Preparation of Ceramic Ultrafiltration Membrane by Nano-Metal Oxides Modified

Zhiwen Hu, Yulong Yang*, Han Liu, Qibing Chang, Fengli Liu and Yongqing Wang

School of Materials Science and Engineering, Jingdezhen Ceramic Institute, Jingdezhen 333403, China

*Corresponding author e-mail: yyl0822@126.com

Abstract. In order to prepare the ceramic ultrafiltration membrane with high-performance, the modification method of nano-metal oxides was chosen. The 19 channel porous ceramic membrane and the ZrCl$_4$ were chosen as the raw materials. The effects of ZrCl$_4$ concentration and modification times on the pore-size, permeability and structure of ceramic membrane were studied in detail. The result shows that the nano-ZrO$_2$ was generated on the surface of the ceramic membrane after being modified and sintered. It can reduce the pore-size and the surface roughness of the ceramic membrane. Meanwhile, this method can improve the permeability. Consequently, the ceramic ultrafiltration membrane has the pore-size of 75nm and the permeability of 1.010.12L/m$^2$·h·bar after sintering at 600°C for 2h with the optimized concentration of modify solution was 10g/L and the modified times was twice.

1. Introduction

In recent years, Porous ceramic membranes have been widely used in the range of food, medicine and industrial fields due to their excellent chemical compatibility, high temperature stability and high separation accuracy [1-3], especially for ultrafiltration membrane [4]. However, low permeability limits its development. Therefore, some researchers work on the preparation of nano-metal oxide modified microfiltration membrane [5, 6], and excellent performance microfiltration membrane was obtained. It has been proved that modification of nano-metal oxide can not only reduce the pore-size but also increase the water flux [7], which provides a reliable scheme for the preparation of high permeability ceramic ultrafiltration membrane.

In this paper, the ceramic ultrafiltration membranes were prepared by the modified method, and the ZrCl$_4$ were chosen as raw materials, the effects of the different concentration of solution and times of modification on properties of ceramic membrane were investigated.

2. Materials and Methods

2.1. Preparation of ceramic ultrafiltration membrane

The tubular Al$_2$O$_3$ microfiltration membranes were prepared by ourselves (19channel; outer diameter was 30mm and the length was 100mm). Its porosity is 40.8%, and the mean pore-size was 124nm.
Preparation of modified membranes by nano-ZrO₂ as follows:

ZrCl₄ (chemical pure) and absolute alcohol (chemical pure) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. ZrCl₄ was dissolved into alcohol, and then mixed directly at room temperature. The concentration of solution was 2g/L, 4g/L, 6g/L, 8g/L and 10g/L. The prepared solution was used to modification the Al₂O₃ microfiltration membranes. The Al₂O₃ membranes were firstly dried at 110°C for 12h in oven, and then were saturated with the prepared ZrCl₄ alcohol solution for 24h at room temperature. After washed by absolute alcohol for three times, the wet Al₂O₃ membranes were dried at 60°C for 4h again. Then the Al₂O₃ membranes were placed above the boiling water and bathed by hot water stream for 6h. The membranes were calcined at 600°C for 2h with the sintering rate of 1°C/min.

2.2. Characterization of the membranes

The surface and cross-sectional morphologies of the membranes were analyzed using scanning electron microscopy (FE-SEM, JSM-6700F, JEOL, and Japan);

Pore size distributions (PSD) of the membranes were obtained by pore size distribution analyzer (PSDA-20, GaoQ Functional Materials Co., Ltd. Nanjing, China);

The water flux of the membrane was tested in a cross-flow filtration apparatus. The apparatus was capable of operating at a variety of temperatures and pressures.

The particles coated by nano ZrO₂ were observed using a Transmission Electronic Microscope (TEM, JEOL-2010, and Japan).

3. Results and Discussion

3.1. Effect of the concentration of modified solution on the pore size distribution and water flux of ceramic membrane

![Figure 1](image_url)

**Figure 1.** Pore size distribution of ceramic membrane with different concentration of modified solution.

Figure 1 shows the pore size distribution of the porous ceramic membrane with different concentration of modified solution by nano-ZrO₂. As it can be seen, the average pore-size of ceramic membrane decreases with the increasing of concentration of modified solution. It is verified that modified by nano-ZrO₂ coating contribute to decrease the average pore-size of the ceramic membrane. It can be explained that the nano-ZrO₂ deposited on the surface and interior of porous support after the solution reacted, and a certain thickness of membrane layer leads to the pore-size decreased [8]. In addition, the nano-ZrO₂ was scattered throughout the porous alumina support and the surface of membrane was more uniformly.
Figure 2. Water Flux of ceramic membrane with different concentration of modified solution.

Figure 2 shows the water permeating flux of ceramic membrane with different concentration of modified solution by nano-ZrO$_2$. As it can be seen, the water flux of ceramic membrane has been improved. And the water flux continues increase as well as the concentration of nano-ZrO$_2$ modification solution improved. This can be explained that the coating membrane is formed and reduce the tortuosity of the membrane surface [9], which weaken flow disturbance and water flow resistance, then increases the water flux. In addition, the increase of solution concentration within a certain range is more effective on reducing the tortuosity, making the membrane surface smoother.

3.2. Effect of the times of modifications on the pore size distribution and water flux of ceramic membrane

Figure 3. Pore size distribution of ceramic membrane with different times of modification by nano-ZrO$_2$ (10g/L).

The pore size distribution of the ceramic membrane depends on the thinckness of membrane layer and the particles sizes of raw materials. For given porous ceramic membrane, the average pore-size will be larger if coating membrane is uneven. Figure 3 shows the pore size distribution of ceramic membrane with different coating times of modification by nano-ZrO$_2$. It can be seen that the pore-size deceases firstly then increases. Which is decided by the thickness of coating membrane, as the times
of modified increases to thrice, the thickness of membrane increased and the smaller pore-size was blocked or disappeared. Therefore, the pore-size of ceramic membrane increased.

![Figure 4. Water Flux of ceramic membrane with different times of modified.](image)

Figure 4 shows the Water flux of ceramic membrane with different times of modification by nano-ZrO$_2$. As it can be seen, the water flux of ceramic membrane that modified by nano-ZrO$_2$ has been improved. However, the water flux decreases rapidly if it continues to increase the times of modification. It can be explained that the transformation was happened after in-situ hydrolysis and calcination of the coating membrane formed by adsorption of ZrCl$_4$. Coating membrane reduced the flow resistance and resulted in higher water flux. When the modified was twice, the coating membrane formed was more uniform and had more significant effects on improve water flux. However, the original coating membrane was damaged if it continues to modification. In addition, the mean pore-size of the modified membranes decreased, and it leads to the fluxes poorer than unmodified.

3.3. Effect of the modifications on microstructure of ceramic membrane

![Figure 5. TEM image of the surface of alumina particles with ZrCl$_4$ solution modified.](image)

Figure 5 shows the TEM of alumina surface with 10g/L ZrCl$_4$ solution modified and the times of modified are twice, as it can be seen that the surface of alumina particles formed a layer of nano-ZrO$_2$
after modifying with the ZrCl₄ solution. It’s verified that the discussed with Figure 2 and the layer of nano-ZrO₂ can reduces the pore-size of ceramic membrane.

Figure 6. SEM image of ceramic membrane with unmodified (A) and modified (B).

Figure 6 shows the SEM image of ceramic membrane with unmodified and modified, and the modified with 10g/L ZrCl₄ solution and the times are twice. It can be seen from the figure 6, the surface of the unmodified ceramic membrane is rougher than that after modification, and a thin layer of ZrO₂ exists on the surface of the modified ceramic membrane. It is verified that the discussed with Figure 6. The thin layer of ZrO₂ can reduces the pore-size of ceramic membrane, the surface of ceramic membrane become smoother and the permeability can be improved.

4. Conclusions
Ceramic ultrafiltration membrane was prepared by membrane modification method. The concentration and the times of modified solution have greatly effects on the properties of the ceramic membrane. With increasing the concentration of modified solution, the pore-size of ceramic membrane decreased; With increasing the times of modification, the pore-size decrese first and then increase. The ceramic ultrafiltration membrane have been obtained after sintering at 600°C for 2h with the concentration of the modified solution is 10g/L and the times of modification are twice.

Acknowledgements
The authors gratefully acknowledge the financial support provided by the National Natural Science Foundation of China (No.21761015, 51662020 and 51772136), Jiangxi Provincial Department of Science and Technology (No. 20165BCB19014), Education Department of Jiangxi Province (GJJ170808 and GJJ170778) and Jingdezhen City Bureau of Science and Technology (No. 20161GYZD011-017).

References
[1] X. Da, J. Wen, Y. Lu, An aqueous sol–gel process for the fabrication of high-flux YSZ nanofiltration membranes as applied to the nanofiltration of dye wastewater, Sep. & Purif. Technol. 152(2015)37-45.
[2] Z. Liu, H. Bai, D. D. Sun, A general method for the fabrication of hierarchically-nanostructured membranes with multifunctional environmental applications, Sep. & Purif. Technol. 107(2013)324-330.
[3] H. J. Lee, H. Yamauchi, H. Suda, Influence of adsorption on the gas permeation performances in the mesoporous alumina ceramic membrane, Sep. & Purif. Technol. 49(2006)49-55.
[4] M. Campinas, M. J. Rosa, Evaluation of cyanobacterial cells removal and lysis by ultrafiltration, Sep. & Purif. Technol. 70(2010)345-353.
[5] J. E. Zhou, J. Q. Wu, Y. Q. Wang, Modification of Al2O3 Microfiltration Membrane by Nano-
ZnO Coating, Key. Eng. Mater. 280-283(2007)1045-1048.

[6] Q. B. Chang, Y. Q. Wang, S. Cerneaux, Preparation of microfiltration membrane supports using coarse alumina grains coated by nano TiO$_2$ as raw materials, J. Eur. Ceram. Soc. 34(2014)4355-4361.

[7] X. B. Hu, J. E. Zhou, Y. Q. Wang, Effect of SnO$_2$ Modification on Permeate Flux of Al$_2$O$_3$ Microfiltration Membrane for Treating Fe(OH)$_2$ Suspensions, Adv. Mater. Res. 189-193(2011)489-493.

[8] J. E. Zhou, Q. B. Chang, Y. Q. Wang, Separation of stable oil–water emulsion by the hydrophilic nano-sized ZrO$_2$ modified Al$_2$O$_3$ microfiltration membrane, Sep. & Purif. Technol. 75(2010)243-248.

[9] H. Bissett, J. Zah, H. M. Krieg, Manufacture and optimization of tubular ceramic membrane supports, Powder. Technol. 181(2008)57–66.