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# Fabrication of a layered hybrid membrane using an organosilica separation layer on a porous polysulfone support, and the application to vapor permeation

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## ABSTRACT

Using 1,2-bis(triethoxysilyl)ethane (BTESE) as a single precursor, a uniform, defect-free and perm-selective organosilica layer was successfully deposited onto porous polysulfone ultrafiltration (PSF-UF) supports via a simple sol-gel spin-coating and thermal-treatment process. The layered hybrid membranes, where BTESE-derived SiO<sub>2</sub> is deposited on polymer supports, were applied to the vapor permeation dehydration of isopropanol–water (90/10 wt%) solutions at 105 °C, and demonstrated a water flux of 1.6 kg/m<sup>2</sup> h and a separation factor of 315 with no selectivity for a PSF-UF support. Long-term stability testing of vapor permeation also confirmed the excellent stability of these BTESE/PSF-UF layered hybrid membranes. Moreover, compared with porous PSF-UF supports, this layered hybrid membrane also showed improved gas separation performance and a moderate ( $\approx 10$ ) separation factor for H<sub>2</sub>/N<sub>2</sub>.

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## 1. Introduction

Membrane separation processes are recognized as one of the most promising separation technologies with energy consumption and operating costs that are both low by comparison with that of conventional separation processes such as distillation [1]. Currently, the improvements in membrane separation technology are mainly focused on the development of advanced separation membranes and the optimization of different membrane processes through process integration [2,3]. The fabrication of advanced separation membranes is one of the most important factors and is attracting great interest. Generally, the separation performance of a membrane is intrinsically determined by the structure and characteristics of the membrane material [4]. Moreover, most membranes are composed of multiple layers with different functions and properties. Only the active top layer plays a vital role, whereas other layers simply act as a mechanical support [5].

A specific example of this active layer would be a hybrid organosilica membrane, which is composed of covalently bonded organic and inorganic moieties. This new class of silica membrane is attracting an ever-increasing amount of attention due to outstanding properties such as excellent hydrothermal stability [6] and silica networks

with adjustable pore sizes [7]. For example, a promising organosilica membrane prepared via a sol-gel process using a bridged precursor, 1,2-bis(triethoxysilyl)ethane (BTESE), has shown excellent stability (at least 2 years) in the dehydration of n-butanol at 150 °C [8]. In our previous report, we described the successful development of silica networks using BTESE that resulted in a highly permeable hydrogen separation layer with hydrothermal stability [9]. Subsequently, our research group applied BTESE membranes to the dehydration of acetic acid aqueous solutions in the pervaporation and desalination of 1500 ppm NaCl aqueous solutions via reverse osmosis as well as confirming an excellent stability in both acid [10] and chlorine [11], respectively, along with a superior molecular sieving ability. Both excellent stability and high separation performance have been ascribed to Si–C–C–Si units. The BTESE membrane showed a stable pervaporation flux and separation factor for more than 10 h even when prepared at a calcination temperature as low as 100 °C [12]. Analogously, potential hybrid organosilica membranes with different bridge and pendant groups have been reported [13–15]. However, all the organosilica membranes were prepared on inorganic supports such as porous Al<sub>2</sub>O<sub>3</sub> supports with a pore size of approximately 200–1000 nm [6–18]. The cost of these ceramic membranes will always be higher than that of polymer-based ones [19]. Therefore, organosilica–Al<sub>2</sub>O<sub>3</sub> membranes with complex fabrication processes [20] and high cost may not be suitable for large-scale industrial utilization. To overcome this potential disadvantage, a new approach to the application of hybrid organosilica layers using a relatively

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low-cost polymeric support was proposed, almost simultaneously, by Ngamou et al. and our research group via an expansion of thermal plasma chemical vapor deposition (ETP-CVD) [21] and a sol-gel spin-coating process [22], respectively. The former requires sophisticated equipment and rigorous conditions in order to deposit a BTESE-derived CVD layer onto a polyamide-imide support for the retention of organic bridges. More importantly, the structure of BTESE was partially decomposed due to the high-energy state of plasma during this process. Reportedly, only 30% of the Si-C<sub>2</sub>H<sub>4</sub>-Si bridges were retained in the silica network, which may degrade the stability of the hybrid membranes.

Therefore, we proposed a layered hybrid membrane by sol-gel processing, where an organosilica layer would be coated onto a polysulfone (PSF) support via simple sol-gel spin coating, and thereby all the Si-C<sub>2</sub>H<sub>4</sub>-Si bridges could be retained in BTESE layer networks. More importantly, the flexibility of these organic bridge groups (Si-C<sub>2</sub>H<sub>4</sub>-Si) resulted in a BTESE layer with a polymeric character and excellent fracture resistance [23], thereby improving the flexibility of a PSF-supported BTESE layered hybrid membrane, which is one of the most important factors for scale-up. The layered hybrid membranes consisted of an inorganic separation layer on a polymeric support and show promise for the fabrication of high-performance, light-weight membranes with low production cost, which would be suitable for large-scale industrial applications. Reportedly, modified mesoporous silica film with pore sizes of 1–2 nm have been prepared on polymeric hollow fibers by static immersion in an acidic silica/surfactant precursor solution followed by a post-treatment of tetraethylorthosilicate (TEOS) vapor [24]. However, mesopores are too large for molecular separation and the thickness of the mesoporous silica layer can be as much as 1.6 μm, which may not be conducive to molecular diffusion in a dense separation layer.

Sol-gel processing is a well-established method for the preparation of hybrid organosilica films at low temperatures (~200 °C), and is suitable for the deposit of organic-inorganic layered hybrid materials on various polymer substrates such as polymethylmethacrylate (PMMA), polyimide (PI), and polycarbonate (PC) [25–27]. These are typically prepared by a combination of metal alkoxides such as tetraethylorthosilicate (TEOS) and organoalkoxysilanes such as methyltriethoxysilane (MTES) or phenyltriethoxysilane (PTES) via sol-gel processing. In our previously mentioned study, we successfully fabricated a thin BTESE-derived silica layer on a non-porous PSF thin film via a sol-gel spin-coating process, which showed promise for large-scale industrial applications due to low cost and a simple fabrication process [22].

In this paper, we proposed a sol-gel spin-coating process for the preparation of porous polymer-supported organosilica layered hybrid membranes where the organosilica separation layer was

deposited onto a porous polymeric support. First, we investigated the effective concentration of BTESE sol for the preparation of a uniform and complete BTESE layer on a non-porous polysulfone (NP-PSF) thin film; this BTESE layer was then deposited onto porous polysulfone ultrafiltration (PSF-UF) membranes. The PSF-UF-supported BTESE layered hybrid membranes were used for the vapor permeation dehydration of an isopropanol-water (90/10 wt %) solution at 105 °C. Moreover, the single-gas permeance of this composite membrane was also investigated.

## 2. Experimental

### 2.1. Materials

Polysulfone (PSF) beads (CAS 25135-51-7; average  $M_n$ : ~22,000) were purchased from Aldrich and porous polysulfone ultrafiltration (UF-PSF) membranes provided by Nitto Denko (Japan) were used as a support. The 1,2-bis(triethoxysilyl)ethane (BTESE) precursor was purchased from Gelest, Inc. (Germany). N-methylpyrrolidone (NMP) and 1-propanol were of analytical grade and were purchased from Sigma-Aldrich and NacalTesque, Inc., respectively. All chemicals were used without further purification.

### 2.2. Sol preparation

Nanometer-sized organosilica sols were synthesized via the hydrolysis and polymerization reaction of a precursor, 1,2-bis(triethoxysilyl)ethane (BTESE), in 1-propanol by following our previous report [22]. Briefly, a certain amount of BTESE was mixed with 1-propanol, and then distilled water and HCl were successively added to this solution under vigorous stirring. The molar ratio of BTESE:H<sub>2</sub>O:HCl was 1:60:0.1, and a 10.0 equivalent wt% of BTESE was maintained in the sol. After continuous stirring for 1.5 h in a closed glass bottle at room temperature, the BTESE sols were diluted with 1-propanol to 2.5, 5.0, 7.5, and 10 wt% of BTESE.

### 2.3. Deposition of the BTESE layer on non-porous PSF thin films

For preparing non-porous polysulfone (NP-PSF) thin films on glass substrates, PSF beads and N-methylpyrrolidone (NMP) were loaded in a sealed glass bottle and stirred with a magnetic stirrer at 70 °C for 3 h until the PSF beads were completely dissolved at a PSF concentration of 15 wt%. The PSF solution was spin-coated onto the glass substrate (18 mm × 18 mm, thickness: 0.12 mm) at 6000 rpm for 5 s and dried at 100 °C for 30 min to evaporate any residual solvent. A comparison of the FTIR spectrums of PSF beads

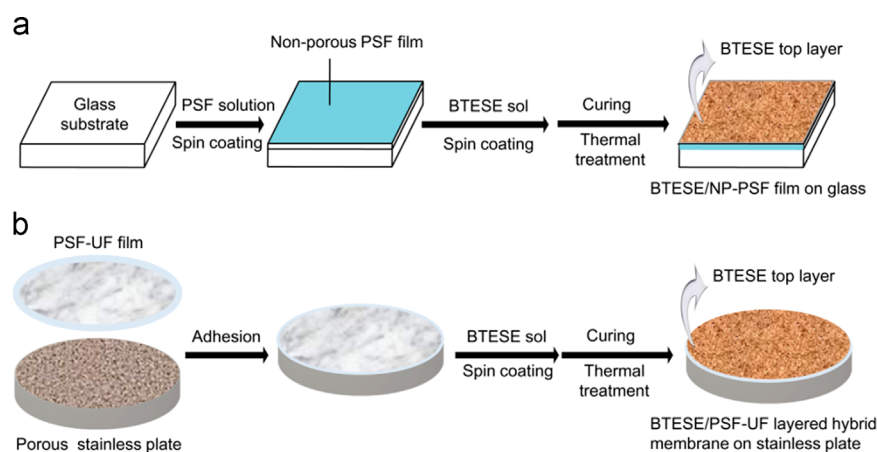


Fig. 1. A schematic illustration of the process for BTESE spin-coating on NP-PSF thin film (a) and porous PSF-UF support film (b).

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