Optimizing polyamide thin film composite membrane covalently bonded with modified mesoporous silica nanoparticles

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A R T I C L E   I N F O

Article history:
Received 23 August 2012
Received in revised form 19 October 2012
Accepted 27 October 2012
Available online 5 November 2012

Keywords:
Mesoporous silica
Particle structure
Interfacial polymerization
Compatibility

A B S T R A C T

Novel modified mesoporous silica nanoparticles (mMSN)/polyamide (PA) thin film nanocomposite (TFN) membranes were prepared via interfacial polymerization of trimesoyl chloride (TMC) and piperazine (PIP). Mesoporous silica nanoparticles were functionalized with amino groups and introduced into PIP aqueous phase. Therefore, reaction between mMSN and TMC would occur during interfacial polymerization, giving rise to a covalent bonding between silica nanoparticles and active layer of TFN membrane. By adding an appropriate concentration of mMSN into aqueous phase (0.03 wt%), the pure water flux of the mMSN/PA TFN membrane reaches to a maximum of 32.4 L/m² h which is almost 1.5 times as high as that of TFC membrane, while the rejection to Na₂SO₄ of TFN membrane keeps at a relative high level (> 80%). Two unique properties of mMSN were favorable for the membrane performance: mesoporous structure for water transport and functional groups for better interaction with polymer matrix. The obtained membrane exhibited a promoted anti-fouling ability as well as a good long-term stability. The effect of the mesopore structures of silica nanoparticles on the membrane performance was also investigated. Modified mesoporous silica nanoparticles with proper pore size was more suitable for the optimization of PA TFN membrane.

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1. Introduction

Membrane technology is considered as an attractive separation approach due to its efficiency and energy-saving process and has been applied in water purification and softening, wastewater reclamation, and food processing, etc. [1–3]. The main effort in optimal design of membrane separation process is to achieve a maximum permeate flow, solute rejection, and operation lifetime. Considerable attempts have been made to improve comprehensive performance of polymeric membrane [4–6]. Nanocomposite membrane, where polymer serve as a host for inorganic nanoparticles, holds a bright promise to improve their synergistic effect on transport properties, selectivity or other properties including hydrophilicity, thermal stability, and mechanical strength [7,8]. Many kinds of inorganic materials such as zeolite, carbon nanotubes, titanium dioxide, and silica, have been applied in nanocomposite membrane [9–18]. Recently, mesoporous silica materials have attracted intensive attention due to their unique properties including uniform pore diameter, good structural flexibility, excellent abrasive, and thermal properties. The pore channels with a diameter range of 2–50 nm can be modified in various ways owing to the reactive silanol groups and high specific surface areas of silica particles. Those mesopores are favorable for rapid diffusion of molecules, resulting in the specific separation applications over a range of molecular sizes. Up to now, great effects have been devoted to the mesoporous silica/polymer membranes for gas separation by many researchers [19–23]. For example, Jang et al. prepared a defect-free mesoporous silica/polymer membrane with high gas flux on a technologically scalable hollow fiber platform [24]. Zornoza et al. prepared mesoporous silica spheres/polyimide Matrimid® mixed matrix membranes and found permeability of the selective gas increased with the filler, and the selectivity reached a maximum at 8 wt% filler loading [25]. There are also some meaningful works about mesoporous silica/polymer ultrafiltration membrane [26–28]. However, to the best of our knowledge, the application of mesoporous silica in the thin film composite membrane has rarely been reported.

Although mesoporous silica spheres have excellent properties and unique structure, one of the greatest challenges during the formation of nanocomposite membrane is the compatibility between inorganic particles and polymer matrix. The non-uniform dispersion of particles and non-selective voids between two phases may seriously decline the membrane performance. So modification of inorganic particles is usually adopted to obtain covalent bonding or better interface compatibility with polymer.
In this paper, mesoporous silica nanoparticles were prepared and functionalized with amino groups. A series of modified mesoporous silica nanoparticles (mMSN)/polyamide (PA) thin film nanocomposite (TFN) membranes were developed via interfacial polymerization of trimesoyl chloride (TMC) and piperazine (PIP) in the presence of mMSN. Herein, mMSN were dispersed in PIP aqueous phase. The amino groups on the mMSN can react with the acid chloride group of TMC during interfacial polymerization. Therefore, silica nanoparticles can be chemically incorporated into the nanocomposite membrane in situ, improving the loading of silica nanoparticles and the compatibility between the silica nanoparticles and the polymer. The influence of the mMSN amount on the membrane performance was investigated. To gain an insight into the effect of the mesopore structures of silica nanoparticles on the membrane performance, various silica nanoparticles including mesoporous silica nanoparticles with different pore sizes and solid silica nanoparticles, were synthesized and incorporated into the PA thin layer. The samples were characterized in terms of pure water flux, rejection, contact angle, FTIR, BET, SEM, TEM, and TGA. Furthermore, the anti-fouling test and running stability of the mMSN/PA thin film composite membrane were also examined.

2. Experimental section

2.1. Materials

The microporous polysulphone support film was supplied by the Development Center of Water Treatment Technology (Hangzhou, China). Piperazine (PIP), N-cetyltrimethylammonium bromide (CTAB), aqueous ammonia (25% w/w) and cyclohexane were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Trimesoyl chloride (TMC) was purchased from Qindao Sanli Chemical Engineering Technology Co., Ltd (China). Tetraethyl orthosilicate (TEOS), mesitylene (TMB) and 3-aminopropyltriethoxysilane (APS) were purchased from Shanghai Chemical Reagent Co., Ltd. NaOH and Na₂SO₄ were analytical grade and used without further purification.

2.2. Synthesis of silica particles

2.2.1. Synthesis of mesoporous silica nanoparticles (MSN)

The MSN were synthesized as follows [29]. An amount of 0.5 g of CTAB was dissolved in a mixture containing 240 mL of deionized water and 1.75 mL of NaOH solution (2 mol/L). 3.0 mL of TEOS was quickly added into the solution. Then, the solution was vigorously stirred at 80 °C for 2 h. The resultant white precipitate was separated by filtration, washing with copious ethanol, and drying overnight in a vacuum at 45 °C. The structure-template CTAB were obtained mesoporous silica nanoparticles was correspondingly named MSN-0. To obtain MSNs with different mesopore sizes, a certain volume of TMB which was used as pore expanding agent was added together with 0.5 g of CTAB in the procedure of preparing MSN. When 1.75 mL and 3 mL of TMB was added respectively, the obtained mesoporous silica nanoparticles was correspondingly named MSN-1 and MSN-2.

2.2.2. Synthesis of solid silica nanoparticles (SiO₂)

To a flask, 50 mL of EtOH, 1 mL of H₂O and 2.7 mL of aqueous ammonia were added. A volume of 1.5 mL of TEOS was rapidly added to the flask and magnetically stirred (200 rpm) for 3 h at 40 °C. Then 1.0 mL of TEOS was dropwise added into the above solution and then kept for 3 h. The SiO₂ was harvested by centrifugation, washing with copious ethanol, and drying in a vacuum at 45 °C for 12 h.

2.2.3. Modification of silica nanoparticles

An amount of 0.1 g of MSN was dispersed in 20 mL of EtOH, and the solution was heated to 80 °C. Then 1 mL of APS was added into the solution to functionalize MSN with amino groups. The reaction mixture was refluxed for 6 h, and followed by centrifugation, washing with ethanol for several times, and drying overnight in a vacuum at 45 °C for 12 h to give modified mesoporous silica nanoparticles (mMSN). mSiO₂ was obtained using the same technique. It should be noted that m-particles is meant to represent the particles which are modified with amino groups.

2.3. Membrane preparation

The mMSN/PA thin film nanocomposite membrane was prepared by interfacial polymerization of PIP and TMC on PSf support membrane in the presence of mMSN. First, the microporous PSf support membrane was immersed into the aqeous phase of PIP (10 mg/mL), NaOH (2 mg/mL) and a certain amount of mMSN for 5 min. The membrane surface was rolled with a soft rubber roller to remove excess solution. Then, the PIP-saturated support membrane was immersed into the organic phase which was composed of TMC (1.5 mg/mL) in cyclohexane for 1 min. Afterwards, the membrane was post-treated at 70 °C for 30 min for further polymerization, leading to the formation of skin layer. The final membrane was washed with deionized water repeatedly and stored in deionized water. The above-mentioned operation of the skin layer formation proceeded in a 35 °C water bath.

2.4. Characterization

The cross-section of membrane was observed using a scanning electron microscope (FE-SEM S-4800, Hitachi). Air-dried membrane sample was prepared for SEM measurement by first cryogenically fracturing in liquid nitrogen and then coating with a conductive layer of sputtered gold. Membrane sample was prepared for TEM imaging by peeling away the polyester backing fabric, gently to ensure polysulfone and polyamide layers remained together. Small pieces of the fabric free membrane sample were embedded in Epon resin, and then were cut on an LKB ultramicrotome and placed on Formvar-coated copper grids. Then, the membrane sample was studied with field emission electron microscope TEM (JEM-2100). The samples of silica particles for TEM imaging were prepared by dropping the as-prepared dispersion of the silica particles at the center of copper grids followed by evaporation of the disperse medium at room temperature. The morphologies of particles were observed using transmission electron microscopes JEM-2100 at an acceleration voltage of 200 kV and Hitachi H-600 at an acceleration voltage of 80 kV.

The surface area of particles was calculated by the Brunauer–Emmett–Teller (BET) method, and the pore size distribution was calculated by the Barrett–Joyner–Halenda (BJH) method. The size distribution of the particles was measured by dynamic light scattering (DLS) using a Zetasizer Nano measurement. The disperse medium of the sample was ethanol. Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer Pyris 1 TGA instrument at a rate of 20 °C/min under a nitrogen atmosphere from 100 to 800 °C. Fourier transform infrared (FT-IR) spectra were recorded on Nicolet Nexus 470. The static contact angles of water on the surfaces of membranes were measured by using...
OCA15 (Dataphysics Co., Germany) and following the sessile drop method at 25 °C and a relative humidity of 65%. The volume of each drop was 2.00 µL. The average value of the contact angle on each polymer membrane was calculated using at least five different locations on each membrane.

The measurements of pure water flux and salt rejection of membrane were performed using a cross-flow membrane module, which can offer a membrane area of 27 cm². Before the measurement, all the membranes were pretreated at 0.8 MPa operation pressure for about 20 min and then the pure water flux and salt rejection were measured at an operation pressure of 0.6 MPa at room temperature. The water flux was calculated in Eq. (1):

\[
F = \frac{V}{At}
\]

where \( V \) is the total volume of permeated pure water, \( A \) is the membrane area, and \( t \) is the operation time.

The rejection was measured with 5 mmol/L Na₂SO₄ solution at an operation pressure of 0.6 MPa. The concentrations of the permeation and feed solutions were determined by electrical conductivity HANA-EC215 (Italy). The rejection was calculated in Eq. (2):

\[
R = 1 - \frac{C_p}{C_f}
\]

where \( C_p \) and \( C_f \) are the concentrations of the permeation and feed solutions, respectively.

3. Results and discussion

3.1. Characterization of mMSN and mMSN/PA nanocomposite membrane

The schematic formation of mMSN is illustrated in Fig. 1. CTAB is used as template during the preparation of MSN. After removing CTAB, MSN is functionalized with amino groups on the both external and internal surfaces by reaction with APS, giving rise to mMSN.

The FT-IR spectra of MSN without removing CTAB (MSN-CTAB), MSN, and mMSN are present in Fig. 1b. Characteristic C–H stretching vibrations at 2926 and 2852 cm⁻¹ and C–H deformation vibration around 1477 cm⁻¹ appear in the spectrum of MSN-CTAB,

![Fig. 1](image_url). (a) Schematic preparation process of mMSN; (b) the FT-IR spectra; (c) TGA curves of MSN-CTAB, MSN, and mMSN; (d) TEM images of mMSN; (e) nitrogen adsorption–desorption isotherms and pore size distribution of mMSN.
owing to the large amount of CTAB present in the channels. These C–H peaks disappear after removal of CTAB in the spectrum of MSN. The broad band located around 3420 cm\(^{-1}\) is assigned to the vibration of the silanol group. This broad band is obviously reduced after reacting with APS and forming a Si–O–Si bond in the spectrum of mMSN. In addition, a new peak at 1551 cm\(^{-1}\) and several peaks in the range of 3000–2800 cm\(^{-1}\) which are assigned to N–H asymmetric bending vibration and C–H stretching vibrations, respectively, appear in the mMSN spectrum. The result of IR confirms the successful functionalization of MSN with amino groups. From the TGA results shown in Fig. 1c, MSN and mMSN, respectively, exhibit a weight loss of 6.5 wt% and 13.5 wt% after heating to 800 ℃. So the amount of amino groups on mMSN can be calculated to be about 7.0 wt%.

As shown in the TEM images (Fig. 1d), the prepared mMSN are uniform spherical nanoparticles with a mean diameter of approximately 100 nm. A highly ordered mesoporous network with a hexagonal array can be clearly observed at high magnification from TEM image (Fig. 1d, inset). The result of DLS measurement suggests mMSN has a mean diameter of 194 nm (PDI = 0.131), which is larger than that observed from TEM due to the hydrate layer in aqueous environment. 

Fig. 1e displays the nitrogen adsorption–desorption isotherms and pore size distribution of mMSN. The isotherms of MSN indicate a typical mesoporous material with uniform mesoporous channels and a relatively narrow pore-size distribution. It can be calculated that mMSN has a BET surface area of 837 m\(^2\)/g, cumulative pore volume of 0.946 m\(^3\)/g and average pore size of 2.2 nm.

When mMSN was introduced into PIP aqueous phase, besides the reaction between PIP and TMC, mMSN with amino groups is considered to react with the acid chloride groups of TMC, forming amide bond and being incorporated into the polyamide network structure during interfacial polymerization process. It is difficult to characterize the formation of amide bond between mMSN and TMC due to the severe overlaps of vibration band in IR spectrum of mMSN/PA TFN membrane. To confirm the chemical reaction between mMSN and TMC, mMSN–TMC compound was obtained by directly adding mMSN into TMC/cyclohexane solution and then washing and drying. The FT-IR results are shown in Fig. 2. Compared with mMSN, mMSN–TMC presents two new peaks located at 1708 cm\(^{-1}\) and 1556 cm\(^{-1}\), respectively. The absorption at 1708 cm\(^{-1}\) is assigned to carboxylic stretching vibration of hydrolyzed TMC. The band at 1556 cm\(^{-1}\) is attributed to the amide II vibration, indicating the formation of amide bond between mMSN and TMC. The band of amide I is overlapped with OH bending vibration in the region around 1634 cm\(^{-1}\).

The performances of TFN membranes incorporated with mMSN and MSN are compared and exhibited in Fig. 3. TFN membrane with MSN possesses higher water flux at the serious expense of rejection. The significant difference in performance between two TFN membranes is mainly attributed to the modification of mesoporous silica nanoparticles, which is closely related to the compatibility between inorganic phase and polymer phase. When MSN is functionalized with amino groups turning to mMSN, the chemical interaction of mMSN with TMC greatly improves the wetting and compatibility of two phases, eliminating most non-selective voids and contributing to a relative high rejection.

Fig. 4 presents the separation properties of mMSN/PA TFN membranes tested with various feed solutions including Na\(_2\)SO\(_4\), MgSO\(_4\), NaCl, and MgCl\(_2\). The salt rejection of the membrane decreases as per the order of Na\(_2\)SO\(_4\), MgSO\(_4\), NaCl, and MgCl\(_2\) for TFN membrane. The result is similar to the sequence of negatively charged membrane reported. As is well known, the rejection to salt for a charged membrane is not only related with the pore size of the membrane, but also largely depends on the electrostatic action between the membrane and the ions in solution. The TFN membrane presents negatively charged membrane character due to the hydrolysis of TMC during the membrane preparation. The negative charge on the membrane surface will attract high-valent cation and repulse high-valent anion, which results in a high rejection to salt with high-valent anion and low rejection to salt with high-valent cation.
The rejections of the mMSN/PA TFN membrane were also examined with different concentrations of Na$_2$SO$_4$ solutions and the results are present in Fig. 5. As the feed concentration increases, the rejection of TFN membrane declines, which is related to concentration polarization.

Fig. 6 demonstrates the morphologies of the cross-sections of mMSN/PA TFN membrane. As is well known, TFN membrane is characterized by a thin selective layer supported on a porous substrate. From the SEM image of cross-section (Fig. 6a), it is easy to distinguish a thin dense polyamide layer from the PSf support membrane with finger-like porous structures. Moreover, it can be observed that mMSN are well dispersed in the membrane without apparent segregation or agglomeration. mMSN are incorporated within the thin layer surrounding by polymer, corroborating the good contact between them. mMSN also appear in the porous substrate because of the absorption when the support membrane is immersed into aqueous phase containing mMSN. Fig. 6b is the TEM image of the cross-section of mMSN/PA TFN membrane. The EDX spectrum in Fig. 6c indicates the Si peak at approximately 1.74 keV, confirming the presence of mMSN in the thin film layer of membrane.

To better investigate the actual loading of mMSN in the TFN membrane, TGA and XPS measurements were performed on mMSN/PA TFN membrane which was prepared with mMSN concentration of 0.03 wt% added into the aqueous phase. From Fig. 7a, the residue at 800°C for TFN membrane is higher than that of TFC membrane, and the decreased weight loss is approximately 0.68% which can be ascribed to the silica loaded in the TFN membrane. Fig. 7b exhibits elemental compositions of TFN membrane by XPS survey scan. The molecular percentage of Si element is 0.32%, so the weight percentage of silica can be calculated to be 0.7%, which is quite close to the results of TGA.

3.2. Effect of mMSN amount on the membrane performance

To gain an insight into the influence of mMSN amount on the membrane performance, mMSN (pore size is about 2.2 nm) with concentration of 0.02 wt%, 0.03 wt%, 0.04 wt%, 0.05 wt%, and 0.07 wt% were, respectively, added into aqueous phase to prepare mMSN/PA TFN membrane. The polyamide thin film composite (TFC) membrane was also prepared for comparison.
reaches to a maximum of 32.4 L/m²h, has a negative effect on the membrane selectivity. In addition, the agglomeration of mMSN at high concentration also contributes to an increase in water permeability. It can be ascribed to the higher hydrophilicity brought by the hydrophilic groups of mMSN. In Fig. 10b, the increased salt rejection may result from the membrane compaction at the operation pressure and the adsorption of BSA on the membrane surface.

3.3. Effect of structures of silica nanoparticles on the membrane performance

Some interesting works concerned with the influence of the structure and morphology of inorganic particles incorporated in the nanocomposite membranes have been reported [31,32]. The mesoporous silica materials take the advantage of well-defined morphology and tunable pore structure, thus various silica nanoparticles including mesoporous silica nanoparticles with different pore sizes and solid silica nanoparticles were synthesized and incorporated into the PA thin layer to investigate the effect of structures of silica nanoparticles on the membrane performance in terms of water flux and salt rejection.

In Section 3.1, modified mesoporous silica nanoparticles with pore size of 2.2 nm (named mMSN-0) were prepared, and herein, two other mesoporous silica nanoparticles were synthesized by using TMB as pore-expanding agent. Modified mesoporous silica nanoparticles with pore sizes of 2.9 nm (named mMSN-1) and 3.4 nm (named mMSN-2) are respectively obtained, which can be confirmed by the results of nitrogen adsorption–desorption measurement in Fig. 11a. To avoid the influence of particle size on the membrane performance, the particle size of mMSN-1 and mMSN immobilization and structure of mMSN/PA TFN membrane. Furthermore, the rejection of the membrane can reach about 90% after a stable running period.

Membrane fouling is usually examined with a mixed solution of salt and organic pollutants [30]. In order to simulate real operating environment, Na₂SO₄/bovine serum albumin (BSA) mixture is used as a feed solution. The membranes are firstly tested with the mixed solution (5 mmol/L Na₂SO₄+50 mg/L BSA), then cleaned with EDTA solution (pH=11), and finally re-tested with the Na₂SO₄/BSA mixture. Fig. 10 illustrates the changes in flux and rejection of TFC and TFN composite membranes within an operation time of 48 h and the recovery performance after cleaning with EDTA solution of 2 h. The flux of TFN membranes declines notably at first and then decreases slightly, reaching a relative stable state, while TFC membrane presents a continuous decrease in flux as shown in Fig. 10a. The result indicates that both normalization flux and rejection of TFN membrane are higher than that of TFC membrane, and after being washed with EDTA solution, the recovery performance of TFN membrane is also better than that of TFC membrane. It suggests the incorporation of mMSN improves the anti-fouling ability of membrane, which may be ascribed to the higher hydrophilicity brought by the hydrophilic groups of mMSN. In Fig. 10b, the increased salt rejection may result from the membrane compaction at the operation pressure and the adsorption of BSA on the membrane surface.

Fig. 8 is a plot of pure water flux and rejection to Na₂SO₄ vs. mMSN concentration in the aqueous phase. The water flux of the membrane significantly increases up to 0.03 wt% of mMSN and then slightly decreases with further increasing of mMSN concentration in the aqueous phase. At the same time, the Na₂SO₄ rejection rate of membranes slightly declines as the amount of mMSN increases. The increase in water flux with increasing mMSN amount could be contributed to the three factors. First, the mesopores of mMSN provide an additional passageway for water molecules passing through. Second, the mobilization of mMSN disrupts polymer chain packing, leading to an increased system free volume. Third, some voids are unavoidably introduced into the thin film layer at the mMSN/polymer interface by the incorporation of mMSN, though the modified mesoporous silica nanoparticles are beneficial to better interaction with polymer matrix. In addition, the incorporation of mMSN can improve the hydrophilicity of the TFN membrane and thus contribute to an increase in water permeability. It can be supported by the results of contact angle measurement. When mMSN with concentration of 0.03 wt% is added, the contact angle of TFN membrane is approximately 47.6°, while that of TFC membrane is about 53.2°, suggesting the enhanced hydrophilicity of TFN membrane. However, water flux slightly decreases when the concentration of mMSN exceeds a threshold value, which may be caused by the agglomeration of mMSN.

The pore size of mMSN is larger than the diameter of water molecule (2.7 Å) and the hydrated sodium and sulfate ion (9–10 Å). Therefore, the presence of mesoporous silica particles provides fast flow paths not only for water molecules but also sodium and sulfate ions, resulting in a loss of salt rejection. In addition, the agglomeration of mMSN at high concentration also has a negative effect on the membrane selectivity.

Seen from Fig. 8, the pure water flux of the TFN membrane reaches to a maximum of 32.4 L/m²h which is almost 1.5 times as high as that of TFC membrane, when mMSN concentration in aqueous phase is 0.03 wt%. And the rejection to Na₂SO₄ of TFN membrane is approximately 47.6%, suggesting the enhanced hydrophilicity of TFN membrane. However, water flux slightly decreases when the concentration of mMSN exceeds a threshold value, which may be caused by the agglomeration of mMSN.

The mechanical property and performance stability are very important for a membrane. Thus, a long-term test was carried out at operating pressure of 0.6 MPa with 5 mmol/L Na₂SO₄ aqueous solution. The fluxes and rejections of the mMSN/PA TFN membrane during 75 h of filtration are shown in Fig. 9. The membrane exhibits a good long-term stability, confirming the stability of the nanocomposite membranes have been reported [31,32]. The mesoporous silica materials take the advantage of well-defined morphology and tunable pore structure, thus various silica nanoparticles including mesoporous silica nanoparticles with different pore sizes and solid silica nanoparticles were synthesized and incorporated into the PA thin layer to investigate the effect of structures of silica nanoparticles on the membrane performance in terms of water flux and salt rejection.

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mMSN-2 is almost the same with that of mMSN-0, which is approximately 100 nm as shown in Fig. 11b and c. Furthermore, solid silica nanoparticles modified with amino groups (mSiO$_2$) were also prepared and the TEM image is presented in Fig. 11d. The performance of TFN membranes incorporated with different silica nanoparticles is summarized in Fig. 12. The concentration of all kinds of silica nanoparticles in aqueous phase is 0.03 wt%. All of the TFN membranes have higher water flux than that of bare TFC membrane with different loss of rejections to Na$_2$SO$_4$. Incorporation of mSiO$_2$ into the thin film layer of TFN membrane results in an increased water flux and decreased salt rejection mainly due to the non-selective void formed at the interface of inorganic particles and polymer phase. Compared with mSiO$_2$/PA TFN membrane, TFN membrane with mMSN-0 exhibits a higher water permeability, which can be attributed to the fast water transport of mesopore. But the rejection to Na$_2$SO$_4$ almost keeps the same level as a result of less non-selective voids and better compatibility with polyamide network owing to the large surface.

Fig. 10. Time-dependent normalized flux (a) and normalized rejection (b) of TFC and TFN membranes (feed solution: 5 mmol/L Na$_2$SO$_4$ + 50 mg/L BSA). The anti-fouling performance test includes three steps: Na$_2$SO$_4$/BSA filtration, membrane washing, and Na$_2$SO$_4$/BSA filtration of the cleaned membranes.

Fig. 11. (a) Pore size distribution of mMSN-1 and mMSN-2 by nitrogen adsorption–desorption measurement; and TEM images of (b) mMSN-1; (c) mMSN-2; (d) mSiO$_2$.

Fig. 12. Performance of TFN membranes incorporated with different silica nanoparticles.
area of mesoporous materials. As the mesopore size increases, water permeation rate of membrane increases while the rejection to Na2SO4 sharply deteriorates especially at the largest pore size, resulting from the additional passageway of mesopores.

4. Conclusions

Novel modified mesoporous silica nanoparticles (mMSN)/polyamide (PA) thin film nanocomposite (TFN) membranes were developed via interfacial polymerization of trimesoyl chloride (TMC) and piperazine (PIP), introducing mMSN in the thin film layer. mMSN is obtained by functionalization of mesoporous silica nanoparticles (MSN) with amino groups which can react with TMC, leading to a covalent bonding with polymer matrix. TFN membrane has an improved overall performance by using an appropriate amount of mMSN, which is attributed to the unique properties of mMSN. When the concentration of mMSN is 0.03 wt% in the aqueous phase, the water flux of TFN membrane reaches a maximum, while maintaining the rejection to Na2SO4 at a relative high level. The obtained TFN membrane exhibits an enhanced anti-fouling ability and a good long-term stability. The pore structures and modification of silica nanoparticles have a great impact on the TFN membrane performance. mMSN with proper mesopore size is more suitable for the optimization of thin film composite membrane property due to the unique properties of mMSN and good interaction between mMSN and polymer.

Acknowledgment

Financial support of this research was provided by the National Natural Science Foundation of China (NSFC) (No. 2011071130001), the Natural Science Foundation of Shanghai (No. 12ZR1401900), and the National Basic Research Program of China (2009CB930000).

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