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A sol–gel-derived α-Al_2O_3 crystal interlayer modified 316L porous stainless steel to support TiO_2, SiO_2, and TiO_2–SiO_2 hybrid membranes

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Abstract A homogeneous α-Al_2O_3 crystal membrane was fabricated by the sol–gel technique on 316L porous stainless steel (PSS) substrate with an average pore size of 1.0 μm. The preparation process was optimized by carefully choosing the binder, the concentrations of the casting solutions and the sintering temperatures of the membranes. Compared to methylcellulose and polyethylene glycol 20000, polyvinyl alcohol 1750 was found to be the most effective binder to fabricate a homogeneously structured Al_2O_3 membrane without defects. The concentration to prepare an uniform coverage membrane with a thickness of ~10 μm was 0.032 mol/L. When sintered at 1000 °C, γ-Al_2O_3 membrane with ~3 μm grains was obtained. When sintered at 1200 °C, γ-Al_2O_3 completely transformed into α-Al_2O_3 and the grains grew to ~5 μm. Accordingly, the process was applied to a bigger pore-sized PSS with an average pore size of 1.5 μm to fabricate an α-Al_2O_3 intermediate layer to initially modify its surface. A single α-Al_2O_3 crystal layer with a thickness of ~5 μm and an average pore size of 0.7 μm was achieved. Subsequently, TiO_2, SiO_2, and TiO_2–SiO_2 hybrid membranes were tried on the modified PSS. Defect-free microfiltration membranes with average pore sizes of ~0.3 μm were readily fabricated. The results indicate that the sol–gel method is promising to initially modify the PSS substrates and the sol–gel-derived α-Al_2O_3 crystal layer is an appropriate intermediate layer to modify the PSS and to support smaller grain-sized top membranes.

Introduction

Membrane filtration is a very effective method for separation/filtration and has been widely used in food, pharmaceutical, wastewater, and electronics industries [1]. Frequently, the membrane employed in a traditional separation membrane device consists of polymeric materials which have significant disadvantages including restricted mechanical, chemical, and thermal stabilities. As an alternative for the polymeric membranes, ceramic membranes with an improved stability have been introduced, but the available membranes still suffer from stability problems such as brittleness and restricted chemical stability in water vapor [2]. To date, more attention has been paid to metallic–ceramic composite membranes which use porous ceramics as top layers and porous metals as substrates. These composite membranes show high chemical stability, good longevity, and high mechanical strength [2, 3].

Porous stainless steel (PSS) has been frequently utilized as the substrate of the metallic–ceramic composite membrane to support silica [4–6], Pd [7, 8], TiO_2 [9, 10], and carbon [11, 12] layers in separation/filtration, membrane reactor, and photocatalysis applications due to its excellent

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mechanical strength, adaptability for fabricating into different shapes, and good corrosion resistance. It also presents the possibility of installing membranes into modules with very simple metal joining techniques such as welding or brazing [2]. The raw PSS substrate has a rougher surface and a wider pore size distribution (PSD) compared to its ceramic counterpart which results in voids or macropores/pinholes on the surface of the resulting membrane. Due to the fact, various approaches have been applied to get rid of these defects. Increasing the thickness of the membrane is obviously a simple way to obtain a macropores/pinholes-free membrane. This method, however, gives rise to other defects such as cracks and desquamations [13, 14]. In addition, a thicker membrane results in strongly increasing flow resistance and transmembrane pressure (TMP). It is believed that surface treatments are effective to prepare defect-free membranes. Gestel et al. [15] utilized a diamond grinding wheel to polish the surface of the α-Al_2O_3 support and obtained a very smooth, nearly mirror-like surface. However, this procedure must be carried out with great care otherwise the surface will be disfigured or the pores on the surface will be clogged irreparably. In addition, too smooth surface results in poor adhesion between the membrane and the support. Lee et al. [16] used nickel or copper submicron powders to polish the PSS. They also used silica xerogel to reduce the pore size and narrow the PSD of the support [17]. These methods do not easily achieve a suitable roughness value determined by the relation between the support particle size and roughness. Surface pre-coating by using an organic binder was explored by Elmaleha et al. [18]. This organic layer, however, increases the risks of membrane desquamations and poor adhesion between the membrane and the support because the temporary organic layer decomposes during the sintering process. A more practical method is to fabricate intermediate layer/layers on the rough surface. The conventional process is based on the suspension pre-coating method [19]. However, the resultant roughness and surface quality of the modification layer are greatly dependent on the morphology and particle size distribution of the powders being used to prepare such a layer. The sol–gel technique is considered as a very promising and versatile method to fabricate ceramic membranes because it is a relatively simple process. It is also suitable for coating films on ceramic and metal substrates of different shapes [20–22]. This method has been used to prepare the intermediate layer to modify the surface of ceramic substrates as well [23–26]. However, there is little written concerning the use of this method to initially modify the surface of the PSS [2, 16]. Therefore, it is worth researching the modification of the PSS by using the sol–gel technique.

Various materials and methods have been tried to modify the surface of PSS according to different pore sizes and different surface qualities of the substrates. Gestel et al. [2] used a rutile-TiO_2 suspension and a colloidal boehmite sol in turn to prepare a macroporous and a mesoporous membrane as intermediate layers to modify a PSS substrate with a $\sim$0.65 μm pore size by the wet-powder spraying technique and the sol–gel method. The rutile-TiO_2 casting solution was homogenized by ball milling of a commercial powder for 20 h. Lee et al. [16] rubbed nickel/copper submicron powders on the PSS support with an average pore size of 0.5 μm to initially modify its surface, and then used boehmite sol and colloidal silica sols to further modify the surface by the sol–gel technique. Metal particles are not versatile to modify inner surfaces of long tubular substrates. Crystalline Al_2O_3 is an excellent ceramic with high thermal, chemical, and mechanical stabilities and has been widely used in the synthesis of ceramic membranes [27–29]. Among the polycrystalline Al_2O_3, α-Al_2O_3 has often been used to fabricate substrates [15, 22–25, 27, 29], while, γ-Al_2O_3 has often been used to fabricate intermediate layers and top membranes [23, 26, 28]. There has been little research on using the crystalline Al_2O_3 to initially modify the raw surface of a substrate by the sol–gel technique.

In this study, we propose a sol–gel-derived crystalline Al_2O_3 layer to initially modify the surface of a bigger pore-sized PSS directly. The impact of the fabrication parameters including organic binders, concentrations of casting solutions, and sintering temperatures on the morphology and phase of such a layer is discussed. Then, top layers including TiO_2, SiO_2, and TiO_2–SiO_2 hybrid are tried to fabricate on the modified PSS by the sol–gel method as well to synthesis metallic–ceramic composite membranes with graded grain sizes. The study is expected to provide an alternative material and a fabrication method to prepare intermediate layer/layers to initially modify raw surfaces of PSS substrates. Our results suggest that the sol–gel-derived α-Al_2O_3 crystal layer is an appropriate interlayer to directly modify the PSS and to support smaller grain-sized top membranes. The preparation processes of both the modification layer and the top layers are based on the sol–gel technique, which can be applied to different shape of surfaces and can be easily adapted to industrial applications as well.

Experimental procedure

Membrane preparation

Substrates

Two different shapes of commercial 316L PSS substrates (Shanghai Yiming Filtration Technology Co., Ltd.) were used as supports to develop the modification layer. One was small PSS pieces of 5 × 5 mm which were wire-cut from a tubular PSS with an average pore size of 1.0 μm (Bubble Point Method, pure water permeance of 10128 L/(h m^2) at 0.1 MPa). The other was tubular PSS pieces 50 cm long, with inner diameters of 8 mm and outer diameters of 10 mm, and with an average pore size of 1.5 μm (Bubble Point Method, pure water permeance of 15192 L/(h m^2) at 0.1 MPa). They were cleaned in dry ethanol (99.7%, Xi'an Chemical Factory) and methyl ketone (99.8%, Xi'an Chemical Factory) in turn using an ultrasonic cleaner, and were dried at 300 °C for 6 h.

Preparation of Al_2O_3 modification layer

The colloidal sol–gel technique was used to fabricate the Al_2O_3 modification layers. The boehmite sol was prepared based on the Yoldas process [30], which included hydrolysis of aluminum isopropoxide ($Al(C_3H_7O)_3$, Shanghai Sinopharm Chemical Reagent Co., Ltd.) with H_2O and subsequent destruction of larger agglomerates with HNO_3 (65–68%, Guangdong Shantou Xilong Chemical Factory) at 85 °C for 12 h in a reflux set under vigorous stirring. The molar ratio of the reactants was $Al(C_3H_7O)_3$:H_2O:HNO_3 = 1:300:0.22. The pH value of the resulting parent sol was 5.42. Casting solutions were prepared by using the resultant boehmite sol with polyvinyl alcohol 1750 (PVA 1750, degree of hydrolysis 99%, Shanghai Shanpu Chemical Co., Ltd.), polyethylene glycol 20000 (PEG 20000, Guangdong Shantou Xilong Chemical Factory), and methylcellulose (MC, Tianjin Yuanhang Chemical Co., Ltd.) as organic additions. The amount of the three additives was 1, 10, and 0.1 wt. %, respectively [31]. The viscosity of the obtained casting solutions was about 0.05–0.07 Pa s (NDJ-5S Viscometer).

Films on the small pieces were prepared by dip-coating the pieces into casting solutions for 30 s, with a withdrawal rate of 0.5 mm/sec. The tubular substrate was also coated by a dip-coating process. The casting solution was poured into the PSS tube and remained for 30 s. It was then effused at a speed of 0.5 mm/sec through a glass valve joined to the PSS tube by a latex pipe. Sintering to the films was executed at different temperatures (i.e., 800, 900, 1000, 1100, and 1200 °C) for 3 h in air in a multi-segment programmable furnace (SX2-4-10, Electric furnace branch of Shanghai motor group, Shanghai) at a speed of 1 °C/min.

Preparation of TiO_2, SiO_2, and TiO_2–SiO_2 hybrid top membranes

Top layers including TiO_2, SiO_2, and TiO_2–SiO_2 hybrid membranes were fabricated on the as-prepared Al_2O_3 layer modified PSS tubular substrates. The TiO_2 membrane was prepared by the colloidal sol–gel technique according to our previous study [32]. The SiO_2 membrane was prepared via the colloidal sol–gel technique as well by using tetraethoxysilane (TEOS, 98%, Xi'an Chemical Factory) as the source of Si and ammonia as hydrolysis catalyst, which was described in another of our previous study [33]. Briefly, the ethanol diluted TEOS solution was heated in a reflux set until the temperature of it reached 50 °C, then ammonia was dropped into the solution. The peptization process was executed in the reflux set at 50 °C for 12 h under vigorous stirring. The molar ratio of the reactants was TEOS:H_2O:EtOH:NH_4OH = 1:52.6:38.2:2.1. The TiO_2–SiO_2 hybrid membrane was fabricated using a casting solution obtained by mixing the two casting solutions of TiO_2 and SiO_2 with a 1:1 volume ratio.

The concentrations of all the casting solutions were calculated by molar of metal atoms (i.e., Ti, Si, and Al) in the systems. All the chemicals were of reagent grade and were used as received. Water was deionized and doubly distilled.

Membrane characterization

Surface and cross-section morphologies of the membranes supported on PSS were determined by scanning electron microscopy (SEM, Quanta200, FEI, Philips) to observe the surface microstructures and the thicknesses of the membranes. The phase developments of membranes were studied by X-ray diffraction (XRD, DMX-2200, Japan) with CuKα radiation. PSDs of the membranes supported on the tubular substrates were measured by using mercury porosimetry (PASCAL 140/240, Thermo Electron). The mercury porosimetry samples with lengths of about 15 cm were taken from the tubular membranes remaining after sampling for SEM observation.

Results and discussion

Preparation of Al_2O_3 modification layer

The Al_2O_3 modification layers were originally developed on the small PSS pieces with an average pore size of 1.0 μm. The preparation process was optimized by regulating the binders, the concentration of casting solutions, and the sintering temperatures.

Figure 1 shows surface morphologies of the resulting Al_2O_3 membranes prepared with MC, PEG 20000, and PVA 1750 as binders. The concentration of the casting solution was 0.032 mol/L. Films were all sintered at 1200 °C. It can be seen from the images that there are many cracks in the membranes when MC (Fig. 1a) and

PEG 20000 (Fig. 1b) were used as binders. But the latter one has fewer cracks than the former one. In addition, the grains in the two membranes are stuck to each other with only a few pores. Dissimilarly, when PVA 1750 was used as the binder (Fig. 1c), the membrane presents no cracks and distinct grains and pores can be clearly seen. When the sol–gel method is employed to prepare membranes, an organic binder is usually required as the drying control chemical additive (DCCA) so as to prevent thin films from cracking during sol–gel transition at the drying stage. Hence the binder is crucial in the synthesis of the membrane by the sol–gel method. It can be concluded from the images that the three binders provide different anti-crack potentials. The images also indicate that the morphologies of the resulting Al_2O_3 membranes are greatly dependent on the binders. For the sol system in this study, PVA 1750 gave rise to a high quality porous microstructure and clear grain morphology without cracks and was chosen as the preferred additive for fabricating the Al_2O_3 membrane on the PSS.

Figure 2 shows the surface and cross-section morphologies of the membranes prepared from different concentrations of casting solutions (0.064, 0.032, and 0.016 mol/L). The sintering temperature to the films was 1200 °C. It is clear that the surface of the membrane is irregular and undulating when the concentration of the casting solution was 0.064 mol/L (Fig. 2a), while evenly smooth membranes were obtained when the concentrations were 0.032 mol/L (Fig. 2b) and 0.016 mol/L (Fig. 2c). Some voids and macropores appear when the concentration was 0.016 mol/L. The cross-section morphologies show that the thicknesses decreased as the concentrations decreased. When the concentration was 0.064 mol/L, the thickness was 12–20 μm and was not quite uniform. When the concentration went down to 0.032 mol/L, the thickness decreased to ∼10 μm and is quite uniform. When the concentration decreased to 0.016 mol/L, the thickness reduced to ∼6 μm. From Fig. 2, it is clear that with different concentrations the thicknesses and flatness of the membranes vary and voids or macropores appear. In terms of both the surface and cross-section morphologies, it can be concluded that the concentration of 0.032 mol/L is the most suitable one to prepare the Al_2O_3 membrane with an uniform thickness and a smooth surface without voids and macropores.

According to our previous study [32], PVA 1750 decomposes completely above 500 °C. Therefore, the calcination temperatures to the Al_2O_3 films were set at 800, 900, 1000, 1100, and 1200 °C. Figure 3 shows the surface SEM images of the resulting membranes sintered at these temperatures. When sintered at 800 °C, the membrane looks like dried mud with many cracks and shows no grains and no pores (Fig. 3a). Some cracks and a few large grains

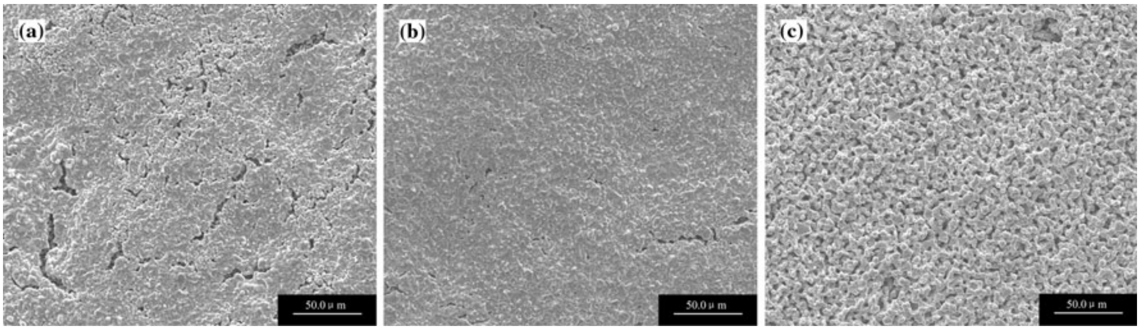

Fig. 1 Surface SEM images of Al_2O_3 membranes fabricated from casting solutions with **a** MC, **b** PEG 20000, and **c** PVA 1750 as binders

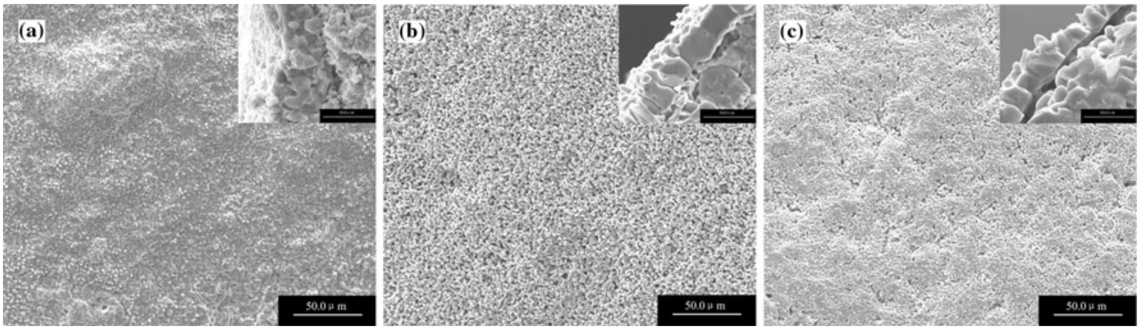

Fig. 2 Surface and cross-section (*insets*) SEM photographs of Al_2O_3 membranes prepared from casting solutions of **a** 0.064 mol/L, **b** 0.032 mol/L, and **c** 0.016 mol/L

dotted in a dried mud-like layer can be seen when the temperature goes up to 900 °C (Fig. 3b). When the temperature reaches 1000 °C, clear grains and homogenous pores among grains can be observed (Fig. 3c). The morphologies of the membranes sintered at 1100 °C (Fig. 3d) and 1200 °C (Fig. 3e) also show grain morphologies. The grains tend to be more regular in rhomb shape when sintered at 1200 °C. The phase structures of the Al_2O_3 membranes sintered at these temperatures are shown in Fig. 4. The spectra of the samples calcined at 800, 900, and 1000 °C exhibit two characteristic peaks at 46° and 67°, the fingerprint peaks of γ-Al_2O_3 (JCPDS #10-0425). This indicates that pure γ-Al_2O_3 phase exists in the membrane. When sintered at 1100 °C, the membrane reveals γ- and α-Al_2O_3 (JCPDS #82-1468) coexistence because of the presence of both α- and γ-Al_2O_3 characteristic peaks. However, the spectrum of the sample calcined at 1200 °C demonstrates that the membrane contains pure α-Al_2O_3 due to the absence of the γ-Al_2O_3 characteristic peak at 46°. From these results, it can be concluded that γ-Al_2O_3 can be fully transformed into α-Al_2O_3 when sintered at 1200 °C, which is in accordance with the result obtained by Lafarga et al. [34]. The SEM studies also show that the grain sizes of the α-Al_2O_3 are bigger than those of the γ-Al_2O_3, i.e., ~5 versus ~3 µm. Our studies suggest an interesting result that both the phases and the sizes of the sol–gel-derived Al_2O_3 crystals can be regulated through sintering temperatures to the films. When compared with the TiO_2 and SiO_2 grains obtained in our previous membranes [32, 33], the size of the α-Al_2O_3 grains is much bigger as well and the grains show a lower tendency for densification when sintered at a higher temperature, which ensures the membrane presenting a porous microstructure.

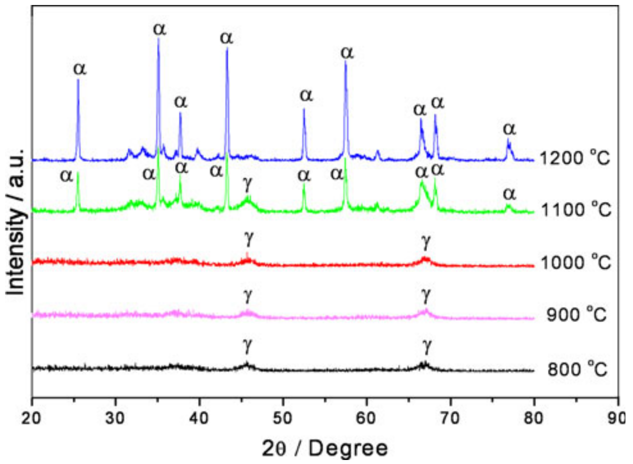

Fig. 4 XRD patterns of Al_2O_3 membranes fired at different temperatures

It is known that continuous membranes without defects are difficult to achieve on big pore-sized substrates because the supports have many big pores on their surfaces which results in defects to the resultant membranes. Yet larger size pores in the substrates yield a more efficient filtration. The most effective measure is to fabricate intermediate layer/layers to modify their surface, keeping permeability

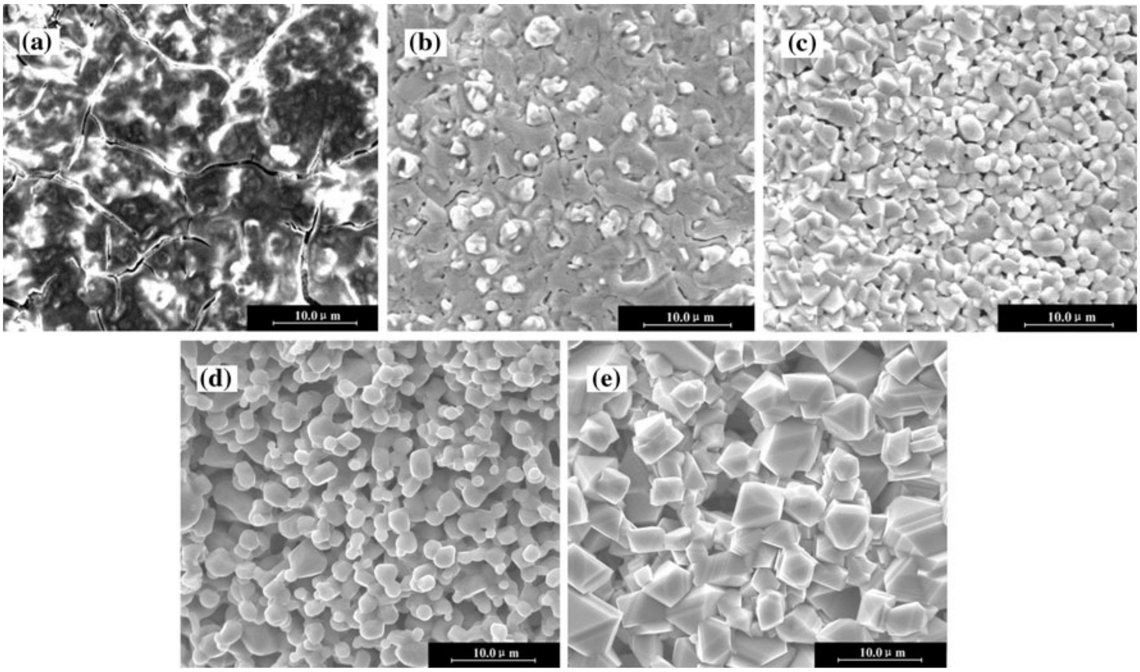

Fig. 3 Surface morphologies of Al_2O_3 membranes sintered at **a** 800, **b** 900, **c** 1000, **d** 1100, and **e** 1200 °C

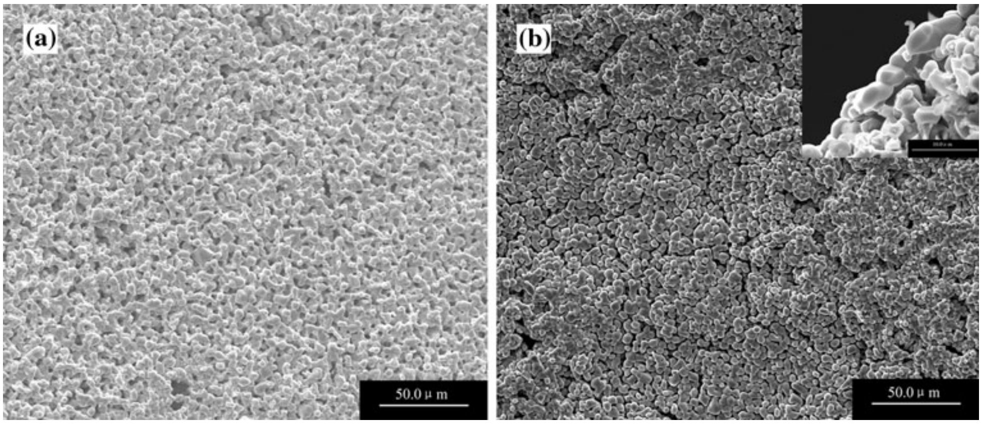

Fig. 5 Surface morphologies of 1.5 μm pore-sized PSS supported α-Al_2O_3 membranes prepared from different concentrations of casting solutions: **a** 0.016 mol/L and **b** 0.008 mol/L. *Inset* cross section of **b**

as high as possible. A small-sized grain modification layer is not recommended because small grains often infix in the big pores on the surface of the substrates and block them. Small grains usually form small pores in the modification layer. Both of these conditions influence the permeability of the substrates. Since the sol–gel-derived α-Al_2O_3 crystals have bigger sizes, we attempted to transfer the process to a bigger pore-sized PSS to fabricate a modification layer.

Bigger pore-sized PSS (1.5 μm, vs. the former 1.0 μm in this study, 0.65 μm [2] and 0.5 μm [16] in other literatures) was tried as the support on which to fabricate an α-Al_2O_3 modification layer. Since we were fabricating an intermediate modification layer, the casting solutions were diluted to 0.016 and 0.008 mol/L to reduce the layer thickness. The surface SEM images of the resulting membranes are shown in Fig. 5. From Fig. 5a, it can be seen that the surface is continuous when the concentration was 0.016 mol/L. Though a few voids and macropores can be observed, we can see that the bigger-sized α-Al_2O_3 grains have the potential to form a continuous membrane on the bigger pore-sized PSS. When the concentration of the casting solution was 0.008 mol/L, more voids and macropores appear (Fig. 5b). Nonetheless, the cross-section morphology of the latter prepared from the concentration of 0.008 mol/L indicates that the membrane consists of a single layer of Al_2O_3 crystals with a thickness of ~5 μm. An appropriate membrane thickness is crucial for practical applications because too thick of a membrane increases flow resistance and TMP. The single-layered α-Al_2O_3 crystal membrane fabricated by using the concentration of 0.008 mol/L is suitable to modify the surface of the substrate. PSD of the Al_2O_3 membrane is shown in Fig. 6. It can be seen that the curve consists of two ranges. The first wide range from 1.0 to 4.1 μm (marked with an “S”) obviously represents the PSD of the substrate. This reveals that the substrate has a quite broad PSD. The second range from 0.2 to 1.0 μm gives a narrow distribution range with a sharp peak (marked with an “A”). This obviously belongs to the PSD of the α-Al_2O_3 layer. This illustrates that the PSD of the α-Al_2O_3 modification layer is comparatively narrow. The peak at 0.7 μm indicates that the average pore size of the α-Al_2O_3 modification layer is 0.7 μm after one modification process. This is about half of the pore size of the PSS substrate with an average pore size of 1.5 μm and, indeed, even smaller than that of the PSS with an average pore size of 1.0 μm, which was used to originally develop the α-Al_2O_3 membranes. Both the morphology and the PSD show that the single-layered α-Al_2O_3 crystal membrane derived from the sol–gel method can be considered as an appropriate modification layer to improve the surface quality of the bigger pore-sized PSS, and the modified PSS can be an appropriate substrate to support even smaller grain-sized membranes.

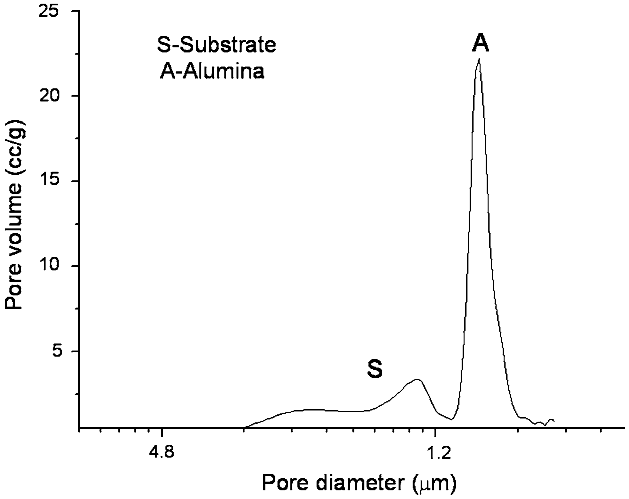

Fig 6 PSD of the sol–gel-derived α-Al_2O_3 modified PSS with an average pore size of 1.5 μm

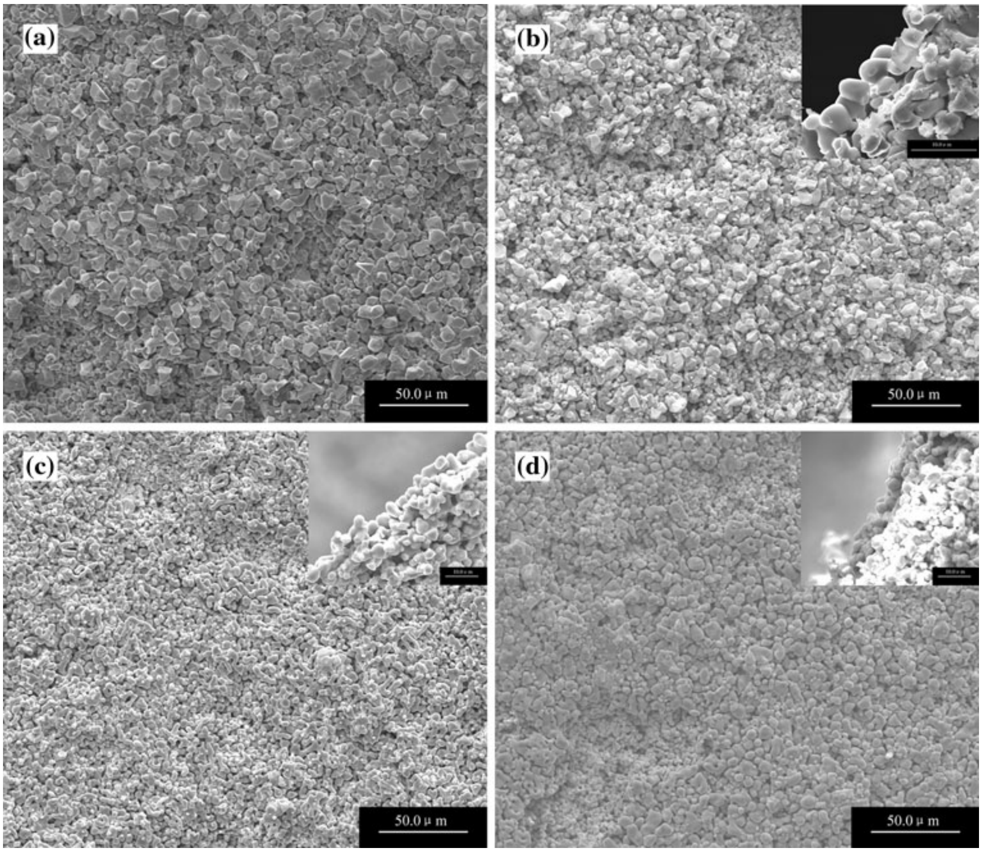

Fig. 7 SEM images of the sol–gel-derived α-Al_2O_3 interlayer supported **a** TiO_2, prepared from casting solution of 0.0005 mol/L, **b** TiO_2, prepared from casting solution of 0.001 mol/L, **c** SiO_2, and **d** TiO_2–SiO_2 hybrid membranes. *Insets* cross sections

From the above results, we conclude that homogenous α-Al_2O_3 crystal membrane is fabricated through regulating the preparation parameters of the binders, of the concentrations of the casting solutions, and of the sintering temperatures to the films. PVA 1750 was found to be preferable when compared with MC and PEG 20000. The most suitable concentration of the casting solution for fabricating a homogeneously structured membrane was 0.032 mol/L. The resulting membrane presents bigger-sized grain morphology and pure α-Al_2O_3 phase when sintered at 1200 °C. The process for preparation of the bigger grain-sized α-Al_2O_3 crystal layer was thereafter transferred onto a bigger pore-sized PSS with an average pore size of 1.5 µm to fabricate an intermediate modification layer. A single α-Al_2O_3 crystal layer with a thickness of ~5 µm and an average pore size of 0.7 µm was successfully fabricated on the substrate.

Preparation of TiO_2, SiO_2, and TiO_2–SiO_2 hybrid top membranes

In order to verify the performance of the modification layer and to fabricate membranes constructed of graded grain sizes, top layers including TiO_2, SiO_2, and TiO_2–SiO_2 hybrid were tried on the α-Al_2O_3 crystal interlayer-modified PSS substrate. These membranes were prepared by a two-step sol–gel procedure. First, an α-Al_2O_3 intermediate layer was fabricated on the raw PSS tube by the sol–gel technique according to the preferred results obtained in "Preparation of Al_2O_3 modification layer". Then, TiO_2, SiO_2, and TiO_2–SiO_2 hybrid membranes were fabricated on the modified PSS tube by the sol–gel technique as well. The sintering temperature to the TiO_2, SiO_2, and TiO_2–SiO_2 hybrid membranes was 850 °C in accordance with our previous studies.

The TiO_2 membranes were fabricated by using casting solutions with concentrations of 0.0005 and 0.001 mol/L. The morphologies of the resulting TiO_2 membranes are shown in Fig. 7a and b. From the image, it can be seen that continuous TiO_2 membranes have been formed on the modified layer by using either of the two casting solutions. A few macropores exist in the TiO_2 membrane when the diluted casting solution of 0.0005 mol/L was used. Continuous membrane with homogenous grains and pores is achieved when the concentration of the casting solution was 0.001 mol/L. The cross-section morphology of the membrane illustrates that the thickness of the α-Al_2O_3/TiO_2 membrane remains almost the same as the original

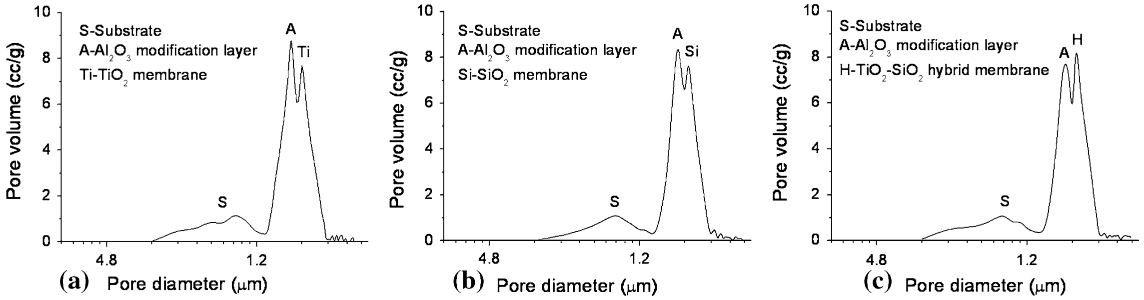

Fig. 8 PSDs of **a** TiO_2, **b** SiO_2, and **c** TiO_2–SiO_2 hybrid membranes on the sol–gel-derived α-Al_2O_3 interlayer modified PSS

α-Al_2O_3 modification layer of ~5 μm. The morphologies of the SiO_2 membrane prepared on the α-Al_2O_3 layer modified PSS are seen in Fig. 7c. The concentration of the casting solution was 0.007 mol/L, which was estimated from the results of our previous study and the experiences of preparations of the TiO_2 membrane on the α-Al_2O_3-modified PSS. From the image, it can be clearly observed that continuous membrane without defects was achieved. The cross-section morphology shows that the α-Al_2O_3/SiO_2 membrane also consists of a single-layered grain membrane with a thickness of about 5 μm. The TiO_2–SiO_2 hybrid membrane was fabricated by using a casting solution obtained by mixing the two previous casting solutions in a 1:1 volume ratio, i.e., 1 volume of TiO_2 casting solution of 0.001 mol/L mixed with 1 volume of SiO_2 casting solution of 0.007 mol/L. The morphologies of the resulting membrane are shown in Fig. 7d. It can be seen that continuous membrane with homogenous grains and pores is obtained. The surface morphology of the membrane shows that the grains in the membrane have higher particle packing density and the pores among the grains look comparatively smaller than those in the TiO_2 and SiO_2 membranes. This can be illustrated by the complementariness of the two different grains. The cross-section morphology of the hybrid membrane also shows that the α-Al_2O_3/TiO_2–SiO_2 membrane consists of almost single-layered grains with a thickness of about 6 μm.

Pore size distributions of the obtained α-Al_2O_3/TiO_2, α-Al_2O_3/SiO_2, and α-Al_2O_3/TiO_2–SiO_2 hybrid membranes on the PSS tubes are presented in Fig. 8. From these graphs, it is obvious that there are three distribution areas in all of the curves. The first ones are in the range of 1.0–4.1 μm, which correspond to the PSD ranges of the substrates (marked with an "S"). The second areas are in the range of 0.4–1.0 μm, which show sharp peaks, corresponding to the PSD ranges of the α-Al_2O_3 crystal-modified layers (marked with an "A"). The peaks at about 0.6 μm indicate that the average pore sizes of the modification layers are 0.6 μm. The third areas in the range of 0.1–0.4 μm obviously belong to the three top layers of TiO_2, SiO_2, and TiO_2–SiO_2 hybrid membranes (marked with a "Ti", a "Si", and an "H", respectively). The peaks at ~0.3 μm show that the average pore sizes of these membranes are 0.3 μm, which confirms that they are microfiltration (MF) membranes.

The thicknesses of the resulting α-Al_2O_3/TiO_2, α-Al_2O_3/SiO_2, and α-Al_2O_3/TiO_2–SiO_2 hybrid membranes on the PSS with an average pore size of 1.5 μm are much thinner than those of the TiO_2 and SiO_2 membranes on the PSS with an average pore size of 1.0 μm achieved in our previous studies. In addition, the concentrations of the casting solutions which were used to fabricate such top membranes are more diluted than those which were used to fabricate TiO_2 and SiO_2 membranes as well. The pore sizes of the three thinner membranes are much smaller than the α-Al_2O_3 membrane supported on the PSS with an average pore size of 1.0 μm (i.e., 0.7 vs. 0.3 μm). This shows that those membranes with α-Al_2O_3 crystal interlayer possess better architecture. It also shows that the bigger grain-sized α-Al_2O_3 crystal layer can act as an appropriate intermediate layer to improve the surface quality of the raw bigger pore-sized PSS and that the sol–gel method is very promising for fabricating such a modification layer. From the results, it can be concluded that the requirement for the pore size limit to the substrates can be less rigid, i.e., bigger pore-sized substrates are acceptable to fabricate continuous membranes without defects when the bigger grain-sized α-Al_2O_3 crystal membrane is applied as the modification layer. From a practical point of view, bigger pore-sized substrate is more economical and easier to obtain since bigger-sized powders are easier to manufacture commercially. In addition, bigger pore-sized substrate has a higher permeability. The preparation processes of the intermediate modification layer and the top layers are both based on the sol–gel technique which can be easily adapted to industrial applications.

Conclusion

This article presents a synthesis method of fabricating a homogenous α-Al_2O_3 crystal membrane on PSS substrate with an average pore size of 1.0 μm by the sol–gel technique. It also presents a two-step sol–gel synthesis method of fabricating smaller grain-sized TiO_2, SiO_2, and TiO_2–SiO_2 hybrid membranes on a bigger pore-sized PSS with an average pore size of 1.5 μm by using a sol–gel-derived α-Al_2O_3 crystal membrane as an intermediate layer. The results indicate several important points. First, the sizes of the sol–gel-derived Al_2O_3 crystals in the membrane can be regulated through sintering temperatures to the films. A bigger grain-sized α-Al_2O_3 crystal membrane is obtained when the film is sintered at 1200 °C. Second, the bigger grain-sized α-Al_2O_3 crystal membrane is an appropriate intermediate layer to initially modify the raw surface of PSS and to support smaller grain-sized membranes with less thicknesses and smaller pore sizes. Third, bigger pore-sized PSS substrates, which are more economical and have a higher permeability, are acceptable to fabricate continuous membranes without defects when the bigger grain-sized α-Al_2O_3 crystal modification layer is applied. This study also shows that the sol–gel method is very promising for initial modifying the surface of raw PSS substrates directly.

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