Journal of Membrane Science 561 (2018) 79–88

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Hierarchical pore architectures from 2D covalent organic nanosheets for efficient water/alcohol separation

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ARTICLE INFO

Keywords:
Covalent organic nanosheets
Hybrid membranes
Hierarchical pore architectures
Water/alcohol separation
Water-selective permeation

ABSTRACT

By mimicking the respiratory system in organisms, hybrid membranes with hierarchical pore structures were constructed by covalent organic nanosheets (CONs) and poly(ether sulfone) (PES). Two kinds of amide modified CONs, TpPa-1 and TpBD, with different pore sizes were facilely synthesized by the Schiff base reactions of 1,3,5-triformylphloroglucinol (Tp) with p-phenylenediamine (Pa-1) and benzidine (BD), and separately incorporated into the PES. The hierarchical pore structures within the hybrid membranes including micropores (0.278–0.289 nm), mesopores (2–50 nm) and macropores (1–10 μm) were generated by the addition of CONs. The microporous structures in top dense layer with high separation accuracy arose from CONs and PES chains. The mesoporous structures and the macroporous structures in porous sublayer with ultralow resistance arose from sponge-like pores and finger-like pores of PES, respectively. A smooth transition of micro-, meso- and macroporous structures rendered the membranes desired level of separation efficiency as well as high stability. Remarkably, the hybrid membrane consisting of TpPa-1 CONs (8 wt%) showed a high water/ethanol separation factor of 1150, while the membrane consisting of TpBD CONs (8 wt%) exhibited a high water/n-butanol separation factor of 2735. The permeation fluxes for both separation systems were higher than 2.5 kg m^{-2} h^{-1}. The links between hierarchical architectures and performance in membranes could facilitate the rational design of novel membrane architectures with advanced properties.

1. Introduction

Nature has developed various composite materials with intriguing hierarchical architectures, which are often attained by organizing components at micro-, meso-, and macroscales [1,2]. The hierarchical architectures with a gradual spatial change in pore structures can prominently facilitate the mass transport efficiency [3–5]. For instance, the human lung comprises a hierarchical architecture that includes a trachea branching into numerous bronchi with alveoli on their ends. The respiratory membranes on alveoli with microporous structures confer precise gas exchange, while the bronchi and trachea with macroporous structures confer fast mass transport pathways [6]. By emulating such design principles in nature, composite materials with hierarchical pore architectures can substantially extend the properties to respond to the demands of emerging technologies such as membrane technology [7,8].

Nonetheless, it remains a significant challenge for exploring a membrane with such hierarchical pore structures. So far, the porous membranes with sponge-like pores (10–50 nm) and finger-like pores (1–10 μm) can be easily achieved by non-solvent induced phase separation (NIPS), a well-documented procedure to prepare asymmetrical membranes [9]. The primary difficulty lies in the formation of microporous structure on membrane surface to discriminate the penetrant molecules with high accuracy. Coating a dense separation layer with microporous structures on a meso- and macroporous support layer to construct a composite membrane seems an ingenious approach in many applications including biofuel production, carbon capture, and seawater desalination [10–15]. The dense layer with microporous structures is favourable to selective permeation of penetrants, while the porous support layer with meso- and macroporous structures contributes to reduced diffusion resistance (e.g., the water permeation rate across large pores (~ 1 μm) could be four orders of magnitude higher

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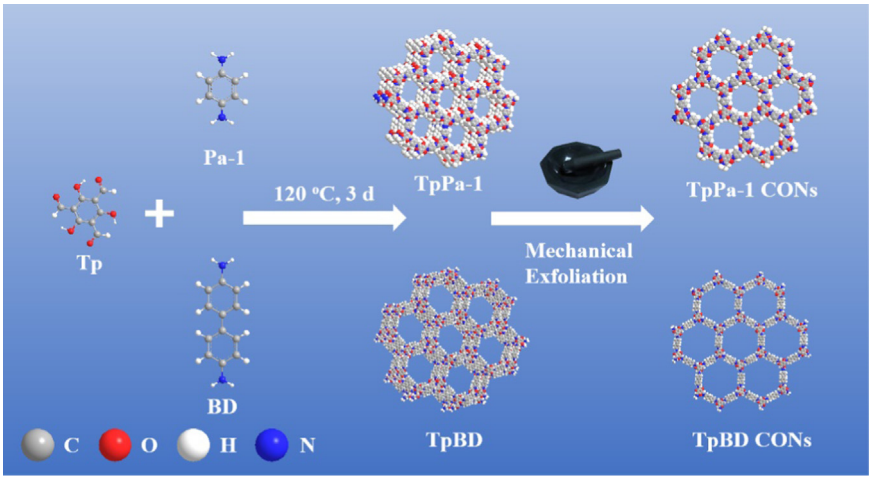
https://doi.org/10.1016/j.memsci.2018.05.036
Received 6 March 2018; Received in revised form 10 May 2018; Accepted 19 May 2018
Available online 22 May 2018
0376-7388/



Scheme 1. The synthesis protocols and chemical structures of the CONs.

than across small pores (~ 10 nm) [16]). However, the premature failure often occurs at the sharp interfaces between dense separation layers and porous support layers due to the stress accumulation [17–19]. A hierarchical architecture that confers a smooth transition of pore structures is highly demanded.

Crystalline microporous materials with delicate structures and complex functionalities have received numerous attention in recent years [20,21]. It is thus conjectured that using microporous materials as additional components for in situ constructing microporous membrane structures on membrane surface could be an effective approach. Covalent organic nanosheets (CONs) derived from the exfoliation of their bulk counterparts such as covalent organic frameworks (COFs), are an emergent kind of two-dimensional (2D) crystalline microporous materials. CONs can be easily designed and functionalized with great potentials in separation applications [22–31]. Compared with other porous materials such as zeolites and metal-organic frameworks (MOFs), CONs feature extremely high chemical and thermal stability as well as good polymer/CON compatibility [21,32,33]. Furthermore, CONs have a low-density nature (the reported lowest density is 0.17 g/cm^3) because they are covalently linked by light elements [21,34]. Such features of CONs are particularly favourable for the development of membranes with the hierarchical architectures. CONs with high hydrophilicity and low density could migrate to the membrane surface along with the solvent during the NIPS processes. Their microporous structures could endow membrane surface with high surface area and separation accuracy. Meanwhile, CONs, similar to the alveoli in organisms, can connect with sponge-like and finger-like pores of polymers to form continuous hierarchical pore structures, which are expected to impart the desired level of efficiency and high stability.

In this study, commercial polymer poly(ether sulfone) (PES) was utilized as a bulk polymer to construct hierarchical pore structures, including micropores in top dense layer and meso- and macropores in porous sublayer. Two kinds of CONs, TpPa-1 and TpBD, with rich amide groups but different pore sizes were synthesized and utilized as building blocks to optimize the hierarchical pore structures of PES membrane. The CONs could adjust the micropore size and optimize physical/chemical properties of the membranes. A smooth transition of porous structures with successive micro-, meso- and macroporous structures was created. These hybrid membranes with hierarchical pore structures adjusted by different CONs were applied to different water/alcohol separation systems including water/ethanol and water/n-butanol systems, which are one of the most important tasks in the advanced biofuel industry [35]. The hierarchical pore structures endow the hybrid membranes with improved water/alcohol separation performance as well as good long-term stability. Our study manifests the great prospects of hybrid membranes with hierarchical pore structures in water/alcohol separation applications.

2. Experimental

2.1. Materials

Distilled water was used for all experiments. Anhydrous acetone (≥ 99.8 wt%) and methanol (≥ 99.8 wt%) were supplied by Tianjin Guangfu Fine Chemical Engineering Institute. Poly (ether sulfone) (PES, Mw = 29000) powders (disk shape, GR) were bought from BASF Co., Ltd (Germany). P-phenylenediamine (Pa-1, ≥ 99.8 wt%), benzidine (BD, ≥ 99.8 wt%) and phloroglucinol (≥ 99.8 wt%) were purchased from TCI Development Co., Ltd. Aqueous acetic acid (≥ 99.5 wt%) and tetrahydrofuran (THF, ≥ 99.5 wt%) were obtained from Tianjin Guangfu Fine Chemical Engineering Institute. Ethanol (99.8 wt%), N, N-dimethylformamide (DMF, 99.8 wt%) and dichloromethane (≥ 99.8 wt%) were supplied by Tianjin Chemart Chemical Reagent Co., Ltd (China). Mesitylene (≥ 99.0 wt%), dioxane (≥ 99.5 wt%), urotropin (≥ 99.5 wt%) and trifluoroacetic acid (≥ 99.0 wt%) were supplied by Aladdin Co. Ltd (China).

2.2. Procedures for preparation of CONs

The synthesis protocols and chemical structures of TpPa-1 and TpBD CONs are shown in Scheme 1.

2.2.1. Synthesis of TpPa-1

Firstly, 1,3,5-Triformylphloroglucinol (Tp) was synthesized from phloroglucinol by Duff formylation [36]. Then COF TpPa-1 was synthesized according to the literature [37]. Typically, a Pyrex tube was charged with Tp (126 mg), Pa-1 (96 mg), 3 mL of mesitylene, 3 mL of 1,4-dioxane and 1 mL of 3 M acetic acid. The mixture was sonicated for 20 min to obtain a homogeneous dispersion. The tube was frozen at 77 K and degassed by three freeze-pump-thaw cycles, and then heated at 120 °C for 3 days. A precipitate with red color was collected by filtration and washed with THF, dichloromethane and acetone, respectively. The powder collected was then solvent exchanged with acetone and dried at 120 °C under vacuum for 24 h to get TpPa-1 in 78% isolated yield.

2.2.2. Synthesis of TpBD

The synthesis procedure of TpBD is similar to that of TpPa-1 only by altering the diamine Pa-1 to BD [28]. The yellow TpBD was obtained in 82% isolated yield.