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Surface-active isoporous membranes nondestructively derived from perpendicularly aligned block copolymers for size-selective separation



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ABSTRACT

Isoporous membranes which have narrow pore size distributions and straight pore profiles promise sharp selectivity at no expense of permeability. However, it remains a challenge to produce isoporous membranes in an affordable and efficient way. In this work, we report on the facile preparation of isoporous membranes based on the nondestructive creation of straight pores in block copolymers of polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP). Thin films of PS-*b*-P2VP are annealed to induce the perpendicular orientation of the P2VP cylinders, and then transferred to macroporous supporting membranes to form mechanically robust composite structures. The copolymer films are treated in hot ethanol to convert the P2VP cylinders into straight pores following the selective swelling-induced pore generation mechanism. The perpendicular alignment of the P2VP cylinders in the PS matrix facilitates the swelling-induced pore generation process, making the membrane highly permeable. Because of its ultrathin thickness, high porosity, and strong hydrophilicity, the membrane exhibits a water flux as high as $1686 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, which is about 10 times higher than that of commercial membranes and also much higher than that of other isoporous membranes with similar effective pore sizes. Furthermore, the membrane has an inherent reversible pH-responsive functionality because of the enrichment of protonizable P2VP chains on the pore wall and membrane surface.

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1. Introduction

Isoporous membranes (IMs) hosting straight and through mesoscale pores with nearly identical pore diameters promise sharp selectivity and enhanced permeability as well as improved fouling resistance [1]. Inspired by the luring features of IMs outperforming conventional membranes with tortuous porosity, a number of strategies have been explored to fabricate IMs based on either top-down or bottom-up techniques [2]. Solution-etching of heavy ions-bombarded polymer films [3] and anodization of aluminum chips [4] are the best known approaches to the polymeric and inorganic IMs, respectively. Lithography-based micro/nanofabrication has been extensively used to fabricate silicon-based IMs with almost arbitrary pore geometries [5,6]. Arrays of vertically aligned carbon nanotubes are also used to produce IMs exhibiting exceptionally enhanced permeability because of the slippery flow of water molecules inside the tubes [7]. These methods provide optional accessibility to IMs with different chemical compositions and physical configurations. However, they suffer from one or more inherent drawbacks, for

example, high cost, complicated fabrication process, poor controllability in pore size and geometry, or limited ranges of available pore sizes.

Very recently, block copolymers (BCPs) have risen as a promising precursor for IMs. Thin films of BCPs are first perpendicularly aligned and the cylinders of the minor blocks are subsequently converted to straight pores traversing the entire thickness of the BCP films [8–14]. The BCP-based approach offers an affordable and flexible alternative to IMs with fine tunability in pore sizes down to sub-10 nm. However, the current methods to BCP IMs are mostly based on the destructive removal of the domains of minor blocks or additives incorporated in these domains. For example, polymethyl methacrylate (PMMA) and polylactide (PLA)-containing BCPs are the most frequently used BCP precursors for IMs and the labile PMMA and PLA blocks have to be chemically etched away by irradiation of short-wavelength UV light plus a rinse with acetic acid or alkaline-catalyzed hydrolysis, respectively. These chemical etching processes carried out in solvents under harsh conditions are usually tedious and produce byproducts. Even worse, as the major blocks are usually hydrophobic PS which constitute the framework of the porous membranes after etching, the obtained membranes are not water wettable. Consequently, additional prewetting or hydrophilic modification steps are typically required for the PS-based membranes to be used in aqueous

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circumstances [9] and the membranes are expected to suffer from reduced permeability and fouling issues because of their strong hydrophobicity [1].

As an alternative to destructive chemical routes to convert domains of the minor blocks into void spaces, we developed a nondestructive pore-making strategy based on the selective swelling of the domains of the relatively more hydrophilic blocks in amphiphilic BCPs [15]. We term it as selective swelling-induced pore generation or confined swelling-induced pore generation if we consider that the swellable domains are confined by the nonswellable matrix [16]. This process is extremely simple and independent of the chemical reactivity of the constituent blocks. Taking the BCPs of PS and P2VP as an example, we obtain porous materials of this copolymer simply by immersing the PS-*b*-P2VP into hot ethanol for hours followed by air drying. In clear contrast to pore generation by chemical etching, no chemical reactions are involved in the swelling-induced pore-making process and thus no byproducts are produced and the chemical composition of the BCP material remains intact. Therefore, both the BCP and the swelling solvent can be directly recycled for repeated use. More importantly, instead of being removed away from the matrix of the major blocks, the relatively hydrophilic blocks migrate to the pore wall and material surface, offering an inherent water wettability and surface activeness for further functionalization to the obtained porous materials generated by the selective swelling process. We successfully produced porous one-dimensional (1D) nanorods [17], 2D micellar monolayers [18], and 3D bulk materials of amphiphilic BCPs [19,20] using this swelling process geared to fit the dimensions of the starting BCP materials.

We previously demonstrated that the selective swelling method was also applicable to solvent-annealed PS-*b*-P2VP films assuming the perpendicular orientation and the perpendicularly aligned P2VP cylinders were converted to straight cylindrical pores with uniform diameters [21]. However, the possibility of using the thin IMs as separation media remains open though the isoporous nature of their pore structure implies excellent separation performances. In this study, we report on the transfer of the perpendicularly aligned BCP films from smooth substrates to macroporous supporting filters, followed by the nondestructive swelling-induced pore-making process, to fabricate two-layered composite membranes using the IMs as the selective layers, and demonstrate the high permeability and sharp selectivity together with a pH-responsive functionality of the IMs (Fig. 1). As far as we know, this is the first report of thin-film composite IMs delivering

a size-selective function prepared by a nondestructive swelling method. Abetz, Peinemann, Nunes and others nicely demonstrated that asymmetrical BCP membranes with a well-ordered, isoporous top layer and a thick sponge-like bottom layer can be prepared by the nonsolvent-induced phase separation (NIPS) method [22–25]. Their method which should also be considered to be ‘nondestructive’ is elegant and might be easily upscaled provided that there is affordable supply of BCP raw materials. However, the isopores only exist in the top layer and this method consumes large amounts of expensive BCP raw materials. It follows the typical NIPS process which requires using thick BCP solutions with a concentration of 20% or higher and produces integral BCP membranes with thicknesses of several hundreds of micrometers. In contrast, the isoporous membrane prepared in our work is in the structure of thin-film composites: the BCP selective layer is less than 100 nm in thickness and only very little amount of BCPs is required as we use extremely dilute BCP solutions typically with a concentration less than 0.6%.

2. Experimental section

2.1. Materials

The PS-*b*-P2VP block copolymer ($M_n(\text{PS})=290 \text{ kg mol}^{-1}$, $M_n(\text{P2VP})=72 \text{ kg mol}^{-1}$, $M_w/M_n=1.10$) and PS-OH ($M_n=6 \text{ kg mol}^{-1}$, $M_n/M_w=1.07$) used in our work were purchased from Polymer Source Inc., Canada. Silicon wafers with a 1000-nm-thick oxide layer were used as smooth substrates on which the BCP solutions were spin-coated. Organic solvents including toluene, chloroform, and ethanol were purchased from local suppliers and used without further purification. Macroporous PVDF membranes (Millipore) with a nominal pore diameter of $0.22 \mu\text{m}$ were used as supporting membranes. Bovine serum albumin (BSA), monodispersed silica particles with a diameter of 12 nm, and dextrans with four different molecular weights (10 kDa, 40 kDa, 70 kDa, and 500 kDa) were purchased from Sigma-Aldrich and used as received.

2.2. Modification of silicon wafers

Firstly, silicon wafers with an oxide layer were cleaned in a piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2=7:3$ (v:v)) at 82°C for 40 min, rinsed with deionized water, and dried in flowing N_2 . Then, solutions of PS-OH in toluene with a concentration of 1 wt% were

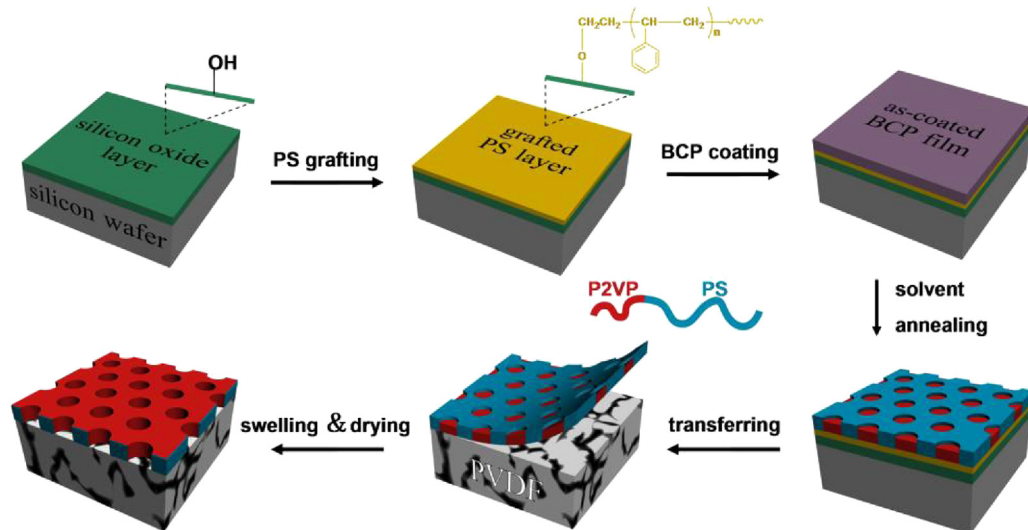


Fig. 1. The schematic illustration of the fabrication process of isoporous BCP membranes supported on macroporous polyvinylidene fluoride (PVDF) membranes.

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