Stretched homoporous composite membranes with elliptic nanopores for external-energy-free ultrafiltration†

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Extremely permeable ultrafiltration membranes with elongated elliptical pores are fabricated by stretching composite membranes with homoporous selective layers and macroporous supports. With simultaneously increased porosities both for the selective layers and supports and the thinned selective layers, the stretched membranes exhibit multifold-enhanced permeability with little sacrifice in selectivity. Thus the produced membranes enable, for the first time, gravity-driven ultrafiltration and discrimination of similarly sized nanoparticles with diameters down to 30 nm.

Ultrafiltration (UF) is extensively used for the supply of clean water and many industrial products based on the size-sieving mechanism of membranes with pore sizes in the range of approximately from 2 to 100 nm.1 UF operates typically under driven pressures larger than one atm, and enormous efforts have been made to improve the permeance of UF membranes at little to no expense to their separation selectivity. Gravity-driven filtration has been realized with filters and membranes with large pores and is extremely energy efficient as it requires no external energy input to generate the pressure required to permeate. However, as UF membranes are defined by pore sizes down to ~2 to 100 nm and usually have a permeance much smaller than that of microfiltration (MF) membranes, gravity-driven UF requiring no external energy has not been demonstrated yet. External-energy-free UF might be possible if the permeability of the membrane can be upgraded to be comparable to that of MF membranes while maintaining the selectivity of the UF category. Pore size and shape are the two key parameters contributing to the water flux and selectivity of UF membranes.2 It has been theoretically predicted that anisotropic pores with a high aspect ratio exhibit higher permeability as well as selectivity than circular pores.2,3 Simulated results further confirm that anisotropic pores with a pore length two or more times larger than their pore width produce superior flux without sacrificing selectivity.4 These theoretical and simulated results have been experimentally verified using microfiltration filters with elongated openings.5–8 Moreover, we prepared UF membranes with long and narrow slit-shaped pores by selective swelling of in-plane aligned block copolymers (BCPs), and demonstrated their remarkably enhanced permeance and high selectivities.9

Also, thinning of the selective layers of UF membranes without introducing defects is very efficient for improving the membrane permeances. Synergetically combining the deformed pores and thinned selective layers may lead to extremely permeable UF membranes, thus enabling gravity-driven UF. Mechanical stretching is capable of controlling the pore shape and size of the membranes in a facile and affordable way,10 however, it is predominantly used to stretch MF membranes.11–14 In addition, stretching will expand the selective layers and reduce their thicknesses.

Herein, for the first time, we fabricate composite membranes with elongated pores by stretching homoporous composite membranes to realize gravity-driven UF. Block copolymer thin films are solvent-annealed to perpendicularly align the micro-domains of the minority blocks.15 The annealed BCP films are then transferred onto macroporous supports, and subsequently subjected to swelling treatment to prepare composite membranes with homoporous BCP selective layers following the mechanism of swelling-induced pore generation.16 The composite membranes are further mechanically stretched along the uniaxial direction to produce membranes with elliptical pores to allow gravity-driven UF (Scheme 1).

A cylinder-forming BCP of polystyrene-block-poly(2-vinylpyrine) (PS-b-P2VP, $M^B_m = 290$ kg mol$^{-1}$, $M^P_{P2VP} = 72$ kg mol$^{-1}$) was used in this work. The as-prepared composite membrane consisted of a BCP selective layer with a thickness of ca. 70 nm and a macro-porous polyethersulfone (PES) membrane with a pore diameter of 0.22 μm as the support. The membrane was subjected to swelling in ethanol at 60 °C for 10 h to produce well-ordered straight
nanopores in the BCP layer (Fig. 1a). The pores exhibit an isotropic circular geometry with a pore diameter of 35 nm. Upon being mechanically stretched along the uniaxial direction, pore deformation selectively occurs in the opening areas of the PES support while in the areas of the PES skeleton, the BCP layers maintained their initial morphology with circular pores (Fig. 1b). Such a selective deformation is caused by the strong adhesion of the BCP layer and the PES support as a result of van der Waals forces. In the deformed areas in the BCP layer, the initially circular pores were transformed into elongated, elliptic pores with an average pore length of ca. 89.6 nm with 20% strain (Fig. 1c). The pore length was further increased to 117 nm as the strain increased to 40% (Fig. 1d). With a strain of 60%, the average pore length was increased to 134.3 nm which is nearly four times the original pore diameter before stretching (Fig. 1e).

As shown in Fig. 1f, the pore lengths of the stretched membranes were progressively increased with the increase of strain. The pore widths were also increased with strain, and 20%, 40%, and 60% strains produce pore widths of 37, 48.6 and 48.2 nm, respectively (Fig. 1f). Therefore, the surface porosities of the stretched BCP layers were gradually improved from 11.7% to 14%, 17.5%, and 19.9% as the strain was increased from 0% to 20%, 40% and 60%, respectively, whereas the porosities of the PES supports were correspondingly increased from 10.2% to 13.2%, 14.3% and 14.2%, respectively (Fig. 1g and Fig. S1 and S2, ESI†). The BCP layers and PES supports both showed an increasing trend in porosity due to their simultaneous stretching using mechanical deformation.

The selective deformation of the BCP layer in the opening areas of the supports resulted in local regions of elongated pores suspended on the supports allowing fast permeation because of the increased porosity and aspect ratios. Moreover, the suspended regions in the BCP layers had reduced thicknesses. The original thickness of the BCP layers after the swelling treatment was 85 nm, and the thickness after stretching can be estimated to be 70.8, 60.7, and 53 nm with strains of 20%, 40%, and 60%, respectively. The reduced thicknesses also noticeably contributed to the increase in permeability. The BCP layers were fixed on the support by attaching on the solid skeleton, thus providing mechanical stability to the composite structure of the membranes. Such a composite structure with localized suspended opening regions is essential to combine high permeability and robustness. Because of the irregularly shaped pores in the PES support (Fig. S1a, ESI†), the sizes of the elongated regions in the BCP layers varied approximately from 1 to 2 μm (Fig. 1b). The pores in the elongated regions were deformed to different degrees and consequently exhibited noticeable scattering in pore lengths and width. This is expected to be improved by using support membranes with homogenous pores.

Since the originally circular pores have been transformed to elliptic pores after stretching, they provide a great opportunity to operate the filtration process merely using the gravity of the feed instead of external pressures. We tried to measure the water fluxes of the composite membranes prepared with different strains (Fig. S3, ESI†). The stretched membranes required much less time to filtrate water with the same volume compared to the pristine membrane prior to stretching (Fig. S4, ESI†). Before stretching, the composite membrane exhibited a flux of 20.4 L m⁻² h⁻¹ as the volume of the water column was decreased from 25 to 20 mL (Fig. 2a). When the volume of the water column was lowered, the flux gradually decreased as a result of reduced gravity, for instance, the flux was 4.3 L m⁻² h⁻¹ when the water column changed from a volume of 5 mL to zero. In contrast, the composite membrane with 20% strain displayed a flux of 85.7 L m⁻² h⁻¹ which was more than four times that of the pristine membrane’s flux at the initial reduction of 5 mL in the water column. Further increasing the strains to 40% and 60%, such fluxes were determined to be 130.4 and 150 L m⁻² h⁻¹, respectively. It should be noted that all the fluxes had linear...
modified gold nanoparticles have electrostatic interactions with stretched with 60% strain. Monodispersed gold nanoparticles increase in flux. For example, the BSA retention dropped by after stretching is greatly compensated for by the remarkable UF category. More importantly, the slight decrease in retention they still implied that these membranes were defect-free and in the 16.5%, respectively. These BSA retentions were modest, however, the stretched membranes exhibited rejection rates of 20, 17.4 and membrane with circular pores. With the strains of 20, 40 and 60%, retention rate was measured as 26.8% for the pristine composite membranes still have the UF performance, as high fluxes might already comparable to that of MF membranes, which may enable gravity-driven filtration.

However, it is necessary to confirm that the stretched membranes are indicating good mechanical robustness of the stretched membranes. We note that the transmembrane pressure was 0.01 bar at the initial 5 mL water column (from 25 to 20 mL, Fig. S5, ESI†), thus the obtained fluxes can be determined to be 2040, 8570, 13 040 and 15 000 L bar\(^{-1}\) m\(^{-2}\) h\(^{-1}\) for the composite membranes with 0, 20, 40, and 60% strain, respectively. That is, after moderate stretching with 20% strain the membrane exhibits more than a four fold increase in flux and this increase is even higher and reaches 7.5 fold at 60% strain. Fluxes exceeding 8000 L bar\(^{-1}\) m\(^{-2}\) h\(^{-1}\) are already comparable to that of MF membranes, which may enable gravity-driven filtration.

As listed in Table S1 (ESI†), upon stretching the porosity of both the separation layer and the supporting membranes is increased as discussed above on one hand, and the thickness of the separation layer is decreased on the other. Moreover, with increasing strains, both the pore lengths and widths become bigger, which leads to increasing the effective pore width if we approximate the elliptic pores to be slit-shaped pores. All these changes in the structural parameters of the composite membranes work in the same direction as can be seen from eqn (1), favoring the significant increase in water flux of the stretched membranes.

We tested the size discrimination of the stretched membrane with 20% strain. The feed solution consisted of 30 and 10 nm gold colloidal nanoparticles and two peaks centered around 32.7 nm and 12.5 nm, respectively can be clearly observed in the size-distribution curve (Fig. 3). However, no peak in the range of 24 nm to 58 nm can be detected in the permeate, indicating the complete rejection of 30 nm gold nanoparticles by the stretched membrane. Meanwhile, the filtrate showed a particle size distribution corresponding to the 10 nm gold nanoparticles. The permeation of 10 nm gold nanoparticles was further evidenced by the presence of gold accounting for 18% of the filtrate.

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J = \frac{\varepsilon}{\tau} \left( \frac{h^2}{3\mu \delta_m} \right) \varepsilon'
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where \(J\) is the filtrate flux, \(\varepsilon\) is the surface porosity of the separation layer, \(\tau\) is the tortuosity of the pores, \(h\) is the width of the pores, \(\mu\) is the solution viscosity, \(\delta_m\) is the thickness of the selective layer, and \(\varepsilon'\) is the surface porosity of the supporting membrane.

The significantly upgraded permeance of the stretched membranes can be understood by the Hagen–Poiseuille equation for membranes with slit-shaped pores which are more similar in geometry to the elongated elliptic pores produced by stretching in the present work:

Fig. 3 The size distributions of the feed and filtrate solutions collected from the size-discrimination of 30 and 10 nm gold nanoparticles.
In conclusion, composite membranes with homoporous BCP selective layers of circular pores atop a PES macroporous support are stretched along the uniaxial direction with different stains. Pore deformation of the selective layer selectively occurs in the opening areas of the support and the initially circular pores are transformed to elongated, elliptic shapes, whereas the selective layer attached on the skeleton of the support remains non-stretched, providing mechanical robustness to the stretched selective layer. The porosity of both the selective layer and the support is increased and the thickness of the selective layer is decreased as a response to stretching, leading to significantly enhanced permeance with little sacrifice in selectivity. Consequently, the stretched membranes can be used for fast UF driven merely by gravity of the feeds instead of external pressures, and they show excellent capability to discriminate similarly sized nanoparticles, with a 100% rejection of 30 nm gold particles while permitting the passing of 10 nm particles.

Notes and references