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Two-dimensional nanofluidic channels towards ion transport

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Electrolytes confined in nanochannels with characteristic dimensions comparable to the Debye length behave very differently from their bulk counterparts [1]. Nanofluidic channels, featuring high surface-to-volume ratio, non-negligible surface charges, and overlapping electric double layers, have attracted strong interest for ion transport due to the emergence of anomalous fluid phenomena and the potential applications in various fields including energy storage and conversion, seawater desalination and biological systems [2,3].

Two-dimensional (2D) nanofluidic channels towards ion transport were first reported in 2012 [4]. By restacking exfoliated nanosheets of graphene or graphene oxide (GO), massive arrays of nanochannels are readily obtained. Such nanofluidic membranes with interlayer spacing of ~1 nm can be used for effective ion transport. Characteristic surface-charge-governed ion transport and higher-than-bulk ion conductivity were observed at low-concentration electrolytes. So far, many other 2D materials beyond graphene and GO have been developed, such as hexagonal boron nitride, transition metal dichalcogenides, MXenes, layered metal oxides, layered double hydroxides, and clays [5,6], which provide a broad platform for the construction of 2D nanofluidic channels. Compared with other nanochannels and angstrom-scale slits, 2D nanofluidic membranes are easy to fabricate and offer numerous uniform and well-structured 2D nanochannels with tunable sizes and varieties, allowing great flexibility in designing devices for specific applications [7].

The unexpected phenomena and exotic properties observed in 2D nanochannels such as ultrafast ion transport and precise ion selectivity mostly stem from the interactions between the ions and the walls of the nanofluidic system. Thus, surface chemistry in particular surface charges plays a critical role in ion transport. By using different 2D nanosheets, it is possible to design 2D nanofluidic channels with different surface charges. Ionizable/polarized functional groups provide an important way to generate surface charges (Figure 1A). Additionally, isomorphous ion substitution and structural defects, such as vacancies, can also allow the walls of the nanofluidic channels to be charged (Figure 1A) [3,8]. For almost all the nanofluidic channels carrying surface charges, there is often an electrostatic force that repels ions with the same charge as the wall (co-ions) while attracting ions with the opposite charge (counter-ions) [1]. No matter ions travel through the nanofluidic membranes horizontally or vertically, their transport behaviors are significantly affected by the surface charges of the 2D nanofluidic channels (Figure 1B). Understanding the interfacial interactions may

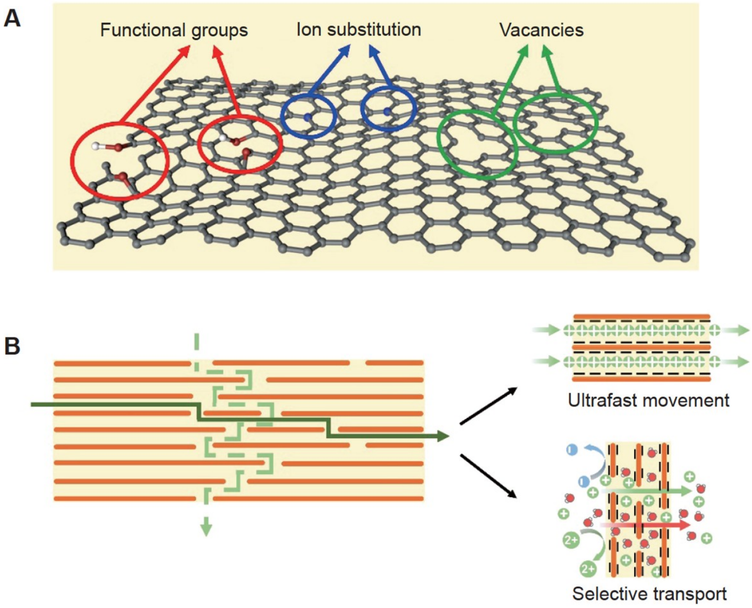

Figure 1 (A) Common surface charging principles; (B) characteristic ion transport phenomena within 2D nanofluidic channels for both vertical and horizontal paths.

enable the rational design of the structure of the nanofluidic channels for different applications.

2D nanofluidic channels decorated with ionizable/polarized functional groups, such as carboxyl, amino, and hydroxyl groups, are among early examples to apply 2D material-based membranes in nanofluidic devices. For instance, the polarized oxygen-containing functional groups on chemically converted graphene from GO can lead to the formation of an excessive cloud of counter-ions near the negatively charged graphene channel wall. Driven by hydraulic flow, both continuous and pulse-shaped ionic currents can be generated depending on the mechanical force waveform provided. This 2D nanofluidic generator shows potential applications in harvesting mechanical energy from foot-steps or monitoring the heartbeat [9]. By further chemical modifications, improved or additional properties can be achieved. In particular, modification of the 2D nanosheets prior to assembly is more efficient and convenient than the chemical modification to nanofluidic channels that have already been formed. Using this method, positively and negatively charged 2D nanofluidic membrane pairs and heterojunction membranes have been constructed for ion-selective transport and asymmetric transport, respectively [10,11], which provides potential applications in energy conversion and water treatment [10–12].

Compared with the 2D nanosheets with pendant functional groups, which might act as obstacles breaking down the continuous paths necessary for fast ion transport, it is more appealing to design and construct 2D nanofluidic channels using defects. For example, transition-metal phosphorus trichalcogenide nanosheets have been designed for nanofluidic membranes by creating abundant transition-metal vacancies with an ion intercalation exchange process [8]. The negatively charged cadmium vacancies on 2D nanofluidic channels not only provide uniform donor centers to absorb protons but also enable easy proton desorption and excellent hydration of the membranes, which boosts the ion conductivity significantly. The proton conduction dominant conductivity of cadmium-containing $CdPS_3$ membranes is several times higher than that of Nafion and one to four orders of magnitude higher than those of the GO-based materials. Similarly, other superionic conductors such as lithium ion conducting membranes can also be fabricated by using the vacancy strategy.

It is also intriguing to explore intrinsically charged layered materials such as clays and layered double hydroxides, a clay-like layered compound, in which the surface charges stem from isomorphous substitution [3,13]. Typically, the substitutional ions of different charges can create a considerable amount of negative or positive charges on the layers, which can promote the exfoliation of clays and the reconstruction of 2D nanofluidic membranes with smooth and well-defined surface structure. It has been demonstrated that the 2D nanofluidic vermiculite membrane has high proton conductivities approaching those of polymeric proton-transport membranes [13].

External stimuli such as electrical gating and chemical stimuli can further modulate the surface charges of nanofluidic channels, which consequently affect the ion transport through the channels [14,15]. Current rectification and increased ion conductivity have been observed when different gate voltages are applied to the membrane. For example, Zhang's group [15] reported reduced GO nanofluidic channels with ultrafast and highly selective ion transport controlled by electrical gating. It was found that the applied voltage creates a high packing density of charges in the graphene channels, imparting strong Coulomb interaction among adjacent ions and promoting their concerted movement with decreased energy barrier, which provides a strategy for designing super-ionic conductors and developing atomic-scale ion transistors. Chemical stimuli, such as pH or ionic strength, can affect the deprotonation/protonation of functional groups and cause an ionic screening effect, respectively, leading to changes in the effective surface charge density as well [14].

Besides surface chemistry, another prominent characteristic of 2D nanofluidic membranes is their nanometer or sub-nanometer interlayer spacing, which is related to ionic/molecular sieving applied in water desalination and purification. The interlayer spacing of 2D membranes can be controlled through various methods, such as physical confinement [16], cation-π interactions [17], chemical modification with small molecules or functional groups [18,19], and specific reduction for GO membranes [20,21]. In some cases, the chemical stimuli mentioned above may also cause variations in interlayer spacing [22]. Although these strategies are generally effective at limiting the permeation of large ions/molecules, it is still possible for cations with hydrated diameters larger than the interlayer spacing to pass through and further narrowing down the interlayer spacing may sacrifice the permeability [16,23]. How to solve the trade-off between the selectivity and permeability of ions is still an open challenge for 2D nanochannels. Innovative design combining surface charges and size effects may offer a promising approach to address the problem [12].

Benefiting from the rapid development of 2D materials, many anomalous fluid phenomena and potential applications have been demonstrated in 2D nanofluidic channels so far. However, most reported 2D nanofluidic channels are designed based on the intrinsic nanosheets. In addition to exploring more new 2D nanosheets as building blocks, modifying the nanosheets for 2D nanofluidic channels with controlled functional groups, substitutions, or defects are highly demanded to improve the ion transport properties. Unexpected phenomena might be observed by constructing asymmetrical nanochannels with different 2D nanosheets as channel walls of the two sides. It is also intriguing to expand the research to more charge carriers beyond proton and Li^+ such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, and Al^{3+} under broader operational conditions, which is essential for exploring more applications and multifunctional devices. Additionally, more theoretical analysis and atomic-level characterizations on the interactions between surface charges and ions within the channels would have a great help in discovering and understanding the unusual nanofluidic phenomena in 2D nanocapillaries. It is reasonable to expect that membranes with superhigh ion transport and excellent selectivity could be achieved by tuning both the physical geometry and the surface chemistry of the 2D nanofluidic channels. Overall, rational design and construction of 2D nanofluidic channels and membranes will have broad implications in advancing the development of batteries, fuel cells, supercapacitors, seawater desalination techniques, atomic-scale ion transistors, sensors, even neuromorphic computing, and bio-inspired nanofluidic devices.

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Conflict of interest

The authors declare no conflict of interest.

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