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Surface micro-patterning as a promising platform towards novel polyamide thin-film composite membranes of superior performance

Ibrahim M.A. ElSherbiny[a,b], Ahmed S.G. Khalil[a,c,d], Mathias Ulbricht[a,*]

[a] Lehrstuhl für Technische Chemie II, and Center for Water and Environmental Research (ZWU), Universität Duisburg-Essen, 45141 Essen, Germany
[b] Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt
[c] Center for Environmental and Smart Technology, Fayoum University, Fayoum, Egypt
[d] Arab Academy for Science, Technology and Maritime Transport, Smart Village Campus, Giza, Egypt

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ABSTRACT

Novel and efficient micro-patterned polyamide (PA) thin-film composite (TFC) membranes are successfully fabricated. Polyethersulfone support membranes are micro-patterned using two microfabrication methods, combined processes of vapor- and non-solvent-induced phase separation micro-molding, as well as micro-imprinting lithography. PA layer is successfully adapted on the developed micro-patterned supports and the impact on the membrane performance as a result of the difference in micro-patterning resolution is explored. The patterned PA TFC membranes exhibit superior water permeability, ~2–2.4 times compared to the flat PA TFC membranes, without sacrificing the membrane selectivity. This is mainly due to the distinguishable enhancement in membrane active surface area (~40–70%) and the increasing of the surface roughness upon micro-patterning. Furthermore, the concentration polarization analysis using different membrane orientations, with patterned grooves "parallel" and "perpendicular" to the direction of feed flow, and various feed concentrations is carried out. The results explicit the merits of implementing the micro-patterned TFC membranes in producing specific surface-induced mixing effects, which are found to reduce the concentration polarization, even at a high feed concentration. Moreover, the fidelity of the micro-patterning methods used in this work is comprehensively studied and different mechanisms for membrane surface patterning are proposed.

1. Introduction

Recently, a number of theoretical and experimental studies have introduced the topographic surface patterning approach as an interesting alternative to yield efficient membranes exhibiting controlled surface roughness along with enhanced fouling resistance [1–4]. Notwithstanding the efforts that have been devoted to develop efficient water desalination membranes, there are still some obstacles that impede its widespread implementation [5,6]. Polyamide (PA) thin-film composite (TFC) membranes are the most prevalently used materials for pressure-driven water desalination processes [7]; nevertheless, they still suffer from being prone to various types of fouling and scaling that limits their performance and increases the operation costs [8–10]. Among many suggested strategies, the application of surface patterning as a new platform towards modifying PA TFC membranes has been introduced firstly by Maruf et al. in 2014 [11].

LIGA method, by Ehrfeld et al., was one of the earliest methods for micro-fabricating membranes of high porosity and high aspect ratio [12]. The method was based on a combination of X-ray lithography, electroforming and micro-molding of polymers. Later, a less complicated and straightforward procedure, namely phase separation micromolding (PSμM), was introduced in 2003 [13]. In PSμM, a thin film of a polymer solution is casted on a mold of the desired features. Thereafter, the change in thermodynamic state disturbs the equilibrium of the polymer film causing precipitation. This can be realized either thermally or by immersion in a liquid (non-solvent-induced PSμM, NIPSμM). Upon solidification, small gap evolves between the molds' features and the membrane as a consequence of the inherent shrinkage in a parallel orientation to the cast film, which facilitates the detachment and preserving the replicated microstructures over extended areas [13,14].

Nevertheless, these techniques are found to be strongly dependent on the experimental conditions; i.e., the aspect ratio, pretreatment of the mold, composition of a polymer solution, casting conditions, and precipitation time. Accordingly, a number of practical challenges are aroused during the application of PSμM. For instance, the orientation of the shrinkage may change during the coagulation process leading to a deformation of the replicated features [14]. Additionally, it is often

* Corresponding author.
E-mail address: mathias.ulbricht@uni-essen.de (M. Ulbricht).

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found that the phase separation induces from the flat side of the cast film, resulting in a pore size gradient [15], and consequently the skin layer is located on the flat side. Therefore, vapor-induced phase separation micro-molding (VIPSμM) was proposed to produce micro-patterned membranes exhibiting isotropic pore size distribution. VIPSμM comprises casting of the polymer solution on water vapor-permeable molds made of polydimethylsiloxane (PDMS) [15]. This modified method guarantees that the demixing process is always starting from the side that is in contact with the mold. In the same context, another modified immersion-precipitation method [16] was presented to prepare isotropic prism-patterned polyvinylidene fluoride (PVDF) ultrafiltration (UF) membranes, and the factors influencing the fidelity of the micro-pattering were investigated [17]. It was revealed that the fidelity can be promoted by employing low molecular weight polymers, and if the work of adhesion between the polymer solution and the mold is minimized.

Nanoimprinting lithography (NIL) has also attracted some interest as a viable micro-patterning procedure for polymeric materials [18]. Maruf et al. [19] investigated the feasibility of using NIL to produce submicron surface patterns on commercial UF membranes without limiting their performance. One year later, they broadened the validation of NIL to develop surface-patterned PA TFC membranes in two steps, nanoimprinting polyethersulfone (PES) supports, and then formation of a thin PA film via interfacial polymerization (IP) method [11]. They found that NIL cannot be directly applied to the commercial TFC membranes because it is almost impossible to plastically deform the membrane's surface without causing a fracture in the barrier PA layer [20].

The advantages of the application of patterned membranes in modifying the flux and the fouling behavior were elucidated in both dead-end and cross-flow filtration modes. Culfaz et al. [21] found that the fouling resistance was higher using micro-patterned hollow fibers in dead-end UF. This was explained by looser particle deposition within the grooves of the surface pattern that was easier to be removed than a compressed deposit in case of un-patterned round fibers. Moreover, the flow distribution and the microbial fouling for prism-patterned UF membranes in cross-flow systems were investigated numerically and experimentally [1]. Less fouling was recorded in the upper regions where the local wall shear stress is higher. In other work, nanoimprinted PES UF membranes were shown to exhibit enhanced resistance towards colloidal silica particles [19]. This was interpreted by the localized turbulences induced by the imprinted features, and the change in the deposition behavior upon varying the orientation angle between the surface features and the feed-flow direction. This improvement in antifouling behavior was also revealed for prism-patterned PVDF UF membranes [17]. The analogous antifouling behavior was recently found in cross-flow yeast filtration employing patterned PES microfiltration membranes [22].

Additionally, the merits of implementing the submicron-patterned PA TFC membranes were also highlighted [11]. The patterned TFC membranes exhibited higher water flux and lower tendency towards scaling by the virtue of modifying the flow behavior near the membrane surface. Nevertheless, these membranes suffered from modest NaCl rejection behavior, ≤90%. In most recent work [20], a more comprehensive investigation regarding the influence of IP conditions on the surface topography and the permselective properties of the patterned TFC membranes was performed. Nevertheless, micro-imprinting lithography (MIL) could potentially be an alternative in order to preserve intrinsic properties of the barrier layer along with promoting the conformity of the surface microstructures.

In the current work, more reliable and detailed fabrication guide for producing high performance micro-patterned PA TFC membranes is introduced. The fidelity of the surface micro-patterning techniques is comprehensively studied and different mechanisms are proposed. The separation performance and concentration polarization experiments are conducted for both dead-end and cross-flow configurations, and all results reveal that substantial improvements of membrane performance can be obtained by the two different fabrication methods for micro-patterned PA TC membranes.

2. Experimental

2.1. Materials

Silicone elastomer and hardener (Sylgard 184; Dow Corning, USA) were used to prepare PDMS molds. Polyethersulfone (PES; Ultrason E6020P; BASF, Germany), and polyvinylpyrrolidone (PVP K-30; Sigma-Aldrich) were dried overnight before use. *N*-methyl-2-pyrrolidone (NMP; 99%; Merck, Germany), and triethyleneglycol (TEG; 98%; Arcos, Belgium) were used as received. For PA synthesis, m-phenylenediamine (MPD; ≥99%), 1,3,5-benzenetricarbonyl trichloride (TMC; 98%), D(+)-camphor-10-sulfonic acid (≥98%) and n-hexane (95%) from Acros, and triethylamine (TEA; 99%; Merck) were used as received. Sodium dodecyl sulfate (SDS; Sigma-Aldrich) was employed for PDMS cleaning/pre-treatment. Sodium chloride (NaCl) was from Fluka. Nitrogen and Argon gasses were supplied from Messer Griesheim GmbH (Krefeld, Germany). Water purified with a Milli-Q system from Millipore (Burlington, MA, USA) was used.

2.2. Fabrication of micro-patterned PA TFC membranes

2.2.1. Preparation and pretreatment of PDMS molds

A 4 in. silicon wafer with parallel lines pattern (i.e., an array of straight grooves with regular branches) fabricated by photolithography at IBM Research, Zurich, Switzerland, was used as master to prepare PDMS molds. Silicon elastomer and hardener were weighed by the ratio of (10:1 w/w). The mixture was vigorously whisked to ensure uniform distribution of the curing agent. Then, the bubble free PDMS solution was poured in a petri-dish containing the master and cured overnight at 65 °C. Only one pattern of fixed features and dimensions was utilized in this paper. An optical microscope image of the employed PDMS mold is presented in Fig. 1a.

Prior to using, PDMS molds were hydrophilized via either oxygen plasma at 0.75 mbar and 100 W for 45 min using plasma cleaner (Femto-QLS, Diener Electronic GmbH), or they were immersed in SDS solution (1 g L^{-1}) and kept under intense stirring for at least 30 min.

2.2.2. Preparation of micro-patterned PES supports using MIL

2.2.2.1. Casting of flat isotropic PES base membranes. The detailed procedure had been optimized and introduced in our previous work [23]. Briefly, NMP (32 wt%) and TEG (43.5 wt%) were mixed, then PVP (12 wt%) was dissolved. Thereafter, PES (12.5 wt%) was added to the solution. The solution was kept under stirring at ambient temperature till clear viscous solution was obtained. The polymer solution was casted at 5 mm s^{-1} using a stainless steel knife of a gap thickness of 250 μm. Then, the polymer film was immediately exposed to humid air (relative humidity: 80% at 22–23 °C) for 3 min. Afterwards, the turbid polymer film was immersed in a coagulation bath containing de-ionized water. The membranes were then immersed in an excess of deionized water overnight for complete precipitation and then dried [23].

2.2.2.2. Micro-imprinting of the prepared flat PES membranes. The aforementioned pattern was imprinted on the prepared flat PES membranes using stainless-steel nanofiltration cell and PDMS mold as a simplified low-cost method. The custom setup was assembled as shown in Fig. 2a. The flat PES membrane was placed on the PDMS mold that was supported by a plain metal plate. Another porous metal plate was added on top to equilibrate the compaction. The normal