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Review

Engineering of nanochannels in polymer membranes for energy and biological applications

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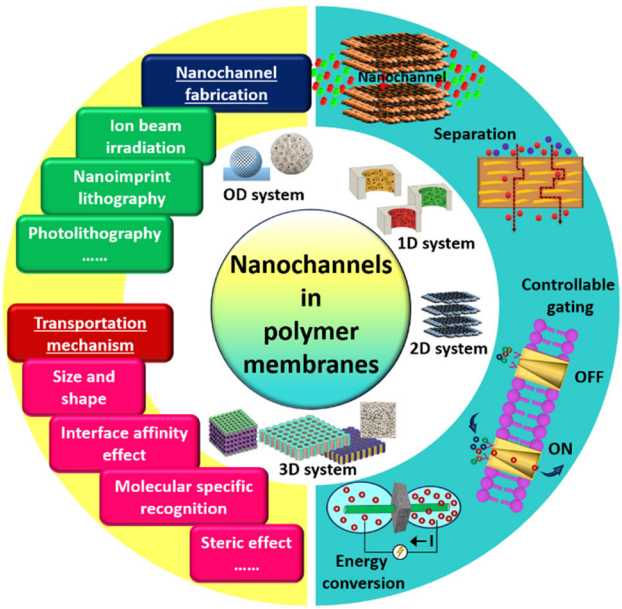
Abstract Nanochannels and their engineering within polymer membranes have emerged as a transformative way to address critical challenges in energy and biological applications. The multidisciplinary approach, through precisely controlling the nanoscale features to modify molecular transport and interactions, provides a range of innovative opportunities. In the realm of energy applications, these tailored nanochannels can enhance ion transport to benefit various energy storage and conversion devices, such as high-performance lithium-ion batteries and fuel cells, due to improved electrolyte management. In the biological domain, these engineered nanochannels with their selective transport of biomolecules provide the potential to revolutionize the treatment of diseases, and personalized medicine by precisely governing the passage of DNA, and proteins and offering unprecedented control in medical and biotechnological applications. The review explores the state-of-the-art techniques for engineered nanochannels within polymer membranes, with a focus on their fabrication methods and applications in various areas. It also discusses various advancements and innovative research going on to enhance the characteristics of nanochannels further. Moreover, it discusses the current challenges and future prospects in harnessing the nanochannels for sustainable energy solutions and advanced biological tools.

Graphical abstract



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Abbreviations

SiO_2	Silicon dioxide
NIL	Nanoimprint lithography
Ag NPs	Silver nanoparticles
PET	Polyethylene terephthalate
PEO	Polyethylene glycol
HMMP-1	High valence metal-induced microporous polymer
MMM	Mixed matrix membranes
GO	Graphene oxide
PEGDA	Poly(ethylene glycol) diamines
Pd	Palladium
PC	Polycarbonate
API	Active Pharmaceutical Ingredients
HVNCs	High-Value Natural Compounds
CMP	Conjugated microporous polymer
PTFE	Polytetrafluoroethylene
AF	Acid fuchsin
SWCNT	Single-walled carbon nanotube
DOPC	1,2-Dioleoyl-sn-glycrol-3-phosphocholine
NaCl	Sodium chloride
COF	Covalent organic framework
PMMA	Poly(methyl methacrylate)
CA	Cellulose acetate
PVDF	Polyvinylidene fluoride
AB	1,4-Diacetylbenzene
CG	Chrysoidin G
FS	Fluorescein sodium
EB	Eosin B
COP	Covalent organic polymer
EB'	Ethidium bromide
RED	Reverse electrodialysis
sPEEK	Sulfonated poly(ether ether ketone)
Am	Americium

1 Introduction

Over the last few decades, membranes have emerged as growing alternatives to conventional methods across a spectrum of industries. Their versatility, efficiency, and eco-friendly characteristics have paved the way for innovative solutions, fostering a paradigm shift in processes ranging from water purification to pharmaceutical separations. Membranes serve at the forefront of technological progress, unlocking new dimensions of sustainability and performance. They have an array of purposes, from water purification and air filtration to fuel cells and artificial organs. These membranes, as a thin and selective barrier, separate and allow the transport of specific substances, making them invaluable in a wide range of applications [1]. Membranes are better than the conventional techniques, which are energy-intensive and require sophisticated instruments as well as create pollution to the environment. Besides cost-effectiveness and environment friendliness, these membranes also offer versatility and simplicity in commercialized system designs due to their easier processing and fabrication techniques [2]. Among various membrane materials, polymeric membrane provides use in various applications, such as food packaging, controlled drug release, separation, and beverage industry [3–5].

Nanochannels within polymer membranes represent a remarkable combination of nanotechnology and materials science [6]. Nanochannels are extremely tiny, well-defined passageways or pores that are intentionally engineered at the nanoscale level within a polymer material. These minute passageways, often on the scale of just a few nanometers, offer the potential to precisely control the movement of ions, molecules, and particles. Their precise size, structure, and surface properties can be controlled and customized to allow specific substances to pass through while blocking others [7, 8]. Their engineered design allows a wide range of applications, spanning energy storage, water purification, and biological sciences. In energy-related applications, nanochannels enable the development of advanced batteries, fuel cells, and membrane-based processes for sustainable power generation and storage [9,

10]. In the domain of biology, these nanoscale channels play a pivotal role in drug delivery, biosensing, protein analysis, and DNA sequencing, offering unparalleled precision and control. As we continue to refine the fabrication techniques and functionalization of these polymer-based nanochannels, their potential to revolutionize a multitude of industries becomes increasingly evident, promising innovation on both microscopic and macroscopic scales [11, 12].

Although nanochannels provide advantages in various fields, they are susceptible to deterioration due to changing external conditions, such as pH, temperature, stress, and more. Also, for the transportation through nanochannels, surface chemistry and geometry should be controlled to regulate the ionic and non-ionic transport phenomenon. The length of these nanochannels should be reduced to around 100 nm along one dimension. Tailoring nanochannel dimensions to specific applications enables precise control over the filtration process, making nanochannels versatile tools across a diverse range of applications. Further, the applications of these nanochannels in the preparation of nanowire fabrication are the availability of nanopores of different shapes, and the control of chemically functionalized inner walls [13].

In this comprehensive review article, we will discuss briefly the diverse array of nanochannels found in polymer membranes and their strategic engineering approaches of designing and manipulating their sizes to harness their potential in both energy and biological applications. Since these nanoscale channels hold great promise in the realm of energy and biology, we aim to shed light on the challenges that have to be faced with the current research process and the outlook for further advancement in the innovative use of nanochannels in diverse applications.

2 Fundamentals of nanochannels

Nanochannels are extremely small channels or pores with dimensions on the nanometer scale, typically ranging from a few nanometers to several hundred nanometers in diameter. These channels can be found in a variety of natural and synthetic materials and possess several unique characteristics and properties, including [14, 15]:

- *Size and Dimension*: Nanochannels typically have dimensions in the range of a few nanometers to several hundred nanometers in diameter or width. Regulating the nanochannel dimensions allows engineers and scientists to tailor these structures to meet the specific requirements of different applications. For example, nanochannel membranes with distinct pore sizes are employed in various filtration processes, including water purification and the separation of nanoparticles. Their small size allows for strictly controlling the flow and transport of molecules or particles at the nanoscale [16].
- *High surface area-to-volume ratio*: The small size of nanochannels results in a high surface area-to-volume ratio, which is required for applications involving adsorption, separation, and reactions, as it provides a large area of contact for interactions with passing molecules.
- *Capillary action*: Nanochannels often exhibit strong capillary forces due to their narrow dimensions. Capillary-driven fluid transport in nanochannels is widely used in various applications, including microfluidics, point-of-care diagnostics, lab-on-a-chip devices, and capillary electrophoresis. It is also useful in fields like nanofluidics for studying the behavior of fluids at the nanoscale. This capillary action can be improvised by manipulating the dimensions of the nanochannels for fluid transport [16].
- *Selective Transport*: Nanochannels can be engineered for the selective transportation of specific molecules or ions based on their size, charge, and chemical properties. This selectivity is beneficial for filtration, separation, and controlled transport. The engineering of nanochannels involves tuning the size and geometry, modification via chemical functionalization, and engineering the surface charge of nanochannel walls.
- *Surface properties*: The surface properties of nanochannels can be modified to control interactions with molecules. Specific applications can be facilitated by certain surface modification processes, such as functionalization or coatings, which can either increase or decrease adsorption [17].
- *Diffusion-driven transport*: In nanochannels, diffusion is a dominant mode of transport for molecules and particles. This can lead to unique transport phenomena and can be important in applications like controlled released systems and drug delivery.
- *Electrokinetic Phenomena*: Nanochannels can take advantage of electrokinetic phenomena, such as electroosmosis and electrophoresis, to manipulate the transport of charged species. Upon applying voltages or modifying the surface charge of the nanochannels, specific ions or molecules can be directed to move towards or away from any particular region of the channel [18, 19]. These phenomena are vital in microfluidic devices and lab-on-a-chip technologies.

2.1 Techniques for nanochannel creation

Nanochannels must be created with precise control and desired properties for their wide range of applications. Several techniques are available for nanochannel fabrication, including ion beam irradiation and chemical etching, optical lithography [20], photolithography, nanoimprinting lithography [21], etc. Out of the various approaches used to create the nanochannels in polymer membranes, top-down approaches can more tightly control the size and distribution of pores within the membranes. These are carried out using lithographic steps to generate predefined patterns on the membranes through focused ion beam, track-etching, reactive ion etching, etc. These approaches involve membranes having pore size depending upon pore design rather than membrane fouling (as done in the bottom-up approach) to create a tortuous path [22].

2.1.1 Ion beam irradiation

Ion beam irradiation is a top-down approach for creating nanochannels in materials. It involves bombarding a material's surface with high-energy ions, leading to the removal of material and the formation of nanoscale features, including channels [23, 24]. This technique is used for both creating permanent nanochannels and for modifying existing surfaces. It offers excellent control over pore size through changing ion beams and dose. The detailed explanation of the process can be given as [25, 26]:

(1) *Irradiation*: The most important step is the irradiation process through high-energy ions, such as protons or helium ions, which are accelerated and directed toward the material's surface. The choice of ions depends on the specific material and the desired channel characteristics such as nanochannel dimensions.
(2) *Sputtering*: When the ions collide with the material's surface, they transfer energy, which can cause atoms to be dislodged from the surface. This process is known as sputtering.
(3) *Pattern Formation*: The ion beam can be precisely controlled to create a pattern on the material's surface. By controlling the beam's intensity and scanning it across the material, nanochannels with well-defined dimensions can be formed.

Through the ion irradiation process, the polymer material surface gets damaged along the transportation path of the ions. These damaged zones can be easily converted into latent tracks upon chemical etching. Under this process, the material is exposed to a chemical etchant that selectively reacts with the exposed regions, removing material and forming the desired channels as shown in Fig. 1a. Depth, shapes, and structural dimensions of the etched channels can be regulated depending on how much faster the track is etched in comparison to the bulk. Figure 1b represents different geometries of the track-etched pores. Etching can be isotropic (uniform in all directions) or anisotropic (directionally dependent). Apart from the ion irradiation, masking typically in the form of a patterned photoresist or a physical mask can be used to protect certain areas from etching while exposing others to etchant [27, 28]. The method of ion irradiation is good where extremely high resolution and precision are required. However, it is less suitable and scalable due to the requirement of specialized instruments and ion accelerators.

2.1.2 Photolithography

Creating nanochannels in polymer membranes using photolithography allows for precise control over channel dimensions and arrangements, making it suitable for various microfluidic and filtration applications [30, 31]. It involves coating the polymer surface with a thin film of photoresist material and exposing it to UV light through a photomask to get the desired nanochannels. The photoresist can be both positive as well as negative depending upon its behavior towards the UV light. The nanochannel width can be determined through the wavelength of UV used. The technique is then followed by the etching process to obtain the required depth of the nanochannels. Shankles et al. in 2015 created 200 nm deep nanochannels in PDMS polymer membrane utilizing the combination of photolithographic and soft lithographic techniques through high-resolution patterning and etching strategies [22]. Spelthahn et al. in 2009 fabricated self-aligned nanopores and fluidic nanochannels of 15–20 nm dimensions on Si-SiO_2 substrate through a combination of photolithography and pattern size reduction technique [32]. Ranjan et al. in 2023 fabricated durable and regenerative nanoporous superhydrophobic surfaces by creating nanochannels into 500 μm thick substrate using the photolithography technique [33]. Photolithography offers good compatibility with a range of materials, such as polymers and metals; however, the choice of photoresists and etchants may restrict the compatibility. Further, the technology offers moderate scalability due to the complex procedure and requirements related to the clean room facilities.

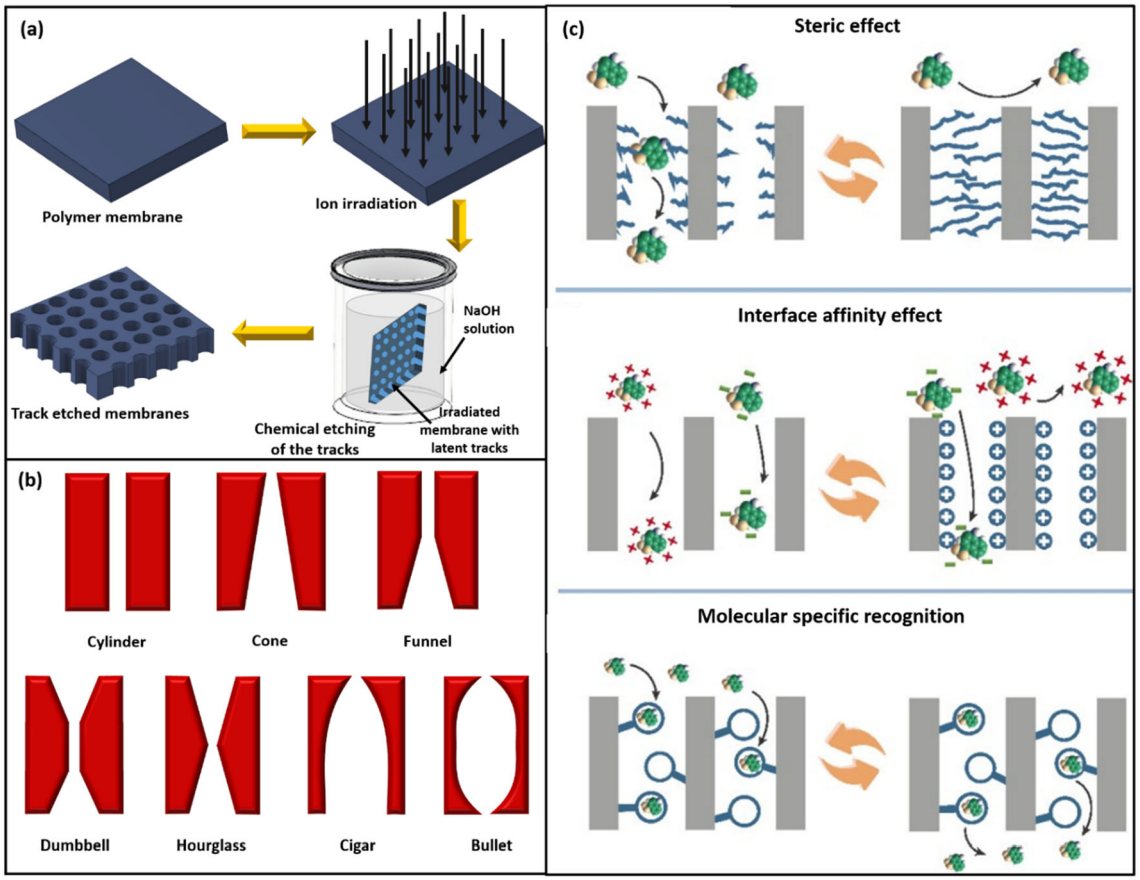

Fig. 1 **a** Creation of nanochannels using ion irradiation and etching process [2], **b** various geometries obtained through the etching process [2], **c** self-regulating mechanisms affecting the transportation mechanism through functionalized nanochannels [29]

2.1.3 Nanoimprint lithography

Nanoimprint lithography (NIL) is a replication technique that uses molds or stamps to imprint nanoscale patterns on a substrate. It offers several advantages including high resolution, simplicity, and the ability to create nanoscale features across wide regions [34]. Its key principle involves the mechanical deformation of a resist material by a template or mold. In the first step, a template or mold (typically made up of silicon or quartz) is created with the desired nanoscale pattern. The template is then attached to the polymer membrane coated with a thin layer of a resist material. The template is then pressed using controlled force or pressure or sometimes heat application. The mechanical deformation causes the resistance to flow and fill the nanoscale features on the template, resulting in the desired pattern transfer. After imprinting, the template is removed and the imprinted resist is subjected to a hard bake to stabilize the pattern. The method offers moderate to high material compatibility and is suitable for polymers, silicon, and metals which are capable of softening under pressure and heat [35, 36].

Sabirova et al. in 2022 used UV nanoimprint lithography to create highly porous membranes of pore size 300 nm with a pore density of 4×10^9 pores/cm^2 and stable permeance of 108,000 Lm^{-2} h^{-1} bar^{-1} towards nanoparticles [21]. Choi et al. in 2019 created conical-shaped nanopores of 10 nm diameter using the NIL technique with a Si microneedle stamp [37]. Ren et al. in 2023 created nanopores of 10–270 nm diameter in a flexible polycarbonate membrane using silver nanoparticles (Ag NPs) as a template and intense pulsed light as a heating source [38]. Feng et al. in 2017 created vertically aligned nanochannels of 1.2 nm–1.5 nm diameter using a combination of molecular templating and directed self-assembling using physical confinement and magnetic fields [39].

2.1.4 Self-assembled block copolymer structures

Self-assembled block copolymers are fascinating materials to create nanochannels of pore diameter in the range from 10 to 50 nm in the membranes with precise control over the size and structure [40]. Block copolymers (BCP) are formed when two thermodynamically incompatible blocks are bonded together via covalent bonds. Hence,

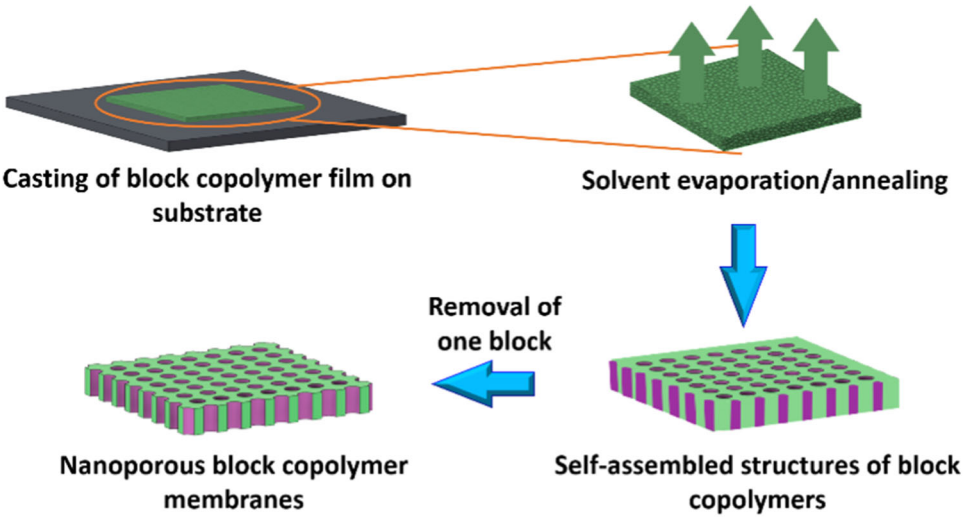

Fig. 2 Schematic of the process of nanopore creation in a block copolymer membrane

these BCPs can undergo precise separation in the range of 10–100 nm [41]. These self-assembled structures can be easily regulated using various factors, such as solvent type, polymer type, concentration of polymer solution, additive aspects, annealing conditions, and many more [42]. In general, the nanochannels can be created into such membranes via certain steps: (1) Preparation of a uniform film using methods like spin-coating, dip-coating, doctor-blade casting, etc., (2) Annealing the solvent through exposing the film to solvent vapor or another method to cause the blocks to self-assemble into the desired nanostructure, (3) Finally, selective removal of one block via etching or other methods to create the nanochannels. The method is compatible mainly with polymer materials. However, the copolymer domains can form inorganic–organic hybrid structures that can expand their compatibility. Figure 2 represents the schematic of the process of nanopore creation in a block copolymer membrane.

The strategy offers the advantages of high density and high order which is significant for the mass transport via membranes. Sharon et al. in 2020 used block copolymer-based ion-selective membranes as separators in concentration cells [43]. Yang et al. in 2021 used PSF-b-PEG block copolymer (made from polysulfone and polyethylene glycol units)-based nanoporous membranes as lithium-ion battery separators. The membrane possesses a rigid and flexible structure with good mechanical stability [44]. In general, the self-assembly of the block copolymer is an efficient way to create nanochannels due to the high control over the shape, size, and spacing of the nanostructures [45].

2.1.5 Template-assisted method

The template-assisted method is a versatile and precise approach to producing tailored nanopore structures of required pore size, shape, and distribution by utilizing a template or scaffold to guide the formation of nanopores [46, 47]. Initially, the polymer is deposited around the template, conforming to its shape and structure. After which, it is cured, and then the template is removed using physical or chemical methods, leaving behind the polymer membrane with nanopores that mimic the features of the template. The method provides the advantages of exact control over the size and shape of the nanopore, together with the uniformity and scalability required for mass production. Ma et al. in 2018 used a templating approach to produce nanovoids in a polyamide layer using Cu nanoparticles loading and later etching them. The membranes showed a 70% increment in water flux without changing the NaCl rejection [48]. In another work, Li et al. in 2021 used the template-assisted method to generate one-dimensional nanochannels using the polyamide layer with Cu nanorods loading and later etching them. The process demonstrated enhanced water purification in RO membranes [49]. Table 1 represents a comparison of different aspects of various techniques of nanochannel creation [40, 50–52].

2.2 Factors affecting nanochannel size and distribution

Size and distribution of nanochannels can be influenced by several factors, including both intrinsic material properties and external processing and fabrication conditions. All of these factors are crucial for controlling and manipulating nanochannel characteristics [53]. Some key factors that affect nanochannel size and distribution are given as:

Table 1 Comparison of various techniques of nanochannel creation

Parameter/ Technique	Ion beam irradiation	Photolithography	Nanoimprint lithography	Self-assembled block copolymer structures	Template assisted method
Cost	High	High	Low	Low	Low
Resolution	Excellent (Sub nanometer)	Excellent (Sub-10 nm)	Good (Sub-10 nm)	Moderate (10–100 nm)	Moderate (10–100 nm)
Control over pore size	Excellent	Good	Good	Moderate	Moderate
Scalability	Low	Moderate	High	Moderate to High	High
Material compatibility	Moderate to High	Moderate to High	Moderate to High	Particularly for polymers	High

(1) *Material Properties*: Various material properties, such as softness/hardness, purity, and crystallinity of the material, play a significant role in determining the nanochannel size and distribution. Different materials may respond differently to fabrication techniques, leading to variations in channel dimensions. For example, softer materials may be prone to more deformation during fabrication, resulting in larger or irregularly shaped nanochannels [16].
(2) *Fabrication techniques*: Fabrication techniques and parameters involved, such as etching conditions (etch rate, temperature, pressure, and exposure time), accuracy and precision of masking and patterning techniques (during photolithography or focused ion beam lithography), and tools and equipment's quality and precision, play a role in achieving the desired channel size and distribution [17].
(3) *Processing parameters*: Apart from the environmental conditions, such as temperature and pressure, the presence of dopants or surface functionalization can alter the material's reactivity and, consequently, size and distribution of nanochannels [12, 54].
(4) *Template Size and Geometry*: Sometimes while using templates or molds for creating nanochannels, the nanopatterning and template properties, such as template's size, shape, and arrangement, can affect the resulting channel dimensions and distribution [15].
(5) *Post-processing treatments*: Several treatments, such as annealing and surface coating/functionalization of the channel walls, may lead to recrystallization or other structural changes and alter the surface interactions [55, 56].
(6) *Control and monitoring mechanisms*: Accurate process control and real-time monitoring of fabrication steps can help maintain tight dimensional tolerances and improve distribution uniformity.

3 Engineering of nanochannels

The engineering of nanochannels plays a pivotal role in enhancing the performance and expanding the range of applications in the realm of nanotechnology. By tailoring the interior surface of these channels with specific functional groups or materials, several crucial benefits can be realized. These include selective separation, precise control over the transportation of molecules, control release of drugs, acceleration of chemical processes in catalytic reactions, and many more [57, 58].

There are several ways for the engineering of nanochannels, such as functionalization, crosslinking, and decoration with other materials [59, 60]. These methods can greatly affect the size, shape, and other surface properties of the channels. Functionalization of nanochannels in the membranes can trigger unique mechanisms, such as the steric effect, affinity at the interface, and special recognition towards specific molecules as shown in Fig. 1c. Functionalization can integrate selective mechanisms toward specific materials [61]. For example, in the separation process, it not only increases the selectivity towards specific molecules but also provides other fascinating properties, such as anti-fouling/self-cleaning, and in situ reaction characteristics. The functionalization of the inner channel can also occur through reprocessing of inner walls. In such cases, the surface acts as a platform for the functional materials. Apart from this, several other pore-filling methods, such as dip coating and dynamic coating, have been used to attach the functional elements to inner nanochannel walls [29].

Espinoza et al. in 2014 created functionalized nanochannels in track-etched PET foils through grafting polymerization of glycidyl methacrylate [13]. Such engineering can also be used to alter the size of the nanochannels. Choi et al. in 2019 reduced the nanochannel pore size using the polymer reflow process to achieve 6 nm pores from

10 nm pores [37]. Choi et al. in 2020 tuned the size of the nanochannels using the chemical approach to control fuel crossover.

4 Nanochannels for energy applications

4.1 Nanochannels for gas separation applications

For the fabrication of high-performance gas separation membranes, the nanochannel environment plays a key role [62, 63]. According to the Knudsen theory, the gas molecules are taken as the mass points and are distinguished based on their molecular weight. However, the gases with the same molecular weight have a significant difference in the flow rate [64]. Qian et al. in 2023 investigated the transport of polyatomic and monoatomic gas molecules through nanochannels using molecular dynamics (MD) simulations. They further confirmed that the geometry of gas molecules effectively influences the collisions through the pore walls and hence affects the flux through nanochannels [65]. There are several ways to create nanochannels in dense membranes for gas separation. Awasthi et al. in 2011 created nanochannels in 25 μm thick polyethylene terephthalate membranes using a Cl^{+9} ion beam of 100 MeV energy at a fluence of 10^7 ions/cm^2 followed by etching in 6N NaOH solution for H_2 separation application. They proved that increasing etching time increased the H_2 selectivity of the membranes in comparison to other gases [66]. Ji et al. in 2023 tuned the graphene oxide nanoribbon nanochannels by adding polyethylene glycol (PEO) polymer. The resultant membranes showed H_2 permeability of 7108 Barrer and H_2/CO_2 selectivity of 10.8. The gas separation performance and the permeation mechanism through the membrane are depicted in Fig. 3a, b [67]. Yuan et al. in 2021 fabricated high valence metal-induced microporous polymer (HMMP-1) @polyvinylamine mixed matrix membranes with amine-rich nanochannels having a high preference towards CO_2 gas [68]. Nanochannels and sub-nanochannels can also be created in mixed matrix membranes (MMM) for efficient gas separation. For example, stacking two-dimensional nanosheets parallelly with each other can create an efficient transportation pathway for good size-sieving ability [69]. Kim et al. in 2013 prepared 3–10 nm GO on porous polyethersulfone support to demonstrate the selective diffusion of gas molecules by controlling gas flow channels and pores via stacking methods. Further, they were able to achieve an H_2/CO_2 selectivity value of 30 due to the well-interlocked GO membranes at higher relative humidity [70]. Such GO layers can also be mixed with other polymers, such as polyethyleneimine [71] and poly(ethylene glycol) diamines (PEGDA), to enhance the gas separation performance. Wang et al. in 2017 reported CO_2 gas separation using GO intercalated PEGDA to generate CO_2-philic and non-CO_2-philic nanodomains in the interlayer channels of graphene oxide. They demonstrated high CO_2 permeance of 175.5 GPU along with CO_2/CH_4 selectivity of 69.5 because of the proper channel size (almost 0.35 nm) exactly between the kinetic diameter of CO_2 and CH_4, i.e., 0.33 nm and 0.38 nm, respectively [72]. Qiao et al. in 2016 prepared montmorillonite /polysulfone MMM with high-speed gas transport channels by aligning the interlayer gaps to obtain a permeance of 800 GPU with good selectivity against N_2, CH_4, and H_2 gases [73]. The nanochannels in MMM reduce the effective diffusion path of the gas molecules [74–76].

Functionalization of nanochannels can greatly affect the transportation of gas molecules inside the membranes by providing active sites for the smooth transportation of certain gas molecules while blocking others. Thereby, enhancing the overall permeability and selectivity of the gases. Awasthi et al. in 2014 reported the functionalization of track-etched polymer PET membranes using carboxyl and amino groups as shown in Fig. 3c for hydrogen purification purposes. Their results demonstrated that amine functionalization could bind more Pd NPs as compared to the carboxylic groups in the PET membranes [77]. Kamakshi et al. in 2018 functionalized nanochannels in track-etched PET polymer membranes through a carboxylic group and further decorated them using Pd NPs. The decorated membranes provided enhanced H_2 gas with a selectivity increment of 109% and 112% towards H_2/N_2 and H_2/CO_2 gases respectively [78]. Filling the nanochannels with other polymer material can be another way of functionalization and increases the permeability of one gas while blocking another depending upon the solubility of gases in the polymer i.e. low permeable gas will hardly permeate through the constrained polymer chains while the transportation of highly condensable gases is enhanced due to high solubility coefficients as shown in Fig. 3d [79]. Kumar et al. in 2020 functionalized the nanochannels and surface of track-etched polycarbonate (PC) membranes using a UV irradiation process. The photo-fries mechanism of the polymer in the presence of UV light leads to bond breaking and hence creates many active sites for the further attachment of Pd NPs. The membrane provided enhanced H_2 permeability as well as selectivity increment of 145% and 151% towards H_2/CO_2 and H_2/N_2 gas pairs as shown in Fig. 3e, f [80].

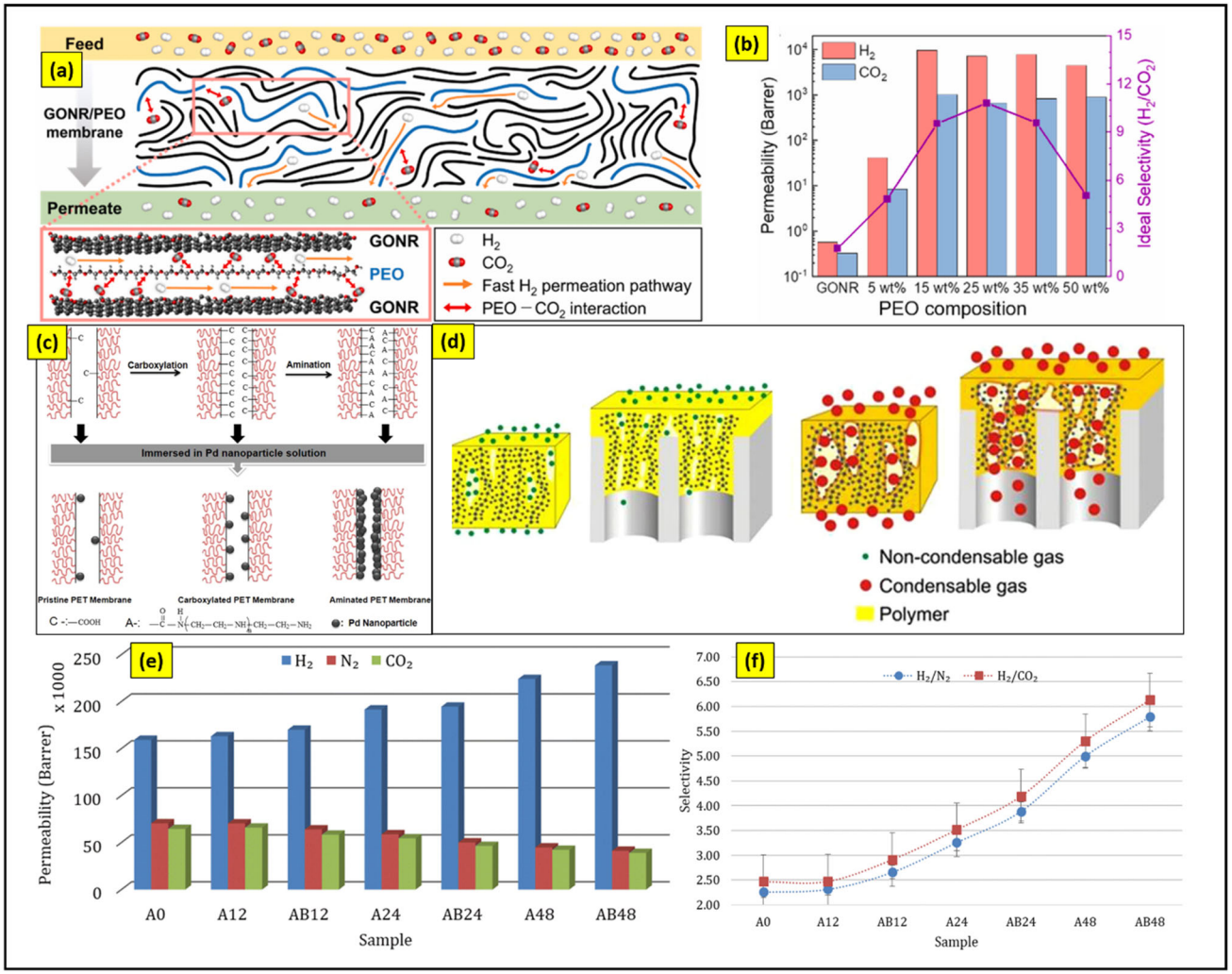

Fig. 3 Representation of gas permeation mechanism through PEO hybridized GO nanoribbon nanochannels [67], **b** H_2 gas separation performance of GO nanoribbon/PEO membranes [67], **c** schematic representation of functionalization of track-etched nanochannels and their decoration with Pd NPs [77], **d** schematic representation of transportation of non-condensable and condensable gas molecules through polymers [79], **e**, **f** gas separation performance of UV-functionalized and Pd NPs decorated track-etched polycarbonate membranes [79]

4.2 Nanochannels for liquid filtration applications

In the realm of daily chemical production, where organic solvents are extensively employed, the separation and purification of high-value substances like Active Pharmaceutical Ingredients (API) and High-Value Natural Compounds (HVNCs) pose significant challenges [81]. To address these, nanochannel within polymer membranes represents a new frontier offering an expansive surface area within a compact space, setting up a stage to separate, purify, and analyze liquids at the molecular and nanoparticle levels. However, the commercial ultrafiltration membranes suffer from low retention and poor solvent resistance making them unsuitable for the application. Su et al. in 2023 reported solvent-resistant C–C bonded conjugated microporous polymer @polytetrafluoroethylene (CCMP@PTFE) composite membranes by portioning channels using space-confined polymerization strategy. The membrane exhibited good permeability up to 80. 7 Lm^{-2} h^{-1} bar^{-1} towards ethanol and small dye molecules, i.e. Chrysoidine G, Mw 249 Da as shown in Fig. 4a [82, 83].

Shi et al. in 2023 fabricated robust covalent organic polymer membranes of uniform pores of 0.7 nm diameter and 20 nm thickness on porous polyacrylonitrile substrate for organic solvent nanofiltration. Further, the membranes showed a high ethanol permeance of 14.5 m^{-2} h^{-1} bar^{-1} and excellent acid fuchsin (AF) rejection of 99% as shown in Fig. 4c, d. Further, it provided rejection rates of $> 95\%$ towards solutes with a molecular weight above 500 $gmol^{-1}$ [84]. Rose et al. in 2022 reported ultra-permeable membrane fabricated using a polymer of intrinsic

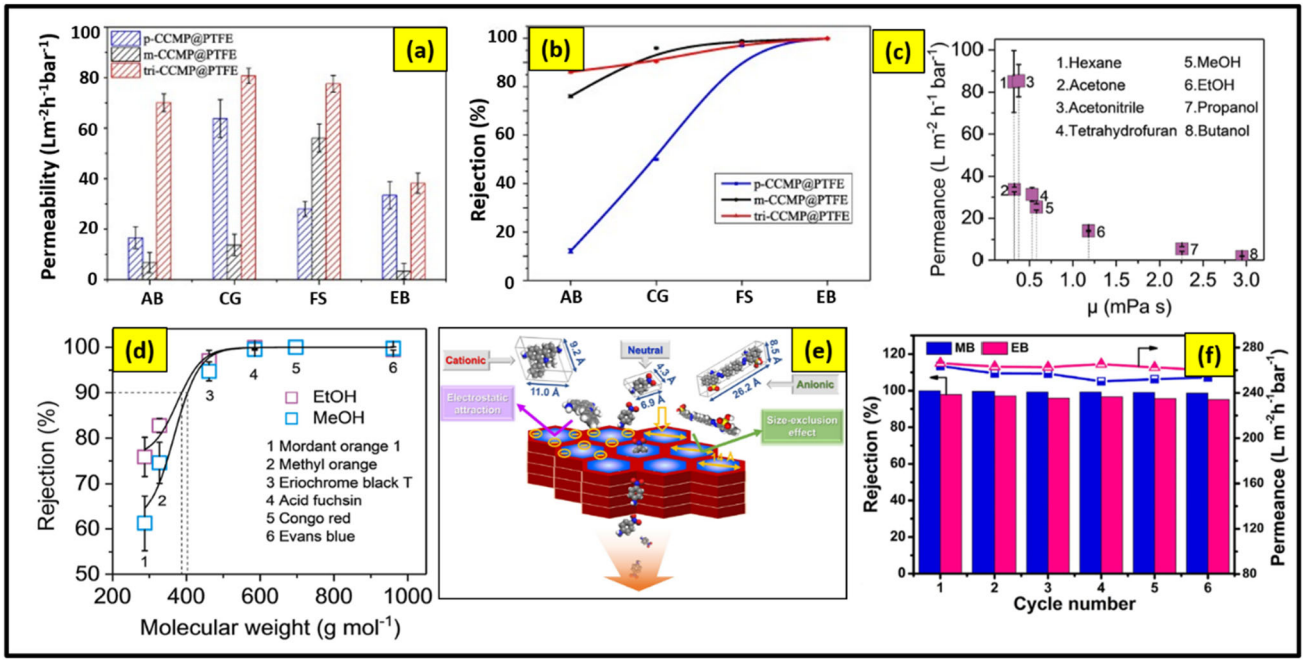

Fig. 4 **a**, **b** Nanofiltration performance of CCMP@PTFE membranes v/s dye molecules (AB: 1,4-diacetylbenzene, CG: Chrysoidin G, FS: Fluorescein sodium, EB: Eosin B) [82], **c** pure solvent permeance of COP membranes as a function of viscosity [84], **d** dye rejection of different molecular weight dyes using COP membranes [84], **e** schematic of selective dye molecule separation mechanism through negatively charged TpPa-SO_3Na membrane [89], f cycle studies of ethidium bromide (EB') and methylene blue (MB) rejection and permeance through TpPa-SO_3Na membrane [89]

microporosity (PIM-TMN-Trip) with a high concentration of channels of small (< 0.7 nm) and large (0.7–1.0 nm) diameter [85].

Furthermore, with the ever-increasing global demand for freshwater resources, the imperative for effective separation and purification processes has become increasingly pronounced [86]. The challenge lies not only in the extraction of water from saline sources but also in the removal of salts and recalcitrant pollutants, notably micropollutants resistant to conventional degradation methods. Elimination of these constant pollutants through traditional means is often challenging and hence necessitates advanced separation and purification technologies. The use of innovative approaches, such as nanochannels in filtration membranes, holds great promise in accomplishing this demand. Nanochannels, with their precisely engineered dimensions at the nanoscale, exhibit an outstanding capacity to selectively filter out salts and micro-pollutants, ensuring a more efficient and sustainable means of water purification. As the urgency to secure freshwater resources grows more pressing, the integration of nanochannels in filtration technologies becomes a crucial avenue to meet the contemporary challenges associated with salt separation and the removal of persistent pollutants from water sources. Yu et al. in 2021 used polypyrrole and graphene oxide-based membranes for dye/water separation process. The resultant membranes provided a rejection rate of 97% towards methylene blue dye and water permeability of 21.14 Lm^{-2} h^{-1} bar^{-1} [87]. Wang et al. in 2023 fabricated the carboxylated-SWCNT incorporated 1,2-dioleoyl-sn-glycrol-3-phosphocholine (DOPC) liposomes @polyamide membranes for efficient filtration properties. With the water channels provided by CNTs, the membrane exhibited an 89% flux recovery rate and 97.6% rejection to NaCl [88]. Yang et al. prepared an anionic COF membrane through a dual-activation interfacial polymerization method for dye wastewater treatment. The separation mechanism is shown in Fig. 4e. The membranes provided water permeability of 270 Lm^{-2} h^{-1} bar^{-1} along with ordered pore structure, and good chemical stability as shown in Fig. 4f [89]. Khan et al. in 2020 fabricated PVDF/PMMA/CA membranes of uniform pore size distribution (0.030 ± 0.005 μm) through Loeb–Sourirajan (L–S) phase inversion and etching mechanism. They utilized SiO_2 NPs in the membrane matrix for the etching purpose. The membrane showed good permeability and selectivity values along with outstanding antifouling ability [90]. Researchers have also fabricated intelligent nanochannel membranes that are responsive to external stimuli, such as pH, light, temperature, and electricity. Ma et al. in 2020 prepared pH-responsive hydrophilic membranes by attaching carboxyl groups on the PVDF surface through amine group bridging. They successfully tested the membranes for the separation of soya bean oil/water emulsion [91].

Different size of nanochannels is favored in different scenarios based on the targeted particles or molecules, flow rates, and desired level of selectivity shown in Table 2 [92, 93]. In general, nanochannels typically in the range of 2–100 nm are used for the ultrafiltration process to filter proteins based on their molecular weights, nanochannels

Table 2 Classification of nanochannels for various applications

Process	Pore dimension	Required pressure	Separable substances
Reverse osmosis	0.1–1 nm	10–100 bar	Monovalent salts
Nanofiltration	1–2 nm	3–20 bar	Sugars, divalent salts, dissociated salts
Ultrafiltration	2–100 nm	0.1–5 bar	Macromolecules, proteins
Microfiltration	100 nm–10 μm	0.1–2 bar	Suspended particles, oil, large colloids, bacteria

with sizes around 50–100 nm can effectively filter out nanoparticles, bacteria and some viruses, for instance, nanoporous membranes are used to separate waterborne pathogens from drinking water sources, nanochannels of 2–50 nm can be designed to control the release of therapeutic agents in drug delivery systems. Nanochannels of size less than 100 nm can be used for capillary-driven fluid transportation without external pumping, polymer membranes with such nanochannel size can be used for lab-on-a-chip devices for point-of-care diagnostics.

4.3 Nanochannels for batteries and fuel cell applications

In electrochemical devices, ion-exchange membranes are the most promising thing which provides a clean and affordable source of energy [94, 95]. The primary requirements are low cost, less toxicity, high output, and large-scale production. Among these, the nanochannel-based proton exchange membrane provides advantages of (i) high proton conductivity, (ii) high mechanical strength, and (iii) working possibility at comparatively high temperatures [96]. Hence, the advancement of these membranes and their nanochannels is required in all of the devices including batteries, electrochemical sensors, fuel cells, and reverse electrodialysis (RED) [97]. Choi et al. in 2020 reported sPEEK/FAA-3 membranes for controlling fuel crossover by tuning membrane nanochannel for reverse electrodialysis application [9]. Prakash et al. in 2020 reported the fabrication of latent tracks in a dense PVDF membrane using swift heavy ion irradiation of Ag^{+} ions and an etching process to generate nanochannels of nearly 80 nm in size. The membrane efficiently removed the radioactive nuclide (Am^{3+}) up to almost 80% from its solution. Further, high exchange capacity, ion conduction, water uptake, and high sorption showed improved results due to functionalization and control over the nanochannel dimension [10].

Polymer nanochannels are important in batteries and fuel cells due to their unique properties and functionalities, offering several advantages that contribute to the overall improvement of these energy storage and conversion devices.

(1) These polymer nanochannels are important because they facilitate the transport of ions between electrodes and electrolytes, which is required for the charge/discharge process in the functioning of batteries and fuel cells. The controllable and tunable nature of nanochannels enables the optimization of ion transport kinetics.
(2) These nanochannels help in managing the electrolyte by selectively allowing the passage of certain ions while blocking others, thereby ensuring precise regulation of electrochemical reactions within the device.
(3) In batteries, such as lithium-ion batteries, nanochannels provide a controlled environment and hence can prevent the formation of undesirable needle-like structures on the electrodes, called dendrites. Thus, enhancing the safety and longevity of the devices.

In general, the polymer nanochannel-based membranes provide superiority in terms of low-cost, faster reaction kinetics, and controllable nanofluidic processes with improved electrolyte management, but they have a certain shortcoming to overcome before their large-scale utilization, such as low ion conductivity and stability. Most research is focused on ion-conducting functional groups, but these are also accompanied by high ion-exchange capacity and water uptake resulting in ion aggregation and reduction of interconnected ion nanochannels, which reduces structure stability and ionic conductivity of the membranes [98, 99].

5 Nanochannels for biological applications

Nanochannels in polymer membranes offer numerous biological applications due to their unique properties including size exclusion, tunable pore size, controlled transport, selectivity, flexibility, and biocompatibility [100–102]. Some notable biological applications include:

5.1 Drug delivery systems

The delivery of a drug in the biological system requires parameters that include drug cargo's mechanical and chemical stability until it reaches its target, uniform pore size that controls drug permeability, and the ease with which the pore size can be adjusted based on the size of the drug [103]. Nanochannels in polymer membranes can be used as efficient drug delivery systems. The controlled release of therapeutic agents through nanochannels allows precise dosage control and sustained release, improving the efficiency of targeted drug delivery [104]. The polymeric nanochannels offer flexibility to customize size, shape, and surface characteristics of the drug delivery systems. Such modifications can tailor the design of carriers for specific requirements of therapeutic agents and patient's needs. Further, their integration into lab-on-a-chip devices propels advancements in portable and efficient drug delivery systems, potentially reshaping point-of-care treatments. Yang et al., in 2010 reported the controlled release of the biotherapeutics, human growth hormone (hGH) using cylindrical nanochannels prepared by self-assembly of PS-b-PMMA block copolymers [105]. Bigham et al. in 2016 reported the delivery of ibuprofen drug using ordered mesoporous magnesium silicate (OMMS) with uniform nanochannels [106]. Their study revealed the effect of calcination temperature on the use of OMMS as a promising local drug delivery system for bone tissue engineering. Dai et al. in 2022 performed molecular dynamics simulations to study the interaction of the anticancer drug methotrexate through CNT nanochannels present in 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC) membrane. They regulated the size of nanochannels and applied an electric field to investigate the translocation behavior and dynamics of the drug [107]. In essence, nanochannels offer a sophisticated platform for redefining the precision, efficiency, and safety of drug delivery, heralding a new era in personalized healthcare solutions.

5.2 Biosensing and diagnostics

Polymer nanochannels can be functionalized with specific molecules to obtain biosensors that can detect biomolecules, pathogens, or specific ions, enabling applications in diagnostics, environmental monitoring, and medical research [108]. Size and charge-based selectivity of nanochannels enable tuning of their morphology which enhances selective transportation. The nanochannels, apart from increasing the surface area, also maximize the binding effect and act as nanowells for biorecognition events to take place. Recently, the biosensing platform based on solid-state nanochannels has been developed rapidly. The nano-porous membranes with tunable pore size and well-ordered channels have been used for the efficient immobilization of biomolecules. The confined space within nanochannels enhances the interactions between target biomolecules and sensing elements, resulting in an improved signal-to-noise ratio. This heightened sensitivity is crucial for early disease detection and monitoring [109]. Within the nanochannels, the detection is based upon the change in transmembrane ionic current due to the change in surface charge and the spacing effect (blockage) of nanochannels. Such changes are very fast and can be easily detected by measuring voltammetric or amperometric currents. Qian et al. detected Pb^{2+} using a PET membrane with conical nanochannels by means of the chelation process between Pb^{2+} and 4'-aminobenzo-18-crown-6. The Pb^{2+} was selectively sensed in ultra-low LOD of 1×10^{-15} m [110]. Liu et al. reported label-free detection of glycan using surface modification of asymmetric PAA membrane with ion channel nanochannel. The electrochemical detector efficiently recognized glycan in the concentration range of 10×10^{-15}–10×10^{-9} m with a LOD of $\approx 10 \times 10^{-6}$ m [111]. Zhao et al. in 2021 detected the microRNA-21 at an ultralow detection limit of 0.5 aM via electrochemical biosensing through a complex formation in nanochannel structure [112]. Zhang et al., in 2022, reported the detection of short-length DNA molecules using a large size (20 nm tip diameter) conic PET nanopore. They were successful in detecting DNA samples as low as 0.5 nM concentrations [113].

5.3 DNA analysis

DNA analysis finds its applications in numerous fields of biomedical discipline including diagnosis, early detection of disease or infections, cancer monitoring, and many more. For instance, optical mapping provides a simple, fast, and affordable method to study DNA molecules. However, the process requires the stretching of molecules to generate fluorescent barcodes which can be achieved using nanochannels [114]. These nanochannels can provide information on the genomic length of DNA molecules with good linear spatial resolution. The basic principle is to bring the DNA molecule inside the nanochannel using electrophoretic or hydrodynamic forces. The dimensions of the nanochannels are such that their cross section is much smaller than the radius of the gyration of DNA molecules, while the length is much greater than the contour length of the DNA molecules, which allows for the inspection of the entire DNA molecule upon elongation. Further, tailoring the surface chemistry and geometry of these nanochannels through various enzymes, ligands, or specific moieties can enhance DNA capture and thus promote single-molecule analysis. In general, the engineering of nanochannels is an innovative approach to DNA analysis with precise control. This method allows extracting information related to length, sequence, and structural features of DNA molecules which finds applications in numerous areas, such as DNA sequencing, genotyping, and detection of genetic mutations [115–117].

5.4 Protein separation and analysis

Nanochannels in polymer membranes can be utilized for the separation and analysis of proteins. This has implications for proteomics research, clinical diagnosis, drug development, and understanding of cellular processes [118]. Nanochannels with dimensions on the nanometer scale enable high-resolution separation of proteins based on size, charge, or other specific properties. The small size of nanochannels enhances the efficiency of the separation process and allows for rapid analysis. Their surfaces can also be functionalized with specific coatings or capture molecules to selectively interact with target proteins. This customization enhances the specificity of protein analysis, allowing for the isolation and detection of specific protein species [119, 120]. Li et al. reported the separation of γ-globulin protein using nanoporous polyethersulfone (PES) membranes. The optimized membrane exhibited high surface porosity with a uniform pore size of 20 nm. The molecular weight cut-off was observed to be as low as 100 kD [121].

These examples showcase the diverse range of biological applications for nanochannels in polymer membranes, highlighting their potential impact on various fields within the life sciences.

6 Ion transport through nanochannels in polymer membranes:

Despite numerous years of investigation, the intricate mechanism governing ion transport through channels remains elusive. Among the captivating phenomena is voltage gating, which encompasses ion current rectification and voltage-dependent fluctuations in ion current. Typically, the current alternates between two values: zero, representing a closed state, and a non-zero value, signifying an open state. The pattern of switching between these states varies among different channels, with voltage-gated channels dependent on external voltage. Swift heavy ion irradiation, followed by etching in polymers, yields materials that exhibit ion transport properties akin to biological channels. A diverse array of ion channels serves various functions. Notably, diode-like ion channels exhibit a preferential direction of ion flow, significantly impeding ions moving in the opposite direction. Many channels display high selectivity for specific ions and can be manipulated by factors, such as an electric field, molecules bound to the membrane, or applied mechanical stress [122, 123].

Understanding the transport of solvents and solutes through membranes necessitates knowledge of membrane characteristics, solution properties, and operating conditions. Commercial membrane characteristics are often undisclosed, and membranes can exhibit various properties. They may be homogeneous or heterogeneous, symmetric or asymmetric in structure, and carry a positive, negative, or neutral charge. Transport through membranes can be influenced by diffusion driven by individual molecules, electric fields, concentration gradients, pressure, or temperature gradients [124].

7 Challenges in nanochannel fabrication and performance

The level of control over transport within polymer membranes has a wide range of applications, from energy storage and water purification to biological processes like drug delivery and DNA sequencing. The manipulation of nanochannels in polymer membranes is a field of materials science that offers great potential for various technological and scientific advancements due to their controllable structures and tunable chemical properties. The track-etched membranes have enabled the creation of single nanopores in polymers. However, it is difficult to position the nanopore at an exact location on the substrate which is essential during nanopore device fabrication and integrating the nanopore devices with additional device components [37]. Also, relying on ion accelerators for experimental endeavors is not a practical approach due to the limited availability and cost associated. Thus, it is imperative that we explore alternative methods and technologies that can effectively address the requirements while remaining economically and operationally viable.

New strategies for high-resolution patterning and etching can tackle the problem, several techniques, such as micromachining and micro-powder blasting, provide high yield but they lack resolution which is required in various chemical and biological systems. Alternatively, the nanoscale resolution can be easily achieved using electron beam lithography and nanoimprinting techniques, but they are comparatively costly and slow. Photolithography and soft lithography possess the advantages between these extremes [22]. However, conventional photolithography requires certain developers and strippers that contain a certain solvent that can dissolve and degrade the polymer material. Hence, nowadays researchers are more focused on the use of light-triggered reactions and other non-photolithographic strategies, such as soft lithography, nanoimprint lithography, and self-assembly of block copolymers [125].

In the stacking of 2-D materials, the nanochannels can also be tuned by intercalating them with other materials, for example, specific polymers having superior properties towards the application. However, producing such 2-D materials-based membranes on a large scale with good reproducibility is a challenge [69].

8 Conclusion and future outlook

High-precision molecular selective separation for various applications, such as seawater desalination, industrial wastewater treatment, gas separation, and concentration of high-valued products, requires a well-defined, internal nanoscale structure of nanochannels in the membranes. The development of intelligent, next-generation nanochannel membranes can advance the separation performance, and open up the possibilities in broad applications prospects in chemical synthesis, environmental, and life sciences. This review article provides a deeper understanding of the creation and functionalization of nanochannels and their application in different areas. Moreover, it also sets the guidelines on the numerous challenges to overcome for the realization of large-scale industrial requirements.

To bridge the gap between academic research and practical and real-world application, more optimizations and investigations are required towards special functionalities to promote the transfer of targeted penetrants.

Some future possibilities associated with the engineering of nanochannels inside the membranes can be listed as.

1. For deeper understanding of the fundamentals and changing specific parameters inside nano-confined channels, more efforts are required in modeling the kinetics and thermodynamics of the mass transfer and reaction process.
2. More research efforts are required to construct nanochannels of uniform shape and morphology while maintaining the long-term stability of the structure.
3. Since the comprehensive performance of the nanochannel membrane under industrial operational conditions will be more sensitive, hence, to bridge the gap between the ideal and practical conditions, the interest in real systems must be enhanced over the lab-scale models.

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