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Plasma activation of porous polytetrafluoroethylene membranes for superior hydrophilicity and separation performances *via* atomic layer deposition of TiO_2

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ABSTRACT

Conformal and smooth TiO_2 thin layers were coated on the surface of porous PTFE membranes subjected to a plasma activation process by atomic layer deposition (ALD). In contrast, TiO_2 was deposited on the PTFE surface as globular particulates without plasma activation due to the inert chemical nature of PTFE surface. X-ray photoelectron spectrometry confirmed the formation of functional groups on the plasma-activated PTFE surface which served as active sites for the homogeneous adsorption and reaction of ALD precursors. Scanning and transmission electron microscopy revealed the uniformity of the deposited layer and the precise control of its thickness by changing ALD cycle numbers. The water contact angle measurement showed that the hydrophobic surface gradually turned to be near superhydrophilic with the increment of ALD numbers. Also, the membrane mean pore size was progressively reduced by simply altering the ALD numbers. At proper deposition conditions, the modified membranes gained an increase of pure water flux of more than 150% and simultaneously a doubled retention compared to the original unmodified membrane. This research provides an efficient approach devoid of any harsh treatments to modifying PTFE membranes for achieving specific functions, which also can be applied to other organic materials especially with chemical inert surface.

1. Introduction

Atomic layer deposition (ALD) has been demonstrated as a mild and effective tool for surface modification of polytetrafluoroethylene (PTFE), a high-performance engineering plastic [1–3]. PTFE generally presents strong hydrophobicity due to its highly symmetrical non-polar linear configuration, where a skeleton constructed of carbon atoms is surrounded by fluorine atoms [4,5]. Therefore, an important purpose for the surface modification of PTFE is to improve its hydrophilicity while keeping its high mechanical strength and good chemical stability, especially when PTFE is applied as the component material to membrane technology for water treatment. Deposition of hydrophilic metal oxides such as Al_2O_3, ZnO, and TiO_2 by ALD on PTFE substrates has been investigated in recent years [1–3]. It is known that an ALD process consists of sequential self-limiting surface reactions [6,7]. Since PTFE is short of active chemical groups on its surface, a model based on the adsorption of ALD precursors onto the PTFE surface and diffusion into its near-surface region was proposed [3]. On nonporous PTFE films, it was observed that globular particulates with a more physically bound oxide/PTFE interface could be deposited on the PTFE surface by both Al_2O_3 and TiO_2 ALD processes. As a result, the adhesion between the deposited layer and PTFE substrates was rather weak. Recently, it was also revealed that the high reactivity of ALD precursors, for example diethylzinc, is possible to initiate an incorporation of zinc into PTFE tapes [2]. This infiltration effect can partly change the molecular structure of PTFE and affect its corresponding mechanical properties. However, the enhancement of hydrophilicity of the PTFE films by the above ALD processes is insignificant.

We recently reported the upgrading of the separation performances of PTFE porous membranes in water systems by improving their surface hydrophilicity *via* ALD of Al_2O_3 [3]. PTFE porous membranes manufactured by using a stretching process are highly porous, exhibiting a net-like structure composed of interconnected nanofibrils. It was found that fine Al_2O_3 particulates were deposited with initial ALD cycles based on subsurface nucleation while continuous thick films were subsequently formed on the surface of PTFE membranes after several hundreds of ALD cycles. The hydrophilicity of the deposited membranes could be progressively improved with the rise of ALD cycle numbers. However, a highly hydrophilic surface was only obtained after 300 Al_2O_3 ALD cycles

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when the morphology of globular particulates gradually evolved to relatively thick continuous layers. In this case, the decrease of water contact angle from initial $131 \pm 3^\circ$ to later $39 \pm 4^\circ$ was accompanied by the formation of a Al_2O_3 ALD layer with a thickness more than 50 nm on the PTFE surface. This indicates that a significant increase of hydrophilicity of the PTFE membranes in the previous experiments had to be achieved at expense of obvious pore shrinkage, which considerably affected the filtration performances, for instance, water flux.

In this work, we demonstrated that a short-time low-power air plasma pretreatment can effectively activate the inert PTFE surface and thus reduce the possibility of subsurface nucleation at the initial ALD stages. As a result, a consistent layer-by-layer ALD growth mode can be achieved throughout the whole ALD cycle window. We investigated the effect of plasma-assisted surface activation of PTFE porous membranes on their surface morphology, adhesion force, hydrophilicity, and separation performances in water systems *via* ALD deposition of TiO_2 with different cycles. The enhancement of the surface hydrophilicity of PTFE was attained by low ALD cycles (*i.e.* 150 cycles) with the formation of conformal and smooth thin TiO_2 layers, which led to a maximal water flux 154% higher than the initial PTFE membrane. Although there are a number of reports on grafting hydrophilic polymer chains on plasma-activated polymeric membranes including PTFE membranes to enhance their hydrophilicity [8,9], our strategy of ALD deposition of TiO_2 on plasma-activated polymeric membranes is distinct in terms of a precise control on the thickness of the deposited layer and a solvent-free process in which no toxic solvents and tedious rinsing and purification steps are involved. Moreover, TiO_2 has superior chemical stability, high photocatalytic activity, and an efficient self-cleaning property, which might find more versatile applications of the modified PTFE porous membranes in harsh operation environments.

2. Experimental

2.1. Materials

Porous PTFE membranes with a mean pore diameter of 0.2 μm in the form of round chips (diameter: 25 mm; thickness: 65 μm) were purchased from Sartorius (Germany) and used as received. The ALD reactants were titanium isopropylate (TIP, 98%, Aladdin) and deionized H_2O, which were used as the Ti and O precursors, respectively. N_2 with high purity (99.99%) was used as both the precursor carrier and the purging gas. Monodispersed SiO_2 nanospheres with a diameter of 142 nm were synthesized by the Stoeber method [10].

2.2. Plasma activation to PTFE membranes

Prior to deposition, PTFE membranes, placed on a glass holder beyond a electrode, were treated by air plasma at a power of 240 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 5 min, and then the other side of the membranes were treated in the same way. After the plasma treatment, the samples were transferred to the ALD chamber for TiO_2 deposition within 5 min. However, the plasma-activated PTFE membrane remained its surface activity for ALD at least for 1 week as ALD on the sample stored in the ambient condition for 1 week exhibited no noticeable difference in surface morphology and performances compared with that of the freshly activated sample subjected to ALD at the same condition.

2.3. ALD on PTFE membranes

TiO_2 ALD was carried out in a hot-wall ALD reactor (S100, Cambridge NanoTech). Plasma-activated PTFE membranes were positioned in the ALD chamber preheated to 150 °C with both sides directly exposed to the nitrogen stream. The ALD reaction was started when the vacuum in the chamber reached 1 Torr. The precursor TIP was heated to 82 °C while the precursor water was maintained at room temperature. These two precursor vapors were alternately delivered into the reaction chamber, and the exposure mode was used to allow the precursors diffuse and adsorb through the samples sufficiently. A typical ALD cycle included (i) TIP pulse for 0.2 s; (ii) exposure for 5 s; (iii) purge for 20 s; (iv) H_2O pulse for 0.015 s; (v) exposure for 5 s; and (vi) purge for 20 s. The plasma-activated membranes were deposited for different cycles up to 300 cycles at 150 °C, respectively, under a steady nitrogen flow rate of 20 sccm. For comparison, the PTFE porous membranes without plasma activation were also deposited for 100, 200, 300, 500 and 800 cycles under the same deposition conditions.

2.4. Microstructure characterizations

X-ray photoelectron spectroscopy (XPS) analyses were carried out on a Thermo ESCALAB 250 system equipped with a monochromatic Al Kα X-ray source ($h\nu = 1486.6$ 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 was approximately 500 μm on samples and the binding energies were calibrated to the C 1 s peak at 284.8 eV. Moreover, Fourier transform infrared spectroscopy (FTIR) characterizations were also performed on PTFE membranes before and after plasma activation on a Thermo Nicolet 8700 FTIR spectrometer in both the attenuated total reflection (ATR) and transmission modes (32 scans, 4 cm^{-1}). Membrane samples were first sputtering-coated with a thin layer of gold, and then were examined to reveal their surface morphology using a field emission scanning electron microscope (FESEM, Hitachi S-4800) at an accelerating voltage of 2 or 5 kV. In order to investigate the growth mechanism of TiO_2, some deposited membranes were microtomed for the examination of transmission electron microscopy (TEM). These samples were soaked in acetone for dehydration for a week at room temperature and then embedded in a Spurr low-viscosity epoxy resin and cured for 1 day. The embedded samples were cut into slices with a thickness of about 50–80 nm by a Lecia Ultracut diamond knife microtome. These thin slices were transferred to copper grids coated with a holey carbon film and observed by a Hitachi H7650 TEM operating at an accelerating voltage of 80 kV.

2.5. Measurements of the membrane water contact angles

Water contact angles of each sample were measured after the ALD process within 30 min by a contact angle goniometer (Dropmeter A-100, MAIST Vision). To keep the sample smooth for measuring, each membrane was first stick to a glass sheet by a double-sided adhesive tape. A 5 μL of water drop was dripped onto the sample surface. The water contact angles were recorded after the droplets kept stable for 30 s. Water contact angles of each sample were measured on 10 different sites of the membranes and the average value of the measurements was presented. In the water contact angles recovery experiment, the samples were exposed to UV irradiation (UVP CL-1000s UV crosslinker with Hg lamps) with the wavelength of 254 nm at a power of 30 W for 60 min, and the distance between the UV source and sample was 15 cm.

2.6. Determination of the amount of TiO_2 deposited on activated membranes

Each piece of standard sized membranes after ALD deposition of different cycles was separately immersed in excessive nitric acid solution (20 wt%) for 2 days to dissolve the TiO_2 layer, then the solution was diluted several folds for the detection of titanium concentration by an inductive coupled plasma emission spectrometer (ICP, Optima 7000DV, Perkin Elmer). Thus the TiO_2 mass uptake of samples prepared at different cycles could be obtained by comparing the amount of TiO_2 and the area of PTFE membranes. Membranes subjected to 50 and 300 ALD cycles were separately immersed in deionized water and treated with a strong ultrasound concussion for 10 min at a power of 300 W and an ultrasound frequency of 40 kHz. After the samples were taken out, an excessive nitric acid solution was added to the water to dissolve the TiO_2 dropped out from the deposition layer and its titanium concentration was measured by ICP. In this way we measured the percentage of TiO_2 detached from the deposited membranes, and higher percentage suggested a poorer adhesion between the deposited TiO_2 and the PTFE membrane.

2.7. Evaluation of the filtration performances

Pure water flux (PWF) was measured to determine the permeability of the membranes in a stirred cell module (Amicon 8010, Millipore) under moderate agitation at room temperature. The hydrophobic membranes were conditioned for 1 min with ethanol prior to water permeation. Membranes were first circulated under a pressure of 16.2 kPa for 30 min to get a relative stable flux, and then the flux was measured every 10 min for three times, so we could obtain the mean value as the final flux. The separation performances of the pristine and deposited membranes were characterized by the filtration of monodispersed SiO_2 nanospheres with a mean diameter of 142 nm measured by dynamic light scattering under modest agitation under a pressure of 8 kPa at 20 °C. The concentration of SiO_2 nanospheres in the feed (C_F) and infiltrate (C_I) was detected by ICP, and then we got the retention (R, $R=1-C_I/C_F$).

3. Results and discussion

3.1. Surface composition of plasma-activated PTFE membranes

Plasma treatment is one of the most efficient processes for activating plastic surfaces [11–13]. The untreated and plasma-activated PTFE samples were examined with XPS to obtain their elemental composition and get an insight in the chemical functions introduced on the surface by plasma treatment. As shown in Table 1, the original PTFE only contains C and F, and the F/C ratio is 2.55 (a little bigger than the theoretical value 2.0), which is probably due to a small portion of $-CF_3$ existing in the PTFE surface [2]. After the treatment of air plasma, a small concentration of oxygen and nitrogen moieties was found on the membrane surface. At the same time, the F/C ratio decreased to 2.26. From the chemical composition of PTFE membranes before and after plasma treatment displayed above, we could conclude that oxidation, nitridation, and defluorination occurred on the PTFE surface, and such elemental composition changes were also reported in other studies [14–16]. As seen in the XPS survey spectrum in Fig. 1a, the pristine PTFE consists of a C 1s peak at 292.07 eV, which can be divided into the peak at 292.08 eV related to the CF_2 species [17,18] and the peak at 293.55 eV related to $-CF_3$ species [19,20] by Gaussian decomposition. A new asymmetric peak at 248.8 eV appeared in Fig. 1b, indicating the presence of several new carbon-derived functional groups. The tentative peak fitting for plasma-treated PTFE has been studied before and the existence of C═N (286.9 eV), C–N (286.3 eV), C–C (284.6 eV), C–O (286.4 eV), *etc.* has been proposed [21–23]. In addition, the plasma-treated PTFE contains an O 1s peak at 533.4 eV in Fig. 1c, which was not present for the pristine PTFE samples. This spectrum could also be decomposed into two peaks: C═O centered at 532.3 eV and C–O centered at 533.8 eV. Therefore, a small amount of O and N was incorporated into PTFE matrix after the plasma treatment on PTFE membranes. In this process, the free radicals or ions produced by plasma introduced certain polar functional groups bonded onto the PTFE surface. However, no new chemical groups of the plasma-activated PTFE were detected by FTIR measurements in both ATR and transmission modes. This result indicates that the plasma process only slightly changed the surface composition of the PTFE membranes. The chemical and physical properties of the bulk PTFE were hardly influenced by this pretreatment.

Table 1
Chemical composition of PTFE surfaces treated with air plasma.

Sample	C (at%)	F (at%)	O (at%)	N (at%)	F/C
Original PTFE	28.15	71.85	0	0	2.55
Plasma-activated	30.22	68.41	1.06	0.31	2.26

3.2. Surface morphology evolution of PTFE membranes with TiO_2 deposition

Pristine PTFE porous membranes manufactured by stretching present a rough net-like structure with a relatively high porosity, as shown in Fig. 2a. No obvious changes of the surface morphology were noticed after plasma treatment at an applied low power of 22 W (Fig. 2b). With the membranes subjected to increasing ALD cycles, the surface morphology of the PTFE gradually changed due to the formation of a layer of TiO_2 by ALD (Fig. 2c–f). In general, the TiO_2 layer consistently grew in a form of continuous and compact layer on the PTFE surface, which became thicker and thicker with increasing ALD numbers. In clear contrast, without plasma pretreatment on the PTFE membranes, TiO_2 were deposited on the PTFE surface as globular particulates having growing particle sizes with increasing ALD cycles (Supporting information, Fig. S1). The globular particulate morphology is similar to our previous investigations on ALD deposition of Al_2O_3 on the same PTFE porous membranes [3]. For the slightly deposited membranes, *e.g.* 50 cycles (Fig. 2c), there is no obvious size change of the stripe-like pores constituted by PTFE nanofibrils due to the relatively slow growth rate of TiO_2 by ALD. When the membrane subjected to 100 ALD cycles (Fig. 2d), most parts of membrane surface were apparently coated by a smooth layer of TiO_2. Compared with the initial PTFE membranes (Fig. 2a), the surface of PTFE subjected to ALD deposition became smoother. This change is attributable to the conformal feature of ALD, which can restore nanoscale rough surfaces by filling the gap with a TiO_2 layer. With further deposition of TiO_2 to 300 cycles (Fig. 2e and f), the membrane surface showed a consistently smooth morphology. The increasing layer thickness with the incremental ALD cycles gradually reduced the average pore size. It is worth mentioning that ALD deposition of conformal TiO_2 films can be achieved even a week after the plasma pretreatment of the PTFE membranes.

3.3. Growth mechanism of ALD TiO_2 on plasma-activated PTFE membranes and the adhesion between the deposited the TiO_2 and PTFE substrate

For polymers with active groups, *e.g.* hydroxyl on the surface, ALD precursors could react with these functional groups, resulting

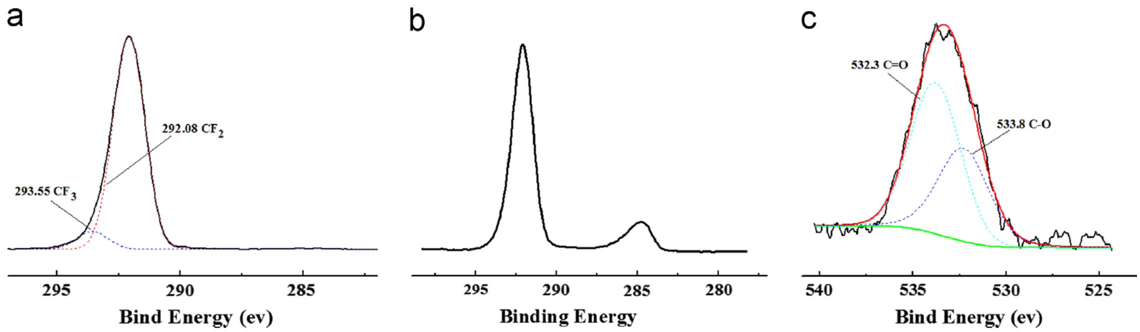

Fig. 1. The C 1s XPS spectra of PTFE membranes: (a) the separated spectrum of the pristine, (b) after plasma treatment, and (c) the separated XPS spectra of O1s after plasma treatment.

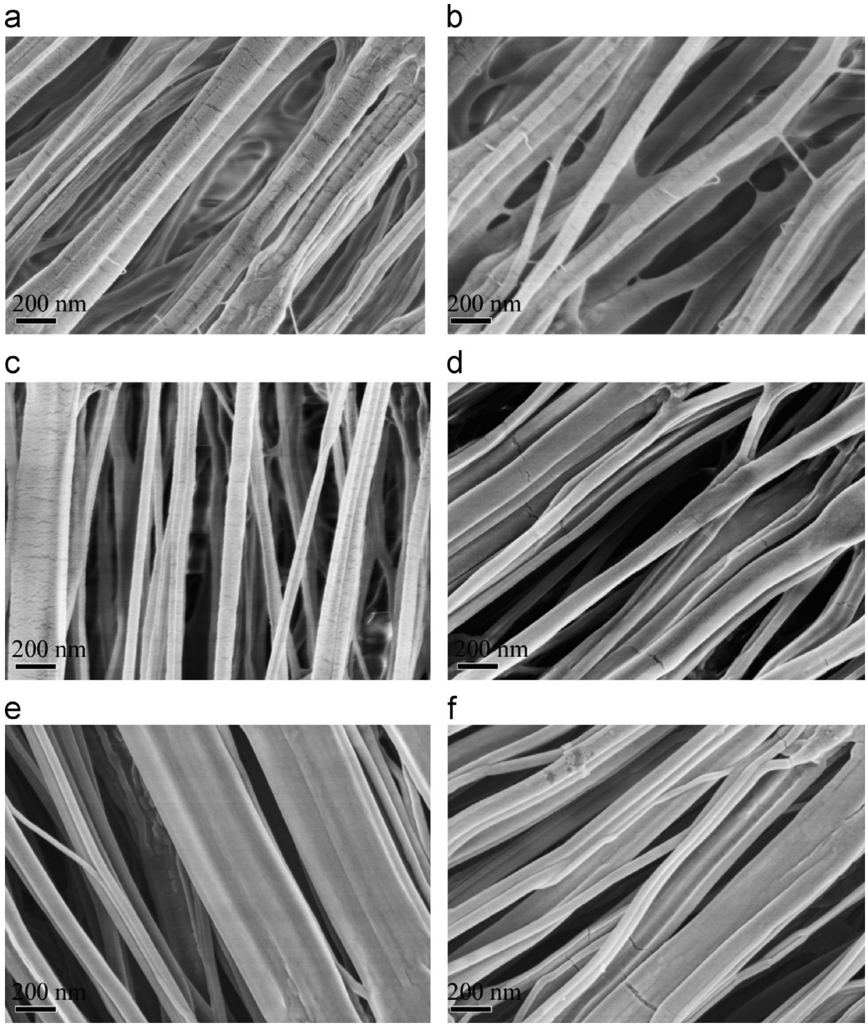

Fig. 2. SEM images of the surface morphologies of PTFE membranes before and after TiO_2 deposition: (a) original, (b) plasma-activated PTFE membrane before ALD, and ALD TiO_2-deposited for (c) 50 cycles, (d) 100 cycles, (e) 200 cycles, and (f) 300 cycles.

in a uniform and conformal initial deposition layer [24–26]. However, the pristine surface of PTFE has no such reactive groups, so deposition can only begin with subsurface nucleation and later grow on these preformed particles, forming a rough and island-like surface morphology [3]. In order to acquire a smooth coating, the glow discharge plasma was applied to generate some active groups on PTFE surface prior to the TiO_2 deposition. For understanding the structure at the TiO_2/PTFE interface, a TEM image of the microtomed PTFE membrane subjected to 50 ALD cycles is presented in Fig. 3a. The coating with a thickness of ~3 nm is very uniform and continuous along the edge of the PTFE slice, confirming the conformal deposition of TiO_2 on the PTFE without apparent subsurface nucleation. When ALD cycles were increased to 100 and 200 (Fig. 3b and c), the coating films with a thickness of ~5 and ~11 nm presented similar smooth and conformal features, consistent with the SEM observations.

For further evaluating the mass uptake of TiO_2 deposited on PTFE membranes during ALD process, membranes subjected to different ALD cycles were dissolved in excessive nitric acid solution and the concentration of TiO_2 was measured by ICP. Fig. 4 shows the plot of mass uptake of TiO_2 as a function of ALD cycles. It can be seen that the average growth rate per cycle (GPC) during

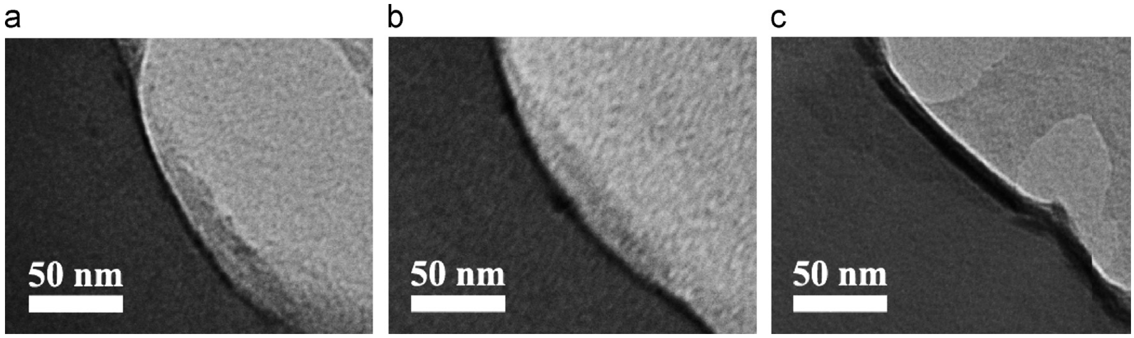

Fig. 3. TEM images of microtomed PTFE membranes deposited at different ALD cycles: (a) 50 cycles, (b) 100 cycles, and (c) 200 cycles.

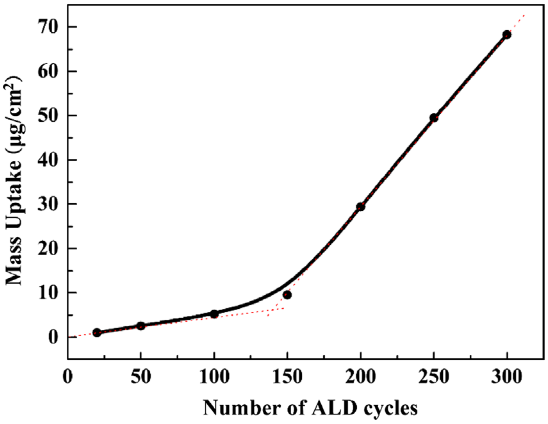

Fig. 4. The plot of mass uptake of TiO_2 as a function of ALD cycles.

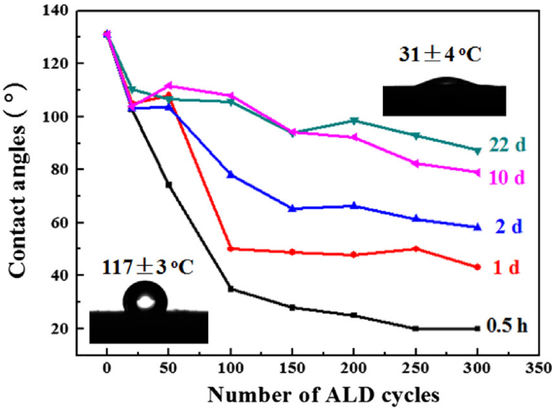

Fig. 5. Curves of average water contact angles of PTFE membranes subjected to different TiO_2 ALD cycles with different aging times in air. The insets at the left-bottom and right-up are the photographs of the water droplet on the membranes corresponding to the one only treated with plasma with a storing time of 0.5 h in air and the other subjected to 150 ALD cycles with a aging time of 10 d in water, respectively.

different stages was not the same. Based on the difference of the growth rates, the whole ALD period can be separated into three stages: 0–100 cycles at a low growth rate with an average GPC of 51.6 ng/cm^2, 100–150 cycles as a transition region with an obviously accelerating growth rate, and 150–300 cycles at a constant and fast growth rate with an average GPC of 319.4 ng/cm^2. Generally, a constant GPC is expected for the oxide growth following the ALD mode [27,28]. In recent years, however, it has been found that the properties of substrate could be changed with the deposition of target materials, so the GPC of ALD is possible to alter at different growth stages [29,30]. In the initial stage of deposition, TiO_2 was deposited on the PTFE surface mainly by the chemical adsorption and reaction between the precursors and the active groups on the PTFE surface generated by plasma treatment. In the following cycles, TiO_2 continued to grow on the preformed TiO_2 layer directed bound on the PTFE surface. Compared to the highly active hydroxyl groups on the TiO_2 surface, the active groups on the surface of plasma-activated PTFE are limited both in reaction activity toward the ALD precursors and density of the available groups. Consequently, TiO_2 deposited at a lower rate at initial stage and speeded up later when growth on preformed TiO_2 dominated, and a moderate growth rate occurred in the transition stage where deposition both on the surface of plasma-activated PTFE and preformed TiO_2 took place. A similar varying trend of GPC has also been found in previous works [31,32].

For enduring some harsh conditions in practical application of the modified membranes, a strong ultrasound concussion was performed to evaluate the bonding force between the deposited TiO_2 layer and the PTFE substrate through the shedding amount of TiO_2. After ultrasonication at a power of 300 W for 10 min, there was a 3.54% content of the total deposited TiO_2 pulled out from the membrane subjected to 50 ALD cycles. When the ALD cycles increased to 300, only 2% of the deposited layer fell off after the same ultrasound concussion. Both of the results exhibited that the TiO_2 films had a good adhesion to the porous PTFE membranes by our ALD processes. However, for membranes without the plasma activation, the percentage of the detached TiO_2 was 9.42% and 7.01% at the cycle number of 50 and 300, respectively. The strong adhesion should be attributed to the active groups generated by the plasma process which led to chemical bonds at the TiO_2/PTFE interface and a spatial stabilizing force (*e.g.* the mechanical interlocking effect) derived from the 3D structure interwoven with the PTFE substrate for the deposited layer.

3.4. *Surface hydrophilicity of the TiO_2-deposited PTFE membranes*

Surface hydrophilicity of porous PTFE membranes is important for their specific applications such as the treatment of drinking and waste water during low pressure microfiltration and ultrafiltration processes. The surface hydrophilicity of membranes subjected different ALD cycles was reliably determined by the static water contact angle in our work. The pristine porous PTFE membrane showed an initial contact angle of $131 \pm 3^\circ$, which is higher than the result from flat PTFE surfaces owing to its porous structure [33]. After plasma treatment, the water contact angle slightly decreased to $117 \pm 3^\circ$ (inset at the left-bottom in Fig. 5), indicating that some hydrophilic chemical groups were produced at the surface. However, the general effect of plasma treatment on the hydrophilicity of the PTFE membranes was very limited.

Fig. 5 summarized the average water contact angles of PTFE membranes subjected to different TiO_2 ALD cycles with different aging times. When the water contact angle was measured 0.5 h after ALD deposition, it rapidly decreased to 35 ± 4° with 100 ALD cycles of TiO_2. On one hand, the surface properties of PTFE substrate were modified by the deposited TiO_2 layer, which is highly hydrophilic. On the other hand, the rough surface of nanofibrils constructing the PTFE membranes was gradually 'repaired' to get smooth. From 100 to 300 ALD cycles, the surface exhibited a similar smooth morphology as 100 cycles (shown in Fig. 2), so the water contact angle decreased slowly to 20 ± 6° with the increasing film thickness, closed to superhydrophilicity. Without plasma pretreatment, the PTFE membrane subjected to 100 TiO_2 ALD cycles is still very hydrophobic (Supporting information, Table S1). Its water contact angle is 132.5 ± 3°, similar to that of the pristine porous PTFE membrane. Moreover, there was no obvious improvement of hydrophilicity by gradually increasing the TiO_2 ALD cycle number till 500 without the aid of plasma activation. When the ALD cycle number was up to 800, only a little enhancement of hydrophilicity was achieved with a water contact angle of 117 ± 4°. According to the particulate morphologies subjected to these ALD processes (Supporting information, Fig. S1), the highly hydrophobic PTFE nanofibrils could not be completely covered by the hydrophilic TiO_2 in the absence of plasma pretreatment. Moreover, the surface of the PTFE membranes became much rougher. Such structural features severely prevented the significant enhancement of hydrophilicity.

In addition, as shown in Fig. 5, the water contact angles were found to gradually increase with aging time in air, which was supposed to be related to the extraction of the hydroxyl groups on TiO_2 surface [34]. We conducted a confirmatory experiment by storing the membrane subjected to 150 ALD cycles in water. It was observed that the water contact angle can still be as low as 31 ± 4° after 10 days (inset at the right-up in Fig. 5), displaying little difference from the freshly deposited membrane. It is well known that TiO_2 has the feature of photo-induced superhydrophilicity under UV irradiation [35]. In our study, we found that no matter how long the TiO_2-modified membranes were exposed in air, their water contact angles could recover to the initial value measured at 0.5 h after ALD deposition, subsequent to UV irradiation with the wavelength of 254 nm at a power of 30 W for 60 min. This result indicated that the current TiO_2-modified PTFE porous membranes are more potential for practical applications due to this 'renewable' feature relative to other oxide-modified systems.

3.5. Separation performances of the deposited PTFE membranes

Fig. 6 presents PWF and retention rate of the TiO_2-deposited PTFE membranes. Relative to the pristine PTFE membrane, the PWF of all the modified membranes was obviously increased. When the membrane was subjected to 20 cycles, the PWF increased 12.4% higher than the original one. When the ALD number increased to 50 cycles, the PWF exhibited a remarkable increase of 101.9%, although the thickness of the deposited TiO_2 was as small as 3 nm, as evidenced in Fig. 3a. Likewise, with further increasing ALD cycles, the PWF of the membranes continued to increase, and reached an increment peak value of 154% at 150 cycles, which has never been achieved in the Al_2O_3-modified PTFE membranes (a maximal increase of 69.2%) [3]. Afterwards, a continuous decrease of the PWF emerged with the increasing ALD cycles. However, the PWF of the membrane subjected to the maximum cycle number (300) within our investigations still had an increase of 64.6% compared to the initial membrane. Based on the structure analysis we conducted above, the thickness of the deposited TiO_2 film in this case had reached more than 10 nm, which led to an obvious shrinkage of the average pore size of the PTFE membranes.

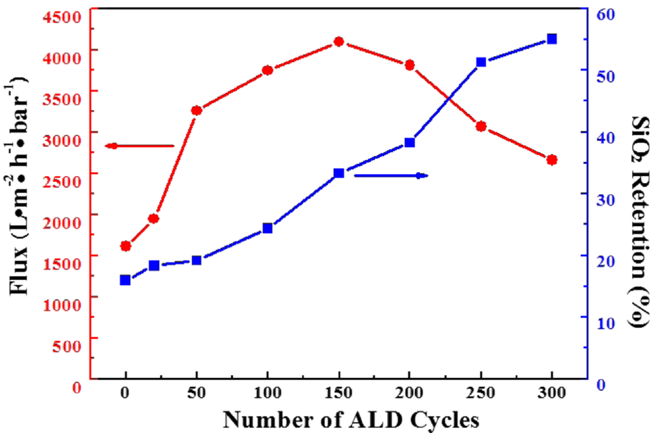

Fig. 6. Pure water flux (PWF) and retention to monodispersed SiO_2 nanospheres with a diameter of 142 nm of PTFE membranes deposited with different TiO_2 cycles.

In the filtration process, two competitive factors, namely the hydrophilicity of the pore surface and the pore size, are responsible for the permeability trade-off change of modified PTFE membranes. A small deposition rate at low ALD cycles (less than 150 cycles) revealed in Fig. 4 only induced slight pore shrinkage, but the hydrophilicity was greatly enhanced with a reduction of the water contact angle from 131 ± 3° to 28 ± 5°. Therefore, at this stage, the increased hydrophilicity could 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. With further increasing the number of the ALD cycles (more than 150 cycles), the deposition was maintained at a fast and constant rate, causing the overgrowth of thicker deposition layer on the wall of membrane pores. However, the hydrophilicity of the modified membranes could no longer be noticeably improved. Because of the more dominating effect of the pore size reduction, the PWF of the modified membranes started to drop from its peak value.

The pristine PTFE membrane has an average pore size of 200 nm. It was also shown in Fig. 6 that it had an initial retention of 16% to the monodispersed SiO_2 nanospheres with a size of 142 nm. As the membrane separation performance was only determined by the pore size, the retention to SiO_2 nanospheres increased along with the increasing deposition cycles to a maximum value of 55.1% at 300 ALD cycles. Therefore, the upgrading of the PWF and separation performance of the membranes could be simultaneously achieved by this ALD deposition strategy. For example, the membranes subjected to 150 ALD cycles gained a 154% increase in water flux and a doubled retention to the 142 nm-SiO_2 nanospheres compared to the unmodified, highly hydrophobic membranes.

4. Conclusions

In this work plasma was introduced to generate active groups on the highly chemically inert surface of PTFE membranes, thus conformal TiO_2 films were successfully deposited by ALD on PTFE surface. The hydrophobic surface progressively changed to approach superhydrophilicity with increasing ALD cycles, demonstrated by water contact angle measurement and pure water flux test. SEM and TEM observations as well as calculation of GPC confirmed that we could precisely control the thickness of the deposited layer and effective pore size simply by changing the number of ALD cycles. Because of a spatial stabilizing force such as mechanical interlocking effect and the additional chemical bond between PTFE and TiO_2, the composite membrane survived strong ultrasonication, indicating its high mechanical stability adaptable to the practical applications. Under proper ALD conditions, the

PWF and retention to SiO_2 nanospheres remarkably increased in a synergistic way, which is difficult to achieve by other methods. With the help of plasma pretreatment, the surface properties of the extremely inert and stable PTFE membrane could be easily modified by ALD with low cycle numbers. Therefore, a significant increase of hydrophilicity is not necessary to achieve at expense of obvious pore shrinkage, which provides a rational approach to modifying PTFE membranes with specific functions.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.memsci.2013.04.061.

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