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Metal oxide nanofibres membranes assembled by spin-coating method

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Abstract

Ceramic membranes are of particular interest in many industrial processes due to their ability to function under extreme conditions while maintaining their chemical and thermal stability. Major structural deficiencies under conventional fabrication approach are pin-holes and cracks, and the dramatic losses of flux when pore sizes are reduced to enhance selectivity. We overcome these structural deficiencies by constructing hierarchically structured separation layer on a porous substrate using larger titanate nanofibres and smaller boehmite nanofibres. This yields a radical change in membrane texture. The differences in the porous supports have no substantial influences on the texture of resulting membranes. The membranes with top layer of nanofibres coated on different porous supports by spin-coating method have similar size of the filtration pores, which is in a range of tens of nanometers. These membranes are able to effectively filter out species larger than 60 nm at flow rates orders of magnitude greater than conventional membranes. The retention can attain more than 95 %, while maintaining a high flux rate about 900 L/m²·h. The calcination after spin-coating creates solid linkages between the fibres and between fibres and substrate, in addition to convert boehmite into γ -alumina nanofibres. This reveals a new direction in membrane fabrication.

Keywords: Nanofibres; Ceramic membrane; High flux, Metal oxide; Spin coating.

1. Introduction

Ceramic membrane modules can withstand elevated temperatures, broad range of pH, and high operating pressure up to 10 bar without concern of membrane structure deformation, such as compaction, lamination and swelling. These unique thermal, chemical and mechanical properties of ceramic membranes have significant advantages over polymeric membranes in many applications [1]. In addition, ceramic membranes have been also reported to have a narrow pore size distribution compared to the polymeric membranes. Ceramic membranes can be significantly resistant to membrane deterioration by microbes and surface abrasion by coarse particles circulation. Nevertheless, it is rare for them to be used in water treatment compared to usage of polymeric membranes [2]. Employing ceramic membranes for both gases and liquids also presents additional economic, environmental and safety imperatives [3].

Normally, the nanofibrous media, made up of organic fibres of diameter ranging from 100 to 1000 nm, can be conveniently produced by electro-spinning technique [4]. These polymer membranes could effectively filter particles of 0.3 μm and above in air and water, which are essential requirements in the control over airborne and waterborne contaminants, hazards biological agents, allergens and pollutants in food, pharmaceuticals and biotechnology processes [5]. Recently free-standing films of nanofibrous composite materials was developed, which could be applied to optical, biological, metallic, and magnetic materials [6].

Our previous communication [7] reported that ceramic nanofilters with a hierarchically structured separation layer were constructed on a porous α -alumina using larger titanate and smaller boehmite (AlOOH) nanofibres. This approach is based on the latest developments within nanostructures of metal oxides. The resulting membranes with layers of randomly oriented fibres (LROF) can effectively filter out species larger than 60 nm at flow rates orders of magnitude greater than conventional membranes, and are inherently “immune” to the structural deficiencies in the conventional ceramic membranes such as cracks, pin-hole and serious sintering.

However, the comprehensive study on the membrane synthesis process and the properties of the membranes has not been presented in details. In this paper, we presents a detailed study on the process of constructing the separation layer by controlled coating procedure, the influence of various substrates and the nanofibres of metal oxides and the texture characterization of the substrates and the LROF membrane. Such a study provides insight into the advantages of these membranes and the compatibility of the top layer of the nanofibres to different supports.

2. Experimental

In ceramic membranes, a thin top layer, which fulfils the actual separation function of the membranes, is usually deposited over porous supports. The porous supports provide mechanical strength for the thin separation layers. The supports can be made from alumina, cordierite, mullite, silica, spinel, zirconia, other refractory oxides and various oxide mixtures, carbon, sintered metals and silicon carbide.

Ceramic membranes can be prepared with different methods: sol-gel coating, spin-coating, in situ hydrothermal synthesis; chemical vapour phase method, spray seed coating, etc. In conventional fabrication of ceramic separation membranes, the particulate sols are applied onto porous supports. Major structural deficiencies under this approach are pin-holes and cracks, and the dramatic losses of flux when pore sizes are reduced to enhance selectivity [8]. Besides, serious sintering of the small metal oxide particles could also reduce the flux.

The inorganic porous support is always required for the ceramic membranes and its nature and structure may affect the quality of the ceramic membrane. A popular support is made of sintered alumina, which is not expensive and easily obtained. Another commercial

product is porous glass disk (Schott, Germany). α -alumina supports with a diameter of 30 mm, thickness of 2 mm and mean pore size of 0.8 μm were obtained from the Membrane Science and Technology Research Center of Nanjing University of Technology. Porous glass supports with a diameter of 30 mm, thickness of 2 mm and mean pore size of 2 μm were purchased from Schott. Both of the supports were used as substrates to investigate their effects on the LROF membranes.

In this research, various nanofibres were prepared and used for assembling LROF structure. NaOH, NaAlO_2 , Tergitol 15S-9 (nonionic surfactant), HNO_3 , ethanol, and acetic acid used in the synthesis were AR grade and from Aldrich. Titanate nanofibres and boehmite nanofibres in this study were prepared as reported in our previous works [9-10]. Titanate nanofibres were synthesized via a hydrothermal reaction between a concentrate NaOH solution and TiOSO_4 [9]. Boehmite nanofibers were prepared by a hydrothermal treatment of aluminium hydrate precipitate in the presence of polyethylene oxide surfactant [10].

The titanate fibres were dispersed into ethanol, forming a suspension containing 0.2 wt% of titanate nanofibres. The suspension was sonicated using an ultrasonic finger for 10 min to achieve a homogeneous dispersion, which was used to apply thin layers on the porous substrate using a spin-coater. The porous substrate was mounted on the chuck of a spin-coat processor (WS-400B-6NPP-Lite, Laurell). The coating was applied at the spinning velocity of 1000 r/min for 2 min. About 0.5 mL of the fibre suspension was used for each coating. The spin-coating process was repeated twice, followed by drying in air at 393 K, calcination at 773 K for 4 h. The heating rate was 1 K/min, starting from 393 K. Similarly, the 0.2 wt% of boehmite nanofibre suspension was prepared and applied on the calcined membrane with the layer of randomly oriented titanate nanofibres.

The membranes were mounted on a filtration set-up to assess their separation efficiency. The 10 wt % dispersion of Latex spheres (Duke Scientific Corporation) was diluted to 0.01 wt% with water. 30 mL of the dilution was used to test permeation passing through a prepared membrane. A pressure difference between the pressures on the feeding fluid and on the permeate was maintained stably at 20 kPa by a vacuum system to drive the filtration. The time taken for filtrating every 5 mL of fluid by the membrane under test was recorded.

The fluids before and after filtration by the membrane were sampled for analysis by two techniques: SEM and UV-Vis spectroscopy [11-12]. SEM images were taken on an SEM (FEI Quanta 200). The specimens from a liquid sample were prepared by dropping 5 μL of solution on a glass slide, which was then dried under vacuum conditions. The specimens were coated with gold using BioRad SC500 sputter coater prior to the imaging. The efficiency of membrane separation could be estimated directly by comparing the numbers of Latex spheres in images of the specimens taken before and after membrane filtration. UV-visible spectroscopy (UV-vis) on a Cary100 (Varian Inc.) spectrophotometer was also utilized to analyse the concentration change of the fluids before and after the filtration. The intensity of the adsorption band at 205 nm was adopted to determine the concentration using a calibration curve. Pore size distribution of the membranes was determined by liquid-liquid displacement method [13]. The pore size distribution function [$f(r)$] demonstrates the corresponding pore numbers. The morphology of the nanofibres was recorded on a Philips CM200 Transmission electron microscope (TEM) employing an accelerating voltage of 200 kV. The specimens were sample powders deposited onto a copper micro-grid coated with a holey carbon film.

3. Results and discussion

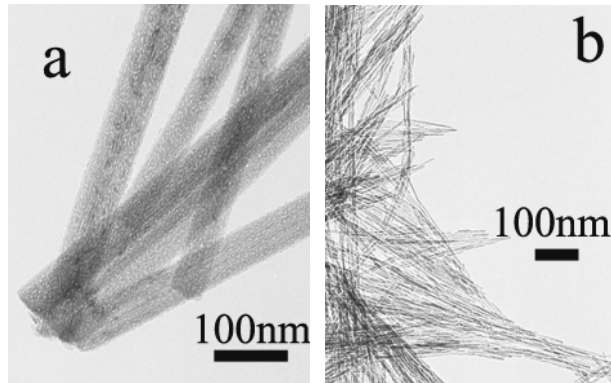


Figure 1 TEM images of titanate nanofibres (a) and boehmite nanofibres (b).

Figure 1 shows the TEM images of synthesized titanate nanofibres and boehmite nanofibres. The titanate fibres were 50-100 nm thick and the boehmite fibres were 5-10 nm thick as shown in the images. The diameter of nanofibres determines the lowest limit of the pore size of the resulting LROF membranes. Use of the thin boehmite nanofibres on the top layer is necessary to reduce the pore size below 100 nm.

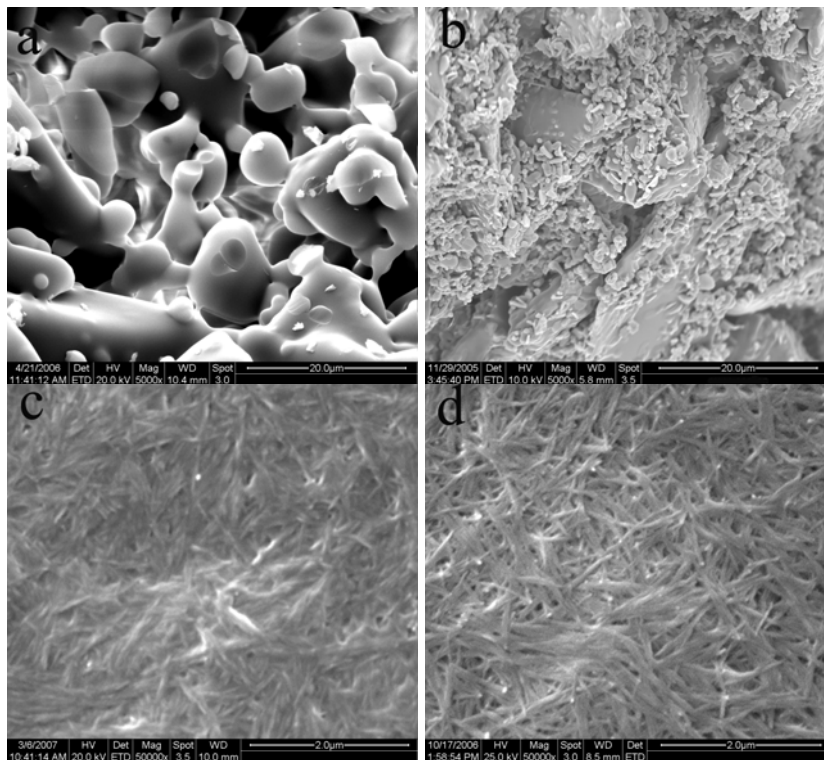


Figure 2 SEM pictures of supports and LROF membranes. a. porous glass support; b. α -alumina support; c. LROF membrane on porous glass support; d. LROF membrane on α -alumina support.

Figure 2 illuminates SEM images of supports and LROF membranes. Larger pores with several microns can be seen on the surface of porous glass supports (Fig. 2a), while the pore size for α -alumina support is less than 1 μm (Fig. 2b). Various supports showed much difference and generally were rather rough. After coating with the large titanate nanofibres

and the thin boehmite nanofibres, the surface of non-woven membranes exhibited no substantial difference. It can be seen that the boehmite nanofibres cover the surface entirely and homogeneously; the pore size of the top layer were below 100 nm without any structure deficiencies, such as pin-holes and cracks.

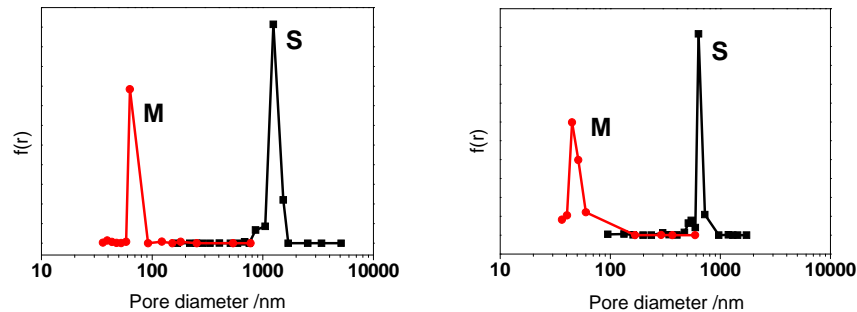


Figure 3 Pore size distributions of supports and LROF membranes. a. LROF membrane on porous glass support; b. LROF membrane on α -alumina support. (S: substrates; M: resulting membranes)

The pore size distributions of supports and LROF membranes are displayed in Figure 3. The mean pore size of porous glass is several microns and that of α -alumina support is 700 nm. However, the resulting membranes on various supports have the similar pore size distributions, centred at about 50 nm.

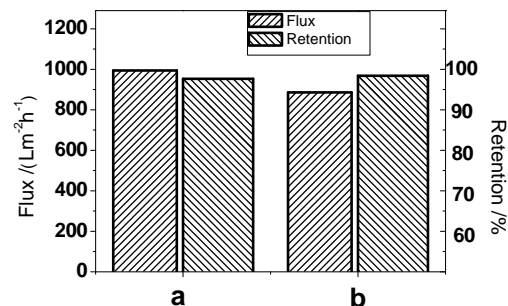


Figure 4 Separation performances of LROF membranes with various supports. a. LROF membrane on porous glass support; b. LROF membrane on α -alumina support.

Figure 4 depicts the separation performances of LROF membranes with various supports. For the LROF membrane on porous glass support, the separation flux is $990 L/m^2 \cdot h$ with the retention of 95.3% for 60 nm latex spheres. Similarly, for the LROF membrane on α -alumina support, the separation flux is about $900 L/m^2 \cdot h$ with the retention of 96.8%. The SEM and separation results confirm that the texture of the top layers of LROF membranes on different supports but formed by the same coating procedures with the large titanate nanofibres and the thin boehmite nanofibres are almost the same.

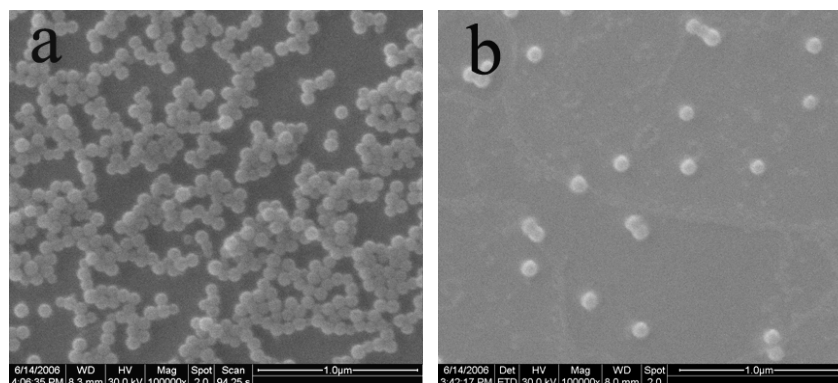


Figure 5 SEM pictures of 60 nm latex dispersion (a) and its filtration (b) using LROF membrane on α -alumina support. Scale bar 1.0 μm .

Figure 5 illustrates SEM images of 60 nm latex dispersion and its filtrate using LROF membrane on α -alumina support. The separation performance of LROF membrane on porous glass support is similar (not shown). More than 95% of latex sphere were cut off [11].

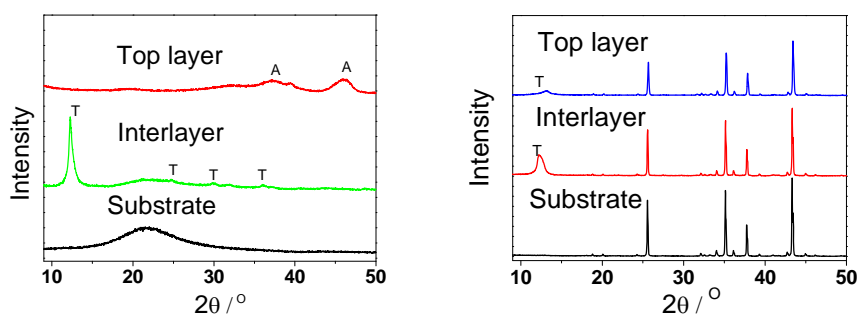


Figure 6. XRD patterns of the supports and the corresponding LROF membranes on various supports. a. LROF membrane with porous glass support; b. LROF membrane with α -alumina support. (T: titanate phase; A: γ -alumina phase)

Figure 6 shows XRD patterns of the supports and the corresponding LROF membranes on various supports. After three coatings with titanate nanofibres on the amorphous glass supports the diffraction peaks from titanate [8] can be seen. Further coating with boehmite nanofibres and calcination result in disappearance of the peaks from titanate phase, meanwhile the γ -alumina peaks can be seen (Fig. 6a), which are from the γ -alumina nanofibres covering the top surface entirely [9]. The membrane on the α -alumina support is similar to that on the porous glass. But the intensities of the XRD peaks from the titanate and the γ -alumina appear weak because of the sharp peaks of α -alumina support (Fig. 6b), the peak of γ -alumina is hardly recognised [8-9].

4. Conclusion

This study clearly demonstrates that the separation efficiency of ceramic membranes can be significantly improved by constructing a top separation layer with metal oxide nanofibres. Such improvements are attributed to the radical changes in the texture of the top-layer. It is also found that the top layers with LROF structure on porous glass and on α -alumina support exhibited striking similarity, in terms of structure and performance. They are able to filter out more than 95 % of 60 nm Latex spheres at a very high flux rate about 900 L/m²·h. Moreover, such a LROF structure is inherently “immune” to cracks, pin-hole and serious sintering with favourable operation process.

Moreover, the fabrication of these membranes is relative simple and economic with low reject rates, compared to the conventional ceramic membrane fabrication. This approach can be scaled-up readily to fabricating ceramic membranes for practical applications. The concept and the approach of constructing a hierarchical LROF structure as separation layer provide new opportunities in developing the next generation of ceramic membranes with high flux. We are also able to tailor the selectivity of the membranes by choosing fibres that meet the requirement of various applications.

References

- [1] R. R. Bhave, *Inorganic Membranes: Synthesis, Characterisation and Applications*, Van Norstrand Reinhold, New York, 1991.
- [2] M. Kazemimoghdam, T. Mohammadi, *Synthesis of MFI zeolite membrane for water desalination*, *Desalination* 206 (2007) 547-553.
- [3] A.J. Burggraaf, L. Lot, *Fundamentals of Inorganic Membrane Science and Technology*, Elsevier, Amsterdam, 1996.
- [4] A.G. MacDiarmid, "Synthetic metal": a novel role for organic polymer (Nobel lecture), *Angew. Chem. Int. Ed.*, 40 (2001) 2581-2590.
- [5] R. S. Barhate, S. Ramakrishna, *Nanofibrous filtering media: filtration problems and solutions from tiny materials*, *J. Membr. Sci.* 296 (2007) 1-8.
- [6] X. Peng, J. Jin, E. M. Ericsson, I. Ichinose, *General method for Ultrathin free-standing films of nanofibrous composite materials*, *J. Am. Chem. Soc.*, 129 (2007) 8625-8633.
- [7] X. B. Ke, H. Y. Zhu, X. P. Gao, J. W. Liu, Z. F. Zheng, *High-performance ceramic membranes with a separation layer of metal oxide nanofibers*, *Adv. Mater.*, 19 (2007) 785-790.
- [8] A. I. Schäfer, A. G. Fane, T. D. Waite, *Nanofiltration-principles and applications*, Elsevier, Oxford, 2003.
- [9] H. Y. Zhu, Y. Lan,; X. P. Gao, S. P. Ringer, Z. F. Zheng, D. Y. Song, J. C. Zhao, *Phase transition between nanostructures of titanate and titanium dioxides via simple wet-chemical reactions*, *J. Am. Chem. Soc.* 2005, 127, 6730-6736.
- [10] H. Y. Zhu, J. D. Riches, J. C. Barry, *γ -alumina nanofibers prepared from aluminum hydrate with poly(ethylene oxide) surfactant*, *Chem. Mater.* , 14 (2002) 2086-2093.
- [11] P. K. Kang, D. O. Shah, *Filtration of nanoparticles with dimethyldioctadecylammonium bromide treated microporous polypropylene filters*, *Langmuir* , 13 (1997) 1820-1826.
- [12] T. Leiknes, H. Ødegaard, H. Myklebust, *Removal of natural organic matter (NOM) in drinking water treatment by coagulation–microfiltration using metal membranes*, *J. Membrane Sci.* , 242 (2004) 47-55.
- [13] J. I. Calvo, A. Bottino, G. Capannelli, A. Hernandez, *Comparison of liquid-liquid displacement porosimetry and scanning electron microscopy image analysis to characterize ultrafiltration track-etched membranes*, *J. Membr. Sci.* , 239 (2004) 189-197.