Microfabricated Ion-Selective Transistors with Fast and Super-Nernstian Response

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Transistor-based ion sensors have evolved significantly, but the best-performing ones rely on a liquid electrolyte as an internal ion reservoir between the ion-selective membrane and the channel. This liquid reservoir makes sensor miniaturization difficult and leads to devices that are bulky and have limited mechanical flexibility, which is holding back the development of high-performance wearable/implantable ion sensors. This work demonstrates microfabricated ion-selective organic electrochemical transistors (OECTs) with a transconductance of 4 mS, in which a thin polyelectrolyte film with mobile sodium ions replaces the liquid reservoir. These devices are capable of selective detection of various ions with a fast response time (≈1 s), a super-Nernstian sensitivity (85 mV dec⁻¹), and a high current sensitivity (224 µA dec⁻¹), comparing favorably to other ion sensors based on traditional and emerging materials. Furthermore, the ion-selective OECTs are stable with highly reproducible sensitivity even after 5 months. These characteristics pave the way for new applications in implantable and wearable electronics.

There is a significant need for miniaturized ion sensors for the real-time monitoring of ion concentrations in applications including fundamental research, health and performance monitoring, agriculture, and safeguarding the food supply and the environment.[1–5] In neuroscience, for example, fast implantable ion sensors could help understand the role of local changes in the extracellular environment in the emergence of seizures.[6] In molecular biology, ion-sensor arrays could potentially enable genome sequencing,[7] identification of single nucleotide polymorphism variants,[8] and real-time monitoring of nucleic acid amplification[9] by measuring hydrogen ions released during nucleotide incorporation. In agriculture, miniaturized sensors inserted in plants, where analytes from soil are purified, could monitor soil nutrient levels to achieve simultaneous improvements in fertilizer use efficiency and crop yield.[5,10,11] This need has driven the development of new sensor platforms, which has largely focused on transistor-based sensors because of inherent advantages that include facile miniaturization and signal amplification. One of the most studied transistor architectures for ion detection is the ion-sensitive field-effect transistor (ISFET), in which the analyte solution is brought in direct contact with the gate insulator.[12,13] A variety of established and emerging materials including silicon, metal oxides, and organics have been investigated in ISFETs, with organics receiving particular attention due to their simple processing, compatibility with flexible substrates, and biocompatibility.[14–16] There has also been recent interest in electrolyte-gated field-effect transistors (EGFETs) that achieve low-voltage sensor operation in aqueous environments.[17–20] In this configuration, a nanometer-thick electrical double layer (EDL) is formed at the electrolyte/channel interface and this provides a high capacitance (typically 1–10 µF cm⁻²), allowing low-voltage operation. In the case of electrolyte-gated organic field-effect transistors in aqueous environments, the devices normally operate in the water-stable operation window <1 V.[18,19,21] Organic electrochemical transistors (OECTs), in which an ion-transporting organic semiconductor is used as the channel, allow further enhancements in performance.[22] This is due to the fact that changes in doping take place not only near the interface with the analyte, but throughout the bulk of the semiconductor layer. As a result, OECTs show a large transconductance, g_m, that translates to high changes in the drain current (I_D) for small changes in the gate voltage (V_G). This makes OECTs excellent transducers for ionic signals.[21–26]

Selectivity in ion sensors is achieved by employing an ion-selective membrane (ISM) that contains ionophores in a plasticized poly(vinyl chloride) (PVC) matrix.[27] The ionophores interact selectively and reversibly with target ions to form complexes,[28] which provides the ion selectivity. Bulky lipophilic ions (so called “ionic sites”) are also embedded in the membrane to facilitate exchange of the target ions while blocking ions of opposite charge through the Donnan exclusion effect.[27] In typical
ISMs, however, ions have a mobility which is around 1000 times lower than that in aqueous solutions since the presence of the PVC matrix hinders their transport.\(^{29,30}\) This makes the direct coupling of ISMs with OECTs challenging, as the limited supply of ions to gate the channel leads to poor performance. The ionic conductivity in the membrane can, in principle, be improved by increasing the concentration of ionic sites.\(^{31,32}\) This was recently leveraged to make OECTs showing a relatively small degradation of the gating performance when coupled directly with ISMs.\(^{40}\) However, exceeding a molar ratio of ionic site to iono-proxy beyond an optimal value, typically in the range of 0.2–0.8, is known to deplete free vacant ionophores in the membrane. This degrades the interfacial kinetics for forming ion-ionophore complexes and thus deteriorates the selectivity and sensitivity of the ISM.\(^{28,29,31,33}\) For this reason, an internal electrolyte reservoir is usually incorporated between the ISM and the channel to supply enough ions to gate the channel effectively and achieve high sensor performance (e.g., sensitivity of 50 µA dec\(^{-1}\)).\(^{34,35}\) However, these liquid or hydrogel electrolyte reservoirs require containment by polydimethylsiloxane (PDMS) or glass chambers, hindering the miniaturization and mechanical flexibility of these devices, therefore, prohibiting their use in wearable/implantable applications. Here, we demonstrate that a thin polyelectrolyte film with mobile sodium ions as the internal ion reservoir enables sensor miniaturization, leading to sensors with fast response time and high sensitivity due to a super-Nernstian response. We show this to be a platform technology, capable of selective detection of different ions by simply using the appropriate ISM. These polyelectrolyte-gated OECTs pave the way for high-performance wearable/implantable ion sensors.

Polyelectrolyte films are polymers consisting of charged polymer chains and mobile counter ions, which leads to ion transport of the counter ions under an applied electric field. We hypothesized that incorporating a polyanionic film with mobile cations between the ISM and the OECT channel would allow a supply of the cations into the channel under a positive gate bias, facilitating efficient gating and addressing the issue of poor ion supply through the ISM. As shown in Figure 1a, the proposed ion-selective OECT consists of a channel made of the poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), an internal ion reservoir made of the polyelectrolyte poly(sodium 4-styrenesulfonate) (PSSNa), and an ISM. Details on the device fabrication are provided in the Experimental Section. Figure 1b shows the transfer characteristics of a conventional OECT before and after depositing the ISM and the ion reservoir. The ISM is shown to effectively act as an ion barrier, hindering ions from the analyte solution from permeating into the PEDOT:PSS channel. Indeed, the device in which there is direct contact between the ISM and the channel shows severe degradation of transfer characteristics (red curve). When the PSSNa layer is inserted between the ISM and the channel, the transfer characteristics (blue curve) are similar to those of the original PEDOT:PSS OECT, indicating successful volumetric gating through the mobile Na\(^+\) ions from the PSSNa layer. The channel in the ion-selective OECT is completely dedoped at gate biases >0.85 V and this results in an on/off current ratio of ≈10\(^5\) with an off-state current of ≈20 nA (Figure S1a, Supporting Information), which is a typical behavior of depletion-mode OECTs based on conducting PEDOT:PSS channels.\(^{23}\) The transfer curves also show small hysteresis (Figure S1b, Supporting Information), which is commonly observed in electrolyte-gated organic transistors.\(^{34,36}\)

A sodium-selective OECT with 100 nm-channel thickness was fabricated by using an ISM doped with sodium ionophores, exhibiting a maximum \(g_{\text{m}}\) of 1.2 mS (see Figure 2a). The \(I_D\) was recorded at a constant gate and drain voltages (\(V_G = 0\) V, \(V_D = -0.5\) V), while the Na\(^+\) concentration in the analyte was varied in a stepwise manner. An increase in the Na\(^+\) concentration leads to an increase in a potential difference at the interface between the analyte solution and the membrane,\(^{37}\) and thus more Na\(^+\) ions from the PSSNa layer permeate into and electrochemically dedope the PEDOT:PSS channel, resulting in a decrease in \(I_D\) as shown in Figure 2b. To extract sensor parameters, \(I_D\) values at equilibrium from Figure 2b and Figure S2a, Supporting Information, were plotted against the Na\(^+\) and K\(^+\) ion concentrations, respectively, as seen in the semilog plot (the left in Figure 2c). Note that the membrane has never been in contact with aqueous solutions, thus the resulting concentration changes are due to the sodium-selective behavior.

![Figure 1](image-url)  
**Figure 1.** Device structure and electrical characteristics. a) Schematic structure of the ion-selective OECT. b) Transfer characteristics of a conventional OECT before and after coating an ISM, and the final ion-selective OECT.
with the primary (Na⁺) ions before measuring in a solution of interfering (K⁺) ions for obtaining an unbiased selectivity coefficient by minimizing primary ion contamination, and the membrane was also preconditioned in the corresponding ion solutions prior to every measurement.[37] Figure 2c (left) shows that while a relatively small $I_D$ response to K⁺ ions is observed from $10^{-2}$ M, the sodium-selective OECT exhibits a linear response to Na⁺ ions in the range of $10^{-4}$ to $10^{-1}$ M with a high sensitivity of 98 $\mu$A dec⁻¹ and a limit of detection (LOD) of $9 \times 10^{-6}$ M. Here, the LOD was extracted from the intersection point between the linear slope of the calibration curve and the horizontal tangent (dotted line) according to the International Union of Pure and Applied Chemistry definition.[38] Assuming that the membrane activity remains constant, the phase boundary potential at the analyte/membrane interface, simply called the membrane potential, is proportional to the analyte activity (i.e., concentration), which is described by the Nernstian equation as follows,[39]

$$E_m = E^0 + \frac{kT}{nF} \ln[M^{n+}]$$  \hspace{1cm} (1)

where $E^0$ and $[M^{n+}]$ denote the formal potential and the concentration of the analyte ion, respectively, $k$ is Boltzmann’s constant, $T$ is the temperature, $n$ is the valency of the analyte ion, and $e$ is the elementary charge. The $E_m$ values for different ion concentrations were calculated from the transfer curve measured with a blank solution (deionised [DI] water) at the same $V_D$ as shown in Figure 2c (right), showing a super-Nernstian slope of 85 mV dec⁻¹. To obtain the selectivity coefficient, the matched potential method was used, which is based on the activity (concentration) ratio of the primary ion and the interfering ion which leads to the same potential change.[40] The selectivity coefficient was calculated to be $-\log k_{Na,K}^{pot} = 3.2$ which is a higher value compared to $-\log k_{Na,K}^{pot} = 1.9$ and $-\log k_{Na,K}^{pot} = 2.7$ of the sodium-selective electrodes employing the same membrane composition.[41,42] In order to test the sensor reversibility, the Na⁺ concentration was increased ($5 \rightarrow 10 \times 10^{-3}$ M) and then decreased ($10 \rightarrow 5 \times 10^{-3}$ M) repetitively in real time as seen in Figure 2d. This shows almost identical $I_D$ when returning back to the previous concentrations, indicating good reversibility.
In order to check whether this proposed architecture is generally applicable to the sensing of different ions, a potassium-selective membrane was used instead of the sodium-selective one as seen in Figure 1a. Note that the PEDOT:PSS channel was thicker (250 nm) in this case with the sensor having a maximum $g_m$ of 4 mS (Figure 3a).[25] Figure 3b represents the real-time current response to various $K^+$ concentrations. In order to provide a quantitative analysis on the sensor performance, as shown in Figure 3c, calibration curves of the measured current at equilibrium (left) and the calculated membrane potential (right) to KCl and NaCl solutions with different concentrations were obtained, and the corresponding $E_m$ values were plotted based on the transfer curve (Figure 3a). Following the same analyses as in the case of the Na+ sensor, the extracted sensor parameters we found are a super-Nernstian slope of 84 mV dec$^{-1}$, a sensitivity of 224 µA dec$^{-1}$, an LOD of $15 \times 10^{-6}$ M, and a selectivity coefficient of $-\log K_{Na}^n = 2.5$, and the sensor also exhibits a reversible response (see Figure 3d).

The most striking result is that the extracted slope in the linear regime is $\approx 85$ mV dec$^{-1}$ which is higher than the theoretically predicted value of 59.2 mV dec$^{-1}$. This super-Nernstian response can be understood by considering the mechanism of the operation of the device: The membrane potential at the analyte/ISM interface induces a potential at the ISM/PSSNa interface, which gates the OECT channel through the PSSNa electrolyte. As a result, an increase in the ion concentration of the analyte solution leads to transport of Na$^+$ ions in the PSSNa layer away from the interface with the ISM and into the PEDOT:PSS channel. The EDL originating from uncompensated PSS$^-$ polyanions at the ISM/PSSNa interface can thus be regarded as an electrochemical gate with a capacitance, $C_{DL}$, which is connected in series with the capacitance of the channel ($C_C$). This configuration has been shown to modify the effective gate voltage, resulting in an effective membrane potential $E_m^{eff}$

$$E_m^{eff} = E^0 + (1 + \gamma) \frac{kT}{nF} \ln [M^{m-}]$$

where $\gamma$ is the capacitance ratio defined as $\gamma = C_C/C_{DL}$. The same phenomenon was demonstrated in OECTs operated by a
polarizable gate electrode, showing super-Nernstian response to ion concentration. This means that the super-Nernstian slope depends on device geometry (the capacitance ratio $\gamma$), which is supported by the fact that both the Na$^+$ and K$^+$ sensors practically show the same sensitivity in mV dec$^{-1}$. The current sensitivity (i.e., the slope of the linear region on the left in Figures 2c and 3c) can also be predicted from the above equation using the definition of transconductance,

$$g_m(E_m) = \frac{\partial I_D}{\partial E_m} = \frac{\partial I_D/\partial \ln[M^+]}{\partial \ln[M^+]}$$

(3)

Note that $g_m$ is dependent on the gate voltage as seen in Figure 2a, and thus $g_m$ is a function of the effective gate voltage, $V_{Geff} = V_G + E_m$. For the sodium-selective OECT, since $V_G = 0$ V and $100 \text{ mV} < E_m < 350 \text{ mV}$ in the linear region on the right in Figure 2c, $V_{Geff}$ varies between 100 and 350 mV, resulting in $g_m \approx 1-1.2 \text{ mS}$ (see Figure 2a). Using Equation (3) and $\partial E_m/\partial \ln[M^+] = 85 \text{ mV dec}^{-1}$, the current sensitivity ($\partial I_D/\partial \ln[M^+]$) is calculated to be $85-102 \mu\text{A dec}^{-1}$. For the potassium-selective OECT, as $V_G = 200 \text{ mV}$ and $50 \text{ mV} < E_m < 300 \text{ mV}$ in the linear region on the right in Figure 3c, $V_{Geff}$ varies from 250 to 500 mV, giving $g_m \approx 2-3.5 \text{ mS}$ (see Figure 3a).

Figure 4. Response time and sensor stability. a) Current response of the sodium-selective OECT to a sudden change in Na$^+$ concentration from $10^{-2}$ to $10^{-1} \text{ m}$ at the fixed $V_G = 0$ V and $V_D = -0.5$ V. Inset shows a fitted line of the curve performed using a double-exponential decay function, resulting in a time constant of $\approx 700$ ms. b) Normalized temporal response of $I_D$ of the PSSNa-coated OECT before (black) and after forming the ISM (red) in response to pulsed $V_G$ of 500 mV. Inset magnifies the region of the $I_D$ response enclosed by the black dashed line. The ion-injection time constants before and after coating the ISM were calculated to be 133 µs and 7 ms, respectively. c,d) Calibration curves for repetitive scans of the Na$^+$ sensor (c) and the K$^+$ sensor (d). The sensitivity values (slopes) are 98 µA dec$^{-1}$ (black squares), 97 µA dec$^{-1}$ (blue circles), and 104 µA dec$^{-1}$ (red circles) in (c) and 224 µA dec$^{-1}$ (black squares), 222 µA dec$^{-1}$ (blue circles), and 254 µA dec$^{-1}$ (red circles) in (d).
Table 1. Performance comparison with several ion-selective transistor technologies.

| Technologies          | Analytes  | $E_{\text{m}}$ sensitivity [mV dec$^{-1}$] | $I_D$ sensitivity [µA dec$^{-1}$] | $-\log_{10}[I]_{\text{Pl}}$ | LOD [× 10$^{-6}$ m] | Response time [s] | $V_{\text{MAX}}$ [V] | References          |
|-----------------------|-----------|------------------------------------------|----------------------------------|----------------------------|---------------------|-------------------|-----------------|------------------|
| ISE                   | Na$^+$    | ≈59                                      | −                               | 1.9, 2.7                  | 3.5, 10              | <20               | −               | [41,42]          |
| Si ISFET              | Ca$^{2+}$, K$^+$ | 26.5, 55.7                             | −                               | −                          | 2, 1, 40            | −                 | −               | [10]             |
| Graphene ISFET        | K$^+$     | 63.6                                     | 35                              | −                          | 1                   | ≈7                | 1               | [53]             |
| AlGaN/GaN ISHEMT$^{(3)}$ | Pb$^{2+}$ | 36                                       | 7                               | −                          | $10^{-3}$            | −                 | 1               | [54]             |
| Dual-gated ISFET      | Cu$^{2+}$ | 98                                       | 0.033                           | −                          | $10^{-8}$            | −                 | 17              | [45]             |
| EGFET$^{(4)}$         | Na$^+$    | 62                                       | 0.5                             | −                          | 1                   | ≈30               | 0.2             | [34]             |
| OECT w/o internal electrolyte | NH$_4^+$, Ca$^{2+}$ | −                                       | 0.06, 0.03                     | −                          | ≈10                | <10              | 0.2             | [4]              |
| OECT with internal electrolyte | K$^+$    | 48                                       | 47                              | 2.7                       | ≈10                | 36                | 0.7             | [35]             |
| OECT with PSSNa electrolyte | Na$^+$, K$^+$ | ≈85                                     | 98, 224                         | 3.2, 2.5                  | ≈10                | ≈1               | 0.5             | This work        |

$^{(4)}$Maximum applied voltage; $^{(3)}$Ion-selective high electron mobility transistor; $^{(4)}$Electrolyte-gated organic field-effect transistor.

and thus the resultant current sensitivity is expected to be 168–294 µA dec$^{-1}$. The experimentally obtained values for sensitivity of 98 µA dec$^{-1}$ (Na$^+$ sensor) and 224 µA dec$^{-1}$ (K$^+$ sensor) are within the predicted range based on Equation (3).

In order to provide a quantitative analysis on the response time, as seen in Figure 4a, a time constant ($\tau$) was calculated by fitting the $I_D$ response of the sodium-selective OECT to a change in Na$^+$ concentration from 10$^{-2}$ to 10$^{-1}$ m with a double-exponential decay function, $I_D(t) = I_0 + A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2}$, and using the amplitude-weighted average method (i.e., $\tau = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$), resulting in $\tau \approx 700$ ms. The average time constant ($\tau_{\text{avg}}$) of the $\tau$ values extracted from every step change in $I_D$ (Figure 2b) was obtained to be $\tau_{\text{avg}} = 1.3$ s which is a much faster value compared to those ($\tau > 30$ s) of the previously reported ion-selective EGFET$^{[34]}$ and OECT$^{[35]}$ using a bulky liquid or hydrogel as an internal electrolyte reservoir. The response time of the ion-selective OECTs can be limited by the three equilibrium processes: 1) ion diffusion across the stagnant solution, 2) ion complexation with ionophores at the membrane surface, and 3) ion injection from the internal electrolyte into the channel. As shown in Figure 4b, the temporal responses of $I_D$ were recorded with a fixed Na$^+$ concentration (10$^{-1}$ m) by applying the gate pulse in the direction of the ion injection, which allows extraction of the time constant related to the ion injection into the channel. Upon introduction of the ISM, the time constant increased from 113 µs to 7 ms. This suggests that the ion injection from PSSNa into the channel is not the dominant factor limiting the response time, and thus this polyelectrolyte-gated ion-selective OECT has room for improvement by equipping it with a flow cell to reduce ion diffusion time in the analyte solution and/or by optimizing the ISM composition to improve the interfacial kinetics for forming ion-ionophore complexes.

In order to investigate the sensor stability, repetitive measurements of $I_D$ versus concentration were performed after 5 months of storage in ambient dry conditions (Figure S3, Supporting Information), and the corresponding calibration curves were obtained as seen in Figure 4c (Na$^+$ sensor) and Figure 4d (K$^+$ sensor). Although a fluctuation of the baseline current, <10% (Na$^+$) and <4% (K$^+$), is observed, the devices exhibit stable sensor performance with highly reproducible sensitivity (average values of 99.7 µA dec$^{-1}$ (Na$^+$) and 233 µA dec$^{-1}$ (K$^+$)) in the range of the linear response (10$^{-4}$–10$^{-1}$ m). The LOD increases slightly to 30 × 10$^{-6}$ m after 5 months, which is also observed in the ISM lifetime tests.$^{[41]}$ The results indicate that the sensors have a remarkably long lifetime and show stable sensitivity.

The performance of the polyelectrolyte-gated OECTs is compared with several ion-selective transistor technologies, along with typical values for ion-selective electrodes (ISEs), in Table 1. The super-Nernstian response can also be observed in dual-gated transistors (e.g., 98 mV dec$^{-1}$ for a divalent ion, Cu$^{2+}$)$^{[45]}$ and the sensitivity in this configuration can be adjusted by the ratio of the top and bottom gate capacitances.$^{[16,46,47]}$ However, dynamic (i.e., real-time) responses have never been reported in the existing literature on the dual-gated ISFETs.$^{[45,48–52]}$ The overall performance of the sensors reported here surpasses that of all transistor technologies, in particular, in terms of the current sensitivity and response time. Perhaps the most striking result we obtained here is that the current sensitivity depends on $g_m$ and hence can be easily increased by controlling $g_m$ through, for example, tuning of channel thickness. The fast response is due to a reduction in ionic resistance resulting from a thin internal electrolyte layer, along with a fast OECT. Together with the fact that the sensor architecture is generic and can be easily coupled with other ISMs to sense different ions, the results shown open new frontiers for the applications of ion sensors.

Experimental Section

Materials: PEDOT:PSS (Clevios PH1000) and Micro-90 cleaning solution were purchased from Heraeus and Cole–Parmer, respectively. Ethylene glycol, 4-dodecylbenzenesulfonic acid (DBSA), (3-glycidoxypropyl)trimethoxysilane (GOPS), PSSNa (molecular weight ≈1000000), 3-(trimethoxysilyl)propyl methacrylate (Silane A174), high-molecular-weight PVC, 2-nitrophenyl octyl ether (2-NPOE), potassium tetrakis(4-chlorophenyl)borate (KT$_4$ClPB), sodium ionophore X, potassium ionophore III, tetrahydrafuran (THF), sodium chloride (NaCl), and potassium chloride (KCl) were acquired from Sigma-Aldrich and were used without further purification.
Polymer Blend Preparation: The PEDOT:PSS blend was prepared by adding 5 vol% ethylene glycol (to improve film conductivity), 0.25 vol% DBSA (to improve film homogeneity), and 1 vol% GOPS (as a crosslinker) to a stock PEDOT:PSS solution. The ISM solution was prepared by mixing high molecular weight PVC (33 wt%), plasticizer (2-NPOE, 66.1 wt%), cation exchanger (KT4ClPB, 0.2 wt%), and a corresponding ionophore in THF (400 mg/4 mL). Sodium ionophore X (0.7 wt%) and potassium ionophore III (2 wt%) were used to prepare the sodium and potassium-selective membrane, respectively. The resultant molar ratio of the ionic site (KT4ClPB) to ionophore was 0.22 (for sodium) and 0.77 for potassium-selective membrane, respectively. The resultant molar ratio of the ionic site (KT4ClPB) to ionophore was 0.22 (for sodium) and 0.77 (for potassium) which were in the range of the optimal value (0.2–0.8).

For the PSSNa mixture, 1 m HCl (1 vol%), DBSA (0.25 vol%), and GOPS (1 vol%) were added to a 1.2 w/v% PSSNa solution. HCl was added to modify pH to enhance the crosslinking reaction.[55]

Device Fabrication: OECTs were fabricated as recently reported (see a detailed fabrication process).[156] Briefly, source/drain electrodes and interconnects were formed on cleaned glass substrates by e-beam evaporation (Kurt J. Lesker PVD-75) on a Ti (5 nm)/Au (100 nm) layer and the lift-off process. A 2 µm-thick parylene C was deposited on the samples to electrically isolate the electrodes after a surface treatment using Silane A-174, an adhesion promoter. A diluted Micro-90 (2% v/v) was added to a 1.2 w/v% PSSNa solution. HCl was added to modify pH to enhance the crosslinking reaction.[55]

Device Characterization: A small PDMS well was placed on top of the ISM to confine an analyte solution. All the electrical measurements were performed using a semiconductor device analyzer (Keysight B1500A) and an Ag/AgCl pellet (World Precision Instruments) as a gate electrode inside a Faraday cage in ambient conditions (40% relative humidity at 20 °C) and ambient light. For obtaining real-time responses (Iₛₜₜ-time) to the stepwise increase in ion concentrations, the PDMS well was first filled with DI water of 50 µL, and then Iₛₜ was recorded at constant Vₛ and Vₛ. After the baseline current was stabilized, either the Naₐ or Kₐ concentration was increased by successively adding the corresponding NaCl and KCl solutions (10⁻³ to 1 m) to the DI water in the well at a 1:1 ratio of the total volume. For the reversibility tests, a chamber (2 mL volume) with a bottom hole was placed on the PDMS well. The ion concentration in the chamber was adjusted from 5 to 10 × 10⁻³ m by adding a calculated amount of the 100 × 10⁻³ m solution, and from 10 to 5 × 10⁻³ m by diluting it with DI water.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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