged SiNPs

281 surface (due to the expulsive force) without the presence of a stronger force. It
282 demonstrates that these mesoporous nanoparticles may indeed act as favorable water
283 transport sites in the nanocomposite fibers.

284

285 **Figure 5**

286 Osmotic flux performance of membranes were tested with 1M NaCl draw solution
287 [46] and DI water feed solution in both orientations (FO and PRO) using a bench-scale
288 forward osmosis system. As shown in Figure 5, adding mesoporous silica nanoparticles
289 significantly improve the water flux of TFN membranes. While Pa-Si5 achieved an
290 insignificant increase in water flux when compared to a zero-particle loading, Pa-Si15
291 had twice the water flux performance in both FO and PRO orientations. The high flux
292 performance were likely attributed to (1) the improved wettability of the supports
293 indicated by the increased water uptake/adsorption of the fibrous mats from 114% (Pa-
294 0Si) to 220% when 15wt% SiNPs are incorporated (Table 1 and Figure 4), compaction
295 [38,39-41] resistant of the silica and (3) the increased water pathways through inter-
296 particles and intra-particles porous channels. The proposed mechanisms are however
297 not intended to be definitive, but possible frameworks for further study. We believe that
298 the first mechanism predominantly governs the high flux of these membranes.
299 Increased support wettability favors a more vigorous polyamidation reaction, forming a
300 thin yet rough polyamide selective layer with high water permeability. High support
301 wettability also led to a decreased effective structural parameter of the supports.
302 Indeed, the exceptionally high flux, which is among the highest recorded for this

relatively low concentration draw solution, suggests enhanced transport is occurring in the support layer.

Structural parameter was obtained using data from reverse osmosis and forward osmosis tests using methods described elsewhere [17,47]. Briefly, S is calculated based on the equation listed below:

$$S = \frac{D}{J_w} \ln \frac{B + A\pi_{D,b}}{B + J_w + A\pi_{F,m}}$$

where D is the diffusion coefficient of the draw solute at 20 °C, J_w is the experimental osmotic water flux measured from the FO test, $\pi_{D,b}$ is the bulk osmotic pressure of the draw solution, and $\pi_{F,m}$ is the osmotic pressure at the membrane surface on the feed side. Table 1 shows the results of that analysis. The TFN membranes exhibited structural parameters that were one-tenth that of HTI membrane. Pa-Si15 obtained an extremely low structural parameter of $64.90 \pm 5.15 \mu\text{m}$. Such an S value obtained from this semi-empirical approach [47] is the lowest obtained today and is amongst the lowest possible value for a membrane of this thickness (~ 60 μm of which ~ 10 - 15 μm is the thickness of the nanofibrous layer).

Figure 5B shows an increase of reverse salt flux J_s of TFN membranes at 10 – 15% SiNPs loading of which the SiNPs clusters appearance are more pronounced. This may be due to the SiNPs clusters protruding from the top nanofibrous layers which may slightly damage the selective layer or impact its mechanical stability [40]. It is also possible that the ions pathways across the porous SiNPs-incorporated supports increased simultaneously with water pathways which then enhanced their chances to partition and diffuse across membrane selective layer. In all, the reverse salt flux of TFN

membranes were as low as that performed by the commercial HTI membrane even though the TFN membranes have higher solute permeability as measured in RO test (Table 1). This is due partly to the reverse coupling of water and salt flux across the membrane. Higher water fluxes draw the salt away from the selective layer, mitigating some of the reverse salt flux [16]. Furthermore, our TFN membranes exhibit a low specific salt flux, J_s/J_w (about 75 - 85 % lower than the HTI membranes) which is desirable in FO to prevent ICP and contamination of the dilute solution [17].

Figure 6

We compare the performance of our membranes against other osmotic membranes in the academic literature in Figure 4. This figure shows a tradeoff between osmotic water permeance, $\frac{J_w}{\Delta\pi_{theo}}$, which relates water flux to the full osmotic potential across the membrane, and specific water flux (inverse of specific salt flux), $\frac{J_w}{J_s}$, which relates water flux to salt flux. High performance membranes should possess a high osmotic water permeance and specific water flux. For a specific membrane, specific water flux is constant with solution properties and operating conditions, and is defined as $\frac{J_w}{J_s} = \frac{A}{B} \beta R_g T$ where β is the van't Hoff constant, R_g is the ideal gas constant and T is the absolute temperature [47-49]. This allows us to compare membranes that have been tested under different conditions, including temperature, draw solution type and concentration. Since these data are not merely obtained from the water and salt transport properties of the membranes, but are indirectly affected by the hydrodynamic conditions, Figure 6 should not be considered to represent the intrinsic membrane properties. However, this comparison allows for a global view of osmotic membrane performances. The figure does represent only those membranes tested with sodium

chloride as the draw agent and DI water as the feed solution. These data are tabulated in the supplementary material (Table S1 [17-19,51,52,58-77]) where references are provided. In general, membranes exhibiting higher water permeance often show lower water/NaCl permeability selectivity and vice versa [50]. Our SiO₂-PAN nanocomposite nanofibrous supported TFN membranes outperformed most up-to-date TFC flat-sheet membranes in terms of water permeance and specific water flux J_w/J_s . These membranes are in the comparable range with newly developed hollow fiber TFC membranes [51-54] or flat-sheet TFC membranes having the polyamide selective layer tuned [55-56].

In all, the incorporation of mesoporous silica nanoparticles into PAN nanofiber supports for TFN membranes yielded some truly promising results. Engineering the support layer to have a low structural parameter is in itself a difficult task. These membranes are going far beyond that, however. They are approaching the theoretical minimum of mass transfer limitations in osmotic transport across a TFC membrane. When considering osmotic membranes, the ideal membrane is one that is perfectly selective and lacks any support layer that generates resistance to mass transport. While no such membrane exist outside of biological membranes, this work demonstrates a synthetic membrane platform that exploits nanocomposite materials for engineering a structure that approaches this ideal form.

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378 **Supporting Information Available:**

379 Table S1: Comparison of FO performance (at 20 – 25 °C) of flat-sheet and hollow fiber FO membranes
380 having been reported in literature.

381 This material is available free of charge *via* the Internet at [http://www.journals.elsevier.com/journal-of-](http://www.journals.elsevier.com/journal-of-membrane-science)
382 [membrane-science](http://www.journals.elsevier.com/journal-of-membrane-science)

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Tables and Figures

Table 1 – Water permeance, salt permeability, and structural parameter of FO membranes; and water uptake capacity of electrospun nanofibrous mats.

	A (*) (L.m ⁻² .hr ⁻¹ .bar ⁻¹)	B (*) (L.m ⁻² .hr ⁻¹)	A/B (bar ⁻¹)	A²/B (L.m ⁻² .hr ⁻¹ .bar ⁻²)	S (**) (μm)	Water uptake (%)
HTI-CTA	0.66 ± 0.04	0.44 ± 0.05	1.50	0.99	790 ± 105	-
Pa-Si0	1.07 ± 0.07	0.35 ± 0.13	3.06	3.27	229 ± 52	114 ± 20
Pa-Si5	2.01 ± 0.44	1.32 ± 0.14	1.52	3.06	155 ± 10	144 ± 1
Pa-Si10	2.42 ± 0.89	1.56 ± 0.55	1.55	3.75	84 ± 10	169 ± 11
Pa-Si15	2.54 ± 0.86	1.66 ± 0.47	1.53	3.89	65 ± 5	220 ± 52

(*) Water permeance A and salt permeance B were obtained from a bench-scale RO crossflow unit at 20 ± 0.5 °C. A was measured at 50, 75, 100 and 125 psi. B was determined at a fixed crossflow velocity of 26.36 cm/s (125 psi) using a 2000 ppm NaCl feed solution.

(**) Structural parameter S was calculated from A and B obtained from RO and FO tests, assuming that the external concentration polarization occurring on the porous side of the membrane during forward osmosis test was insignificant.

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Figure 1. (A) Schematic diagrams of: mesoporous silica nanoparticles (left, adapted from [54]), clusters of mesoporous silica nanoparticles (right, adapted from [57]) and their dispersion in nanofibers in our hypothesis (right); (B, E) Representative transmission electron microscope (TEM) image of: (B) as-received mesoporous silica nanoparticles and (E) nanoparticle-embedded PAN nanofibers; (C,D,G) - Representative FESEM images of: (C) - silica nanoparticles-embedded PAN nanofibrous mats, (D) - zoom-in nanocomposite domains where fibers are embedded with silica nanoparticles or clusters and (G) - surface morphology of polyamide selective layer deposited on PAN-SiO₂ nanocomposite; (F) - Energy-dispersive X-ray point analysis showing the chemical identity of the selected PAN-SiO₂ domain.

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Figure 2. Mechanical properties of (A) – electrospun PAN nanofibrous and SiO₂-PAN nanocomposite nanofibrous supports, and (B) – nanocomposite-supported TFC membranes. PET nonwoven fabrics were removed before testing.

Figure 3. N_2 adsorption-desorption isotherms, BET surface area (SSA) and pore size analysis of electrospun nanofibrous materials and mesoporous silica nanoparticles.

Figure 4. (A) – Microscopic images of water-saturated fibers after removing excess water with kimwipe; (B) - UV-vis spectra of solutions extracted from PAN and Pa-Si15 nanofibers after being immersed in 10 μ M direct blue 71 dye solution for 10 hours and dried with kimwipe. The inset shows the UV-vis spectra of control samples: deionized water and 10 μ M direct blue 71 dye solution.

Figure 5. (A-C) Membranes performance in osmotic flux tests: (A) osmotic water fluxes, (B) reverse salt fluxes and (C) specific salt fluxes across the membranes. *Experimental conditions:* 20°C, 1M NaCl as the draw solution, DI water as the feed solution, cross-flow velocities of 15.82 cm/s on both sides of the membranes. Data was obtained from six tests on independent samples. Note that while the errors for measured variables (i.e. J_s and J_w) are standard deviations, those for the function of J_s/J_w were calculated based on the standard deviations of J_s , J_w , assuming a zero covariance.

Figure 6– Correlation between osmotic water permeance, $\frac{J_w}{\Delta\pi_{theo}}$, which relates water flux to the full osmotic potential across the membrane and water/NaCl permeability selectivity, $\frac{J_w}{J_s}$, which relates water flux to salt flux of FO membranes have been reported in open literature so far [58-82]. Temperature: 20 – 25 °C, DI water as feed solution, NaCl (0.5 – 2M) as draw solution, zero transmembrane pressure, FO orientation (draw solution contacts the porous support). The difference in crossflow velocities used in these studies was not taken into account.

Graphical Abstract