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Preparation of Hydrophilic UHMWPE Hollow Fiber Membranes by Chemically Bounding Silica Nanoparticles

Lian-Lian Fan^a, Jia-You Quan^a, Hao Zhang^b, Jun-Rong Yu^{a*}, Zu-Ming Hu^a, and Yan Wang^a

^a Shanghai Collaborative Innovation Center for High Performance Fiber Composites, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

^b Sinochem International Corporation, Shanghai 200126, China

Abstract In this work, ultra-high molecular weight polyethylene (UHMWPE) microfiltration hollow fiber membranes prepared via the thermally induced phase separation (TIPS) method were modified by chemically bounding hydrophilic silica (SiO₂) nanoparticles onto the surface to improve anti-fouling performance. A range of testing techniques including attenuated total reflection Fourier transformed infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FE-SEM), water contact angle, mechanical test, filtration and anti-fouling performance were carried out to discuss the influence of different modification conditions on the properties of the membranes. The prepared hollow fiber membranes display the significantly excellent performance when the vinyl trimethoxy silane (VTMS) concentration was 13%, the pH value of the hydrolyzate was 4 and the hydrolysis reaction time was 6 h. In particular, the hydrophilicity of modified membranes was improved effectively, resulting in the enhancement of membrane anti-fouling properties. The results of this work can be consulted for improving the anti-fouling performance of the UHMWPE microfiltration hollow fiber membrane applied in the field of water purification.

Keywords Hollow fiber membrane; Hydrophilic; Anti-fouling; Silica (SiO₂) nanoparticles; Water purification

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INTRODUCTION

Microporous polymeric membranes have been prepared by several methods, including melt stretching, phase transition and phase separation of a variety of polymers.^[1,2] Generally, there are two ways to prepare polymeric membranes by phase separation: nonsolvent induced phase separation (NIPS) and thermally induced phase separation (TIPS).^[2,3] In the NIPS process, phase separation occurs during the exchange of a non-solvent for the solvent from polymer solution, while phase separation is caused by cooling the polymer solution in the TIPS process.^[3,4] UHMWPE microporous membranes are usually prepared by TIPS method, which is perhaps the most versatile and simplest technique for the preparation of microporous membranes.^[5] Generally, TIPS method can provide membranes with high porosity and mechanical strength as the microstructure of the membranes can be easily controlled during TIPS process, which meets the needs of the application in water treatment; accordingly, they have attracted great attention of many scholars and experts in the last decades.^[6]

Membrane material is the core and key for the technology of membrane separation. Compared with traditional commer-

cial polymer materials, UHMWPE exhibits excellent mechanical properties, thermal and physicochemical stability and low cost, which makes it one of the most widely used materials in membrane separation.^[7–9] However, the UHMWPE membrane has limitation in water treatment application, as it is very susceptible to fouling by absorbing organics in the separation process owing to its inherent hydrophobicity and deletion of polar groups on the polymer chain;^[10–12] the fouling issue may decrease the capacity of separation and increase the operation cost. It has been proved that hydrophilic polymer membranes are more normally favored with respect to the prevention of membrane fouling than the hydrophobic ones.^[13–18] Thus, to improve the anti-fouling performance of the UHMWPE membrane, one efficient approach is to modify its hydrophilic property.^[19]

Among the wide variety of approaches, surface modification is one of the most commonly investigated methods for reducing the fouling of the hydrophobic polymer membrane, such as graft polymerization of hydrophilic monomers,^[19] plasma surface treatment,^[20] ozone treatment^[21] and dip-coating.^[22] Since the inorganic nanoparticles possess unique physicochemical properties, incorporating them into polymer matrix of membranes to improve anti-fouling performance has attracted more and more concern in the field of membrane technology in recent years. Nanoparticles widely used in inorganic polymer membranes mainly include ZrO₂,^[23]

* Corresponding author, E-mail: yjr@dhu.edu.cn

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Al₂O₃,^[24] SiO₂,^[25] silver,^[26] zeolite,^[27] ZnO^[28,29] and TiO₂.^[30,31]

In this work, we prepared UHMWPE hollow fiber membrane *via* the TIPS method and improved its hydrophilicity and anti-fouling performance by immobilizing nano-SiO₂ on the membranes surface. The process and mechanism of nano-SiO₂ graft modification were described. In detail, we discussed the effects of different modification conditions on morphology, hydrophilicity, filtration and anti-fouling performance and mechanical property of the modified hollow fiber membranes. The results with higher flux recovery ratio (FRR) values indicated that nano-SiO₂ significantly improved the anti-fouling performance of the membranes.

EXPERIMENTAL

Materials

UHMWPE (weight-average molecular weight=1.6×10⁶) was supplied by Celanese Corporation with white oil used as a diluent (70#, purchased from Sinopec Hangzhou Refinery). Dichloromethane was used as extractant and without further purification (provided by Zhiqin Chemical Technology Co., Ltd.). Hydrophilic nano-SiO₂ (particle size of *ca.* 15 nm) were purchased from Keyan Industrial Co., Ltd. (Shanghai, China).

Preparation of the UHMWPE Hollow Fiber Membranes

Preparation of pristine gel hollow fibers

First, 20% UHMWPE resin powder ($M_n=1.6\times10^6$) and 0.7 wt% antioxidant 1076 (BASF, Shanghai) were dissolved in white oil, followed by stirring manually for several minutes to prepare a homogeneous spinning solution and then filling into twin-screw. The pristine hollow fibers were fabricated by gel-spinning and double ring casing type spinneret was used. The air-gap distance was 1–2 cm and the take-up velocity was 8.6 cm/s. The gel hollow fibers were extruded from the spinneret into coagulation bath (pure water, 20 °C), and solid-liquid phase separation occurred. Subsequently, they were stored at room temperature for more than 48 h.

Stretching of pristine gel hollow fibers

The spun pristine gel hollow fibers were subjected to 3 times cold stretching and then 2 times hot stretching. The process of cold stretching was directly carried out at room temperature using spinning rolls, and the step of hot stretching was as follows: Firstly, prepare samples. The spun pristine gel hollow fibers were cut into a length of about 7.5 cm; Secondly, preheat samples. A sample was placed between the clamps of the universal testing machine and the temperature was set to 100 °C and held for 5 min; Thirdly, hot stretch the samples. The hot stretching temperature was raised to 110 °C. When the set temperature was reached, a hot stretching test was performed at a rate of 20 mm/min; Fourthly, heat set the samples. After stretching, the temperature was further increased to the heat setting temperature (120 °C), and held for 5 min; Finally, remove the samples. After the samples were cooled to room temperature, they can be removed for subsequent testing.

Hydrophilic Modification of UHMWPE Hollow Fiber Membranes with Silica

Grafting of silane coupling agent

The unextracted hollow fiber membranes prepared above were

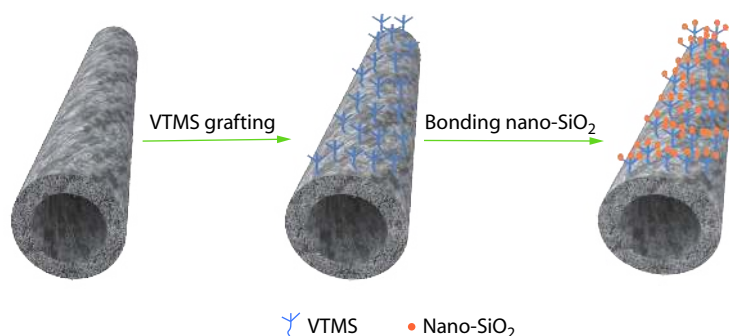
placed in dichloromethane, and ultrasonically extracted twice with an ultrasonic cleaner. The dichloromethane was replaced by each extraction to remove the white oil from the gel hollow fiber membranes. The extraction time was 8 min each time. During the third extraction, the extract was changed to a modified extract of benzoyl peroxide (BPO) and vinyl trimethoxysilane (VTMS) at a mass ratio of 1:10. The water temperature in the ultrasonic cleaner was controlled to be 35 °C, the ultrasonic frequency was 50 Hz, the bath ratio was 10 mL/g, and the extraction time was more than 30 min. The extracted membranes were taken out to dry in air in order to remove dichloromethane, and then placed in an oven at 80 °C for 4 h. Thus, the silane coupling agent grafted UHMWPE hollow fiber membranes were successfully obtained.

Grafting of hydrophilic silica nanoparticles

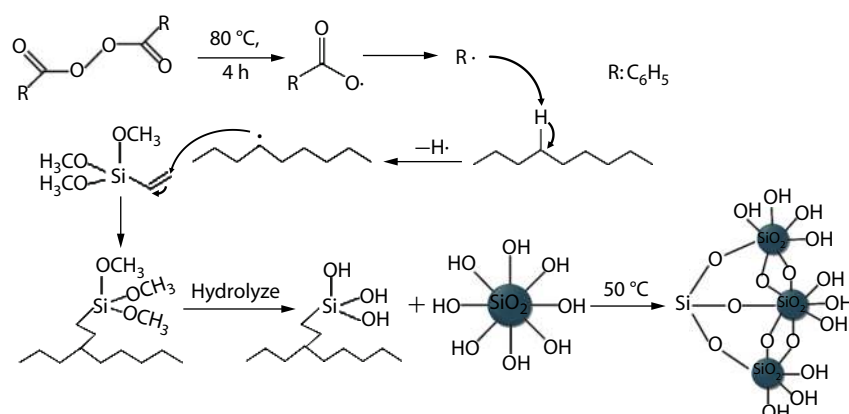
The procedure of grafting hydrophilic nano-SiO₂ was as follows. First, nano-SiO₂ was added into the hydrolysate made of 1:18 deionized water and ethanol to configure a nano-SiO₂ dispersion at the concentration of 3.0 g/L; the pH value was controlled with acetic acid to 3, 4, 5, 6 and 7, respectively. Then, the silica nanoparticles were uniformly dispersed by ultrasonication for 30 min. After that, the hollow fiber membranes grafted with VTMS on the surface were immersed in the nano-SiO₂ hydrolyzate, and shaken in a constant temperature water bath at 50 °C. The —OCH₃ on the membranes surface was hydrolyzed to —OH after certain hours, and bonded with nano-SiO₂ completely. The duration of hydrolysis was controlled to 1.5, 3, 6 and 8 h, respectively. After the graft reaction was completed, the modified membranes were taken out and rinsed repeatedly with deionized water to remove unreacted nano-SiO₂, and then the membranes were warily kept in deionized water for subsequent testing. Scheme 1 shows the preparation process of nano-SiO₂ modified UHMWPE hollow fiber membranes, and the grafting mechanism of nano-SiO₂ is presented in Scheme 2. In the graft process, the initiator BPO was first decomposed under heating conditions to produce free radicals, which captured H atoms on the molecular chain of PE to form free radicals and grafted with silane coupling agent VTMS, and then hydrolyzed to form silanol. Finally, inorganic nano-SiO₂ was bonded to the surface of hollow fiber membranes by reaction with silanol.

Membrane Characterization

The surface morphology and structure of the membranes were characterized through FE-SEM (SU8010, Nitachi, Japan). Before observation, all membrane samples were coated with gold by sputtering to make them conductive. Membrane surface pore size distribution was determined by software Image J using SEM images. ATR-Fourier transform infrared (FTIR) spectra of membrane samples were measured by a Nicolet 6700 spectrometer (USA). In order to analyze the composition of elements in the surface of membrane, X-ray photoelectron spectroscopy (XPS) was performed by an ESCALAB 250Xi X-ray photoelectron spectrometer (USA, Al K α radiation with 1486.6 eV). Water contact angle was tested by automatic video micro contact angle measuring instrument (OCA40Micro) to assess the surface hydrophilicity of the modified UHMWPE hollow fiber membranes. The tensile strength was measured by a universal mechanical testing machine (Model 44, MTS Criterion, USA) at a stretching velocity of 20 mm/min.



Scheme 1 The preparation process of nano-SiO₂ modified UHMWPE hollow fiber membranes.



Scheme 2 Schematic diagram of the preparation of UHMWPE hollow fiber membranes grafted nano-SiO₂.

To quantify the filtration and antifouling performance of the membranes, we conducted the separation experiments with a homemade cross-flow filtration device (Fig. 1). The structure of the membrane module made of 2–3 pieces of hollow fiber of 15–20 cm length is shown in Fig. 1(a). Each end of the module was a piece of nylon tube with an outer diameter of 10 mm, an inner diameter of 8 mm and a length of 5 cm. The potting compound used was epoxy resin. Fig. 1(b) shows the whole test equipment. The sample membranes were first precompactd for 30 min at 0.2 MPa. Then the deionized water flux was recorded every 5 min for 30 min at 0.1 MPa when it was stable, and calculated using the equation as follows:

$$J_{w1} = \frac{V}{S \times \Delta t} \quad (1)$$

where J_{w1} , V , S , and Δt represent deionized water flux, the volume of collected water (L), effective membrane area (m²) and the operation time (h), respectively. Then, the deionized water was replaced with 1 g/L bovine serum albumin (BSA) solution as an important water pollutants. The permeate was collected at 0.1 MPa. The concentration of BSA was measured by UV spectrophotometer (LabTech, UV-9100 D, Beijing). The rejection (R) was calculated as below:

$$R\% = \left(1 - \frac{c_p}{c_f}\right) \times 100\% \quad (2)$$

where c_p and c_f are the BSA concentrations in permeate and feed solution, respectively. In the next step, the membranes contaminated were rinsed repeatedly with deionized water for

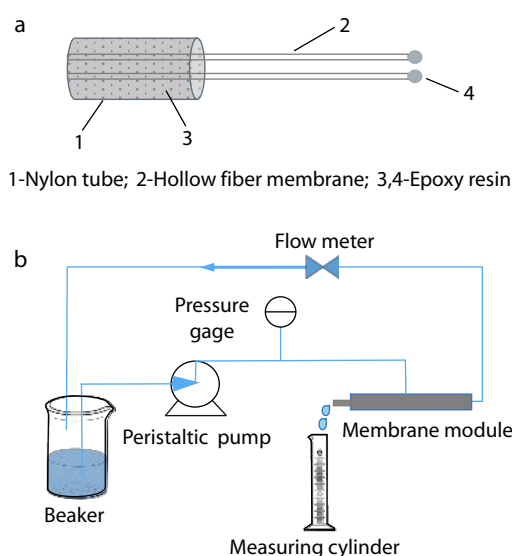


Fig. 1 Experimental setup for measuring filtration and anti-fouling properties for UHMWPE hollow fiber membrane: (a) the structure of membrane module; (b) the whole measuring setup.

20 min. We performed the second deionized water flux test and recorded it as J_{w2} . The flux recovery ratio (FRR) and flux attenuation rate of irreversible pollution (IFRR) used to evaluate the antifouling characteristics quantitatively were calculated by the Eqs. (3) and (4). And it is worth mentioning that the higher FRR value (the lower IFRR value) indicated that the

membranes have the better anti-fouling performance.^[32,33]

$$\text{FRR} = \frac{J_{w2}}{J_{w1}} \times 100\% \quad (3)$$

$$\text{IFRR} = \left(1 - \frac{J_{w2}}{J_{w1}}\right) \times 100\% \quad (4)$$

Furthermore, we also performed the carbon ink rejection performance of the membranes using the homemade device above. The average particle size of the ink particle measured by a laser particle size analyzer (Nano ZS, Malvern Co., Ltd., Britain) was 77.0 nm. Deionized water was replaced with 0.5 mg/L carbon ink solution and the rejection was determined according to Eq. (2). The permeate concentration could be calculated from the turbidity measured by the turbidimeter (HACH, 2100Q, America).

RESULTS AND DISCUSSION

Membrane Characterization

ATR-FTIR spectroscopy

The ATR-FTIR spectra of original and modified UHMWPE hollow fiber membranes at different conditions are shown in Fig. 2. In comparison with original UHMWPE membranes, there appears a very broad band in the range of 3600–3100 cm^{-1} in the spectrum of the modified membranes, which is ascribed to the stretching vibration of $-\text{OH}$ in nano- SiO_2 . Additionally, the absorption bands at 1127 and 769.45 cm^{-1} are assigned to the $\text{Si}-\text{O}-\text{Si}$ anti-symmetric and symmetric stretching vibration, respectively. From Fig. 2(a), we can find that the intensity of characteristic bands with silica is strengthened with the increase of the VTMS concentration. As seen in Fig. 2(c), when the duration of hydrolysis is less than 6 h, the band strength of silicon hydroxyl group and $\text{Si}-\text{O}-\text{Si}$ bond increases gradually with the prolongation of hydrolysis time, which indicates that more silica nanoparticles were grafted onto the UHMWPE hollow fiber membrane surface. However, the intensity of silica characteristic bands becomes weaker with the further extension of reaction time, which may be because that partially incomplete graft or unstable nano- SiO_2 fell off from membrane surface under stress due to the protracted water bath oscillation. As a result, six hours seems to be the reaction time with the maximum graft amount of nano- SiO_2 on the surface of hollow fiber membranes, which has also been corroborated by filtration performance test being talked over in the latter sections.

X-ray photoelectron spectroscopy (XPS)

To further confirm that nano- SiO_2 had been grafted on the membranes surface successfully, the surface elemental composition of the membranes was determined by XPS analyses. The results are reflected in Table 1 and Fig. 3. Table 1 gives the surface element distribution of original and modified UHMWPE hollow fiber membranes. It is obvious that the surface of original membranes contains a large amount of C 1s (97.27%) and only a small amount of O 1s (2.73%). The slight O 1s may be derived from the organic contaminations in the air or external environment. When the nano- SiO_2 was bonded to the surface of hollow fiber membranes, the content of C 1s of the modified membranes reduced to 77.68%, while that of the O 1s and Si 2p rose to 15.69% and 6.63%, respectively. The XPS wide scans in Fig. 3 also illustrate the same situation. It can be seen from

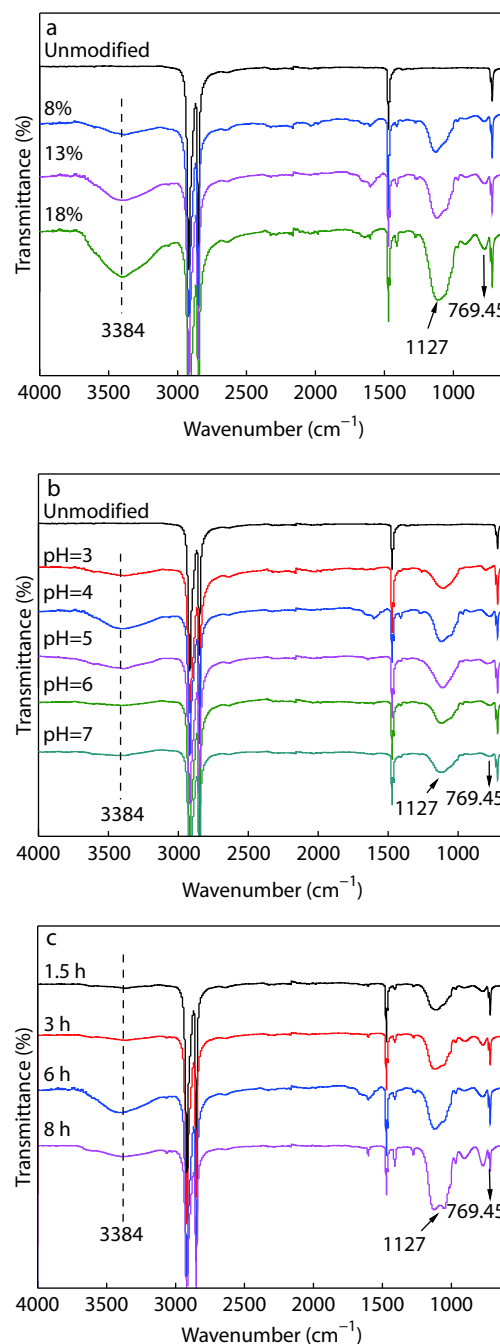


Fig. 2 ATR-FTIR spectra of nano- SiO_2 grafted membranes with different modification conditions: (a) different VTMS concentrations (pH=4, hydrolysis time 6 h); (b) different pH values of silica hydrolysis solution (VTMS concentration 13%, hydrolysis time 6 h); (c) different reaction time (VTMS concentration 13%, pH=4).

Table 1 Surface elemental percentages of the original and modified membranes after immobilizing nano- SiO_2 .

Sample	C 1s (%)	O 1s (%)	Si 2p (%)
Original membrane	97.27	2.73	0
Modified membrane	77.68	15.69	6.63

the spectra that the new O 1s and Si 2p peaks appear on the surface of modified membranes compared with the original

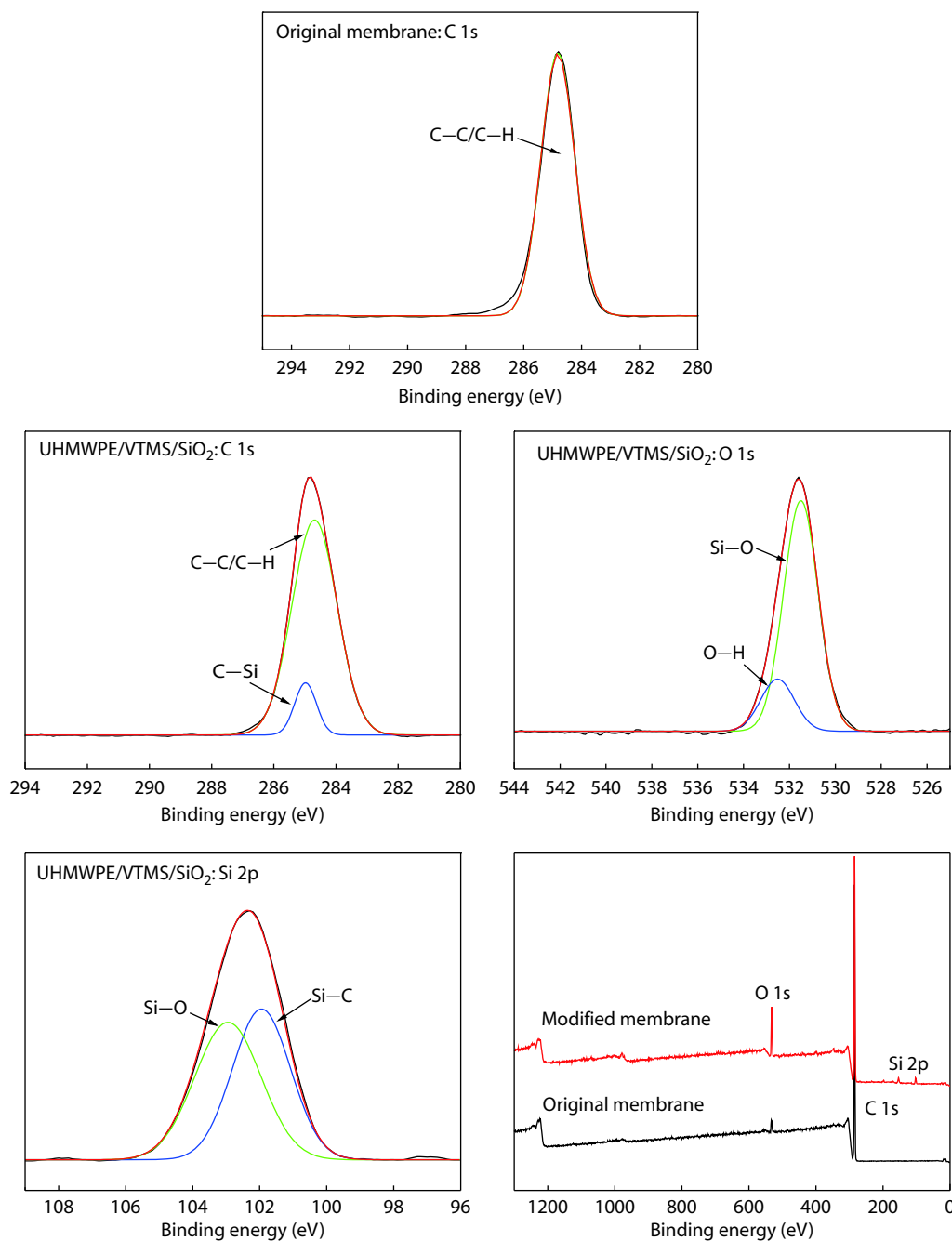


Fig. 3 XPS wide scan and narrow scan spectra of original and modified membranes after immobilizing nano-SiO₂ (C 1s, O 1s and Si 2p).

membranes. The results of XPS and element distribution imply that hydrophilic nano-SiO₂ were successfully grafted onto the surface of UHMWPE hollow fiber membranes.

The C 1s, O 1s and Si 2p curves are fitted respectively and indicated in Fig. 3. The C 1s curve of the original UHMWPE hollow fiber membrane presents the characteristic peak of C—C/C—H groups at the binding energy of about 284.7 eV, which is in accordance with the chemical component of UHMWPE membranes. The C 1s energy spectrum of the modified membrane can be curve-fitted with two peaks at the binding energy of about 285.5 and 284.7 eV, which are

attributed to C—Si and C—C/C—H species separately. Fitting the O 1s core-level spectrum, we can find Si—O peak at 532.5 eV and O—H peak at 533.1 eV. Furthermore, the Si—C and Si—O peaks appear at 102.8 and 103.5 eV in the Si 2p spectra of XPS, respectively. Based on the above results, we can see that the results of XPS and peak-fitting spectra are conforming to those obtained from ATR-FTIR spectra, that is, silane coupling agent (VTMS) was initially grafted onto the membranes surface by initiator, and then nano-SiO₂ was incorporated into the hollow fiber membranes surface by hydrolysis reaction of VTMS.

Morphology

The thickness of UHMWPE membrane significantly affects its filtration performance.^[34] The wall thickness of the hollow fiber could be controlled by the spinning conditions including UHMWPE concentration, fiber's take-up velocity and the stretching condition. In this research, the wall thickness of the resultant UHMWPE hollow fiber was 0.15 mm. As shown in Fig. 4, the hollow fiber membranes have an asymmetric structure. It is easy to find that the cross section near the outer surface gradually becomes denser than that near inner surface. During the spinning process, as the polyethylene melt was extruded from the spinneret and entered the coagulation bath, the outer surface of the nascent hollow fiber was first exposed to a large amount of water, which was rapidly cooled and solidified in a short time, promoting the growth of polymer-rich phase and inhibiting the growth of polymer-lean phase. Consequently, there are fewer pores near the outer surface, while the section near the inner surface is loosely porous. Comparing Figs. 4(b1) and 4(b3), we can find that the average pore size of the fiber membranes increased after stretching.

The surface morphology and pore distribution of original and modified membranes with different duration of hydrolysis are exhibited in Fig. 5. Compared with original membranes, the surface of modified membranes becomes rough. Along with the prolongation of hydrolysis time, the surface roughness increases and the number of micropores somewhat decreases, which is caused by the coverage of grafted nano-SiO₂ on the surface. According to the graft reaction mechanism that VTMS was grafted on the surface by conducting hydrolysis reaction to convert the silane to silanol and then inorganic nano-SiO₂ particles were bonded to the surface of the membranes, we can know hydrolysis reaction takes a certain amount of time. Only sporadic nanoparticles are dispersed on the surface of membranes when the reaction time is 1.5–3 h (Fig. 5b). After 6 h (Figs. 5c and 5d), the membrane surface has

been already covered with more nanoparticles, which distribute uniformly and orderly without large-scale agglomeration. However, the number of inorganic nanoparticles on the surface of the membrane is reduced and agglomeration occurs when the reaction time is further prolonged to 8 h. This phenomenon can be attributed to the fact that partial nano-SiO₂ particles are not grafted completely or stable enough to fall off from the membrane surface under stress due to the protracted water bath oscillation, which is consistent with the results of ATR-FTIR spectroscopy. The pore size of the original membranes is about 0.36 μm , and the pore size of the modified membranes decreases first and then increases with the increase of the hydrolysis time.

Surface hydrophilicity

As the UHMWPE surface skin layer is the major area to separate and filter and lead to membrane fouling, surface hydrophilic modification is a widely used and effective way to render the membranes favorable anti-fouling property. In our work, the hydrophilicity of the modified membranes was investigated by the measurement of the surface water contact angle. Fig. 6 demonstrates the water contact angles of the modified membranes surface at various modification conditions. It is easy to see that the contact angle of original membrane (0% VTMS) is relatively high (121.8°), showing the characteristics of conventional hydrophobic membrane materials. However, the water contact angles of the modified membrane surfaces decrease significantly owing to the —OH groups introduced by hydrophilic nano-SiO₂. Along with the increasing concentration of VTMS, the surface contact angle decreases. When the concentration reaches 18%, the modified membranes own the smallest contact angle (74.6°). When the pH value is 4 and the hydrolysis time is 6 h, the water contact angle is 75.5°, showing fairly good hydrophilicity. The results show that the construction of hydrophilic layer of inorganic particles plays a positive role in improving the wettability of the membranes surface, which lays

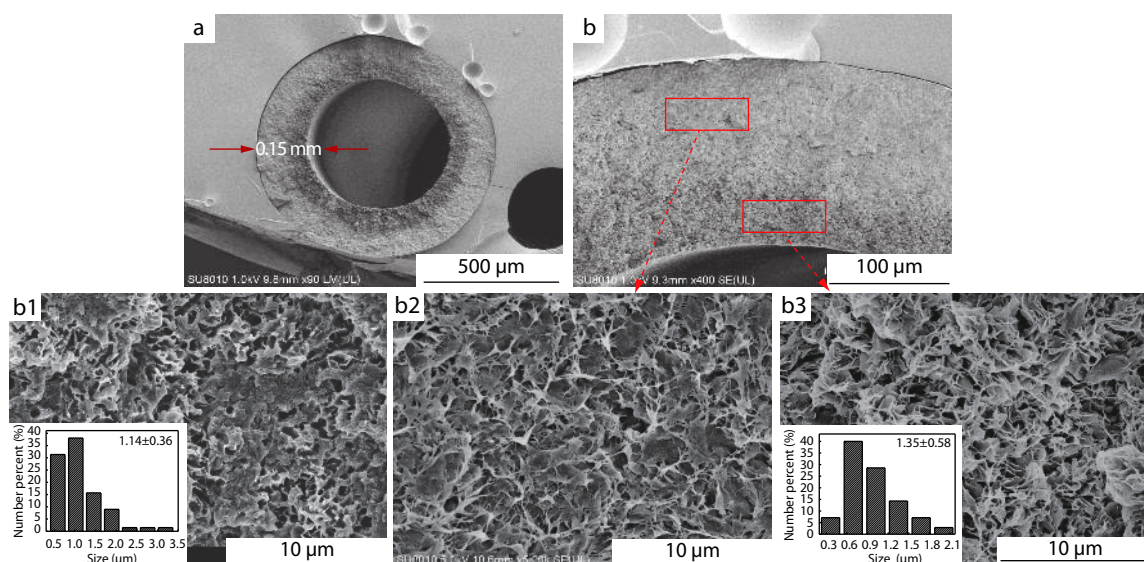


Fig. 4 Cross section morphology of UHMWPE hollow fiber membranes: (a) overall cross section; (b) partial cross section, (b1) local enlargement of near inner surface before stretching, (b2) local enlargement near outer surface after stretching, (b3) local enlargement near inner surface after stretching.

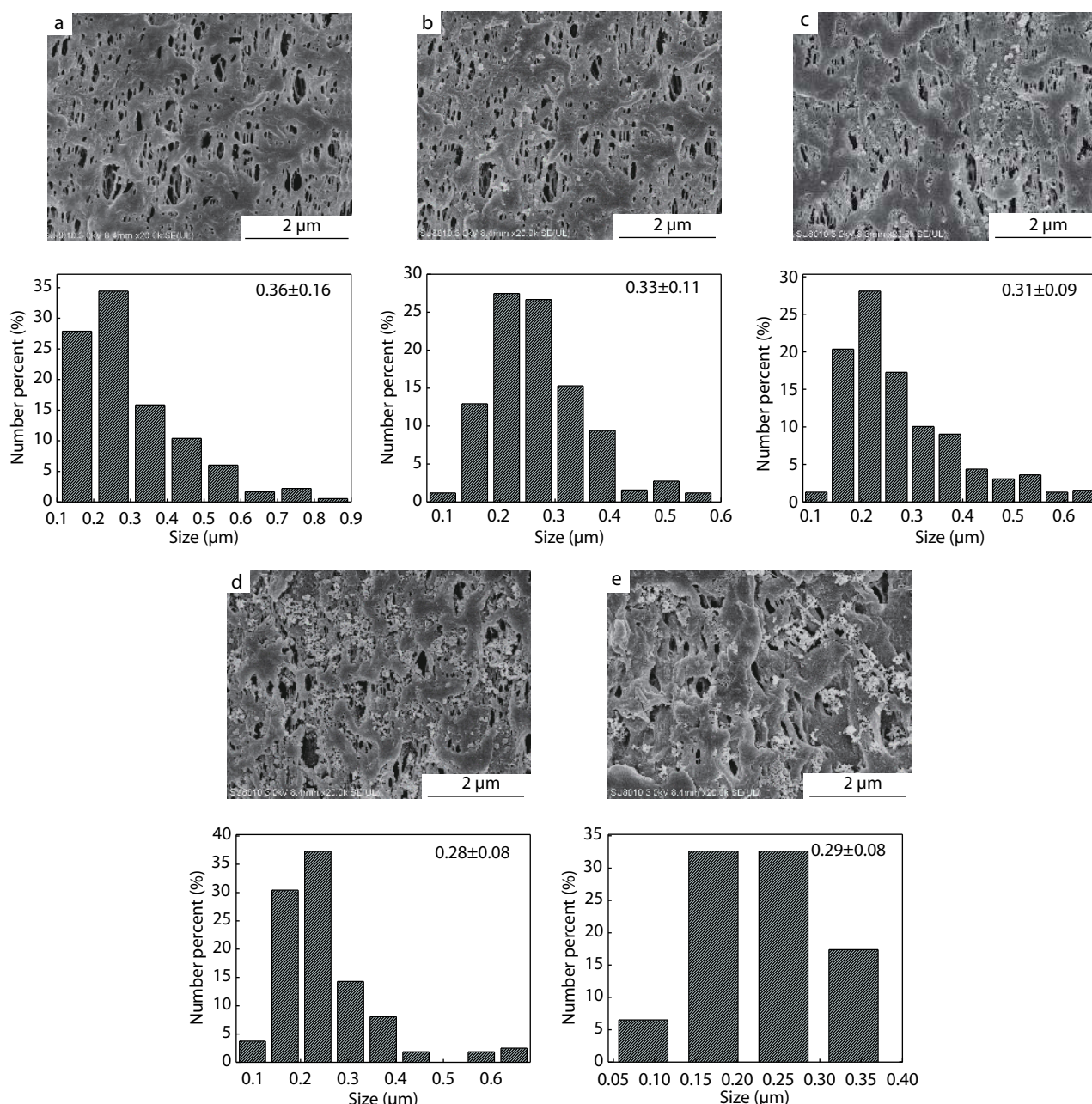


Fig. 5 FE-SEM images of UHMWPE hollow fiber membranes surface (upper) and pore size distribution (lower) of (a) original membranes, (b–e) nano-SiO₂ grafted membranes with different duration of hydrolysis: (b) 1.5 h; (c) 3 h; (d) 6 h; (e) 8 h (VTMS concentration 13%, pH=4).

the foundation for improving the anti-fouling performance of UHMWPE hollow fiber membranes.

Membrane Performance

Effect of VTMS concentration

The graft of silane coupling agent VTMS on the membranes surface is essential for the construction of hydrophilic layer of inorganic particles. Therefore, we explored an optimal concentration of VTMS by studying the effect of different VTMS concentrations on filtration performance, anti-fouling performance and mechanical properties of modified hollow fiber membranes.

The effect of VTMS concentrations on filtration performance of modified hollow fiber membranes is depicted in

Fig. 7(a). The pure water flux and BSA rejection rate of the original UHMWPE hollow fiber membranes are 172.89 L/(m²·h) and 45.04%, respectively. With the increase of VTMS concentration, the pure water flux successively increases to 242.28, 310.90 and 313.23 L/(m²·h) after the incorporation of nano-SiO₂, which is consistent with the trend of surface hydrophilicity. At the same time, the BSA rejection rate of corresponding samples increases to 48.32%, 81.47% and 83.03%, respectively, indicating that the filtration performance of the modified hollow fiber membranes has been significantly improved. This is mainly because the content of silanol groups increases with the growing number of VTMS molecule, resulting in an

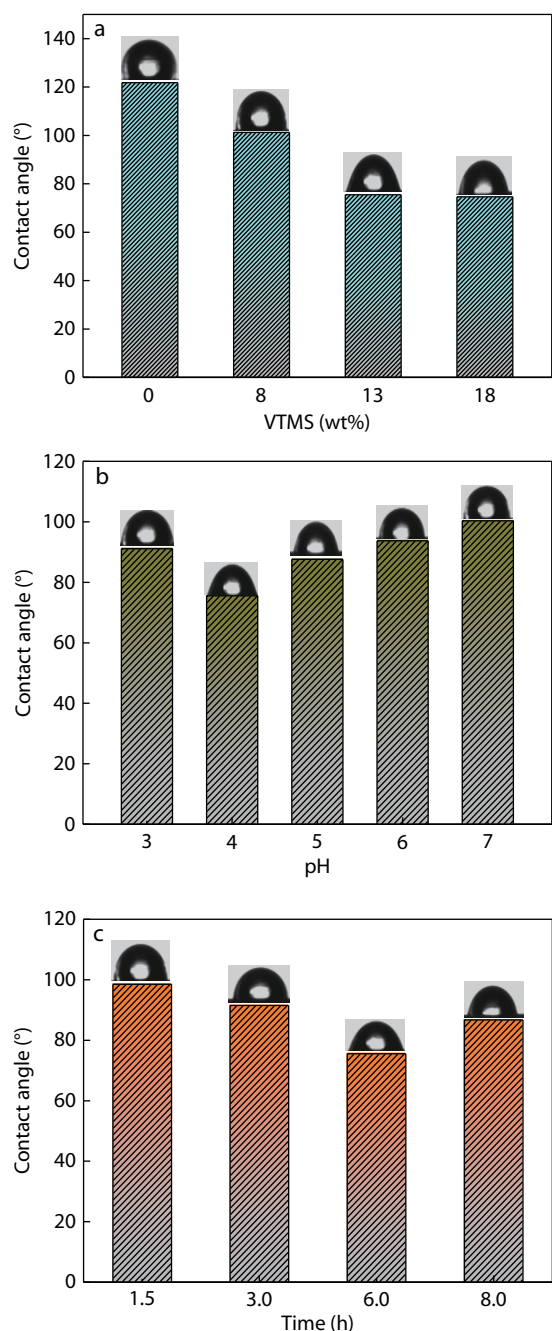


Fig. 6 The water contact angles of the nano-SiO₂ grafted membrane surfaces at various modification conditions: different (a) VTMS concentrations (pH=4, hydrolysis time 6 h), (b) pH values of silica hydrolysis solution (VTMS concentration 13%, hydrolysis time 6 h) and (c) reaction time (VTMS concentration 13%, pH=4).

increase in the number of nano-SiO₂ grafted on the surface. The introduction of nano-SiO₂ hydrophilic layer changes the separation mechanism of UHMWPE hydrophobic membranes. When the membrane surface becomes hydrophilic enough, water molecules can be adsorbed on the surface of the hydrophilic membranes under hydrogen bonding during the separation process, and pressure can accelerate the passage of water molecules, thereby the water flux is greatly increased. Be-

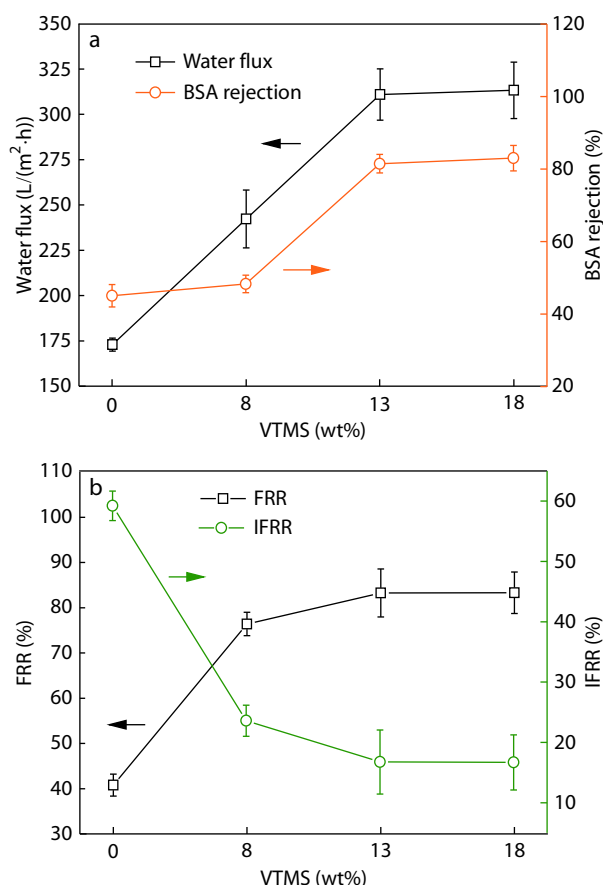


Fig. 7 Effect of VTMS concentrations on (a) filtration performance and (b) anti-fouling performance of modified hollow fiber membranes (pH=4, hydrolysis time 6 h).

sides, the nanoparticles distribute orderly on the membrane surface, which form a tight physical barrier to reject BSA molecules, showing a high rejection effect.^[32]

Fig. 7(b) presents the effect of VTMS concentrations on anti-fouling performance of modified hollow fiber membranes. The flux recovery rate (FRR) of original UHMWPE hollow fiber membranes is about only 40%, which means the membranes can be easily fouled by protein molecules. It can be seen that the FRR of the modified membranes is higher (more than 80%) than that of original membranes. With the increase of VTMS concentration, the FRR of modified membranes shows an increasing trend, indicating that the anti-fouling performance of UHMWPE hollow fiber membranes has been effectively enhanced by grafting nano-SiO₂.

VTMS in the modified extract also has a huge impact on mechanical strength of hollow fiber membranes. As indicated in Fig. 8, the tensile strength of original membranes is as high as 19.5 MPa, while it decreases significantly in modified membranes. When the concentration of VTMS increases from 8% to 13%, the strength decreases slightly, while it is reduced to 12.8 MPa when the concentration reaches 18%, which is considerably lower than that of the original membranes. It can be explained as that the graft of silane coupling agent on the surface of membranes does great damage to the structure of UHMWPE itself. Studies by Pollet *et al.*^[33] prove that

when vinyl trimethoxysilane (VTMS) is used as coupling agent and ditertiary butyl peroxide is used as initiator to graft low-density polyethylene (LDPE), the number of VTMS grafted on the PE macromolecular chain varies from 1 to 8, and the structure of the grafts is mainly 2,4,5-grafted. Therefore, the concentration of VTMS affects the strength of modified membranes negatively. Considering comprehensively, the optimum concentration of VTMS is obtained as 13%.

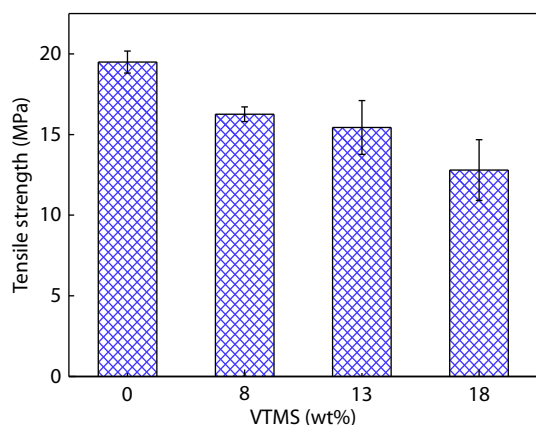


Fig. 8 Effect of VTMS concentrations on mechanical strength of modified hollow fiber membranes (pH=4, hydrolysis time 6 h).

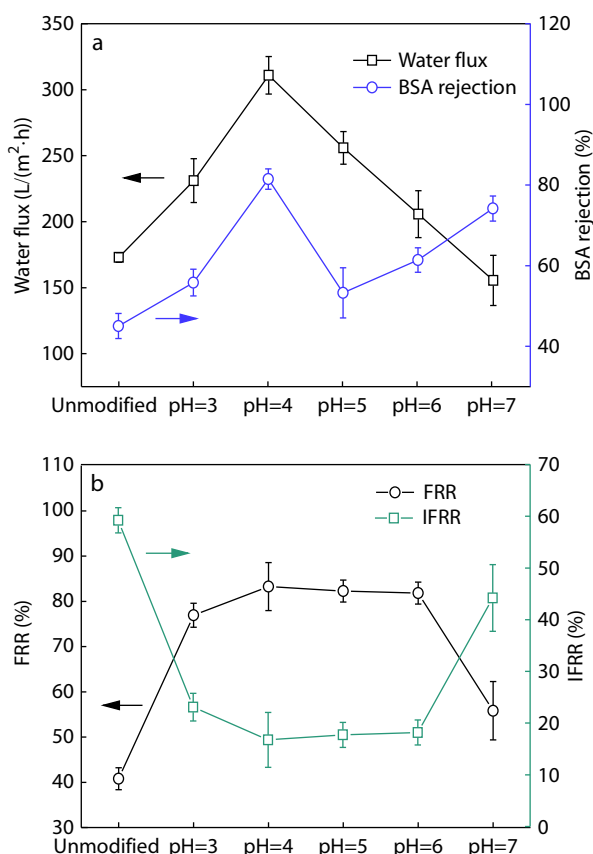


Fig. 9 Effect of pH values of silica hydrolysis solution on (a) filtration performance and (b) anti-fouling performance of modified hollow fiber membranes (VTMS concentration 13%, hydrolysis time 6 h).

Effect of pH values of silica hydrolysis solution

The effect of pH values of SiO₂ hydrolysate on the performance of modified membranes is also discussed, which is presented in Fig. 9(a). We can obviously see that the water flux of modified membranes first increases and then decreases with the increase of acidity of hydrolysate. It can be explained with the theory that as the acidity increases, the reactions of silane hydrolyzing to silanol and silanol condensing to form Si—O—Si are speeded up, which makes the content of residual silanol the highest and the number of nano-SiO₂ bonded on the surface of the membranes the largest at the pH value of 4. At this point, the modified membranes own the strongest hydrophilicity, the largest pure water flux (310.9 L/(m²·h)) and BSA rejection rate (81.47%), which are about twice as high as those of the original membranes. When the pH value of the hydrolysate was continuously increased to 3, the acceleration of silanol condensation reaction is much higher than that of silane hydrolysis, resulting in the decrease of residual silanol content and nano-SiO₂ content bonded on the membranes surface. Therefore, the pure water flux and BSA rejection rate of the modified hollow fiber membranes come down. In addition, when the pH value of the hydrolysate is 4, the FRR of modified membranes reaches the maximum value (Fig. 9b), that is, the membranes own the most outstanding anti-fouling performance. All the observations underscore the optimum pH value of SiO₂ hydrolysate is 4.

Effect of the duration of hydrolysis

The duration of hydrolysis is also one of the most important parameters, which can influence the filtration and anti-fouling performance of membranes. As discussed in the previous sections, the hydrolysis of VTMS takes time, while the reaction time of 1.5–3 h is so short that there are only a small number of nanoparticles grafted on the membrane surface. Hence, the water flux, BSA rejection rate and FRR of the modified membranes are slightly higher than those of the original membranes. When the hydrolysis reaction time reaches 6 h, the membrane surface has been covered with more nanoparticles, which distribute uniformly and orderly without large-scale agglomeration. At this time, the pure water flux, BSA rejection rate and FRR of the modified membranes arrive at the maximum (Fig. 10). When the hydrolysis time is further extended to 8 h, the number of inorganic nanoparticles on the membrane surface decreases and agglomeration occurs. The reason is also mentioned in the previous part. As a result, the filtration and anti-fouling performance of the modified membranes become poorer.

The membranes we prepared in this work are microfiltration membranes. In order to assess the rejection effect of the modified membranes, carbon ink with larger particle size was used to characterize the rejection performance of the membranes. The particle size of carbon ink was characterized by SEM (Fig. 11a) and laser particle sizer (Fig. 11b). From the results, we can know that the carbon particle size is mainly in the range of 50–225 nm, and the average particle size is about 77 nm. Therefore, ink also was used as the rejection test material. The effect of hydrolysis time on the carbon particle rejection performance of modified membranes is shown in Figs. 11(c) and 11(d). It can be obviously seen from

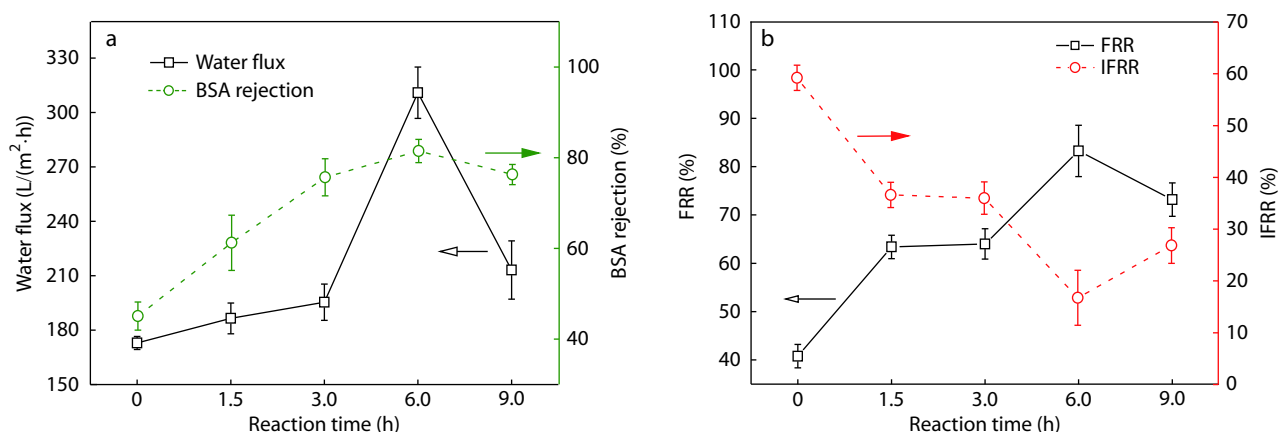


Fig. 10 Effect of the duration of hydrolysis on (a) filtration performance and (b) fouling resistance of modified hollow fiber membranes (VTMS concentration 13%, pH=4).

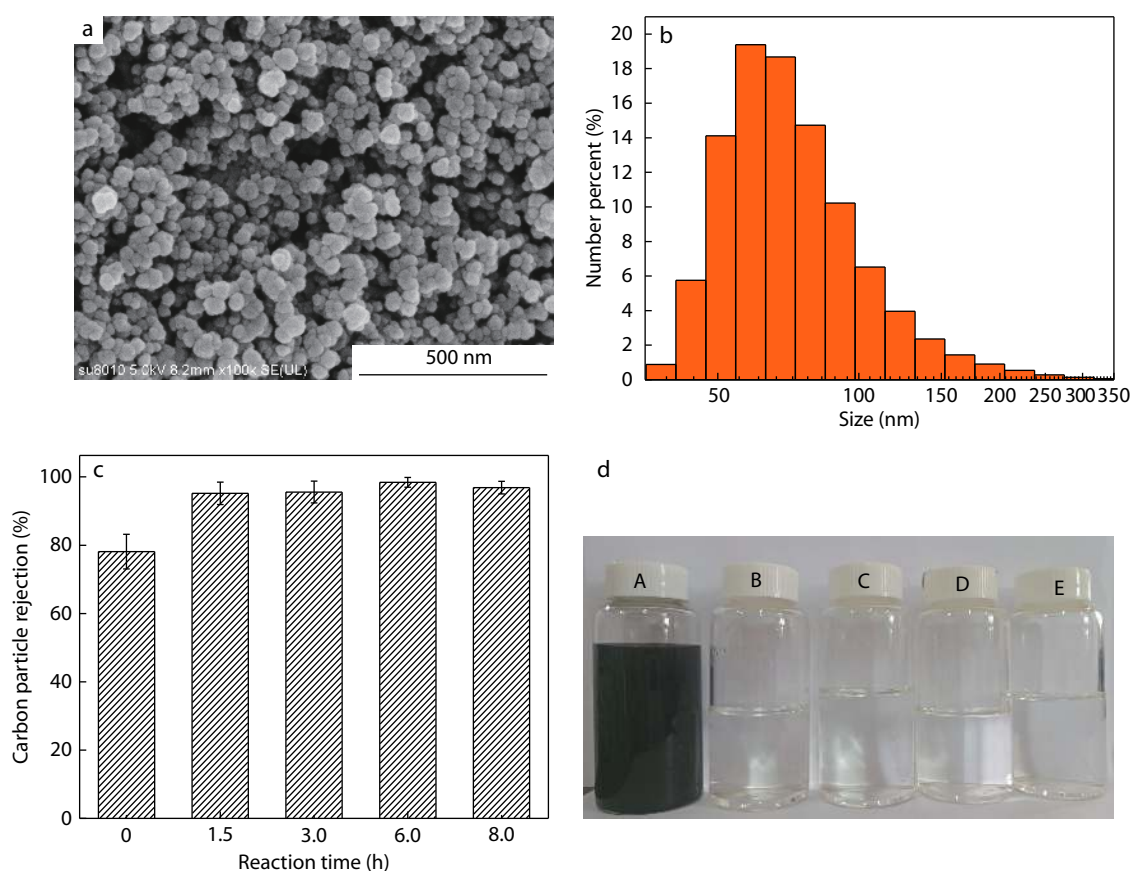


Fig. 11 Carbon particle size distribution spectra measured by (a) FE-SEM and (b) laser particle size and (c, d) the effect of the duration of hydrolysis on carbon particle rejection of modified hollow fiber membranes: (A) original ink solution; (B–E) permeate solution with hydrolysis for (B) 1.5 h, (C) 3 h (D) 6 h, and (E) 8 h (VTMS concentration 13%, pH=4).

Fig. 11(d) that the permeate becomes clarified, which indicates that UHMWPE hollow fiber microfiltration membranes can be provided with excellent rejection to carbon particles. Observing Fig. 11(c), we can find that with the increase of hydrolysis time, the rejection rate of modified hollow fiber membranes increases first from 95.2% to 98.4%, and then decreases to 96.9%, which is in agreement with the results of pure water flux. Furthermore, the rejection effect of the modi-

fied membranes is enhanced significantly compared with the original membranes (the rejection rate is increased from 78.1% to over 95%). It is well known that the microfiltration process requires a higher rejection ratio. Therefore, the immobilization of nano-SiO₂ on the membranes surface can exert active influence on microfiltration performance. In general, our observations suggest that the hydrolysis reaction should be lasted for six hours.

CONCLUSIONS

UHMWPE microfiltration hollow fiber membranes were prepared via the TIPS method and hydrophilically modified by immobilizing with nano-SiO₂ to the membrane surface in this work. The results of ATR-FTIR spectroscopy, XPS and FE-SEM images confirmed the successful grafting of nano-SiO₂ on the membrane surface. The effects of different modification conditions such as VTMS concentration, pH value of silica hydrolysis solution and hydrolysis time on filtration and anti-fouling properties were investigated. The results demonstrated that the modified hollow fiber membranes possessed the optimum performance including hydrophilicity, filtration and anti-fouling performance when the concentration of VTMS was 13%, the pH of the hydrolyzate was 4, and the hydrolysis reaction time was 6 h. By comparison with original membranes, water contact angle of the grafted membranes decreased from 121.8° to 75.5°, which indicated that the hydrophobic membranes were converted into hydrophilic membranes. The pure water flux rose from 172.89 L/(m²·h) to 310.9 L/(m²·h), the BSA rejection rate also increased by leaps and bounds, from 45.04% to 81.47%, and the rejection rate of carbon particles can reach more than 95%, which showed that the graft of nano-SiO₂ effectively improved the filtration performance of UHMWPE hollow fiber membranes. Furthermore, the FRR value of modified membranes was up to 83.3%, revealing that the construction of the nano-SiO₂ hydrophilic layer on the membranes surface has imparted excellent anti-fouling performance to the UHMWPE hollow fiber membranes. The tensile strength of modified membranes decreased slightly, but it could still reach higher than 15 MPa. Therefore, it can be seen that the hydrophilic modification process of UHMWPE hollow fiber membranes described in this work is a promising approach for the application in the field of water purification.

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