Bioinspired nanochannels based on polymeric membranes

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ABSTRACT Bio-nanochannels in living organisms participate in the physiological activities by selectively transporting ions through cell membranes. The structure and function of biological ion channels inspire the development of artificial ion nanochannels with practical applications. The bioinspired nanochannels based on polymer materials present good mechanical stability, high-performance ion transport and designability, which have attracted much attention. In this review, we mainly focus on the fabrication and application of polymer-based biomimetic nanochannels especially in environmentally responsive biosensor and energy conversion. We firstly introduce the basic understanding of nanochannels in ion regulation and osmotic energy conversion. Then, we discuss the fabrication methods of polymer-based nanochannels and highlight their advantages compared with other materials. The practical applications of polymer-based biomimetic nanochannels, especially in energy conversion and environmentally responsive biosensor, are detailedly discussed. Finally, we summarize the unsolved problems in bioinspired nanochannels and overview the further developing direction in this field.

Keywords: bioinspired nanochannel, polymeric membrane, environmentally responsive biosensor, energy conversion

INTRODUCTION

In organisms, biological nanochannels regulate the ion transport across cell membranes to achieve complex life activities, such as maintaining cell ion homeostasis, signal transduction, and energy generation [1]. For example, electric eels can utilize ion channels in the plasma membrane [2] to convert the salinity gradient energy into bioelectricity [3], generating an action potential of up to

600 V for hunting or self-defense [4]. These biological nanochannels seem to be powerful assistants in many fields [5], such as molecular separation, biosensing and energy conversion. However, the lipid bilayer is fragile and sensitive, and it is difficult to artificially adjust working environment to biological systems. Inspired by biological nanochannels, researchers have developed artificial nanochannels functioning like the ion channel or nanopore in biological system membranes [1,6,7], called “bioinspired nanochannels” [8–12]. Bioinspired nanochannels have significant advantages over nanochannels embedded in lipid membranes: chemical and physical stability, flexibility in size and shape, and easy fabrication of high-density arrays [13,14].

The materials of biomimetic nanochannel are mainly divided into biological materials, inorganic materials, organic and composite materials [14,15]. The application of biological materials is limited due to their low strength and harsh requirements for external working conditions [16]. Inorganic materials, which have the advantages of high strength, stable structure and physicochemical properties, play an important role in the construction of nanochannels [17–19]. For example, anodic alumina membrane (AAO) has a pore density up to 10^9 cm^{-2} , and its shape and size are relatively controllable. In addition, the exposed hydroxyl groups on the inner surface of the channel can be used to further modify functional groups to achieve more complex functions [20]. Zhang *et al.* [21] introduced the redox-active polypyrrole into the channel of AAO to form an intelligent unipolar nanofluid diode. Zhang *et al.* [22] explored the effect of the length of functional molecules on gating performance with symmetric AAO channels. In addition, two-dimensional (2D)

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inorganic materials are also widely concerned because of their unique layered structures. For example, carbonitride, as an excellent semiconductor and photocatalyst material, has strong light absorption. Efficient photoelectric conversion can be realized by the layered structure designed from carbon nitride [23,24]. Organic materials can be used to prepare nanochannels of different shapes by using an etching process, and then different functional groups can be grafted on the channels to achieve different functions, such as responding to external stimuli and energy conversion [25–27]. Composite materials based on the combination of biological, inorganic and organic materials [28,29] achieve multifunctional nanochannels, combining the advantages of different materials [30,31]. For example, Chen *et al.* [32] modified the AAO nanochannels with the cyclic 3',5'-adenosine monophosphate (cAMP) response molecule. The biomimetic nanochannel with high controllability and excellent reversibility provides a great potential in the application of nanofluidic devices. The superb intelligent behavior of ion channels in organisms originates from the symmetric or asymmetric structure and chemical composition. The interface characteristics of the bioinspired nanochannels between the electrolyte solution and the inner surface of channels strongly depend on the surface adjustment of the nanochannels containing symmetric and asymmetric chemical modification, particularly in the application of biosensors [33]. Different techniques including chemical electroless deposition [34], solution chemical reaction [35,36], self-assembly modification [37], ion sputtering [38], electron beam evaporation [39] and plasma [40] are usually utilized for modification.

Bioinspired polymer nanochannels with excellent

properties and designability have attracted much attention. Polymeric nanochannel membrane is advantageous over other materials in many aspects: (1) polymer membranes can solve the mechanical problems of inorganic films and limited variety of inorganic materials [41]; (2) the track-etched technology for polymer nanochannel is a feasible way for artificial nanochannel fabrication for many advantages such as a defined size and geometry [42]; (3) the inner surface of polymer nanochannels exposes active chemical groups under specific condition, enabling further functionalization [43–45]; (4) the stable polymer membrane overcomes the mechanical problems of lipid bimolecular membrane, and the polymer membrane can withstand higher transmembrane potential, which can theoretically improve the accuracy of chemical detection [13,14,46]. Herein, we systematically demonstrate the development of bioinspired nanochannels based on polymer membranes, and mainly discuss the construction methods and practical applications (Fig. 1). This review consists of four sections: first, we briefly introduce the bioinspired nanochannels and their basic properties; then, we overview the construction methods of the polymer-based systems including homopolymer membrane and block copolymer (BCP) membrane. The third section summarizes the applications of the polymer membranes, including biochemical sensing and energy conversion. This section introduces the nanochannels with environmental responses, such as pH-response, photo-response, temperature-response, ion-response and multi-response. The applications in energy conversion mainly include photoelectric conversion and osmotic energy conversion. Finally, we outlook the future development of the polymer-based systems.

Figure 1 Diagram of the strategy to construct the polymer-based bioinspired nanochannel membranes.

BASIC CHARACTERISTICS OF NANOCHANNELS

Biological ion channels constructed by membrane proteins can get open and closed in response to external stimuli to regulate ion transport across the cell membrane [9,47], which is an important physiological activity in the metabolism of living cells. Like biological ion channels, bioinspired nanochannels also have three basic characteristics associated with wide biological roles: ion selectivity, ion gating and ionic rectification [14]. The interaction between the transmembrane ions and the charges on the inner surface of the channel is the main reason why ion transport can be regulated. Ion selectivity is a main functional property of biological ion channels, which can precisely control the transportation of ions. Biological ion channels usually select ions of different sizes to enter and exit the cell membranes by volume exclusion. However, bionic nanochannels mainly use electrostatic effects to distinguish ions [48,49]. The electrochemical property of nanochannels is determined by the electric double layer (EDL) when ions transport through suitable size nanochannels. Fig. 2 shows that when the size of the channel is compressed to the nanometer level, EDL can effectively control the ion transmission, which endows the system with ion selective property [50,51]. When the length of Debye shielding (λ_D) is similar to the size of channel cross-section in dilute electrolytes [48], the surface charge would control the transmission by repelling co-ions and concentrating counterions. It means that these nanochannels are selective for counteracting ions [52].

The ionic rectification of nanochannels usually refers to that ion currents preferentially transmit under bias in one direction and are suppressed under bias in the opposite direction, which is caused by the electrostatic interaction between the ions and the surface charges inside the channel [48]. The rectification effect must meet three conditions [49]: first, structurally asymmetric nanochannels are required [53], and the diameter of the smaller entrance should be commensurate with the length of the Debye layer. Secondly, there should be charges on

Figure 2 Ion transport in channels with dimensions $d \gg \lambda_D$ and $d \approx 2\lambda_D$. Reprinted with permission from Ref. [51], Copyright 2018, John Wiley and Sons.

the inner surface of the channel. Finally, the interaction between the ions and charges in the channel wall should be asymmetric at the two ends of the channel [54]. The open and closed properties of biomimetic nanochannels to various external stimuli are called ionic gating [49,55]. The ionic gating characteristic is mainly controlled by the properties of the inner surface of the channel, including clogging [37], surface charge distribution [56,57], wettability and geometry [58,59]. Of course, for some specific nanochannels, ionic gating may be affected by multiple factors simultaneously.

At present, the design and preparation processes of bioinspired nanochannels are usually implemented through two schemes. One is to utilize the characteristics of certain materials, such as the responsiveness to specific external conditions. If these materials can be directly used to fabricate nanochannels, the nanochannels will inherit the similar characteristics. The other is to functionalize some nanochannels [14]. We can use functional molecules to achieve the control of various stimulating ion migrations in the nanochannels [9,56,60,61]. In next section, we will briefly introduce the preparation processes of polymer-based nanochannels.

PREPARATION OF BIOINSPIRED NANOCHANNELS BASED ON POLYMER

Homopolymer nanochannels

Polymer-based nanochannels are the most available and functionalized substrates in solid nanochannels. Track etching technology is the most commonly used method for the preparation of polymer-based nanochannels for two main reasons: nanochannels of various shapes can be prepared by track etching [9,62], such as cylinder [63,64], dumbbell type [65], hourglass type [66–68], cigar type [60], cone type [69], and bullet type [26] (Fig. 3). The other is that activated carboxylic acid groups can be generated on the inner wall of some polymer nanochannels after chemical etching which can be used for some simple amidation or esterification reactions, providing convenience for further functionalization of nanochannels [44]. Firstly, the polymer film is penetrated by high-energy heavy ions to form a pen diameter trace at the scale of several nanometers [70]. Then, selective chemical etching is carried out on the damaged high-energy ion trace area to ensure that other areas are basically unaffected, so as to prepare nanochannels with controllable pore size. The usual preparation process is as follows (Fig. 4) [3,71]. For polyethylene terephthalate (PET) films, NaOH solution is used as the etching agent

Figure 3 Different shapes of nanochannels. (a) Cylinder. Reprinted with permission from Ref. [64], Copyright 2016, American Chemical Society. (b) Bullet. Reprinted with permission from Ref. [26], Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Dumbbell. Reprinted with permission from Ref. [65], Copyright 2018, The Royal Society of Chemistry. (d) Cigar. Reprinted with permission from Ref. [60], Copyright 2013, American Chemical Society. (e) Hourglass. Reprinted with permission from Ref. [67], Copyright 2014, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (f) Cone. Reprinted with permission from Ref. [69], Copyright 2009, American Chemical Society.

Figure 4 Schematic diagram of an etched ion track and simple schematic diagram of the etching conductivity device. Reprinted with permission from Ref. [3], Copyright 2001, Elsevier Science B.V.

and KCl or a mixture of KCl and HCOOH (1:1 by volume) is used as the terminating agent [72,73]; for polyimide (PI), the main reagent for oxidation etching is NaClO, and KI solution is used as the terminating reagent; for polycarbonate (PC), the typical etching condition for producing cylindrical holes is 6 mol L⁻¹ NaOH at 50°C [3]. The tapered nanochannel can be obtained by changing the process conditions, such as adding 20%–30% methanol to the 9 mol L⁻¹ NaOH solution [74] or increasing the working voltage during the etching process. The pore density of nanochannels depends on the number of incident irradiated ions. By selecting the appropriate etching solution, temperature and etching time, the diameter of the produced nanochannel can be controlled [75] within the range of several nanometers to several microns. Moreover, the chemical etching condi-

tions also determine the specific shape of the nanochannel.

PET membranes have significant advantages over other membranes and have been used to study the physical property of ion transport across membranes [76,77]. The etching process is very simple, and at the same time, the diameter of the nanochannel can be easily controlled by changing the conditions [78]. In addition, the PET surface can be etched by high-concentration sodium hydroxide and generates carboxyl groups *in situ*, which can be used for further modification [79]. PET nanochannels can be used to manufacture various nanodevices in response to various stimuli, such as specific ions and molecules [25,66,80–86], pH [65,67,68,87–90], temperature [91,92], and multiple stimuli [11,56,60,93–95] (Table 1). For example, inspired by the light/pH-switched

Table 1 The functional group for various nanodevices in response to various stimuli

Stimuli	Functional groups	Stimuli	Functional groups
pH	Chondroitin-4-sulfate (ChS) [96]	Temperature	Pillar[5]arene [97]
	Poly(acrylic acid) (PAA) [88]		PNIPAAm-co-PBA [22]
	Polydopamine [98]		Poly(benzyl methacrylate) (PBzMA) [99]
	Histidine [100]		PNIPAAm [91]
	Polyelectrolyte (PE) [101]		Elastin-like polypeptide (ELP) loops [102]
Light	Azobenzene (Azo)-DNA [103]	Ion	4-Amino benzamidoxime (ABX) [104]
	C4-DNA motors and malachite green carbinol base (MGCB) [105]		Poly[(N-isopropylacrylamide-co-4-(3-acryloylthioureido)acid) _{0.2}] (PNI-co-ATBA _{0.2}) [106]
	Spiropyran [107]		4'-Aminobenzo-18-crown-6 (4-AB18C6) [80]
	Azobenzene ligands [108]		mercaptoacetic acid-pillar[5]arene (MAP5) [81]
	Poly(N-isopropylacrylamide-co-(S)-(4-acrylamido-1,2,3-triazol)-5-guanidino-pentanoic acid) [32]		poly[2-(dimethylamino) ethylmethacrylate]-co-[4-vinyl phenylboronic acid] (P(DMAEMA-co-VPBA)) [109]
Molecule	CAMP	Multi	Temperature, pH and sugar
	Bovine serum albumin		pH and temperature
	Cocaine		Na ⁺ and K ⁺
	MicroRNAs		Hg ²⁺ and Ag ⁺
	TiO ₂ and cysteine enantiomers [110]		PNIPAAm and PAA [56]
	Capture DNA aptamers (C-aptamers) [25]		4'-Aminobenzo-15-crown-5 and 4'-aminobenzo-18-crown-6 [27]
	Phosphorodiamidate morpholino oligos [111]		T-/C-rich single-strand DNA (ssDNA) [20]

channelrhodopsin-2 (ChR2) ionic gate in mammalian cells (Fig. 5a), Xiao *et al.* [94] grafted an environmental stimulus-responsive molecule 8-hydroxypy-1,3,6-trisulfonate (HPTS) onto the solid-state nanochannel, and prepared a light and pH cooperative stimuli ionic gate. The single conical-shaped PET nanochannel was prepared by a common method (Fig. 5b) and the modification process was carried out by a two-step reaction. With coupling reaction between the carboxyl groups on PET and the amino groups of ethylenediamine (EDA), EDA can be grafted onto the inner surface of the nanochannel. Then, they further grafted HPTS onto the nanochannel modified by electrostatic interaction with EDA (Fig. 5c). The HPTS-modified nanochannel displayed four gating states from open to close under different pH and light conditions (Fig. 5d).

Although PI films [97,112–114] were not applied as frequently as PET films, PI nanochannels can provide a highly stable ion current signal [115,116] and high surface charge density [54] comparable to PET. For example, Guo *et al.* [117] demonstrated the salinity gradient energy harvesting on a non-biological single channel nanofluidic with PI membrane, and achieved ultrahigh power density. In addition, two more common polymer materials are introduced, PC and polyethyleneimine (PEI). Deng *et al.*

[118] used polyvinyl alcohol (PVA) to modify the track-etched PC (TEPC) membranes and constructed a biomimetic nanodevice for cascade response of borate and *cis*-hydroxyl compounds. Morones-Ramírez [11] grafted opt-thermally responsive polymer-nanoparticle nanocomposites onto the PC track-etched porous membrane, realizing the engineering design, mathematics modeling and manufacturing of a reversible fast-responding porous membrane. Lokuge *et al.* [119] reported that the nanocapillary array membrane (NCAM), prepared by modifying poly(N-isopropylacrylamide) (PNIPAAm) brushes onto the surface of Au-coated PC, achieved adjustment of the effective pore size towards temperature response. PEI usually functions as the responsive groups in bioinspired nanochannels. For example, Li *et al.* [83] prepared responsive polymer PEI-g-glucopyranoside (Glc-PEI)-modified nanochannels (Fig. 6a, b), which are promising for developing the device with high sensitiveness to sialylated glycans (Fig. 6c).

The track etching method to prepare nanochannel is usually limited by equipment. The functional groups are usually modified additionally. In this review, we summarized more methods such as casting, vacuum filtration, self-assembly, electrospinning, and phase separation for constructing nanochannels. The combination of casting

Figure 5 (a) Scheme of the biological ChR2 gate. (b) Base side and tip side scanning electron microscopy (SEM) of the conical PET single nanochannel. Scale bar: 200 nm (left) and 100 nm (right). (c) The preparation process of HPTS-modified nanochannel. (d) Four gating states under different pH or UV light stimulations. Reprinted with permission from Ref. [94], Copyright 2014, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figure 6 (a) Chemical structure of Glc-PEI. (b) Schematic of the Glc-PEI-modified nanochannels. (c) Glycan-induced nanochannel “OFF-ON” gates, showing the competition between polymer-glycan binding and the polymer shrinkage. Reprinted with permission from Ref. [83], Copyright 2020, Royal Society of Chemistry.

and phase separation is a facile strategy to construct nanochannels. For example, Zhu *et al.* [120] designed and synthesized a Janus membrane based on two ionomers with tunable surface charge density and porosity (Fig. 7a). They firstly synthesized positively charged poly(ether sulfone) with pyridine pendants (PES-Py) and negatively charged hexasulfonated poly(aryl ether ketone) (PAEK-HS) [121]. Then, the Janus membrane can be achieved by spin-coating these polymers sequentially. By tuning the contents of the ionomers, the nanochannel membranes

with different pore sizes and porosities can be obtained, which was applied for energy conversion, and achieved 2.66 W m^{-2} output power density. Zhao *et al.* [122] synthesized a sulfonated poly(ether ether ketone) (SPEEK) nanochannel membrane involving numerous nanochannels by utilizing nonsolvent induced phase separation (NIPS) technique (Fig. 7b). The membranes, which have been charged negatively, include a spongy porous layer as the supporting agent and also a dense shell layer, which is plenteous in parallel contiguous nanochannels.

Figure 7 (a) Preparation process of the Janus polymer membrane by combining PES-Py (left) and PAEK-HS (right). Reprinted with permission from Ref. [120], Copyright 2018, American Association for the Advancement of Science. (b) Fabrication of the asymmetric SPEEK membrane with the thin skin layer and supporting layer. Reprinted with permission from Ref. [122]. (c) Schematic fabricating process of silk nanofibril/AAO membranes. SEM image of natural silk cocoons, degummed silk fiber, transmission electron microscopy (TEM) image of silk nanofibril with a diameter of ~20 nm and cross-sectional of the hybrid membrane (from left to right). Scale bars from left to right: 20, 2.5, 0.2 and 10 μm . Reprinted with permission from Ref. [123], Copyright 2019, Springer Nature. (d) 3D hydrogel membrane for ion transportation. Reprinted with permission from Ref. [126], Copyright 2020, Springer Nature.

The parallel nanochannels with great space charges exhibit magnificent cation-selectivity, which is able to be enhanced *via* modifying the charge density and length of nanochannels. In addition, the SPEEK membranes divulged desirable mechanical features, rendering the possible creation of membranes with high-endurance scale-up property.

More functional polymers such as biological polymers, BCPs, and hydrogels are developed in recent years. For example, bombyx mori (silkworm) silk is a natural polymer material with many excellent properties, such as abundant surface groups, excellent mechanical properties, and easy modification with functional groups. Xin *et al.* [123] prepared a silk-based hybrid membrane and applied it for energy conversion. The results showed that the membrane performed good energy conversion efficiency and long-term stability. The author used a variety of solvents to dissolve the sericin wrapped around the silk to obtain the required nanofibers (Fig. 7c). Then, the silk membrane was fabricated by vacuum filtration. The silk nanofibril membrane with negative surface nanochannels was suitable for ion transport. Furthermore, Chen *et al.*

[124] constructed a silk fibroin membrane through the spin coating method within three layers. The prepared silk fibroin membrane could be simply regulated by adjusting the layers of the membrane. Electrospinning is a well-established method for preparing fibrous 3D material for constructing nanochannel membranes [125].

To make further improvement of ion transport efficiency in the interface, they presented the use of 3D polyelectrolyte hydrogel on the research of ion transport [126,127]. The hydrogel membrane can provide a charged 3D network for ion transportation, and the interface transmission efficiency can be greatly improved (Fig. 7d) [128,129]. Schroeder *et al.* [130] introduced polyacrylamide hydrogel compartments consisting of cation- and anion-selective hydrogel. They used it as an electric-eel-inspired soft power source, generating total open-circuit potential up to 100 V and power densities of 27 mW m^{-2} per gel cell. Chen *et al.* [129] used 2-hydroxyethyl methacrylate phosphate (HEMA-P) which was negatively charged as the key monomer and synthesized a hydrogel film by using space-charged and 3D interconnected nanopores through the photopolymerization

method. This HEMAP hydrogel membrane performed great conductivity as well as magnificent energy conversion behavior.

Block copolymer nanochannels

BCPs play a key role in the construction of nanochannels [87]. BCP self-assembly technology has been developed as one of the most promising methods for preparing porous polymers with well-ordered nanochannel structures and tunable sizes [131]. BCP is a special polymer prepared by connecting two or more polymer segments with different properties together. They have thermodynamic incompatibilities between different polymer chains [132,133], displaying unique phase separation structure. Compared with other nanochannel materials, amphiphilic BCP membranes show great advantages due to their diverse and multifunctional macromolecular blocks [131,134]. These mobile, stable and extensible macromolecular groups perform as intelligent effectors [135–138], for energy conversion and storage [87,139], responsive gating [93,134] and other fields [10,140].

Functional BCP to prepare ordered nanochannels is the key to achieve high-performance ion transport. Our group designed the functional BCP with the chalcone liquid crystal element to chemically crosslink continuous phase and nitrobenzyl ester structure capable of degradation under ultraviolet (UV) light. Thus, we successfully prepared large-scale membrane with excellent mechanical strength and well-defined nanochannel structure [4,139,141]. The molecular design concept is as follows: (1) the design of liquid crystal polymer. The liquid crystal segment should stabilize and maintain the

nano-ordered structure during the self-assembly process of the BCP, which is important for membrane up-scaling. (2) Design of cross-linkable groups. Since the chalcone structure can undergo a “2+2” cycloaddition reaction under UV irradiation, this structure is introduced into crystal structure and to crosslink the continuous phase, which would improve the mechanical strength and stabilize the nanostructure. (3) The design of degradable groups. Two separate polymer chains are chemical bonded by the nitrobenzyl ester structure, which would be degraded by UV light and generate carboxylic acid *in situ*. In addition, the UV conditions of the chalcone cycloaddition reaction and the degradation reaction of nitrobenzyl ester are the same. The cross-linking of the block and the bond cleave of the connection point can be achieved simultaneously in a “one-step” method. (4) Design of the flexible section. The flexible section is polyoxyethylene (PEO) with good solubility in lots of solvents. It can be easily cleaned from the nanostructure after breaking the chain, which benefits the formation of nanochannels in the film.

Based on the above design ideas, we reported an organic-inorganic hybrid nanochannel using a BCP and AAO (Fig. 8a). It has the characteristics of nanofluid diodes in a wide pH range [137], and displays a high energy conversion efficiency over a wide pH range [4]. To improve the performance, our group prepared an ultrathin and ion-selective Janus membrane using phase separation of BCPs (Fig. 8b, c) [139]. The membrane can convert osmotic energy with high power density by mixing natural seawater and river water [142], which provides a new idea for constructing high-energy ion

Figure 8 (a) The BCP-based nanochannels prepared by self-assembly and UV degradation. The BCP molecule contains a UV-degradable linker between the blocks and UV-crosslinkable chalcone groups in one block. Reprinted with permission from Ref. [4], Copyright 2019, American Chemical Society. (b) Fabrication process of the ultrathin ion-selective Janus membrane based on BCPs and atomic force microscopy (AFM) images of the back side (left) and front side (right) of the Janus membrane (c). Reprinted with permission from Ref. [139], Copyright 2017, American Chemical Society.

concentration battery [143]. The bottom-up preparation scheme can also realize ultra-density nanochannel arrays, overcoming the channel density limit of the top-down designed membranes in the past [40,68,144,145]. Obviously, BCPs have made breakthroughs in osmotic energy conversion, and have also achieved good results in other aspects, such as reversible pH response behavior [134], multiple response characteristics [93], which are introduced in subsequent chapters.

Fig. 9 shows the time line of bioinspired polymer nanochannels. Etched polymer nanochannels play an important role in the early stage of the development of biomimetic nanochannels [146–149]. Recently, more and more methods and materials are developed to satisfy more demands in application.

APPLICATIONS

Responsive channels

The development of nanochannels responding to external stimuli like pH, temperature, light, ions, molecules, and multiple stimuli has made rapid progress in recent years. We illustrate the ion regulation of nanochannels by the common stimuli in the following sections.

pH-responsive nanochannels

Presently, pH-responsive nanochannels are the most extensively studied [3,150]. There are two major reasons: (1) the first one is the wide applicability along with their high application value. This is due to that pH is a very important parameter for all the electrochemical reactions. It is considered as an important indicator of biochemical changes taking place in the ion channels of the living

system [13,14,40]. (2) The second reason is the relatively simpler construction of pH-responsive channels [9,151]. Among the various materials used for the construction of pH-responsive channels, polymeric materials are widely applied. As early as in 2003, Siwy's group [70] constructed single asymmetric nanopores such as PET and PI films with carboxy groups using the track etching technology. It was found that the electrolyte has different rectification phenomena in presence of different pH values, clearly indicating that these nanopores have obvious pH-responsive properties. Zhang *et al.* [60] grafted two polyelectrolytes with opposite pH responses to the left and right tips of a cigar-shaped nanochannel, constructing an ion pump with a cooperative pH-responsive double-gate nanochannel. The two electrolytes are polyelectrolyte-polyvinylpyridine (PVP) and polyacrylic acid (PAA). The swelling and collapse state of the nanochannel can be controlled by adjusting the pH value, and then the opening and closing of the channel can be controlled (Fig. 10a). Because PVP and PAA have functional groups with opposite charges [40,63], these reverse pH-responsive conformational transitions can well induce the on/off, off/on, on/off, and off/off gating states of the PVP/PAA gate, thereby producing three unique ion migration characteristics of the bio-ion pump.

Zhao *et al.* [96] prepared pH-regulated nanochannels by a layer-by-layer self-assembly method utilizing PEI and chondroitin-4-sulfate (CHS), which is a good example for the use of polyelectrolytes to achieve specific functions. The polyelectrolyte CHS, which has two anionic functional groups, i.e., sulfonic and carboxyl groups, can be strongly adhered to the branched PEI. The experimental result shows that when the salt concentration

Figure 9 The time line for the development of bioinspired polymer nanochannels.

Figure 10 (a) Cross-sectional schematic of the pH-responsive double-gate nanochannel in which acid-driven PVP gate and alkali-driven PAA gate are grafted on the two sides of the channel, respectively. Reprinted with permission from Ref. [60], Copyright 2013, American Chemical Society. (b) Schematic of reversible pH-responsive behavior of the BCP nanochannels and AFM images of the BCP membrane at different pH values. Reprinted with permission from Ref. [134], Copyright 2015, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Schematic diagram of controlling functional groups in nanochannels through photoresponsive host-guest interaction. Reprinted with permission from Ref. [113], Copyright 2018, Springer Nature. (d) Scheme of the sensing principle for Pb²⁺ detection and the ion selectivity of the morpholino-DNA-functionalized PAA membrane. Reprinted with permission from Ref. [183], Copyright 2015, Elsevier B.V. (e) Above the lower critical solution temperature (LCST) in ionic liquid electrolyte ([EMIm][NTf₂]), the polymer brushes with conformational collapse will block the pathway for ion transportation. Reprinted with permission from Ref. [99], Copyright 2012, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (f) Schematic illustration of the on-demand release system and the time-concentration curves of molecules transporting through nanochannels. Reprinted with permission from Ref. [84], Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

is low, the nanopores are almost closed at pH > 4, and the gate is open to anions only at lower pH (< 4). Moreover, the pH response of the nanochannel disappears with increasing salt concentration. Further, significant results have also been achieved in the domain of pH responsive nanochannels using BCPs [87,95,134,152,153]. Zhang *et al.* [134] combined asymmetric BCP and porous anodic aluminum oxide to prepare a multifunctional heterogeneous membrane, showing an obvious pH response. Apart from utilizing the high mechanical strength of the inorganic material, this heterogeneous membrane is also able to overcome the inherent defect of the inorganic

material having monotonous functional group. Fig. 10b shows that when the inner wall of the nanochannels (pK_a ≈ 5.2) containing poly(4-vinylpyridine) (P4VP) chains are exposed to a solution with a pH value lower than 5.2, they become swollen, positively charged, and hydrophilic. Otherwise, they are in collapsed, neutral and hydrophobic states [154,155], clearly indicating the pH-responsive characteristic of the nanochannels [134,156].

Photo-responsive nanochannel

Compared with the other responsive channels, photo-responsive nanochannels have certain unique advantages.

First, light can be quickly turned on or off [107,113,155], and thereby achieving precise control of the nanochannels; second, higher space-time accuracy of the light-responsive channels [157] due to precise projection ability of light; third, since the light can penetrate through the tissues, the remote and non-invasive *in-situ* control can be achieved [158,159], which minimizes the invasiveness and potential damage to the subject. Spiropyran [107,160], azobenzene [108,113,158,161] malachite green derivatives [105] are some of the common light-responsive molecules. Liu *et al.* [113] utilized the host-guest interaction between azobenzene and β -cyclodextrin to construct a photo-responsive nanochannel based on PI membrane (Fig. 10c). When irradiated by visible light, the azo group bonded with β -cyclodextrin (β -CD) and transformed into the *trans* conformation, resulting in an increase in positive charge. Consequently, there was an increase in the ion current from 0.065 to 5.65 nA at pH 3 under a positive voltage (+2 V). However, the ion current recovered to ~0.065 nA when UV irradiation was carried out, because the azo group was converted to a *cis* conformation and peeled off the pore surface. The nanofluidic diode realizes reversible switching based on the light response after being irradiated by visible or UV light, and also shows good stability and reversibility.

However, poor biocompatibility of these photochromic molecules (spiropyran, azobenzene, malachite green derivatives) severely limits their further applications [162]. In this regard, DNA is considered as an excellent candidate by its supramolecular property of duplex formation through complementary pairs [163,164]. As a special polymer, DNA molecule in photo-responsive nanochannels has wide range of applications. Wen *et al.* [105] grafted C4-DNA motors onto a PET membrane and achieved photo-responsive characteristic. The conformation of DNA changed *via* receipt or release of protons generated by UV radiating the malachite green methanol base (MGCB). The film was repeatable as well as stable in nature even after many cycles of alternate measurements under UV and dark conditions. Li *et al.* [162] obtained a new type of functional nanochannel *via* integration of the Azo-DNA strands with the PET film. The nanochannel displayed short response time and reversibility as other light-responsive devices. Besides, it also had the advantages of good biocompatibility and universal design [165], with the potential for use in light-controlled drug release and other fields [166].

Ion-responsive nanochannels

Diverse ion-responsive nanochannels such as K^+

[112,167], Pb^{2+} [80], Zn^{2+} [66,86,168,169], Ca^{2+} [106,170], Hg^{2+} [81], and Cl^- [171] have been investigated in the recent years. Yang *et al.* [104] prepared a single conical nanochannel from 4-amino benzamidoxime (ABX) and PI membrane. This channel has detection ability for ultra-trace uranyl ions in a complex environment with simultaneous uranyl removal properties [172–175]. Furthermore, a Zn^{2+} -responsive nanochannel based on the salicylaldehyde Schiff base (SASB) was prepared by Sun *et al.* [66]. This channel can not only provide an effective and reversible “on/off” state, but also can be modified unilaterally. This provides a greater experimental basis for further promotion of the asymmetric chemical modification of molecules with various complex functionalities.

In addition, label-free DNA analysis has been widely used in biochemical analysis [176–179]. Researchers have proposed various amplification strategies to improve the high-sensitivity analysis of DNA in nanochannels [180–182]. One of the strategies is to fix neutral biological probes (peptide nucleic acid (PNA), morpholino, etc.) with capture property in the nanochannel, and then use low ion intensity for amplifying the target signal to reduce the background signal [150–152]. Chen *et al.* [183] established a new type of Pb^{2+} bionic logic gate sensor *via* modification of a porous alumina membrane by morphine and DNA. Nanochannel devices functionalized with DNA can achieve the opening and closing of nanochannels by the use of 1,4,7,10-tetraazacyclododecane-*N,N',N',N'*-tetraacetic acid (DOTA), and Pb^{2+} , and have objective repeatability and stability (Fig. 10d).

Temperature-responsive nanochannel

PNIPAAm occupies an extremely important position in temperature-responsive nanochannels. Researchers have designed many temperature-sensitive channels by the sharp volume transition that occurs near the critical solution temperature of PNIPAAm [6,92,119]. Reber *et al.* [36] grafted PNIPAAm hydrogel onto the etched PET channel membrane, and studied the local transport characteristics by measuring the current of the single pore membrane, which provided a good example for studying the application of responsive membranes in the field of drug release. Lokuge *et al.* [119] prepared an NCAM by grafting PNIPAAm brush onto the outer surface of Au-coated PC to achieve active controlled transport. Yameen *et al.* [6] proved that the PNIPAAm-modified PI membrane can act as thermally driven molecular gate with a closed stage, which can be remotely controlled by simple adjustment of the operating temperature in the range of

23–40°C. Zhang *et al.* [22] constructed a macromolecular nanochannel system *via* grafting poly(NIPAAm-acid) onto the AAO solid-state nanochannel using the typical surface-induced atomic transfer radical polymerization (ATRP) process and explored the effect of the length of the gated molecule on its gating performance.

Zhou *et al.* [99] created a temperature-responsive nanochannel which can operate in room-temperature ionic liquid system by attaching the molecular brush of poly-benzyl methacrylate (PBZMA) to the surface of the polymer *via* the surface-induced ATRP process. The conformational change of PBZMA molecular brush contributed to the thermal shutdown behavior of the modified nanochannel (Fig. 10e) [184]. The changes in electrical conductivity and the effective porosity of the channel with temperature indicate that the nanochannels have good thermal response characteristics. In addition, Wang *et al.* [97] constructed a temperature-sensitive artificial channel using the host-guest interaction of the Pillar[5]arene. The selectivity of ion transport can be converted from cation to anion by controlling the degree of host-guest binding *via* regulation of the temperature. This study not only opens up a new means for better understanding of the mechanism of temperature-sensitive characteristics, but also shows a broader prospect for biomedical research.

Molecule-responsive nanochannel

Molecule-responsive nanopores have attracted wide attention due to their possible applications in molecular recognition, biosensors and drug separation [9,13,14,151]. The core element of the sensor nanofluidic device is the control of the transmission of the nanochannels *via* utilizing their specific interactions [44,185]. The specific interaction between the target ion or molecule and the functional group fixed on the surface of the channel is responsible for the change of the ion current of the responsive channel [186–188]. Most interaction processes are based on non-covalent bonds, such as electrostatic interactions, and hydrogen bonds [189–191]. However, due to these weak non-specific interactions, subtle interference with ligands on the channel surface may reduce the accuracy of the response to specific ions or molecules. Consequently, these systems cannot guarantee good accuracy in complex matrices and real environments.

Sun *et al.* [73] developed bioinspired nanochannels with high Cys specificity and sensitivity by a click reaction strategy. The results show that the channel selectivity is very high even in the presence of complex substrates

(interfering substances such as Arg, Asp, PHE, Met, Trp, Ser, His, Pro, Leu, Ala, Thr, Val, Lys, Tyr, Glu, AA, UA). In addition, due to the presence of strong covalent bonds [192], the channel can also achieve a highly specific response in complex environments and actual samples. This nanochannel was used for detecting different concentrations of Cys in urine samples [193], with no significant alteration of the current change ratio of Cys being observed in urine samples in comparison to that in the electrolytes resulting in a standard error of ~2.51%. Therefore, this channel achieves high Cys selectivity and strong non-interference in complex matrices and human urine. Though various triggering systems have been constructed [194,195], these systems can only control the transmission of molecules in burst mode rather than controlling the continuous transmission performance. In order to satisfy the clinical translation, a release system with on-demand, reproducible, repeatable and controllable molecular transport is required to be developed. Xiao *et al.* [84] introduced peptides as gatekeepers on the inner surface of PET film, which was able to achieve on-demand molecular transport based on the response characteristics of peptides to dithiothreitol (DTT). The process of on-demand release of molecules can be evaluated by measuring the flux rate of fluorescein between the two reservoirs (Fig. 10f). For the unmodified nanochannel membrane, there was a linear increase of the fluorescence intensity. However, the change in fluorescence intensity for the nano-gating system was different with sharp increase in the first 2 h followed by slowing down. The data of the release amount and release rate also directly indicated that the channel can achieve molecular control at an adjustable rate and dose-controlled release.

Multi-responsive nanochannel

The biological ion channels in nature usually respond to a variety of physical and chemical stimuli, which are crucial in physiological processes. Inspired by this, scientists have developed intelligent multifunctional responsive nanochannels and made breakthroughs in the fields of controlled drug release [9,84,196], random DNA sequencing [197–199], and molecular recognition [46,84,114,200–202]. For example, Guo *et al.* [186] synthesized a temperature- and pH-responsive nanochannel by grafting poly(NIPAAm-co-acrylic acid) brush onto the inner wall of a tapered polyimide [186,193,203]. The current-voltage (*I*-*V*) curves show different behaviors at different temperatures and pH values, indicating obvious pH- and temperature-responsive behaviors of the nanochannel. In

addition, the authors evaluated the influences of NI-PAAm and acrylic acid contents in the copolymer on the gate ratio and current rectification ratio. DNA as a special polymer has also been studied for multi-responsive nanochannels. We all know that mercury and silver are the two most toxic metal ions existing in the natural environment, posing huge danger to the health of the human being. Accurate and sensitive measurement of the Hg^{2+} and Ag^+ ion concentrations has always been a hot topic. Studies have found that stable metal-ion-mediated base pairs are formed by the Hg^{2+} and Ag^+ ions in combination with specific nucleotide bases. Based on these characteristics, Wang *et al.* [20] designed a new type of bionic ion-responsive nanochannel *via* immobilization of single-stranded DNA (ssDNA) in a funnel-shaped alumina nano-channel (Fig. 11a). They selected a series of interfering ions for comprehensive experimental analysis, including Zn^{2+} , Mg^{2+} , Fe^{2+} , Fe^{3+} , Cd^{2+} , Pb^{2+} , Mn^{2+} and Cr^{2+} ions. The results show that the nanochannel still has good selectivity to Hg^{2+} and Ag^+ in a complex environment (Fig. 11b, c).

The use of BCPs in the multi-responsive nanochannels has been reported. Zhang *et al.* [93] demonstrated the construction of a functional nanofluidic system using the confined swelling-induced surface reconstruction method. The combination of the BCP membrane with PET led

to a new heterogeneous membrane (Fig. 11d). The system was able to respond to the changes in pH and temperature simultaneously, and showed excellent stability and controllability (Fig. 11e, f). The hybrid system will greatly help the development of biosensing, water purification and sustainable power generation. In addition to the dual-response nanochannels, Zheng *et al.* [109] modified poly[2-(dimethylamino) ethyl methacrylate]-*co*-[4-vinyl phenylboronic acid] (P(DMAEMA-*co*-VPBA)) on the wall of a single glass tapered nanochannel to demonstrate a triple-responsive nanofluidic diode. The functional groups of the copolymer brush are sensitive to pH, temperature, and sugar, causing changes in the charge and configuration of the copolymer. As a consequence, these changes would affect the properties of the pore wall, which leads to the triple response under the experimental condition.

Energy conversion

Salinity gradient energy conversion

Salinity gradient energy, the Gibbs free energy [204] in the salt solutions of varying concentrations, is known as the blue energy and can be converted into electrical energy by reverse electrodialysis (RED) [205,206]. Considering the great potential of marine resources, the

Figure 11 (a) Schematic illustration of Hg^{2+} and Ag^+ ions-responsive nanochannels. *I-V* curves of ssDNA-modified AAO nanochannels in complex ion solutions at pH 7.0 (b) and 4.5 (c). Reprinted with permission from Ref. [20], Copyright 2015, Royal Society of Chemistry. (d) The fabrication process of the PET and polystyrene-*b*-PDMAEMA-based asymmetric membrane. (e) Schematic diagram of charge, wettability, and spatial configuration changes of PDMAEMA brushes under different pH and temperature environments. (f) The carboxylic groups on the inner walls of the PET nanochannels are also pH sensitive. Reprinted with permission from Ref. [93], Copyright 2016, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

salinity gradient has great potential in alleviating the energy crisis in the future. By regulating the migration of monopolar ions inside their confined spaces, the solid-state nanochannels [123,207,208] can realize energy conversion [3,209].

Guo *et al.* [117] demonstrated the harvesting of salinity gradient-driven energy for the first time on a completely abiotic single-channel nanofluidic system. They pointed out two distinct advantages for the use of a single nanopore system. The first advantage is to research the influence of pore size on power generation performance by regulating and characterizing the geometry of the nanochannel, which is crucial to confirm the appropriate pore size for power generation [54,78,210,211]. The other advantage is achieving a stable current output throughout the measurement process. The experiment systematically measured the dependences of the zero-volt current (I_0) and the reversal potential (V_{rev}) on the concentration gradient, surface charge density and pore size. In addition, the collected power from the nanopore system was used as output for the external circuit in the experiment. The experimental results indicated that individual nanopores reached the maximum power output ($(P_L)_{\text{max}}$) of ~ 26 pW. Zhang *et al.* [87] also obtained considerable energy output *via* BCP, which can be attributed to the elimination of the concentration polarization by using asymmetric bipolar structure and excellent anion selectivity. The harvested power from the experiment was transferred to an external circuit, which yielded a maximum output as high as 0.35 W m^{-2} for the heterogeneous membrane and exceeded the power efficiency generated by some commercially available cation exchange membranes [212].

Huang *et al.* [213] employed a phase separation method to construct a polyether sulfone/sulfonated polyether sulfone (PES/SPES) membrane with large nanochannels and applied it for the salinity gradient power generation. Meanwhile, the authors also discussed the effects of SPES content, thickness and polymer concentration on the surface structure and charge density of the PES/SPES membranes, which determines the ionic conductance and ionic selectivity of the membrane (Fig. 12). The experimental results showed maximum output power density of the PES/SPES film to be about 2.48 W m^{-2} in presence of 500-fold salinity gradient (NaCl solution). In addition, the cost of PES/SPES membranes was about 6.2 USD m^{-2} , which is lower than the commercial cost target (11 USD m^{-2}) of the ion exchange membranes based on RED [214]. The improved mechanical properties of the PES/SPES membrane, and simpler membrane prepara-

tion process, provide the possibility of large-scale industrial production of salinity gradient power [215].

Hsu *et al.* [205] further broadened the scope of research, focusing on the shape of the channel and the influence of external experimental conditions on energy harvesting, which provided an experimental and theoretical basis for further improvement of the energy collection efficiency. The pH-adjusted nanochannels were selected by the authors for evaluation of the power generated by Gibbs free energy mixed by RED, concentrating on the effects of bulk salt concentration, the non-uniform distribution of H^+ , along with the size and shape of the nanochannels. And the article mentions that, the details of the convection transport of ions are considered which have been neglected by the scientific researchers in the past. For this reason, the authors also compared three different shapes of the nanochannels (bullet-shaped, conical and trumpet-shaped nanochannels). The results showed that the trumpet-shaped nanochannel has the best ion selectivity in comparison with the other two shapes. This is because the smaller the nanochannel space, the more pronounced the overlap of the EDL; for the bullet-shaped nanochannel, the maximum generated power had a local maximum due to the change in the ratio of nanochannel length/radius of curvature. Long *et al.* [216] studied the role of asymmetric temperature and its dependency in nanofluid-based power generation. A difference in negative temperature could considerably augment the potential of the membrane and also greatly enhance the power. Furthermore, a difference in positive temperature could obstruct the power at great intensities of transmembrane concentration and improve the power at low intensities of transmembrane concentration. The result indicated the significance of the temperature that has been ignored for decades in harvesting nanofluid energy, and supplied the manufacturing and optimization of high-performing power devices.

Photoelectric conversion

The bio-light driven ion pump uses the concentration gradient of ions to create a membrane potential [23], and converts the energy stored in sunlight into an osmotic potential. The application of nanochannels to participate in the photoelectric conversion process, directly or indirectly, has received increasing attention [24,79,217,218]. Wen *et al.* [219] introduced amino ($-\text{NH}_2$)-terminated groups (EDA) onto the inner surface of PET to prepare a functionalized nanochannel membrane, showing the typical response characteristics of photoelectric conversion measured in presence of radiation and darkness. The

Figure 12 Salinity gradient power generation property of PES/SPES nanochannel membrane. Reprinted with permission from Ref. [213], Copyright 2019, Elsevier Ltd.

study found that when the system was in the dark, the diffusion potential (E_{dif}) and electrons (I_p) tended to be constant. But under radiation, immediate photochemical reaction occurred which resulted in change of E_{dif} and I_p . When the light was removed, both E_{dif} and I_p fell rapidly, and they could not be restored to their original state, showing a significant drop in the peak value when the cycle test was carried out. Further, the authors used photoelectric conversion technology and Gibbs free energy diffusion technology to calculate the conversion performance of the energy conversion system and found them to be 0.00825% and 36%, respectively.

Unlike previous research, Meng *et al.* [79] used PSII complexes extracted from green plants and certain bacteria, the natural photoelectric conversion materials, as a “pump” to convert light into ion current (Fig. 13a). Furthermore, the authors introduced a PET film with a tapered nanochannel array into the photoelectric conversion system to adjust the light-induced ion current. It shows that the photocurrent generated by the system remains stable under radiation. The current was found to fluctuate violently and behave irregularly when the porous membrane was removed from the system, indicating that the PET nanochannel array can directly adjust the ion migration (Fig. 13b).

Electrokinetic energy conversion

Electrodynamic effect implies the situation that external pressure drives the electrolyte solution through the nanochannel with net charges and the charge separation of anion and cation occurs in the double electric layer [220,221]. Further, the asymmetric transport of anion and cation occurs in the channel, and subsequently the dynamic current and voltage will be generated [222]. When the current passes through an external load resistor within the fluid system, energy can be accumulated. Thus, the system of the nanochannel energy conversion found on the electrodynamic effect is capable of providing a novel choice for the conversion of fluid mechanical energy to electrical energy. In 1970s, the concept of energy conversion system based on the electrodynamic effect was proposed by Osterle's, Burgreen's and Nakache's groups [223–226]. It was expected that new findings pave the way for the energy conversion system of micro/nano fluid devices based on the electrodynamic effect more and more [227]. However, numerous investigations have indicated that the efficiency of actual energy conversion related to the conversion system based on the electrodynamic effect is relatively low and this issue has restricted its application as power devices and so on [228,229]. The future of energy issue in this field, directly

Figure 13 (a) Light-induced artificial ion channels prepared by using the PSII compound extracted from green plants and certain bacteria (natural photoelectric conversion materials) as a “pump”. (b) The photocurrent of the PECS in cyclic “ON-OFF” illumination. Reprinted with permission from Ref. [79], Copyright 2013, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

depends on the study of the meticulous structure optimization of nanofluid mechanics, surface chemical modification, interface slip and other surveys attributed to the construction of a fluid transport accurate control of the core of the essential circumstances which led to the break through the traditional solid-liquid interface under the limit of the bottleneck of low conversion efficiency and power output [230,231].

CONCLUSION

Polymer materials play an important role in the development of bioinspired nanochannels for their unique advantages (e.g., variety, controlled structure, active surface groups). This review summarizes several preparation methods of nanochannels based on polymers, such as track-etching, self-assembly, and cross-linking, including the preparation process, design of functional groups, and schemes of novelty nanochannels. Practical applications of polymer nanochannels in biochemical sensing and energy conversion are illustrated. These applications are based on the basic properties of bioinspired nanochannels including ionic selectivity, ionic gating and ionic rectification, which are related to their particular chemical and physical structures. We hope this review will provide overall information for the scientific community on the research of bioinspired nanochannels based on polymer.

Although the research of bioinspired nanochannels has made significant progress and breakthroughs in recent years, there are still great challenges in theory and practice. We still lack the theoretical basis and models to

explain the ion transport mechanism in the channel and understanding of the complex ion and molecular transport behavior, which obviously has guiding significance for the design of future nanofluidic devices. For instance, the distribution and density of charges in the nanospace, the modification status of the functional groups in the nanochannel and the development of new response mechanisms. In order to study these, it is essential to discover more appropriate systematic representation methods. Currently, to investigate the power density and the current change under various resistances is the most principal method to characterize the behavior of ion transportation within the nanochannel. Since the aforementioned cases are not obviously sufficient to achieve the considered objective, direct visualization and quantitative analysis of the ion transport behavior by using a visualized nanofluidic device is essential and it requires many novel assessment and control methods. Fortunately, molecular dynamic simulation has represented a plethora of valuable insights. To achieve a thorough understanding of the ion transport in nanospace status, considering a combination of various techniques, including molecular dynamics, statistics, and new concept such as quantum-confined superfluidics, is indispensable [232,233]. Moreover, although many different high-performance nanochannel membranes such as ultra-trace detection of ions, and high-performance energy conversion have been synthesized in the laboratory, it is estimated that the application of nanochannel membranes will encounter substantial challenges owing to the com-

plexity of the actual environment. In practical application, limited by the stability, reversibility, and durability of nanochannels, nanochannels are rarely used in actual working environment, and the result does not meet the experimental expectations. More cross-linked polymers with designable chemical structures are needed to be developed to solve this problem.

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基于聚合物膜的仿生纳米通道

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摘要 在生物体内, 细胞膜上的离子通道可以通过选择性地传输离子参与生命活动. 受生物体内传输通道结构和功能的启发, 具有实际应用价值的人工离子纳米通道备受关注. 基于高分子材料的仿生纳米通道具有机械稳定性、离子输运性能优异和可设计性强等特点. 本文主要介绍了基于聚合物的仿生纳米通道的制备及其在环境响应性生物传感和能量转换方面的应用. 首先介绍了纳米通道在离子传输调控和能量转换方面的基本特性. 之后, 我们讨论了聚合物基纳米通道材料的制备方法, 并强调了它们相对于其他材料的优势. 详细讨论了聚合物基仿生纳米通道在能量转换和环境响应生物传感器中的实际应用. 最后, 总结了仿生纳米通道研究中尚未解决的问题, 并对该领域的进一步发展方向进行了展望.