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REVIEW

Fundamental studies and practical applications of bio-inspired smart solid-state nanopores and nanochannels

Huacheng Zhang[a], **Ye Tian**[b], **Lei Jiang**[a,b,*]

[a] *Laboratory of Bio-Inspired Smart Interfacial Science, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China*
[b] *Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China*

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Summary Biological ion channels intelligently controlling ions across cell membranes serve as a big source of bio-inspiration for the scientists to build bio-inspired smart solid-state nanopores and nanochannels with practical applications. In this review, we mainly focus on fabrication and application of the bio-inspired smart solid-state nanopores and nanochannels. At the beginning, we introduce the nature-inspired strategy for developing bio-inspired smart solid-state nanopores and nanochannels. In the following, specific emphasis is put on recent advances in nanotechnologies and methods for fabrication and modification of the synthetic nanopores/nanochannels. Meanwhile, the fundamental understandings of the smart ion transport properties including ionic selectivity, ionic gating, and ionic rectification inside these artificial functional nanopores and nanochannels are discussed in detail. Moreover, the focuses are placed on practical applications of the bio-inspired smart nanopore and nanochannel materials in molecular filters, biosensors, nanofluidic logic devices, and energy conversions. Finally, some perspectives are provided for future developments and directions of this fantastic research field.

* Corresponding author at: Laboratory of Bio-Inspired Smart Interfacial Science, Technical Institute of Physics and Chemistry, No. 29 Zhongguancun East Road, Beijing 00190, PR China. Tel.: +86 82621396.
E-mail address: jianglei@iccas.ac.cn (L. Jiang).

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Introduction

Biological ion channels embedded within cell membranes are used to intelligently regulate ions across cell membranes, playing vital roles in life processes [1]. Ion channels, potassium channels for example, are membrane proteins that have three crucial functional elements: an ion conduction pore that has unique structure at the nanoscale; an ion selectivity filter that can distinguish ions; and a functional gate that can control the flow of ions (Fig. 1A) [2,3]. Based on these functional elements, regulations of ionic transport inside biological ion channels are mainly comprised of three characteristic features including ionic selectivity, ionic gating and ionic rectification. First of all, the ionic selectivity of biological ion channels is determined by their ion selectivity filters, and the selectivity filter is the central structural element that defines the type of the channel. For example, the K^+ selectivity filter of the K^+ channel has four potential binding sites where K^+ ions, but not other ions, can be bond in an essentially dehydrated state, surrounded by eight oxygen atoms from the protein (Fig. 1B) [4]. The ionic selectivity of the ion channel is generally investigated by measuring the ionic current of the ion channels under different ion solutions. Such as K^+ channel that shows much higher ion current in K^+ solution than in Rb^+ solution and the ion current increases obviously with the increase of the concentration of K^+ [4]. This indicates that K^+ channel conducts K^+ much higher than any other biologically abundant ions (Fig. 1C). Furthermore, gating of the biological ion channels is controlled by the stimuli sensors that can detect changes in environmental stimuli and trigger opening and closing of the gate of the ion channels [5]. For instance, the voltage-gated K^+ channel opening follows a very steep function of membrane voltage. To allow channel to switch to the open state, charged amino acids on the channel protein move within the membrane electric field to open the pore (Fig. 1D) [6]. Under the open state, ion channel conducts ion, resulting high ion current, while precludes ion movement under the closed state (Fig. 1E) [1,7]. The last but not the least, ionic rectification widely exists in the biological ion channels that have a preferential direction for ion flow [8—11]. Such as the inward rectifier K^+ channel conducts more inward than outward ionic current [10]. Ionic rectification of the inward rectifier K^+ channel is observed as asymmetric macroscopic current trances (Fig. 1F) and asymmetric current—voltage (I—V) curves (Fig. 1G) [12], with the ionic current recorded for one voltage polarity higher than the current recorded for the same absolute value of voltage of opposite polarity. Fig. 1F and G show macroscopic current traces and I—V curves of a strong and a weak inward rectifier K^+ channels, respectively [10].

Inspired by the intelligent biological ion channels, building bio-inspired smart nanopores and nanochannels with smart ion transport properties similar to those observed in the biological ion channels, have attracted extensive research interests in the last two decades [13—22]. Unlike the fragile biological ion channels, the artificial solid-state nanopores and nanochannels are of mechanical and chemical robustness, stability, controllable channel shape, and tailorable surface properties. These advantages allow them to be useful for a wide range of practical applications. As shown in Fig. 2, three routes are suggested to develop bio-inspired smart solid-state nanopores and nanochannels: the symmetric and asymmetric design of the shapes of the nanopores and nanochannels, the asymmetric and asymmetric functionalization of the inner surface of the nanopores and nanochannels, and the symmetric and asymmetric construction of the external stimuli of the nanopores and nanochannels. These three routes can be used independently or cooperatively to fabricate bio-inspired smart nanopores and nanochannels, and the idea of asymmetric design provides more flexible approaches for building much more functional nanopores and nanochannels. In this review, we mainly focus on recent advances in fabrication and functionalization techniques of the synthetic solid-state nanopores and nanochannels, fundamental studies of the smart ion transport functions including ionic selectivity, ionic gating and ionic rectification in the solid-state nanopores and nanochannels, and the practical applications of these nanopores and nanochannels in molecular filters, biosensors, nanofluidic logic devices, and energy conversion devices.

Advances in nanofabrication

From a structure point of view, nanopore is defined simply as a pore having diameter of 1—100 nm, with the pore diameter larger than its depth. If the pore depth is much larger than the diameter, the structure is generally referred to as ''nanochannel' [17]. According to the number of pore or channel they have, here we divide the solid-state nanopore and nanochannel materials into five kinds: single-nanopore, single-nanochannel, multi-nanopore, multi-nanochannel, and composite nanopore/nanochannel materials. Single nanopore or nanochannel materials are membranes with only one nanopore or nanochannel, while multi-nanopore or nanochannel materials are membranes with many nanopores or nanochannels. Composite nanopore and nanochannel materials generally comprise of more than two different nanopore and nanochannel materials. At present, various methods have been used to fabricate artificial nanopores and nanochannels in diverse synthetic materials, nanopores and nanochannels can be obtained in a variety of different shapes and structures (Fig. 3).

Single nanopore membranes can be made by using different approaches (Fig. 3A). First, ion beam sculpting reported by Golovchenko and co-workers has been used to create single nanopores in thin free-standing silicon nitride (SiN) membranes where an ion beam is focused at the membrane to open up a tiny hole with a diameter down to a few nanometers [23]. Alternatively, an electron beam from a transmission electron microscope (TEM) or a scanning electron microscope (SEM) can be used to drill and shape pores down to nanometers or sub-nanometer in the ultrathin free-standing Si, SiN, or SiO_2 membranes [24—28], 1—5 nm thick graphene membranes [29—32], and graphene monolayers [33]. Besides, laser technology was used to fabricate a conical nanopore in a thermoplastic material [34], atomic force microscopy (AFM) was adopted to prepare a ultrathin nanopore in the 9.50 nm thick mica membrane [35], and electrochemical etching method was used to make a single conical nanopore in glass or quartz capillaries [36]. The glass nanopores can be further decorated with a gold layer through electrochemical deposition methods