



Novel methodology for facile fabrication of nanofiltration membranes based on nucleophilic nature of polydopamine



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ARTICLE INFO

Article history:

Received 16 December 2015

Received in revised form

19 March 2016

Accepted 21 March 2016

Available online 26 March 2016

Keywords:

Polydopamine

Nanofiltration membrane

Grafting

Trimesoyl chloride

Poly(ethyleneimine)

ABSTRACT

Novel methodology for facilely fabricating nanofiltration (NF) composite membrane has been successfully developed by employing nucleophilic nature of polydopamine (PDA) chemistry. The self-polymerized PDA coating over polysulfone (PSf) substrate was utilized as a key intermediate layer for trimesoyl chloride (TMC) grafting followed by poly(ethyleneimine) (PEI) deposition to construct the hierarchically structured separation layer of NF membrane. In contrast to the electrophilic quinone moieties of PDA layer usually involved in the Michael addition and Schiff base reactions with polymeric amines for membrane preparation in previous reports, the phenolic hydroxyl groups of catechol moieties as well as amine groups at the PDA layer possess nucleophilic nature, which are capable of quickly coupling with the highly reactive acyl chlorides to form ester and amide bonds in the step of TMC grafting, resulting in TMC moieties covalently anchored at the PDA layer with free acyl chloride groups. Such created acyl chlorides are further coupled with the amine groups of branched PEI polymer in the PEI deposition procedure to form the stable amide bonds linking the PDA base layer and PEI upper layer in the resulting hierarchical separation layer. The properties of membranes prepared at different stages were characterized with respect to surface chemistry, pore properties, and separation performances to understand deeply the newly developed methodology for membrane preparation. Further studies focusing on NF properties and stability of the developed NF membrane revealed that such membrane shows high efficiencies in retention of divalent cations, small organic molecules as well as heavy metal ions, and exhibits desirable thermal stability and long-term performance stability.

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1. Introduction

Over the past few decades, nanofiltration (NF) membrane with properties between ultrafiltration (UF) and reverse osmosis (RO) has attracted considerable research interests because of its distinguishing characteristics such as low rejection of monovalent ions, high rejection of multivalent ions and small organic species, as well as low energy consumption [1]. In general, most of NF membranes have a charged selective layer with negative or positive characteristic due to the ionization of surface functional groups. During the NF process, rejection of uncharged solutes is mainly governed by the size exclusion mechanism; while the electrostatic interaction based Donnan mechanism plays a key role in determining the separation behaviors of the charged solutes [2]. To date, most commercial NF membranes are thin film composite (TFC) membranes comprising polyamide separation layers

fabricated by interfacial polymerization (IP) technique. However, great deals of research efforts have been sustainably made for developing novel materials and methodologies to fabricate the NF membranes with enhanced separation properties over the decades [1]. It is believed that the deep understanding towards the novel methodologies for membrane fabrication is definitely necessary to enable the rational design of advanced membranes for practical applications [3,4].

In 2007 Messersmith and co-workers reported breakthrough research in the chemistry of surface modifications inspired by the composition of adhesive proteins in mussels. Since then, dopamine, one kind of such catecholamines, has received a significant interest in the field of material science [5–7]. It has been demonstrated that dopamine could undergo self-polymerization in alkaline environment to form a thin and hydrophilic polymer coating on a wide variety of materials with great adhesive strength. Moreover, the formed multifunctional polydopamine (PDA) film could serve as an extremely versatile platform for secondary surface-mediated reactions to build up additional layers with specific functionalities [5,8]. To date, the detailed polymerization and

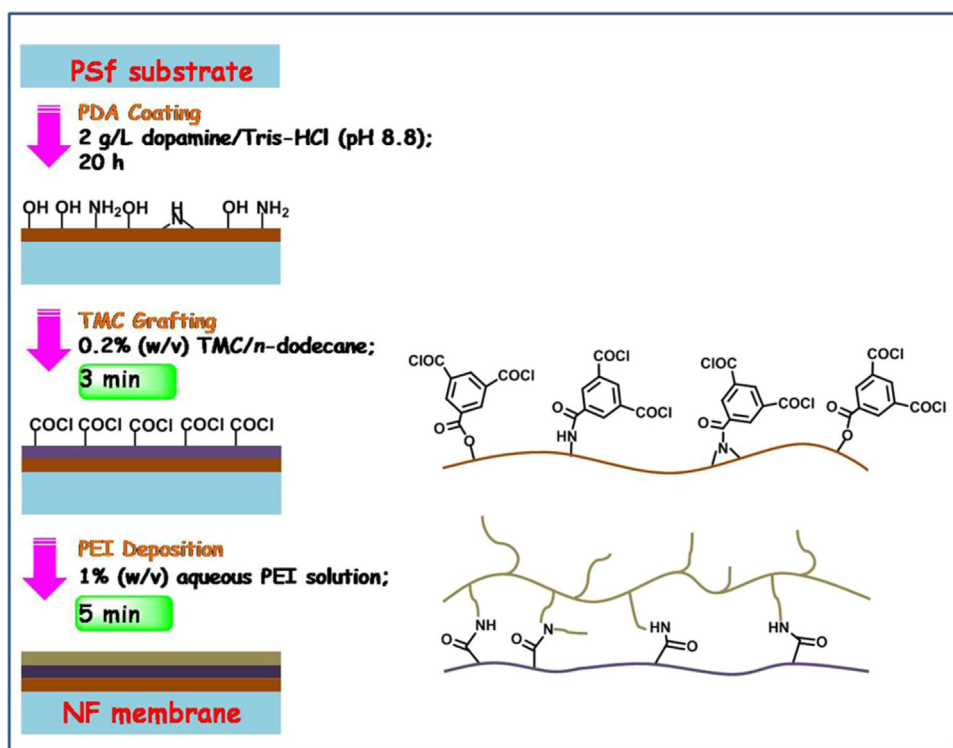
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binding mechanisms of dopamine are not well understood. It is believed that dopamine undergoes a complicated process of self-polymerization based on both covalent and non-covalent interactions, accordingly introducing plenty of functional groups including free amine groups, phenolic hydroxyl groups of catechol moieties, as well as carbonyl groups of *o*-quinone moieties at the resulting PDA layer surface [9–11]. Owing to such unique properties of PDA, numerous studies have focused on the application of dopamine chemistry into surface modifications and fabrications of membranes for water treatment [7,12]. On one hand, dopamine can be utilized as hydrophilic surface modifier by simple coating approach. The self-polymerized PDA layers formed on the surfaces of various membranes such as microfiltration [13], UF [14–16] and RO [17,18] endow the resultant modified membranes with enhanced surface hydrophilicity and fouling resistance. In addition, the modification of the support layer with PDA film prior to the conventional interfacial polymerization has also been proved as an effective approach to improve the separation properties of the resulting TFC membranes for forward osmosis (FO) [19], pressure retarded osmosis (PRO) [20], pervaporation [21], as well as NF applications [22]. On the other hand, PDA can be utilized as a functional intermediate layer for further construction of hierarchically structured separation layers of membrane with advanced filtration properties [7]. A great deal of research activities has been focusing on the development of functionalized desalination membranes by applying the chemistry of Michael addition and/or Schiff base reaction between thiol or amine groups of functional polymers and *o*-quinone moieties of the mediating PDA layer. For example, thermo responsive UF membrane, high flux and anti-fouling NF membrane, as well as positively charged NF membrane have been successfully fabricated by grafting the amino-terminated poly(*N*-isopropylacrylamide) [23], fluorinated polyamine [24], and poly(ethylene imine) at the PDA coated precursor layers [25,26], respectively. Such chemistry of Michael addition and Schiff base reactions is based on the electrophilicity of PDA due to the electrophilic nature of quinone carbonyl groups.

However, to ensure such reactions proceed to completion, long reaction times, high temperatures and alkaline conditions are required in the membrane fabrication procedures. Nevertheless, in contrast to the quinone carbonyl groups, the phenolic hydroxyl and amine groups of the PDA have nucleophilic nature, which could facilely react with active electrophiles such as acyl-chloride groups to form covalent ester and amide bonds [27–29]. Compared with the reactant system of quinone moieties and amines involved in Michael addition and Schiff base reactions, the polar phenolic hydroxyl and amine groups possess higher reactivity to couple with acyl-chloride groups, enabling the reaction to take place at room temperature and accomplish within a short time. However, up to now, there are very few reported works focusing on the utilization of such nucleophilic nature of PDA chemistry to facilely construct the membrane separation layers [29].

In order to further extend the variability of PDA layer as an effective platform for constructing functional separation layers of desalination membranes, in this work we herein report the successful usage of self-polymerized PDA film as a key intermediate layer for fabricating novel NF membrane based on the nucleophilic nature of PDA chemistry. As illustrated in Scheme 1, the fabrication process started with coating PDA layer onto the polysulfone (PSf) substrate, followed by employing trimesoyl chloride (TMC) as active electrophilic modifier to be covalently grafted at the surface of the PDA layer via the coupling of acyl chlorides with phenolic hydroxyl and amine groups. Finally, branched poly(ethyleneimine) (PEI) polymer comprising plenty of free primary and secondary amine groups was anchored on the surface of TMC grafted PDA layer through the reaction of amino groups with acyl chlorides to produce the defect free separation layer with hierarchical structure. The membranes prepared at different stages were characterized in terms of surface chemistry, pore properties, and separation properties to better understand the feasibility and mechanism of the newly developed methodology for membrane preparation. Additionally, separation efficiencies of the as-prepared NF membrane for retention of dyes and heavy metal ions,



Scheme 1. Schematic illustration of the procedure for NF membrane preparation.

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