Silica ultrafiltration membrane with tunable pore size for macromolecule separation

Fengjing Jiang, Haibin Li, Zhigang Di, Sheng Sui, Qingchun Yu, Junliang Zhang*

Institute of Fuel Cell, Key Laboratory for Power Machinery and Engineering of Ministry of Education, Shanghai Jiao Tong University, Shanghai 200240, China

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ABSTRACT

An innovative and facile approach for preparing mesoporous silica membranes is described. The prepared membranes possess abundant, accessible, wormlike pores across the membrane. Narrow pore-size distribution and tunable pore sizes ranging from 2 to 6 nm have been obtained by using a sol–gel method with phosphoric acid as pore-forming agent. The prepared membranes have a potential application in ultrafiltration.

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1. Introduction

Recently, inorganic membranes have attracted much attention for their superior thermal and chemical stability compared to organic membranes [1–4], and they can be used in a variety of applications such as gas and liquid filtrations, catalysts and sensors [5–9].

Mesoporous inorganic membranes with pore sizes ranging from 2 to 50 nm and narrow pore-size distributions are particularly promising for membrane-based separation processes. State of the art commercial ultrafiltration inorganic membranes, such as porous silicon (Microsieve®, Aquamarijn), anodic aluminum oxide (Anodisc™, Whatman) and Cera Mem® ceramic membranes, are expensive as compared with polymer ultrafiltration membranes, because of their complex, costly preparation processes. On the other hand, most research works have been focused on the preparation of asymmetric multilayer membranes composed of a thin mesoporous or microporous film (or skin layer) on a porous support [2,5,10,11].

The thin skin layer imposes mass or ion transmission resistance, while the support provides the required mechanical strength. The conventional technique for preparing the mesoporous skin layer is the sol–gel process, which is typically carried out through a simple spin-coating or dip-coating step. Different approaches are applied in order to obtain mesoporous membranes with finely controlled pore sizes, narrow pore distributions, and high surface area. To make an ordered or shape controlled pore structure, surfactants or polymers are normally used as pore-forming templates [10–15]. To make a thin film with granular pore-structure, the pore sizes are controlled mainly by changing the sizes of colloidal sol because the void spaces of packed-particle layers form pores for water permeation [16].

It has been reported that when the pore size of the porous support is larger than the colloidal sol size, the sol solution tends to penetrate into the support pores. The most commonly utilized method is to deposit one or more additional intermediate layers [17–19]. The intermediate layers coated on the porous support reduce pore sizes for the further coating of the top layer so as to prevent the infiltration of the top layer material into the pores below it. Recently, Kim et al. made progress in this area by filling the pores of an alumina tube support with water-soluble PVA [3,20]. After the silica film was formed on the modified support surface, the pore-filling PVA could be removed by calcination. Although these methods are interesting and can effectively solve the problem, they increase the complexity of the membrane-forming process. However, when the pore size of the support is similar to (or smaller than) the colloidal size, ultrafiltration membranes can be prepared successfully via sol–gel processing without using intermediate layers.

In this work we demonstrate an innovative and facile approach for preparing continuous mesoporous silica membranes. The prepared membranes possess symmetric structures (without support) and contain abundant accessible pores running through the entire membrane thickness. The pore-size distributions are narrow and the pore size can be precisely adjusted in the range of 2–6 nm. These characteristic features make the membranes particularly suitable for size-exclusive separation of proteins, colloids, and macromolecules.

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* Corresponding author. Tel.: +86 21 34207439; fax: +86 21 34206249.
 E-mail address: junliang.zhang@sjtu.edu.cn (J. Zhang).

2. Experimental

2.1. Preparation

The mesoporous silica membranes were prepared via a sol–gel method. A mixture of tetraethylorthosilicate (TEOS, Sinopharm, Analytical reagent), deionized water, and hydrochloric acid (TEOS: H_2O:HCl) in a molar ratio of $1:4:4 \times 10^{-3}$ was first prepared and stirred for 20 min at room temperature to obtain a homogeneous silica sol solution. The sol solution was cooled in an ice bath and then a certain amount of H_3PO_4 was added slowly into the sol solution under stirring over a period of 2 min. The mixture was then stirred vigorously for another 2 min. The resulting transparent mixture was then transferred into a Teflon vessel and aged at 30 °C for 3 weeks. The obtained gel was then annealed at 120 °C in an oven for 12 h in a humid atmosphere. After the hydrothermal treatment, the gel was immersed in water to wash out the H_3PO_4 contained in the membrane. Finally, the silica membrane was dried in ambient conditions. Mesoporous silica membranes with different pore sizes can be prepared by varying the molar ratio of H_3PO_4:TEOS in the sol mixture.

2.2. Characterization

Photos of the samples were captured in flash mode by using a digital camera (DSC-W50, Sony). SEM images were obtained on a LV UHR FE-SEM (NOVA NanoSEM 230) using a low-vacuum mode. The surfaces of the membranes were observed directly without spraying the samples with a thin layer of gold or platinum nanoparticles.

TEM images were recorded on a JEM-2010HT (JEOL) operated at 200 kV. The membranes were ground into small particles less than 1 μm in size.

Small-angle X-ray diffraction (XRD) patterns were recorded in reflection mode ($\lambda = 0.154250$ nm) on a D8 Advance X-ray diffractometer (Bruker, Germany). Wide-angle XRD was carried on a D/max-2200/PC X-ray diffractometer equipped with Cu Kα radiation (Rigaku, Japan).

N_2 adsorption–desorption isotherms were measured on a Micromeritics ASAP 2010M+C instrument. The samples were degassed at 150 °C under vacuum before measurement.

Solid-state ^{31}P-NMR spectra were measured on a 400 MHz Nuclear Magnetic Resonance Spectrometer (Avance III, Bruker) to determine the residual H_3PO_4 in the membranes. The samples were ground into powders and dried in oven at 200 °C for 24 h to remove the adsorbed water.

For the filtration experiments, the silica membrane was placed on an ultrafiltration apparatus (Stirred cell 8003, Millipore). Filtrations of all the samples were carried out under a transmembrane pressure of 3 bars. Poly(ethylene oxide) (PEO) with molecular weights of 300, 1500, 4000, 6000, and 20,000 g mol^{-1} (Sinopharm, Analytical reagent) was dissolved in deionized water to prepare 1 g L^{-1} PEO aqueous solutions for the filtration test. The rejection rate (R) was calculated by using the equation

$$R = ((C_1 - C_2)/C_1)100\%$$

where C_1 is the PEO concentration of feed solution and C_2 represents the PEO concentration of filtrate.

Water flux (F) was obtained by measuring the volume of the water that permeated through a unit area of membrane per unit time, namely

$$F = V/At$$

where V is the total volume of permeated water, A represents the membrane area, and t is the measuring time. Deionized water was used to measure the pure water flux of the membrane. The silica membrane used for water flux measurement has an average pore size of 3.7 nm and pore volume of 0.5 cm^3 g^{-1} according to the N_2 adsorption–desorption evaluation.

3. Results and discussion

3.1. Preparation of mesoporous silica membranes

The symmetric mesoporous silica membranes were fabricated using a conventional sol–gel method. The silica sol was prepared by acid-catalyzed hydrolysis and condensation of the tetraethylorthosilicate (TEOS). Particularly, we used phosphoric acid (H_3PO_4) as the pore-forming agent by adding a suitable amount of H_3PO_4 to the silica sol. The obtained sol mixtures were then cast onto polytetrafluoroethylene (PTFE) plates. After a moderate gelation process of the cast sol mixture, continuous mesoporous silica membranes with designed pore sizes can be obtained. The procedures for preparing the membranes are described in detail in the experimental section. The pore size of the silica membrane can be precisely adjusted in the range of 2–6 nm by simply changing the amount of added H_3PO_4 (the pore sizes are measured by N_2 adsorption–desorption isotherms). In order to improve the mechanical strength of the membranes, a hydrothermal treatment of the silica gel membranes is necessary, which was carried out at 120 °C in humid atmosphere. Usually, silica membranes should be annealed at 400–600 °C for sufficient condensation of the silanol groups. However, in this work, the silica membranes were heat treated only at 120 °C because cracks happen when the annealing temperature was higher than 150 °C. A noteworthy advantage of the present approach is that the pore-forming agent can be easily washed out by rinsing the silica membranes with water. Solid-state ^{31}P-NMR spectra were measured to determine the residual H_3PO_4 in the membrane. In Fig. 1, the peaks in the spectrum of the sample before wash can be assigned to H_3PO_4 and the products of H_3PO_4 self-condensation. After wash, these peaks disappeared. It can be concluded that H_3PO_4 was completely removed from the membranes after washing procedure.

Fig. 2 shows a photo of the appearance of the obtained mesoporous silica membrane. Large areas of the silica membrane can be fabricated and the prepared silica membrane is crack-free, homogeneous, and transparent. Membranes with various areas and thicknesses can be obtained by changing the vessel size and thickness of the cast sol film, respectively.
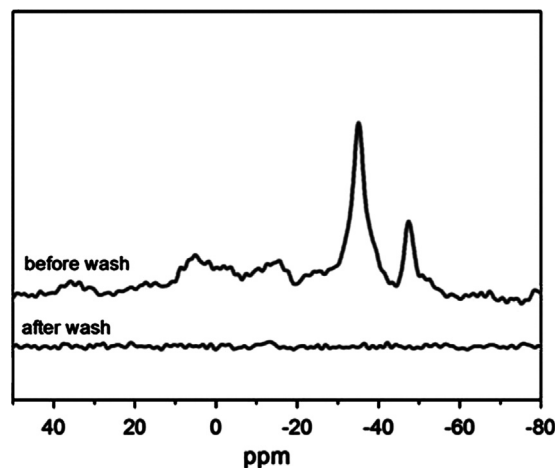

Fig. 1. Solid state ^{31}P-NMR spectra of SiO$_2$ mesoporous membrane before and after removing H_3PO_4.

3.2. Morphology and structure of the mesoporous silica membrane

After removing H_3PO_4, the silica membranes show significant liquid-absorbing capability. Polar liquids (e.g. water, ethanol, methanol, tetrahydrofuran (THF), and ionic liquids) diffuse rapidly in the membrane and penetrate through the membrane. A considerable amount of the liquid can be absorbed by the membrane. This phenomenon implies that the synthesized membranes possess abundant accessible pores across the membrane. Fig. 3 shows scanning electron microscopy (SEM) images of the mesoporous silica membranes. The SEM images were taken using a low vacuum mode, where the surface of the membrane was observed directly, without first spraying a thin layer of gold or platinum nanoparticles onto the sample. In Fig. 3(a, b, and c), nano-sized pores can be observed on the surface of the silica membranes.
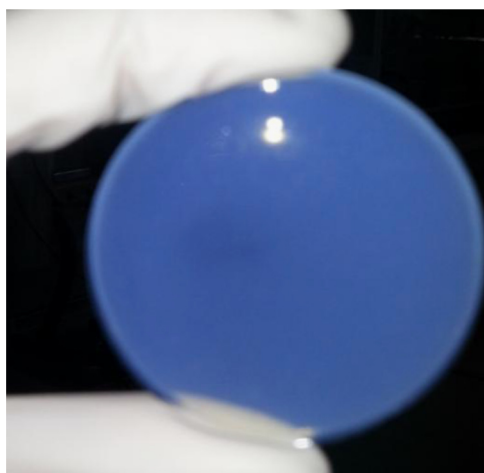

Fig. 2. Digital photo of the silica membrane obtained after gelation.

As the amount of H_3PO_4 in the sol solution increases, the pore size and pore density on the surface increase accordingly. Fig. 3 (d) indicates a pore-rich structure inside the membrane. It should be noticed that the pore sizes determined by the adsorption–desorption measurement are different from that observed with SEM. There are two possible reasons: (a) the pore size by N_2 adsorption–desorption measurement is based on modeling and calculation, and the difference between the model and the real pore geometry may lead to the deviation; and (b) the pores observed by SEM are all near the surface of the membrane. The pores near the surface could be larger than the inner ones due to the solvent evaporation during the gelation process. The pore sizes of the membrane mentioned in this work are all results of N_2 adsorption–desorption measurement and estimated by using the Barrett–Joyner–Halenda (BJH) analysis.

The mesoporous structure of the silica membranes was evaluated by N_2 adsorption–desorption measurement (see Fig. 4). It can be seen from Fig. 4 that the prepared mesoporous silica membranes have narrow pore-size distributions, which is important for filtration membranes.

The pore diameter of the membranes can be tuned by simply adjusting the molar ratio of H_3PO_4:TEOS in the sol mixture. The effects of the H_3PO_4:TEOS molar ratio on average pore size and pore volume of the membranes are demonstrated in Figs. 5 and 6. Both the average pore size and pore volume of the silica membrane increased as the molar ratio of H_3PO_4:TEOS in the sol mixture increased. When increasing the H_3PO_4:TEOS molar ratio from 0.1 to 1, the average pore sizes of the membranes could be precisely controlled in the range of 2.5–4.8 nm and the pore volume increased accordingly from 0.36 to 0.81 $cm^3\,g^{-1}$.

It can be assumed that H_3PO_4 plays the role of a template in the pore-forming process. Hydrogen bonds may be formed between H_3PO_4 molecules and the silanol groups on the surface of the pore wall. H_3PO_4 aggregations along with pore walls could be formed and retained within the membrane during gelation. Thus, pore
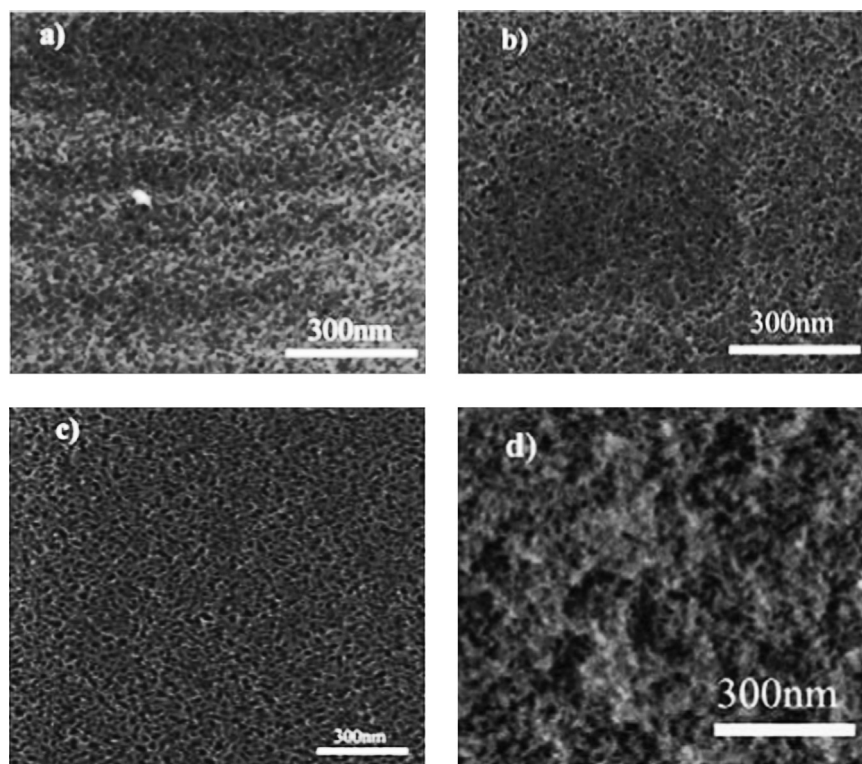

Fig. 3. SEM images of mesoporous silica membranes. (**a**, **b** and **c**) Top view of the mesoporous silica membrane. (**d**) Cross-sectional view of the mesoporous silica membrane. The molar ratios of H_3PO_4:TEOS in the sol mixture are 0.1 (**a,d**), 0.3 (**b**), and 0.5 (**c**).
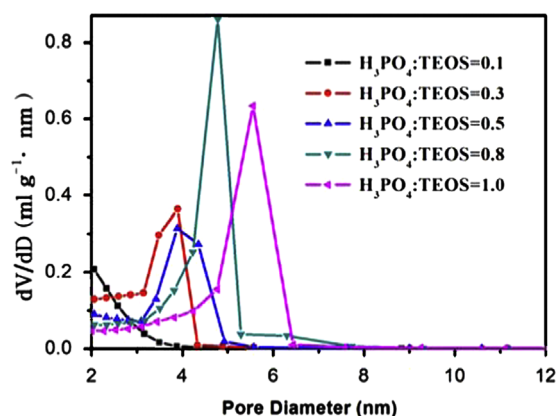
Fig. 4. Pore-size distribution of the silica membranes evaluated by N_2 adsorption–desorption measurement and estimated by using the Barrett–Joyner–Halenda (BJH) analysis.
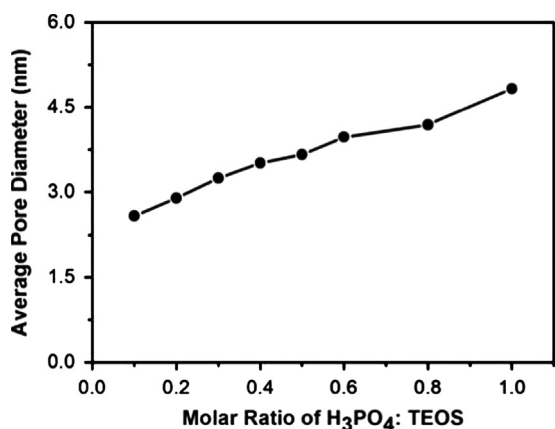

Fig. 5. Average pore diameter of the silica membranes versus the molar ratio of H_3PO_4:TEOS in the sol solution. The average pore size was measured by the N_2 adsorption–desorption method.
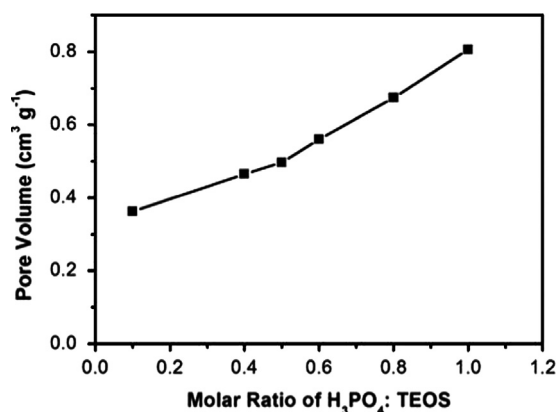

Fig. 6. Pore volume of the silica membrane versus the molar ratio of H_3PO_4:TEOS in the sol solution. The pore volume was measured by the N_2 adsorption–desorption method.

channels with widths of several nanometers are formed in the membranes. The H_3PO_4 aggregations increased with the H_3PO_4 content in the sol mixture. Consequently, both the pore size and pore volume increase. The porous structure of the silica membrane can also be observed with transmission electron microscopy (TEM), as shown in Fig. 7. It can be assumed from Fig. 7 that the silica membrane contains abundant, disordered, and wormlike pore channels, most of which are three-dimensionally interconnected. The white parts in the
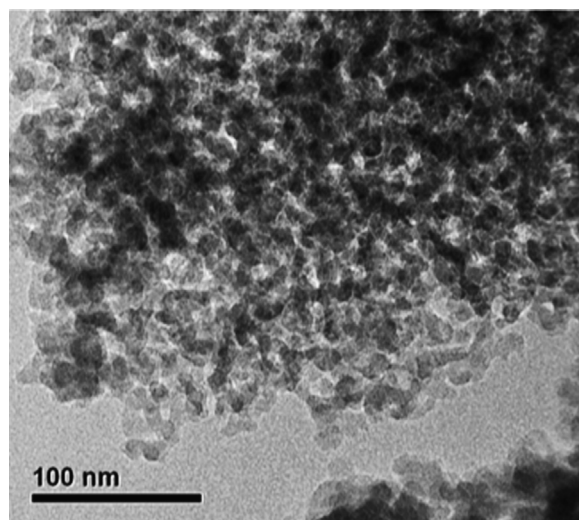

Fig. 7. TEM image of the mesoporous silica membrane with an average pore size of 4.8 nm according to the N_2 adsorption–desorption measurement.

image are pores and channels, while the dark parts are pore walls (SiO_2).

The mesoporous structure of the prepared silica membranes is evidenced by a small-angle XRD peak at 0.7° (Fig. 8a), which is attributed to the partially ordered mesoporous structures of the sample [21,22]. The wide-angle XRD peak corresponds to the amorphous SiO_2 structure (Fig. 8b). The d-spacing calculated from the diffraction peak is 12.6 nm.

3.3. Separation properties of the mesoporous silica membrane

The molecular transport across the membrane was examined using a series of PEO with varying molecular weights. PEO molecules are usually applied to determine the molecular-weight cut-off (MWCO) of the ultrafiltration membranes and to estimate their pore size. In this work, the silica membrane used for ultrafiltration had an average pore size of 3.7 nm and a pore volume of 0.5 $cm^3 g^{-1}$ according to the N_2 adsorption–desorption evaluation. PEO with molecular weights of 300, 1500, 4000, 6000, and 20,000 Da was dissolved in deionized water to prepare 1 g L^{-1} PEO aqueous solutions for filtration. A plot of the rejection rates of the silica membrane versus PEO molecular weight is shown in Fig. 9. The MWCO of the measured membrane was estimated to be 5100 Da.

The pure water flux through the membrane was measured under different transmembrane pressures. It can be calculated from Fig. 10 that the water flux of the membrane was 0.48 L m^{-2} h^{-1} bar^{-1}, which is relatively low, because the silica membrane was rather thick (0.57 mm) as compared with the skin layer in an asymmetric membrane. Considering the fact that the silica membranes are self-supported membranes, a thickness of 0.3–0.5 mm is necessary to provide the required mechanical strength. In addition, due to the moderate thickness of the silica membranes, small defects in the silica membranes are tolerable, while the same defects may cause failure in ultrathin filtration films. In order to improve the flux of the silica membrane, further efforts need to be made to optimize the pore structure of the membrane, or alternatively, to prepare asymmetric membranes with a much thinner mesoporous silica film (< 50 μm) supported on a membrane with larger pore sizes.

Since SiO_2 membranes are not very stable in aqueous solutions, applications of the silica membranes for aqueous systems might be limited. For use in non-polar solvents, surface modification of the
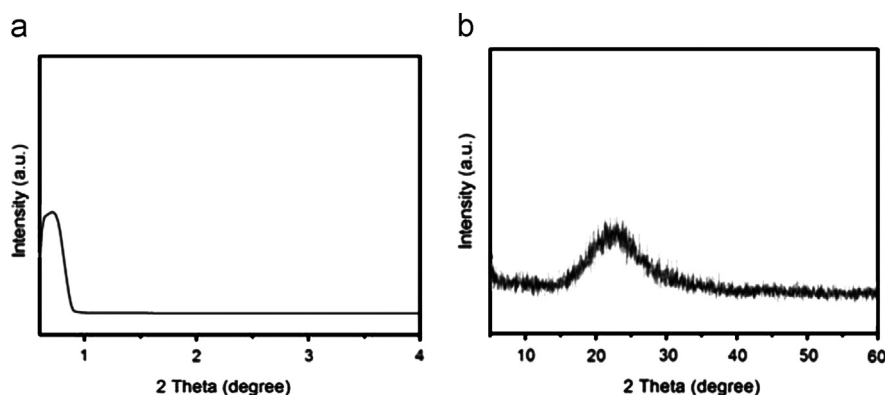
Fig. 8. Small-angle (a) and wide-angle (b) patterns of the mesoporous silica membrane with an average pore size of 3.7 nm and pore volume of 0.5 cm^3 g^{-1} according to the N$_2$ adsorption–desorption evaluation.
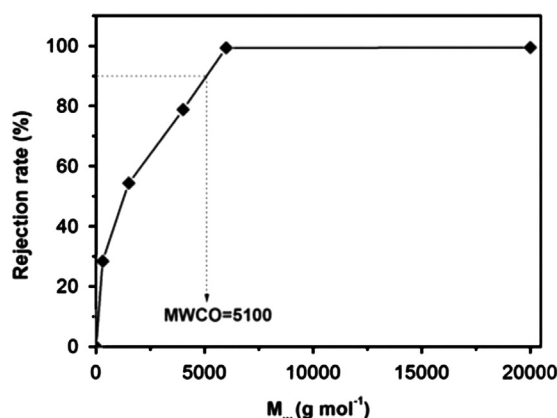

Fig. 9. Rejection rates of the silica membrane evaluated using a series of poly (ethylene oxide) molecules with varying molecular weights.
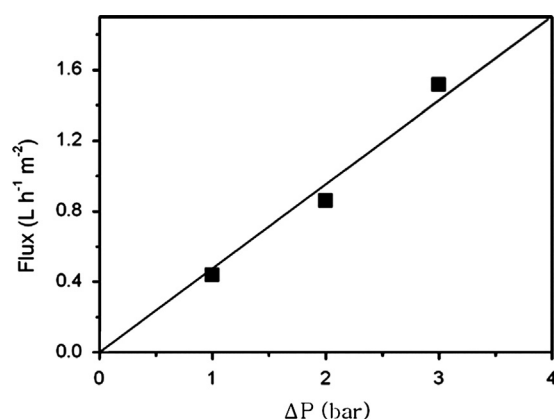

Fig. 10. Water flux versus transmembrane pressure. The silica membrane used for measurements has an average pore size of 3.7 nm and pore volume of 0.5 cm^3 g^{-1} according to the N$_2$ adsorption–desorption evaluation.

hydrophilic silica membranes may be necessary to improve the permeate flux [23].

4. Conclusions

The method of fabricating mesoporous silica membranes described in this work is innovative and a simple process as compared with the conventional approaches. Mesoporous silica membranes have been prepared successfully by using H$_3$PO$_4$ as the pore-forming agent, which is cheap and easily removed. The pore size of the silica membranes can be continuously adjusted by simply changing the H$_3$PO$_4$ content in the sol solution. The prepared SiO$_2$ mesoporous membranes may have a potential application as inorganic ultrafiltration membranes. Further efforts need to be made to improve the permeate flux of the mesoporous silica membrane.

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