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Journal of Membrane Science

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

Plasma activation of porous polytetrafluoroethylene membranes for superior hydrophilicity and separation performances *via* atomic layer deposition of TiO₂

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ARTICLE INFO

Article history:

Received 14 September 2012
Received in revised form
10 April 2013
Accepted 26 April 2013
Available online 9 May 2013

Keywords:

Atomic layer deposition
PTFE
Plasma activation
Porous membranes
Surface modification

ABSTRACT

Conformal and smooth TiO₂ thin layers were coated on the surface of porous PTFE membranes subjected to a plasma activation process by atomic layer deposition (ALD). In contrast, TiO₂ 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.

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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 Al₂O₃, ZnO, and TiO₂ 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 Al₂O₃ and TiO₂ 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 Al₂O₃ [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 Al₂O₃ 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 Al₂O₃ 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 $^\circ\text{C}$ 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 $^\circ\text{C}$ 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 $^\circ\text{C}$, 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 $K\alpha$ 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 (Drop-meter 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.

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