TiO₂ Nanofiltration Membranes Prepared by Molecular Layer Deposition for Water Purification

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ABSTRACT

In this study, molecular layer deposition (MLD) was used as a novel and highly controllable method to prepare TiO₂ nanofiltration membranes with approximately 1 nm pores for water purification. Number of deposition cycles and precursors (TiCl₄ and ethylene glycol) were used to control membrane quality and final pore sizes, respectively. Optimized TiO₂ nanofiltration membranes had a pure water permeability as high as ~48 L/(m²·h·bar). Salt and dye rejection measurements showed moderate rejection of Na₂SO₄ (43%) and MgSO₄ (35%) and high rejection of methylene blue (~96%). In addition, natural organic matter (NOM) removal testing showed high rejection (~99%) as well as significantly improved antifouling performance and recovery capability. MLD, as a new TiO₂ nanofiltration membrane preparation technique, has great potential to realize excellent control of membrane composition, thickness, and potentially pore sizes in a scalable way.

Keywords: Membranes; Nanofiltration; TiO₂; Molecular layer deposition

1. Introduction

Water scarcity is one of the most serious global issues because of the growing freshwater use and depletion of usable fresh water resources.[1] It is, therefore, in a great need to develop various energy-efficient water treatment technologies to realize water purification for different water sources and at different levels. Nanofiltration membranes are now widely used in drinking water and wastewater treatment, as well as pretreatment for desalination because of their ability to remove viruses, hardness, dissolved organic matter, and salts, especially multivalent ions.[2-5] Currently, polymers, such as cellulose acetate, polyamide, polyimide, and poly(ether)sulfone, are dominant materials in nanofiltration.[4, 6] Most of the polymeric nanofiltration membranes have advantages of flexibility, simple preparation process, and relatively low cost.[2] Compared with

polymeric nanofiltration membranes, ceramic nanofiltration membranes, usually manufactured from Al_2O_3 , ZrO_2 , and TiO_2 , [7] have better chemical, thermal and mechanical stability and long lifetime, and thus may be used in applications under extreme operating conditions. [2] Ceramic nanofiltration membranes are usually prepared by solution-based sol-gel method, [8-12] which needs careful control of the deposition process to produce high quality membranes. Typically, in this process, a gel needs to be carefully prepared from a colloidal or polymeric solution by adding organic additives to control the hydrolysis and condensation of alkoxides. [10, 13] In addition, membrane thickness cannot be precisely controlled at the sub-nanometer scale. This may severely limit sol-gel method for preparing ultrathin, high flux nanofiltration membranes. More importantly, pore sizes of ceramic nanofiltration membranes, prepared by the sol-gel method, are difficult to be precisely controlled at about 1 nm, especially for stable metal oxides, such as TiO_2 . Attempts to prepare TiO_2 nanofiltration membranes started from 1990s, and the average pore sizes obtained in these studies were in the range of 1.5~4.0 nm. [8-11, 13-16] To date, the tightest reported TiO_2 nanofiltration membranes, prepared by optimizing the sol-gel processing conditions, had a pore size of ~0.9 nm. [12, 13] Hydrolysis conditions of titanium alkoxides, however, need to be strictly controlled because of the extremely fast hydrolysis rate to avoid any local excess of water at any moment. [12]

Molecular layer deposition (MLD), a gas phase deposition technique, is a subset of atomic layer deposition (ALD) and has been developed very recently. [17, 18] Similar to ALD, in MLD, two self-limiting surface reactions are conducted alternately to deposit organic-inorganic hybrid coatings on a substrate. During each surface reaction, precursor molecules react with surface reactive groups, such as -OH, and chemically bond a layer of precursor molecules on the surface; new reactive sites/functional groups on the linked precursor molecules will be utilized for further layer growth. [19] Compared with the dense inorganic coatings prepared by ALD, MLD growth has been demonstrated for a variety of organic-inorganic hybrid coatings by using suitable metal and organic precursors. [20] The obtained organic-inorganic hybrid coatings can subsequently be converted into porous coatings by removing the organic compound [18, 21, 22]. The potential of using ALD technique to reduce pore size of porous support has been investigated by several research groups. [23-26] However, it is difficult to precisely control the resulting pore size at nanometer level. This resulted from the unavoidable pore size distribution of the porous support, and smaller pores were completely sealed first, leaving the larger pores still open. Transport

resistance was also expected to increase dramatically, because of the deposited dense coating by ALD. Molecular layer deposition has already been used to deposit ultra-thin porous coatings for metal catalysts stabilization[27] and highly selective catalysts.[28] Very recently, we have shown that forming an ultrathin, microporous MLD coating on 5A zeolite external surface greatly improved its size-selective adsorption via appropriate pore misalignment at the interface of the MLD coating and zeolite[21, 22]. Various microporous materials, such as Al_2O_3 , SiO_2 , and TiO_2 , can be deposited by MLD technique. One reason we chose TiO_2 as the coating materials in this study is that TiO_2 has been considered as a more stable material, especially its water stability[12, 29]. Figure 1a illustrates two surface reactions in one cycle of MLD using TiCl_4 and ethylene glycol (EG) as precursors to deposit titanium alkoxide coating. The self-limiting nature of the surface reactions of MLD offers advantages of exquisite control over coating thickness at sub-nanometer level, conformal pinhole-free coatings on high aspect ratio structures, and scale-up capability.[30-32] Here, we report an innovative use of MLD to fabricate TiO_2 nanofiltration membranes by depositing microporous TiO_2 coating on mesoporous support with excellent control of coating quality, thickness and nanometer-sized membrane pores, and their potential for water purification. We expect MLD will become a new method for preparing TiO_2 nanofiltration membranes with well controlled thickness, composition, and membrane pore sizes in a scalable way.

2. Experimental methods

2.1 Molecular layer deposition process

Titanium alkoxide MLD coatings were deposited using titanium tetrachloride (TiCl_4 ; 99.9%, Sigma Aldrich) and ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$; 99%, Alfa Aesar) as precursors. The MLD coating process was carried out in a tubular reactor, as shown in Fig. 2. A LabVIEW software was used for programmed control of pneumatic valves for transient dosing. Each MLD cycle started with 240 sec vacuum. TiCl_4 was then gradually introduced into the reactor as a vapor, based on the driving force of its room-temperature vapor pressure, until a pressure of 20 Pa and settled for 120 sec to allow the surface reaction; 240 sec vacuum was followed to evacuate extra unreacted TiCl_4 . Ultrahigh purity N_2 (Airgas) was used to purge the reactor with a flow rate of 20 sccm (standard cubic centimeters per minute) for 30 sec controlled by a mass-flow controller (Aera FC-7800) to further clean the reactor. Then, 240 sec vacuum was applied to evacuate N_2 . The

above operation was repeated except that TiCl_4 was replaced by ethylene glycol (EG) at 6.7 Pa. A typical coating cycle consisted of the following sequence: evacuation, TiCl_4 dose, evacuation, N_2 purge, evacuation; EG dose, evacuation, N_2 purge, evacuation. The MLD reactor was wrapped by a heating tape covered by a thermal insulation tape. All MLD processes were conducted at 100°C controlled by a homemade temperature controller.

2.2 Membranes preparation

Proposed MLD membrane forming process was shown schematically in Fig.1b. We used flat anodic aluminum oxide (AAO) membranes (Whatman) as the starting model support. These AAO membranes have an asymmetric structure with a diameter of 47 mm. The main body of AAO membranes is composed of large pores, ~ 100 nm, with ~ 60 μm thickness. The top selective layer has a thickness of approximately 300 nm and pore size of ~ 20 nm. Before MLD, AAO membrane was outgassed under vacuum at 200°C for 1 h to remove adsorbed water. Different cycles of MLD were subsequently conducted to deposit titanium alkoxide coating in AAO support pores. After completely filling AAO pores by hybrid titanium alkoxide, microporous TiO_2 membrane was generated by removing organic compound in the dense hybrid coating by calcination in air in a muffle furnace at 250°C for 4 h with a heating and cooling rate of $1^\circ\text{C}/\text{min}$ as reported before[21].

2.3 Membranes characterization

Field emission scanning electron microscopy (FESEM, Zeiss Ultra Plus) was used to observe the morphology of AAO before and after MLD. Surface roughness of AAO before and after MLD was measured using atomic force microscopy (AFM, AFMWorkshop). Surface chemical composition of AAO support and TiO_2 coated AAO was analyzed by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD instrument equipped with a monochromated Al $\text{K}\alpha$ x-ray source and hemispherical analyzer capable of an energy resolution of 0.5 eV). N_2 adsorption isotherms at 77 K were measured using a Micromeritics ASAP 2020 unit to determine pore size distribution of the MLD membrane. Prior to adsorption measurement, samples were ground to a fine powder and degassed in situ at 250°C for 4 h. Pore size distribution was calculated using adsorption branch of the isotherms. X-ray powder diffraction (XRD) measurements were carried out using a Rigaku MiniFlex II diffractometer with Cu $\text{K}\alpha$ radiation ($\lambda = 0.15418$ nm). Diffraction data were recorded for 2θ angles between 5° and 50° .

2.4 Membrane permeation tests

Liquid permeation was conducted using a dead end, stirred cell filtration system (Sterlitech Corp.) with 300 mL total feed volume. Feed side was connected to a high-pressure nitrogen tank to control feed pressure in the range of 0-7 bar. A magnetic stir bar inside the tank was used to stir the feed liquid at a spinning rate of 1000 rpm to minimize concentration polarization. An electronic scale (Ohaus, CS Series) was used to measure mass of permeated liquid. DI water (pH: 5.3; conductivity: 0.86 μ S) was used in all permeation measurements. Pressurized filtration of aqueous solutions of methylene blue (MB) (6.4 mg/L), NaCl (10 mM), Na₂SO₄ (10 mM), MgCl₂ (10 mM), and MgSO₄ (10 mM) was performed to evaluate water purification performance of the prepared TiO₂ nanofiltration membranes. All chemicals were obtained from Sigma-Aldrich, and no pH was adjusted in the prepared solutions. In each rejection test, liquid permeation was stabilized for 3 h before taking any measurement. Concentration of MB in the collected permeate was analyzed using a UV-vis spectrophotometer (Shimadzu UV-1800). Concentration of NaCl, Na₂SO₄, MgCl₂, and MgSO₄ was measured by a conductivity meter (Pour Grainger International, Lake Forest, IL, USA).

Suwannee River humic acid (SRHA) standard, as a model natural organic matter (NOM), was purchased from International Humic Substance Society (St. Paul, MN, USA) and used to evaluate anti-fouling performance of the TiO₂ nanofiltration membranes. Feed concentration SRHA in all filtration measurements was 5 mg/L. Permeate was collected at different water recoveries for flux and composition analysis. Concentration of SRHA was determined by UV-vis at a wavelength of 292 nm.

3. Results and discussion

3.1 TiO₂ nanofiltration membrane characterization

Surface morphology of the blank AAO support and gradual pore filling by TiO₂ MLD coating were observed by FESEM. The top surface view of the blank AAO support exhibited a porous structure consisting of 20-50 nm pores, the estimated porosity of AAO top selective layer is approximately 60%, as shown in Fig.3a. After 20 and 40 cycles of MLD on AAO support (AAO-20TiO₂ and AAO-40TiO₂; corresponding abbreviations for AAO with different cycles of MLD were used in the following description), the effective pore size of the AAO support gradually

reduced (Fig.3b) due to the conformal TiO_2 MLD coating deposited on the pore wall as well as on the surface of the support. However, after 40 cycles of MLD coating, open pores were still visible. This is apparently because deposited MLD coating was not thick enough to completely fill support pores. Our previous work showed a TiO_2 MLD growth rate of ~ 0.42 nm/cycle at 100°C [21]. Therefore, only pores smaller than approximately 32 nm are expected to be completely filled after 40 cycles of MLD. Since pore size distribution (20-50 nm) of the AAO support (Fig. 3a) exists, pores larger than 32 nm were only partially filled after 40 cycles of MLD. When 60 cycles of MLD was applied, a dense, continuous coating was deposited on the AAO support free of visible defects (Fig. 3c), and higher magnification revealed a much thicker coating and complete filling of AAO pores (inset in Fig. 3c). Fig. 3d showed the cross-sectional view of the AAO-60 TiO_2 membrane. The top AAO layer with 20-50 nm pores and a thickness of approximately 300 nm, which was supported on the bottom layer with larger pores of about 100 nm, has been completely filled with the TiO_2 MLD coating. Pressurized pure water permeation also confirmed that the MLD coating before calcination was dense and impermeable to water, as discussed below. The membrane surface properties, including surface roughness and chemical composition, of AAO before and after MLD were summarized in Table 1. Bare AAO support had an average roughness (R_a) of 24.5 nm; as we applied MLD coatings, the surface became smoother and the surface roughness decreased gradually to 16.7, 13.3 and 8.7 nm, respectively, after 20, 40 and 60 cycles of MLD... This decrease in the value of R_a is consistent with the fact that MLD has the advantage to deposit coatings with smooth morphologies[33]. XPS was used to detect the surface elements of the AAO and MLD modified AAO membranes. For bare AAO support, it is composed of Al and O, and no Ti was detected on the surface as shown in Table 1. After 60 cycles of MLD, surface Al concentration drastically decreased to 1.3% and Ti concentration increased to 28.8% due to the TiO_2 coating on the surface (Table 1). We found that the deposited TiO_2 MLD coating was amorphous by showing a large bump distributed in the range of 20 to 25° instead of high intensity narrow peaks with respect to XRD. Figure 4 showed the pore size distribution of TiO_2 MLD coating after calcination at 250°C , which was centered at approximately 1 nm. This is consistent with our previous work of TiO_2 MLD coated 5A zeolite composite adsorbents[21] and Patel's work on porous TiO_2 MLD films[34]. Organic dye rejection was also measured to probe the effective pore size of TiO_2 nanofiltration membranes, as discussed below.

3.2 Effect of MLD cycles on pure water permeation

Besides direct observation of the MLD coating on AAO support by FESEM, pressurized pure water permeation was also measured and used to determine number of MLD cycles that ensures a continuous, dense coating. Pure water permeability through AAO coated with different cycles of MLD was measured before and after calcination at 250°C. The permeability was calculated by the ratio of the volumetric filtrate flux (volume flow rate per membrane area) to the applied pressure. As shown in Fig. 5, before calcination, water permeability through bare AAO support (feed pressure: 1 bar) was 1520 L/(m²·h·bar), and decreased to 595 and 195 L/(m²·h·bar) after 20 (feed pressure: 2 bar) and 40 cycles of MLD (feed pressure: 4 bar), respectively. This is due to the gradual reduction of the AAO pores by the hybrid MLD coating deposited on the AAO pore walls. Apparently, after 40 cycles of MLD, the AAO support pores were still not completely filled. After 60 cycles of MLD, no observable water flux was found after 24 h permeation under pressure drop of 7 bar, corresponding to a pure water permeability lower than 0.1 L/(m²·h·bar) (detection limit of our system). This suggests 60 cycles of MLD formed a defect-free, dense titanium alkoxide MLD coating on the AAO support. This is consistent with the SEM images of AAO-60TiO₂ in Fig.3c. After calcination in air at 250°C, a pure water permeability as high as 48 L/(m²·h·bar) was obtained (feed pressure is 7 bar for all AAO-60TiO₂ and AAO-80TiO₂ membrane filtration test). This is comparable with the water permeability of reported TiO₂ nanofiltration membranes in the range of 25–50 L/(m²·h·bar)[10, 35], and in strong contrast with the low pure water permeability of commercial polymer membranes that is between 1-7 L/(m²·h·bar)[36]. Further increasing MLD cycles to 80 also generated a defect-free, hybrid MLD coating with pure water permeability lower than our detection limit, and after calcination pure water permeability increased to 13 L/(m²·h·bar). The decreased water permeability is apparently due to the thicker TiO₂ coating on AAO surface and thus increases transport resistance. It is interesting to find that the pure water permeability of calcined AAO-20TiO₂ membrane was even higher than calcined bare AAO support, although pores of AAO are expected to become narrower after MLD coating. This may be attributed to the better stability of TiO₂ at elevated temperature[37]; alumina is much easier to dehydrate after thermal treatment, and thus its surface becomes less hydrophilic.

3.3 Water purification by TiO₂ nanofiltration membranes

We first investigated water purification performance of the AAO-60TiO₂ nanofiltration membranes by measuring permeability and rejection for aqueous solutions of NaCl, Na₂SO₄, MgCl₂, and MgSO₄. AAO-60TiO₂ membrane showed permeabilities of 7.2-10.5 L/(m²·h·bar) for studied aqueous salt solutions (Fig. 6). The decline of permeability compared with pure water is probably because of the increased hydrodynamic resistance by ions adsorption in membranes, which was also observed in Tsuru's previous work[29]. The slightly higher permeability of NaCl than other salt solutions might be due to the smaller ion size of chlorine and sodium compared with sulphate and magnesium[38]. For the salt rejection, decent rejection for Na₂SO₄, 43%, was observed, while moderate rejection (35%, 29%, and 24%) of MgSO₄, NaCl, and MgCl₂ was obtained, respectively, as shown in Fig.6. This observed order of salt rejection (Na₂SO₄ > MgSO₄ > NaCl > MgCl₂) can be ascribed to the Donnan exclusion[2, 38] for slightly negatively charged TiO₂ nanofiltration membranes[39]. According to Donnan exclusion theory, co-ions, which have the same charge of membrane surface, tend to exclude from the membrane, and the repulsive force for divalent co-ions is greater than for monovalent co-ions. Counter-ion is also rejected in order to keep the electro-neutrality.[2] We also measured organic dye permeation, AAO-60TiO₂ membrane showed a high rejection (96%) for MB (cationic dye, MW = 373.90 g·mol⁻¹) after 3 h filtration; much longer time permeation only slightly decreased its rejection (93% after 18 h). The high rejection of rigid dye could be mainly attributed to sieving by membrane pores.[40] But, the MB permeability was only ~3.3 L/(m²·h·bar) (Fig. 6). We speculate the low permeability during MB filtration might be because the size of MB (0.7 × 1.6 nm)[41] is comparable to the pore size of AAO-60TiO₂ nanofiltration membrane (~1 nm) and thus blocked membrane pores. Bare AAO support did not show rejection of the organic dye and salt solutions.

3.4 Antifouling performance of TiO₂ nanofiltration membranes

Titanium dioxide (TiO₂) has received much attention in recent years to improve the antifouling property of membranes due to its hydrophilicity and great stability.[42, 43] Natural organic matter (NOM) is one of the major contributors to membrane fouling.[44] NOM fouling tests were conducted using AAO-60TiO₂ membranes. Figure 7 showed the normalized fluxes in three cycles to evaluate the antifouling performance and recovery capability. Normalized flux is defined as the measured permeation flux at different water recovery divided by the initial flux in the first cycle.[45] As shown in Fig. 7, during the first cycle of NOM filtration, after collecting

10 mL (i.e., 20% water recovery) of SRHA solution, the permeate flux decreased by 62% for AAO-60TiO₂ membranes. Similar trend was also observed in the second and third cycle. After each NOM filtration cycle, we opened the module and conducted a simple membrane cleaning process by flushing the membrane surface with water at a rate of 4.0 L/min for 30 min. We found that AAO-60TiO₂ membrane showed a good flux recovery (77-84%), and this recovery capability was also superior to the reported polysulfone nanofiltration membrane[46]. NOM rejection was around 99% in each cycle for AAO-60TiO₂ membranes (Fig. 7).

4. Conclusions

TiO₂ nanofiltration membranes were prepared for the first time by using a novel technique, MLD. Influence of cycles of MLD on hybrid coating quality was investigated. Our results showed a defect-free, dense titanium alkoxide MLD coating was formed after complete support pore filling, and approximately 1 nm pores can be effectively generated by calcination at 250°C in air. The AAO-60TiO₂ membrane showed a high pure water permeability of 48 L/(m²·h·bar) and high rejection for MB and NOM, moderate rejection for salts, and good antifouling performance as well as recovery capability. Compared with traditional sol-gel method, MLD has the potential advantages of precise pore size control, simple fabrication process, and ability to scale up. We expect MLD will become a new method for preparing TiO₂ nanofiltration membranes with well controlled thickness, composition, and membrane pore sizes.

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Table 1. The surface properties of AAO before and after MLD

Membrane	Surface roughness (nm)	Atomic concentration (%)		
		<i>Al</i>	<i>Ti</i>	<i>O</i>
AAO	24.5	40.0	-	60.0
AAO-20TiO ₂	16.7	17.3	17.3	65.4
AAO-40TiO ₂	13.3	6.8	24.4	68.8
AAO-60TiO ₂	8.7	1.3	28.8	69.9

Fig. 1. Schematic diagrams of MLD surface reactions for titanium alkoxide coating growth using TiCl_4 and EG as precursors (a) and a step-by-step procedure to prepare the TiO_2 nanofiltration membrane using an AAO support by MLD and subsequent calcination to open pores (b).

Fig. 2. Schematic illustration of the deposition system used for molecular layer deposition.

Fig. 3. FESEM images of the top-surface of AAO support (a); AAO-20TiO₂ membrane (left) and AAO-40TiO₂ membrane (right) (b); AAO-60TiO₂ membrane (c) (the inset SEM image showed a higher magnification of AAO-60TiO₂ membrane); and cross-section of AAO-60TiO₂ membranes (d). All MLD coatings have been calcined at 250°C in air.

Fig. 4. Pore size distribution of the AAO-60TiO₂ membrane.

Fig. 5. Pure water permeation through AAO with different cycles of MLD coatings before and after calcination at 250°C.

Fig. 6. Permeation through AAO-60TiO₂ membrane (black bar) and rejection of AAO-60TiO₂ membrane (red bar).

Fig. 7. Three filtration cycles of NOM on AAO-60TiO₂ membrane: flux decline (first row) and NOM removal for the corresponding cycle (second row).