

# Hydrophilic modification of poly(vinylidene fluoride) ultrafiltration membranes by surface UV photo-grafting with N,N'-methylene-bisacrylamide as monomer and Ce(IV) as initiator

Baoli Shi, Zheng Li and Xing Su

## ABSTRACT

A UV photo-grafting method was utilised to enhance the hydrophilicity and anti-fouling property of self-made poly(vinylidene fluoride) (PVDF) ultrafiltration membranes. N,N'-methylene-bisacrylamide (MBAA) was used as monomer and Ce(IV) was used as initiator to obtain balance between grafting treatment consumption and enhanced performance. MBAA could be grafted onto the surface of pure PVDF membranes through a water-phase grafting method under UV photoradiation. When the MBAA concentration was 0.07 mol/L, the Ce(IV) concentration was 0.04 mol/L, and the irradiation duration was 3 min, the membrane surface was grafted with a sufficient amount of monomer under a UV photoradiation intensity of 5.0 mW/cm<sup>2</sup>. The water contact angle on the surface of the modified membrane decreased by approximately 16°, and flux recovery increased by approximately 40% compared with the pure PVDF membrane when treating river water. For bovine serum albumin rejection and porosity measurements no significant changes were observed between pure PVDF and graft-treated membranes. The enhanced performance of the modified membrane in this work was moderate, but the UV irradiation duration (3 min) was short. The integrative effects of UV modification in this work were satisfactory when both irradiation duration and enhanced performance were considered.

**Key words** | hydrophilic, PVDF, ultrafiltration, UV photo

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## INTRODUCTION

Poly(vinylidene fluoride) (PVDF) separation membranes are widely utilised in water treatment facilities and are extensively studied by researchers to further enhance performance and expand the application of these membranes. However, the weak hydrophilicity of PVDF results in the poor anti-fouling ability of PVDF membranes. Increasing the hydrophilicity of PVDF membranes to enhance their anti-fouling ability is an important research direction (Liu *et al.* 2011; Kang & Cao 2014).

Grafting several hydrophilic groups or molecular chains onto the surface of membranes through UV photoradiation technology is a convenient method to prepare hydrophilic

membranes (He *et al.* 2009). Many polymer membranes can be easily modified through this technology. However, PVDF can resist UV photoradiation (Liu *et al.* 2011). Therefore, studies on the hydrophilic modification of pure PVDF membranes through UV photoradiation technology are limited. Hilal *et al.* (2004) modified a commercial PVDF microfiltration membrane through UV photo-grafting polymerisation with quaternised 2-(dimethylamino) ethyl methacrylate and 2-acrylamido-methyl-propane sulfonic acid as monomers and benzophenon (BP) as the initiator. However, the authors did not discuss the change in the water contact angle or water flux recovery of the

membranes. Rahimpour *et al.* (2009) utilised acrylic acid, 2-hydroxyethylmethacrylate, 2,4-phenylenediamine and ethylene diamine as monomers. BP was also adopted as the initiator (Rahimpour *et al.* 2009). In their work, the water contact angle decreased by  $10^{\circ}$ – $27^{\circ}$ , and the water flux recovery of the modified membranes was 31%–57%. Gu *et al.* (2013) adopted 4-vinylpyridine and *n*-butyl chloride as monomers and BP as the initiator to treat PVDF membranes. The water contact angle decreased by  $13^{\circ}$ – $20^{\circ}$ , but the water flux recovery was not measured.

Li *et al.* (2012) employed Ce(IV) (tetravalent cerium ions) as the initiator instead of the common BP to graft N,N'-ethylene bisacrylamide (EBAA) onto polyHEMA-g-PVDF membrane. The water contact angle and water flux recovery of the modified membrane were  $22.1^{\circ}$  and 96.3%, respectively, but the irradiation duration was extremely long (nearly 5 h). The photocatalytic ability of cerium ions was comprehensively studied by Cheng *et al.* (2015). The authors confirmed that the photocatalytic ability of Ce(IV) is stronger than that of Ce(III).

Mono- and multi-functional monomers can be utilised to graft monomers. Unlike mono-functional monomers, multi-functional ones (e.g., EBAA or N,N'-methylene-bisacrylamide (MBAA)) produce a cross-linking structure when used; thus, a stable hydrophilic layer is formed on the surface of the matrix (Yang *et al.* 2005; Deng *et al.* 2009).

In this study, MBAA was utilised as the monomer and Ce(IV) as the initiator to modify self-made PVDF ultrafiltration membranes. The main objective is to enhance the hydrophilicity and anti-fouling property of these membranes within a short irradiation duration; the modified membranes would have a relatively high water flux recovery (e.g., over 80%). The effects of monomer and initiator concentrations and irradiation duration on water contact angle, water flux recovery, membrane porosity and BSA rejection were comprehensively studied.

## MATERIALS AND METHODS

### Materials

PVDF 6010 was purchased from Solvay, Belgium. Polyvinylpyrrolidone (PVP) K30 purchased from BASF, Germany,

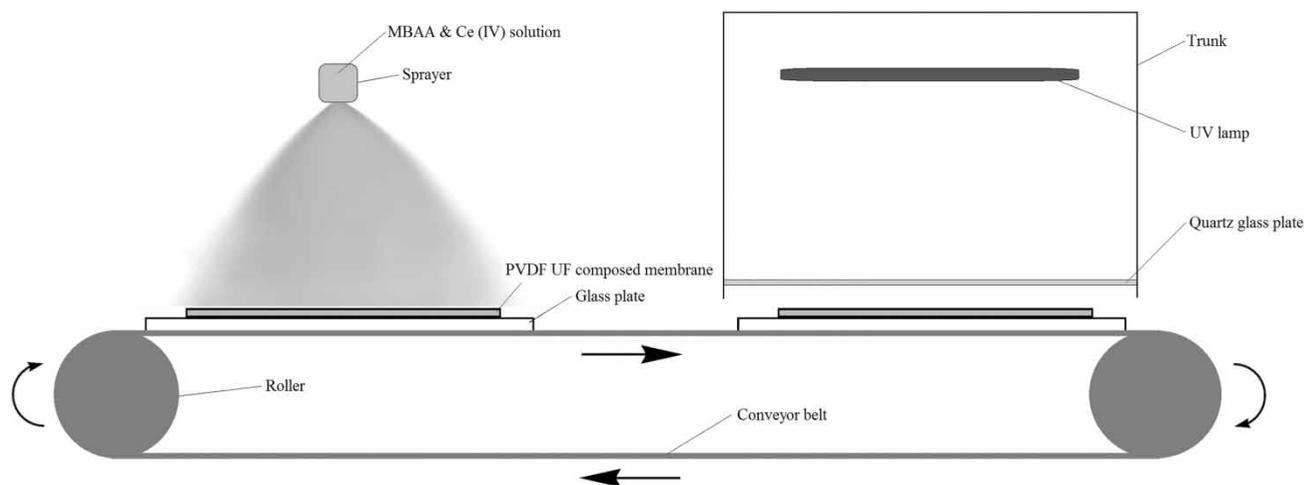
was utilised as the pore former. Dimethylacetamide (DMAc) purchased from Tianjin Kermel Chemical Reagents Development Centre, China, was used as the solvent. MBAA (AR) was purchased from Maya Reagent Co. Ltd, China.  $\text{Ce}(\text{SO}_4)_2$  was purchased from Tianjin Bodi Chemical Regent Co. Ltd, China.  $\text{H}_2\text{SO}_4$  and *n*-butanol were purchased from Beijing Chemical Reagents Development Centre, China. Bovine serum albumin (BSA;  $M_w$  68,000 g/mol) was purchased from Beijing AoBoXing Bio-tech Co., Ltd, China.

### Preparation of PVDF membranes

The membranes were prepared through the immersion precipitation phase inversion method, as described by He & Shi (2014). PVDF powder was dried at  $80^{\circ}\text{C}$  for at least 24 h before use. A casting solution was prepared by blending PVDF, PVP and DMAc. The PVDF and PVP concentrations in the casting solution were 16 and 5 wt%, respectively. After complete dissolution and degassing, the solution was cast on a polyethylene terephthalate nonwoven fabric support ( $80\text{ g/m}^2$ ) by using a hand-casting knife with a knife with a  $350\text{ }\mu\text{m}$  knife gap. The membrane formed with the nonwoven fabric support was then immersed in a coagulation water bath to form an asymmetric membrane. The membrane was rinsed with distilled water and stored in distilled water for 48 h before the next modification by UV photo-grafting.

### Modification by UV photo-grafting

A UV photo-grafting reaction was stimulated with a self-made device. Figure 1 presents a schematic of the experimental setup. The device comprises three parts. The first part is a spray unit. A total of 5 mL of grafting aqueous solution containing MBAA,  $\text{Ce}(\text{SO}_4)_2$  and 0.3 mol/L  $\text{H}_2\text{SO}_4$  was sprayed onto the upper surface of a  $30\text{ cm} \times 30\text{ cm}$  piece of the prepared PVDF composite membrane at room temperature. Five MBAA monomer concentrations, namely, 0.04, 0.07, 0.10, 0.13 and 0.15 mol/L, were selected. The concentrations of Ce(IV) were 0.01, 0.02, 0.03, 0.04 and 0.05 mol/L. The second part is a UV photoradiation trunk. A UV lamp (40 cm length, 500 W) was installed in the trunk. The distance between the lamp and the membrane

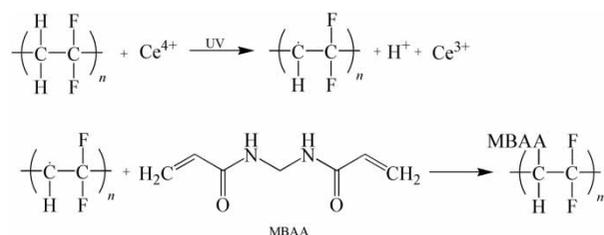


**Figure 1** | Schematic of the experimental set-up for the modification of PVDF membranes through a UV photo-grafting reaction.

was 20 cm. The lamp produced approximately  $5.0 \text{ mW/cm}^2$  irradiation intensity on the membrane surface. Intensity was measured with a UV irradiance meter (model XYI-V, Hangzhou Xinye Optoelectronic Engineering Co. Ltd, China). The third part is an auto-conveyor system. The membrane sprayed with the grafting solution was sent to the radiation trunk via a conveyor belt and was UV-irradiated for a certain period of time.

Figure 2 presents the reaction mechanism of grafting MBAA to PVDF chains, as proposed by Huang *et al.* (2014).  $\text{Ce}^{4+}$  initially oxidises C–H bonds on the polymer membrane surface to produce surface carbon radicals which release  $\text{H}^+$  and change to  $\text{Ce}^{3+}$  during the process. Vinyl groups of MBAA then react with carbon radicals, forming grafted groups.

Five irradiation durations, namely, 1, 3, 5, 7 and 9 min, were set. After UV irradiation, the grafted membrane was rinsed three times with distilled water within 48 h and then stored in distilled water for the next measurement.



**Figure 2** | Reaction of grafting MBAA to the PVDF chain.

## Characterisation of the membranes

The top surface and cross-section morphologies of the unmodified and modified membranes were observed with a scanning electron microscope (SEM; FEI Sirion, The Netherlands). The top surface groups of the unmodified and modified membranes were analysed through attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) technique performed with a Nicolet FT-IR 360 spectrometer. The surface of the membranes was in contact with a ZnSe crystal with a  $45^\circ$  angle of incidence. The absorption spectra were obtained in the region of  $650\text{--}4,000 \text{ cm}^{-1}$  with  $4 \text{ cm}^{-1}$  resolution. The water contact angle on the top surface of the dried membranes was measured with a contact angle instrument (DSA 100, KRÜSS, Germany). The dried membranes ( $20 \text{ mm} \times 20 \text{ mm}$ ) were measured with this equipment with deionised water as the probe. Ten locations were randomly selected for each membrane and the average value was calculated to minimise errors.

## Measurement of water flux recovery

The prepared PVDF membrane without a UV grafting reaction was utilised to treat river water. Figure 3 shows the change in the appearance of river water before and after the treatment. Muddy water became clear after filtration with the membrane. To further evaluate the effect of the



**Figure 3** | Change in the appearance of river water before and after treatment with a self-made pure PVDF membrane.

UV grafting reaction, a water flux recovery experiment was performed to compare the difference in the anti-fouling ability of the membranes by using the river water as feed water in the laboratory. The turbidity of the feed water was 80–100 NTU, as measured with an SGZ-1 digital turbidimeter (Shanghai Yuefeng Instruments & Meters Co. Ltd, China).

The water flux recovery experiment was performed with self-made dead-end filtration equipment. The effective area of each membrane was 20 cm<sup>2</sup>. First, the membrane was pre-pressed with pure water for 30 min at 0.3 MPa. Second, the pressure was changed to 0.1 MPa, and the initial water flux ( $J$ ) was measured within the first 10 min of operation. After this measurement, pure water was changed to river water. After collecting 60 mL of permeation, the membrane was removed from the membrane cell and cleaned three times with pure water in an ultrasonic bath for 3 min. After cleaning, the membrane was reloaded into the membrane cell, and the second water flux ( $J_1$ ) was measured under the same conditions as that in the first measurement. The water flux recovery operations were measured five times for each piece of membrane. Three pieces of each type of membrane were measured. The average flux recovery was calculated with the following equation:

$$R_n = \frac{J_n}{J} (n = 1, 2, 3, 4, 5) \quad (1)$$

### Measurement of porosity and BSA rejection

The porosity of the membranes and rejection to 100 mg/L BSA ( $M_w$  68,000 g/mol) solution were measured to provide more information on the membrane structure. For the porosity measurement, the membranes were placed in an air circulating oven at 60 °C for 24 h to measure the dry mass. The dried membranes were then immersed in *n*-butanol for 24 h at 20 °C to obtain the wet mass. Membrane porosity ( $\epsilon_p$ ) was calculated with the equation:

$$\epsilon_p = \frac{(m_w - m_d)/\rho_w}{(m_w - m_d)/\rho_w + m_d/\rho_p} \times 100\% \quad (2)$$

where  $m_w$  and  $m_d$  are the mass of wet and dry membranes, respectively.  $\rho_w$  and  $\rho_p$  are the densities of *n*-butanol (0.81 g/cm<sup>3</sup>) and PVDF (1.78 g/cm<sup>3</sup>), respectively. For each type of membrane, five samples were measured to obtain the average result.

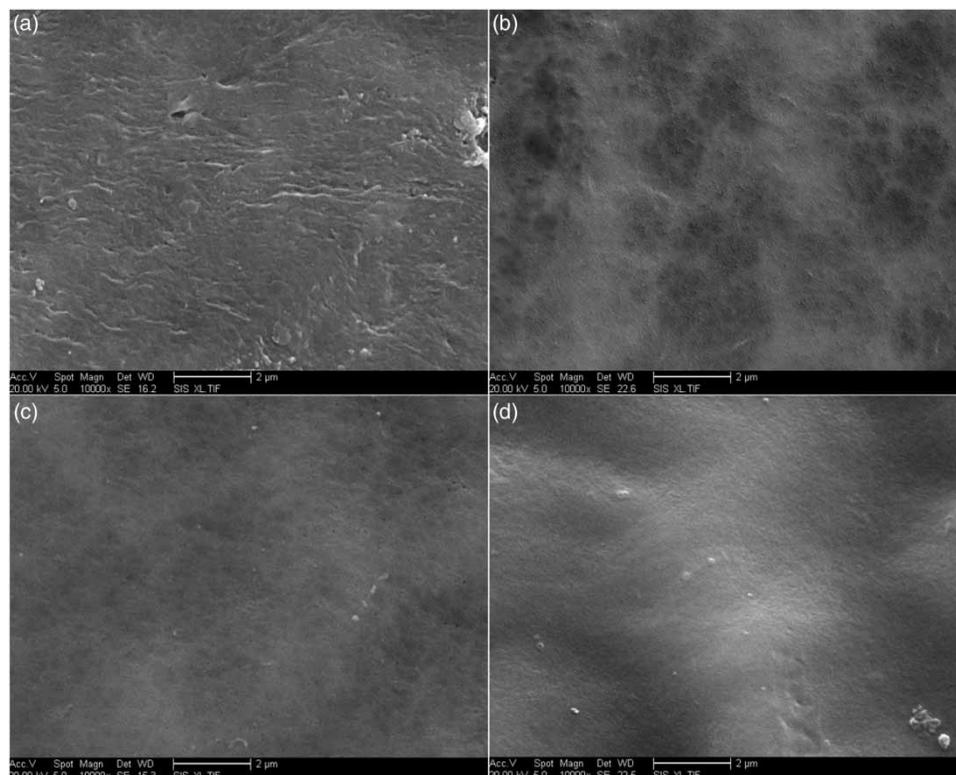
The same filtration equipment utilised in the water flux recovery experiment was used to measure BSA rejection. The permeation operation was performed only once. Three samples were measured for each type of membrane, and the average rejection (%) was calculated with the equation:

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

where  $C_p$  and  $C_f$  (mg/L) are the BSA concentrations in the permeation and feed sides, respectively. The BSA concentration in the permeation solutions was measured with a UV-vis spectrophotometer (T6, Beijing Purkinje General Instrument, China) at 280 nm.

## RESULTS AND DISCUSSION

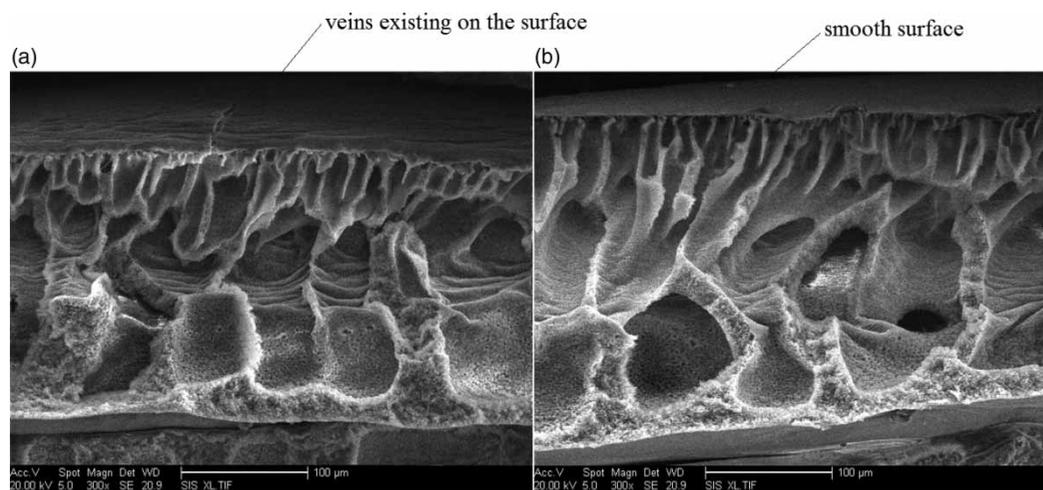
Figure 4 shows the top surface SEM morphologies of the pure PVDF and three modified membranes prepared under the following conditions: MBAA concentration of 0.07 mol/L, Ce(IV) concentration of 0.04 mol/L and irradiation duration of 1, 3 and 9 min. The surface of the pure membrane was not smooth. By contrast, the surface of the modified membrane was smooth, and no veins existed



**Figure 4** | Surface SEM morphologies of PVDF membranes: (a) pure membrane; (b) modified membrane (MBAA concentration of 0.07 mol/L, Ce(IV) concentration of 0.04 mol/L, irradiation duration of 1 min); (c) modified membrane (MBAA concentration of 0.07 mol/L, Ce(IV) concentration of 0.04 mol/L, irradiation duration of 3 min); (d) modified membrane (MBAA concentration of 0.07 mol/L, Ce(IV) concentration of 0.04 mol/L, irradiation duration of 9 min).

on the surface. Evidently, the surface was covered with a dense grafted layer as the irradiation duration lengthened. Grafting modification improved the smoothness of the membrane surface.

Figure 5 shows the cross-section SEM morphologies of the pure PVDF and modified membranes prepared under the following conditions: MBAA concentration of 0.07 mol/L, Ce(IV) concentration of 0.04 mol/L and



**Figure 5** | Cross-section SEM morphologies of PVDF membranes: (a) pure membrane; (b) modified membrane (MBAA concentration of 0.07 mol/L, Ce(IV) concentration of 0.04 mol/L, irradiation time of 3 min).

irradiation duration of 3 min. No obvious change occurred in the cross-section morphology of the membrane after the grafting treatment. The grafting reaction occurred mainly on the membrane surface.

Figure 6 presents the ATR-FTIR spectra of the top surfaces of the pure PVDF and modified membranes prepared under the same conditions. The absorption peak at around  $1,180\text{ cm}^{-1}$  is attributed to the stretching vibration of C–F. The absorption peak at  $1,660\text{ cm}^{-1}$  is the stretching vibration of C=O of the amide group and that at  $1,530\text{ cm}^{-1}$  is the bending vibration of N–H of the amide group. The ATR-FTIR spectra proved that MBAA was successfully grafted onto the surface of the membrane.

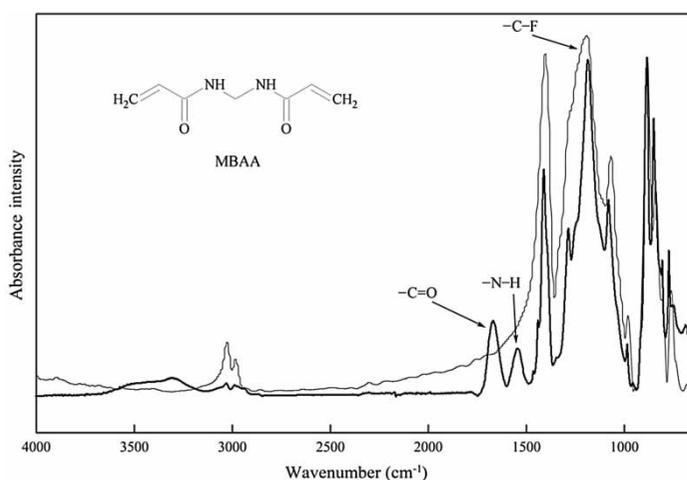
Figure 7 shows the plots of flux recovery versus cleaning time for the modified membranes prepared at different irradiation times when the MBAA and Ce(IV) concentrations were 0.07 and 0.04 mol/L, respectively. For the modified membrane prepared at 1 min irradiation, flux recovery decreased sharply when only three cleaning operations were performed. When the cleaning times reached four and five times, flux recovery no longer decreased. However, the flux recovery of the other modified membranes decreased gradually as the cleaning time increased because the very short irradiation duration (e.g., 1 min) resulted in a considerably low grafted monomer content on the membrane surface. Compared with the grafted location on the membrane surface, the location without grafted MBAA induced a stronger fouling effect by adsorbing pollutants.

When the irradiation duration was longer than 5 min, a sufficient amount of MBAA was grafted onto the membrane surface. Consequently, the flux recovery of the membranes prepared at 5, 7 and 9 min decreased gradually with cleaning time because the grafted MBAA covered the entire surface of the modified membranes.

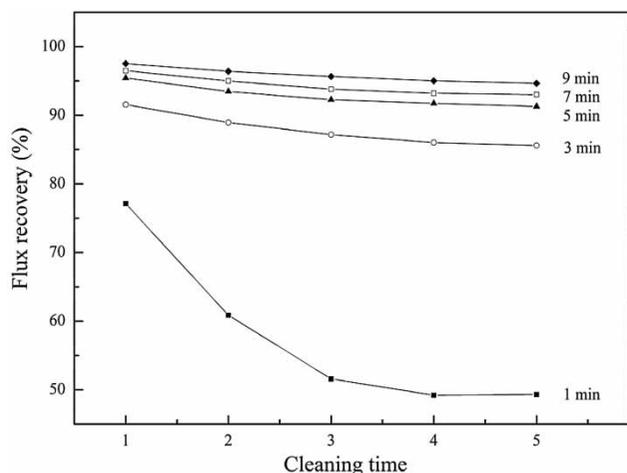
Figure 8 shows the plot of fifth flux recovery versus the irradiation duration for the preparation of the modified membranes. The flux recovery of the pure PVDF membrane is also plotted in the figure. When the irradiation duration changed from 1 min to 3 min, flux recovery increased sharply from 49.3% to 85.6%. When the irradiation duration increased from 5 min to 9 min, flux recovery increased from 91.2% to 94.7%. Therefore, for a grafting solution containing 0.07 mol/L MBAA and 0.04 mol/L Ce(IV), 3–5 min of irradiation duration is sufficient to obtain a grafting reaction.

Figure 9 shows the plot of water contact angle versus irradiation duration for the preparation of the modified membranes. The water contact angle decreased with the irradiation duration. Therefore, the hydrophilicity of the modified membranes was enhanced compared with that of the pure PVDF membrane.

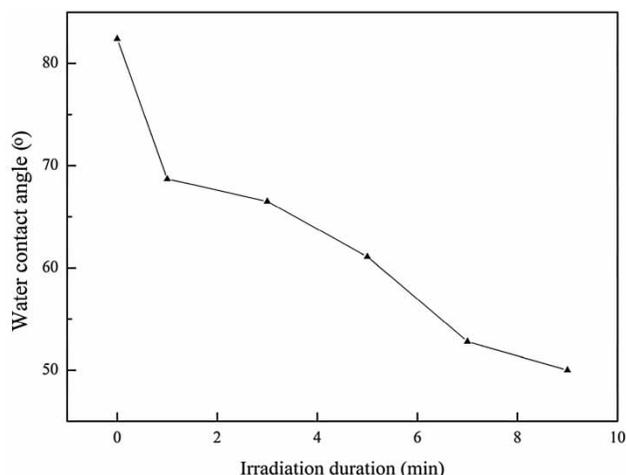
Figure 10 shows the plot of porosity versus irradiation duration for the preparation of the modified membranes. Porosity decreased slightly as the irradiation duration lengthened. Given that MBAA molecules do not contain the F element, grafting MBAA to PVDF would decrease



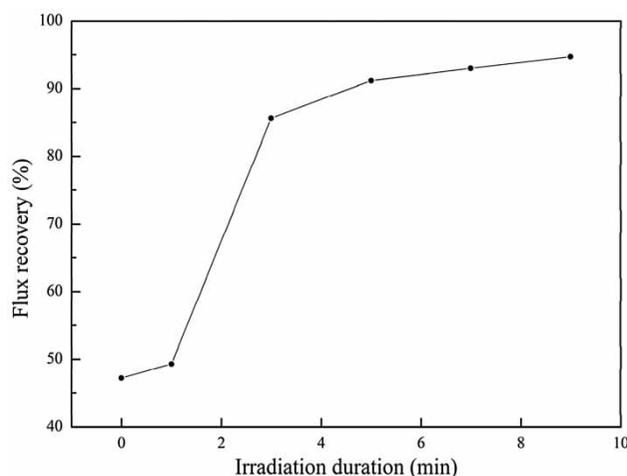
**Figure 6** | ATR-FTIR spectra of the top surfaces of the PVDF membranes: thin line, pure membrane; thick line, modified membrane (MBAA concentration of 0.07 mol/L, Ce(IV) concentration of 0.04 mol/L, irradiation duration of 3 min).



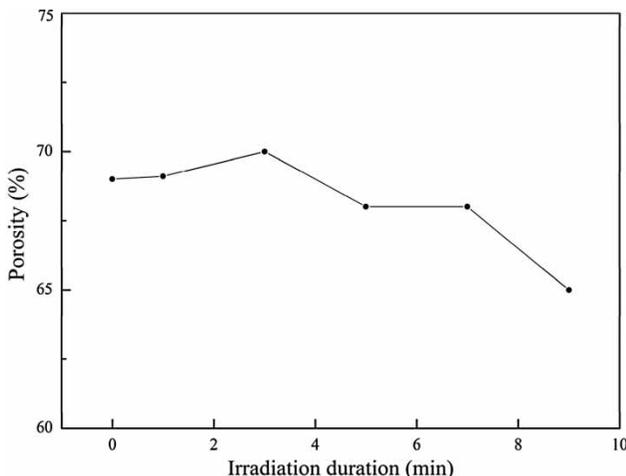
**Figure 7** | Plots of flux recovery versus cleaning time for the modified membranes prepared at different irradiation durations (MBAA concentration of 0.07 mol/L, Ce(IV) concentration of 0.04 mol/L).



**Figure 9** | Plot of water contact angle versus irradiation duration for the preparation of the modified membranes (MBAA concentration of 0.07 mol/L, Ce(IV) concentration of 0.04 mol/L).



**Figure 8** | Plot of fifth flux recovery versus irradiation duration for the preparation of the modified membranes (MBAA concentration of 0.07 mol/L, Ce(IV) concentration of 0.04 mol/L).



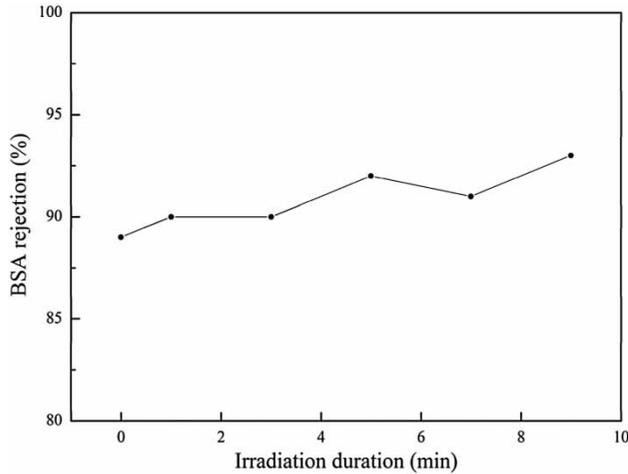
**Figure 10** | Plot of porosity versus irradiation duration for the preparation of the modified membranes (MBAA concentration of 0.07 mol/L, Ce(IV) concentration of 0.04 mol/L).

the density parameter ( $\rho_p$ ) in Equation (2) (smaller than  $1.78 \text{ g/cm}^3$ ). Therefore, the calculated porosity decreased when MBAA was grafted onto the membranes.

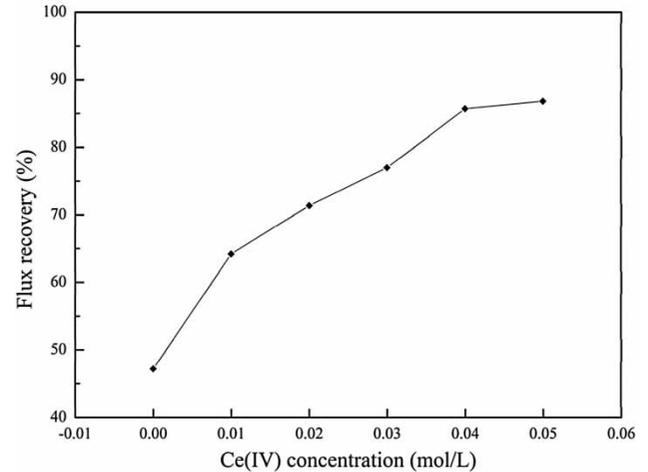
Figure 11 shows the plot of BSA rejection versus irradiation duration for the preparation of the modified membranes. BSA rejection increased slightly with irradiation duration because the size of the surface pores of the membranes decreased when MBAA was grafted onto the pore edges.

Figure 12 shows the plot of the fifth flux recovery versus MBAA concentration for the preparation of the modified

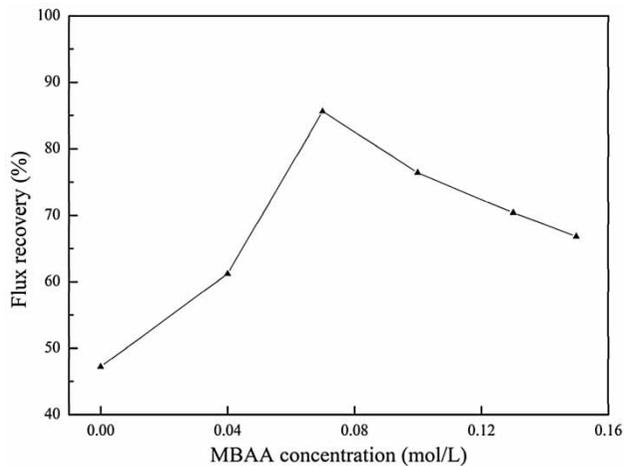
membranes when the Ce(IV) concentration was 0.04 mol/L and the irradiation duration was 3 min. The maximum flux recovery occurred when the MBAA concentration was 0.07 mol/L. Adding more monomers into the grafting solution decreased flux recovery because MBAA is a multifunctional monomer. The self-crosslinking reaction in the grafting solution strengthened as the solution concentration increased. Thus, more monomer molecules were consumed, and the amount of MBAA grafted onto the surface decreased.



**Figure 11** | Plot of BSA rejection versus irradiation duration for the preparation of the modified membranes (MBAA concentration of 0.07 mol/L, Ce(IV) concentration of 0.04 mol/L).



**Figure 13** | Plot of fifth flux recovery versus Ce(IV) concentration for the preparation of the modified membranes (MBAA concentration of 0.07 mol/L, irradiation duration of 3 min).



**Figure 12** | Plot of fifth flux recovery versus MBAA concentration for the preparation of the modified membranes (Ce(IV) concentration of 0.04 mol/L, irradiation duration of 3 min).

Figure 13 shows the plot of the fifth flux recovery versus Ce(IV) concentration for the preparation of the modified membranes when the MBAA concentration was 0.07 mol/L and the irradiation duration was 3 min. Flux recovery always increased as the Ce(IV) concentration increased because more Ce(IV) meant more reaction sites for grafting on the membrane surface. However, when the Ce(IV) concentration was higher than 0.04 mol/L, flux recovery increased slightly because the potential reacting sites on the membrane surface were almost activated by Ce(IV).

Certain key preparation conditions were selected from four studies (Table 1) to compare the changes in the hydrophilicity and flux recovery performance of the modified PVDF membranes prepared at different UV conditions. The water contact angle in this work decreased by about  $16^\circ$ , and flux recovery increased by about 40%. Compared with that in other published studies, the performance enhancement of the modified membrane in the current study was moderate, but the UV irradiation duration (3 min) was significantly shorter. Consequently, the UV modification in the current work generated satisfactory integrative effects in consideration of both irradiation duration and enhanced performance.

## CONCLUSION

When Ce(IV) is used as the initiator and MBAA as the monomer, MBAA can be grafted onto the surface of pure PVDF membranes through the water-phase grafting method under UV photoradiation. At 0.07 mol/L MBAA concentration, 0.04 mol/L Ce(IV) concentration and 3 min irradiation duration, the membrane surface can be grafted with a sufficient amount of monomer under  $5.0 \text{ mW/cm}^2$  UV photoradiation intensity. Compared with that in the pure PVDF membrane, the water contact angle on the surface of the modified membrane decreased by

**Table 1** | Surface UV grafting modified PVDF membrane

Membranes	Initiator	Monomer	UV lamp	Irradiation duration (min)	Water contact angle (°)	Flux recovery (%)	Reference
Unmodified pure PVDF					89.6	–	Gu et al. (2013)
Modified PVDF	BP	4-VP/ BCl	700 W	40	76.4–69.8	–	Gu et al. (2013)
Unmodified pure PVDF					92.3	24	Rahimpour et al. (2009)
Modified PVDF	–	AA	160 W	5	74.0	45–46	Rahimpour et al. (2009)
Modified PVDF	–	HEMA	160 W	5	66.0	52–57	Rahimpour et al. (2009)
Modified PVDF	BP	PDA	160 W	5	82.7	29–31	Rahimpour et al. (2009)
Modified PVDF	BP	EDA	160 W	0.5	78.6	32	Rahimpour et al. (2009)
Unmodified PVDF/ PES					73	32.8	Zhang et al. (2009)
Modified PVDF/PES	–	NVP	500 W, 3.44 mW/cm <sup>2</sup>	1–10	70–32	83.3–93.4	Zhang et al. (2009)
Unmodified polyHEMA-g- PVDF					75.3	42.4	Li et al. (2012)
Modified polyHEMA-g- PVDF	Ce(IV)	EBAA	–	300	22.1	96.3	Li et al. (2012)
Unmodified pure PVDF					82.4	47.2	This work
Modified PVDF	Ce(IV)	MBAA	5.0 mW/cm <sup>2</sup>	3	66.5	85.0	This work

BP, benzophenone; 4-VP, 4-vinylpyridine; BCl, *n*-butyl chloride; AA, acrylic acid; HEMA, 2-hydroxyethylmethacrylate; PDA, 2,4-phenylenediamine; EDA, ethylene diamine; NVP, N-vinyl-2-pyrrolidone; EBAA, N,N'-ethylene bisacrylamide; MBAA, N,N'-methylene-bisacrylamide.

approximately 16°, and flux recovery increased by approximately 40%. With regard to BSA rejection and porosity measurements, no significant changes were observed between the pure PVDF and the graft-treated membranes. Compared with that in other published studies, the enhanced performance of the modified membrane in the current work was moderate, but the UV irradiation duration (3 min) was significantly shorter. This work is significant because the integrative effects of the UV-grafted membranes were satisfactory when both irradiation duration and enhanced performance are considered.

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