Bio-Inspired Smart Nanochannels: Toward Improved Nanofluidic Devices

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Biological ion channels are the essential excitable elements in the membranes of living cells that facilitate chemical and electrical communication with the extracellular environment[1,2] by acting as a 'smart' gate for selective ion transport.[3,4] Development of artificial nanochannels, which can simulate ionic transport processes and enhance the functionality of biological ion channels,[5] is a challenging yet rapidly progressive area of research. Nanochannels are structures containing nanopores having diameters of 1 to 100 nm, with the pore depth larger than the pore diameter.[3] Artificial nanochannels are more flexible than their biological counterparts due to their shape, size, robustness, and tunable surface properties.[2] Currently multipore membranes with pore diameters ranging from 10 nm to 10 μm and pore densities ranging from 10^5 to 10^9 pores per cm^2 are commercially available.[6] These artificial nanochannels have potential real world applications such as making functional materials like analytical sensors,[6] nanofluidic devices,[2] semiconductors,[7] diodes,[8,9] and transistors.[10]

Biological ion channels have two main functional characteristics: ion selectivity and stimuli response.[7] Artificial nanochannels are therefore designed to be ion selective,[8] and respond to external stimuli such as specific ions,[8] pH,[2,11] temperature,[2,12] voltage,[8,9,10] light,[13] and mechanical stress.[6] Ion channels respond to a stimulus by gating which opens or closes the pores. There is a selective flow of counterions in the pores due to electrostatic interactions with the charged surface walls resulting in a fluctuation in current (Figure 1).[14] Ionic rectification of the ion current is also observed in these nanochannels. This is a current-voltage relation which is non-linear.[7] Ionic rectification in artificial nanochannels can be achieved by four modes: designing a homogenously charged surface with an asymmetric geometry, designing an inhomogenously charged surface, controlling the current flow using an external voltage bias, and electromechanical gating.[7] The size and shape of the pores also affect the voltage response. Ideally the pores should be small with an asymmetric, conical shape.[6]

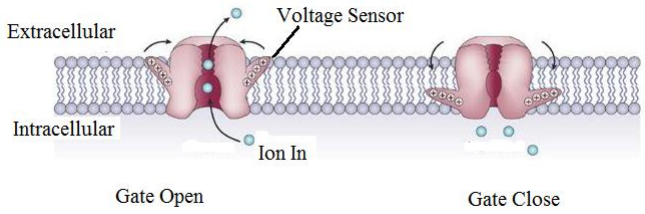

Figure 1: Schematic Illustration of Voltage Gating in Biological Ion Channels[14]

Biological and non-biological nanopore systems have been developed to make the artificial nanochannels. OmpF, from the outer membrane of Gram-negative bacteria, was one of the first protein pores engineered into a nanofluidic diode.[7] Also α-hemolysin, with a 10 x 10 nm external dimension, is another protein pore that has been incorporated into a biosensor to detect a single DNA polynucleotide.[3] These biomolecules exhibit desirable characteristics, such as size and ion selectivity. However these systems are not practical, since lipid bilayers are fragile and are unable to withstand a wide range of pH, temperature, potentials, and solvents and are sensitive to vibrations.[6] Non-biological systems, such as electrochemically etched glass nanopipettes,[16] ion beam sculpted silicon nitride pores,[7] chemically etched nanopores in polymer films,[2] and electroless plated gold in conical pores,[7] have proven to be better platforms for making artificial nanochannels. The fabrication of these non-biological systems still poses a challenge in that the precise functionalization of a small area and control of surface coverage can be difficult.

Recently Hou *et al*. addressed this issue and precisely functionalized a small area of a 12μm thick polyethylene terephthalate (PET) film by plasma induced polymerization.[2] PET films have been extensively used to embed nanochannels by track-etching.[16] PET is suitable for this process because it is a polyester thus using concentrated sodium hydroxide as an etchant deprotonates the carboxylic acid groups making the surface negatively charged thus voltage responsive. Plasma induced polymerization[17] was used to embed the pH responsive poly(acrylic acid) (PAA) and the temperature responsive poly(N-isopropylacrylamide) (PNIPA) in an asymmetric conical pore with a tip diameter of 10 – 30 nm and a base diameter of 250 – 300 nm (Figure 2).[2] Although the pH response was greater than the temperature response, this system marks the beginning of fabricating multiresponsive systems and moves one step closer toward the development of a "smart" nanochannel system.[2]

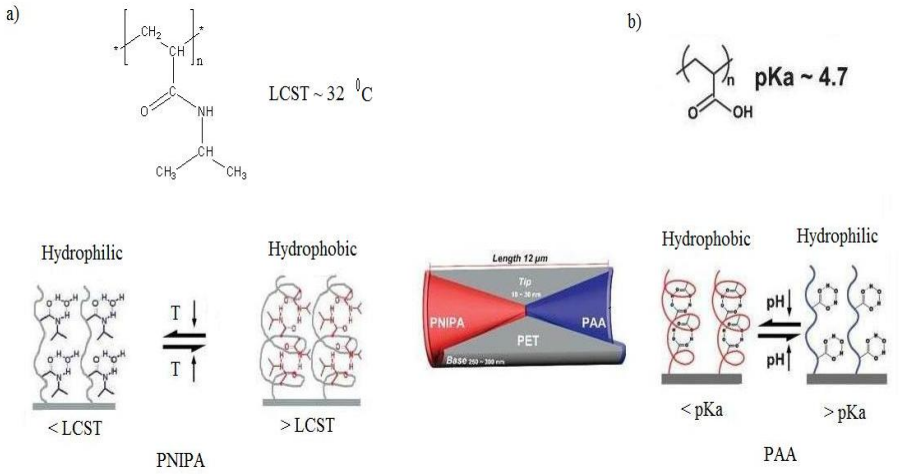

Figure 2: Schematic Illustration of dual responsive asymmetric system a) Mechanism for temperature responsive PNIPA[12] b) Mechanism for pH responsive PAA[2]

PET polymer films have also been modified by coupling the carboxyl groups with positively charged amines by Vlassiouk *et al*.[7] and Kalman *et al.*[8] to make a diode and a transistor respectively. Mubarak *et al.* also fabricated a diode by attaching the pH tunable L-lysine to a PET film which varied in ion selectivity with pH change above and below the pKa.[6]

Development of 'smart' artificial nanochannels is an area of interest because of their real world applications. Although the fabrication methods have been improved considerably over the years, better techniques and more responsive biological and non-biological molecules need to be developed and eventually commercialized. Artificial nanochannels can model biological ion channels and will lead to advancement in the field of nanotechnology.

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