Hydrophilization of porous polypropylene membranes by atomic layer deposition of TiO$_2$ for simultaneously improved permeability and selectivity

Qiang Xu, Jun Yang, Jiawei Dai, Yang Yang, Xiaoqiang Chen, Yong Wang *

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, PR China

A R T I C L E   I N F O

Article history:
Received 26 May 2013
Received in revised form 7 August 2013
Accepted 12 August 2013
Available online 19 August 2013

Keywords:
Atomic layer deposition
Hydrophilization
Polypropylene membranes
Surface modification

A B S T R A C T

The uses of porous polypropylene (PP) membranes are limited in water-based separations because of their strong hydrophobicity. To improve the separation performances of polypropylene membranes by hydrophilization, we deposited TiO$_2$ on their pore surface using the atomic layer deposition strategy with and without a pretreatment to the membrane by plasma. The direct deposition without plasma pretreatment led to slightly enhanced hydrophilicity because TiO$_2$ was slowly deposited on the membrane as discrete particles due to the lack of active groups on the bare polypropylene surface. In contrast, after a short exposure to plasma generated in air, oxygen-containing active groups were formed on the membrane and subsequent atomic layer deposition yielded conformal thin layer of TiO$_2$ on the pore walls. The deposited membranes showed remarkably enhanced hydrophilicity and higher deposition cycles led to stronger hydrophilicity. As a consequence of the enhanced hydrophilicity, the permeability and retention of the deposited membrane were simultaneously improved with big amplitudes. For example, an increase in pure water flux of ~60% and a more than doubled retention ratio were obtained by deposition of TiO$_2$ for 150 cycles on the plasma-activated polypropylene membrane. Furthermore, the TiO$_2$-deposited membranes showed improved resistance to protein fouling compared to unmodified membranes also because of the enhanced hydrophilicity. Such a hydrophilization strategy of plasma pretreatment and subsequent atomic layer deposition of metal oxides is expected to be also effective in the upgrading of performances of other membranes with inert surfaces.

1. Introduction

Polypropylene (PP) is superior compared to many other polymers in mechanical strength, chemical stability, thermal and chemical resistance, and low cost. Moreover, PP can be easily processed to porous fibers and thin films through the melt spinning or extrusion process and a subsequent stretching step in which no solvents are involved. Therefore, PP is a very promising material for separating membranes. Porous PP membrane has found potentially important applications such as water treatment [1], separators of lithium-ion batteries [2–4], pervaporation [5], blood purification [6]. However, its strong hydrophobicity and consequently easy fouling characteristic generate a series of problems in its practical application processes. When used as separation membranes in water systems such as waste water treatment using the membrane bioreactor (MBR) technique, PP membranes are prone to be fouled, causing the degradation in permeability and increment in cost and energy. This is one of the main reasons why PP membranes have not been widely used in water treatment in the industry scale. Hence, extensive efforts have been made to improve the hydrophilicity of PP membranes.

A number of physical and chemical methods have been adopted to modify the surface properties of PP membranes aiming at improving their hydrophilicity. The principle of surface modification is direct and simple: to cover the original hydrophobic surface of PP with an additional layer of hydrophilic materials, triggering the transition of the PP surface from hydrophobic to hydrophilic. The hydrophilic materials can be either physically deposited on the membrane pores, e.g., by adsorption [7–5] or by plasma treatment in which oxygen-containing polar groups are generated on the pore walls [10]. However, these physical methods frequently suffer a poor durability because the introduced hydrophilic materials are easily lost during application and storage. Alternatively, covalent bonds are used to tightly link the external modifiers to the pore walls by chemical reactions. To this end, PP backbones are first activated by thermal initiators [11,12] or high energy irradiation such as UV,
effective in keeping the surface hydrophilic for a long time [17].

However, these chemical modification routes typically involve harsh pretreatment, tedious and complicated synthesis and purification processes. Moreover, as these methods are usually carried out in liquid solutions, monomers are not easy to diffuse into every small membrane pore, leading to inhomogeneous grafting of polymer chains on membrane pores. Some small pores might be blocked by extraordinarily long grafting chains whereas some others might not be grafted at all, leading to a loss of permeability. Therefore, it is in urgent need of a simple and efficient approach to boost the hydrophilicity of PP membranes at no expense of their permeability.

Recently, atomic layer deposition (ALD) has emerged as an effective technique to deposit conformal and thin films on various substrates with a precision of atom level [18]. The nucleation and growth behaviors of metal oxides (e.g. Al2O3, ZrO2, TiO2 and so on) have been investigated on various types of polymer substrates during the ALD process [18–25]. A model was proposed for the ALD precursors’ adsorption on surface and diffusion into the subsurface of polymers without active groups [19], and it was found that the process temperature significantly affected the interface between the deposition layer and the substrate [26,27]. There are some reports on the deposition of metal oxides by ALD on PP substrates but most studies are focused on the deposition of metal oxides, mainly Al2O3, on nonporous PP films [19,27–30]. One work was reported on the ALD deposition of Al2O3 on porous PP membranes with the purpose to improve the wettability of electrolyte solutions and the thermal stability of the PP membrane in the use of lithium ion batteries [31]. For the lack of active chemical groups on the PP surface, a rough and graded interface observed through TEM usually appears between the deposition layer and the PP substrate [27]. ALD has been demonstrated to be very effective in tuning the pore size and surface properties of porous membranes with different chemical nature by depositing thin layer of Al2O3 or TiO2 on pore walls [22,25,32]. However, there is no report on the modification of PP membranes by ALD deposition of metal oxides with the aim to improve their liquid separation performances.

In the present work, we first directly ALD-deposited TiO2 on nascent PP membranes and observed slightly enhanced hydrophilicity because of the growth of discrete TiO2 particles on the pore surface. We then generated oxygen-containing groups on the membrane surface by plasma activation. A conformal and uniform TiO2 ALD coating was then achieved on the surface of the plasma-activated PP membranes. During each half reaction of ALD, the “exposure mode” was adopted to enhance the diffusion efficiency of ALD precursors [33], guaranteeing the full implementation of reaction and precise control of the deposited layer. TiO2 was chosen as the depositing material instead of other metal oxides because of its good hydrophilicity and strong resistance to acids and alkalis as well as the convenient ALD operation of TiO2 using cheap and less sensitive precursors. After ALD coating, the PP membranes showed notably strengthened hydrophilicity and fouling resistance. Moreover, at wide range of ALD cycles, the water flux and rejection of the deposited membranes simultaneously increased with big amplitudes.

2. Experimental

2.1. Materials

Porous PP membranes (Celgard 2400) with a mean pore size of 43 nm and a porosity of 41% as claimed by the manufacturer were received as sheets with a thickness of 25 μm. We cut round chips with a diameter of 25 mm from the PP sheets and these PP chips were used as porous membranes for the ALD of TiO2. Titanium isopropoxide (TIP, 98%, Aladdin) and deionized H2O were used as precursors for the ALD of TiO2 and N2 with a purity of 99.99% was used as both the precursor carrier and the purging gas. Monodispersed SiO2 nanospheres with the average diameter of 22 nm dispersed in water purchased from Aldrich were used as probes to test the retention of PP membranes. Bovine serum albumin (BSA) with a molecular weight of 67k obtained from General Material with a purity > 97% was used as the model protein to reveal the fouling resistance of the membranes.

2.2. Plasma activation

Some PP membranes were activated by air plasma before ALD deposition. The plasma activation was first carried out on one side of the membrane at a power of 50 W in a vacuum chamber of the sub-atmospheric pressure glow discharge plasma generator (HPD-280, Nanjing Suman Electronics Co. Ltd) with a pressure of 10 mbar for 20 s. The other side of the PP membrane was then treated by air plasma in the same way. The PP membranes were shifted to the ALD chamber for TiO2 deposition within 10 min after the plasma treatment.

2.3. TiO2 ALD

ALD of TiO2 on PP membranes with or without plasma activation was performed in a Savannah S100 ALD reactor (Cambridge NanoTech) with a substrate temperature of 80 °C. PP membranes were fixed in a holder in the ALD reactor and dried at 80 °C in vacuum (~0.5 Torr) for 10 min before deposition. TIP was heated to 82 °C and water was maintained at room temperature. TIP and water vapor were pulsed into the reaction chamber alternatively, and the exposure mode was introduced in this experiment to make the precursors diffuse and be adsorbed in the samples sufficiently. In a typical ALD cycle TIP was pulsed into the chamber for 0.2 s. After a waiting time of 5 s, the chamber was purged with nitrogen for 30 s. Then the second precursor, water, was pulsed into the chamber for 0.015 s, followed by a waiting time of 5 s and purging time of 30 s. Thus we finished one ALD cycle. In the ALD process, a steady N2 flow with the rate of 20 sccm was maintained. The plasma-pretreated PP membranes were deposited up to 200 cycles, respectively. For comparison, porous PP membranes without plasma pretreatment were deposited with 100, 150, 200, 250, 500, and 800 cycles using the same deposition conditions, respectively.

2.4. Characterizations

X-ray photoelectron spectroscopy (XPS) analyses were performed on a Thermo ESCALAB 250 system equipped with a monochromatic Al Kα X-ray source (hv = 1486.6 eV). The X-ray anode was run at 150 W, and the pass energy for survey spectra was set at 20 eV with a step size of 0.05 eV. The diameter of the analysis area on samples was approximately 50 μm and the binding energies were calibrated to the C 1 s peak at 284.8 eV. The surface morphology of PP membranes was observed with field emission scanning electron microscopy (FESEM, Hitachi S-4800) operated at 5.0 kV. Prior to SEM observation, the samples were sputtering-coated with a thin layer of Pd/Au alloy. The elemental compositions of the deposited PP membranes were obtained from an Oxford INCA 350 energy dispersive X-ray microanalysis system (EDS) coupled to the SEM and operated at 20 kV. Water contact angles (WCAs) of each sample were measured on ten different sites of the membrane by a contact angle goniometer (Dropmeter A-100, Maist) and the average value of the measurements was
represented. Thermogravimetric (TG) analysis was performed with a NETZSCH TG209F1 thermal analyzer in air with a heating rate of 10 °C/min from 30 to 700 °C. We challenged the TiO$_2$-deposited PP membranes with strong ultrasound oscillation to examine the stability of the deposited TiO$_2$. The nascent and plasma-activated PP membrane subjected to 200 cycles of TiO$_2$ ALD were separately immersed in 20 wt.% nitric acid for 48 h to dissolve all the deposited TiO$_2$ and the amount of titanium in the solution was measured by an inductive coupled plasma emission spectrometer (ICP, Optima 7000DV, Perkin Elmer). Other pieces of the two deposited membranes were separately immersed in deionized water and ultrasonicated for 10 min at a power of 150 W and an ultrasound frequency of 40 kHz. We then removed the samples from the water and added excessive nitric acid to the water to dissolve TiO$_2$ dropped out from the deposition layer and its titanium concentration was measured again by ICP. In this way we obtained the percentage of TiO$_2$ detached from the deposited membranes.

2.5. Evaluation of fouling resistance

The fouling resistance of the membranes was evaluated by protein adsorption [34]. PP membranes subjected to different ALD cycles of TiO$_2$ were separately placed in a glass vial filled with BSA in phosphate buffer solution with a concentration of 1 g/L. The glass vial was then incubated in a water bath at 25 °C for 12 h to reach the adsorption equilibrium. The amount of BSA adsorbed on PP membranes was determined by comparing the concentrations of the BSA solutions before and after adsorption. The concentrations of BSA were obtained by a NanoDROP 2000C UV–vis spectrophotometer at the wavelength of 280 nm.

2.6. Evaluation of the filtration performances

The pure water flux of membranes was determined using a stirred filtration cell (Amicon 8010, Millipore Co., Billerica, MA) under the pressure of 0.05 MPa. The hydrophobic membranes were prewetted for 1 min with ethanol prior to water permeation. Membranes were first circulated for 10 min to get a relative stable flux, and then the flux was measured every 5 min for 3 times, so we could obtain the mean value as the final flux. The retention performances of the PP membranes were evaluated by filtering monodispersed SiO$_2$ nanospheres with a diameter of 22 nm through the membranes under a pressure of 0.05 MPa with moderate agitation. The concentration of SiO$_2$ nanospheres in the feed ($C_f$) and permeate ($C_p$) was detected by an inductive coupled plasma emission spectrometer (ICP, Optima 7000DV, Perkin Elmer), and the retention, $R$, was obtained using the equation $R = 1 - C_p/C_f$.

3. Results and discussion

3.1. Deposition of TiO$_2$ on nascent PP membranes

We first investigated the effectiveness of ALD coating of TiO$_2$ on the as-received nascent PP membranes which were not subjected to any surface activation treatment. We deposited the nascent PP membranes at 80 °C using TIP and water as the precursors for different ALD cycles up to 800 and then examined their surface morphology under SEM. As shown in Fig. 1a, the as-received membranes are composed of isolated porous regions embedded in continuous solid skeletons and the porous regions are formed by parallel ribbons with both ends connected on the solid skeletons. These membranes have the diameter and length in the range of $\sim$20–50 nm and $\sim$200–500 nm, respectively. The gaps between neighboring ribbons are $\sim$30–60 nm, defining the membrane pores. The surface of the ribbons is smooth and free of any particulates. TiO$_2$ ALD deposition with 100 cycles does not noticeably change the smooth surface of the ribbons (Fig. 1c). However, when the cycle number is increased to 200, small particles with a diameter less than 10 nm appeared on the surface of the ribbons (Fig. 1c). These particles expand their

Fig. 1. (a–d) Surface SEM images of nascent PP membranes before (a) and after TiO$_2$ deposition with 100 (b), 200 (c), and 500 (d) ALD cycles. (a)–(d) have the same magnification and the scale bar is shown in (a).
sizes with increasing ALD cycles and their sizes grow to ~15–20 nm at 500 cycles (Fig. 1d). These particles are TiO$_2$ produced by the ALD process which is confirmed by the presence of evident Ti and O peaks in the EDS spectrum of the PP membrane subjected to 500 ALD cycles (data not shown).

It has been reported that ALD of metal oxides on the surface of nonporous films of highly hydrophobic polymers takes place through the subsurface nucleation mechanism [19,20]. Moreover, our previous work demonstrated that ALD of Al$_2$O$_3$ on porous polytetrafluoroethylene (PTFE) membranes also followed the subsurface nucleation mechanism [22]. In these works, metal oxides were always grown on the substrate surface as discrete particulates which can be regarded as a direct indicator for the occurrence of subsurface nucleation. In the current work, the presence of fine particles on the surface of the ribbons of PP membranes suggests that the ALD deposition of TiO$_2$ on the as-received PP membranes follows the subsurface nucleation mechanism because of the scarcity of active groups on the surface. We already made a detailed investigation on the nucleation and growth of metal oxides on PTFE membranes in our previous work and we believe the behavior of nucleation and growth of TiO$_2$ on porous PP membranes is similar to the case of Al$_2$O$_3$ on PTFE as both PTFE and PP are highly chemically inert and hydrophobic. On polymers containing active groups, e.g., –OH or –COOH, ALD precursors like TIP can directly chemosorb on the polymer surface by forming chemical bonds, and subsequent exposure to the second precursor, water, which reacts with the pre-adsorbed TIP, leads to the formation of thin layers of TiO$_2$ tightly adhered to the substrate polymer surface. In contrast, for polymers with inert surfaces, e.g., PP, instead of chemosorbing on the polymer surface, precursor molecules diffuse into the subsurface regions of the polymer and are entrapped in the free volumes between the polymer chains as the ALD process is performed at elevated temperatures (e.g. 80 °C). At elevated temperatures both the mobility of the polymer chains and their affinity to precursors are enhanced, allowing the accommodation of precursors. The second precursor subsequently pulsed into the reaction chamber will also diffuse into the subsurface regions of the polymer and react with the first precursor previously entrapped between polymer chains, leading to the subsurface nucleation of TiO$_2$. The subsurface nucleation proceeds at the initial stage of ALD with low cycle numbers. As TiO$_2$ grows underneath the polymer surface at this stage the PP membrane subjected to 100 ALD cycles does not show a noticeable morphological change compared to the nascent one (Fig. 1a vs. Fig. 1b). Further increase in ALD cycles results in the continuous growth of the preformed TiO$_2$ nuclei which finally expand their size outside the subsurface regions and appear as globular particulates on the outer surface (Fig. 1c). Once TiO$_2$ particulates form on the membrane surface, ALD occurs on the surface of the exposed TiO$_2$ particulates following the normal surface growth mode, leading to the ever-increasing of the particle sizes (Fig. 1c vs. Fig. 1d) until the coalescence of neighboring particles.

We then examine the hydrophilicity of the TiO$_2$-deposited PP membranes by measuring their water contact angles. The nascent PP membrane without any pretreatment shows a relative high contact angle of 113°. This hydrophobic characteristic is mainly related to two reasons: the inert chemical nature of PP and the porous structure composed of nanoscale ribbons with a porosity of 41%. As shown in Fig. 2, WCAs of the deposited PP membranes maintain almost unchanged at the ALD cycle number lower than 200. A cycle number of 300 leads to a slightly reduced WCA of 108°. Only with very high cycle numbers, for example, 500 or 800, a moderate reduction in WCAs can be obtained. The poor enhancement in hydrophilicity of the deposited PP membranes at low ALD cycles can be easily understood as at low cycles TiO$_2$ particles are still in the subsurface nucleation stage or just sparsely deposited on the membrane surface. In this situation, the surface of the PP membrane is still predominantly covered by hydrophobic –CH$_3$ groups. Therefore, its WCA is close to that of the pristine, unmodified PP membrane. At higher cycle numbers, the coverage of the TiO$_2$ on the membrane surface enlarges, yielding moderately reduced WCAs. However, even at a cycle number as high as 800 the PP membrane still has a quite high WCA which is just slightly lower than 90° and the membrane yet cannot be regarded as hydrophilic. It is not likely that PP membranes subjected to direct ALD deposition of TiO$_2$ will exhibit noticeably improved flux because their hydrophilicity only increases slightly or moderately while the formed TiO$_2$ particles significantly reduce the effective pore size of the membranes.

3.2. Surface properties and morphologies of plasma-activated and TiO$_2$-deposited PP membranes

To avoid the particulate morphology of the deposited TiO$_2$ and consequent problems, the plasma activation is adopted to produce active groups on the inert PP surface. Because of the thin and fragile nature of the ribbons in PP membranes, we applied a very low power (50 W) and short processing time (20 s) to prevent the damage to the fine structures. We used XPS to determine the element compositions of the surface of samples subjected to different treatments. As can be seen in Fig. 3, the surface of the original membrane is mainly composed of carbon and trace amount of oxygen less than 1 at% which should be originated from contaminants. After plasma activation, the content of oxygen increases to 4.72 at%, indicating that oxygen-containing groups were generated on the surface. No obvious change of the surface morphology is noticed after plasma treatment, as seen in Figs. 1a and 4a. Strong peaks of Ti 2p at the binding energy of 458.6 eV appear on the XPS spectra of the 50-, and 100-cycle-deposited membranes, and the intensities of Ti and O both increase continually with increasing ALD cycle numbers. Therefore, we conclude that TiO$_2$ has been successfully deposited on the plasma-treated PP membranes and higher ALD cycles lead to larger amounts of deposited TiO$_2$. In clear contrast to the nascent membrane, SEM examinations showed that the plasma-treated membranes subjected to ALD deposition with a cycle number up to 200 maintain its original smooth surface and no particulates could be observed (Fig. 4b–f). Therefore, ALD of TiO$_2$ on the plasma-treated PP membranes forms conformal layers on the surface as precursor molecules can be easily chemosorbed on the active groups on the surface generated by plasma treatment.

We perform TG analysis on the nascent and modified membranes to measure the content of TiO$_2$ in the deposited membranes by heating them up to 700 °C in air. There is 0.02% of ash
left after burning the pristine membrane at 700 °C, and the 50-, 100- and 200-cycle deposited membrane has a remaining weight of 0.73%, 3.49%, and 8.40%, respectively, after subtracting the ash weight of the original PP membrane. The remaining weight corresponds to the mass of TiO$_2$ deposited on the membrane as burning the deposited membranes in air degrades all the organic components and the deposited TiO$_2$ remains. We can estimate the average mass uptake per cycle in three stages: 0–50, 51–100, 101–200 cycles of ALD, which are 0.015%, 0.055%, and 0.049%, respectively. TiO$_2$ grows at a much higher rate in the subsequent stages (51–100 and 101–200 cycles) than the initial stage (0–50 cycles). In the initial stage, the low deposition rate is mainly because of the relatively low rate of the reaction between the precursors and the active groups generated by plasma treatment on the PP surface. Then the growth occurs on the performed TiO$_2$ in the layer-by-layer mode, resulting in a relative large deposition rate in the subsequent stage. The growth rate of 101–200 cycle stage is slightly lower than that in the stage of 51–100 cycles, which is due to the increasing diffusion resistance of precursors into the membrane pores (gaps between the neighboring ribbons) as the membrane pores become smaller with increasing ALD cycles. Although it is technically difficult to directly measure the thickness of the TiO$_2$ layer deposited on porous PP membranes with irregular pores and rough surface, we can roughly estimate the thickness of the deposited TiO$_2$ layer.

Fig. 3. The XPS wide-scan spectra of the original PP membrane, the plasma-activated membrane, and the plasma-activated membranes further subjected to 50 and 100 ALD of TiO$_2$.

Fig. 4. SEM images of the surface morphology of plasma-activated PP membranes after TiO$_2$ deposition with different ALD cycles: (a) 0 cycle, (b) 20 cycles, (c) 50 cycles, (d) 100 cycles, (e) 150 cycles, and (f) 200 cycles. (a)–(f) have the same magnification and the scale bar is shown in (a).
according to the cycle numbers because the growth rate of TiO$_2$ on polymer surfaces with active groups is typically in the range of 0.5–10 angstrom per cycle [35]. For example, the thickness of the TiO$_2$ layer for the activated PP membrane subjected to 200 ALD cycles is estimated to be ~10–20 nm.

After the deposition of TiO$_2$, the initially hydrophobic PP surface has been changed as the TiO$_2$ surface is terminated by hydrophilic Ti–OH groups. We examine the surface hydrophilicity of membranes subjected to different ALD cycles by measuring their static water contact angles. Fig. 2 also summarized the average water contact angles of plasma-activated PP membranes subjected to different TiO$_2$ ALD cycles. It is clear that the WCA continuously decrease with rising ALD cycle numbers. In the initial stage of ALD, e.g., only at a low ALD cycle numbers of 20, the WCA rapidly decreases to 98° from 113° of the pristine PP membrane. When the cycle number further increases to 100, a significantly reduced WCA of 57° is observed, and moreover, the PP membrane subjected to 200 cycles exhibits a WCA as low as 33°. However, in stark contrast, ALD of TiO$_2$ on PP membranes without the plasma activation does not yield any noticeable reduction in WCA at cycle numbers <200. Therefore, the plasma activation is essential for obtaining significantly enhanced hydrophilicity. Plasma treatment of the PP membranes in air produces active groups on the membrane surface, and the following ALD of TiO$_2$ on the treated membrane yields conformal thin layers on the membrane surface. Full coverage of the original PP surface by TiO$_2$ can be achieved at a relatively low cycle number, for example, 200, leading to a strongly hydrophilic surface.

3.3. Separation performances of plasma-activated PP membranes subjected to different TiO$_2$ ALD cycles.

The surface hydrophilicity of porous membranes plays a significant role in determining the permeability of the membrane as the interaction between the liquid and pore walls strongly influences the filtration resistance. Therefore, it is expected that the permeability of the TiO$_2$-deposited PP membranes will be greatly improved as ALD of TiO$_2$ on the plasma-activated PP membranes remarkably enhanced their hydrophilicity even at slight or moderate ALD cycle numbers. Fig. 5 presents pure water flux (PWF) and retention of PP membranes subjected to different ALD cycles. Relative to the pristine PP membrane, all the modified membranes exhibit remarkably enhanced PWF. For the membrane subjected to 20 cycles, the PWF increases from 250 L/(m$^2$ h bar) of the original unmodified membrane to 304 L/(m$^2$ h bar). When the ALD number increases to 50 cycles, the PWF exhibits a notable increase of 68% and reached to 420 L/(m$^2$ h bar). With further increasing ALD cycles, the PWF of the membranes continue to increase, and reach an increment peak value of 74% at 100 cycles. Afterwards, a continuous decrease of the PWF occurs with increasing ALD cycles. However, the PWF of the membrane subjected to the maximum cycle number (200) within our investigations still has an increase of 22% compared to the initial unmodified membrane.

In the filtration process, the permeability of modified PP membranes is mainly controlled by two competitive factors: the hydrophilicity of the pore surface and the pore size. At low ALD cycles, for example, 20 and 50 cycles, the membranes have very limited reduction in pore size because the deposited TiO$_2$ is very thin which is revealed by SEM examinations. However, the hydrophilicity is greatly enhanced with the water contact angle which decreases from 113° for the initial unmodified membrane to 91° for the 50-cycle-deposited membrane. Therefore, at this stage, the increased hydrophilicity will dominate water permeability despite the very limited negative effect due to the pore reduction by TiO$_2$ deposition, resulting in the remarkable increase of PWF. At higher ALD cycles (50–100 cycles), the deposition TiO$_2$ layers grow thicker and the effect of the pore size reduction progressively increases in determining the permeability. Consequently, the PWF keeps increasing but at a lower increasing rate. At even higher ALD cycle numbers (>100 cycles) the effect of pore size reduction becomes more pronounced compared to the effect of the enhancement in hydrophilicity, and the latter effect plays the dominating role in determining the permeability. Therefore, the PWF of the modified membranes starts to drop from its peak value. It should be noted that a moderate ALD cycle number, for example, 200, does not generate a very thick layer of TiO$_2$ on the pore walls and correspondingly the membrane pore is not visibly reduced. On the contrary, the 200-cycle-deposited membrane becomes highly hydrophilic as revealed by the contact angle measurements. Therefore, the membrane subjected to the highest ALD cycle (200 cycles) in this study still exhibits an obviously improved PWF compared to the unmodified, highly hydrophobic PP membranes. The PP membranes modified by TiO$_2$ ALD at varying cycle numbers all display noticeable or even significant increase in water flux. This is remarkable and superior to other modification methods. For example, the grafting method which is extensively used to improve the hydrophilicity of PP membranes frequently results in a decrease in water flux as it is difficult to finely control the length of the grafted chains in liquid phase [11].

The pristine PP membrane has an average pore size of 43 nm and it shows a retention of 31% to monodispersed SiO$_2$ nanospheres with a diameter of 22 nm. As shown in Fig. 5, there is a constant increase in retention for the PP membranes with increasing ALD cycles and the 200-cycle-deposited membrane exhibits the highest retention of 97%. The ever-increasing retention with ALD cycle numbers is simply because higher cycles lead to thicker deposited retention of 97%. The ever-increasing retention with ALD cycle numbers is simply because higher cycles lead to thicker deposited layers on the membrane pores and consequently reduces effective pore sizes. Therefore, the upgrading of the permeability and retention of the membranes can be simultaneously achieved by this ALD deposition strategy on the plasma-activated PP membranes. For most membranes prepared at different ALD cycles, they all demonstrate a notable improvement not only in water flux but also in retention. For example, the membrane subjected to 150 ALD cycles gains a ~60% increase in water flux and a more than doubled retention compared to the unmodified, highly hydrophobic membranes. In our work on ALD of TiO$_2$ on plasma-activated PTFE membranes, we obtained a 150% increase in water flux and a doubled retention after 150 ALD cycles [36]. The enhancement in permeability is more pronounced at the similar level of improvement in retention in the case of PTFE than PP, which should be explained by the reason that PTFE is more hydrophobic than PP and the effect of hydrophilicity enhancement induced by the deposition of TiO$_2$ is more pronounced for PTFE membranes. Anyway, such a simultaneous improvement in permeability and selectivity in
a broad window of experimental conditions achieved by ALD both in the case of PTFE and PP is remarkable as other methods of surface modification are difficult to improve the selectivity at no expense of permeability or vice versa because of the frustrating tradeoff effect between them [37,38].

3.4. Antifouling properties of plasma-activated PP membranes subjected to different TiO2 ALD cycles and the stability of the deposited TiO2

The anti-fouling properties of TiO2-deposited PP membranes are expected to be greatly enhanced due to the coverage of the membrane surface by thin layers of hydrophilic TiO2. We investigated the static protein adsorption of the deposited membranes to evaluate their anti-fouling properties. As shown in Fig. 6, the saturated mass of BSA static adsorption of the pristine membrane was 102.9 μg/cm² whereas all the PP membranes with different ALD cycles displayed apparently reduced adsorption of BSA. Moreover, there is a trend that membranes with higher ALD cycles adsorb less BSA because higher ALD cycles give rise to stronger hydrophilicity. For the membrane subjected to 100 ALD cycles, the BSA adsorption sharply decreases to 78.5 μg/cm². The membrane with 200 ALD cycles exhibits an even lower BSA adsorption of 51 μg/cm² which is only one half of that of the original unmodified membrane. Finally, we note that TiO2 deposited on either the nascent or plasma-activated PP membranes is mechanically very stable and cannot be easily detached from the PP substrate because of the strong adhesion between them. For example, only 0.98% and 0.74% of the deposited TiO2 on the nascent and plasma-activated PP membranes subjected to 200 ALD cycles detached from the PP substrates after a harsh challenging with ultrasoneication at a power of 150 W for a duration of 10 min, respectively. Such a strong stability guarantees that the improved performances of the PP membrane endowed by the deposited TiO2 will maintain for long-term usage.

4. Conclusions

We deposited TiO2 on porous polypropylene membranes using the atomic layer deposition technique. TiO2 was grown on the pore surfaces as discrete particles because of the scarcity of active groups on the surface of PP membranes and thus-obtained membranes exhibited a slightly enhanced hydrophilicity. To generate active groups on the pore surface we applied a plasma activation step to PP membranes before TiO2 ALD. XPS analysis confirmed the successful formation of oxygen-containing groups on the PP surface after a very short plasma treatment in air. TiO2 was deposited on the plasma-treated PP membranes as smooth and conformal thin layers and the amount of the deposited TiO2 was dictated by the number of ALD cycles. ALD deposition of TiO2 on plasma-activated PP membranes significantly improved the hydrophilicity and consequently the fouling resistance of the membranes. Importantly, the deposited membranes exhibited greatly enhanced permeability and retention at the same time because the deposition of thin layer TiO2 slightly reduced the effective pore sizes but remarkably enhanced the hydrophilicity of PP membranes.

Acknowledgments

This work is financially supported by the National Basic Research Program of China (2011CB612302), the National Natural Science Foundation of China (21176120), the Jiangsu Natural Science Funds for Distinguished Young Scholars (BK2012039) and the Natural Science Research Program of the Jiangsu Higher Education Institutions (13KJA430005).

References


