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Room-temperature development of thin film composite reverse osmosis membranes from cellulose acetate with antibacterial properties

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ABSTRACT

A cellulose acetate thin film composite (CA TFC) membrane was developed by direct casting of CA onto an ultrafiltration membrane support. The flux through the CA TFC membrane was, as expected, inversely proportional to the selective layer thickness. The membrane with the lowest thickness of the CA film (217 nm) initially had poor salt rejection (\sim 55%) but relatively high permeability (\sim 0.5 l m⁻² h⁻¹ bar⁻¹). In contrast to asymmetric CA reverse osmosis membranes that are developed in 4 °C water baths, the CA TFC membranes were developed by subsequent swelling in room temperature water baths, thermal annealing at 81 °C, and with room-temperature incorporation of silver nanoparticles onto CA TFC surfaces by chemical reduction. The change in the physical properties as a result of the swelling process was examined with ellipsometry, grazing incidence X-ray scattering and contact angle measurements. A combined swelling and annealing treatment was found to improve salt rejection to an acceptable reverse osmosis salt rejection level (\sim 94%) without significant deterioration of flux. The swelling time was found to generally improve the membrane performance in terms of flux and surface roughness whilst the silver nanoparticle treatment reduced bacterial surface coverage by four orders of magnitude.

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1. Introduction

Desalination of sea water and brackish water using reverse osmosis (RO) has become an increasingly important process to address the issue of depleting global fresh water resources [1–3]. A number of strategies for using polymer based membranes have been developed over the past 40 years, seeking to control the porosity and mode of diffusive and pseudo-convective transport in pore sizes in the sub 2 nm regimes with application to reverse osmosis and tight nanofiltration membranes [4–7].

Cellulose acetate (CA) is commonly used for RO membranes and also being investigated with other desalination techniques such as forward osmosis and membrane distillation [8–10]. It is a semicrystalline thermoplastic that, despite being insoluble in water, remains swellable due to hydrophilic – OH moieties and acetyl groups on the polymer backbone. This polymer can be made into asymmetric membranes using tailored casting solutions and phase-inversion in ice-water baths (at 4 °C). The latter developmental process is key to the final performance of the membrane and determines the evolution of porosity through the membrane [6,7,11–14]. A critical choice of solvents is often required for the development of the relatively porous interior of the film via solvent-water exchange while maintaining a dense surface skin layer. Hence water is a major component in both the development and operation of any CA based RO membrane. As such, CA-water interaction has received significant attention: for example it is thought that at low relative humidity, CA absorbs water vapor which remains bound to the carbonyl groups on the acetate sites of the polymer [15,16]. As the relative humidity increases, more water gets absorbed and expands the polymer to accommodate water up to the maximum saturation [15,17]. This water absorption is a long-term molecular relaxation process [18] and water can remain in the polymer matrix as both free water and polymer-bound water [15,19]. However, the effect of absorption of water on the evolution of the dense selective layer in CA RO membranes is still not well understood due to the complexity in the asymmetric membrane development process. Here we investigate the effect of absorbed water on the evolution of the CA selective layer in a RO membrane while developing a CA thin film composite (TFC) membrane. TFC structures are also advantageous







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for RO membranes due to the ability to tailor the selective layer without compromising the porosity of the support.

Previous studies on CA TFC membranes for RO applications show that these membranes can be successfully made by different wet-casting techniques such as float casting and meniscus coating methods, but only with nanoporous supports [20]. In this article, we show that a CA TFC membrane with desalination properties can successfully be developed on an ultrafiltration support by direct deposition (dry-casting via spin coating) of the CA selective layer and swelling it in water. We also investigate the effect of absorption of water on the surface roughness, which is a significant factor that needs to be taken into account when developing low-fouling RO membranes.

We further improve the CA TFC by incorporating silver nanoparticles onto the CA selective layer. Silver nanoparticles are well known for their antibacterial properties and silver–polymer nanocomposites have been successfully used to reduce biofouling in membranes, eliminating the need for biocides [21–24]. Here we use CA as the template for in-situ synthesis of silver nanoparticles which provides a specific platform for dense and uniform distribution of nanoparticles on the membrane surface [25,26]. This method is more effective than a nanocomposite where incumbent nanoparticles, submerged below the active surface, do not contribute towards the reduction of surface biofouling. The CA TFC incorporating silver nanoparticles (Ag-CA TFC) had good resistance to biofouling.

2. Experimental details

2.1. Materials

Polacrylonitrile ultrafiltration membrane (PAN UF membrane, 20 kDa molecular weight cut-off) was purchased from Sepro Membranes Inc, USA. Cellulose acetate (CA, 30 kDa molecular weight and 39.8 wt% acetyl content), acetone, sodium chloride (NaCl, > 99%), silver nitrate (AgNO₃, > 99%) and sodium borohydride (NaBH4, 99.9%) were purchased from Sigma-Aldrich and used as received. Tryptic Soya Agar with Polysorbate 80 and Lecithin, and Luria–Bertani (LB) medium (Sigma Aldrich) were sterilized by autoclaving at 120 °C for 15 min and stored under sterile conditions.

2.2. Preparation of the CA TFC membrane

Casting solutions containing different CA concentrations were prepared in acetone, filtered through $0.45 \,\mu m$ glass fiber filters, and degassed. For dry-cast CA TFC membranes, casting solutions were spun coated onto the PAN UF membrane at 4000 rpm for 30 s at an acceleration speed of 2720 rpm/min. The membranes were immediately stored in a Petri dish for about 1 h for complete evaporation of the solvent and annealed in an oven at 81 °C for 5 min. In preparing water-swollen CA TFC membranes, dry-cast CA TFC membranes were kept in room temperature water baths (at 20 °C) for a predetermined time before annealing. All the membranes were stored in deionized water overnight before testing for the desalination properties.

2.3. Membrane physical characterization

2.3.1. Grazing incidence wide angle X-ray scattering (GIWAXS)

GIWAXS studies were performed at beam-line 107 at the Diamond Light Source (Harwell Science and Innovation Campus, U.K.) with energy E=12.5 keV. The beam was focused to a size of $200 \,\mu\text{m}^2$ at the sample position, with a footprint on the sample averaging over ca. 3 cm length, and the scattering was detected

with a Pilatus 2D detector. Water swollen CA thin films were made on silicon wafers using identical preparation steps applied for CA TFC membranes. By changing the incidence angle of the incoming X-ray beam from 0.12° to 0.2° – i.e. below and above the critical angle (α_c) of CA – one can alter the total depth of sample from which scattering occurs. This allows a measure of how the CA crystal structure might vary near the surface of the sample and through the whole film thickness as well.

2.3.2. Ellipsometry

Ellipsometric data of the CA thin films on silicon wafers was acquired via Nulling Ellipsometry at angles from 42° to 86° using selected wavelengths in a range from 900 to 360 nm with an Imaging Ellipsometer (Accurion Nanofilm EP3; Accurion GmbH, Germany). The data was fit using Accurion EP4 software applying a model consisting of the Si substrate with a 2 nm native oxide, the cellulose layer with a variable refractive index and a top layer using a Bruggeman effective medium layer accounting for the roughness [27]. The effective medium approach utilized a 50% composition of air within the surface of the cellulose layer.

2.3.3. Contact angle measurements

The static water contact angle was determined by the sessile drop method using a KSV CAM 200 contact angle instrument (KSV Instruments) with deionized water [28]. At least ten measurements were taken on the CA thin films made on Si wafer.

2.3.4. Scanning electron microscopy (SEM)

CA TFC membranes were freeze-fractured and observed using a XL30 SFEG SEM (Hitachi). For surface profiles, CA thin films were made by spin coating CA solutions onto Si wafer, treated under the same conditions as in the making of CA TFC membrane and measured using a surface profilometer (Dek-Tak, Veeco Instruments, USA). The data was analyzed using the statistical software Igor Pro6 (WaveMetrics Inc., USA).

2.4. Membrane performance characterization

The membrane performance was evaluated using a magneticallystirred dead-end filtration cell (Sterilitech Corporation, USA) using nitrogen as the pressurizing agent. A feed solution containing 2000 ppm NaCl was filtered through the CA TFC membrane with an active area of 14.6 cm². Conductivities of the feed and permeate, C_f and C_p respectively, were measured using a conductivity meter (SevenGo Pro, Mettler Toledo) and considered directly proportional to the ionic concentration in the solutions. Hence the overall rejection of salt by a membrane was calculated as $(1 - C_p/C_f)$ where C_f was calculated for each pressure increment to correct the feed salt concentration increase due to the loss of water from the feed-side during consecutive pressure-ramped tests.

2.5. Synthesis of silver nanoparticles loaded CA TFC (Ag-CA TFC) membrane

Silver nanoparticles were directly synthesized onto the CA selective layer using a modified version of the method used by He et al. [25]. In summary, a degassed 0.1 M AgNO₃ (aq) solution was contacted with the active surface of the water-swollen CA TFC membranes clamped with a rubber gasket. After 30 s of contact time, excess AgNO₃ (aq) was removed and the membrane was washed in distilled water. Excess water was removed from the membrane surface and the active surface was contacted with degassed 0.1 M NaBH₄ (aq) solution for 30 s. The membrane was thoroughly washed and stored in distilled water.

UV–visible absorption spectra were recorded over the range of 400–800 nm for the as-prepared Ag-CA films on glass slides using a Cary WinUV UV–visible spectrophotometer. For TEM micrographs of silver nanoparticles the Ag-CA films were delaminated from the glass and transferred onto carbon-coated copper grids in water, dried at room temperature, and observed with TEM (FEI Technai G2, Hillsboro OR) at 200 kV.

2.6. Characterization of the antibacterial properties of Ag-CA TFC membrane

To evaluate the antibacterial properties of the active surface of the Ag-CA TFC membrane, *Escherichia coli* strain W3110, which was used as the model microorganism, was inoculated from LB agar plates into LB liquid medium (5 ml) in 30 ml tubes and incubated at 37 °C for 16 h on an orbital shaker set at 250 rpm. Ag-CA TFC membranes were cut into 1.18 cm² discs, sterilized with 70% ethanol and securely placed into the wells of a sterile 36-well plate. 30 µl of the diluted bacterial suspension containing 4×10^6 colony forming units (CFU)/ml were placed on each membrane and incubated statically for a specified time at 37 °C. Bacterial suspensions from the membrane surfaces were diluted and plated onto tryptic soya agar with lecithin where lecithin was used as a deactivator for silver ions in the solution. Colonies were counted after incubation at 37 °C overnight.

The effect of silver nanoparticles on biofouling of the membrane was evaluated according to De Prijck et al. [29]. Briefly, sterile membrane coupons fixed onto sterile glass supports were introduced into stationary phase cultures of *E. coli* W3110 diluted to 2.4×10^3 CFU/ml and incubated at 37 °C for specified time periods in a rotary shaker set to 250 rpm. Glass supports were useful to avoid bacterial adhesion onto the polyester backing of the membrane. After incubation, the membranes were removed from the bacterial medium and from the glass supports, and briefly rinsed with sterile distilled water. The membranes were placed in 0.25 ml of fresh LB medium, vortexed vigorously for 30 s and placed in a sonication bath for 30 s. The vortexing and sonication steps were performed twice each. Samples were taken from the LB medium, diluted as required, spread on to soy agar plates with lecithin, and colonies were counted after incubation at 37 °C overnight.

3. Results and discussion

3.1. Desalination performance of dry-cast CA TFC membranes

Dry-cast CA TFC membranes were made on PAN UF membrane supports by spin coating solutions containing different concentrations of CA in acetone, followed by solvent evaporation and thermal annealing. Casting solutions containing low polymer concentrations (3% and 2% (w/v) CA) resulted in CA TFC membranes with relatively rough surfaces compared to the films made from higher CA

concentration solutions (7%, 6% and 5% (w/v) CA). Table 1 shows the properties and desalination performance of these dry-cast CA TFC membranes. All the membranes except the CA TFC from 2% (w/v) CA casting solution were stable as indicated by improvement in the salt rejection and flux under increasing feed pressure. Table 1 shows that the thickness of the CA selective layer and the salt rejection of the membrane are positively correlated with concentration of CA in the casting solution. In contrast, the water permeability of the membrane varies inversely with the polymer concentration.

This relationship is expected due to the increase in the viscosity of the casting solution with higher polymer concentrations, which results in thicker CA selective layers and more resistance to the water flow through the membrane [30–33]. However it should be noted that this direct correlation between the thickness of the selective layer and the water permeability is valid only if the same flow mechanism occurs in all these membranes. The type of water flow, which can be either pore-flow or solution-diffusion flow, is generally associated with the structure of the CA selective layer that also governs the selectivity of these CA TFC RO membranes. Thus selectivity to salt becomes useful to understand the structure of the CA selectivity layer. To distinguish the effect of the PAN UF support membrane on the selectivity, the support alone was treated and tested under the same conditions of the CA TFC membrane. As this support membrane showed no selectivity to salt and significantly higher fluxes, we confirm that the salt rejection in these CA TFC membranes can be completely attributed to the CA selective layer and its structural arrangement.

The dry-cast CA TFC membranes reside in two main categories according to the selectivity; membranes with moderate to high salt rejection (from casting solutions containing polymer concentrations of or greater than 5% (w/v) and membranes with low salt rejection (from casting solutions containing 2% and 3% (w/v) CA). Generally, a defect-free selective layer on a RO membrane results in high salt rejection (>98%) for monovalent salts, with a principle water transport mechanism of solution-diffusion. This appears to occur in the CA TFC membranes made by 7% (w/v) CA solutions. The dry cast CA TFC membranes from 2% and 3% (w/v) CA solutions resemble nanofiltration membranes with low NaCl rejection, where pore-flow dominates the solution-diffusion flow resulting in a higher water flux [6]. Thus we assume that the CA selective layer in the thinner membranes is a more open structure (at the 1 nm length scale) possibly due to a non-equilibrated molecular packing in a confined thin film. Such effects are known to be exacerbated in thinner polymeric films during the spin-coating process [34].

3.2. Effect of swelling in water on the physical state of CA TFC membranes

The effect of water in the CA selective layer was studied using the dry-cast CA TFC membranes from CA 2% casting solution. CA thin films on PAN support or on Si wafer were treated in room-temperature

Table 1

Physical properties and desalination performance of the dry-cast CA TFC membranes from different concentrations of CA in the casting solutions.

CA concentration in the casting solution $(w/v\% \text{ of acetone})$	Thickness of CA thin film ^a (nm)	Feed pressure (bar) and feed NaCl concentration (g/l)	Water Permeability ^b $(l m^{-2} h^{-1} bar^{-1})$	NaCl rejection ^b (%)
2%	$\begin{array}{c} 217 \pm 7.6 \\ 363 \pm 29 \\ 767 \pm 16 \\ 1067 \pm 48 \\ 1228 \pm 347 \\ - \end{array}$	32, 2.31	0.439	56.4
3%		20, 2.19	0.096	72.8
5%		32, 2.51	0.025	94.3
6%		32, 2.29	0.029	96.1
7%		32, 2.45	0.015	98.2
GE osmonics CE ^c		28, 2.66	1.07	93.6

^a The mean and standard deviation of the film thickness measured on Si wafer (n=5).

^b The optimum performance measured at 20 °C using a dead-end filtration cell.

^c Commercial CA asymmetric membrane tested in our lab. Manufacturer's specifications: 1.43 l m⁻² h⁻¹ bar⁻¹ and 97% salt rejection at 28 bar (feed: 2000 ppm NaCl).



Fig. 1. SEM images of the CA TFC membrane prepared using 2% (w/v) CA casting solution: (a) dry-casted CA layer on PAN UF membrane, and the same membrane after keeping in the water bath (b) for 30 min, (c) for 60 min and (d) for 72 h. The images show the changes in the surface morphology of the CA TFC membrane.



Fig. 2. Changes in surface properties of the CA thin layer made from 2% (w/v) CA casting solution on Si wafer as a function of water swelling time. (a) Contact angle. (b) Surface roughness and film thickness. (c) Refractive index change in the CA thin films as a function of the time in water bath. The inset shows the ellipsometry data and fit lines measured for the dry-cast film for different incident angles (α). The error bars represent the standard deviation ($n \ge 5$).

water baths before the annealing treatment. The SEM images of the CA TFC membranes (Fig. 1) clearly show that the surface roughness of the films is reduced with the time in the water bath suggesting a possible swelling. These changes were confirmed with Dek-Tak measurements as shown in Fig. 2(b). This observation is imperative as low surface roughness is key to reduced colloidal and bio-fouling in RO membranes [35–39]. The thickness of the film slightly increased with the treatment time by ca. 5% (Fig. 2(b)). This also suggests a possible absorption of water into the polymer matrix.

However, this extent of swelling due to the water absorption is a lower estimate since these CA films were subjected to annealing prior to thickness measurements which may reduce the net amount of water absorbed into a polymer matrix [15,40,41]. The local thickness variations due to the spin coating process may also have a dominant effect here.

Contact angle measurements (Fig. 2(a)) showed no significant change with the time in the water bath suggesting no appreciable change in surface chemistry or wetting energy of the polymer



Fig. 3. (a) 2D GIWAXS map, as a function of the scattering vector q, of the as-prepared cellulose acetate thin film, taken at an incident angle α_i =0.18°. The lines in the image indicate the sectors used for the radial integration of the scattering peaks. (b) Radial integration profiles along q_z for different treatment time at α_i =0.18°. The nearly unchanged scattering peaks rising from the semi-crystalline CA are indicated and labeled with the corresponding d-sapcing. (c) 1-D GIWAXS profiles of the sample swelled for 240 min in water, taken at different incident angles. In figures (b) and (c), the period breaks seen in the data correspond to blank areas in the 2D detector grid (as also seen in figure (a)) and the curves are shifted vertically.

surface. The slight changes observed in the contact angles are supposed to be an effect of the surface roughness.

Ellipsometry studies of the thin CA films on Si wafer were performed by fitting into a model that considered a rough layer of CA on a dense film of the same polymer. The refractive index of the film treated for 30 min in water showed a significant increase in the refractive index compared to the dry-cast thin film (Fig. 2(c)). However the change in refractive index was observed to be smaller after this point. This can be correlated to an increase in the density of the polymer considering the roughness changes observed in SEM and Dektak however there are also other parameters, such as the residual water content in the film after the water treatment and annealing that also affect this change.

The crystallinity of the CA thin films under the treatment was studied with GIWAXS. The pattern in Fig. 3(a) shows prominent Bragg reflections at positions which correspond to d-spacing within the semi-crystalline structure of the CA thin film. Here the complete structural properties of the CA thin films were investigated by employing a wide *q*-range. The scattering profiles of the bulk films showed no significant change in the semicrystalline structure with the treatment as indicated by the unchanged scattering shoulder centered at $\approx 1.1 \text{ Å}^{-1}$, which is due to the amorphous backbone of CA. Further studies with the radial integration profiles of the CA thin films showed a minute differences at *q*-values higher than 3 Å^{-1} (i.e. d-spacing lower than 2 Å). These peaks are indicated and labeled with the corresponding d-sapcing in Fig. 3(b). The full width at half maximum (FWHM) of one of the scattering peaks rising from the crystal structure (at $q \approx 3.35 \text{ Å}^{-1}$ corresponding to a d-spacing of 1.87 Å) was compared for the dry-cast CA thin film and the film that was treated in water for 240 min. The FWHM values changed within a region of 0.0285–0.0315 $Å^{-1}$ but the 120 min sample showed relatively less scattering at the high end of this region. This may suggest a slight increase in crystallinity of the sidechains crystal structure of the 120 min sample. Similar minute changes were also observed in the depth profiling (Fig. 3(c)). However the changes were still not prominent suggesting any

significant structural differences as a function of the film penetration depth.

3.3. Effect of swelling in water on the desalination performance of CA TFC membranes

There is always a trade-off between the flux and salt rejection in RO membranes [2,30]. Therefore, only the dry-cast CA TFC membranes made from 2% (w/v) CA casting solution resulted in an acceptable flux but poor salt rejection (56.4%). Thus, such dry-cast CA TFC membranes were swollen in water baths at 20 °C for specified time durations before thermal annealing in an effort to enhance its salt rejection.

Fig. 4(a) shows that the salt rejection of the dry-cast CA TFC membrane is significantly improved after a 60 min water swelling time. Fig. 4(b) clearly shows that swelling in water improves the stability of the dry-cast CA TFC membrane. The dry-cast CA TFC was highly unstable under applied pressure as shown by the reducing flux up to 28 bar and increasing flux thereafter. This can be attributed to the open non-equilibrated porosity of the initial dry-cast selective layer that is subjected to re-arrangement under applied pressure.

Fig. 5 summarizes the permeability and selectivity of the waterswollen membranes as a function of the water swelling time. Up to 30 min swelling time, the permeability and salt rejection are highly fluctuating and resemble the performance of the dry-cast CA TFC membrane. A 60 min swelling time improves the salt rejection to 90.6% with a dramatic reduction in the permeability to $0.26 \text{ I m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. The flux-selectivity trade off is clearly visible at this point. These results suggest that the major reconfiguration in the CA selective layer occurs within the first 60 min in the water bath.

The increase in the water swelling time to 120 min results in a gradual improvement in the permeability with a slight increase in the selectivity to 93.5%. Fig. 5 also shows that prolonged swelling time further improved the water flux to return to values close to the drycast CA TFC membrane while keeping the salt rejection at a high value.



Fig. 4. Desalination performance of the water-swollen CA TFC membranes (a) NaCl rejection (measured at 20 °C, feed concentration 2000 ppm NaCl) and (b) flux. The different curves show different water swelling times. The fit curves are for visual guidance only.



Fig. 5. Permeability and NaCl rejection of the water-swollen CA TFC membranes as a function of time in the water bath comparing at 32 bar (at 20 °C, feed concentration 2000 ppm NaCl). Both permeability and salt rejection improved after 60 min. Error bars represent standard error of the mean.

Therefore it is evident that the dry-cast CA TFC membrane can be improved to achieve performances of an RO membrane by swelling in room temperature water baths for more than 60 min.

A reasonable interpretation of these swelling results is that the structure of the initial dry-cast film, made at a 2% CA concentration, contains significant nanoporous defects. However, the ability of these 'defective' films to heal under the act of swelling results in the generation of films where the principal mode of solute rejection is due to the dominant mode of solvent-diffusion of water through the membrane. It is notable for example in Fig. 5, that there is a persistent improvement, via water swelling, in six independently made dry-cast membranes (from 60 min swelling times onwards). This indicates that although defective by virtue of nanoporous structure within the dry-cast films, there is some repeatability to this defective character, which can subsequently be improved by programmable swelling. The ellipsometric results indicate that the largest of the improvements in rejection correlate with an increase in refractive index (and hence film density) after 60 min; this can be ascribed to the swelling of the polymer phase with water and closing of nanoporous channels. It is notable that the detailed GIWAXS results do not indicate any significant change of crystallinity within the sample, and indeed the degree of crystallinity in all films is fairly low, with respect to reported studies of thermally equilibrated CA films [43-45]. This might be expected for a spin-cast film where film formation is rapid and highly non-equilibrated and the annealed time is relatively short. The large amorphous shoulder at low q-values is unaltered either within the sample depth or as a result of the swelling process. This is reasonable since the degree of water swelling in the membrane may not induce significant crystal coarsening whilst it does enable sufficient reduction of the local glass transition to enable the closing of the nanoporous defect structures.

These observations suggest that we might optimize the performance of this method further by the control of three key characteristics; crystallinity, film thickness, and nanoporous defect concentration in the film. The crystallinity effectively controls density variations within the film and the ability of the remaining amorphous domains to participate in defect healing. In principle all of these can be controlled through a choice of a solvent with the appropriate volatility and level of solubility for the CA as well as through subsequent annealing to enhance crystallinity. However whilst annealing for 12–24 h would increase the CA crystallinity [43,44], the practical use of such longer times is limited due to the physical limitations of the support.

3.4. Effect of cold water as the swelling medium

When the temperature of the water bath was reduced to 0–4 °C and swelling proceeded for 120 min, the resulting CA TFC membrane had a permeability of $0.26 \ lm^{-2} \ h^{-1} \ bar^{-1}$ whereas the membrane developed under the same conditions but in room-temperature water baths produced a higher permeability of $0.34 \pm 0.03 \ lm^{-2} \ h^{-1} \ bar^{-1}$. The salt rejection of the membrane developed in the room-temperature water bath treated membrane was $93.5 \pm 3.6\%$ while that of the ice-water bath treated membrane was 90.7%. Thus the temperature of the water bath did not affect the salt rejection of the membrane. This is probably due to the reduced macromolecular mobility at low temperatures, which may reduce opening of water channels through the selective layer.

Therefore, for the development of the CA TFC membranes, room-temperature water baths would be preferred over low temperature baths. This also suggests that though low temperature water baths would support developing the porous structure in asymmetric CA membranes, it would negatively affect the selective skin layer, limiting the water flux through the CA asymmetric membranes.



Fig. 6. (a) TEM micrograph of silver nanoparticles from 30 s reduction time showing the crystallographic planes of silver on the amorphous CA background. (b) The particle size distribution histogram of the silver nanoparticles evaluated from the corresponding TEM micrograph. (c) UV-vis absorption spectra of in-situ synthesized silver nanoparticles on CA thin films at different reduction times.



Fig. 7. Antibacterial and antifouling effects of silver nanoparticles: (a) bacterial growth in a solution in contact with the membranes and (b) bacterial attachment onto the membrane surface. Ag-CA TFC membrane shows strong antifouling effects while significantly reducing the solution bacterial density.

3.5. Characterization of Ag-CA TFC and its antibacterial properties

UV–vis spectrophotometry of silver nanoparticles synthesized at different reduction times is demonstrated in Fig. 6(c). The narrow peak at 425 nm, which corresponds to the surface plasmonic effect of silver nanoparticles [22], maximized at a reduction time of 60 s possibly due to the high binding site density on the CA thin film. With the high binding site density and the efficient reducing agent, nanoparticles would rapidly grow and exceed the nano-dimensions by attaching to each other which would lead to loss of the characteristic plasmonic effect. However, a 30 s reduction time was selected for development of the Ag-CA TFC membrane to avoid excess coverage of the active surface with nanoparticles, while still producing a large absorbance peak at 425 nm.

TEM images confirmed that the silver nanoparticles on the CA thin film had a narrow size distribution, with a mean diameter of 4.15 ± 0.87 nm (Fig. 6(a)). The particles were also fairly uniformly distributed across the surface of the membrane. We believe that this is due to the specific site selection for silver ions on the CA thin film via strong electrostatic attractions with the oxygen groups on the polymer [26]. With this method, high surface distribution of nanoparticles can be attained with low silver

loading as only the surface of the selective layer is covered by the nanoparticles. In an Ag-CA nanocomposite, a very high silver loading would be needed to achieve this surface coverage [42].

The Ag-CA TFC membrane was tested for both antibacterial properties towards a bacterial suspension in contact with the membrane surface and the antifouling properties of the active membrane surface. The bacterial suspension placed on the control membrane (CA TFC with no silver nanoparticles) followed a classical bacterial growth curve and appears to reach the exponential phase within 4 h as shown in Fig. 7(a). In contrast, the bacterial suspension on the Ag-CA TFC membrane failed to grow and the bacterial density was reduced by an order of 2 compared to the initial bacterial density in the solution. These results indicate that the Ag-CA TFC membrane can effectively reduce the bacterial growth in a feed solution even over short time scales.

To assess the effect of silver nanoparticles on biofouling, membranes were incubated with bacterial solution for a longer time. Here the control showed a high growth rate with a sharp increase in the colony density on the membrane surface while the Ag-CA TFC membrane showed a slowed growth rate (Fig. 7(b)). The Ag-CA TFC membrane maintained a reduced biofouling density four orders of magnitude lower than the control, over

Table 2

Effect of silver nanoparticles on the desalination performance of CA TFC membrane (measured using dead-end filtration at 20 °C with a feed concentration of 2000 ppm NaCl, operating pressure 32 bar). The incorporation of silver nanoparticles does not show an effect on the water flow or the salt rejection of the CA TFC membrane.

Membrane	Flux $(l m^{-2} h^{-1})$	Permeability $(l m^{-2} h^{-1} bar^{-1})$	Salt rejection (%)
CA TFC Ag-CA TFC	$\begin{array}{c} 10.88 \pm 1.01 \\ 9.59 \end{array}$	$\begin{array}{c} 0.34 \pm 0.03 \\ 0.30 \end{array}$	$\begin{array}{c}93.5\pm3.6\\90.0\end{array}$

48 h. The bacterial density on the Ag-CA TFC membrane reached almost zero after 72 h probably due to the eradication of the bacterial cells in both the solution and on the membrane surface.

These results confirm that Ag-CA TFC membrane effectively reduces bacterial density in both the feed solution and on the surface of the membrane. Generally the average bacterial density in a practical desalination process is about 2.69×10^2 CFU/ml in chlorinated feed or 6.46×10^2 CFU/ml in non-chlorinated feed [46]. This is around 10 times lower than the initial bacterial density used here. Therefore, we conclude that the Ag-CA TFC membrane would be highly effective against biofouling in RO desalination membranes.

Table 2 shows the desalination properties of the Ag-CA TFC membrane compared to a CA TFC membrane. Considering the error bars, the permeability and salt rejection of the silver-incorporated CA TFC membrane were within the values of the CA TFC membrane. Thus the incorporation of nanoparticles only onto the surface of the selective layer seems to reduce any possible contamination of permeate while not restricting the flux through the membrane. Therefore, we believe that the incorporation of silver nanoparticles would improve the lifetime of the membrane with no significant effect on the desalination performance.

4. Conclusions

Dry-cast CA TFC membranes, which initially had low NaCl rejection, were developed into brackish water RO membranes by swelling in room-temperature water baths before the annealing treatment. This is considered to be due to a combined effect of polymer swelling and thermal annealing, which support the CA thin film to reach the equilibrium state while closing the open non-equilibrated network of polymer chains. This treatment further resulted in a smoother surface for the CA TFC membrane which is advantageous for a low fouling RO membrane. The effect of swelling of these films were studied with GIWAXS, contact angle and ellipsometry measurements. Whilst the former two studies showed minimal changes, ellipsometry revealed that the films were subjected to a large change in density as a result of the water-swelling-induced healing of air-filled nanosized defects within the film. This then infers an interesting method to generate RO type membranes via thin-film-composite schemes since the partially healed portions of such defects will allow for rapid water transport whilst the remainder of the dense film contributes a solution-diffusion based separation of the salt. In principle one could alter the size and fraction of such defects in a fairly controlled manner, perhaps through an appropriate choice of solvent. Furthermore we found that incorporation of silver nanoparticles onto the active surface of the CA TFC significantly enhanced the membrane's resistance to biofouling with no deterioration in the flux or the salt rejection. For future work, the CA TFC membrane is suggested as a good platform for studying the CA selective layer in RO membranes and the Ag-CA TFC membrane is supposed to be a good candidate for fouling-resistant RO membranes.

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