

Surface Modification of Polyamide Nanofiltration Membrane by Grafting Zwitterionic Polymers to Improve the Antifouling Property

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ABSTRACT: A simple two-step surface modification method of polyamide nanofiltration membrane, involving the activation of amide groups by formaldehyde and the subsequent cerium [Ce (IV)]-induced graft polymerization of zwitterionic 3-(methacryloylamino) propyl-dimethyl-(3-sulfopropyl) ammonium hydroxide (MPDSAHA) monomers, was employed to improve membrane antifouling property. The membranes before and after modification were characterized by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscopy, and atomic force microscopy. The changes in both surface chemical composition and morphology of membranes confirmed the successful graft polymerizations of MPDSAHA onto polyamide nanofiltration membrane. The static water contact angle measurements showed that surface hydrophilicity of the modified membranes was significantly enhanced. As the MPDSAHA concentration increased, the water flux of grafted membrane decreased gradually, while salt rejection increased slightly. The fouling experiments with bovine serum albumin solution demonstrated that modified membranes exhibited better resistance to protein fouling. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41144.

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INTRODUCTION

Nanofiltration process is currently the worldwide-used separation technology in many application fields such as desalination, wastewater treatment, pharmaceutical concentration, dye removal, and so on.^{1–4} Nanofiltration membranes have gained great research interest due to their high permeate flux with suitable salt rejection, low operation cost compared with reverse osmosis membranes.⁵ At present, most nanofiltration membranes are thin film composite membranes prepared with a polyamide skin layer on porous support by interfacial polymerization.⁶ However, the further application of polyamide membranes is badly limited by its vulnerability to fouling, which is believed to result from the accumulation of foulants like proteins, natural organic matters and bacteria on the relatively hydrophobic polyamide surface or even inside the membrane pores.^{7,8} Membrane fouling causes undesirable flux decline temporarily or permanently, which leads to an inevitable increase in the cleaning frequency and ultimate decrease in membrane lifetime.⁹ Hence, the development of polyamide nanofiltration membranes with good antifouling property has become an important subject of academic and industrial research.

The surface characteristics (e.g., chemical structure, hydrophilicity, surface roughness, and charge) of membrane have significant influence on its antifouling property.^{10–12} It is commonly accepted that membranes with hydrophilic smooth surface and similar charge to foulants can restrain the adsorption and deposition process of foulants.¹³ Therefore, the modification of membrane surface characteristics is a promising way to improve the fouling resistance of polyamide membranes. There are multifarious methods including physical and chemical treatments to modify the surface characteristics of polyamide membranes, such as physical coating of hydrophilic polymers or inorganic nanoparticles,^{14,15} UV-induced (or initiated) grafting antifouling polymers on membrane surface^{10,16} and chemical grafting by the activation of terminal amino or carboxylic groups.^{17,18} Physical coating is a simple and easily handled method. However, the coating layers are adhered to the polyamide active layer only by weak physical attraction forces which cannot avoid the desorption and peeling of coating layers during the long-term operation.¹⁹ UV grafting method is desirable but complicated as special setups are needed to activate membrane surface that restricts the actual application.²⁰ In addition, since polyamide membrane contains limited number of terminal amino groups,

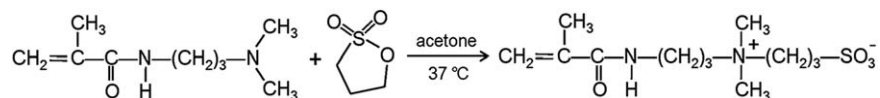


Figure 1. schematic diagram of MPDSAH synthesis.

chemical grafting antifouling polymers on these groups leads to low ligand densities and therefore unobvious performance improvement.²¹

In recent years, the zwitterionic polymers such as phosphorylcholine, polysulfobetaine methacrylate, and polycarboxybetaine methacrylate have attracted increasing attentions for the surface antifouling modification because of their high hydration capability and excellent resistance to protein adsorption and bacterial attachment.^{22,23} The structure speciality of the zwitterionic polymers is that they have both positively and negatively charged functional groups within the same monomer unit, but maintain overall charge neutrality.²⁴ Compared with those hydrophilic materials achieving surface hydration via hydrogen bonding (for example, polyethylene glycol, an extensively studied hydrophilic and antifouling material), the zwitterionic polymers can attract water molecules more strongly via electrostatic interaction to form a hydration layer on membrane surface, which helps inhibit the attachment of protein or bacteria.²⁵ This makes zwitterionic polymers the desired antifouling material for membrane surface modification. Till now studies in this field have been mainly reported in ultrafiltration and microfiltration area.^{26,27} Nevertheless, as far as we know, only few studies have been carried out to employ zwitterionic polymers on polyamide nanofiltration membrane surface for membrane fouling reduction^{28,29} and the methods they proposed are too complicated for practical application.

Based on the discussion above, the objective of our present work is to provide a simple two-step method without special equipments for grafting zwitterionic polymer on the surface of conventional polyamide nanofiltration membrane to enhance its antifouling property. The polyamide membrane was firstly activated by formaldehyde to provide initiating sites at surface amide groups. Then, the zwitterionic monomer 3-(methacryloylamino) propyl-dimethyl-(3-sulfopropyl) ammonium hydroxide (MPDSAH) was covalently grafted on these activated sites through Ce (IV)-induced graft polymerization. Membrane characterizations including Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscopy (SEM), atomic force microscopy (AFM), and water contact angle were employed to confirm the successful grafting of MPDSAH. The effect of MPDSAH concentration on the performance of polyamide nanofiltration membranes was investigated. Membrane antifouling property was also evaluated through fouling experiments.

EXPERIMENTAL

Materials

Polysulfone (PSf) Udel-3500 was provided by Amoco Company. Poly(ethylene glycol) ($M_w = 400$) (PEG400) was purchased from Kermel Chemical Reagent (Tianjin, China). *N,N*-dimethylacetamide (DMAC) was obtained from Tianjin Bodi Chemical

Reagent (Tianjin, China). The monomer 2-(Dimethyl amino) ethyl methacrylate (DMAPMA) and 1,3-propanesulfonate (1,3-PS) were purchased from Aladdin-reagent (Shanghai, China). 1,3,5-Benze-netricarbonyl trichloride (TMC) was purchased from Acros (Belgium) and *m*-phenylenediamine (*m*-PDA) was purchased from J&K Scientific Ltd. (Beijing, China). *N*-hexane was purchased from Xingyue Chemical (Tianjin, China). Triethylamine (TEA) and phosphoric acid (H_3PO_4 , >85 wt %) were purchased from Fuyu Fine Chemical (Tianjin, China). Formaldehyde solution (37–40 wt %) was purchased from Xilong Chemical (Guangdong, China). Ceric ammonium nitrate (CAN) was supplied from Sinopharm Chemical Reagent (Shanghai, China). Analytical reagent sodium sulfate (Na_2SO_4) was used without further purification. Bovine serum albumin (BSA) was purchased from Aoboxing Bio-tech (Beijing, China).

Synthesis of MPDSAH Monomer

The zwitterionic monomer MPDSAH was synthesized from DMAPMA and 1,3-PS following the similar ring opening reaction as reported in literature³⁰ and the synthesis pathway was shown in Figure 1; 0.052 mol (8.805 g) DMAPMA and 100 mL acetone were added into a 250 mL flask and the mixture was stirred at 37°C. During the stirring period, 0.057 mol (6.916 g) 1,3-PS dissolved in 20 mL acetone was added dropwise into the flask within 30 min. The reaction mixture was stirred at the same temperature for 4 h followed by cooling the whole mixture at 5°C for 3 days. The precipitated white power was then collected by filtration, washed with dry acetone for three times to remove surplus reagents, and subsequently dried under vacuum at 40°C to obtain zwitterionic MPDSAH.

Preparation of Polyamide Nanofiltration Membrane

PSf ultrafiltration membrane used as support substrate in this work was fabricated by immersion-precipitation phase inversion method.³¹ The PSf casting solution containing 15 wt % PSf and 6 wt % PEG400 in DMAC was cast on a clean glass plate at room temperature using a film applicator, and then the glass plate covered with a thin cast solution layer was immersed into deionized water bath at ambient temperature. The obtained membrane was thoroughly washed with deionized water to remove residual DMAC and PEG400.

The polyamide nanofiltration membrane was prepared via conventional interfacial polymerization between aqueous *m*-PDA and organic TMC solutions.³² The simple process for the formation of polyamide active layer was as follows: an aqueous phase solution containing *m*-PDA (0.5 wt %) and TEA (0.3 wt %) was poured and stayed on the top of the wet PSf support membrane for 3 min at room temperature. Extra aqueous phase solution was drained off with filter paper until no liquids remained on the membrane surface. Then, the organic solution composed of TMC (0.2 wt %) and *n*-hexane was poured onto the wet membrane for 2 min. After removing excess TMC solution, the membrane underwent heat treatment in an oven at

80°C for 10 min. Then, the obtained membrane was thoroughly washed with deionized water and stored in deionized water.

Surface Modification of Polyamide Nanofiltration Membrane

The amide groups of the polyamide membrane were firstly activated by formaldehyde according to a similar procedure described in the literatures.^{21,33} Polyamide membrane was kept in a mixed solution of 150 mL formaldehyde and 3 mL phosphoric acid at 60°C for 7 h. After the reaction, the activated polyamide membrane was washed several times with a large amount of deionized water to remove residual formaldehyde.

The graft polymerization of MPDSAHA on activated polyamide membrane surface was carried out as follows:^{34,35} at first a series of solutions containing CAN (2 mmol/L) and different concentrations of MPDSAHA (3, 10, and 20 g/L) were prepared and degassed with nitrogen; then, the activated polyamide membrane was immersed in this solution and the system was heated at 40°C with constant supply of nitrogen to remove oxygen from the solution; at the end, the obtained membrane was thoroughly washed with and then stored in deionized water for the continued experiments. The fabricated polyamide nanofiltration membranes were named as PA-g-MPDSAHA_x, where *x* indicated the MPDSAHA concentration with a unit of g/L. The membrane samples used for grafting degree measurement were dried under vacuum at 40°C to gain constant weight. The grafting degree was calculated by the following equation:

$$\text{Grafting degree} = \frac{W_1 - W_0}{A} \quad (1)$$

where W_0 and W_1 are the weights of the dried original and grafted polyamide membrane (μg); A is the surface area of the membrane (cm^2), respectively. Each result was an average of at least three parallel samples.

Membrane Surface Characterization

ATR-FTIR, Nicolet iS5 measurements were performed to investigate the changes of chemical composition of unmodified and modified polyamide membranes and confirm the grafting of MPDSAHA onto membrane surface. The background spectrum in air was measured and subtracted from the membrane samples spectrum.

Surface morphologies of the original and grafted polyamide membranes were observed by SEM (JSM-6360LV, Japan). All membrane samples were frozen in liquid nitrogen and sputtered with gold to produce electric conductivity before SEM observation.

Quantitative surface roughness analysis of the membranes was measured using AFM (Nanoscope IIIa) in the tapping mode to prevent any possible damage to the membrane surface morphology. The root mean square roughness (Rms) values in an area of $10 \times 10 \mu\text{m}^2$ for each membrane were calculated to describe the membrane surface roughness. All three-dimensional AFM images were obtained under room temperature.

Water contact angle measurement was performed by a contact angle meter (JC2000C Contact Angle Meter, Powereach, Shanghai, China) to evaluate membrane surface hydrophilicity after the membrane samples were dried at room temperature.

The average value of water contact angle was obtained by five measurements for each membrane sample to reduce error.

Membrane Performance Evaluation

The filtration performance in terms of water flux and salt rejection for the fabricated membranes was tested at room temperature with a cross-flow filtration system. The effective membrane area was 28.26 cm^2 . Before testing, each membrane loaded in the filtration cell was prepressurized under 0.8 MPa with deionized water for at least 30 min to ensure the membrane is in a steady state. Then the test pressure was lowered to 0.6 MPa. The water flux (J) of each membrane sample was calculated by the following equation:

$$J = \frac{V}{At} \quad (2)$$

where V is the total volume of the permeate solution (L); A is the effective membrane area (m^2); and t denotes the filtration time (h).

The aqueous solution containing 0.01 mol/L Na_2SO_4 was used to evaluate the salt rejection of fabricated nanofiltration membranes and the rejection ratio (R) was calculated using the following equation:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (3)$$

where C_p and C_f are the solute concentrations in the permeate and feed solutions, respectively. Na_2SO_4 solution concentrations were determined by measuring the electrical conductivity of the salt solution using a conductivity meter (DDS-12DW, Shanghai Bante Instruments, China). All the obtained values of water flux and salt rejection were averaged values from at least three samples for each membrane.

Membrane Fouling Experiments

The membrane fouling experiments were conducted through the filtration system as described above. BSA was selected as model organic foulant to represent effluent organic matter that significantly contributes to organic fouling in wastewater effluent.^{16,36} Each membrane fouling experiment consisted of three stages: First, the compacted membrane was measured with deionized water for 1 h to obtain its average pure water flux (J_0); subsequently the reservoir was refilled with 1 g/L BSA solution and then the permeate flux was measured; after 4 h of filtration, the membrane and reservoir were washed with deionized water for 20 min and this period was not included in the test time; at the end the pure water flux of cleaned membrane was measured again for 1 h with deionized water. The membrane flux (J_t) as a function of time during the whole experiment was tested under the same conditions as used in the filtration performance test. The relative flux (J_t/J_0) was calculated to evaluate antifouling behavior of the membrane to BSA.

RESULTS AND DISCUSSION

Preparation of MPDSAHA Grafted Membrane

In this study, surface modification of polyamide nanofiltration membrane was achieved by a simple two-step method comprising the activation of amide groups and the graft polymerization of zwitterionic MPDSAHA onto polyamide membrane surface.

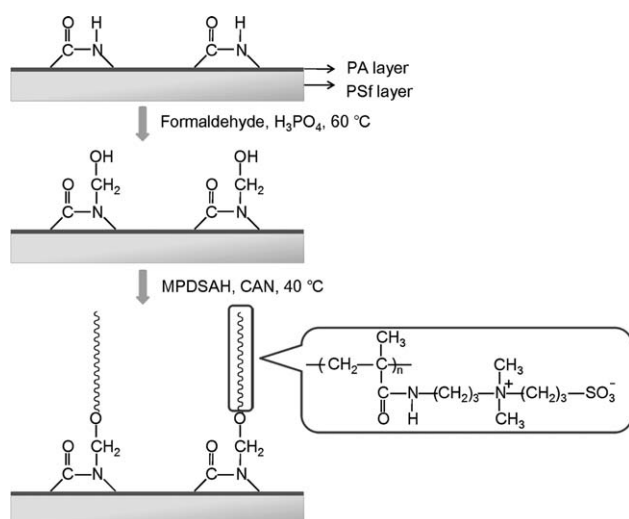


Figure 2. The reaction process for activation of amide groups and graft polymerization of MPDPAH on the surface of polyamide membrane.

The surface amide groups on polyamide membrane were activated by formaldehyde to produce *N*-methylol polyamide membrane. It has been confirmed that the *N*-methylol reaction of polyamide probably occurs at its low order segment since this area shows a loose structure, which will allow effective penetration of formaldehyde.³³ Moreover, the formation of *N*-methylol polyamide will be obviously facilitated in an acidic environment.

In the second step, the zwitterionic MPDPAH was covalently immobilized on polyamide membrane surface via Ce (IV)-induced graft polymerization. As shown in Figure 1, the synthetic MPDPAH contained a positively charged quaternary amine group and a negatively charged sulfonic group in the monomer unit. The two oppositely charged groups from this zwitterionic molecule lead to a homogenous mixture of balanced charge groups. During the graft polymerization, the grafting of polyMPDPAH onto polyamide membrane was achieved based on the interaction between hydroxyl groups on *N*-methylol polyamide membrane surface and vinyl groups of MPDPAH monomers using CAN as an initiator. It is reported that as a living radical polymerization, the Ce (IV)-induced graft polymerization had a high grafting efficiency of initiator and a minimal extent of ungrafted homopolymer in solution,^{37,38} which was beneficial for the successful grafting of zwitterionic MPDPAH on the surface of polyamide membrane. The detailed reaction process for activation of amide groups and graft polymerization of zwitterionic MPDPAH on the surface of polyamide membrane was illustrated in Figure 2.

Table I. Grafting Degrees of the Original and Modified Polyamide Membranes

Membrane sample	Grafting degree ($\mu\text{g}/\text{cm}^2$)
PA-g-MPDPAH0	0
PA-g-MPDPAH3	33.76 ± 10.19
PA-g-MPDPAH10	113.59 ± 23.57
PA-g-MPDPAH20	170.49 ± 18.02

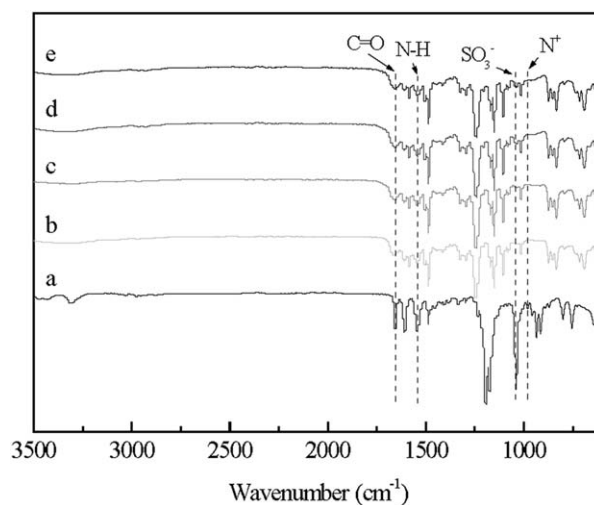


Figure 3. ATR-FTIR spectra of (a) zwitterionic MPDPAH, (b) PA-g-MPDPAH0, (c) PA-g-MPDPAH3, (d) PA-g-MPDPAH10, and (e) PA-g-MPDPAH20.

Table I presents the effect of MPDPAH monomer concentration in aqueous solutions on the grafting degree of polyamide membrane. As seen from these results, the grafting degree increased with the increase of MPDPAH concentration. It is well known that the monomer concentration is an important influencing factor for the grafting degree. At low monomer concentration, there was not enough MPDPAH to contact with active sites on membrane surface, thus caused a lower grafting degree. While at high monomer concentration, there were more opportunities for numerous MPDPAH to contact with active sites and graft on membrane surface, leading to high grafting degree. However, the increasing rate of grafting degree slowed down with the increase of MPDPAH concentration. This could be attributed to the formation of long grafted chains through graft polymerization of MPDPAH monomers. The large number of long grafted chains covered on membrane surface induced steric repulsion and hindered the ungrafted monomers from approaching active sites. In addition, the increase of MPDPAH concentration may accelerate the monomer homopolymerization in aqueous solution. Therefore, further grafting of monomers was prevented by the combined effect of long grafted chains steric repulsion and monomer homopolymerization.

Characterization of Surface Modification on Polyamide Membrane

Changes of chemical groups in original and surface modified polyamide membranes were characterized by ATR-FTIR. As shown in Figure 3(a), there were characteristic adsorption peaks at 1655, 1540, 1038, and 935 cm^{-1} , which correspond to the C=O stretching vibration of the amide groups, the N—H in-plane bending vibration of secondary amines, O=S=O stretching vibration of sulfonic groups and C—N stretching vibration of quaternary ammonium groups on MPDPAH,^{31,39} respectively. Figure 3(b) exhibits the spectra of original polyamide membrane surface. Compared with the original polyamide membrane, the MPDPAH modified polyamide membrane [Figure 3(c)] had a new peak at 1038 cm^{-1} , which was attributed to

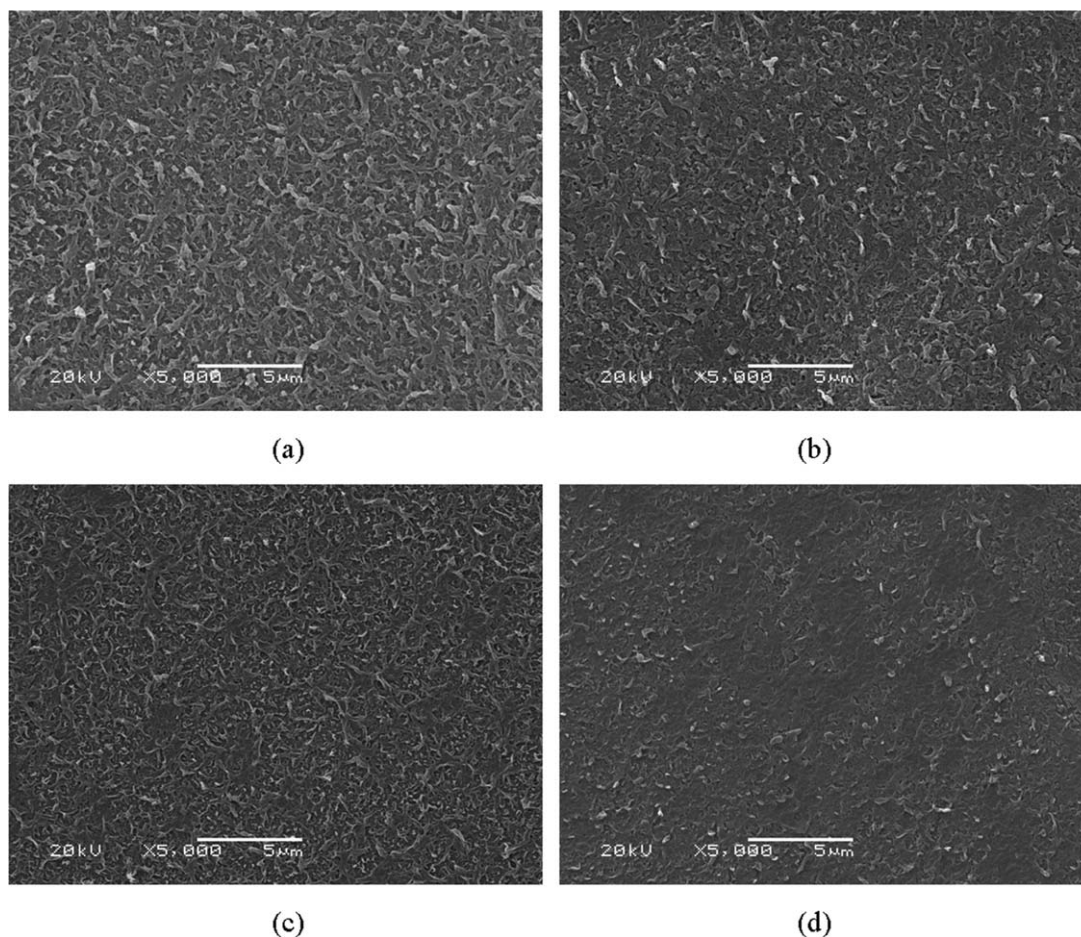


Figure 4. Surface SEM images of (a) PA-g-MPDSAH0, (b) PA-g-MPDSAH3, (c) PA-g-MPDSAH10, and (d) PA-g-MPDSAH20.

O=S=O stretching vibration of sulfonic groups, indicating that zwitterionic MPDSAH had been successfully grafted onto the polyamide membrane surface. Moreover, as seen in Figure 3(d,e), the intensity of this characteristic peak of sulfonic group became stronger with the increase of monomer concentration. It was noted that there was no evident absorption peak of C—N stretching vibration of quaternary ammonium groups on the modified polyamide membrane because this absorption peak was weak for MPDSAH.

The surface microstructures of polyamide membranes before and after MPDSAH grafting were examined using SEM. As shown in Figure 4, the membrane surface of original polyamide membrane was rough. There were no significant morphological variations between unmodified PA-g-MPDSAH0 and modified PA-g-MPDSAH3 and PA-g-MPDSAH10 except very small nodular structure that could be found after MPDSAH was grafted on membrane surface. However, the changes in the structure of membrane surface were more observable with the further increase of MPDSAH concentration. It was clearly seen that the formed grafting layer almost fully covered the surface of polyamide membrane and the membrane surface became much smoother and denser when the grafting concentration increased to 20 g/L. Therefore, the surface microstructures of polyamide

membranes before and after modification confirmed the successful MPDSAH immobilization on membrane surface.

To further quantitatively investigate the surface morphologies of original and modified polyamide membranes, the AFM analysis was carried out and the corresponding results were shown in Figure 5. As it can be seen in Figure 5(a), the surface of original polyamide membrane had evident ridge-and-valley structure and the calculated Rms value was as high as 104.020 nm. The Rms value slightly increased to 114.820 nm by grafting of MPDSAH with a concentration of 3 g/L on the surface of the polyamide membrane. Under low grafting concentration, poly-MPDSAH chains on the membrane surface were dispersed and kept in a stretching state, which would cause space steric hindrance to resist the further grafting of MPDSAH. Therefore, the surface region of modified membrane covered by grafted MPDSAH was relatively high, while the surface region not covered by grafted MPDSAH was relatively low, thus led to a small increase of surface roughness. However, with the increasing grafting concentration of MPDSAH from 10 to 20 g/L, the membrane surface became smoother and at the same time the Rms values significantly lowered from 65.561 to 34.169 nm. This result could be attributed to the fact that a large number of polyMPDSAH chains covered most of the surface region of

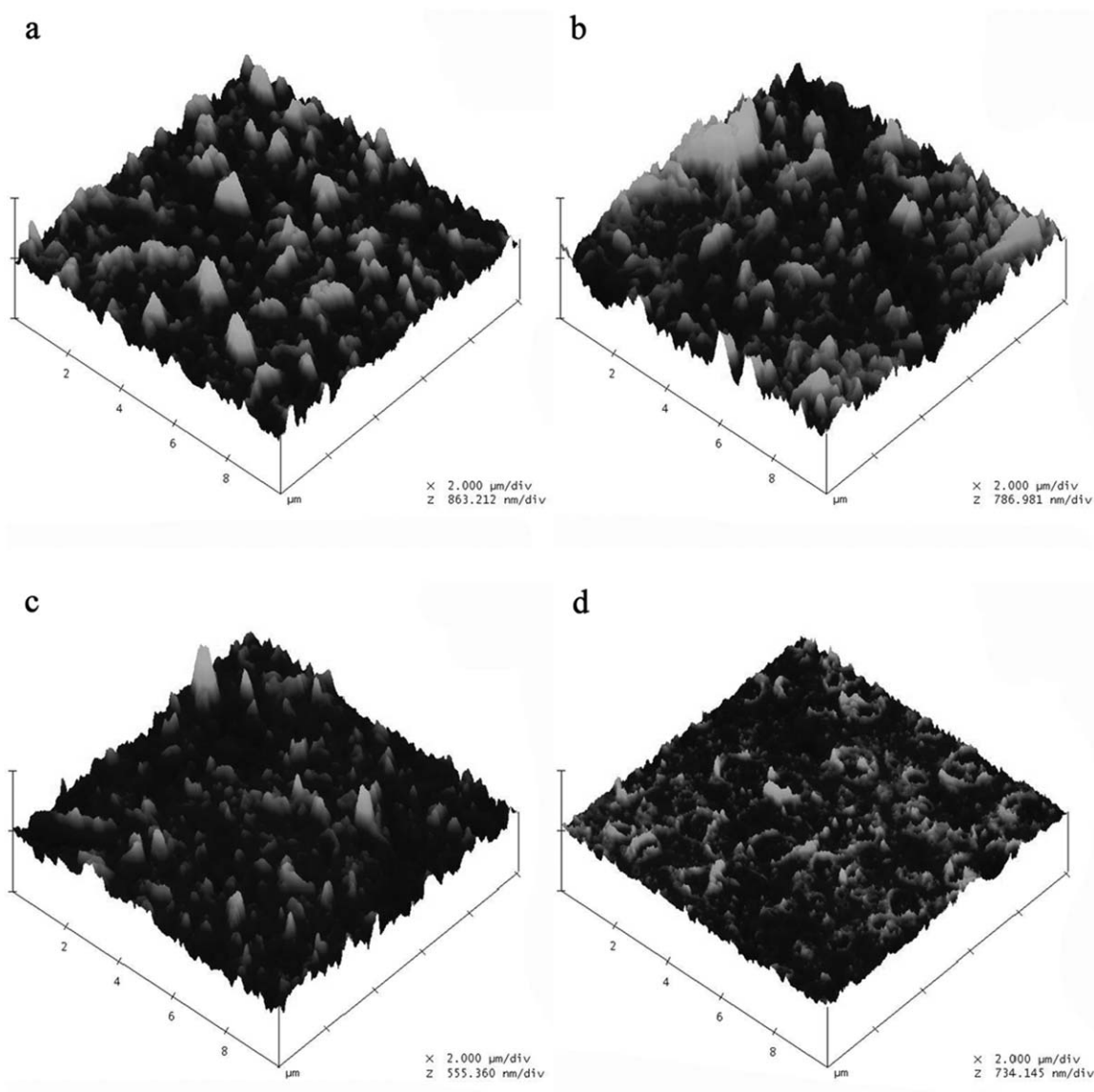


Figure 5. Three-dimensional AFM images of (a) PA-g-MPDSAH0, (b) PA-g-MPDSAH3, (c) PA-g-MPDSAH10, and (d) PA-g-MPDSAH20.

the polyamide membrane under high grafting concentration. Similar decrease of surface roughness after modification on membrane surface has been observed in previous works.^{40,41} It was reported that rough membrane surface is more vulnerable to fouling than smooth membranes as particles preferentially accumulate in the valleys of rough membranes, leading to “valley clogging” and a more severe flux decline.¹¹ Therefore, the modified polyamide membranes with smoother surface in this work could have a better antifouling property.

Water contact angle is usually used to assess the hydrophilicity of the membrane, which is an important property affecting the flux and antifouling ability of the membrane. Figure 6 presents the water contact angle measurement of original and modified polyamide membranes. It can be seen that the water contact angle value of original polyamide membrane PA-g-MPDSAH0

was 58.8°, and compared with it, all the grafted polyamide membranes had lower water contact angles and showed a decrease tendency with the MPDSAH concentration increase. A minimum value of 35.5° was achieved for membrane PA-g-MPDSAH20. Generally speaking, lower water contact angle of membrane surface indicates that more water molecules in aqueous solution can penetrate into membrane surface and correspondingly improve the membrane hydrophilicity, which is in favor of membrane antifouling property. Therefore, the decrease of water contact angle value with the increasing concentration of MPDSAH demonstrated that the MPDSAH grafted membranes were much more hydrophilic than the original polyamide membrane, which can be attributed to the strong hydration effect between its hydrophilic zwitterionic groups and water molecules.

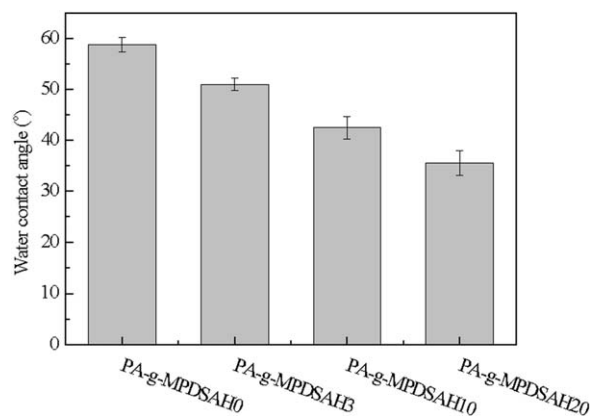


Figure 6. Surface water contact angle values of the original and modified polyamide membranes.

Membrane Performance

The water fluxes and Na_2SO_4 rejections of the original and modified polyamide membranes after grafting with different concentrations of MPDSAH were tested and presented in Figure 7. The pure water flux of PSf support membrane was about $150 \text{ L/m}^2\text{h}$ at 0.1 MPa. After the formation of a thin polyamide layer by interfacial polymerization, the pure water flux exhibited an obvious drop to around $38.9 \text{ L/m}^2\text{h}$. As shown in Figure 7, the grafted membrane of PA-g-MPDSA3 had almost the same water flux as original membrane, while the fluxes decreased for modified membranes of PA-g-MPDSA10 and PA-g-MPDSA20. Surface hydrophilicity and hydraulic resistance (related to membrane pore size) are two main but conflicting factors affecting the variation of water flux.¹⁰ That is to say, on one hand, the increase of surface hydrophilicity can promote water molecules penetration into membranes which results in the enhancement of membrane water flux; however, the increase of hydraulic resistance due to pore blocking caused by the grafting of MPDSAH will become an obstacle for water permeability and lead to a decrease of water flux. Although during the water contact angle measurement, we found that the surface hydrophilicity of membranes was enhanced with the increase of MPDSAH concentration, unfortunately water flux was running

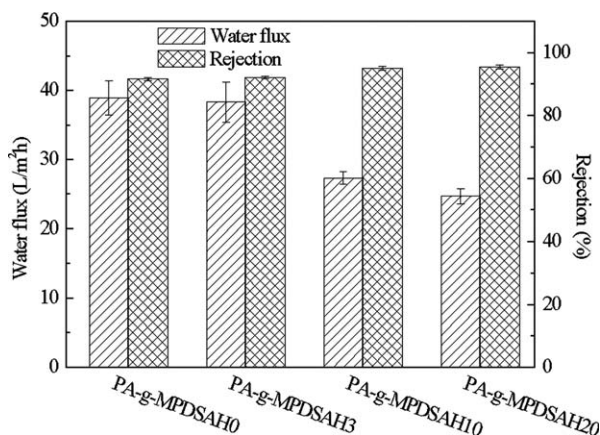


Figure 7. Nanofiltration performance of the original and modified polyamide membranes.

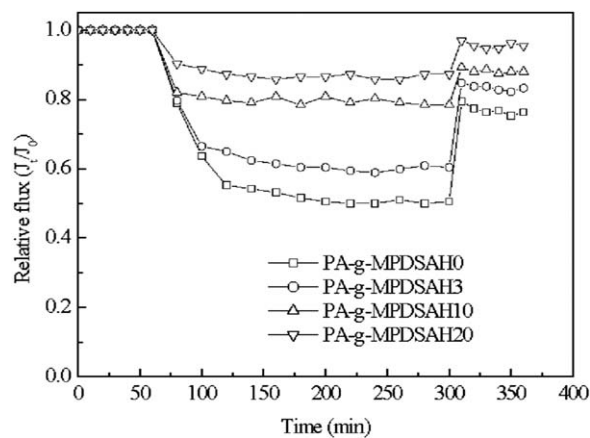


Figure 8. Time-dependent fluxes of the original and modified polyamide membranes during the BSA filtration process.

to an opposite direction. It indicates that negative impact of increased hydraulic resistance has unexpectedly overwhelmed the positive impact of increased surface hydrophilicity in term of water flux change. Moreover, the corresponding salt rejection of grafted membranes slowly increased with the increase of MPDSAH concentration, which is likely due to the densification of obtained thin layer since more polyMPDSAH chains were grafted on membrane surface. It is concluded from the membrane filtration performance results that a smaller amount of MPDSAH grafting onto the membrane surface had less impact on membrane performance, especially for water flux.

Antifouling Property of the Polyamide Membranes

Membrane fouling is always being considered as a severe problem for membrane filtration. In this section, the effect of MPDSAH monomer grafting on the antifouling property of polyamide membranes was investigated using BSA as a model protein foulant. The variation of water flux with time for the unmodified and MPDSAH grafted polyamide membranes during the fouling experiments were presented in Figure 8. It is clearly seen that the fluxes of all membranes decreased when BSA solution was filtered through membranes. It is speculated that protein molecules deposited on membrane surface could form a cake layer and prevent water from permeating through the membrane. However, flux decline of all modified polyamide membrane was smaller than that of the original polyamide membrane. After cleaning with deionized water, the relative water fluxes of all modified polyamide membranes were higher than that of unmodified polyamide membrane, which indicated that all the grafted membranes were less susceptible to be fouled by BSA compared with the unmodified membrane. Moreover, fouling on the modified polyamide membrane grafted with 20 g/L MPDSAH was almost reversible as water flux of this modified membrane could significantly be recovered to about 95.5% of its original flux after cleaning. These results demonstrated that the grafting of MPDSAH has successfully enhanced the fouling resistance of polyamide membranes.

It is well known that the antifouling property of membranes is mainly determined by their surface characteristics (including hydrophilicity, chemical structure, surface charge and roughness,

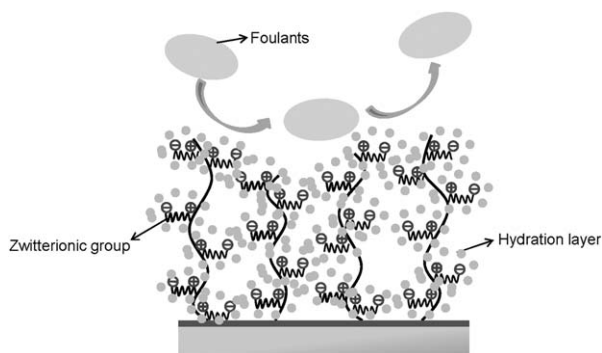


Figure 9. Schematic representation of antifouling mechanism of zwitterionic MPDSAH grafted on polyamide membrane.

etc.). For the MPDSAH modified polyamide membrane prepared in this work, its excellent antifouling property can be attributed to the following four points as presented in Figure 9:

1. First, the surface hydrophilicity of polyamide membrane was effectively improved after grafting MPDSAH onto membrane surface, since zwitterionic MPDSAH had strong hydration capability to form a stable hydration layer via electrostatic interactions. Thus, the adsorption of foulants on membrane surface was prevented by the hydrophilic repulsion force between foulants and membrane;
2. Second, the grafted polyMPDSAH chains on polyamide membrane surface were flexible and long polymer chains. When foulants approached to the surface, the steric repulsion effect was enhanced due to the compression of long-chain polymers. This resulted in resistance of large BSA molecules from closely approaching and adsorbing onto the membrane surface, while the small water molecules could easily pass through the membrane;
3. Third, zwitterionic MPDSAH was electroneutral as it contained both positive ammonium group and negative sulfonic group in the same monomer unit, which shielded negatively charged carboxyl groups in polyamide membrane. Under this case, the charge interaction between foulants and membrane was reduced and that ultimately led to a weaker adsorption to foulants;
4. Finally, the surface of modified polyamide membrane became smoother with the increase of MPDSAH grafting. Therefore, there were less foulants on membrane surface as it was not easy for them to deposit on the valleys of smooth membranes.

All these points indicated that the surface characteristics of polyamide membrane were modified in a desirable way. In summary, the antifouling performance of polyamide membrane has been improved via grafting zwitterionic polyMPDSAH chains onto the membrane surface as expected.

CONCLUSIONS

In this study, surface modification of the polyamide nanofiltration membrane was successfully performed through a simple two-step method composed of the activation of surface amide groups with formaldehyde followed by Ce (IV)-induced graft

polymerization of MPDSAH on the *N*-methylol polyamide membrane. Membrane characterization analysis had confirmed the successful grafting of MPDSAH on polyamide membrane surface. The water flux decreased but the salt rejection increased for modified polyamide membrane with the increase of MPDSAH concentration. The antifouling experiments data demonstrated that the MPDSAH-grafted polyamide membrane had strong resistance to BSA fouling. The improvement of membrane antifouling property was related to a combination of the enhanced hydrophilic repulsion force between foulants and membrane, steric repulsion effect imparted by the compression of long-chain polymers, the shielding of negatively charged carboxyl groups with electroneutral MPDSAH and smoother layers formed on the membrane surface. Grafting of MPDSAH on polyamide nanofiltration membrane had a positive influence on its fouling resistance, suggesting that the simple two-step method proposed in this study may open a new way to prepare highly antifouling polyamide membranes for desalination and water purification.

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