Properties and Potential Applications of Biomimetic and Bio-derived Nanofluidic Systems

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Synopsis report

Chapter 1: Introduction to biomimetic and bio-derived nanofluidic channels:

The branch of fluid dynamic that explore the flow of liquid in structure constrained to nanometer size regime (1-100nm) is defined as nanofluidic. Fluidic transport in and around nanofluidic structures is dominated by interactions of otherwise weak effects such as the formation of electrical double layers (EDL), attractive or repulsive forces of charged species, and entropic barriers. Typically, transport of charged species through nanometer-sized channels are dominated by the overlapping electrical double layers. One of the major difficulties in designing nanofluidic devices is the inherent complexity. The overall transport characteristics are determined by the interplay of various nanoscale or even molecular level physical, geometric, and chemical factors. Biological ion channels, however, are known for their capability of elaborately manipulating these factors to regulate the transmembrane ionic flow, which plays a crucial role in a number of physiological processes. Mimicking the biological systems researchers has tried to demonstrate its artificial counterparts. In light of this feature, various ion-channel-mimetic smart 1D nanofluidic systems have been developed that can reproduce functions analogous to its parent biological systems. Although systematic research in single-pore devices makes the physical picture of this nanofluidic process much clear, it is still far from competent for practical applications. Toward practical applications, one major challenge is to extrapolate individual nanofluidic devices to macroscopic platform in a cost-efficient way. Interestingly solution to the above mentioned dilemma was also resolved from natural inspirations in the form of lamellar microstructure of nacre, in which soft materials (polysaccharides and proteins) are sandwiched between hard inorganic layers (aragonite platelets), forming an alternatively arranged layered structure. This novel method of material designing and large-scale integration of individual artificial nanofluidic channels into a macroscopic platform give birth a new research filed known as the 2D nanofluidics. Via a simple vacuum filtration process, colloidal dispersions of individual 2D nanosheets can be reassembled into a densely stacked multi-layered structure. The interstitial space between opposite 2D nanosheets can be treated as lamellar channels for mass and charge transport.

With the rising global climate change and resource shortage, increased attention has been paid to design environmentally friendly materials. Bio-derived materials, being abundant, renewable and environmentally friendly are considered attractive alternatives that can potentially meet some of these challenges. Biopolymer nanofibrils are universal nano-building blocks in natural materials and there lies a significant possibility to extract this biomaterial to design and create new materials and nanostructures. Outstanding properties of biopolymer materials profit from their multiscale hierarchical structures. The common property of natural structural materials is the nanoscale interaction between polysaccharides and silk-like protein, where the structural proteins confer the mechanical properties, structure and function of biological systems. Nature creates sophisticated materials with such hierarchical structure with assembly of interconnected nanofibrils and elementary fibrils that make the percolated nanochannel networks. The abundant hydroxyl and carboxyl groups on the surface of these nanofibers and elementary fibrils provided the nanochannels permanent negative surface charges that can attract layers of counter ions adjacent to the fibres and ensure a surface charge-governed ion transport.

Chapter 2: Nanofluidic transport through humic acid modified graphene oxide nanochannels:

In this chapter we have exploited the chemical similarity of graphene oxide (GO) and humic acid to fine-tune the ionic and molecular transport properties of a lamellar GO membrane. Even

though layered material based lamellar membranes panoply excellent selectivity for ionic and molecular separation but they suffer from lower permeability issues. The sub-nanometer-size pores of lamellar membranes that facilitate unprecedented ionic/ molecular selectivity also impede molecular permeability. The natural choice to overcome the problem of low permeability is to increase the channels' heights by applying spacers between the sheets. However, application of incompatible inert spacers could sacrifice the selectivity and robustness of the pristine membranes. Here, we have explored the possibility of tuning the transport characteristics of GO membranes without sacrificing their lamellar structure or altering the channels' heights. Humic acid, a naturally occurring organic material, is applied here to tune the structure of GO nanochannels. With a structure chemically and physically similar to that of GO, humic acid causes an all-round improvement of the GO lamellar membrane. Humic acids, the mixtures of acidic organic polymers that are believed to be a product of the natural break-down process of plant- and animal based materials, were extracted and purified following the standard alkaline-acid treatment-based procedure. Introduction of humic acid (in 10, 15 and 20 wt. %) is found to improve the nanofluidic transport characteristics, such as ionic mobility, molecular selectivity, diffusivity and permeability, of the GO membrane. Remarkably, the membrane prepared with 15% humic acid displayed superior proton mobility ($\mu_H = 1.04 \times 10^{-4}$ cm^2 V^{-1} s^{-1}), in-plane diffusivity ($D = 4.8\times10^{-6}$ cm^2 s^{-1}), and cross-plane permeability ($P_L = 2.03\times10^{-4}$ mm g cm^{-2} s^{-1} bar^{-1}) to the pure GO and other composite membranes. The favorable nanofluidic characteristics of the 15% membrane are attributed to the larger effective heights of the 2D nanochannels, derived from the onset point of the surface charge governed ionic conductivity of the membranes. The activation energy of proton transport (0.07 to 0.1 eV) confirmed the occurrence of a Grotthuss-like hopping mechanism in all the GO-HA membranes. Introduction of humic acid into two-dimensional GO channels also improved the solution stability and mechanical robustness of the pristine GO

membrane. The lamellar GO-HA membranes were also found to be suitable for energy harvesting applications such as direct methanol fuel cells and reverse electrodialysis.

Chapter 3: Uphill anion pumping through triangular nanofluidic device of reconstructed layered double hydroxide:

The synchronous growth in the research related to the novel 2D nanomaterials boosted diverse real time application related to two-dimensional nanofluidics. After the initial demonstration with graphene oxide, numerous other layered materials such as h-BN, clay minerals, Mxenes, carbon nitride were utilized to create nanofluidic devices with unique characteristics, mostly via reconstruction of their respective exfoliated layers. Remarkably, till date, most of these nanofluidic studies are limited to only cation-selective nanochannels. However, complimentary regulation of both the cation and anion is essential for futuristic applications such as osmotic power generation, seawater desalination, and regulated ionic/molecular transportations. Several indirect approaches, like modification of the reactive surface groups (-COOH or -OH) of the 2D sheets and intercalation of cationic polymers were adopted to imbue anion selectivity to the nanofluidic channels. The application of foreign materials/molecules not only involves tedious chemical processes but also disturb the well-defined 2D structure of the nanochannels. Along with decreasing nanofluidic confinements, it also exerts adverse effects on the mechanical, chemical, and thermal stability of the nanofluidic membranes. Therefore, direct utilization of positively charged 2D sheets for the fabrication of anion-selective nanofluidic nanochannels is the need of the hour. In the present work, we have utilized the inherent positive charges of the cationic Co-Al layered double hydroxide (CoAl LDH) to create anion-selective nanofluidic channels. The lamellar membrane of CoAl LDH was exploited for preparing a triangular ion-pump capable of transporting anions against the concentration gradient, as well as to fabricate salinity gradient-driven energy harvesting devices.

Nanofluidic membranes prepared by self-assembling exfoliated layers of CoAl LDH exhibit excellent anionic transport characteristics. At the surface-charge-governed regime, the positively charged CoAl LDH membrane (p-LDHM) showed a remarkable OH^- ion conductivity of ~ 2 mS cm^{-1}. The remarkable mobility of OH^- ions (4×10^{-4} cm^2 V^{-1} S^{-1}) in the atomically thin channel of p-LDHM is attributed to the tiny activation energy (0.09 eV) required for Grotthuss-like hopping of the ions between the positive charges of densely packed CoAl LDH layers. The lamellar p-LDHM was also found to be suitable for energy harvesting via salinity gradient, and power density up to 0.7 Wm^{-2} was achieved under a 1000-fold concentration gradient. The triangular p-LDHM displays a diode-like non-linear *I*-*V* curve, attributed to a combination of unipolar conductivity of counter-ions inside the 2D nanochannels and geometrical asymmetry. The triangular p-LDHM pumps anions against the concentration gradient (up to 1000 fold), under fluctuating external potentials of zero means.

Chapter 4: Disposable fluidic devices of bio-nanochannels for enzymatic monitoring and energy harvesting:

While artificial devices and machineries are providing countless conveniences to modern life, their disposals are creating major havoc in the environment. Therefore, in recent years, numerous research efforts are being dedicated to replace unsustainable materials and devices with environmentally benign alternatives of similar functionalities. For example, different kind of electronic devices such as solar cells, diagnostic tools, sensors, and artificial tissues, etc. have been developed based on sustainable materials obtained from the environment. Similarly, the outstanding new properties of liquids confined inside nanometer sized containers promise numerous technological breakthroughs in the areas of water treatment, energy harvesting, and molecular sieving. Studies on confined liquid also open up an avenue to understand the activity of biological nanochannels creating a platform to exploit them for various biomedical and chemical applications. However, in practice, the excellent properties of numerous biological

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channels readily available to us have not been explored yet for the technological applications. Here, we have the possibilities of employing large number of bio-channels readily available in our surroundings for the technological advancements in multiple directions.

Solanum tuberosum or potato, taken here as a model system exhibits very interesting internal features in the micro and nanometer regime just like any other biological system. It also possesses a highly active fluidic network across the cell walls to facilitate communications and transport of materials between the plant cells. The nature of molecular/ ionic transport through the narrow (3-5 nm) channels of the cell walls are not free or bulk-like, and it is strongly influenced by the interactions with the non-diffusible anions of the cell wall, like the carboxyl groups of the galacturonic acids of pectin. These characteristics of the bio-nanochannel based nanofluidic devices give rise to various nanofluidic phenomena like surface-charged-governed ionic conductivity and development of the transmembrane potential. The cation-selective nature of the bio-channels was also exploited to harvest a continuous supply of power up to 74 mW m^{-2} for 3h from the enzymatic decomposition of urea. The transmembrane potential across the bio-channels was also explored for label-free electrical monitoring of the enzymatic reaction inside the biological medium. Electrical monitoring on the kinetics of urease at different reaction temperatures suggested that inside biological medium the reaction goes through a pathway of lower activation energy (31.1 kJ) than that in the bulk environment (34.1 kJ).

Chapter 5: Remarkable Rate of Water Evaporation through Naked Veins of Natural Tree-leaf:

In the last few decades, numerous unforeseen properties and phenomenon specific to systems confined in nanometer size regime have been uncovered, and many of them were also exploited for technological applications. One of the recently discovered astonishing nano phenomena are

the enormous rate of evaporation from capillary nanochannels. In this article, we have studied evaporation behaviour through the hierarchical structure of the vein network extracted from the fallen leaves and exploited the same for seawater desalinations. We observed that even in the absence of photoactive materials, the naked vein network exhibited an evaporation rate at par with the man-made systems with highly efficient photo-thermal materials. A remarkable kinetically controlled evaporation process powered by extended evaporation area, decreasing thermal resistance between the solid substrate and the liquid/vapour interface, and efficient exchange of heat and mass between water molecules confined inside porous biological channels and atmosphere is accounted for the remarkable performance of the leaf vein based natural evaporator. The network of hierarchical channels, precisely designed by nature for efficient transportation of liquids were extracted from matured and fallen leaf samples collected directly from nature. To begin with, the leaves of *Ficus religiosa* (Peepal tree) were soaked in tape water for around 25 days. During the prolonged soaking period, most of the soft cells of the leaf blade (cuticle, epidermis, the mesophyll) were digested by the microbes releasing a funky smell. Remarkably, the vein structure of leaf epipodium was not affected by the digestion process. The naked leaf veins exhibit remarkable flux (evaporation rate 1.5 kg m^{-2} h^{-1}) of capillary evaporation under ambient condition (25 °C and 30 % RH), close to the photothermal material-based evaporators reported in the recent literature. Even, inside a dark box, naked veins exhibit an evaporation rate up to 4.5 kg m^{-2} h^{-1} (at 30 % relative humidity (RH), and wind speed of 22 km h^{-1}). The evaporation rates can be further improved by tuning the environmental conditions like temperature, humidity, and wind speed. The mechanistic studies performed with variable atmospheric conditions (temperature, humidity, wind-speed) suggest the evaporation process through the naked veins to be a kinetic-limited process. Naked veins with remarkable evaporation efficiency are found to be suitable for applications like water desalination and streaming potential harvesting. Experiments with the naked veins also shows

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that the biofluidic channels in leaf not only exhibit the characteristics of surface-charge-governed ionic transport but also support an exceptional water transport velocity of 1444 μm s^{-1}. Looking at the variety and abundance, the vein-based evaporator could provide an ideal platform for futuristic water treatment and energy harvesting devices.

Conclusion:

In conclusion, we have explored the properties of biomimetic and bio-derived nanochannels and of utilized the same to fabricate nanofluidic conduits for multiple application purposes, notably for manipulating molecular/ionic transportation, concentration gradient based energy harvesting, uphill ion pumping, level free monitoring of enzymatic reactions and water steam generation. Chapter-1 describes a general overview of biomimetic nanochannels with special emphasis on their structural integrity and peculiar electrokinetic properties. Chapter-2 demonstrates fabrication of mechanically robust composite membranes using graphene oxide and humic acids. Introduction of humic acid into two-dimensional GO channels was found crucial in improving the nanofluidic properties of the pristine GO membrane. The percolated network of ultra-thin nanochannel exhibiting fascinating transport properties could find applications in the areas of selective molecular/ionic transport, catalysis, energy harvesting and storage, methanol fuel cell and gas sensing. Chapter-3 demonstrated the direct utilization of positively charged 2D sheets (CoAl LDH) for the fabrication of anion-selective nanofluidic nanochannels. A biomimetic strategy was utilized to fabricate the anion selective lamellar membrane (p-LDHM). The lamellar membrane was exploited for preparing a triangular ion-pump capable of transporting anions against the concentration gradient, as well as to fabricate salinity gradient-driven energy harvesting devices. In chapter-4 we have we have demonstrated the utilization of bio derived disposable nanofluidic conduits extracted from potato tuber for nanofluidic study. The cation-selective nature of the bio-channels was also exploited to harvest electrical energy from concentration driven process aided by an enzymatic decomposition reaction of urea. The transmembrane potential across the biochannels was also explored for label-free electrical monitoring of the enzymatic reaction inside the biological medium. In Chapter-5 we have demonstrated another bio-derived material in the form of precisely designed leaf network and exploited its technological applications. The naked leaf veins exhibit remarkable flux of capillary evaporation under ambient condition (25 °C and 30 % RH), close to the photothermal material-based evaporators reported in the recent literature. This feature makes our bio-derived evaporator a potential candidate to be utilized as low grade steam generator. Naked veins with remarkable evaporation efficiency are found to be suitable for applications like water desalination and streaming potential harvesting.

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