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Engineering superhydrophobic surface on poly(vinylidene fluoride) nanofiber membranes for direct contact membrane distillation

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ABSTRACT

Recently membrane distillation (MD) has received intensive interests for a range of applications such as desalinations of seawater and brine. One of the major obstacles for MD application is the lack of an optimized MD membrane that can produce a high and stable flux in long-term operation. Two types of superhydrophobic PVDF nanofiber membranes, integrally-modified and surface-modified PVDF membranes, have been successfully fabricated by electro-spinning followed by surface modification, which includes dopamine surface activation, silver nanoparticle deposition and hydrophobic treatment. The modification is convenient because of mild reactions and wide applicability. These novel composite nanofiber membranes have been characterized by a series of measurements and benchmarked against commercial PVDF flat sheet membrane for MD application.

The characterizations reveal that the modifications have altered the membrane surface morphology and topology and made the membrane superhydrophobic due to their hierarchical structures. Compared with unmodified membrane, the integrally-modified membrane (I-PVDF) can achieve a high and stable MD water flux of 31.6 L m^{-2} h^{-1} using a 3.5 wt% NaCl as the feed solution while the feed and permeate temperatures were fixed at 333 K and 293 K, respectively. To the best of our knowledge, this result is superior to all other PVDF flat-sheet membranes tested under the same or similar conditions, which is believed to be attributed to the open-surface pore structure and thin thickness of the PVDF nanofiber membrane with the aid of electro-spinning. The superhydrophobic nature of the membrane surface brought by the integral modification on all nanofibers renders the membrane anti-wetting property while remaining high water flux.

1. Introduction

Superhydrophobic surfaces exhibit both a high water contact angle above 150° and a low water roll-off angle below 10° [1]. Water droplets are able to roll off on such a surface with some slip, providing the surface self-cleaning property known as "Lotus Effect" as the contaminants on the surface can be taken with them [2,3]. Since the 1990s, materials and biological scientists began to investigate natural superhydrophobic surfaces such as Lotus [4,5]. The Lotus leaves have a hierarchical structure with microscale roughness composed of papillose epidermal cells and nanoscale asperities consisting of three-dimensional epicuticular waxes which are long train hydrophobic hydrocarbons. This hierarchical structure facilitates the formation of air pockets on the solid surface, making applied water droplets have the lowest contact surface with the solid. As a result, the adhesive force between the solid surface and water can be reduced significantly [6–8].

Materials with a superhydrophobic surface can find many applications. For example, membrane distillation (MD) requires the membrane to exhibit extreme water repellence. MD is a non-isothermal membrane process driven by the vapor pressure difference across the membrane caused by the temperature gradient between the feed and permeate solutions [9]. The mild operating conditions in MD process, such as lower operating temperatures than that of conventional distillation, lower operating hydrostatic pressure as compared with pressure-driven processes (i.e. nanofiltration, reverse osmosis), less mechanical strength requirement of membranes and theoretically 100% rejection, make MD more attractive than other separating processes. However, most of the membranes used in MD process were fabricated originally for other processes such as microfiltration [10]. The availability of specially designed MD membranes, which can fulfill the requirements for MD process such as high hydrophobicity to avoid membrane wetting and high porosity to enhance vapor permeation, is one of the issues to be tackled for MD industry applications.

Fundamentally, the methodologies used to achieve superhydrophobic surfaces are to increase surface roughness and then modify the surface with low-energy and non-polar molecules. It is worth mentioning that surface roughness is usually more critical than the low surface energy, as both moderately hydrophobic and

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very hydrophobic materials can possess similar superhydrophobic property when roughened. Among various technologies to prepare MD membranes, electro-spinning is a simple and effective way to fabricate continuously polymeric nanofiber membranes with microscale and nanoscale fibers. The electrospun membranes have high porosity and a high surface-to-volume ratio, which are thus widely applied in filtration processes, battery technology, tissue engineering and optical devices [11–13]. However, the uniform nanofiber structures fabricated by pure polymer dopes without hydrophobic additives are usually not superhydrophobic [14]. In particular, the micro- and nanostructured surfaces provide a high adhesive force with water. The water droplet cannot roll off even if the membrane is turned upside down, which is so-called petal effect [15]. Thus, in order to obtain superhydrophobic nanofiber membranes, more steps are needed to optimize surface roughness and modify surface chemistry of the membranes.

To date, the layer-by-layer (LBL) assembly has been introduced into the electrospun fibers to construct a superhydrophobic surface [16]. In this approach, the nanofiber membranes need to be immersed in TiO_2 colloid solution for 15 min, rinsed in three pure water baths and then placed into an anionic solution for another 15 min. The adsorptions and rinsing steps need to be repeated more than 10 times to achieve enough roughness. Later the membranes were dried to immerse into fluoroalkylsilane (FAS) solution for 6 h to modify the surface to be superhydrophobic. The entire procedure is complicated and time-consuming. It was also reported that combining electro-spinning with initiated chemical vapour deposition (CVD) is an effective approach to prepare superhydrophobic fabrics [17]. Moreover, Yoon et al. have demonstrated that CF_4 plasma is an alternative method to fabricate superhydrophobic micro/nanofibrous cellulose triacetate (CTA) membrane [18]. However, these modification processes require the usage of special equipments, such as chemical vapour deposition reactor and CF_4 plasma equipment.

In this work, a facile method for preparation of superhydrophobic nanofiber membranes by surface modification was explored. It involves three steps of modification: (1) the nanofiber surfaces were firstly coated by poly-dopamine (PDA) to improve the adhesive force between the fibers and silver nanoparticles which were deposited on the fiber surface at the second step; (2) the PDA activated nanofibers were coated by silver nanoparticles during chemical reduction to optimize the morphology and roughness of the membrane; (3) in order to alter the surface chemistry, 1-dodecanethiol (C12) was applied to react with silver nanoparticles in mild conditions. The whole modification procedure could be finished in 3 h. The PDA modification method is versatile because of its applicability to many types of materials with complex shapes, simple ingredients, mild reaction conditions and strong binding force [19]. Moreover, the PDA-coating layer performs well as a binding agent even with metals [20,21]. These advances make this modification method available for all types of nanofiber membranes including poly(vinylidene fluoride) (PVDF) nanofiber membranes used in current study. Subsequently the modified membranes were evaluated in direct contact membrane distillation (DCMD) process to compare with commercial membranes for potable water production.

2. Experimental

2.1. Membrane materials and chemicals

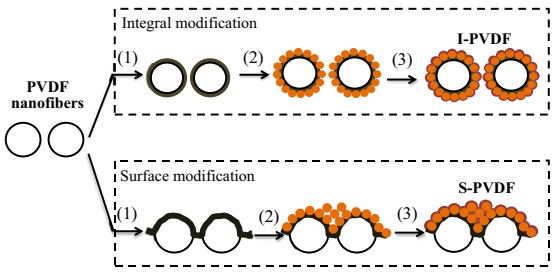
Commercial polymer poly(vinylidene fluoride) (PVDF) Kynar HSV 900 was purchased from Arkema Inc., Singapore and was dried at 50 °C under vacuum for at least 1 day before use. *N*,*N*,*N*-Dimetylformamide (DMF) and acetone from Fisher, Singapore were used as solvents. Lithium chloride (LiCl) as an additive in electrospun dope solutions was obtained from Merck, Singapore. Isopropyl alcohol (IPA) with analytical grade was obtained from VWR Co. Ltd, Singapore. Dopamine hydrochloride, tris(hydroxymethyl) aminomethane (tris), 1-dodecanethiol (C12), D-(+)-glucose and silver nitrate plant cell were purchased from Sigma-Aldrich, Singapore. Ethanol and ammonia solutions used in the modification process were received from Merck, Singapore. All the reagents were used as received. Water was purified with a Milli-Q system (Millipore Co. Singapore). Commercial PVDF membranes, Durapore® Membrane filter, were purchased from Millipore, Singapore to compare with the nanofiber PVDF membranes in the DCMD experiments.

2.2. Electro-spinning of PVDF nanofiber membranes and post-treatment

A 5 wt% PVDF polymer dope solution for electro-spinning was prepared by dissolving a pre-weighted PVDF HSV 900 in a mixture of DMF and acetone with a weight ratio of 6 to 4. A desired amount of LiCl (0.004 wt%) was added into the dope solution to improve dope electro-spin ability, optimize the nanofiber membrane's porosity and control membrane pore sizes [22,23]. The dope solution was stirred mechanically for at least 1 day at 60 °C. The homogenous dope solution was then cooled down and degassed at room temperature for overnight before electro-spinning. Then, the polymer solution was electrospun into nanofiber webs using an electro-spinning setup equipped with a high voltage supply. A positive voltage of 28 kV was applied across a distance of 12 cm between the tip of the sprayers and the grounded drum. The spinning sprayers can be moved slowly and evenly by a motor during electro-spinning. Nanofibers were spun over a course of 3 h to prepare continuous fibrous membrane. In order to eliminate the affect from residual solvents in the membrane, the PVDF nanofiber membranes were subsequently placed in a fume cupboard under vacuum condition at 60 °C for overnight to ensure all solvents evaporated from the fresh membranes. The dry PVDF nanofiber membranes were then pressed between two flat glass panes and placed in an oven at 170 °C just below polymer melting point for an hour to compress all the nanofiber layers together.

2.3. Membrane modification

Two types of modification which are integral and surface modifications were carried out as shown in Fig. 1. The difference between the integral and surface modifications lies in the pre-activation by the DPA. Nanofiber membranes were firstly wetted by a mixed solution of IPA and water to ensure that the chemical solution can flow inside the membranes and react on all fibers, which were used to make integrally modified PVDF membranes (designated as I-PVDF). Compared with the I-PVDF membrane,



(1) PDA modification; (2) Silver nanoparticle coating; (3) 1-dodecanethiol hydrophobic modification

Fig. 1. Schematic diagram of preparing superhydrophobic PVDF nanofiber membranes by silver nanoparticle and 1-dodecanethiol hydrophobic modification.