In-situ construction of antifouling separation layer *via* a reaction enhanced surface segregation method

Mingrui He, Yanlei Su, Runnan Zhang, Yanan Liu, Shiyu Zhang, Zhongyi Jiang *

Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China
Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

HIGHLIGHTS

- A reaction enhanced surface segregation method was first explored.
- An antifouling separation layer was *in-situ* constructed at membrane surface.
- The thickness and the effective pore size of the layer could be manipulated.
- The resulting membranes exhibited good ultrafiltration performance.

GRAPHICAL ABSTRACT
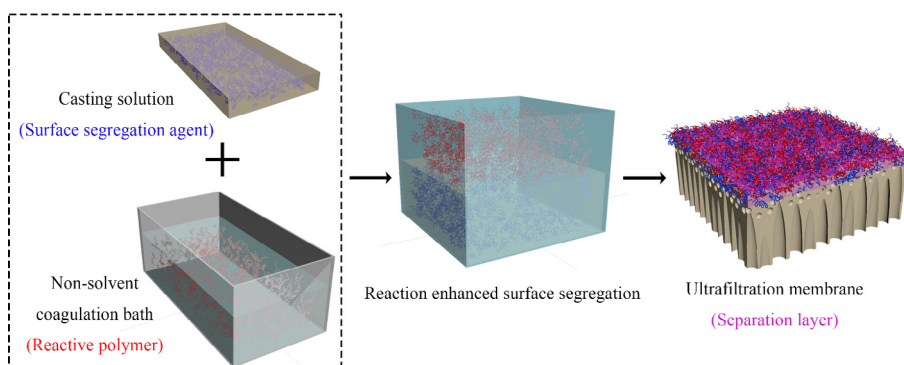
ABSTRACT

In this study, a reaction enhanced surface segregation method was explored for *in-situ* construction of antifouling separation layer on membrane surface. Polyvinyl pyrrolidine (PVP) is used as the surface segregation agent in the casting solution and polyacrylic acid (PAA) is used as the additive in the coagulation bath. During the membrane formation process, PVP and PAA spontaneously migrate to the surface of the polyvinylidene fluoride (PVDF) support in an opposite direction and form a crosslinked separation layer based on the hydrogen bonding interaction. The resultant layer has smaller effective pore size and higher hydrophilicity compared with the PVDF control membrane, which renders enhanced antifouling and separation performance. In the ultrafiltration of oil–water emulsion, the rejection was 100%, the initial water flux was 695 ± 33 L m^{-2} h^{-1} bar^{-1}, and the FRR was 95.2%; meanwhile, in the ultrafiltration of BSA solution, the rejection was 90.3%, the initial water flux was 603 ± 18 L m^{-2} h^{-1} bar^{-1} and the FRR was 92.3%. This study offered a novel and facile method for antifouling membrane surface construction.

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1. Introduction

Membrane separation technology has been widely applied in the field of water treatment (Shannon et al., 2008). High selectivity and persistent high flux are the critical parameters of separation membranes, therefore, the construction of properly sized membrane pores and antifouling membrane surfaces always lies in the heart of membrane materials development (Howorka, 2017; Rana and Matsuura, 2010).

Surface segregation, as an *in-situ* method to construct antifouling membrane surfaces which is inspired by the self-assembly process of cell membranes, has been more and more actively exploited

* Corresponding author at: Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China.

E-mail address: zhyjiang@tju.edu.cn (Z. Jiang).

(Zhao et al., 2014). As two kinds of most popular surface segregation agents (SSA), polyethylene oxide (PEO)-based and zwitterionic polymers can be enriched at the membrane surface by free or force surface segregation process, which bind water molecules *via* hydrogen bonding and electrostatic interactions to generate a robust hydration shell as "water barrier" (Tielrooij et al., 2010; Waluyo et al., 2011; Wang et al., 2006; Zhao et al., 2016). Till now, the surface segregation method has been successfully used in preventing the fouling of oil, protein and bacteria in a broad range of seawater desalination and wastewater purification applications (Hester et al., 1999; Liu et al., 2016; Wang et al., 2011). For a typical surface segregation method, SSA, often an amphiphilic polymer, is blended with the hydrophobic membrane bulk material in the casting solution. During the non-solvent (often water) induced phase separation process, the exchange of solvent and non-solvent forms a concentration gradient near the membrane surface which spontaneously drives the surface segregation of the SSA. As a result, majority of the SSA is enriched at the membrane surface with the hydrophilic segments stretching outwards to form a brush layer and the hydrophobic segments anchoring inside (Zhang et al., 2016). In this process, the SSA also acts as the pore-forming agent, which affected the porosity and pore sizes of the membrane *via* the mediation on the phase separation process of the membrane bulk material (Kim and Lee, 1998; Zhao et al., 2008). Usually, the surface modification effect and the pore-forming effect of the SSA are strongly coupled, which is not convenient for the manipulation of the membrane antifouling and separation performance independently. For example, the enhancement of the anchoring stability of the SSA often accompanied with the undesirable increase of membrane pore sizes and the decline of the membrane selectivity (He et al., 2016; He et al., 2017).

In this study, a reaction enhanced surface segregation method (named as RESS) was proposed to uncouple the surface modification effect and the pore-forming effect of the SSA. The key point of RESS is that a hydrophilic polymer can quickly crosslink the SSA (referred as the reactive polymer). The reactive polymer added in the non-solvent coagulation bath can freely migrate onto the membrane surface, meanwhile, the SSA in the casting solution can spontaneously segregate to the membrane surface in an opposite direction. Upon the contact of the reactive polymer and the SSA, the *in-situ* crosslinking reaction occurs and forms a nascent layer at membrane surface. With the further migration of the reactive polymer and the surface segregation of the SSA, the nascent layer is gradually developed into a compact and thick layer with selective separation performance, which is basically independent of the primary membrane pores. In a sense, the RESS method shares much similarity to that of interfacial polymerization method, thus the selectivity of the resultant separation layer can be controlled by the types and concentration of both the reactive polymer and the SSA. However, the major differences are that the RESS is an assembly of polymers and the two phases (solvent and non-solvent) have no strict phase boundary, which lead to the looser separation layer compared with that formed *via* interfacial polymerization layer. Consequently, the separation layer will be more suitable for ultrafiltration. In consideration of the quick reaction rate, low manufacturing cost and excellent environmental safety, the crosslinking reaction between polyvinyl pyrrolidine (PVP) and polyacrylic acid (PAA) based on hydrogen bonding was chosen in this study. PVP as utilized as the SSA, and PAA was utilized as the reactive polymer. The negative conjugation effect in PAA lowered the electron cloud density of the hydrogen atom, increasing its ability as the hydrogen bonding donor (Zheng et al., 2017), and the keto-enol tautomerizing in PVP elevated the electron cloud density of the oxygen atom, increasing its ability as the hydrogen bonding accepter (Kothari et al., 2015; Song

et al., 2016). Accordingly, the resulting membranes exhibited tunable separation performance and superior long-term antifouling performance.

2. Experimental

2.1. Materials

Commercial PVDF (R904) was purchased from Shanghai 3F New Material Co. Ltd. (China) and was dried at 70 °C for 24 h before use. Polyvinylpyrrolidone (PVP, M_w = 10 kDa) was purchased from Tianjin Heowns Biochemical Technology Co. Ltd. (China). Polyacrylic acid (PAA, M_w = 5, 50 kDa) was purchased from Shanghai Macklin Biochemical Co. Ltd. (China). N, N-dimethyl formamide (DMF) was purchased from Kewei Chemicals Co. (Tianjin, China). Deionized water was produced by Elix® Essential 5, which was purchased from Merck Millipore Co. (America). A series of dextran with different molecular weight (Mw 70, 150, 250 kDa) was purchased from J&K Scientific (China).

2.2. Membrane preparation

The formulations of the casting solution, the coagulating bath and the post treatment were listed in Table 1. Since PVP could be also the pore-forming agent, in order to eliminate its influence on the membrane separation performance, the molecular weight and content of PVP were fixed. The PAA content varied from 0.1 wt%, 0.2 wt%, 0.3 wt% to 0.4 wt% and the PAA molecular weight of 5 kDa and 50 kDa were chosen as the major variables, and the resulting membranes were denoted as Membrane 1#, 2#, 3#, 4#, 6#, 7#, 8# and 9#, respectively. Membrane 0# was the blank control group with no reaction. Membrane 5# and 10# were the post treatment control groups with the reaction happened after the coagulation bath step. The detailed membrane preparation steps were as follows: Firstly, the casting solution was stirred at 80 °C for about 4 h for homogeneous mixture, and stewed for 2 h for complete bubble release. Then, the casting solution was cooled down to about 25 °C and uniformly casted on a glass plate with the thickness of 240 μm using a knifing stick. At last, the glass plate with the liquid membrane was quickly immersed in the coagulation bath at 25 °C for 10 min. In order to ensure that PVP was only able to contact and react with PAA at the membrane top surface in the coagulation bath, the glass plate was modified with tapes to prevent the peeling of the membrane from the glass plate. The post treatment was conducted also at 25 °C for 10 min. The pristine membrane was rinsed with deionized water to remove the unreacted PAA and PVP on the surface, and kept in water to remove residual solvent for at least 12 h before utilization.

2.3. Characterizations

The surface and cross-section morphologies of the membranes were observed using the Field emission scanning electron microscopy (FESEM, Nova Nanosem 430, FEI Co., USA). The element composition variation with the distance from membrane surfaces were measured using the Energy dispersive spectrometer (EDS, Genesis XM2 APEX 60SEM, EDAX Co., USA) at the line scanning model. The membrane samples freeze-dried with the vacuum freeze dryer (Alpha 1-2 LD plus, Christ Co., German) were broken in liquid nitrogen and sputtered with gold for generating electric conductivity. The thermal properties of the membranes were measured using the Differential scanning calorimetry (DSC, 200F3, NETZSCH Co., Germany) at the heating and cooling rate of 10 °C/min under a nitrogen (N_2) atmosphere. The mechanical performance of the membranes at the dry state was investigated by the electronic