Applied Surface Science 356 (2015) 659–667

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

# Tailoring interlayer structure of molecular layer-by-layer assembled polyamide membranes for high separation performance

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## ARTICLE INFO

*Article history:*
Received 23 June 2015
Received in revised form 2 August 2015
Accepted 14 August 2015
Available online 18 August 2015

*Keywords:*
Molecular layer-by-layer assembly
Polyamide
Thin film composite membranes
Multilayered coatings
Reverse osmosis desalination
Water purification

## ABSTRACT

A molecular layer-by-layer (mLbL) technique was recently developed to fabricate polyamide (PA) thin film composite (TFC) membranes for water purification. In this study, the interlayer structure between the selective and support layers of the mLbL-assembled TFC membrane was tailored to achieve high performance applicable to seawater desalination. Introducing interlayers on porous supports prior to mLbL deposition allowed the effective PA growth by preventing monomer deposition within the support pores. The PA layers were grown *via* mLbL on supports coated by a series of interlayers: poly(piperazine-amide), cross-linked poly(ethyleneimine) (PEI) and a polyelectrolyte bilayer of PEI and poly(acrylic acid) (PAA) (PEI/PAA). The density and distribution of surface carboxyl groups of the interlayer were found to be key parameters that determine the structure and performance of the mLbL-assembled membranes. Among the interlayers examined, the PEI/PAA interlayer not only yielded membranes with superior performance but also with a highly smooth surface beneficial for antifouling.

## 1. Introduction

Membrane-based reverse osmosis (RO) has become a predominant technology for desalination and wastewater treatment [1,2]. Contemporary RO membranes are fabricated as a polyamide (PA) thin film composite (TFC) platform comprising an ultrathin PA selective layer sitting on top of a porous support, where membrane performance is determined primarily by the topmost PA selective layer. This selective layer has been conventionally prepared *via* interfacial polymerization (IP) of trimesoyl chloride (TMC) in the organic phase and *m*-phenylenediamine (MPD) in the aqueous phase on a porous support [1–3]. When the immiscible aqueous and organic phases are brought into contact, the two monomers immediately react at the interface to form a highly cross-linked PA layer. Due to the fast reaction rate and reasonable solubility of MPD in organic phase, IP takes place in the organic phase and proceeds by MPD diffusion from the aqueous phase to the organic phase [4–7]. Subsequent MPD monomer diffusion and reaction lead to film growth, which restricts additional monomer diffusion [8]. This multi-staged IP process typically results in the formation of a relatively thick and rough (so called "ridge and valley" structure) PA selective layer with a highly depth-heterogeneous structure [6,7]. In addition, many process parameters, including the reactivity, diffusivity, and solubility of the monomers and the types of solvents, affect the selective layer structure and thus membrane performance [9,10]. Due to its diffusion-controlled and complex nature, IP process provides little control over the selective layer structure, which greatly limits membrane separation performance and thus necessitates the development of a new membrane fabrication technique.

Recently, we devised a molecular layer-by-layer (mLbL) assembly to prepare the PA selective layer in a highly-controlled manner, which is not achievable by the conventional IP process [11,12]. In this mLbL process, two reactive monomers (e.g., MPD and TMC) are alternatively cross-linked at the molecular level to produce a tightly compact PA selective layer with well-defined structure, tunable thickness, and minimal surface roughness. To assemble

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http://dx.doi.org/10.1016/j.apsusc.2015.08.119
0169-4332/

the PA selective layer on a porous support *via* mLbL, we applied an ultrathin *interlayer* on top of the porous support prior to the mLbL deposition. This strategy allows the fabrication of defect-less TFC membranes that exhibited superior separation performance and antifouling properties when compared to those prepared by conventional IP.

In our previous studies [11,12], we focused on understanding the structure and properties of the mLbL-assembled PA selective layer and their relationships with membrane performance. However, there are two main reasons for studying the effects of the interlayer structure and chemistry on membrane performance. First, it has been reported that the selective layer does not solely dictate membrane performance, but that the interface between the selective layer and the support plays a crucial role as well [13,14]. Second, the structure and integrity of the mLbL-assembled PA selective layer could be affected significantly by the physical and chemical structure of the interlayer on which the PA layer is grown [15]. Hence, it is imperative to understand the role of the *interlayer*, which serves as an interface in the mLbL-assembled TFC membrane, in determining the selective layer structure and thus membrane performance in order to rationally design the TFC membrane *via* mLbL.

In the present study, we investigated the effect of the structural and chemical properties of the interlayer on the structure and performance of the resulting mLbL-assembled TFC membrane. A porous polyacrylonitrile (PAN) ultrafiltration membrane was selected as the support due to its excellent chemical stability and tunability in surface functionality, hydrophilicity, and charge properties [10,16]. The PA selective layers were fabricated on the uncoated porous PAN supports as well as the interlayer-coated PAN supports *via* mLbL. A series of interlayers, including interfacially polymerized poly(piperazine-amide) (PIPA), cross-linked polyethyleneimine (PEI) (xPEI), and the electrostatically assembled polyelectrolyte bilayer of PEI and poly(acrylic acid) (PAA) (PEI/PAA), were prepared prior to mLbL. Finally, we correlated the physicochemical structures of the interlayers with the structures and separation performances of the mLbL-assembled membranes to elucidate the role of the interlayer.

## 2. Experimental

### 2.1. Materials

Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

The following chemicals were used as received: branched polyethyleneimine (PEI, $M_w = 750{,}000\,\mathrm{g\ mol^{-1}}$, Sigma-Aldrich), poly(acrylic acid) (PAA, $M_w = 100{,}000\,\mathrm{g\,mol^{-1}}$, Sigma–Aldrich), piperazine (PIP, Sigma–Aldrich), *m*-phenylenediamine (MPD, Sigma–Aldrich), trimesoyl chloride (TMC, Sigma–Aldrich), HPLC-grade toluene (J.T. Baker), *n*-hexane (J.T. Baker), acetone (J.T. Baker), sodium chloride (NaCl, Junsei Chemical Co.), sodium hydroxide (NaOH, Daejung Chemical Co.). Deionized (DI) water (18.2 MΩ cm) was prepared in a Millipore Milli-Q purification system. Polyacrylonitrile (PAN) membranes (PAN 50) as supports were purchased from Sepro Membranes, Inc. A PAN support is mechanically reinforced by a polyester nonwoven fabric layer to ensure the mechanical strength of the membrane that can withstand the highly-pressurized operating conditions.

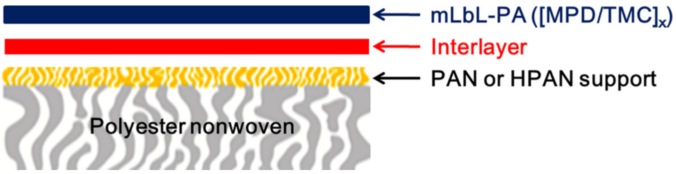

**Fig. 1.** Schematic illustration of the fabrication of the mLbL-assembled PA TFC membranes. Membranes are denoted as support (interlayer)[MPD/TMC]$_x$.

### 2.2. Membrane preparation

#### 2.2.1. Interlayer preparation

A series of mLbL-assembled TFC membranes were fabricated by creating PA selective layers on interlayer-coated PAN supports *via* mLbL deposition of MPD and TMC as illustrated in Fig. 1. Four different interlayer systems were systematically designed: interlayer-free, interfacially polymerized, cross-linked poly(piperazine-amide) (PIPA), PEI cross-linked with TMC (xPEI), and electrostatically assembled polyelectrolyte bilayer of PEI and PAA (PEI/PAA).

For the interlayer-free case, a pristine PAN or hydrolyzed PAN (HPAN) was used as a support on which the PA selective layer was grown *via* mLbL. HPAN was prepared by soaking a PAN support into an aqueous solution of 1.5 M NaOH at 45 °C for 2 h, which is known to increase its surface negative charge and hydrophilicity [17]. The PIPA interlayer was prepared by interfacial polymerization of PIP and TMC on a PAN support. A PAN support was soaked into an aqueous solution of PIP (2.0 wt%) for 3 min and excess PIP was removed with a rubber roller. Then, a TMC (0.05 wt% or 0.5 wt%) solution in *n*-hexane was poured onto the membrane and allowed to react for 30 s. The remaining solution was drained off, and subsequently the membrane was rinsed with pure *n*-hexane several times. To prepare the xPEI interlayer, a negatively charged HPAN support was first dipped into an aqueous solution of cationic PEI (0.1 wt%, pH 10.6) containing 0.5 M NaCl for 15 min and subsequently washed with DI water. Cross-linking PEI with TMC was carried out by immersing the PEI-coated HPAN support into a TMC solution in toluene for 5 min [18]. For the fabrication of PEI/PAA interlayer, the PEI-coated HPAN was dipped into an aqueous solution of anionic PAA (0.1 wt%, pH 3.5) containing 0.5 M NaCl for 10 min, followed by rinsing with DI water.

#### 2.2.2. Selective layer preparation

TFC membranes were prepared by fabricating the PA selective layers on the interlayer-coated PAN supports *via* mLbL as described previously [11,12]. The first step started with immersing the uncoated support or the interlayer-coated PAN support into a MPD (1.0 wt%) solution in toluene for 30 s and subsequent rinsing it with acetone to remove the unreacted MPD. Then, the membrane was dipped into a TMC (1.0 wt%) solution in toluene for 30 s, followed by rinsing with toluene to complete one mLbL deposition cycle. This process was repeated to obtain the desired mLbL cycle number, which controls the growth of the PA layer. The resultant mLbL-assembled TFC membrane consists of a PAN support, an interlayer and a mLbL-PA selective layer and they were denoted as support(interlayer)[MPD/TMC]$_x$, where the subscript *x* represents the mLbL cycle number. For example, the PAN(PIPA)[MPD/TMC]$_{10}$ membrane consists of the PA selective layer prepared with 10 mLbL cycles on top of a PIPA interlayer-coated PAN. In addition to the mLbL-assembled membranes, the conventional TFC membrane was prepared *via* IP as a control. A PAN support was immersed into an aqueous solution of MPD (2.0 wt%) for 3 min and rolled with a rubber roller to remove excess MPD solution. Then, a TMC (0.05 wt%) solution in *n*-hexane was poured onto the membrane and allowed