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Controlled deposition of MOFs by dip-coating in thin film nanocomposite membranes for organic solvent nanofiltration

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ABSTRACT

ZIF-8 and ZIF-67 particles, with sizes of 70 ± 10 nm and 240 ± 40 nm, respectively, were deposited by dip-coating on top of polyimide P84® asymmetric supports. In the best conditions, this gives rise to a MOF (metal-organic framework) monolayer which remains on the polyimide support during the interfacial polymerization of polyamide carried out to produce a thin film nanocomposite membrane for organic solvent nanofiltration (OSN). This method is simple, shorter and is environmentally friendly, since no excess MOF is lost during the interfacial polymerization, exhibiting good OSN results: dye rejection of 90% together with a high methanol permeance of 8.7 L m^{-2} h^{-1} bar^{-1}.

Introduction

In recent decades, organic solvent nanofiltration (OSN) with membranes has been very attractive due to its high separation efficiency and low equipment costs and energy consumption [1]. Materials that have been explored for the manufacture of high-performance composite membranes include carbon nanotubes [2], graphene [3], metal-organic frameworks (MOFs) [4], and covalent organic frameworks (COFs) [5], among others. MOFs are of great interest due to the exceptional properties of the design and functionalization of their pores, their high specific surface area and their easy synthesis, contributing to several membrane applications such as gas separation (GS) [6], reverse osmosis (RO) [7], pervaporation (PV) [8], nanofiltration (NF) [4,9,10] and wastewater treatment [11]. Two types of polymer membranes can be found for NF and RO processes in terms of structure: integrally skinned asymmetric (ISA) membranes and thin film composite (TFC) membranes. ISA membranes consist of a selective thin layer supported on a more porous layer of the same material [12]. TFC membranes comprise a non-woven support at the bottom, an intermediate layer with an asymmetric porous structure, and a selective ultrathin film at the top. One of the most commonly used porous supports are polyimides (PI) owing to their unique physicochemical properties such as their resistance to high temperatures, radiation and chemical attack, their good mechanical strength and their superior insulation properties [13,14]. The ultrathin selective layer is fabricated by the interfacial polymerization (IP) method [15]. This is carried out through a polycondensation reaction between two monomers present in two immiscible solutions: *m*-phenylediamine (MPD) aqueous and trimesoyl chloride (TMC) organic phases. As a consequence of this process, a thin barrier of polyamide (PA) is formed at the interface of the immiscible solutions giving rise to high solvent permeance and good retention of solutes [16,17].

Abbreviations: ATR, attenuated total reflection; BET, Brunauer–Emmett–Teller; COF, covalent organic frameworks; CR, Congo Red; DC, dip-coating; DMF, *N,N*-dimethylformamide; EA, ethyl acetate; EDX, energy-dispersive X-ray spectroscopy; ETD, Everhart–Thornley detector; FEG, field emission fun; FIB, focused ion beam; FTIR, Fourier transform infrared spectroscopy; GS, gas separation; HAD, hexanediamine; HKUST-1, Hong Kong University of Science and Technology-1; H-MeIm, 2-methylimidazolate; IP, interfacial polymerization; IPA, isopropyl alcohol; ISA, integrally skinned asymmetric; ISG, in situ growth; LBL, layer-by-layer; MeOH, methanol; MMM, mixed matrix membrane; MOF, metal-organic framework; MPD, *m*-phenylediamine; NF, nanofiltration; OSN, organic solvent nanofiltration; PA, polyamide; PDMS, polydimethylsiloxane; PEG, polyethylenglycol; PI, polyimide; PP, polypropylene; PS, polystyrene; PSF, polysulfone; PV, pervaporation; RB, Reactive Black; RO, reverse osmosis; SDTA, single differential thermal analysis; SEM, scanning electron microscopy; SO, styrene oligomers; SOD, code for the ZIF structure with the same topology than zeolite sodalite; SY, Sunset Yellow; TFC, thin film composite; TFN, thin film nanocomposite; TGA, thermogravimetric analyses; THF, tetrahydrofuran; TLD, through lens detector; TMC, trimesoyl chloride; UV, ultraviolet; XRD, X-ray diffraction; ZIF, zeolite imidazole framework.

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With the aim of increasing the permeate flux without affecting the rejection, porous nanoparticles can be incorporated within the PA layer of TFC membranes producing the so-called thin film nanocomposite (TFN) membranes [18]. However, there remain several limitations such as the thickness of the skin layer [19,20], and the difficulty of nanoparticle (MOF) positioning in the TFN [21]. In fact, conventional interfacial polymerization is poorly controllable because the reaction is completed in a few seconds, which represents a great challenge for forming a thin but defect-free skin layer. Therefore, the development of a method which initially controls the formation of a MOF monolayer avoiding aggregation is essential. In this context, Gevers et al. [22,23] tested the dispersion of silica, carbon and zeolite (ZSM-5) inorganic fillers in a PDMS polymer matrix. Besides the enhancement of OSN, this strategy led to the reinforcement of the polymer and its anti-swelling properties. The incorporation of MOFs as fillers for the preparation of OSN membranes was first explored by Basu et al. [24] who incorporated $Cu_3(BTC)_2$, MIL-47, MIL-53(Al) and ZIF-8 dispersed into PDMS. This resulted in enhanced permeances with lower solute rejections compared with the pure PDMS/PI membrane (due to the poor adhesion of MOFs to PDMS). Campbell et al. [25] produced composite membranes by the in situ growth (ISG) method of HKUST-1 crystals on PI P84® asymmetric supports. These membranes demonstrated higher rejections in the treatment of styrene oligomer suspensions in acetone with a lower flux decline than those observed without the MOF. Sorribas et al. [4] prepared TFN membranes on PI P84® asymmetric supports by dispersing several MOFs (ZIF-8, MIL-53(Al), NH_2-MIL-53(Al) and MIL-101(Cr)) in the organic phase before the IP reaction. These TFN membranes showed higher methanol and THF fluxes than commercial OSN membranes. Wang et al. [26] reported a similar procedure with ZIF-8 nanoparticles in the aqueous phase, in the organic phase, or in the two phases to produce a modified PA selective layer on asymmetric polysulfone (PSF). Wang et al. [27] used a layer-by-layer (LBL) method via ZIF-8 in-situ growth followed by IP to obtain TFN membranes containing ZIF-8.

These studies indicate that the development of OSN membranes faces challenges mainly in terms of the formation of defect-free skin layers with minimal thicknesses and of highly stable and selective operation. In this work, we propose a dip-coating method [28] for the controlled dispersion of MOF nanoparticles in TFN membranes. MOFs ZIF-8 [29] and ZIF-67 [30] (see Fig. 1) were chosen to create homogeneous monolayers on the surface of an asymmetric porous PI P84® support after which the IP was carried out to produce PA-based TFN membranes. The membranes were applied in the OSN of methanol-dye solutions.

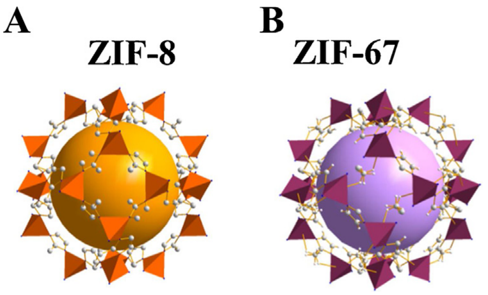

Fig. 1. Building blocks of: (A) ZIF-8 and (B) ZIF-67. These structures were made with software Diamond 3.2 using the corresponding CIF files [30].

Experimental

Materials

Polyimide P84® (PI — HP Polymer GmbH), $Zn(NO_3)_2{\cdot}6H_2O$ (99% purity, Sigma–Aldrich), $Co(NO_3)_2{\cdot}6H_2O$ (99% purity, Sigma–Aldrich), 2-methylimidazole (mIm, 99%), methanol (99% purity, Scharlab), *m*-phenylediamine (MPD — 99%, Sigma–Aldrich), DMF (99.5%, Scharlab), dimethylsulfoxide (DMSO — synthesis grade, Scharlab), trymesoyl chloride (TMC — 98%, Sigma–Aldrich), hexane (99%, Scharlab), isopropyl alcohol (IPA — 99.5%, Scharlab), hexanediamine (HDA – 98%, Sigma–Aldrich), polyethylenglycol (grade of PEG synthesis, Scharlab), Sunset Yellow (SY — 90% dye content, Sigma–Aldrich) and polypropylene (PP, Freudenberg Performance Materials) were used as received without further purification.

Synthesis of MOFs

ZIF-8 was synthesized based on the methodology reported elsewhere [31]. The following molar composition was used: 1 Zn: 8 H-MeIm: 700 MeOH. $Zn(NO_3)_2{\cdot}6H_2O$ (0.47 g) and 2-methylimidazole (1 g) were separately dissolved in 22.37 mL of methanol each. Then the solution of the ligand was poured on that of the salt and the resulting solution was stirred for 10 min. This produced a white dispersion containing ZIF-8 nanosized crystals.

ZIF-67 was synthesized based on a previously reported molar composition [32], with an adaptation to 1 Co: 8 H-MeIm: 700 MeOH (from 1:4:700) $Co(NO_3)_2{\cdot}6H_2O$ (0.47 g) and 2-methylimidazole (1 g) were separately dissolved in 22.67 mL of methanol each. Then the solution of the ligand was poured on that of the salt and the resulting solution was stirred for 10 min. A purple coloration indicated the formation of ZIF-67. The ZIF-8 and ZIF-67 suspensions were directly used for support dip coating without any modification.

Preparation of porous substrates of P84®

A polymer dope solution was prepared by dissolving 24 wt.% polyimide (P84®) in DMSO and stirring it overnight until complete dissolution. The viscous solution formed was allowed to stand until complete removal of the air bubbles. The dope solution was then cast on a non-woven PP sheet attached to a glass plate using the casting knife set Elcometer 4340 Automatic Film Applicator, at a thickness of 250 μm and at a speed of 0.04 m s^{-1}. Immediately after casting, the polymer membrane was immersed in a distilled water bath at 20 °C where phase inversion occurred. After 10 min, the coagulation bath was replaced with fresh distilled water and the substrates were left there for 1 h.

The asymmetric P84® supports were then immersed in two successive baths of IPA for 1 h each to remove any remains of water and DMSO [33]. Afterwards, a cross-linking process took place consisting of immersion in a bath of 120 g L^{-1} of HDA in IPA for 16 h to increase the stability of the support in organic solvents. Four successive baths with IPA were then applied to remove traces of HDA from the supports. The supports were then immersed overnight in a PEG/IPA solution at a volume ratio of 3:2 to prevent pore collapse [9] and subsequently wiped with tissue paper to remove PEG excess.

Preparation of homogeneous MOF@PI support by dip-coating technique

Small disk supports of PI P84® (12.0 cm^2) for characterization and large disk supports of the same material (60.8 cm^2) for nanofiltration testing were dip coated with the suspensions of

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