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Enhancing the hydrophilicity and water permeability of polypropylene membranes by nitric acid activation and metal oxide deposition



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ABSTRACT

Activation by nitric acid oxidation has been combined with atomic layer deposition (ALD) to modify microporous polypropylene (PP) membranes. Nitric acid oxidation with prewetting of *t*-butanol generates active groups on the inert surface of PP membranes. Metal oxides including Al₂O₃ and TiO₂ are subsequently ALD-deposited on the activated membrane. Nitric acid oxidation is a mild approach to activate PP membranes. A short immersion in nitric acid for 10 min is able to generate oxygen/nitrogen-containing active species on the membrane surface, which leads to an evident increase (38%) in the membrane permeability. The mechanical stability and the integrity of the porous structure are well preserved after activation. Surface elemental analyses and microscopy observations confirm the successful deposition of metal oxides thin layers onto the activated membranes. In the deposition of either Al₂O₃ or TiO₂, the hydrophilicity of the deposited membranes is continuously improved with increasing ALD cycles, resulting in further increase in water flux. After 100 ALD cycles, the flux is doubled compared to that of the bare membrane. Al₂O₃ is more efficient in enhancing the hydrophilicity and permeation than TiO₂ under identical deposition conditions because of the faster growth of Al₂O₃ on the activated PP surface.

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1. Introduction

Polypropylene (PP) membranes are widely used in a diversity of fields such as wastewater treatment, lithium-ion batteries, and pharmaceuticals, due to their low cost, excellent mechanical robustness, and good chemical resistance [1,2]. However, membrane fouling and the decline of filtration flux arising from the strong intrinsic hydrophobicity of PP materials remain a major challenge which hinders the scale-up applications of PP membranes. Extensive research results indicated that membrane fouling could be effectively reduced by increasing the surface hydrophilicity of the membrane [3–7]. So far, great research efforts have been carried out to modify the surface property of PP membranes to increase its hydrophilicity and these modification methods basically involved coating the bare hydrophobic surface with a thin layer of hydrophilic materials, which turns the hydrophobic surface into hydrophilic. Conventional methods such as surface adsorption have been utilized for physical deposition of hydrophilic materials on the membrane [8–11]; however, the structure suffers from poor durability since the hydrophilic materials tend to detach from the membrane skeleton during long-term

usages in aqueous environment. Alternatively, grafting polymerization could covalently combine the external polymeric materials of strong hydrophilicity with the membrane though reactive groups are prerequisite on the membrane surface. To this end, a variety of surface pretreatment steps are essential for covalent grafting which mainly include UV irradiation, plasma treatment, ion beam, and γ -ray irradiation [12–17]. Such pretreatment proves as an effective approach to generate active species on the surface of PP membranes for the subsequent grafting of hydrophilic polymer chains; nevertheless, these techniques typically require expensive instruments and/or complicated and tedious procedures [18]. Moreover, the following grafting reactions usually take place in solutions, and inhomogeneous grafting of polymer chains on the fine membrane pores is inevitable, which leads to a loss of permeability, as it is difficult for monomers to thoroughly diffuse into membrane pores. Therefore, a simple and efficient methodology to improve the hydrophilicity of PP membranes meanwhile not sacrificing the permeability would be highly preferable.

A thin layer of metal oxides can dramatically improve the water wettability of intrinsically hydrophobic substrates including PP membranes, owing to the presence of large amount of strongly hydrophilic hydroxyl (–OH) groups on the surface of metal oxides. Atomic layer deposition (ALD) technology has been demonstrated as an effective way to deposit conformal yet ultrathin layers on many substrates with the precise control over the thickness of the deposition layer at the

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atom level [19]. A few reports have been published focusing on the deposition of metal oxides by ALD on polymeric substrates [20–24]. Jung et al. used ALD to deposit Al_2O_3 on polypropylene separators to improve their thermal stability and wettability towards electrolytes and they obtained rough membrane surface after the deposition due to the island-like growth of Al_2O_3 on chemically inert surface of bare polypropylene [25]. In our previous work, TiO_2 was ALD-deposited on both bare and plasma-activated PP membranes, and the deposition on bare PP membranes slightly enhanced the hydrophilicity of the membrane since the chemically active groups rarely existed on the membrane surface, somehow deposition on the activated membrane did drastically improve hydrophilicity [26]. Nevertheless, the complicated plasma instruments are required to treat on both sides of the membrane since the plasma could only penetrate limited depth of the sample surface and the intermediate part may remain unactivated if plasma treatment was applied only on one side or was not sufficient in power or duration. Furthermore, the unacceptable damage to the microstructure and mechanical stability of the substrate may occur if harsh conditions of plasma activation are used [27].

Here we apply nitric acid as the surface oxidation/activation agent without expensive and/or specialized equipment or reagents involved. Known as a cheap and widely used chemical with strong oxidation ability, nitric acid has been reported to oxidize nonporous polymeric material [28]. However, there is no report on the activation of porous membranes by taking the advantage of nitric acid oxidation. In this work, we first prewetted the porous PP membranes with *t*-butanol to facilitate the complete contact of the membrane pores with nitric acid in the following activation step which produced nitrogen- and oxygen-containing active groups on the surface of PP membrane. Subsequently, a conformal and uniform Al_2O_3 or TiO_2 layer is coated on the surface of the nitric acid-activated PP membranes by ALD. The nitric acid-activated PP membranes after ALD of either Al_2O_3 or TiO_2 exhibit noticeably enhanced hydrophilicity and water permeability. However, Al_2O_3 was more efficient in the modification of PP membranes than TiO_2 as Al_2O_3 was deposited on the substrate with a higher growth rate on the activated PP membrane under the same deposition conditions.

2. Experimental

2.1. Materials

Porous PP membranes (Celgard 2400) with a thickness of 25 μm and an average pore size of 43 nm were used as substrate membranes in this study. Trimethylaluminum (TMA, 99.99%, Metalorganic Center, Nanjing University) and Titanium isopropoxide (TIP, 98%, Aladdin) were used as metal precursor for Al_2O_3 and TiO_2 , respectively; whereas deionized water for oxygen source in the ALD process. N_2 with a purity of 99.99% was used as the precursor carrier and purging gas. Nitric acid with a concentration of 65%, *t*-butanol with a purity of 98%, ethanol with a purity of 99.7% and other reagents used in this work were purchased from local suppliers and used without further purification. Monodispersed SiO_2 nanospheres with a diameter of 12 nm obtained from Sigma-Aldrich were used to test the retentions of modified PP membranes.

2.2. Nitric acid activation of PP membranes

PP membranes were treated with nitric acid for a preset period of time (typically 10 min) after prewetted in *t*-butanol for 1 min at room temperature. Ethanol was then used to wash out the residual nitric acid and *t*-butanol for 5 times, eventually the nitric acid-treated membranes were dried in the oven at 70 °C for 4 h.

2.3. ALD deposition of Al_2O_3 and TiO_2 on PP membranes

The membrane sample was fixed on a sample holder in the ALD reactor (Savannah S100, Cambridge NanoTech) and dried at 80 °C for 10 min before deposition in vacuum ($\sim 1.33 \times 10^{-3}$ bar). Both TMA and deionized water were maintained at room temperature, while TIP was heated to 82 °C. Metal precursors (TMA or TIP) and water vapor were transferred into the reactor alternatively, and the “exposure mode” was utilized in this study to ensure sufficient diffusion of precursors into the porous membranes [29]. Taking Al_2O_3 for instance, for one ALD cycle, the sequential pulsing of precursors was 0.03 s/5 s/40 s/0.015 s/5 s/30 s with the order of TMA pulsing/exposure/purge/ H_2O pulsing/exposure/purge with a steady N_2 flow rate of 20 sccm; while one TiO_2 ALD cycle was composed of 0.2 s/5 s/30 s/0.015 s/5 s/30 s with the sequence of TIP pulsing/exposure/purge/ H_2O pulsing/exposure/purge under the same condition. The nitric acid-activated PP membranes were deposited for different cycles up to 500. The bare PP membranes without nitric acid treatment were also deposited under the same experimental conditions for comparison in the thermal analysis and filtration measurements.

2.4. Characterizations

Fourier Transformation Infrared (FTIR) spectra of the bare, nitric acid-activated PP membrane and the deposited membranes for various cycles were obtained from a Nicolet 8700 FTIR spectrometer in the mode of attenuated total reflection (ATR). All the spectra were measured within the wavenumber range of 4000–500 cm^{-1} at a resolution of 1.0 cm^{-1} . Surface chemical compositions of different membrane samples were characterized by X-ray photoelectron spectroscopy (XPS) performed on a Thermo ESCALAB 250 spectrometer. X-rays of energy $h\nu = 1486.6$ eV used a monochromatic rotating anode Al-K α source and a charge neutralizer. The ejected photoelectrons were analyzed by an electron energy analyzer at pass energy of 30 eV and the effective instrumental step size is 0.05 eV. A field emission scanning electron microscope (FESEM, Hitachi S-4800) was used to observe the surface morphologies of PP membranes being treated in different conditions, and the operating voltage was 5 kV. Sample surface was first sputtering-coated with a thin layer of Pt/Pd alloy to avoid the electron charging during SEM observations. The energy dispersive X-ray spectroscopy (EDS) attached to the microscope was employed to detect the elemental composition of membrane surfaces. Thermal gravity analysis (TGA) was performed on a NETZSCH TG209F1 thermal analyzer in air with a heating rate of 10 °C/min from 30 to 700 °C. An electronic tensile tester (CMT-6203, Shenzhen Sans Test Machine Co., Ltd.) was used to measure the tensile strengths of PP membranes before and after nitric acid treatment with a tensile rate of 1 mm/min. The samples were prepared with the size of 40 mm \times 30 mm. For both the bare and nitric acid-activated PP membrane, three samples were tested and the average value of the tensile strength was reported. The tensile strength (σ_t) of the membrane was calculated via the following equation:

$$\sigma_t = p/(b \times d)$$

where p is the maximum load, b the width and d the thickness of the membrane. We used a contact angle goniometer (Dropmeter A-100P, MAIST Vision Inspection & Measurement Co. Ltd., Ningbo) to measure the contact angles of water droplets on the bare and nitric acid-activated PP membrane deposited with different ALD cycle numbers. For each sample, the contact angle of a water droplet with a volume of 5 μL on five different positions was measured to obtain the average value. To test the stability of the metal oxides deposited on activated PP membranes, we challenged both Al_2O_3 - and TiO_2 -deposited membranes with 400 cycles with ultrasonic oscillation at a power

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