Contents lists available at ScienceDirect



Separation and Purification Technology



journal homepage: www.elsevier.com/locate/seppur

A new route to mixed matrix membranes: Atomic layer deposition of TiO_2 on membrane-forming polymers followed by nonsolvent-induced phase inversion

Xiaoqi Xu^a, Hongcheng Song^a, Sen Xiong^{a,*}, Yong Wang^{a,b,*}

^a State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 211816 Jiangsu, PR China ^b School of Energy and Environment, Southeast University, Nanjing 210096 Jiangsu, PR China

ARTICLE INFO

Editor: Junyong Zhu

Keywords: Atomic layer deposition (ALD) Mixed matrix membranes (MMMs) TiO₂ nonsolvent-induced phase inversion Ultrafiltration

ABSTRACT

Mixed matrix membranes (MMMs) are emerging as a novel class of advanced membranes. Versatile nanofillers are usually applied to improve the separation performance of MMMs. However, the poor compatibility and dispersibility of nanofillers cause inner defects in the polymeric matrix, which degrades the separation performance of MMMs. To solve this problem, we introduce atomic layer deposition (ALD) to modify polyacrylonitrile (PAN) powders and use them to fabricate high-performance PAN-TiO₂ MMMs by the nonsolvent-induced phase separation method. Thanks to the advantages of ALD, the thickness of TiO₂ is precisely tuned and the interaction between TiO₂ and PAN matrix is established during the ALD process. Therefore, the fine size and non-covalent interactions make TiO₂ disperse homogeneously in the membrane matrix and enhance the porosity of PAN-TiO₂ MMMs. The PAN-TiO₂ MMMs fabricated by 500-cycle-deposited PAN powders show a 46.5 % higher permeance without consuming the selectivity. Moreover, MMMs possess better antifouling properties, which show lower contaminant adsorption and a better permeance recovery of 86.4 % in dynamic antifouling tests.

1. Introduction

The continuous population growth, rampant environmental pollution, and rising global temperatures make the world perpetually thirsty, therefore, improving the access to available water resources is urgent [1–3]. Among water production technologies, membrane separation is an effective method for freshwater production and wastewater treatment due to the low energy consumption, high separation efficiency, and environmental friendliness [4]. As a common membrane separation process in industries [5-7], ultrafiltration (UF) membranes with pore sizes ranging from 2 to 100 nm can effectively remove colloids, natural organic matter, macromolecules, and many other substances from water [8]. Polymeric UF membranes are more attractive than their inorganic counterparts, because of lower costs and excellent processability. Various polymers, including polysulfone (PSF), polyethersulfone (PES), polyvinylidene fluoride (PVDF), and polyacrylonitrile (PAN), have been used as membrane materials. However, most of these polymers are bothered by their hydrophobic nature, which leads to low water production efficiency and inevitable membrane fouling [9–11]. With the development of membrane fouling, the water production efficiency

keeps decreasing. Therefore, promoting separation performance and alleviating membrane fouling in polymeric membranes are formidable issues.

Mixed matrix membranes (MMMs) are emerging as a novel class of advanced membranes that address the challenges faced by conventional polymeric membranes [12]. Nanofillers with different morphologies, such as Al₂O₃ [13], TiO₂ [14], MgO [15], and SiO₂ nanoparticulates [16] (0-dimensional), carbon nanotubes [17], cellulose nanofibers [18], polyaniline nanorods [19] (1-dimensional), graphene oxide [20], MXenes [21] (2-dimensional), metal-organic frameworks (MOFs) and covalent-organic frameworks (COFs) [22,23] (3-dimensional), are usually applied to improve the separation performance of MMMs. By dispersing nanofillers into a polymeric matrix, MMMs combine the processability and mechanical properties of polymers with the advantages of nanofillers, such as permeability, selectivity, and wettability [24], potentially overcoming the "trade-off" effect and natural hydrophobicity that limit the polymeric membranes in terms of permeability and selectivity [25]. The performance of MMMs is not only influenced by the properties of the polymers and nanofillers, but also affected by the interactions between them [26]. The compatibility between the

* Corresponding authors. *E-mail addresses:* xiongsenhg@njtech.edu.cn (S. Xiong), yongwang@seu.edu.cn (Y. Wang).

https://doi.org/10.1016/j.seppur.2025.132737

Received 4 February 2025; Received in revised form 20 March 2025; Accepted 26 March 2025 Available online 1 April 2025

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Fig. 1. The schematic diagram of the TiO2-ALD on PAN powders and the preparation process of MMMs.

polymeric matrix and the nanofillers, as well as the dispersion of nanofillers within solvents and the polymeric matrix, are the most significant factors [27]. The poor compatibility will lead to non-selective interfacial defects, and the nanomaterials may leak out during longterm storage. The inferior dispersion of the nanofillers will cause severe agglomeration, which undermines the mechanical stability and separation performance of the MMMs [28]. Therefore, finding methods to improve the dispersion of nanofillers and enhance the compatibility between the nanofillers and polymers are crucial for advancing the development of MMMs.

Atomic layer deposition (ALD) is a gas-phase thin film deposition technique based on unique self-limiting reactions and a sub-class of chemical vapor deposition (CVD) [29]. Currently, applications of ALD in the modification, functionalization, and preparation of inorganic and polymeric membranes have being extensively investigated [30]. The ALD can deposit ultrathin metal oxide layers on almost any substrate, even the inert polytetrafluoroethylene (PTFE) [31,32], polypropylene (PP) [33], and PVDF membranes [34], due to the high reactivity of organometallic precursors [35]. After ALD deposition, the pore sizes of membranes were finely tuned by the deposition layers, and the wettability of polymeric membranes was also enhanced [31,34]. As a consequence, the selectivity and permeability of polymeric membranes were promoted simultaneously. However, ALD also has some disadvantages in membrane modification, such as the high cost of precursors, low production efficiency, and the need for additional modification steps.

To address the aforementioned impediments in the fabrication of MMMs and expand the application range of ALD, we propose to use ALD to modify raw materials of polymeric membranes. ALD has been proven to be an effective way to modify powder materials [36-38]. As one of the most commonly used polymers for preparing MMMs via the nonsolventinduced phase separation (NIPS) method, PAN powders are selected as the raw material. Moreover, the PAN molecular chains contain polar functional groups that greatly facilitate the TiO₂ deposition. Thanks to the self-limiting nature of ALD and the high reactivity of ALD precursors, the TiO₂ is deposited with precisely controlled dimensions and tightly bound to PAN powders with strong non-covalent interactions [39], which will break into nano-sized fillers during the NIPS process. Finally, the fine size and non-covalent interactions between nanofillers and polymeric matrix make TiO₂ disperse homogeneously in PAN-TiO₂ MMMs, and the high-performance mixed matrix UF membranes are acquired. This work demonstrates for the first time that the ALD can be easily introduced into the mainstream polymeric membrane industries, and this strategy will accelerate the development of high-performance MMMs at the same time.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN, Mw = 150 kDa) powder purchased from

Taicang Keldar Plastic Raw Materials Co., Ltd. *N*,*N*-dimethylformamide (DMF, \geq 99.5 %) was supplied by Shanghai Lingfeng Chemical Reagent Co., Ltd. Bovine serum albumin (BSA, Mw = 66 kDa, 99 %) was obtained from MP Biomedicals, and phosphate-buffered saline (PBS) tablets were provided by Shanghai Acmec Biochemical Co., Ltd. TiO₂ nanoparticulates (25 nm, rutile structure) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. Titanium isopropoxide (TTIP, 95 %) was purchased from Alfa Aesar Chemical Co., Ltd. Deionized (DI) water was sourced from Wahaha Group Co., Ltd. High-purity nitrogen (>99 %) was provided by Air Liquide. All chemicals were used without further purification.

2.2. Fabrication of PAN-TiO₂ MMMs

An ALD reactor (MNT Micro-Nano Technology Co., Ltd., China) was employed for powder deposition. Before deposition, the PAN powder was dried in a vacuum oven at 70 °C overnight. TTIP and DI water were used as precursors to deposit TiO2. To guarantee the successful volatilization of precursors, the TTIP was stored in a steel cylinder and heated to 90°C, while the H₂O was kept at room temperature due to its high volatility. During the deposition processes, a vacuum pump was connected to the reaction chamber to control the pressure at 1 Torr. All experiments were conducted at 110 °C, and the high-purity nitrogen with a flow rate of 20 sccm was used as carrier gas and purge gas. The PAN powder was placed in the ALD reaction chamber and preheated under vacuum (~1 Torr) for 30 min before the ALD process. In the two half-cycles, the sequence of precursor pulsing (TTIP and H₂O), exposure, and N₂ purge were 2 s, 30 s, and 40 s, respectively. Different ALD cycle numbers (100, 200, 300, 500, 750 and 1000) were applied to the PAN powder (Fig. 1), and the ALD-deposited PAN-TiO₂ materials were named PAN-X, where X represents the number of ALD cycles.

The pristine PAN membranes and PAN-TiO2 MMMs were fabricated using the NIPS method [40]. The casting solutions were prepared by dissolving 15 wt% pristine or ALD-deposited PAN powders in DMF. The casting solutions were stirred mechanically at 70 °C for 6 h to form homogeneous solutions (Fig. 1). During the stirring, the deposited TiO₂ layers were pulverized into nanofillers. The PAN powders were directly contacted with the DMF and the deposited TiO2 layers showed almost no impact on the dissolution of PAN powders. Then, the casting solutions were placed in a vacuum oven statically overnight. Then, the casting solutions were turned into 200-µm-thick liquid films on automatic knife coater (JFA-II, Shanghai Modern Environment Engineering Technique Co., Ltd., China). The liquid films stood in the air for 10 s before the NIPS process. After the solvent exchange step started, the self-supporting membranes were gradually formed. The obtained membranes were thoroughly washed and soaked in DI water for 24 h to remove residual DMF. Finally, the membranes were stored in fresh DI water and the DI water was replaced daily. The obtained PAN-TiO2 MMMs originated from PAN-X were named PAN-X MMMs (Fig. 1). For example, PAN-100 MMMs meant that the MMMs were fabricated by PAN powders which underwent 100 cycles of TiO_2 deposition.

2.3. Characterizations

The morphology of prepared membranes and all other specimens was characterized by scanning electron microscopy (SEM, S-4800, Hitachi). At least 70 pores on the membrane surface of each sample were measured using NanoMeasurer software (version number: 1.2.5) to estimate average pore sizes. The element distribution of PAN-TiO₂ MMMs was analyzed using energy-dispersive X-ray spectroscopy (EDX, Oxford INCA 350). The PAN-500 powder was calcined in a muffle furnace and the morphology of the residual material was observed by SEM and EDX. The thermal stability and actual TiO2 amount in the PAN powder were tested by thermal gravimetric analysis (TGA, STA 449F3, NETZSCH). All samples were placed in an air atmosphere and heated from 25 °C to 1000 °C with a heating rate of 10 °C min^{-1} . The dispersion of different TiO₂ nanofillers in the casting solution can be observed by using an optical microscope (MD50, Mshot). A small amount of the casting solution prepared with 0.75 wt% nano-sized TiO2 and PAN-1000 powder was examined. A water contact angle goniometer (WCA, DropmeterA100, Maist) was employed to characterize the wettability of the prepared membranes. Each sample was measured at least three times, and the average value was taken as the WCA. The zeta potentials of selected membranes were measured by an electrokinetic analyzer (SurPASS, Anton Paar). An X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) was employed to examine the PAN-1000 membranes. The viscosity of casting solutions was assessed at ambient conditions using a rotational viscometer (DV2T, Brookfield) at a rotational speed of 100 rpm. Additionally, the overall porosity of each membrane was determined through a gravimetric technique, which can be calculated using the following equation [14,41]:

$$\varepsilon = \frac{m_1 - m_2}{A\rho d} \tag{1}$$

where ε (%) represents the overall porosity of the membranes, m_1 (g) and m_2 (g) refer to the wet and dry weights of the membranes, respectively. *A* (cm²) denotes the effective area of the membranes, while *d* (cm) is the thickness of the membranes, and ρ (g cm⁻³) is the density of water.

2.4. Performance tests

The pure water permeance (PWP) and the rejection rate of BSA in PAN-TiO₂ MMMs were evaluated using a crossflow filtration system (SF-SB, Hangzhou Saifei Membrane Separation Technology) under a pressure of 0.1 MPa. The effective membrane area for testing was 22 cm². The feed solution temperature was controlled at 25 °C and the volumetric flow rate was maintained at 35 L h⁻¹. Before testing, all membranes were pre-pressed at 0.15 MPa for 30 min. The PWP (*J*, L m⁻²h⁻¹ bar⁻¹) was calculated using Eq. (2):

$$J = \frac{V}{A \cdot P \cdot \Delta t} \tag{2}$$

where *V* (L) is the volume of water permeated through the membrane, *A* (m²) is the effective membrane area, Δt (h) is the permeating duration, and *P* (bar) is the transmembrane pressure.

The rejection rate was measured with a BSA solution (0.5 g L^{-1}) as the feed solution, and the absorbance of the permeate and feed solutions at a wavelength of 280 nm was measured using a UV–vis absorption spectrometer (UV-8000, Shanghai Yuanxi Instrument Co., Ltd.). The rejection rate (*R*, %) was calculated based on the concentration change between the feed and permeate solutions, as shown in Eq. (3):

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{3}$$

where R (%) is the BSA rejection, C_p (g L⁻¹) and C_f (g L⁻¹) are the BSA



Fig. 2. The TG curves of PAN and PAN-TiO₂ powders with different deposition cycle numbers. The insert shows the magnified view of different TG curves.

concentrations of the permeated and feed solutions, respectively.

2.5. Static adsorption and dynamic antifouling performance tests

The static adsorption experiments were conducted in a sealed glass vial with 10 mL of BSA solution (1.0 g L⁻¹). The PAN membranes and PAN-TiO₂ MMMs were cut to 2×2 cm², and thoroughly immersed in BSA solutions. The glass vials were then placed in a thermostatic shaking bath at 25 °C and incubated for 24 h. Afterward, the membrane was removed from the glass bottle, and the equilibrium concentration of the BSA solution was measured. The static adsorption value of BSA on the membrane, q (mg cm⁻²), was calculated using the Eq. (4) [42]:

$$q = \frac{(C_0 - C)V}{A} \tag{4}$$

where C_0 (g L⁻¹) and *C* (g L⁻¹) represent the initial and equilibrium concentrations of BSA solutions, respectively. *V* (L) is the volume of the tested BSA solution, and *A* (cm²) is the membrane area.

Dynamic BSA filtration experiments were conducted under a transmembrane pressure of 0.1 MPa to evaluate the antifouling performance. The membrane was pre-pressed at 0.15 MPa for 30 min and then lowered down to 0.1 MPa for testing. The 40-min water permeance and 40min BSA solution permeance were tested in an interleaved mode, and each test was repeated 3 times. Eq. (5) was used to calculate the flux recovery ratio (FRR):

$$FRR = \frac{F}{F_0} \times 100\% \tag{5}$$

where *F* (L m⁻²h⁻¹ bar⁻¹) represents the PWP of the membrane after each cycle, while F_0 (L m⁻²h⁻¹ bar⁻¹) is the initial PWP of the membrane.

3. Results and discussion

3.1. TiO₂-deposited on PAN powders

TGA was performed to quantitatively assess the content of TiO_2 deposited on the PAN powders. The mass loss curves and the final residual mass are shown in Fig. 2. According to the TGA curves, all specimens exhibited negligible weight loss before 300 °C. Then, an obvious mass loss appeared in all specimens around 300 °C due to the decomposition of the polymer chains in PAN. The samples underwent more pronounced pyrolytic reactions when the temperature increased to 500 °C, which meant that the PAN backbone started pyrolysis. With the



Fig. 3. The surface, cross-sectional SEM images and surface pore size distribution of (a) PAN membranes; (b) PAN-100 MMMs; (c) PAN-200 MMMs; (d) PAN-300 MMMs; (e) PAN-500 MMMs; (f) PAN-750 MMMs; (g) PAN-1000 MMMs. All SEM images are presented with the same scale bar, which is demonstrated in (a).



Fig. 4. Overall porosity of different membranes.

increasing temperature, the polymer chains broke and promoted the movement and rearrangement of the molecular chains [43]. To investigate the morphology change, the PAN-500 powder was subjected to a calcination treatment at 500 °C for 5 h, and the residual was analyzed. The morphology of the calcined PAN powder changed obviously (Fig. S1a-b), the original structure was replaced by rod-like stacking structures, and some smaller particles were on the rods. EDX-mapping showed that the Ti element was easily found on the residual (Fig. S1c), which proved the successful deposition of TiO₂.

When the temperature exceeded 550 °C, the decomposition of the PAN backbone accelerated and a significant weight loss was found in all specimens. Interestingly, the decomposition rate of ALD-modified PAN was prompted with more ALD cycles. As shown in Fig. 2, the pyrolysis rate from the quickest to the slowest was PAN-500, pristine PAN, PAN-300, and PAN-100. This phenomenon was attributed to the protective effect of TiO₂ at lower deposition cycles and the catalyzing effect with more deposition cycles [34]. The TiO₂ content in deposited PAN powders was calculated based on the residual mass. The TiO₂ loading for PAN-100, PAN-300, and PAN-500 was 0.25 %, 0.59 % and 1.27 %, respectively. At the initial ALD stage, the precursors required a longer time to diffuse into the polymer matrix and nucleated in the subsurface area, thus the mass increase of the first 300 cycles was slow. Once the nucleation was completed, TiO2 grew rapidly along the nucleation sites [32], therefore, the TiO₂ mass ratio in PAN-500 powders was doubled when compared with the PAN-300 powders.

3.2. Characterization of PAN-TiO₂ MMMs

The microstructure of membranes has a significant influence on the UF performance. The top surface morphology and cross-sectional morphology of PAN membranes and PAN-TiO₂ MMMs were characterized by SEM (Fig. 3a–g). Both PAN and PAN-TiO₂ MMMs exhibited a coarse surface with small pores. The surface mean pore sizes of PAN membranes and PAN-TiO₂ MMMs showed an increasing and then decreasing trend (Fig. 3). The surface pore size of PAN membranes was 10.2 nm, and it kept increasing to 16 nm in PAN-300 MMMs. Then the pore size decreased to 13.8 nm in PAN-1000 MMMs. This phenomenon was attributed to the addition of TiO₂, which altered the diffusion rate between the solvent and the nonsolvent during the NIPS process [44].

According to the cross-sectional morphology depicted in Fig. 3, the membranes displayed a characteristic hierarchical structure [45], which was composed of a dense top layer, a finger-like middle layer, and a macrovoid-containing lower layer. After being immersed in the DI



Fig. 5. The viscosity of different casting solutions.

water, the surface of the casted film solidified immediately and formed the dense top layer. With the processing of solvent exchange, finger-like channels were formed and widened gradually. Some macrovoids appeared around the lower part of the pristine PAN membranes. After bringing in the ALD-deposited TiO2 nanofillers, the cross-sectional morphologies of the PAN-TiO₂ MMMs showed obvious changes. With the increasing amount of TiO₂ nanofillers, the top layer became more and more porous, and the finger-like area in $PAN-TiO_2$ MMMs was compressed. Compared with other parts, the lower part of MMMs exhibited the most significant changes. The macrovoids expanded continuously with the increasing amount of TiO₂. The overall porosity of PAN membranes and PAN-TiO₂ MMMs was tested using the weighing method (Fig. 4). The pristine PAN membranes exhibited the lowest porosity of 60.4 %. After introducing TiO₂, the porosity of PAN-TiO₂ MMMs showed a similar trend with the surface pore size. The porosity increased from 64.3 % (PAN-100 MMMs) to 77.6 % (PAN-500 MMMs) and then decreased to 62.3 % (PAN-1000 MMMs).

In the MMMs, the nanofillers acted as a "double-edged sword", which could be an enhancer or a reducer with different concentrations. With fewer ALD cycles, the amount of TiO₂ nanofillers in the casting solutions was low. In the NIPS process, the hydrophilic TiO₂ accelerated the exchange rate between the solvent (DMF) and nonsolvent (H₂O) [46], which caused the formation of solvent-rich nuclei in the polymer matrix. Then the nuclei facilitated the pore formation in the MMMs, therefore, the porosity of PAN-TiO2 MMMs rose in conjunction with ALD cycles. With a certain amount of TiO2, the thermodynamic stability of casting solutions decreased, and the phase separation rate was accelerated. However, the more TiO₂ deposited on the PAN powders, the more viscous the casting solution. The high viscosity of the casting solution impeded the solvent-nonsolvent exchange rate, leading to reduced porosity in the MMMs [47]. As shown in Fig. 5, the viscosity of pure PAN casting solution was 820 mPa·s. With the ALD cycles rising from 100 to 500, the viscosity of PAN-TiO₂ casting solution gradually increased to 1227 mPa·s. As the amount of TiO2 increased, the physical entanglement between PAN chains in the casting solution was enhanced, thereby increasing the viscosity [48]. However, the viscosity of the casting solution was suddenly increased to 1713 mPa·s and 2000 mPa·s after 750 cycles and 1000 cycles of ALD deposition, respectively. Therefore, the formation of micro-pores was suppressed by the excessive amount of TiO_2 in the casting solution and the porosity began decreasing (Fig. 4). This result also explained the changes in cross-sectional morphologies.



Fig. 6. SEM and EDX mapping images of the cross-section of MMMs prepared by ALD deposition of TiO₂ on PAN powder.

3.3. The dispersibility of TiO₂

The dispersion of TiO₂ in PAN casting solutions was characterized by comparing with the traditional blending method. Two casting solutions were prepared for comparison: one composed of PAN-1000 powders in DMF, and the other containing pristine PAN powders and 0.75 wt% TiO₂ nanoparticulates (according to the polymer mass) in DMF. After the solutions were prepared and allowed to stand overnight, the bottom layer of the two casting solutions was carefully examined using an optical microscope. There was severe agglomeration in the TiO₂ nanoparticulates blended solutions, while slight agglomeration of nanofillers was found in the PAN-1000 casting solution (Fig. S2). This result confirms the better dispersion of our strategy. During the ALD processes, the TTIP molecules would form intermediate complexes with the $-C \equiv N$ groups, thus the TTIP molecules were weakly bound to the PAN chains. With the proceeding of ALD processes, the intermediate complexes and $-C \equiv N$ groups became the preferred nucleation sites for the deposited TiO₂ [49,50], thus the interaction between TiO₂ and PAN was established and enhanced the dispersibility of TiO₂.

To investigate the dispersibility of TiO₂ in the membrane, EDX mapping was performed on the PAN-300 MMMs (Fig. 6). The image clearly showed a wide distribution of Ti element, which was attributed to the uniform deposition of TiO₂ on the PAN matrix. Moreover, the top and bottom surfaces of PAN-1000 membranes were characterized by XPS to analyse the uniformity of TiO₂ distribution in the PAN-TiO₂ MMMs. As shown in XPS spectra (Fig. S3) and the atomic ratio of different elements (Table S1), there were no obvious differences between the top surface and bottom surface of the PAN-1000 membranes. The C 1s and N 1s peaks observed in the spectra were attributed to the carbon and nitrogen elements within the PAN matrix. These two elements constituted over 96 % atomic ratio of the entire composition. The O 1s in the spectra came from the adsorbed moisture, carbon dioxides, and the doped nanofillers. According to the XPS result, the Ti atomic ratio on the top and bottom surfaces was 0.15 % and 0.18 %, respectively (Table S1). Therefore, no obvious Ti-related peak was found in the XPS spectra due to the low Ti atomic ratios. The similar Ti concentrations of the top and bottom surfaces further confirmed that the deposited TiO2 were uniformly dispersed in the PAN-TiO2 MMMs across the membrane.

To further investigate the form of ALD-deposited TiO_2 existing in the PAN-TiO₂ MMMs, the PAN-1000 MMMs were dissolved in the DMF and the precipitate was collected. The precipitate was characterized by SEM and EDX after being thoroughly washed by DMF (Fig. S4). The precipitate was composed of agglomerated nanomaterials and its size reached the micrometer level. As shown in Fig. S4a, the EDX result showed the Ti element distributed evenly on the precipitate, which confirmed the major composition of the precipitate was TiO₂. In high magnification (Fig. S4b), the precipitate exhibited sharp edges. Therefore, it could be inferred from the SEM and XPS results that the ALD-deposited TiO₂ layers were broken into fragments during the NIPS process and evenly distributed in the PAN-TiO₂ MMMs.



Fig. 7. PWP and BSA rejection rate of different membranes.

3.4. Separation performance of PAN membranes and PAN-TiO₂ MMMs

The wettability of PAN membranes and PAN-TiO₂ MMMs was investigated by WCA, which was used as a reference to investigate the membrane surface hydrophilicity. The WCA of PAN membranes was 68.7° , and that of PAN-TiO₂ MMMs exhibited similar values until 1000 cycles of ALD deposition were completed (Fig. S5). Considering the doping amount and homogeneous dispersion of TiO₂, this result was reasonable. Moreover, similar WCAs also showed that the introduction of ALD-deposited TiO₂ had no adverse effect on the wettability of PAN-TiO₂ MMMs.

The PWP and BSA rejection rates of PAN membranes and PAN-TiO2 MMMs are shown in Fig. 7. The PAN membranes exhibited a PWP of 417 L m⁻² h⁻¹ bar⁻¹ and a BSA rejection rate of 98.7 %. The PWP of PAN-TiO₂ MMMs showed a pattern of ascent followed by descent, which aligned with the pore size and porosity of the membranes. After introducing TiO₂ into the PAN matrix, the PWP of PAN-TiO₂ MMMs increased gradually with more ALD cycles until 500 ALD cycles. Among the PAN- TiO_2 MMMs, the PAN-500 MMMs showed the highest PWP of 611 L m⁻² h^{-1} bar⁻¹, which was 1.46 times higher than the pristine PAN membranes. Fortunately, the increase in PWP had no adverse influence on the BSA rejections. For all PAN-TiO2 MMMs, the rejection towards BSA fluctuated between 97.9 % and 99.5 %. BSA was a frequently used probe molecule in membrane separation processes, which showed an ellipsoidal shape with a dimension of 14 nm \times 3.8 nm \times 3.8 nm [51]. The higher rejection showed that the surface pore size of all membranes was close to the BSA molecular size, which was in good accordance with the statistical results from SEM images. Moreover, the separation performance showed that introducing ALD to modify PAN powders endowed unilateral improvement in the permeability of the PAN-TiO2 MMMs without undermining their selectivity. According to the TGA result, the



Fig. 8. (a) Dynamic antifouling performance of PAN membranes and PAN-500 MMMs, (b) Performance comparison between the PAN-500 MMMs and other membranes.

TiO₂-blended MMMs were prepared by adding 1.25 wt% TiO₂ nanoparticulates (diameter: ~20 nm) into the casting solution. Compared with the PAN-500 MMMs, the TiO₂-blended MMMs showed a similar BSA rejection (98.4 %) and ~47 % lower PWP (322.9 L m⁻² h⁻¹ bar⁻¹). As shown in Fig. S6, many irregular protrusions were detected on the surface of TiO₂-blended MMMs. Combined with the optical microscope image of the casting solution, these protrusions were caused by the uneven dispersion of agglomerated TiO₂ nanoparticulates, thus some pores were blocked and led to low PWP. This comparison further illustrates the importance of homogeneous dispersion of nanofillers in the MMMs.

During the separation process, contaminants continuously accumulate on the membrane surface, leading to a decline in separation performance. Therefore, the antifouling property of PAN-TiO2 MMMs should be taken into consideration. As shown in Fig. S7, static BSA adsorption experiments were conducted on all membranes. It could be observed that the static adsorption value of BSA on the PAN membrane was approximately 0.603 mg cm⁻². After doping with ALD-deposited TiO₂, the adsorption values on all MMMs decreased. The ALDdeposited TiO₂ surface exhibited positive charging at lower pH values and negative charging at higher pH values [52], therefore, the PAN matrix mixed with positively charged TiO₂ or less negatively charged TiO₂ led to reduced negative charging on the PAN-TiO₂ MMMs. Nevertheless, the PAN-TiO₂ MMMs still possessed a negatively charged surface (Fig. S8). Due to the hydrophilic and negatively charged surface, BSA molecules, which are also negatively charged, were difficult to adsorb onto the membranes. This result demonstrated the improved antifouling property of PAN-TiO₂ MMMs.

Compared with the static BSA adsorption, the dynamic antifouling is more practical. As shown in Fig. 8, both the PWP and BSA solution permeance for PAN-500 MMMs were higher than that of PAN membranes. At the first cycle, the initial PWP of the PAN-500 membrane was $611 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. After being contaminated by BSA, the permeance decreased to 119 L m⁻² h⁻¹ bar⁻¹, and the PWP recovered to 590 L m⁻² $h^{-1}\,\text{bar}^{-1}$ through backwashing with DI water, which resulted in an FRR of 96.6 %. In contrast, the permeance of the PAN membrane decreased from 417 to 104 L m⁻² h^{-1} bar⁻¹ after BSA contamination, and the FRR of PAN membranes was only 46.4 % after backwashing. After the thirdcycle test, the FRR for PAN-500 MMMs was 86.4 %, and that of PAN membranes was only 31.5 %. This result indicated that the antifouling performance of the PAN-500 MMMs was significantly enhanced compared to the PAN membranes. As confirmed by the static BSA adsorption experiments, the introduction of TiO2 alleviated the adhering of BSA molecules, therefore, the contaminated membrane surface of MMMs was easier to clean during the backwashing processes and led to higher FRR values. A summarization of the membrane performance in terms of PWP and BSA rejection was provided in Fig. 8b, which disclosed that our membrane performance was at the forefront of ultrafiltration membranes (Table S2).

4. Conclusions

In this study, the PAN powder was modified by ALD-deposited TiO₂ and then used as raw material to fabricate high-performance MMMs. Compared with the traditional doping method, the ALD-deposited TiO₂ on PAN powders showed better dispersion in casting solutions and the agglomeration of nanofillers was relieved. Thanks to the hydrophilicity of TiO₂, the exchange rate between the solvent and nonsolvent during NIPS processes was accelerated, which improved the porosity of the MMMs without consuming the selectivity. The PAN-500 MMMs exhibited a 1.46 times higher PWP (611 L m⁻² h⁻¹ bar⁻¹) than the pristine PAN membranes and a similar BSA rejection (97.9 % to 98.7 %). Moreover, the results of static and dynamic antifouling experiments towards BSA solutions explained that introducing ALD-deposited TiO₂ also improved the antifouling property of PAN-TiO2 MMMs. The FRR of PAN-500 MMMs was 86.4 % and that of pristine PAN membranes was only 31.5 % after the three-cycle experiment. In summary, this study shows that introducing ALD to modify raw polymer materials for MMMs will enhance the adaptability of applying ALD to the membrane industry, as well as provide a new strategy to fabricate high-performance MMMs. In future works, this strategy will be brought into other polymer systems to promote the further development of MMMs.

CRediT authorship contribution statement

Xiaoqi Xu: Investigation, Data curation, Writing – original draft, Writing – review & editing. Hongcheng Song: Investigation, Validation, Writing – review & editing. Sen Xiong: Methodology, Validation, Writing – review & editing. Yong Wang: Conceptualization, Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was financially supported by the National Key Research and Development Program of China (2024YFE0112300) and the Key Research and Development Program of the Jiangsu Provincial Department of Science and Technology of China (BE2022056-3).

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2025.132737.

Data availability

Data will be made available on request.

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