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Introduction

Reverse osmosis (RO) is a key energy-efficient and costeffective desalination protocol,¹⁻³ and thus, there has been considerable attention towards the development of membranes with improved separation performance.⁴⁻⁷ Based on a survey of available data it is evident that A (the "permeance", *i.e.*, the water flux, J_w , eqn (2) in ESI,[†] per unit area per unit pressure drop across the membrane), and sodium chloride (NaCl) rejection, R_s , (eqn (5) in ESI[†]) are often inversely correlated. By analogy with gas separations there may be an upper bound (UB),⁸⁻¹¹ but these are not intrinsic material plots since A and Rs depend on membrane thickness. Polymer membrane-based RO^{12,13} and nanofiltration (NF) membranes^{14,15} have been extensively developed since the 1960s.7,16-22 Thin film composite polyamide (TFC-PA) membranes are the stateof-the-art ubiquitous platforms to desalinate water at

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Enhanced efficiency of water desalination in nanostructured thin-film membranes with polymer grafted nanoparticles*

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Polyamide composite (PA-TFC) membranes are the state-of-the-art ubiquitous platforms to desalinate water at scale. We have developed a novel, transformative platform where the performance of such membranes is significantly and controllably improved by depositing thin films of polymethylacrylate [PMA] grafted silica nanoparticles (PGNPs) through the venerable Langmuir-Blodgett method. Our key practically important finding is that these constructs can have unprecedented selectivity values (i.e., ~250-3000 bar⁻¹, >99.0% salt rejection) at reduced feed water pressure (*i.e.*, reduced cost) while maintaining acceptable water permeance A (= $2-5 \text{ Lm}^{-2} \text{ h}^{-1} \text{ Bar}^{-1}$) with as little as 5–7 PGNP layers. We also observe that the transport of solvent and solute are governed by different mechanisms, unlike gas transport, leading to independent control of A and selectivity. Since these membranes can be formulated using simple and low cost self-assembly methods, our work opens a new direction towards development of affordable, scalable water desalination methods.

> scale^{8,11,23-31} Recently, surface modification has become a popular approach for improving the desalination performance of the popular class of PA membranes.^{23,32-35} In particular, anchoring a hydrophilic PA layer on to the membrane surface via physical adsorption, or polymer grafting ("grafting to" and "grafting from") is efficacious in improving performance,28 while aiding in antifouling^{7,36,37} and dye rejection.⁶⁰ Tethered polymer layers can increase $R_{\rm S}$, but at the expense of (reduced) water permeability. Nanofiltration (NF) based on TFC-PA membranes are typically used to separate small solutes from liquid solvents.^{28,38-40} The active layer of a PA-based NF membrane is formed by interfacial polymerization (IP) on a porous support.⁴¹ Despite considerable interest, the lack of a thorough understanding of IP makes it difficult to rationally improve membrane performance.^{28,29,42} The surface pore structure, such as surface pore size, could affect the IP-based PA TFC membrane performance through influencing the skin layer formation.³² While recent studies have explored ways of improving perm-selectivity, achieving precise separation of ions and small molecules requires enhancing pore size homogeneity, which entails a paradigm shift in engineering the PA active layer.43

> Here, we demonstrate the fabrication of an ultra-selective TFC-PA membrane with remarkable salt rejection performance even at desirably large J_w . We achieve this goal by depositing a controlled number, $N (1 \le N \le 7)$, of PGNP layers on modified TFC-PA membranes using the Langmuir–Blodgett (LB)

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method^{44–46} (see Methods section, ESI Fig. S4†). Significantly, the use of a commercially available TFC-PA platform (Toray flat RO membrane, USA) modified to create a hybrid nanostructured membrane using the large area transfer of PGNPs using the LB method (ESI Fig. S4†) suggests these templates to be ready for scale up towards potential practical implementation.

2 Methods

A support surface pore structure re-construction method was developed to enhance the flux of TFC RO membranes. With this method, an aqueous solution of a suitable organic solvent was used to swell the support for a period of time and then the swelled support was immersed in water to complete the whole surface pore structure re-construction process. Dimethylformamide (DMF) was employed as the organic solvent. It was shown that under proper conditions, *i.e.*, an organic solvent content of 87% v/v, the re-constructing agent contacting time less than 30 s and re-constructing agent contacting temperature of 25 ± 2 °C, allows us to increase the support surface porosity and surface pore size. The process of creating the modified PA-TFC membrane is illustrated schematically in Fig. 1(a).

Polymethylacrylate (PMA) grafted spherical silica particles (PMA-g-SiO₂) were synthesized by the surface initiated reversible addition-fragmentation chain transfer polymerization (SI-RAFT) technique. More details are provided in the ESI (Fig. S1[†]). A PGNP monolayer was created at the air-water interface in a Langmuir-Blodgett (LB) trough (KSV NIMA) using the following procedure: \approx 400 µL of homogeneous

Table 1 Specifications of PGNP monolayers used for desalination membranes

Sample ^a	M _n [kDa]	$\delta_{ m SAXS} \left[m nm ight]$	$\kappa_{\rm f}$ at 35 [mN m ⁻¹]
S-PA	29	24.5	84
M-PA	88	35.3	45
L-PA	132	38.3	50

^{*a*} The grafting density of PMA chains on silica nanoparticles, $\sigma \approx 0.47$ chains per nm², while the dispersity in chain length is ≤ 1.1 . δ_{SAXS} is the size of the respective PGNPs (Fig. S1[†]), M_n is the PMA graft chain molecular weight and κ_f is the isothermal compression modulus of the respective PGNP Langmuir monolayers evaluated using eqn (1) in ESI.[†]

PGNP solution in toluene (0.75 g L⁻¹) was spread on the water surface using a Hamilton syringe. A monolayer of connected granules of PGNPs was formed upon the evaporation of solvent. A dense film of PGNPs was then obtained by compressing the monolayer to a surface pressure of Π = 35 mN m⁻¹. The ability to follow the changes in surface pressure during compression allowed us to measure $\kappa_{\rm fr}$, the isothermal compressibility modulus (Table 1). The $\kappa_{\rm f}$ at the transfer pressure of Π = 35 mN m⁻¹ (Table 1 and shown in Fig. S5†) is a signature of the material's softness,⁴⁶ or equivalently the flexibility of these membranes. However, intriguingly, $\kappa_{\rm f}$ depends non-monotonically on the graft molecular weight of the PGNPs (Table 1).

3 Results and discussion

Water is only transported under a relatively large pressure gradient through the pristine semipermeable PA membrane, *i.e.*,



Fig. 1 Illustration of membrane preparation process and microscopy images. (a) Schematic of membrane preparation process starting from pristine PA-TFC membrane (ESI Fig. S2 \dagger), to processed membrane and finally with added PGNP layers transferred by the Langmuir–Blodgett (LB) method (ESI Fig. S4 \dagger). Optical images of (b) chemically modified PA membrane, (c) N = 3 and (d) N = 5 M-PGNP layers transferred on modified PA membranes.

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the up stream side is at high pressure. The need for high pressure indicates that, although more efficient than previous thermal-based desalination methods, it is still energetically expensive. Thus, challenges still exist in enhancing water permeability, which can reduce energy demand, chemical consumption for cleaning, and operating cost. Specifically, we chose a state-of-the-art TFC-PA membrane to perform water desalination experiments at a canonical NaCl concentration of 2000 ppm. The performance of this membrane over an upstream pressure range of 75–120 psi is shown in Fig. S8 and S9.†⁶³ The water permeelectivity (*A*/*B*) is shown in Fig. S9.† These values are below the upper bound curve. Further, it is difficult to get permeate below this pressure without chemical methods of pore reconstruction. No permeate was collected on reduction of input pressure to 60 psi.

Therefore, we have modified the pristine PA membrane using methods discussed in ESI[†] to improve its performance, *i.e.*, its water flux. This permits the possibility of creating more energy efficient media. Comparing the modified [Fig. 2(a)] and untreated [Fig. S2[†]] PA-TFC membranes, respectively, shows that while this modification procedure resulted in considerably enhanced water permeability at 60 psi, the salt rejection was significantly reduced (Fig. S10[†]). As such, this membrane (without the PGNPs) is a high flux support with poor selectivity, Fig. S10.[†] To improve the selectivity of these modified PA membranes we resort to the LB method to transfer compact PGNP layers by the layer-by-layer method on top of the modified PA membrane. We use the layer-by-layer technique because we can tune various parameters like the number of layers and surface pressure; most importantly the technique is very easy and time-saving as compared to others like vapour deposition, spin-coating, and interfacial polymerization.^{47-49,62} For the deposition we have used PGNP because we can vary the grafting density, chain length, and the polymer and nanoparticle chemistry.

We then transferred packed layers of PGNPs comprised of chains of different M_n, termed short (29 kDa; S-PA), medium (88 kDa, M-PA), and large (132 kDa, L-PA) [Table 1], respectively, at fixed surface pressure, $\Pi = 35 \text{ mN m}^{-1}$ on the modified TFC-PA membrane as shown in Fig. 2(b)-(c) and also in ESI Fig. S5.[†] As Fig. S5[†] shows, $\Pi = 35$ mN m⁻¹ yields a well packed monolayer as evidenced by the sharp rise in Π vs. area in this range. The Π can be varied to control the packing of the PGNPs, which allows control over A and perm-selectivity, A/B, where B is the salt permeability. Optical microscopy images, Fig. 1(c) and (d), show that the film surfaces are made smoother by the deposition of additional PGNP layers, and Fig. 2(b) and (c) show corresponding scanning electron microscopy (SEM) images. Transmission electron microscopy (TEM) images in Fig. 3(a-c) reveal the evolution of the lateral morphology during the layer-by-layer deposition. Since the average thickness of a M-PGNP layer is ~36 nm, as can be seen from the cross-sectional SEM images in Fig. 3(d and e), the TEM images in Fig. 3 (b and c), average over more than one NP layer.

We now consider the desalination performance of these various thin film membranes. The modified membrane



Fig. 2 Scanning electron microscopy (SEM) images of PGNP layers on modified PA membranes. SEM images of (a) modified PA membrane, (b) after transferring of N = 1 and (c) N = 5 layers of M-PGNP on top of modified PA membrane. Scale bars correspond to 1000 nm for all the images.

without any PGNP gives $J_{\rm w} \sim 100 \text{ L M}^{-2} \text{ h}^{-1}$ but very poor salt rejection, $R_{\rm S} < 10\%$ (Fig. S10[†]). Depositing 1–2 PGNP layers does not yield significant improvements (Fig. S11[†]), likely because of pinholes. However, systems with 3 or more PGNP layers have systematically reduced $J_{\rm w}$ but increased $R_{\rm S}$ as shown in Fig. 4(a) for the specific case of the M-PA. [S and L based membranes behave similarly, Fig. S11[†]]. Further, inde-



Fig. 3 Transmission (TEM) and cross-sectional scanning electron microscopy (SEM) images of PGNP layers. TEM images of (a) N = 1 M-PGNP layer with inter-particle distance, δ_{TEM} , of ~33 nm, (b) N = 3 M-PGNP layers with apparent δ_{TEM} of ~16 nm, (c) N = 5 M-PGNP layers with apparent δ_{TEM} of ~12 nm. The δ_{TEM} values are obtained from the histograms in ESI Fig. S7.† Typical cross-sectional SEM images of (d) N = 5 and (e) N = 3 M-PGNP layers transferred on to silicon wafers. The total thickness of ~186 nm and ~107 nm of PGNP layers in (d) and (e), respectively, corresponds approximately to an average PGNP layer thickness consistent with the δ_{SAXS} (Table 1 and Fig. S1†) and δ_{TEM} values reported. Scale bars correspond to 200 nm in (d) and (e).

pendently fabricated membranes show reasonable reproducibility [Fig. S11(b)[†]]. In addition, typical membranes also demonstrate the ability to produce sustainable desalination performance (Fig. S11(c), \dagger especially for those with N = 4 layers or greater) over prolonged usage when being recycled continuously; this strongly suggests that these constructs are viable for technological applications. Fig. 4(b) shows the same data on a permeance vs. salt rejection plot. With 4 added layers the rejection, R_s , reaches >85%; addition of one more layer results in R_s > 99% while retaining $J_{\rm w} \sim 10$ L m⁻² h⁻¹. This is the desired remarkable improvement in performance. We were able to reach even higher $R_{\rm S}$ > 99.5% for a 7 layer M-PA membrane with a $J_{\rm w} > 2$ L m⁻² h⁻¹ with successful operation not only at 60 psi but also at 75 psi. We further benchmark the performance of some of the membranes through perm-selectivity (A/B)vs. permeance (A) plots where we compare the performance of some of the membranes with respect to the so called UB line indicative of the best available desalination membrane performance,¹⁰ Fig. 4(c). Perm-selectivity, A/B, and water permeance, A for an input pressure of 60 psi (closed symbols) for several membranes based on M-PGNP clearly lie above the cur-

rently accepted UB¹⁰ for all RO membranes indicated by the dashed line. This includes N = 7 and N = 4 at higher input pressure (75 psi) (half open symbols). These data were obtained from water-salt separation tests (2000 ppm NaCl, 25 °C, 60 psi). The A/B, of M-PGNPs with various N values at transfer pressure, Π , of 35 mN m⁻¹ (closed symbols) and 37 mN m⁻¹ (open symbols) are also shown (also refer Fig. S12[†]). In all cases higher Π leads to enhanced A/B value suggesting this to be an additional control parameter apart from M_n , N and input pressure. While the membrane with 5 M-PGNP layers stands out, at least two other membranes operating at either 60 or 75 psi also exceed the UB line. While a 4 layer M-PA membrane falls below the UB line at 60 psi, it exceeds the UB line at 75 psi, although with only a reduced $R_{\rm S}$ value of ~80%. The 7 layer M-PA membrane also exceeds the UB line at both 60 and 75 psi operating pressure. Most importantly, the 7 layer M-PA membrane significantly exceeds the separation performance [Fig. 4(d)], in terms of achieving a permselectivity value >1000 while maintaining a $A \sim 2 \text{ Lm}^{-2}$ h⁻¹ Bar⁻¹, across all available desalination membranes.⁵⁰ Hence, apart from exceeding the UB line for M-PA membranes



Fig. 4 Comparison and novelty with other RO membranes. (a) Histogram of salt rejection, R_5 , and flux, J_{wr} , for all membranes for M-PA of different layer number *N*. (b) R_5 , *vs.* water permeance, *A*, for all the membranes. (c) Correlation between water perm-selectivity, *A*/*B*, and water permeance, *A* for two input pressure 60 psi (closed symbols) and (75 psi) (half open symbols). Several membranes based on M-PGNP with N = 5 or more and N = 4 at higher input pressure (75 psi) (half open symbols) clearly lie above the currently accepted empirical upper bound (UB)¹⁰ for all RO membranes indicated by the dashed line. These data were obtained from water–salt separation tests (2000 ppm NaCl, 25 °C, 60 psi). The permselectivity, *A*/*B*, of M-PGNPs with various *N* values at transfer pressure, Π , of 35 mN m⁻¹ (closed symbols) and 37 mN m⁻¹ (open symbols) is also shown (also refer Fig. S12†). In all cases, higher Π leads to enhanced *A*/*B* value suggesting this to be an additional control parameter apart from M_{nr} . *N*, and input pressure. (d) Comparison of separation performance of the most efficient currently available desalination membranes across diverse platforms⁵⁰ (indicated by different closed symbols) with the best performing membranes reported by us here consisting of N = 5 (M-PA-51, red) and 7 (M-PA-71, red) layer of M-PGNP based membranes, with the significance of symbols as explained in 3(a) above. The significant improvement in *A*/*B* values, especially for N = 7 layer membranes, while maintaining relatively high *A*, can be clearly seen.

with N = 5 and 7 layers, these unprecedentedly high A/B values make these modified membranes attractive desalination alternatives with reduced energy costs.^{51,61} Thus, we have demonstrated that both the layer number, N (also Fig. S13†) and the operating pressure are facile handles to control the desalination properties of the PGNP membranes.

In terms of applications, it is necessary that the membranes have good mechanical properties, chlorine tolerance, fouling resistance and that they display minimal aging effects. The stability of PGNP layers after flux experiments has been checked by using SEM, Fig. S16.† We have also checked the membrane stability by running the MPA-7L membrane for 7 days continuously. While we find a mild decrease in performance over this time, our membrane demonstrates a steady performance of >90.0% NaCl rejection throughout the experiment shown in Fig. 5(a). In Fig. S17,† we also show the comparison plot of the desalination performance of some M-PA membranes having different PGNP layers when these were run continuously for up to 7 days. We notice that for the M-PA N = 4 membrane rejection comes down considerably after 7 days of continuous usage while the drop in corresponding membranes with N = 5 and above is less significant. As is evident from the optical images in Fig. S18[†] the M-PA N = 4 membranes still have some voids as compared to M-PA N = 5 membranes. This in turn reflects the compactness of the respective membranes which in turn imparts both long-term stability and ensures better efficiency of the corresponding membranes.

Low resistance to chlorine attack is a major bottleneck for RO water purification applications because it precludes easy and cheap solutions to the problem of membrane biofouling. The unstable amide bonds that are present in the TFC RO membrane show poor chlorine resistance. Here, the induced



Fig. 5 Stability and fouling resistance through various PGNP layers on modified PA membranes. (a) The J_w and R_S for M-PA N = 7 membranes showing the performance with time evolution for 7 days continuous running the experiment for the stability checking and (b) J_w and R_S of the membrane of N = 7 layers of M-PA for 8 days expose with NaOCl to check the chlorine susceptibility and 7 days expose with BSA for the protein fouling to see the PGNPs layer stability.

physio-chemical changes by chlorination reaction are the primary degradation mechanisms in the TFC RO membranes. So, the induced changes in the physio-chemical structure of the membrane by chlorination control the membrane characteristics and performance evaluation.

In terms of biofouling it is better to always clean with some chemical reagent. The effect of chlorination on membrane performance was studied by soaking M-PA-7L RO membrane in an aqueous solution of sodium hypochlorite (NaOCl solution pH 7.5, active chlorine 2000 ppm) at 22 °C for 8 days. The flux and rejection do not change, which proves that these membranes have good chlorine tolerance. We have also checked the fouling resistance by using bovine serum albumin (BSA) for 7days. The performance is good, as found after cleaning the membrane with DI water and checking for its flux and rejection, Fig. 5(b). Thus, this construct is more stable as compared with PVDF-based membranes.^{52,53}

We now focus on understanding this dramatically enhanced performance, and specifically we separately examine the water and the salt fluxes in these different supported PGNP membranes, Fig. 6. Fig. 6(a) illustrates that 1 NP layer gives a water permeance result that is similar to the PA layer likely because of layer imperfections ("pin holes"). Beyond 3 NP layers, however, both Fig. 4(a) and 6(a) illustrate that the permeance decreases effectively inversely with the PGNP membrane thickness. This is consistent with expectations from the solution–diffusion model. Similarly, N = 5 PGNP layers yields a permeance that goes through a maximum in the vicinity of $M_{\rm n}$ \approx 88 kDa, Fig. 6(b). (Similar results are also found for N = 3 PGNP layers, Fig. S13(b), S14 and S15[†]). In this context we note that the gas permeability shows a maximum for materials that are similar to the M series 56-59 – the water permeance measurements thus seem to follow expected trends. We have not explored desalination behaviour with other $M_{\rm n}$ systems because we instead probed variations in Π , N and input pressure.

To help understand this behaviour we explore the variation of the $\kappa_{\rm f} = -A_{\rm M} \left(\frac{\partial \Pi}{\partial A_{\rm M}}\right)_T$ ($A_{\rm M}$ is the total available area in between the limiting mechanical barriers used to compress the monolayers and T is the temperature) of the PGNP monolayers on the water surface as depicted in the inset of Fig. 6(b) (also in Fig. S5[†] for Π vs. A_M data). Careful scrutiny of the three curves for the three grafting molecular weights reveals that at Π = 35 mN m⁻¹ $\kappa_{\rm f}$ is minimized for the M-PGNP. From standard thermodynamics the $\kappa_{\rm f}$ is an inverse measure of density fluctuations and hence to available free volume. This suggests that amongst all the equally compact PGNP layers the one with the lowest $\kappa_{\rm f}$ has the highest $J_{\rm w}$. This is consistent with the conclusions drawn for gas transport in these PGNP layers. In contrast to water transport, which is facilitated by free volume, the salt flux decreases exponentially with increasing number of layers [Fig. 6(c)] and increasing graft chain length [Fig. 6(d)]. Thus, the salt rejection rate increases monotonically with increases in the amount of polymer through which the ions have to travel. This result is quite different from the corresponding gas permeation results. Previous work⁵⁴ has shown that the transport of ions in a non polar polymer (in that case a composite with graphene) relies on the presence of defects. Direct application of that model in this context rationalizes the results obtained for salt permeability, and therefore the rejection rates. Most importantly these results illustrate that the two components of a saline solution use distinctly different mechanisms to transport through a GNP layer with hydrophobic graft polymers. Further, the new methodology we introduce can be further tuned by varying grafting density, σ , and the grafted chain or nanoparticle chemistry - in particular, varying the chain hydrophobicity could have profound consequences. These intriguing issues remain to be explored.

The LB deposition of neat PMA always yields pin holes shown in Fig. S19† (likely because PMA is a rubber under deposition conditions) and hence low R_s (Fig. S20†), PGNPs have strongly improved thermomechanical properties which ensures a robust membrane so long as 3 or more LB layers are deposited. As has been presented in recent work this is

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Fig. 6 Water permeance (*A*) and salt permeability (*B*) for polymer nanocomposite modified PA membranes. Dependence of *A* on (a) number of PGNP layers (*N*) in the membrane for M-PA and on (b) M_n , for N = 5 layers of PGNPs. Inset shows dependence of κ_f on Π for Langmuir monolayers of all PGNPs used here. Dependence of *B* on (c) *N* for M-PA membranes and on (d) M_n for N = 5 PGNP layered PA membranes.

because the PGNPs (at least up to a $M_n \approx 88$ kDa) behave akin to a jammed colloidal solid with an unusually long relaxation time.⁵⁵ Thus, these materials behave more akin to elastic solids with reinforced, soft-solid-like mechanical behavior. This mechanical reinforcement gives us additional motivation to use these materials in the context of membrane applications, even under circumstances where the base polymer itself cannot form a stable membrane construct. Perhaps it is precisely because of their long relaxation times that PGNP membranes show minimal aging effects in the context of gas separation, and hence, presumably for water desalination.

4 Conclusion

Our work demonstrates that modified PGNP multilayers can be produced on PA membranes by the venerable Langmuir-Blodgett method. In contrast to most current studies, focused on using conventional surface treatments on PA membranes, this LB strategy offers complete coverage of the surface and hence opens new avenues for materials development. The water permeance of these membranes scale inversely with their thickness as long as they are at least 3 NP layers thick, but the more interesting result is that the permeability goes through a maximum as a function of graft chain molecular weight. Through measurements of the osmotic compressibility we show that these effects are driven by the non-monotonic dependence of membrane free volume as a function of graft molecular weight, consistent with our previous findings on gas permeability. Since the transport of solvent and solute are governed by different mechanisms these constructs offer two independent handles to control solvent permeance and permselectivity and thereby suggests an alternate route towards development of a new, low-cost, energy efficient paradigm for water desalination membrane technologies. Our methodology, in principle, can also be extended for other membrane separation applications including gas separation due to the versatility of the LB methodology used in preparing these GNP based multilayers.

Conflicts of interest

The authors declare no conflict of interest.

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