1 Introduction

Separations of biological and chemical species have great value in industrial processes, biopharmaceutical production, medical care, and water purification. Semipermeable membranes that are classified as ultrafiltration sieves, with approximately 10–100 nm pores, are commonly used to address these needs [1]. Conventional polymeric ultrafiltration membranes are limited in their ability to separate two or more species similar in size due in part to a log-normal distribution of pore sizes [2]. Tortuous path polymeric membranes also have significant surface area that can lead to adsorption and loss of desired product [3]. Additionally, most ultrafiltration membranes are orders of magnitude thicker than the pore diameter resulting in low permeability [4]. Improvements in nanofabrication and recent interest in nanomanufacturing offer promise in making significant improvements in ultrafiltration [5]. The ideal molecular or protein sieve is a membrane with a uniform distribution of pores in an ultrathin film, while fabricated and supported in a manner that is scalable and robust enough for practice use. Through-pores and the use of inorganic materials might also enable membranes that can be cleaned, sterilized, and reused far more readily than tortuous path polymeric membranes currently in use today.

The classic Mehta and Zydney Selectivity-Permeability plot has long predicted an upper bound on selectivity for ultrafiltration membranes with log-normal distributions of pores [6]. While uniform pore size or isopore membranes currently exist that would push the limits of this plot, such as commercially available track-etched membranes, their low porosity and significant thickness results in very low permeability [7, 8]. Ultrathin membranes, ≤100 nm thickness, present unique transport efficiency not normally found in much thicker polymeric membranes considered in the Mehta

Review

Fabrication techniques enabling ultrathin nanostructured membranes for separations

The fabrication of nanostructured materials is an area of continuous improvement and innovative techniques that fulfill the demand of many fields of research and development. The continuously decreasing size of the smallest patternable feature has expanded the catalog of methods enabling the fabrication of nanostructured materials. Several of these nanofabrication techniques have sprouted from applications requiring nanoporous membranes such as molecular separations, cell culture, and plasmonics. This review summarizes methods that successfully produce through-pores in ultrathin films exhibiting an approximate pore size to thickness ratio of one, which has been shown to be beneficial due to high permeability and improved separation potential. The material reviewed includes large-area, parallel, and affordable approaches such as self-organizing polymers, nanosphere lithography, anodization, nanoimprint lithography as well as others such as solid phase crystallization and nanosphere lens lithography. The aim of this review is to provide a set of inexpensive fabrication techniques to produce nanostructured materials exhibiting pores ranging from 10 to 350 nm and a pore size to thickness ratio close to one. The fabrication methods described in this work have reported the successful manufacture of nanoporous membranes exhibiting the ideal characteristics to improve selectivity and permeability when applied as separation media in ultrafiltration.

Keywords: Membrane / Nanofabrication / Nanoporous / Nanostructured / Ultrafiltration

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Electron and ion beam lithography are examples of top-down features with excellent control in shape, size, and distribution. Shaping of a macroscopic layer into an array of microscopic features is, to some degree limited, these processes provide a good trade-off between cost and functionality. In contrast, bottom-up processes are more affordable and although feature size and distribution limits their application. In summary, conventionally used high cost top-down fabrication methods, serial and parallel, remain an unlikely candidate for the advancement of low-cost and large-area membrane fabrication. Conversely, bottom-up methods offer closer control while bottom-up methods are inexpensive.

Figure 1. Schematic comparison of top-down and bottom-up nanofabrication techniques used for the production of nanoporous membranes. Top-down methods allow closer control on feature size and distribution while providing a large area of fabrication to ensure mass manufacture feasibility. Fabrication techniques can be divided into two categories according to their overall approach being top-down or bottom-up; Fig. 1 shows a schematic comparison of these two directions. Top-down processes allow closer control on feature size and distribution; however, their high cost often limits their application. In contrast, bottom-up processes are more affordable and although feature size and distribution is, to some degree limited, these processes provide a good trade-off between cost and functionality.

Top-down methods offer close control of feature size and distribution, whereas bottom-up methods allow parallel and self-assembly.
Table 1. Comparison of techniques resulting in free-standing or released membranes with a pore size to thickness aspect ratio close to one

<table>
<thead>
<tr>
<th>Technique</th>
<th>Pore dimension (nm)</th>
<th>Aspect ratio (size: thickness)</th>
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</thead>
<tbody>
<tr>
<td>Self-organizing polymers</td>
<td>15–95</td>
<td>80–100</td>
</tr>
<tr>
<td>Nanosphere lithography</td>
<td>70–350</td>
<td>75–500</td>
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<tr>
<td>Anodization</td>
<td>100–115</td>
<td>190–540</td>
</tr>
<tr>
<td>Nanoimprint lithography</td>
<td>200</td>
<td>280</td>
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approaches allow the formation of arrays of nanoscopic features through the use of atomic, molecular or particle building blocks, often resulting in a parallel process. These are efficient and spontaneous processes that under the right conditions promote materials self-structuring into nanoscale patterns that can be controlled through indirect environmental parameters.

This review will discuss processes that have enabled the fabrication of nanostructured membranes at a reasonable cost, highlighting those producing released or free-standing membranes with a pore size to thickness aspect ratio close to one. These techniques have been utilized to produce membranes with thicknesses in the range of 70–540 nm, demonstrating the feasibility and great potential of achieving ultrathin membrane fabrication. Table 1 summarizes pore dimensions and aspect ratio of the highlighted membrane reports. The use of self-organizing polymers [23–29] and nanosphere lithography [30–35] are discussed first; these methods are being increasingly applied for ultrathin membrane fabrication. Nanosphere lithography can be considered a hybrid approach; however, it is based on a bottom-up self-assembly of nanospheres. Anodization [36–40] will be presented next; although, not widely applied for the fabrication of ultrathin membranes, this very well researched process has been successfully used for the production of nanoporous patterns and thick membranes. Although commonly considered a top-down approach, nanoimprint [41–43] techniques that utilize low-cost or unique master molds have been included in this review. Finally, an overview of other applied or developing fabrication methods is also offered. Figure 2 shows micrographs adapted from publications reporting the production of membranes processed through the nanofabrication techniques reviewed in this work. These techniques correspond to bottom-up or affordable top-down strategies which are favorable for the production of nanoscale patterns over large-areas at low-cost. The aim of this review is to provide a critical analysis of nanofabrication methods enabling the production of ultrathin nanoporous membranes to be used as separation media.

2 Challenges of bottom-up membrane fabrication

Bottom-up techniques provide a platform for the production of porous patterns at the nanoscale. One of the major quality and usability challenges when applying these patterns for the fabrication of separation membranes is the presence of defects. Point defects found in porous membranes can be summarized as defects resulting in pore absence as well as defects resulting in altered pore size. The absence of pores can potentially increase flow resistance while reducing yield; however, this will not significantly hinder the functionality of the membrane. On the other hand, the variation in pore size or merging of pores directly impacts the selectivity by allowing unwanted particles to move across the membrane, which can compromise its functionality, particularly in applications...
such as virus removal in bioprocessing. Simple methods can be implemented to tune the pore size distribution. Decreasing the pore size can be accomplished by placing a conformal layer through techniques such as atomic layer deposition. Increasing the pore size is often achieved by isotropic etching and develop fewer defects [95]. Templated self-assembly has been used to promote long-range order in self-organizing polymers by using templated substrates that guide the arrangement and decrease the defect concentration. The templates consist of shallow steps; however, sidewall defects in the template can lead to domain vacancies and changes in the width can create dislocations; both point defects contribute to the absence of pores [96], an acceptable defect for separations.

Nanosphere lithography is based on the periodic arrangement of nanoparticles over a monolayer which can represent a challenge. Polysilare solutions of nanoparticles translate into polydisperse pore sizes. Overabundant quantities of nanoparticles, hinder the formation of monolayers which can potentially result in larger pore sizes. Both effects result in defects related to pore size and significantly affect separation processes based on size. Several methods addressing the periodicity of the assembled beads have been reported [67, 97]. Another factor increasing the concentration of defects is the plasma treatment used to decrease particle size. This type of defect arises from the formation of a pedestal that results in the nanoparticles tipping over to a side [35], which has a minimal effect on pore arrangement and does not generally impact membrane functionality.

In the case of anodization, the most common defect is disorder of the generated pores which is affected by the anodizing voltage, temperature, solution, and pre-existing defects in the metallic substrate used [98, 99]. High-purity aluminum foils yield nanoporous structures with a higher ordering degree than low-purity aluminum or aluminum alloys. Long-term anodization can increase the order by rearranging the pores [40]. However, the improved order might be the result of pore enlargement [100], a type of defect that directly affects the size exclusion capability of a membrane.

Defects occurring in nanoimprint lithography can be repeated or random [101]. Repeated defects are those created from a defective nanoimprint master mold; random defects are those produced as a result of particles, non-uniform contact or residue. The non-uniformity causes incomplete pattern development due to non-ideal contact with the mold. Presence of residue arises from the adhesion of the polymer to the mold. The latter can be minimized with the use of a fluorinated monolayer to decrease the surface energy of the mold [102]; however, the anti-adhesive character has been found to decrease when in contact with air [103]. Non-uniformity and residue cause the increase of defects related to pore size which have a detrimental effect on membranes applied as separation media. Defects have many origins and achieving a defect-free membrane is impractical. Therefore it is important to study the defect concentration related to a particular nanofabrication route. These versatile techniques can be integrated into processes enabling the fabrication of organic and inorganic based membranes; where the active area closely depends not only on the fabrication method but on properties such as strength and stability of the selected membrane material. As usual, optimization must be application driven since it is the application which determines the active area, type and level of accepted defects.

3 Self-organizing polymers

Traditional ultrafiltration membranes typically made by solvent casting polymeric materials have been used and studied for several decades. These asymmetric membranes have a selective skin over a mechanically strong porous substructure [26]. Parameters such as a solvent to polymer ratio, temperature, and gelation medium effectively control the characteristics of the resulting membranes [46]. However, these membranes exhibit a tortuous pore structure which increases flow resistance and surface area, impacting the flow and resulting in product loss. The self-organizing quality of polymers has attracted much interest since it provides an efficient path for the formation of nanostructures exhibiting well aligned and through-pores. The most studied self-organizing polymers are the block copolymers (BCP), macromolecules composed of two or more distinct units that undergo microphase separation due to their positive enthalpy of mixing; hence self-organizing into well-defined arrays in the nanoscale [47, 48]. Membrane fabrication technologies have benefited from BCP research, applying its findings into the fabrication of nanopores. After the polymers undergo self-organization, removing one of the components in the array results in nanostructured porous materials [49].

Self-organizing BCP is a versatile technology yielding nanoporous membranes of polymeric nature such as polystyrene (PS) or poly (methyl methacrylate) (PMMA); and non-polymeric nature such as silicon nitride (Si₃N₄). The general fabrication process can be divided into three main steps. First the BCPs are synthesized in solution, then the solution is casted polymeric materials have been used and studied for several decades. These asymmetric membranes have a selective skin over a mechanically strong porous substructure [26]. Parameters such as a solvent to polymer ratio, temperature, and gelation medium effectively control the characteristics of the resulting membranes [46]. However, these membranes exhibit a tortuous pore structure which increases flow resistance and surface area, impacting the flow and resulting in product loss. The self-organizing quality of polymers has attracted much interest since it provides an efficient path for the formation of nanostructures exhibiting well aligned and through-pores. The most studied self-organizing polymers are the block copolymers (BCP), macromolecules composed of two or more distinct units that undergo microphase separation due to their positive enthalpy of mixing; hence self-organizing into well-defined arrays in the nanoscale [47, 48]. Membrane fabrication technologies have benefited from BCP research, applying its findings into the fabrication of nanopores. After the polymers undergo self-organization, removing one of the components in the array results in nanostructured porous materials [49].

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optimizing the concentration plays an important role in achieving a determined BCP nanoarchitecture.

Polystyrene-block-poly(ethylene oxide) (PEO) was used by Altinpinar et al. [47] to produce PS membranes supported on silicon wafers. The use of UV light as a cleaving agent was reported. Ortho-nitrobenzyl ester was used as the BCP junction which was later photocleaved. The PEO was washed in ultrapure water to reveal the nanoporous PS layer exhibiting 10 nm pores with a thickness of 24 nm. It is important to mention that the washing process distorted the morphology of the nanoporous film obtained; therefore, further investigation is required. Moreover, the nanoporous films remained supported on the silicon wafer; hence, integration of a releasing step is also required.

A PMMA membrane was successfully lifted-off a silicon wafer and transferred onto a microfiltration membrane (Fig. 3A). In this case, the addition of PMMA homopolymer caused the BCP to self-organize around the PMMA homopolymer cylindrical structures which was then removed in acetic acid. The latter resulted in a nanoporous PS-PMMA film supported on a sacrificial silicon oxide (SiO$_2$) layer dissolved in hydrofluoric acid (HF). The released membrane was transferred to a microfiltration polysulfone membrane. The obtained nanoporous membrane exhibited 15 nm pores with a thickness of 80 nm. The process was reported and applied by Yang et al. [14] to produce a device designed for the retention of human rhinovirus type 14 (HRV14) 30 nm in size. The virus was successfully separated from a solution containing bovine serum albumin (BSA) 7 nm in size. Regardless of the very thick (150 μm) microfiltration membrane used as a support, the authors reported high flux when compared against an anodized alumina membrane (60 μm thick and 200 nm pores). The increased selectivity was attributed to improved hydrodynamic interaction with the nanopore walls.

Montagne et al. [5], reported the fabrication of a Si$_3$N$_4$ membrane through the use of self-assembled micelles (Fig. 3C). The micellar arrangement represents a negative template and therefore must be inverted before it can be directly transferred to create nanopores. After etching the polymeric residue between micelles, the pattern was transferred into an underlying silicon film. The latter results in silicon nanopillars on top of a Si$_3$N$_4$ film. A chromium thin film was then selectively deposited on the Si$_3$N$_4$ only and the silicon nanopillars dissolved in potassium hydroxide (KOH), leaving a chromium layer with a nanoporous pattern which was then transferred into the Si$_3$N$_4$ through RIE. Finally, the back of the wafer was etched by deep-RIE (DRIE) to yield a free standing membrane with 95 nm pores and a thickness of 100 nm; showing improved transport rate compared to track-etched membranes.

The fabrication of another double-layered filtration device was reported by Nuxoll et al. [51], where a polymeric nanoporous membrane was fabricated on a Si$_3$N$_4$/Si microporous support (Fig. 3B). The method involved a PS-poly(isoprene)-poly(lactide) (PS-PI-PLA) triblock copolymer spin coated onto a Si$_3$N$_4$ surface, where the polymeric mixture self-organized into PI-PLA cylinders perpendicular to the substrate and embedded in a PS continuous layer. Then, the PLA domain was removed to reveal a nanoporous pattern exhibiting 45 nm pores with a thickness of 80 nm. Micrographs taken with a scanning electron microscope (SEM) showed irregularly shaped pores due to fluoropolymer deposition during reactive ion etch (RIE). Nevertheless, the authors demonstrated a successful nanofabrication method to produce a double-layered filtration device that showed a 50-fold increased selectivity of methyl orange over dextran blue when compared against an anodized alumina membrane (60 μm thick and 200 nm pores). The increased selectivity was attributed to improved hydrodynamic interaction with the nanopore walls.

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Popa et al. [52], followed a similar micellar approach by using polystyrene-block-poly(2-vinylpyridine) (PS-P2VP) deposited on a full 4” silicon wafer previously coated with SiO$_2$ followed by 100 nm of Si$_3$N$_4$ (Fig. 3D). A thin chromium etching template was produced in a similar fashion as described above and transferred into the Si$_3$N$_4$ layer to produce 80 nm pores with a thickness of 100 nm. The membrane release was accomplished by a KOH through-wafer etch that created exposed membrane windows. The SiO$_2$ film was used as an etch stop to prevent etching of the membrane; lastly, the SiO$_2$ was removed by a quick buffered oxide etch (BOE). In sum, the authors reported a nanofabrication process executed at the wafer scale (50% yield) containing several $10 \times 10 \mu$m$^2$ nanoporous membranes.

BCPs are able to attain several different nanopatterns, hence it is important to exert control over their self-organizing process. Several scientific reviews have tackled the task of outlining the chemical and physical details governing BPC technology [23, 24, 27–29]. Solvent evaporation or annealing, [54] applied electric field, [55] chemical (chemoepitaxy) or topographical (graphoepitaxy) treatment of surfaces are a few examples of strategies developed for the control of the self-organization of BCPs [23, 24]. The dimensions of the domains or micelles formed in the self-organized BCPs films determines the size and distribution of the pores; which can be tuned by varying the molecular weight as well as the deposition parameters such as spinning speed, humidity, and temperature [5, 52].

Overall, several research groups have demonstrated a straightforward BPC process for the fabrication of ultrathin free-standing or released nanoporous membranes that are integrated with conventional silicon technologies. The scalable nature of semiconductor manufacturing gives promise for the production of ultrathin membranes using these approaches.

4 Nanosphere lithography

Nanosphere lithography (NSL) is a patterning process that has been used and developed for the past three decades. It is a simple and inexpensive method that has found many applications in the fabrication of nanostructured materials [35]. This technique enables spheres to be used as templates to create nanoscale features. Most employed spheres are polystyrene but the use of silica has also been reported. In addition to producing nanoporous membranes, this technique has been used to produce silicon nanopillar arrays for fuel cells [56], chromium nanorings potentially applicable to optical and electro-optical devices [57], plasmonic patterns on graphene [58], gold nanohole arrays for electrochemical sensors [59], among many others.

A solution containing the spheres is first prepared to then be deposited on a surface where the self-assembly forms a 2D colloidal crystal film with hexagonal symmetry [35]. Spin-coating, drop casting, dip coating, electrochemical or electrophoretic deposition, assembly at an interface and template-guided assembly are some deposition techniques used [32, 63]. Many works have aimed to expand the control over the order of the nanospheres by depositing them on substrates placed at a tilt angle [32]. Additionally, controlled size reduction of the nanospheres after deposition has also been reported through the use of isotropic plasma etching; achieving a 65% reduction in diameter [64]. This shrinking effect is a simple and reliable process employed to achieve smaller feature sizes and increased spacing between features. Non-optimal etching parameters result in heterogeneous size and shape as well as the movement of the nanospheres and ultimately loss of symmetry [63].

After deposition and post-treatment of the nanospheres, the areas that are left uncovered are most commonly etched for pattern transfer; however, Kang et al. [60] functionalized them in order to selectively direct the deposition of a modified poly(hydroxyethyl methacrylate) (PHEMA) hydrogel to those open areas between nanospheres (Fig. 4A). A porous hydrogel was obtained exhibiting ~215 nm pores with a thickness of ~75 nm as estimated from atomic force microscopy micrographs. The produced nanoporous hydrogel membrane was detached from the substrate by UV-initiated cleavage. After membrane detachment, the authors reported a thickness decrease of about 2.5–3 times and an increase in pore diameter due to lateral stretching.

A more commonly taken approach is to etch the open areas which transfers the nanospheres pattern into an underlying film. This results in nanodots (2D) or nanopillars (3D) depending on the etch depth; hence, the pattern must be inverted in order to produce nanopores. The latter can be accomplished by deposition of a metallic film on top of the nanospheres; followed by their removal usually assisted by sonication. The process results in a nanoporous metallic layer which can then be used as an etch mask for pattern transfer. This was the approach taken by Klein et al. [61] in order to produce Si$_3$N$_4$ nanoporous membranes (Fig. 4B). The authors employed PS spheres that underwent a RIE process in an oxygen atmosphere to reduce their size. A thin chromium layer was used to produce the nanoporous etch mask to transfer the pattern into an underlying Si$_3$N$_4$ film. After membrane release in a KOH bath to etch the exposed silicon wafer from the backside, free-standing membranes exhibiting 350 nm pores with a thickness of 100 nm as estimated from SEM micrographs were obtained.

Interestingly, NSL has also been used to aid in the anodization of aluminum. Lipson et al. [62] reported a fabrication process for creating a nanoporous tungsten pattern on an aluminum layer deposited on silicon, acting as an etch mask to create ordered aluminum pits (Fig. 4C). After tungsten removal, anodization was performed as a one-step process to produce 70 nm pores with a thickness of 300 nm. This work demonstrates an efficient approach to ensure vertical sidewalls on anodized aluminum oxide (AAO), an alternative to the usual two-step anodization commonly used to achieve the same goal.

Finally, Acikgoz et al. [44], employed silica nanoparticles assembled as a close packed film embedded in a polymeric
matrix (Fig. 4D). Argon sputtering was used to etch both the polymeric matrix as well as the silica nanospheres to half their thickness. Then, the silica spheres were removed in HF leaving a porous nanopattern in the polymeric matrix. The nanopattern was then transferred by an oxygen plasma etch into an underlying film of polyethersulfone (PES). The described process was carried out on a silicon wafer coated with cellulose acetate (CA) as a sacrificial layer for membrane release; after membrane fabrication the CA was easily dissolved in acetone. The obtained PES nanoporous membrane exhibited 230 nm pores with a thickness of 500 nm.

Since characteristics such as size, ordering, and spacing of the deposited nanospheres directly determine the pore size and distribution of the resulting membrane, several groups have studied the role of the deposition processes. Jian-Hong Lee et al. [65], followed the evolution of a metallic mask deposited on PS spheres and found the PS spheres to move as a result of metallic growth underneath, eventually resulting in a continuous metallic layer rather than a nanostructured layer. This finding offers a simple parameter that can be used to obtain a feature size smaller than the spheres used. The use of isotropic plasma etching achieves sphere size reduction and consequently smaller feature size than the starting spheres; RIE is usually employed for this purpose. However, a combination of RIE-ICP (inductively coupled plasma) has shown to decrease the etch rates offering a closer control on the sphere shrinking process [64]. Jie Yu et al. [66], fabricated silver nanoparticles by depositing a thin layer of silver over close packed PS spheres. The nanoparticles exhibited sizes small as 50 nm. This method can be applied as a way to obtain secondary nanospheres of much smaller size. Furthermore, nanosphere assembly at the liquid-liquid interface has also been reported to yield non-close packed arrangement in which the spacing is easily tuned by setting the interface area constant while varying the number of particles introduced for self-assembly [67]. NSL is a versatile process used to fabricate nanostructured materials for a wide variety of applications.

5 Anodization

As fabrication has moved from the micro into the nanoscale, special interest has been given to spontaneous fabrication methods that yield nanostructured materials; naturally, anodization has come into play. In addition to commonly used Al, other anodized materials include Ti [68–72]; Ta [73]; Zr [74]; Nb [75]; GaN [76]; and have been studied for applications such as drug release [77], electrically active membranes [68], solar cells [71], and protein-releasing conductive membranes [78], among many others.

Anodization is a spontaneous process that oxidizes a material while creating cylindrical nanoperes parallel to each other and perpendicular to their underlying metallic substrate [36]. The layer anodized during the initial step is allowed to reach symmetry and then dissolved, leaving ordered concave pits in the substrate which serve as nucleation sites during the second anodization step [39]. The anodized aluminum oxide (AAO) layer presents open nanopores on one side and closed bottoms on the interface with the metallic substrate. This interface is referred to as the barrier layer and its chemical composition is the same as the AAO. When applied to membrane fabrication, the barrier layer and the metallic substrate can be dissolved to release a nanoporous AAO membrane [36].

One key characteristic of the anodization process is the achievement of very high aspect ratios of pore size to thickness while maintaining vertical sidewalls and periodic order [40]. Anodized materials have been widely employed because of their high aspect ratios; however, their very thick nature limit them to low transport rates [52]. More recently,
Anodization

Increasing interest over small aspect ratios has emerged because of the mass transport advantages it offers. The latter expands the reach of anodized materials and calls for further research and development.

Successful preparation of anodized titanium oxide (ATO) from a Ti foil, followed by transfer from the foil to a foreign substrate has been reported by Lv et al. [69] (Fig. 5A). After anodization, the ATO/Ti foil is immersed in water to undergo detachment. The authors believe that hydrogen trapped under the barrier layer further develops H₂ bubbles allowing water to penetrate this interface, releasing the H₂ present and resulting in complete membrane detachment. The ATO released membrane of 539 nm thickness with 115 nm pores achieved in this work as an efficient and low-cost alternative to electrodes for photoelectrochemical applications. Furthermore, this fabrication process exhibits great potential to apply ATO as separation media since it successfully produces a released nanoporous membrane that can be transferred onto a supporting frame and be used for separation strategies.

Yanagishita et al. [79], employed a two-step anodization process to fabricate a free-standing porous alumina membrane. Anodization was carried out in H₂C₂O₄ and H₂SO₄ for the first and second step, respectively. First anodization creates a highly soluble alumina layer selectively dissolved in a mixed solution of CrO₃ and H₃PO₄ which detaches the second alumina layer without pore widening. Although high aspect ratio AAO membranes were fabricated in this study, it is a promising approach for membrane detachment that can be readily applied to thinner AAO films.

Wen-Jeng Ho et al. [45], fabricated AAO from an Al foil which, after anodization, was immersed in a solution containing CuCl₂, HCl, and H₂O to etch the remaining Al foil (Fig. 5B). They then used H₃PO₄ to remove the back barrier layer to fully open the pores. The process resulted in a free standing AAO ultrathin film with a pore diameter of 80–100 nm and a thickness of 190 nm. The ultrathin AAO was used as a template for the growth of silver nanoparticles [45].

Nanoimprint lithography

Nanoimprint lithography is a relatively new fabrication technique enabling patterning at the nanoscale with high throughput at a reasonable cost [42]. It requires thermoplastic materials such as PMMA to be heated above its glass transition temperature while being pushed into a mold. The polymer is cooled down after filling the mold retaining the developed shape. This process is also referred to as hot embossing. A variation of this process is the use of UV light to...
Nanoimprint lithography offers a wide variety of patterning processes such as lift-off, direct nanoimprint, stamping, transfer, stripping, and reversal [41].

Nanoimprint technologies are occasionally classified as expensive since the nanostructured master molds used are commonly fabricated through costly techniques such as e-beam lithography. This significantly increases the budget of research and development, since the master mold can only cover a small area and the patterns cannot be easily modified. Nevertheless, reported works have demonstrated the feasibility of using nanoimprint technologies for the fabrication of nanoporous membranes. Sainiemi et al. [89], fabricated silicon nanoporous membranes by UV-assisted nanoimprint lithography. The master mold presented circular patterns with a diameter of 300 nm, fabricated by e-beam lithography, from which a PDMS stamp was made. More recently, Nabar et al. [90] demonstrated the fabrication of Si$_3$N$_4$ nanoporous membranes through a thermal nanoimprint process. In their work, a commercially available silicon master mold presenting nanopillars with a diameter of 200 nm was used to imprint a photosensitive material on a Si$_3$N$_4$ layer. The resulting membrane exhibited 385 nm pores with a thickness of 1 μm. The authors studied the occurrence of defect events, namely connected and malformed pores and found the wafer average % of damaged pores to be 13.81% when evaluated on a single wafer over a 10 × 10 μm area.

Wong et al. [22] recently reported a strategy to tune pore thickness and diameter by utilizing a PDMS mold to imprint a nanoporous pattern on a polymeric film using capillary force driven mold-based lithography (Fig. 6A). The PDMS master mold is brought in contact with the polymeric layer to produce pores exhibiting oval, circular or rod shapes with a pore size ranging from 80 to 400 nm; by controlling imprinting time and temperature. The fabrication technique reported includes the use of a sacrificial layer of poly(sodium 4-styrenesulfonate) (PSS) which is dissolved in water to mediate the release of the membrane. This simple nanoimprint fabrication process successfully expands the versatility of a single master mold to be used for the fabrication of membranes with a wide range of pore dimensions.

Furthermore, the ever increasing catalog of nanofabrication techniques has allowed the cost reduction of nanoimprint master molds as well. Several authors have reported the use of AAO for the fabrication of nanoimprint master molds. To the best of our knowledge, this alternative route has been rarely used to fabricate nanoporous films applied as membranes; however, it has been used for the fabrication of nanostructured materials for other applications that require a porous surface which illustrates its promising potential for the fabrication of nanoporous membranes.

The use of AAO templates hot-pressed against a polymeric or platinum-based metallic alloy to create a master mold of nanorods has been reported by Jianjun Li et al. [88] (Fig. 6B). The obtained nanorods were subsequently used to produce nanopore arrays on a resist layer by hot embossing. The nanoporous resist film corresponding to SU-8 exhibited 207 nm pores with a thickness of 300 nm, fabricated from a PMMA-based master mold. Moreover, the AAO template has been used as a nanoimprint master mold itself [91].

Nanoimprint lithography has also been used to enable the fabrication of AAO with different morphologies, where the porous pattern is duplicated or even triplicated. The latter was achieved by nanoindentations on a PMMA layer through the use of a nanoimprint stamp, which was found to be closely correlated to the morphology of the AAO obtained [92]. Furthermore, the shape of the pore faces can also be controlled as reported by Masuda et al. [93], through the use of a SiC nanoimprint mold to produce square or triangular nanoindentations from which the anodization process develops to form square or triangular pore faces. Additionally, a mild-hard cyclic anodization has been shown to produce pores where the diameter fluctuates with depth [94]. These techniques demonstrate the versatility of the well-known anodization process, expanding the catalog of AAO based nanoimprint master molds that can be produced.

One of the challenges of nanoimprint lithography is the correct alignment of the template and substrate, which if not done with precision can result in misalignment of the subsequent layers [42]. However, the fabrication of nanoporous membranes usually requires a single step of nanopatterning, hence the overlay is not a limiting factor. Furthermore, nanoimprint lithography is a great candidate for scalable nanomanufacturing, by potentially enabling roll-to-roll processes. Master molds can be fabricated as spinning rods...
that when in contact with a moving substrate can imprint a pattern [41]. Roll-to-roll processes are highly desirable for mass manufacture because of significantly reduced costs.

7 Other applied or promising techniques

Other innovative mechanisms have also been studied with the goal of creating ultrathin membranes. Solid phase crystallization is a spontaneous phenomenon driven by the thermodynamics of materials crystallization which has been integrated into nanofabrication processes through similar pathways to produce free-standing nanoporous membranes. Similarly to NSL, lens lithography utilizes spherical beads to focus UV light and expose a nanoscale area on a photoresist layer. The well-known Stöber process offers a promising technique to produce nanoporous membranes through an approach very similar to self-organizing polymers. Furthermore, the self-assembly of molecules or nanoparticles has been reported for the fabrication of nanoporous membrane. Additionally, carbon nanotubes embedded in a matrix have been used as a nanoporous membrane and carbon nanotube removal from the matrix is another promising nanofabrication approach. Lastly, metal-assisted chemical etching is a promising tool to produce nanopores by etching a layer through the use of nanoparticles. These applied or promising techniques are discussed in this section.

7.1 Solid phase crystallization

Our collaborative teams have been researching the fabrication and application of ultrathin silicon-based porous membranes for over ten years. Striemer et al. [4], designed an innovative fabrication process driven by the spontaneous formation of voids in ultrathin silicon films due to solid phase crystallization (Fig. 7A). The process requires the deposition of a three layer stack consisting of SiO\(_2\)/amorphous-Si/SiO\(_2\) which undergoes a rapid thermal treatment to develop nanopores. The nanoporous silicon films were accessed by etching the back of the silicon wafer resulting in free-standing nanoporous membranes exhibiting pore sizes from 9 to 35 nm with a thickness of 15 nm. Parameters related to film deposition and thermal treatment were found to influence the pore size and distribution [105]. Membranes with pore diameters between 5 and 55 nm with 0.5 to 6.6\% porosities and even >20\% have been achieved by replacing SiO\(_2\) with Si\(_3\)N\(_4\) [106]. This fabrication method allows for carbonization as a post-fabrication means of controllably reducing the pore size by 1 to 25 nm. Moreover, the thin carbon coat further improves the chemical stability to alkaline solutions that rapidly etch silicon otherwise [107]. The nanoporous silicon membrane described has also been used as an etch mask to produce large-scale SiN membranes [108], which have been successfully released through wet and dry lift-off techniques [109]. The scale-up capability of this fabrication process has enabled us to consistently deliver nanoporous membranes with larger active area and improved mechanical stability while remaining ultrathin.

Another successful fabrication process was reported by Liu et al. [110], utilizing the self-assembly of cesium chloride (CsCl) islands. In this case, a CsCl layer was evaporated on a sacrificial layer of polydimethyl glutarimide (PMGI); the samples underwent moisture exposure to promote the formation of islands. The obtained pattern was transferred into the PGMI film and reversed to form a chromium etch mask. The pattern was transferred into the Si\(_3\)N\(_4\) layer and the produced membrane was accessed by etching the back of the silicon wafer. The obtained free-standing Si\(_3\)N\(_4\) membranes exhibited pores in the range from 80 to 200 nm with a thickness of 200 nm. It has been reported that size and interpore spacing can be controlled by changing processing parameters such as CsCl thickness, relative humidity, exposure time, and temperature [111, 112].

7.2 Nanosphere lens lithography

This is a maskless patterning process that enables the fabrication of nanopores or nanopillars through the use of conventional photolithography tools; using UV light focused by PS or silica nanospheres [113]. Wu et al. [114], reported the successful patterning of positive and negative photoresists through this approach, obtaining nanopores or nanopillars with a diameter between 500 and 700 nm by adjusting the exposure time through an assembled monolayer of 0.97 \(\mu\)m spheres (Fig. 7B). Moreover, the lattice period was increased from 500
to 4000 nm through the use of larger nanospheres without impacting the size of the pores, due to the fact that the focused area is a very weak function of the sphere size. Feature sizes with a diameter of 180 nm and sexfoil-shaped features have been obtained through process optimization [104, 115]. Furthermore, feature size down to 75 nm has been obtained by using an interlayer of silver to enhance the evanescent wave by surface plasmon excitation [116]. Although, more research needs to be done to explore its reach, lens lithography stands as a straightforward technique that can be readily applied to membrane fabrication.

7.3 Stöber-process

The Stöber process is an example of a sol-gel method through which molecules from a precursor reorganize in solution to form new structures; it remains as a commonly used process for the production of silica nanostructures since it was first reported by Werner Stöber in 1968 [117]. Porous silica films can be produced by the addition of a surfactant to promote initial micellar formation that evolves into well-aligned pores. Zhaogang Teng et al. [53], reported the successful formation of mesoporous silica films formed on silicon with aligned pores of 2.3 nm average size. Film thickness was varied from 34 to 240 nm when adjusting the water/ethanol or precursor/surfactant ratio and deposition time. The use of similar porous silica films as separation media was reported by Lin et al. [118]. In their work, the porous silica film was synthesized on an ITO substrate and then transferred to a microporous Si₃N₄ membrane supported on a silicon wafer. Thickness was controlled by adjusting the deposition time between 4 and 24 h to yield a final thickness of 14 to 118 nm. Produced porous silica of all thicknesses were successfully transferred without breaking or wrinkling.

The Stöber process offers a simple approach to obtain quality porous silica that can be transferred to a foreign substrate and has already been applied for molecular separation based on size and charge [13]. Variation of pore size may be attained through the use of different surfactants that create larger micelles; however, this remains a subject to be studied.

7.4 Metal-assisted chemical etching

The use of metallic nanoparticles in etching solutions has been implemented as a simple method for the production of morphologies of nanopolars or nanopores. Zhu et al. [119], utilized a colloidal gold solution in HF/H₂O₂ to produce random porous structures (20 nm wide) on the surface of a silicon wafer where the pores followed the <100> planes when propagating below the surface. More recently, an array of gold nanoparticles was employed for the fabrication of nanowires and nanopolars [120]. A similar approach utilizes gold nanoparticles heated close to their melting point, promoting their diffusion perpendicularly into amorphous substrates such as SiO₂ and Si₃N₄. De Vreede et al. [121] found that under optimized conditions, nanoparticle diffusion leaves nanopores 25 nm wide. Additional research and development of this process should be done since it represents a valuable tool that can be integrated into a nanofabrication process for the creation of pores.

7.5 Membranes based on the assembly of nanoparticles/molecules

Protein-based membranes have achieved very small pore sizes through simple assembly processes. These membranes are formed by proteins such as ferritin that assemble around metal hydroxide nanostrands which are then removed; the protein film is crosslinked to yield a robust membrane, although the pores formed are not always through-pores. Peng et al. [122], reported the fabrication of a ferritin membrane exhibiting 2.2 nm pores in a 60 nm thick membrane. Van Rijn et al. [123], reported another ferritin-based membrane; however, in their work the protein is embedded in a polymer matrix assembled at an air/water interface. The ferritin is then denaturized, leaving a polymeric nanoporous 7 nm thick membrane exhibiting pores with selectivity to particles below 20 nm. Similarly, dodecanethiol-ligated gold nanocrystals were reported by He et al. [124], to assemble at a water/air interface to form a thin nanoporous film after drying. These membranes consisted of four layers sequentially deposited to a final thickness of 34 nm; hence, a 100% population of through-pores is not expected. The obtained membrane exhibited >99% rejection of nanoparticles with a diameter ≥2 nm. Although membranes presenting through pores remain to be obtained, this approach shows future promise.

7.6 Carbon based membranes

Carbon nanotube (CNT) based membranes have also been investigated since very small diameters can be achieved. Hinds et al. [125], fabricated an array of aligned CNT embedded in a polymeric matrix and released from the quartz substrate in HF leaving the CNT tips opened. The resulting membrane exhibited 7.5 nm pores with a thickness of 5 to 10 μm. Moreover, functionalizing the open ends of the CNT allows controlled chemical or ionic separations. Although these membranes are very thick, gas and liquid transport show a 15–30 and 1000–10 000 fold increase from the values predicted by Knudsen diffusion and no slip hydrodynamic calculations respectively [126].

Holt et al. [127], reported the fabrication of a CNT-based membrane grown on a silicon substrate with iron as a catalyst. SiNₓ was then deposited to fill in the bulk of the CNT without losing alignment. The membrane was accessed by wet etch removal of exposed silicon on the back of the wafer. This CNT membrane exhibited a lower molar flux than predicted due to the bamboo morphology. Additionally, the CNTs were removed through an oxidation process leaving a SiNₓ nanoporous membrane; exhibiting an estimated average pore
size of 66 nm. Nanofabrication involving CNT remains an interesting approach to achieve very small pores; however, further investigation and development need to be done in order to achieve a CNT morphology free of defects that hinder mass flow.

Graphene membranes have also been fabricated by treating graphene layers with an oxygen plasma producing nanopores exhibiting a diameter of 1 nm as reported by Surwade et al. [128]. The pore formation could be tracked by Raman spectroscopy by evaluating the intensity ratio and shape of the D and G peaks. Similarly, introduction of defects by ionic bombardment causes the formation of pores which can be further enlarged through etching to form pores with diameters of <1 nm. Pore density reaches a maximum equivalent to ionic bombardment density, suggesting each ion acting as a seed from which a single pore is created [129]. Graphene based membranes provide an aspect ratio close to one for very small pore sizes (≤1 nm), hence are of great interest for the separation of very small molecules.

7.7 Controlled breakdown

Another promising technique for the fabrication of nanopores of <2 nm in size takes advantage of the dielectric breakdown of thin films when exposed to high electric fields. The successful formation of single nanopores has been demonstrated by Briggs et al. [130], in Si$_3$N$_4$ films in the presence of aqueous and organic environments. The main interest in single nanopore membranes derives from their potential application as DNA analysis and sequencing platforms.

8 Conclusion

Advancement of nanofabrication techniques continues to enable the production of nanostructured materials in many areas of science and for a wide range of applications. The techniques reviewed here correspond to processes yielding through-pore nanoporous membranes with a pore size to thickness ratio close to one, ensuring efficient mass transport due to improved selectivity and high permeability. These membranes have been fabricated thorough large-area and low-cost methods that are inherently scalable to large scale manufacturing. Most separation applications can tolerate some variation in pore size and distribution. The most common point defects found during membrane fabrication are related to the absence of pores or variation of pore size. The former is not significant for ultrafiltration strategies and the latter can be optimized to ensure membrane functionality and optimal efficiency. The nanofabrication techniques reviewed show great versatility and can be utilized for organic and inorganic materials to produce membranes exhibiting a wide range of geometries. These processes can be easily performed in research laboratories and integrated into more complex assemblies, showing great potential for a variety of applications, advancing many areas of research. The catalog of nanofabrication processes will continue to expand and allow for increasingly sophisticated and reliable membranes applied in ultrafiltration technologies.

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9 References


