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Review Article

Bionic iontronics based on nano-confined structures

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ABSTRACT

The Moore's law in silicone-based electronics is reaching its limit and the energy efficiency of the most sophisticated electronics to mimic the iontronic logic circuit in single-celled organisms is still inferior to their natural counterpart. Unlike electronics, iontronics is widely present in nature, and provides the fundamentals for many life activities through the transmission and conversion of information and energy via ions. Moreover, as nanotechnology and fabrication processes continue to advance, highly efficient iontronics could be enabled by creation of asymmetry from nano-confined unipolar ion transport through various nanohierarchical structures of materials. The introduction of bionic design and nanostructures has made it possible for ions to demonstrate numerous anomalous behaviours and entirely new mechanisms, which are governed by complex interfacial interactions. In this review, we discuss the origins, development, mechanism, and applications of bionic iontronics and analyze the unique benefits as well as the practicality of iontronics from a variety of perspectives. Iontronics, as an emerging field of research with innumerable challenges and opportunities for exploring the theory and applications of ions as transport carriers, promises to provide new insights in many subjects covering energy and sensing, etc., and establishes a new paradigm in investigating the ionic-electric signal transduction interface for futuristic iontronic logic circuit and neuromorphic computing.

KEYWORDS

iontronics, electronics, nano-confined ion transport, nanofluidic, asymmetry

1 Introduction

Over the past few decades, the rapid advances in electronics have had a profound impact on people's lives [1]. However, even today the most sophisticated electronics could hardly do bionic brain operation, let alone the human brain, which only consumes 12 W of energy [2]. The urgent need for producing higher-performing and more energy-efficient electronics has promoted the search for new materials or architectures for electronic systems, and size reduction to nanoscale has become an important strategy to achieve this goal [3]. Nowadays, nanoelectronics based on semiconductor physics has become an essential component of electronics, playing a crucial role in fields such as energy and information technology [4]. However, due to the limitations of quantum mechanics laws and the current state of manufacturing technology, it becomes harder and harder to improve existing silicon-based electronic devices [5]. Meanwhile, nanoelectronics is gradually extended from pure computing or memory storage to include artificial intelligence and human–machine interfaces [4]. Even if nanoelectronics makes breakthroughs in manufacturing technology, synthesizing new materials with new structures, it will be difficult to achieve advanced information processing functions in an energy efficient way, such as highly efficient pattern recognition, intelligent reasoning, embedded sensing and computing, and brain–machine interfaces. This is mainly due to the fundamental differences in working principles between nanoelectronic systems and biological systems. The carriers of information transfer in nanoelectronics are electrons and holes, and the structure as well as the system's properties are invariant over time. In comparison, information is transmitted by a variety of molecules and ions in biological systems, and biological processors have extremely dynamic structures and functions in a non-linear fashion [4]. For example, the formation and maintenance of synapses in neural networks are sensitive to constant bidirectional communication between pre- and postsynaptic neurons, but the wire connections and resistance between solid-state logic gates in electronics remain constant after circuit formation [6]. With the development of iontronics, the existing electronic systems built primarily on silicon semiconductors may undergo a dramatic transformation: As the chip size reduces from 14 to 2 nm, contemporary semiconductor-dominated electronics that follows Moore's law is approaching the limitations of processing capability. Iontronics opens a new scenario to offer possibility of building highly-efficient brain-like neuro-iontronics in areas such as in-sensor computing devices and human–computer interfaces, etc. (Fig. 1) [7, 8].

The concept of iontronics could be traced back to Luigi Galvani's attempts to link electrical current with muscular contraction in the 18th century, which gave rise to the subject of electrochemistry [9]. Later, iontronics was introduced as a fusion of "ion" and "electronics" when scientists investigated the conjugated polymers, which were awarded the 2000 Nobel Prize in Chemistry as synthetic metals [10, 11]. Doping conjugated polymers with ions can considerably increase their electric

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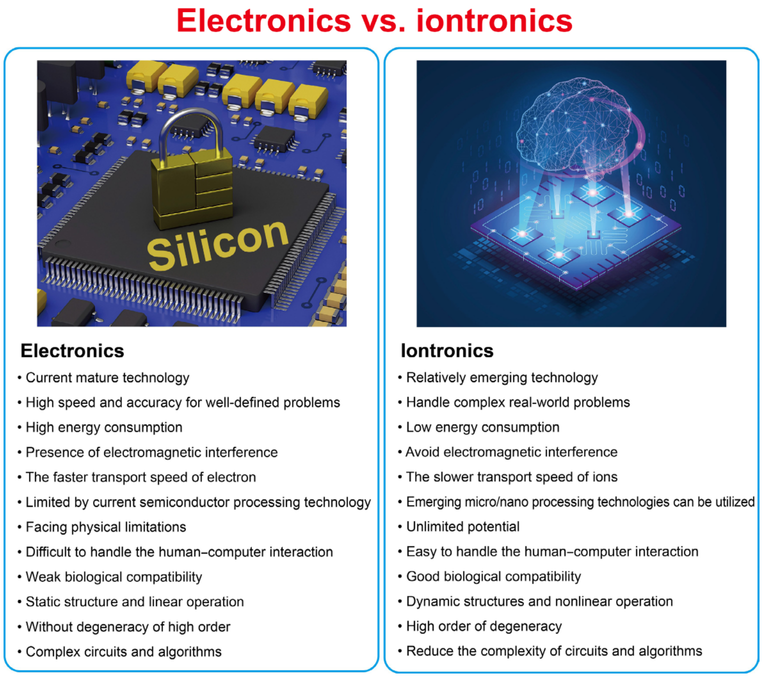

Electronics	Iontronics
• Current mature technology	• Relatively emerging technology
• High speed and accuracy for well-defined problems	• Handle complex real-world problems
• High energy consumption	• Low energy consumption
• Presence of electromagnetic interference	• Avoid electromagnetic interference
• The faster transport speed of electron	• The slower transport speed of ions
• Limited by current semiconductor processing technology	• Emerging micro/nano processing technologies can be utilized
• Facing physical limitations	• Unlimited potential
• Difficult to handle the human–computer interaction	• Easy to handle the human–computer interaction
• Weak biological compatibility	• Good biological compatibility
• Static structure and linear operation	• Dynamic structures and nonlinear operation
• Without degeneracy of high order	• High order of degeneracy
• Complex circuits and algorithms	• Reduce the complexity of circuits and algorithms

Figure 1 The comparison between electronics and iontronics.

conductivity, making them an appropriate ionic-electric signal transduction medium [10, 12]. Iontronics was further referred to organic semiconductor devices with conjugated polymers such as, organic light-emitting devices, field-effect transistors (FETs), sensors, and actuators (Fig. 2(a)) [11]. As research progressed, iontronics was no longer limited to the study of organic electronics but gradually began to draw inspiration from nature and expanded to a broader field of study. Materials were also no longer limited to the conjugated polymers or ionic conducting elastomers. Instead broader choice of materials with bionic nanostructures, for example, nanofluidic structures were introduced into iontronics, forming the bionic iontronics [11, 13]. Many information transfer and energy conversion processes in living organisms are based on iontronics, which is a prevalent phenomenon in nature [14]. Our human body itself is iontronics *per se*, through the regulation of ions to achieve various life activities [15–17]. Nature's ultimate selection of ions to sustain all biological life activities during biological evolution is inextricably linked to the processes of energy conversion and information transfer in living organisms and serves as the basis for low-energy consumption and efficient bionic iontronics [18]. In addition, ions with the same unit charge are at least 1000 times heavier than their electron counterparts. Unlike electrons, the ionic charge carrier is well protected from electrical or magnetic noises. Moreover, the electron is singular as a carrier; in contrast, ions have different valences, sizes, polarizabilities, and other properties that can be utilized to create more efficient and diversified iontronics [14]. In general, iontronics combines ionic and electronic charge transfer and signal exchange at the interfaces of ionic and electronic conductors, differentiating it from electronics that employ electrons and holes as primary carriers [13]. Iontronics is based on the control of ions by ion regulation components and creates a bridge between conventional electronics and biological systems [19].

The creation of asymmetric factors in nanoscale has recently become a fundamental means to achieve efficient iontronics [14, 20–24], for example, osmotic power devices [25–30], ionic gates [31–33], ionic diodes [34–36], ionic sieves [37–40], supercapacitors [21, 41, 42], as well as transistors and artificial synapses [43–46], etc. as Fig. 2(b) shows. Bionic iontronics could also establish complementary ionic circuits and energy harvesting capability as integrated systems (Fig. 2(c)) like biological systems for more complicated and advanced functions [47–49]. It is noted that effective iontronics could be generated at the nanoscale or sub-nanoscale because ions exhibit anomalous ion transport behaviour in charged nanofluidic channels different from that observed in bulk systems [20, 50, 51]. For instance, when a material with a surface charge is placed in an electrolyte solution, ions opposite to the surface charge (counter-ions) of the material are electrostatically attracted, while ions of the same charge (co-ions) are repelled from the surface [52]. The thermal energy and Boltzmann distribution will create a graded electrical double layer (EDL), which consists of two parts, Stern layer and the diffusion layer (Fig. 2(d)). An exponential decay potential between the surface and any location in the electrolyte solution typically serves to simplify the EDL. The characteristic length of the EDL is referred to as the Debye screening length (λ). When the size of the nanochannel is similar to the Debye screening length, the kinetic path of ion diffusion in confined space changes significantly, and the selective and high-speed transport of ions can be observed [53, 54]. These anomalies provide a theoretical foundation for the design and development of bionic iontronics. Formation of the EDL is recently proven by electron transfer and ion transfer in the liquid–solid contact electrification (CE) [55, 56]. This brings the study of the electron–ion transducer layer into the nanoscale, same aperture size in the biological systems. Bionic iontronics is not an isolated field, and it develops as an interdisciplinary subject with nanoelectronics [57], nanoionics [14], and bionics [58]. It is a tool for signal processing that combines electronic characteristics and ionic conductivity to enable advanced information processing and transfer (such as pattern recognition, intelligent reasoning, neural devices, and human–computer interfaces) for daily life or clinical medicine with excellent biocompatibility and biodegradability [4, 8, 16, 59–61].

In this paper, efficient bionic iontronics based on creation of asymmetric factors by ion gradient in nano-confined structures, different nanohierarchical structures, and external signals (e.g., light, heat, electricity, pressure, etc.) were reviewed. The iontronic biological systems, the development of iontronics, and perspectives were thoroughly discussed.

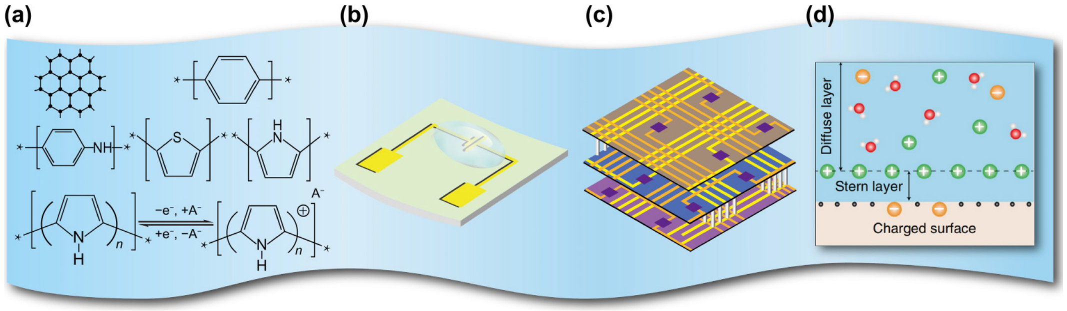

Figure 2 The concept of iontronics. (a) Illustration of representative conjugated polymers. (b) The representative iontronics. (c) Schematic illustration of ionic circuits and intrgrated systems. (d) Schematic diagram of the EDL. Reproduced with permission from Ref. [55], © Lin, S. et al. 2020.

2 Biological systems: Iontronics in nature

Most creatures are made up of cells, which are the basic units that constitute living organisms and the fundamental units that support life processes [62]. As an important part of the cell, organelles achieve precise control of various complex functions through the precise control of biomolecules (such as ions, proteins, nucleic acids, and phospholipids) at nanoscale. Among them, ions, as an important mediator of information transfer and processing, play a critical role in exocytosis, fertilization, muscle contraction, pH balance, nerve conduction, cell volume regulation, and modulating adenosine triphosphate (ATP) hydrolysis and synthesis [63–67], etc. For instance, the electric eel is a neotropical freshwater fish that can use its electric organ to generate potential differences up to 600 V and peak currents of about 1 A to stun and incapacitate its prey or natural predators. The electric organ of the electric eel consists of many electrocytes, which can achieve a small action potential of about 150 mV per electrocyte upon stimulation through the periodic closing and opening of Na$^+$ and K$^+$ channels in the cell membranes (Fig. 3(a)). By connecting thousands of electric cells in series and parallel, eighty percent of the rear area of the electric eel is covered with electrocytes, resulting in both high voltage and high current output [25, 26]. Moreover, during nerve impulse conduction, the transmission of information between neurons is achieved through the structure of the synapse. At chemical synapses, the action potential will open voltage-gated Ca^{2+} channels, and a large influx of Ca^{2+} ions will trigger the rapid emptying of neurotransmitters contained synaptic vesicles into the synaptic cleft, enabling the transmission of information between neurons (Fig. 3(b)) [68]. Another example is the stomach as an important digestive organ, in which gastric juice plays an essential role in food digestion and preventing the invasion of pathogens. The pH of gastric juice will decrease to 1 with food intake, and this highly acidic environment is attributed to the gastric H$^+$/K$^+$-ATPase (Fig. 3(c)). H$^+$/K$^+$-ATPase transports H$^+$ with a roughly 10^6-fold H$^+$ gradient from the parietal cell's neutral cytoplasm (pH 7) to the stomach's acidic environment (pH 1) [69]. To provide energy, ATP needs to be synthesized by chemoismotic coupling in organisms, where the ion pump in the mitochondria would capture the electron energy generated by the decomposition of nicotinamide adenine dinucleotide (NADH) and pump the protons into the intermembrane space. As depicted in Fig. 3(d), the conversion of adenosine diphosphate (ADP) to ATP is connected by the effective return flow of protons across the membrane, driven by the proton motive force, to create the proton translocating redox chain. The processes driven by proton gradients in chemiosmotic coupling are the primary source of energy for living organisms [70–73].

All of these aforementioned information transfer and energy conversion processes rely on precise ion transport through protein nanopores. Ion transport proteins are broadly classified into two types based on their ability to transport ions thermodynamically uphill against the electrochemical potential gradient: passive conduits known as ion channels, through which ions flow along concentration and potential gradients, and ion pumps, which can

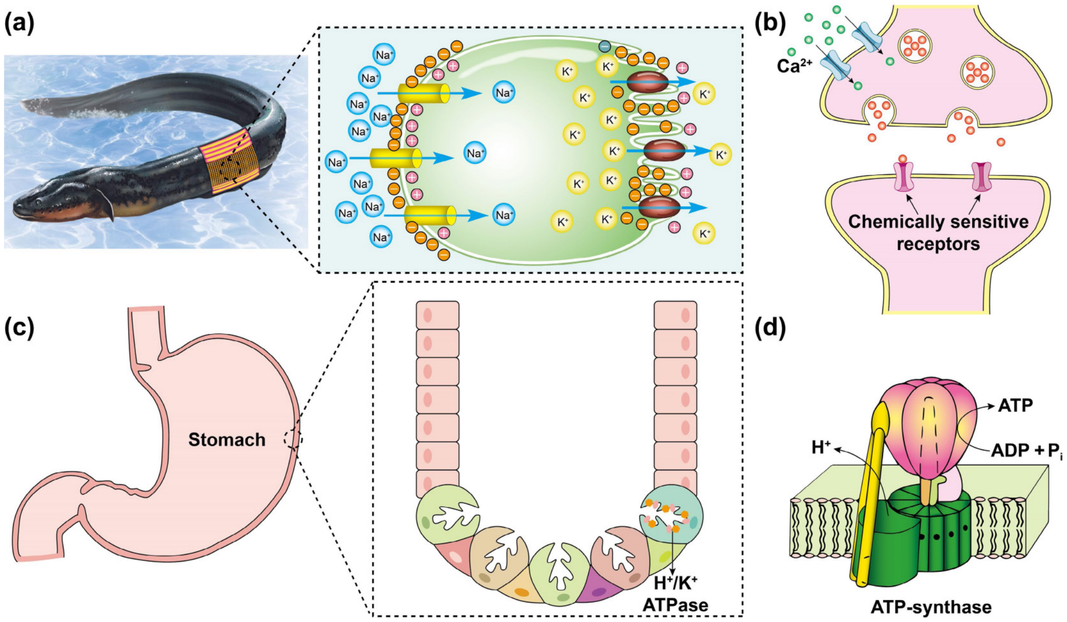

Figure 3 Typical examples of biological iontronics. (a) Illustration of structures of the electric eel's electrocytes. Reproduced with permission from Ref. [25], © Yang, L. et al. 2021. (b) Schematic diagram of the structure of a chemical synapse. (c) Schematic of structures of the stomach and gastric H$^+$/K$^+$-ATPase. (d) Schematic illustration of the chemiosmotic coupling process to produce ATP.

actively push ions against concentration gradients by releasing energy from ATP or other sources [63]. Both ion pumps and ion channels have one thing in common: Ions can be transported selectively, which is thought to be the fundamental function of ion transport proteins [74]. Energy for ion pumps could be supplied by ATP hydrolysis, redox processes, or external energy such as light [63]. Typically, ion pumps establish an ion gradient by consuming energy, which is then used by ion channels as a source of energy for various life activities, such as pumping nutrients into cells, generating electrical signals, regulating cell volume, etc. [74]. Ions themselves also carry information and have specific functions in biological systems. For instance, the signals of Ca^{2+} have crucial roles in activating neurotransmitter release, triggering alterations in neuronal function, and the efficient relaxation of cardiac muscle cells [75, 76]. The Na^+ and K^+ not only affect blood pressure, blood volume, and osmotic equilibrium but also enable the spread of excitation by controlling the rate and duration of the action potential [77, 78]. Membrane potentials are frequently stabilized by ionic currents of Cl^- ion flow in places like skeletal muscle fibers and inhibitory synapses [63].

3 Iontronics

Inspired by the above biological systems in nature, numerous iontronics enabled by nanotechnologies and nanomaterials have received extensive attention recently [8, 79]. In contrast to ion diffusion in bulk systems, ion transport in nano-confined space exhibits a variety of peculiar characteristics [23, 53, 80]. The aforementioned ion transport is frequently affected by pore size, size distribution, pore connectivity, ion gradient, and charging dynamics. Among them, the pore size exerts the greatest influence on ion transport due to its effect on the type of interactions [14]. Therefore, the function of ionotronics could be determined by different enhanced ion transport kinetics in different nano-confined pore sizes either in range of 2–100 nm or in smaller pores (< 2 nm).

3.1 Mechanisms of ion transport in different confined systems

Ion interactions in liquid systems mainly include van der Waals (vdW) force, electrostatic force, hydrogen bonding, etc., and they behave differently at different scales of the confined system (Fig. 4) [14]. In the first confined system with diameters larger than 100 nm, the ions demonstrate bulk free diffusion behaviour as in the conventional electrolyte systems. The kinetics of ion transport and migration follow the general physiochemical rules, i.e., solvated cations and anions simultaneously move along opposite directions to generate ionic current under electric filed. In the second confined system with a diameter between 2 and 100 nm, electrostatic forces will predominate, and the transport of ions is mainly regulated by the EDL. In the third confined system with diameters less than 2 nm, the hydration and weak interaction forces (like hydrogen bonding and vdW force) will play an increasingly important role in the regulation of ions, and the effects of steric interactions and hydration on ions and fluid flow should be analyzed by stochastic dynamics and/or molecular dynamics (MD), which give rise to a range of anomalous ionic behaviours such as EDL overlapping, ionic coulomb blockade, finite size of ions and resolvation, superionic states, drastic changes in diffusion coefficients, ion–ion correlation, ultra-dense packing of ions, and electroneutrality breakdown, etc. [37, 81–85]. Meanwhile, the classical mechanical and thermodynamic equations, such as the Navier–Stokes equation, Kelvin equation, and Hertz–Knudsen equation, are challenged in the small pore size (< 2 nm) system [24]. If such small pore size system itself is charged, in channels narrower than the Debye length of the electrolyte, the surface charges on the inner walls repel ions of the same charge and attract counter ions, making them the dominant charge carriers [50].

3.2 Ionic gates

Inspired by asymmetric ion channels embedded in cell membranes, a number of ion gating devices that operate as gates in nanofluidic systems and respond to certain stimuli or signals upon reception have been developed [86]. For instance, Liu et al. reported an ionic gate system that could be activated by Na^+ and K^+ to regulate ion conduction in nanochannels. By immobilizing 4′-aminobenzo-15-crown-5 and 4′-aminobenzo-18-crown-6 onto conical nanochannels, respectively, Na^+ activated ionic gates and K^+ activated ionic gates were developed. The Na^+ activated ionic gate might open and close to regulate the behaviour of ion conduction in the nanochannel (Fig. 5(a)). The K^+ activated ionic gate can be employed to selectively conduct cations and anions through the nanochannel [77]. Meanwhile, Jiang et al. designed a cigar-shaped double-gated ion gating with pH-drive. Two pH-responsive molecules, acid-responsive polyvinyl pyridine (PVP) and base-responsive polyacrylic acid (PAA), were immobilized on both sides of the channel, respectively. When the pH reached the predetermined level, the PVP gate and the PAA gate would alternately open and close, successfully simulating the transport

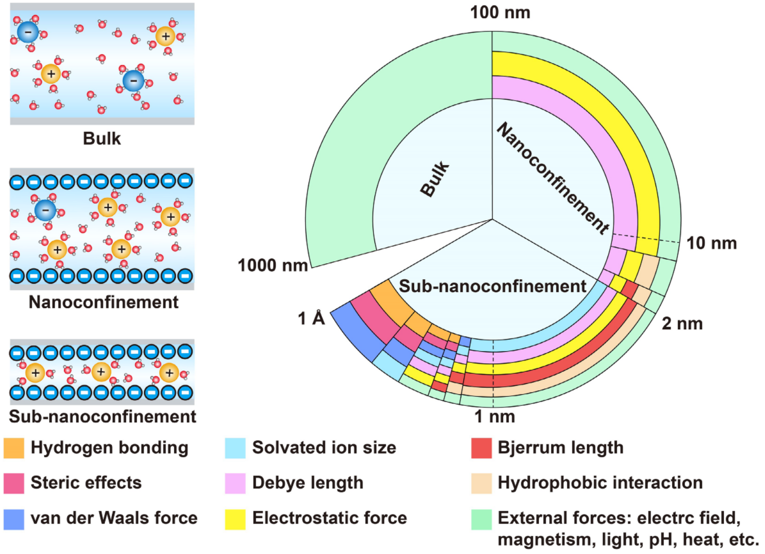

Figure 4 Ion interactions in different confined systems.

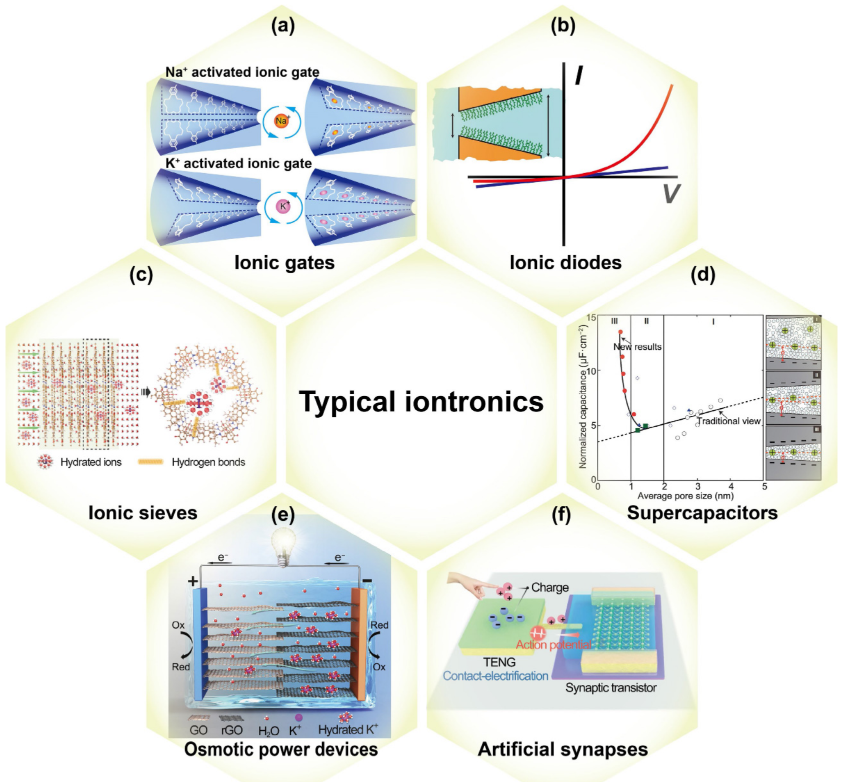

Figure 5 Typical iontronics. (a) Schematic demonstration of the simplified Na^+ activated ionic gate and K^+ activated ionic gate. Reproduced with permission from Ref. [77], © American Chemical Society 2015. (b) *I–V* curve and the illustration to indicate the configuration of conical nanopores for ionic rectification (red: high surface charge density; blue: low surface charge density). Reproduced with permission from Ref. [143], © The Royal Society of Chemistry 2017. (c) The MD simulation model of metal ions transport through COF nanochannels. Reproduced with permission from Ref. [38], © Wiley-VCH GmbH 2021. (d) The normalized capacitance of supercapacitor decreased with decreasing pore size until a critical value was reached, unlike the traditional view which assumed that capacitance continually decreased. Reproduced with permission from Ref. [21], © American Association for the Advancement of Science 2006. (e) Schematic of structures of the moisture-enabled power source. Reproduced with permission from Ref. [25], © Yang, L. et al. 2021. (f) Schematic illustration of the CE-EDL-activated artificial afferent. Reproduced with permission from Ref. [132], © Yu, J. et al. 2021.

characteristics of a biological ion pump [87]. In addition, numerous other stimuli or signals, such as light [88, 89], pH [31, 86], electric [78, 88, 90], magnetism [32], thermal [91], specific molecules or ions [33, 92, 93] could also activate the ionic gate.

For ionic gates driven by different energy sources, asymmetric structure-driven ionic gates have the lowest ion transport efficiency, which can only drive ion transport against a small electrochemical potential gradient and require the help of an oscillating electric field to achieve continuous ion transport. Both pH-driven ionic gates and light-driven ionic gates are more energy efficient and easy to implement, but pH-driven ionic gates are often difficult to control precisely, so light-driven ionic gates are more feasible. Electric field-driven ionic gates have the longest operating times, but the process of ion reverse transmission requires a lot of energy, making it unsustainable. Therefore, the first challenge is to develop ionic gates that are energy-efficient and can operate continuously. The solution may lie in developing novel materials and cleverly designing multiple stimuli. Regardless of the external stimuli or signals, the driving force should ultimately be the electrical field [94]. Meanwhile, in contrast to biological ion pumps, which are capable of transporting thousands of ions per second, artificial ionic gates are still in their infancy. One option for enhancing the performance of ionic gates is to design a stronger electric potential within the channel in order to reduce the energy barrier caused by the chemical potential. In addition, there are many challenges that need to be addressed in future research, such as improving the performance of ionic gates based on nanostructures to that of biological ion pumps, developing related large-scale processing and fabrication technology, and selection of suitable ionic gate materials for system integration, etc.

3.3 Ionic diodes

Ion current rectification is the phenomenon that occurs in asymmetric nanofluidic devices where unipolar ions can be efficiently transported in one direction [36]. Typically, it is influenced by the surface charge of the channel, concentration gradient, and asymmetric geometry. The rectification property is expressed as the rectification ratio, which is the ratio of the forward bias current to the reverse bias current (Fig. 5(b)) like in semiconductors [22]. Ion rectification is widely used in living organisms to control ions for applications such as mass transfer, signal transmission, and energy conversion, and it also provides inspiration and ideas for artificial ion rectification systems [95]. Siwy et al. reported an artificial ion pump driven by an asymmetric structure, which formed asymmetric conical structured nanochannels with large openings of approximately 500 nm and small cone tips of approximately 2 nm on a single polymer by high-energy heavy ion bombardment and chemical etching. This ion pump could exhibit cation selectivity (preferential flow of K^+ from the narrow to the wide opening) due to the negative charges distributed on the walls of the channels [96]. Meanwhile, Zhang et al. also constructed a non-homogeneous membrane with an asymmetric conical structure for ion rectification, demonstrating an engineered heterogeneous membrane with chemical, geometric, and electrostatic heterogeneous structures. By combining a porous block copolymer (BCP) membrane with an etched asymmetric porous polyethylene terephthalate (PET) membrane, this membrane enabled the anion-selective heterogeneous membrane to show an ultra-high ion rectification ratio of 1075 with improved overall anion selectivity [95]. In addition to asymmetric structures, the introduction of asymmetric surface properties (surface charge density, wettability) can also enable ion rectification [35, 86, 97]. Inspired by the responsive ion transport and asymmetric structure of biological ion channels, Zhai and colleagues introduced conjugated polymers into porous nanochannels and successfully constructed artificial nanochannels with synergistic effects of pH modulation and light modulation. Over a wide range of pH values, the surface charge distribution of the channel is asymmetric, providing conditions for ion rectification. Furthermore, asymmetry could also be introduced by light, which creates a photo-responsive ionic current through the nanochannel to construct both pH and light-sensitive ionic rectification systems [97].

However, the mechanism of ion rectification remains controversial, and there are currently two popular mechanisms. The "ratchet" mechanism relies on electrokinetic trapping of mobile ions in an asymmetric nanochannel. The model attributes the state of poor conductivity to a potential well near the tip of the conical pore, which traps ions and inhibits current flow. The presence of the potential well is confirmed by numerical simulations inside the nanopore. The other mechanism proposes that ion rectification is caused by the disparity in transference numbers of counterions surrounding the nanopore tip. The theory has also been verified by a numerical analysis of the Poisson–Nernst–Planck equations and calculations based on a narrow pore membrane model. Therefore, the mechanism of ion rectification needs further exploration.

3.4 Ionic sieves

The presence of sub-nanometer scale protein channels creates a particular polarity environment for ion electrostatic and hydrogen bonding interactions, enabling biological membranes to exhibit efficient ion transport properties [98]. Inspired by this phenomenon, a series of artificial membranes with precisely sized sub-nanochannels for ion sieving have been developed [37–39]. The artificial membranes for ion sieving have sub-nanopores or two-dimensional (2D) lamellar structures with sub-nanometer layer spacing, which can be adjusted to achieve sieving of ions of different sizes by adjusting the pore size or layer spacing. The effects of coordination, cation–π interaction, electrostatic force, and hydrogen bonding make the target ions pass through the membrane with a lower energy barrier, further improving the selectivity and permeability of ions. Sheng et al. designed and synthesized covalent organic framework (COF) membranes with a channel size of 1.4 nm and an abundance of hydrogen bonding sites. Due to the fact that divalent cations have a higher energy barrier than monovalent cations when passing through the COF channel, the monovalent cation permeation rate is maintained with ion selectivity for monovalent cation/divalent cations significantly enhanced (Fig. 5(c)) [38]. Wen et al. utilized GeV heavy ion irradiation and ultraviolet (UV) radiation to prepare negatively charged polymer sub-nanopores measuring 12 μm in length and 0.3 nm in diameter. Transport rates were on the order of $Li^+ > Na^+ > K^+ > Cs^+ > Mg^{2+} > Ca^{2+} > Ba^{2+}$, with heavy metal ions such as Cd^{2+} and anions blocked. As confirmed by MD simulations, the selective transport of this sub-nanopore could be attributed to the size sieving of partially dehydrated ions [39]. Nanoporous graphene oxide (GO) membranes could also sieve metal ions through coordination, cation–π interactions, and electrostatic forces [37, 38]. Chen et al. made use of cation–π interactions between hydrated cations and aromatic rings to achieve 1 Å precision control of the interlayer spacing of GO membranes by different cations, enabling accurate ion sieving. The ultraviolet absorption spectroscopy and first-principles calculations indicate that the most stable cation adsorption occurs where oxide groups and aromatic rings coexist [37]. Meanwhile, Abraham et al. also achieved the preparation of GO membranes with layer spacing from 9.8 to 6.4 Å by physical confinement, exhibiting accurate and tunable ion sieving properties. In the regime that the layer spacing is smaller than the diameter of hydrated ions, the permeation rates decrease exponentially with decreasing sieve size but water transport is weakly affected. The exponential suppression of ion permeation combined with fast water transport makes such GO membranes interesting candidate for water filtration [99].

An energy barrier exists for the transport of ions in sub-nanopores, and it can be adjusted by creating asymmetric elements and introducing external stimuli [100, 101]. Meanwhile, when ions are hydrated by the shell layer of dipolar water molecules, the mobile entity is the ion with the hydrated shell layer rather than the bare ion [40]. The energy barrier at the pore entrance is dependent on the hydration radius or hydration energy, when the hydration radius is larger than the effective pore radius, the transport of ions is greatly hindered, and ions must be deformed or dehydrated prior to entering the pore [39]. The free energy of the ions in the channel is compensated by the electrostatic interaction of the dehydrated ions with the specific configuration of charges on the inner surface of the pore [102]. Despite many theoretical and modeling studies on the transport behaviour of ions in sub-nanopores, the origin of some of the anomalous phenomena remains unclear, and the role of EDL in sub-nanopores still needs further exploration [42].

3.5 Supercapacitors

It has been demonstrated that a decrease in the average pore size of carbonaceous materials can increase the capacitance of the electrical double-layer capacitors, particularly when the pore size is commensurate with that of the bare ions of the electrolyte [21, 103]. Gogotsi and colleagues discovered that when sub-nanometer pores are smaller than ion size, they can still absorb electrolyte ions and even achieve a higher capacitance. They explained this anomaly as a distortion of the solvation shell layer of ions in the sub-nanometer pores, which brings the ions closer to the pore surface (Fig. 5(d)) [21]. Later, several studies also demonstrated that the desolvation of ions also contributes to the increase in capacitance in sub-nanopores [104–106]. Moreover, Kornyshev et al. have attempted to explain this phenomenon by the "superionic state" in metallic nanopores, where image forces exponentially screen the interactions of ions within pores [107]. Meanwhile, the phenomenon of the partial break of the Coulombic ordering of ionic liquids in carbon nanopores, as reported by Kaneko and colleagues, provided direct evidence for the theory of superelectronic states [108]. In addition, Jiang et al. investigated the size dependence of capacitance of ionic liquids in pores by the density functional theory, revealing that oscillation of capacitance is a function of pore size, similar to the interaction potential between two charged surfaces. The oscillatory behaviour is due to interference from overlapping EDLs, with peak capacitance occurring when there is maximum constructive interference from EDLs at the two walls [109].

The phenomenon that the reduction of the average pore size of carbonaceous materials can increase the capacitance of double-layer electric capacitors has not reached a uniform conclusion. In this regard, monitoring the dynamics of nano-confined ions in supercapacitors is required to better understand the mechanism. It is especially necessary to map the temporal and spatial distribution of ions during dynamic ion transport, preferably *in situ* and with high spatial resolution. However, conventional characterization techniques are often limited to achieve these goals. It may be necessary to have recourse to some *in situ* characterizations including *in situ* infrared spectroscopy in electrochemistry, *in situ* nuclear magnetic resonance (NMR), *in situ* electrochemical quartz crystal microbalance (QCM), *in situ* X-ray transmission measurements, etc.

3.6 Osmotic power devices

There are numerous applications for ionic gradients in nature, such as the electric eel that was previously discussed [25]. In this regard, pressure-retarded osmosis (PRO) and reverse electrodialysis (RED) systems have been developed to harvest osmotic energy in seawater and river water, providing a theoretical basis for future large-scale applications [110]. However, there are still many problems with the membrane materials in terms of contamination resistance, output power density, mechanical stability, ion selectivity, etc., so it is particularly important to develop new materials for the efficient use of osmotic energy [59, 110, 111]. Recently it is found that many 2D nanofluidic materials with bionic nanoscaled-ion channels can exhibit excellent ion selectivity and enhanced ion diffusion kinetics, such as GO [25, 112–117], MXene [118, 119], molybdenum disulfide (MoS_2) [120, 121], boron nitride [28, 122], framework materials (metal-organic frameworks (MOFs), COFs, zeolitic imidazolate frameworks (ZIFs)) [27], etc. These 2D nanofluidic materials have been extensively studied and applied due to their abundant functional groups, ease of fabrication, high chemical modification rates, and more efficient structures than conventional ion-exchange membranes, which have the potential to drive the practicability of the osmotic power source [117].

One typical example of 2D nanofluidic materials is GO. When used in osmotic power sources, it can form 2D nanofluidic channels when restacked, enhancing the unipolar transport behaviour of ions in it [117]. It presents a negative charge due to its surface having functional groups such as hydroxyl, carboxyl, etc., which reduces the activation energy of ion dehydration and achieves cation selectivity within the Debye length [117, 123]. Kim et al. constructed GO films with channels similar in size to biological channels using confined van der Waals crystals, reducing the dehydration energy barrier of cations and achieving unipolar ion transport with ion selectivity of 95.8%, energy conversion efficiency of 41.4%, power density of 5.26 $W\cdot m^{-2}$, and a good structure with operation stability of over 150 h [114]. Inspired by the electric eels, Wei et al. successfully developed a printable solid-state osmosis energy power source based on GO ink (Fig. 5(e)). With the high K^+ ion gradient, a single cell can achieve an open-circuit voltage of 1.2 V. By optimizing the printing parameters, an ultra-high voltage of 192 V was achieved by connecting 175 cells in series on a small strip of paper. By introducing the concept of mathematical fractal design to increase the effective length of GO ink, the planar cell can achieve a power density of 2.5 $mW\cdot cm^{-3}$ and an energy density of 0.41 $mWh\cdot cm^{-3}$, which is comparable to lithium thin-film batteries. This new design strategy provides a safe, reliable, and cost-effective green pathway for future wearable electronic devices [25]. It should be noted that the power of most current osmotic power sources is typically very low (ranging from 10 $\mu W\cdot cm^{-3}$ to 4 $mW\cdot cm^{-3}$) and is constrained by temperature and humidity. In order to solve these challenges, Wei et al. also reported an ultrathin and printable osmotic power source based on fine-tuned interfacial electrochemical reactions driven by the ion gradient of K^+. Such an osmotic power source exhibited a power density of 28 $mW\cdot cm^{-3}$ and a volumetric specific energy density of 6 $mWh\cdot cm^{-3}$ with a total thickness of only 10 μm. Benefiting from the antifreeze and self-healing room temperature ionic liquid (RTIL) ionogels, the power source could also operate at −40 °C, taking it one step further to practical applications [117].

In addition to GO, $Ti_3C_2T_x$ MXene has also been used for osmotic power sources. It is similar to GO, which also has numerous oxygen-containing functional groups on its surface, providing tunable surface chemistry that allows the material to be negatively charged in aqueous solutions, greatly facilitating the confined transport of water and ions [118, 119]. Zhang et al. developed an MXene/aramid nanofiber (ANF) nanofiber composite membrane for a nanofluid osmotic power source. The ANF acts as an intercalating and interlocking agent between MXene nanosheets, and the synergistic effect between the space charge brought by it and the surface charge of MXene is the key to achieving high power density. By mixing river water and seawater, the osmotic power source can reach a power density of 4.1 Wm^{-2}. This MXene-based composite membrane also has excellent mechanical strength and stability [118]. Moreover, Ding et al. designed and synthesized a bioinspired heterogeneous MXene membrane (BHMXM) consisting of a negatively charged MXene (NCM) layer and a positively charged MXene (PCM) layer, achieving the selective transport of ions. The power density of this MXene-based osmotic power source was 8.6 Wm^{-2} under the salinity gradient of synthetic seawater and river water and up to 17.8 Wm^{-2} at a 500-fold salinity gradient [119]. Other 2D nanomaterial, such as MoS_2, also exhibits a superior water transport characteristic as a promising 2D nanofluidic material for osmotic power generation [120, 121]. Feng et al. created an osmotic ion flux within the nanopore of the 0.65 nm-thick monolayer MoS_2 membrane. If the monolayer MoS_2 membrane with a uniform pore size of 10 nm and 30% porosity is created, it is anticipated that the power density could achieve 10^6 Wm^{-2} [120]. In addition, Graf et al. used a similar monolayer MoS_2 nanopore membrane with light modulation. The introduction of light can change the MoS_2 membrane surface charge and effectively improve the ion selectivity and surface conductivity of MoS_2 nanopores. Such device can double the osmotic power generated by a single nanopore at neutral pH by increasing the surface charge of MoS_2 membrane with light [124].

In general, effective conversion of gradient energy (ions) to electrical energy (electrons) is achieved by artificial nano/sub-nano channels or 2D nanofluidic materials with dimensions smaller than the Debye screening length of the electrolyte. In contrast to 1D nanotubes and biological channels, the 2D nanofluidic channels provide capillaries with little chemical interaction with ions that function purely as geometric confinement. In general, cations and anions diffuse at different rates, creating the ion diode effect [125]. The ionic diode effect of the heterogeneous membrane enhances unidirectional ion diffusion, thereby significantly boosting the interfacial transport efficiency. The osmotic energy could derive from the asymmetric charge gradient, particularly the surface charge of the nanochannel, which is crucial for the ion selectivity in osmotic energy harvesting [28, 126]. The surface charge carried by the pores on the membrane prevents the entry of ions with the same charge and permits the passage of ions with the opposite charge, achieving cation selectivity or anion selectivity under the combined effect of surface charge and pore size. Moreover, the counterions are concentrated within the channels to balance the surface charge, increasing the ionic conductivity, so in such unipolar ionic transport, the ionic conductivity can be considerably improved [127]. In addition to selectivity, membrane permeability is also important, as it has a direct impact on the output power density of the device. However, there is a competitive relationship between membrane selectivity and permeability, so the trade-off between selectivity and permeability is a tricky challenge for osmotic membranes today, for which a popular solution is to develop ultrathin films with a thickness of less than 1 μm [59]. The osmotic power source, as a typical example of iontronics, is present in the majority of biological organisms and has superior biocompatibility, safety, and mechanical flexibility compared to conventional lithium-ion batteries, which could be used in the future for wearable or implantable neuronal computer interface devices [26, 128].

3.7 Transistors and artificial synapses

Transistors play an essential role in microelectronics [129, 130]. Iontronic transistors operate via ion penetration or ion accumulation induced by double layer capacitance [45, 79]. Gao et al. discovered that current electrolyte-gated FETs efficiently control charge carriers in semiconductor channels by forming an EDL that induces a large local electric field. In order to further enhance the performance of FETs and realize their diverse applications, they reported a triboiontronic transistor with MoS_2 that enables carrier control by triboiontronic potential without external gate voltage. This triboiontronic transistor could achieve an on/off ratio over 10^7 and an ultralow cutoff current below 0.1 pA in both depletion/enhancement mode. The developed triboiontronic logic inverter also exhibited a desirable gain of 8.3 $V \cdot mm^{-1}$, with a high stability and low power consumption. This work proposes a low-power, active, and general method for modulating semiconductor devices with mechanical instructions, which has significant applications in biological interfaces [45]. Moreover, Zhang et al. proposed a dual-mode field-effect transistor with enhanced performance by means of EDL capacitive coupling, which was realized with ion gels, graphene, and silicon-based materials. Its first mode can be considered as a tribotronic transistor with capacitively coupled ion gel, and the capacitively coupled ion gel increases the on-state current by double and the on/off ratio by fourfold. In the second mode, it can also be utilized as a multiparameter distance sensor with a mechanical displacement of 0.25 mm, an increase in drain current of 600 μA, and a threshold voltage shift of 0.8 V. The diverse and versatile transistor design ideas in this work make it possible to go beyond Moore's law [129].

The human brain is the central organ in the neurological system [79] that has a very complex structure and composition, including a biological neural network with around 10^{15} synapses and 86 billion neurons, as well as low-power interactive perception and information processing capabilities [15]. Therefore, a comprehensive research of artificial bionic interacting neuromorphic devices and systems may provide an effective solution to the real-world issues of bionic iontronics [131]. Yu et al. reported low-power artificial afferents with biological afferent properties that activate ion-gel-gated MoS_2 synaptic transistors by triboelectric electrical signals, providing afferent-like capabilities for spatiotemporal recognition and transmission of external inputs (Fig. 5(f)). Its energy dissipation is lowered to 11.9 fJ per spike due to the absence of the gate voltage supply. This study indicates a direction for the investigation of low-power bionic neuromorphic devices [132]. Moreover, Yu et al. constructed a mechano-photonic artificial synapse with an optically plastic graphene/molybdenum disulfide heterostructure to modulate the photocurrent, persistent photoconductivity, and photosensitivity after the artificial synapse via triboelectric potential. With the assistance of mechanical plasticity, high precision image recognition accuracy was obtained by developing an artificial neural network [133]. Similarly, Tan et al. revealed a device-level multifunctional sensing platform based on triboelectric potential-tuned dual-gate transistors that not only provide high-sensitivity distance and pressure sensing but also function as artificial photonic synapses. The updated synaptic weights can be easily implemented for image edge detection with the aid of synergistic triboelectric potential modulation. This study is important for the development of multifunctional, high-sensitivity sensing, image analysis, and neuromorphological techniques [46].

The aforementioned iontronics with ion and electron transfer behaviour through the EDL are able to perform not only simple signal acquisition, transmission, and modulation, but also advanced functions such as sensing, image recognition, and low-power computing through the construction of artificial neural networks [15, 131]. However, the majority of current research stays at the level of individual iontronics or simple ion logic circuits, and few constructs more complicated ion logic circuits or artificial neural networks to accomplish more complex and diversified functions [134]. Moreover, urgent action is required to address compatibility issues between sensors and synaptic devices, signal decoupling for multi-sensing coupling, interference, and on-chip integration. Optimized sensors, bionic neuromorphic iontronics, and hardware integrations with compatible algorithms are essential. At the material level, there are two main research directions. One is to investigate growth conditions and modification techniques to enhance the interface quality and physical properties of materials, and the other is to explore the novel materials with the help of software simulations and machine learning. In addition, it is essential to develop iontronics interfaces with good compatibility between artificial neural networks and biological neural networks to achieve two-way diverse and complex information exchange with high spatial and temporal separation rates to achieve a real sense of human–computer interface, and it is anticipated that new human–computer interaction means and novel solutions for treatment of several mental diseases might be developed in the future [47, 79].

4 Perspectives

Due to the ubiquitous existence of iontronics in nature, bionic iontronics have become a hot topic, and it is especially interesting to observe how the ionic-electric signal transduction was implemented by creating the asymmetry in nanoscale. In biological systems, ions are the main charge carriers. The action potential across cell membranes to transfer data based on the time- and voltage-variant ionic conductivity modulation of ion channels results in the precise coordination and timing of physiological outputs. These outputs range from simple muscular contractions to complex brain processes. In conventional electronics, state switching in semiconductors is achieved by altering the population of charged electrons and holes, and their drifting and filling behaviours are invariant in space and time once the wires in circuits are coupled. In contrast to conventional electronics, iontronics could conduct electricity like nerves that govern ion flow direction and magnitude, thereby amplifying small input signals into huge output signals with capability of operating at high frequencies, biocompatible and stretchable. Inspired by the Å-size ion channels in cellular membranes, artificial channels with similar dimensions have been developed, but it is still challenging to fabricate and study them in a controlled manner. Numerous bionic iontronics, such as ionic gates, ionic diodes, ionic sieves, supercapacitors, osmotic energy devices, transistors, and artificial synapses were recently reported and reviewed in this paper. The creation of asymmetry is essential to iontronics to enhance ion and electron transduction. Such asymmetry could be a structural asymmetry, salinity gradient, asymmetric surface properties (e.g., wettability, surface charge density, molecular configuration, etc.), or asymmetry created by external signals such as light [89], pH [135], electric field [78], and magnetic field [32], etc. They may also play a synergistic role to enhance the performance of iontronics (Fig. 6) [34, 87, 95, 96]. Materials with controlled and defined nanostructures are particularly interesting to be used in iontronics, avoiding the complicated E-beam or lithographic methods. Such materials, including 1D nanotubes, 2D nanofluidic GO, MoS_2, MXene materials, etc., and 3D nanoporous ion conducting membranes, play an essential role in regulating the motion of ions. When going to the nanoscale, one of the most important scientific questions in iontronics is the mechanism of EDL formation, which functions as the essential transduction of ions and electrons. Wang et al. recently proposed a "two-step" EDL formation model [55]. Firstly, the electrons transfer between the water molecules and the atoms of solid materials on contact electrification, accompanied by ionization that produces electrons and ions. Secondly, ions will be attracted by electrostatic interactions and migrate toward the charged surface, resulting in the formation of EDL. This provides a foundation to fine-tune the ionic–electronic transfer kinetic process by choosing various types of materials with different surface structures and designs.

The charge attraction and steric effects in the nano-confined space could restrict the disordered motion of ions, thus achieving the ordered superfluidity of ions like in biological membranes [136]. Stable, precise, and controllable regulation of ions could be effectively achieved by using such anomalous behaviours in the nano-confined structure. However, a series of challenges still exist and they are also interesting directions for developing future iontronics: (1) how to effectively build highly efficient nanofluidic systems, including optimizing their length, surface charge, conductivity of unipolar ions, etc. These factors play a dominant role in controlling the transport behaviour of ions in the confined nanofluidic system and have a significant impact on the iontronic performance. The charge attraction and steric effects in the nano-confined space restrict the disordered motion of ions to form an ordered superflux within the confined pores. Therefore, designing the optimized nano-hierarchical structure to carry on ionic superflux is one of the challenges in the future. (2) The preparation methods for nanofluidic channels also need to be optimized. Currently, many methods have been proposed and applied to synthesize artificial nanofluidic channels, e.g., ion beam and electron beam sculpting can be applied to form nanopores in atomically thin materials, with a thickness comparable to lipid bilayers. Ion-track etching techniques can be used to prepare nanochannels with different geometries (e.g., conical, bullet, cigar, and funnel shapes), similar to the various shapes of biological ion channels. However, these preparation methods are complex and costly, making it difficult to achieve industrial production. Therefore, it is necessary to develop a simple, economic preparation process that enables the construction of precise nanofluidic channels for effective control of ion transport and the commercialization of iontronics. Currently, 2D nanofluidic materials possibly offer a viable route to solve this problem. They could be made in ink formula and have the advantages of controllable surface modifications through chemical functionalization. The 2D nanofluidic channels could also be effectively rebuilt/restacked by cost-effective printing/drop-casting methods. (3) More *in situ* characterization techniques need to be applied. The nano/sub-nanostructures actually have many defects or disorders (e.g., in-plane micropores, microscopic corrugation in nanosheets, and inhomogeneous layer spacing in nanosheets), which may also have some impact on the mechanism and performance of ion transport. Furthermore, the nanostructure may change over time under different stimuli, so the information obtained by commonly used characterization techniques (scanning electron microscopy, transmission electron microscopy, X-ray diffraction, etc.) may be incomplete and even inaccurate, and the use of *in situ* techniques to probe the interface, such as *in situ* electrochemical-Fourier transform infrared spectroscopy (FTIR) based on attenuated total reflectance (ATR) of IR, surface plasmon resonance (SPR), QCM, surface enhanced Raman spectroscopy (SERS), X-ray transmission, or NMR, etc. can address this issue by investigating the dynamic ion transport behaviour. (4) How to create iontronic networks or develop neuronal–computer interfaces in the future is also critical. It firstly needs precise and effective control of ion transport by constructing asymmetry factors through nano-confined structures and developing new materials. Conveying different messages through different kinds of ions needs designing effective signal transduction interface for iontronic integrated systems. (5) Last but not least, recent work reported that the storage of life information could be realized by four-dimensional modes within nano-confined spaces of ions [137]. Therefore, bionic iontronics

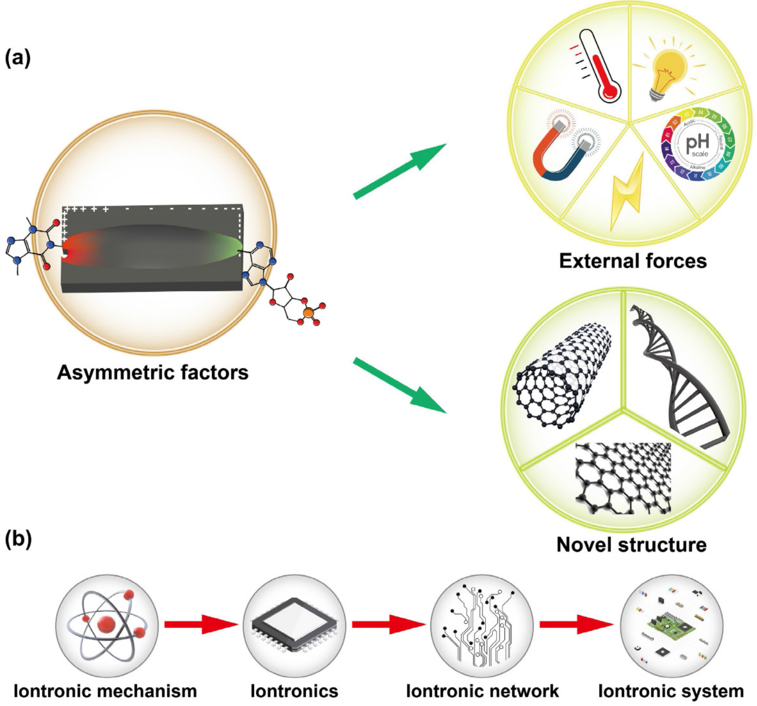

Figure 6 (a) Creation of asymmetry in iontronics. (b) Roadmap of bionic iontronics.

based on nano-confined systems, is an interdisciplinary subject, and could extend to a wider range of perspective applications.

In recent decades, the interaction between electrons and ions at the interface of bionic iontronics has been studied to understand the mechanism and develop more efficient devices. By iontronics integration, ion logic circuits with distributed parallel processing capability and good biocompatibility may be formed, building iontronic networks as shown in Fig. 6. Iontronic networks could effectively reduce the complexity of algorithms and data, enabling numerous more advanced functions such as image recognition, speech recognition, computational decision-making, and so on. This provides a paradigm for building a brain-like computer that has compatible ion-based signals with neurons, allowing higher signal processing efficiency and lower power consumption. It opens a new scenario for the creation of implantable or wearable iontronics, as well as neuronal–computer interfaces (Fig. 7). For example, Song et al. have developed an electrochemical method to activate or inhibit a nerve by electrically modulating ion concentrations *in situ* along the nerve. On the basis of the role of K^+, Na^+, and Ca^{2+} in neural processes, they used ion selective membranes to modulate the ion concentration *in situ* to change the nerve excitability locally at the site of electrical stimulation for more efficient stimulation, or along the nerve fibre for more efficient on-demand suppression of nerve signal propagation [138]. These biological-artificial hybrid iontronics move a significant step forward in neuronal–computer interfaces by translating electrical signals, through ionic or molecular signals, into neuronal responses [138–141]. Moreover, biological signals could also be understood by biological-artificial hybrid iontronics. Meanwhile, Keene et al. reported a dopamine-mediated organic neuromorphic iontronics, which can mimic the synaptic cleft as well as the dopamine recycling process. In such iontronics, dopamine exocytosed by dopaminergic cells at the presynaptic end is locally oxidized at the postsynaptic gate electrode, and the resulting change in the charge state of the gate electrode induces ion flow in the aqueous electrolyte, thus altering the conductance of the postsynaptic channel. This dopamine-mediated iontronics constitutes a fundamental building block for artificial neural networks that can be directly modulated based on biological feedback from live neurons and is a crucial step in realizing neuronal–computer interfaces [61]. In addition, Dobashi et al. designed and fabricated a piezoionic sensor composed of hydrogel to perform peripheral nerve stimulation and demonstrate the possibility of self-powered piezoionic neuromodulation. Currents are generated by tapping on the piezoionic sensor directly, eliciting hindlimb movement in rodent models. The high charge density of piezoionics is particularly attractive for use in neural interfaces, where charge injections at tens of microcoulombs per square centimeter are routinely required while maintenance of low voltages is a key safety requirement. Piezoionics could be tailored to produce a wide temporal range of transient signals and provide much higher charges at low voltages. Therefore, piezoionics, as one of iontronics, is a good match for neural interfacing applications [142].

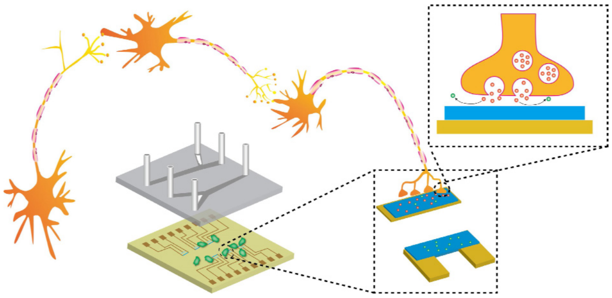

Figure 7 Iontronic neuronal–computer interfaces.

It is noted that transistors for electronics have been introduced for about seven decades, and silicon-based electronics already attained a vast array of previously inconceivable capabilities. With the emergence of iontronic transistors less than a decade, it is hard to imagine what kind of world will be created by iontronics in the next 60 years.

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