

Supporting Information

Sensitivity-tunable and disposable ion-sensing platform based on reverse electro dialysis

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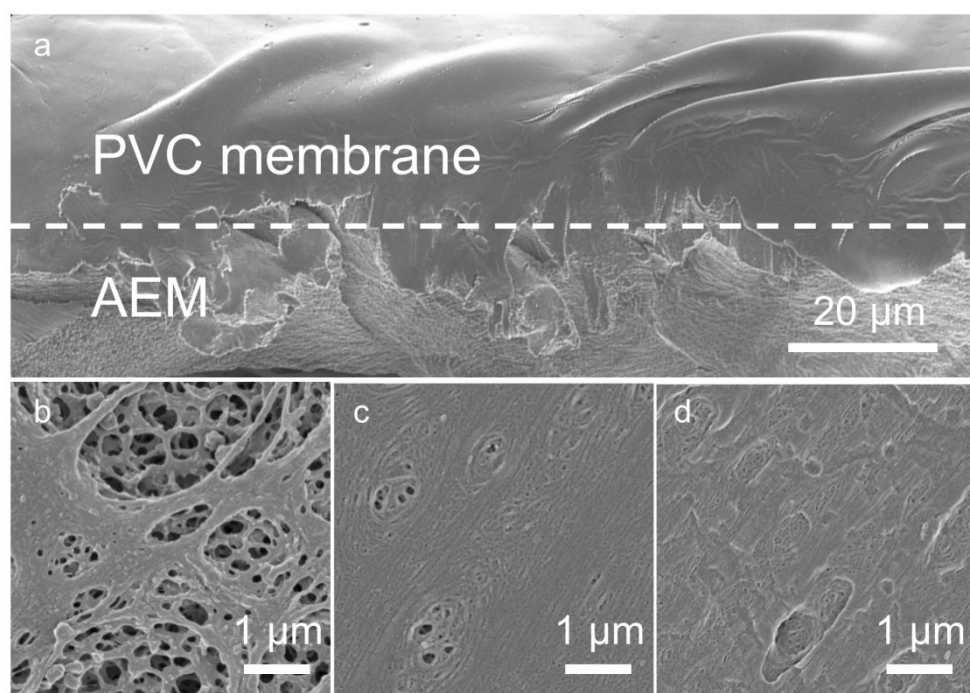


Figure S1. FESEM images of Membranes: a. Cross-section view of NSM. Top view of b. 1,000 kDa DM, c. 100 kDa DM, and d. 10 kDa DM.

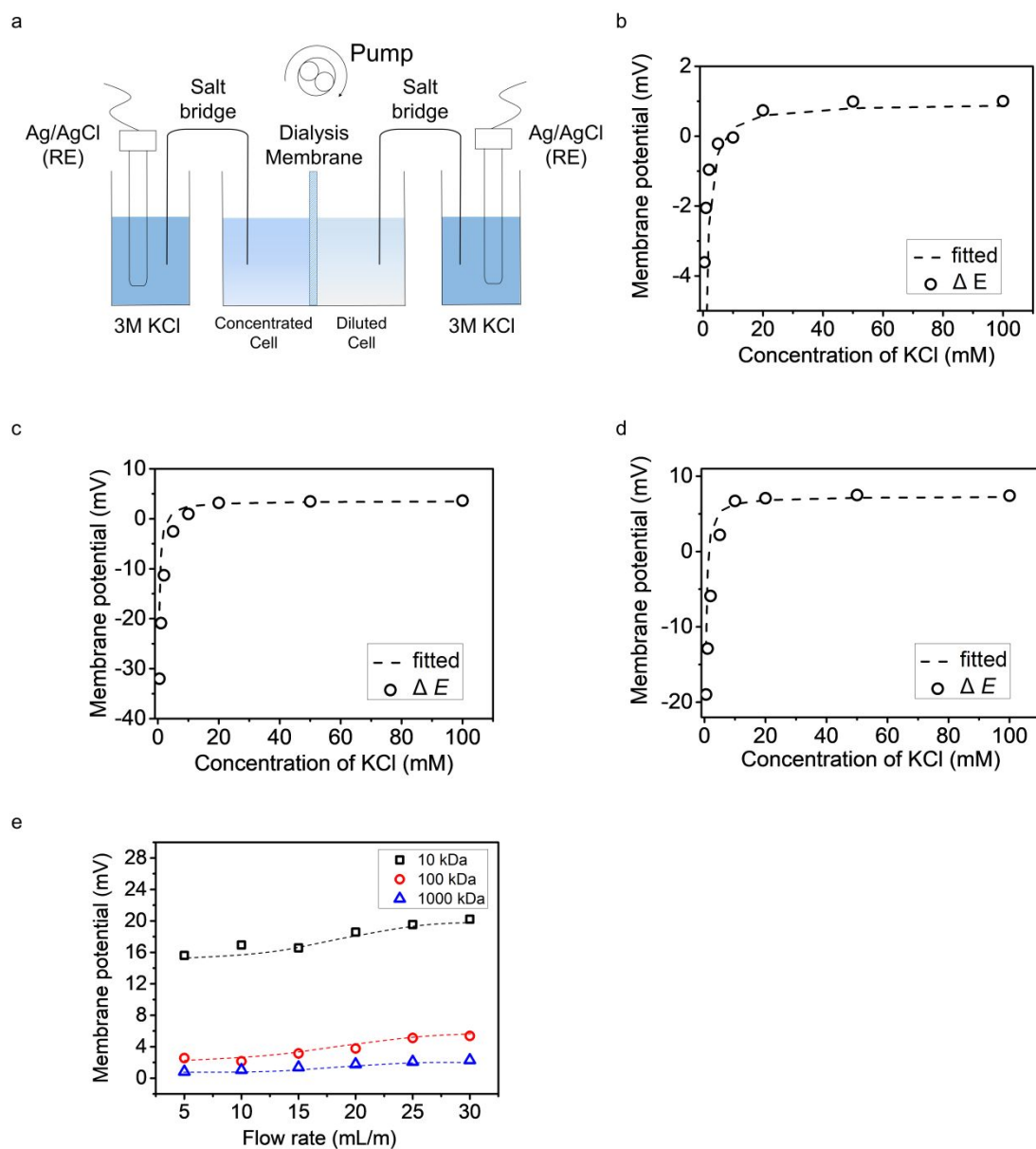


Figure S2. a. Setup for measurement of DM charges. A dialysis membrane separates concentrated and diluted cells containing aqueous KCl solutions. An external pump keeps the concentration ratio between the two solutions constant. Ag/AgCl reference electrodes were immersed into 3 M KCl solutions and connected to the two solutions via a salt bridge. Membrane potential of b. 1,000 kDa, c. 100 kDa, and d. 10 kDa DM is measured as a function of KCl concentration (diluted side). The high-to-low concentration ratio was maintained as 10. Experimental values of E at high KCl concentrations were plotted against $1/C$ to obtain the value of charge density (θ). e. DM potentials measured as a function of flow rate. Positive correlation between the observed potential and flow rate was obtained at 5–30 mL/min. Membrane potential was saturated at 25 mL/min, which was selected for measuring membrane charge density.

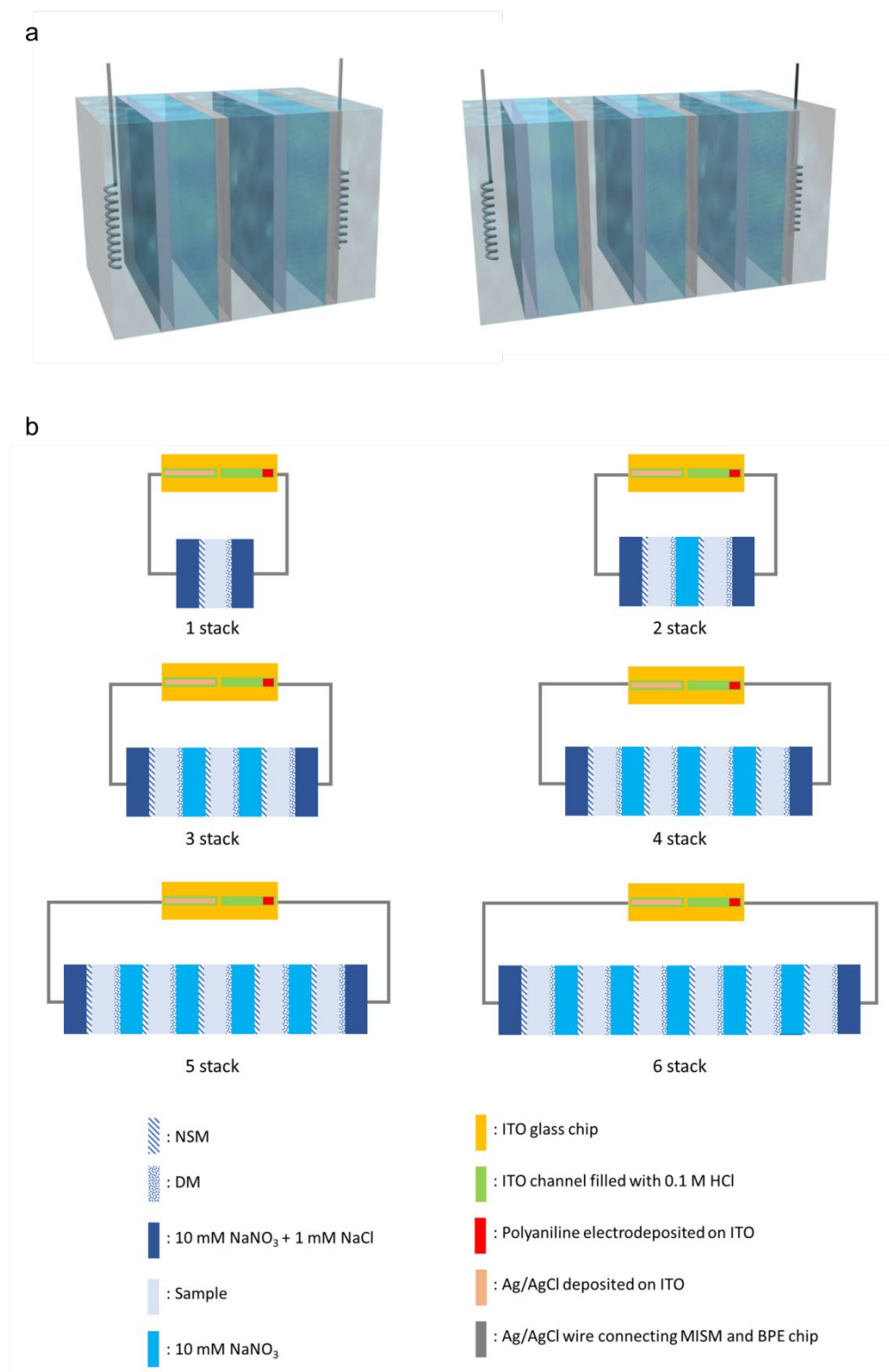


Figure S3. a. Schematic diagram of 2 stack and 3 stack MISMs. b. Schematic diagram of 1 to 6 stack MISM.

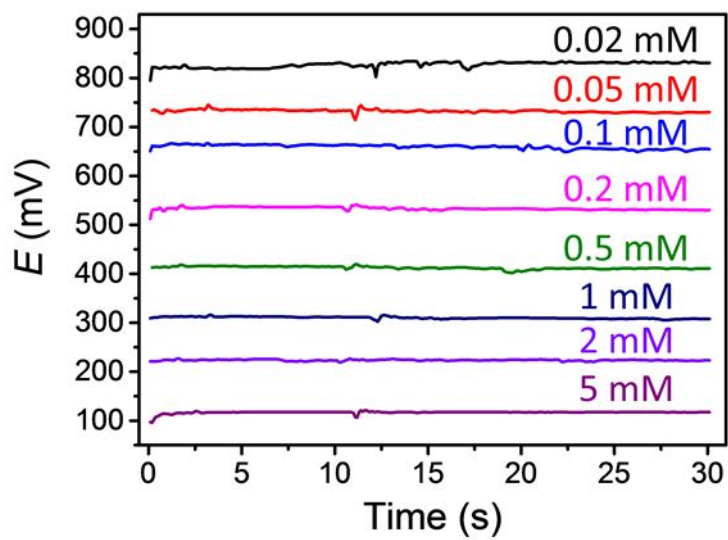


Figure S4. The potential of 6 stack MISM for 30 s. To check MISM stability and robustness, we conducted experiments on potential equilibration and time-dependent fluctuation, revealing that the potential of a six-stack cell reaches ± 1 mV of the stabilized value within 5 s after electrolyte injection and decreases by only 1.3% after 30 s on average.

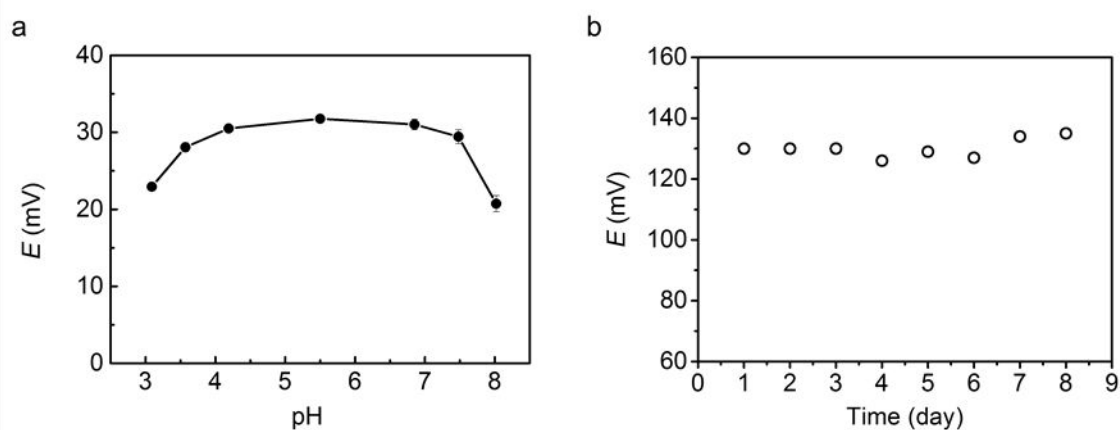


Figure S5. Stability of single stack MISM. a. The effect of sample pH (3.2–8.6; 2×10^{-3} M nitrate solution) for a single-stack MISM, demonstrates the potential output remains stable and largely constant at pH 3.5–7.8 and critically decreases outside this range. b. Daily OCP of MISM recorded for 0.02 mM nitrate solution with 0.1 mM chloride ions. Only insignificant MISM selectivity and potential deteriorations are observed within eight days of dry storage under ambient conditions. The error bars in a. represent \pm SD ($n = 3$).

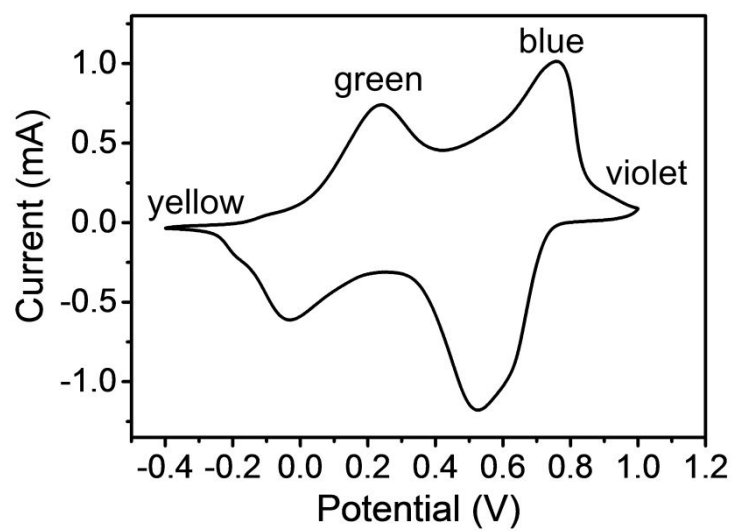


Figure S6. Cyclic voltammogram of polyaniline that has four oxidation states and respective colors.

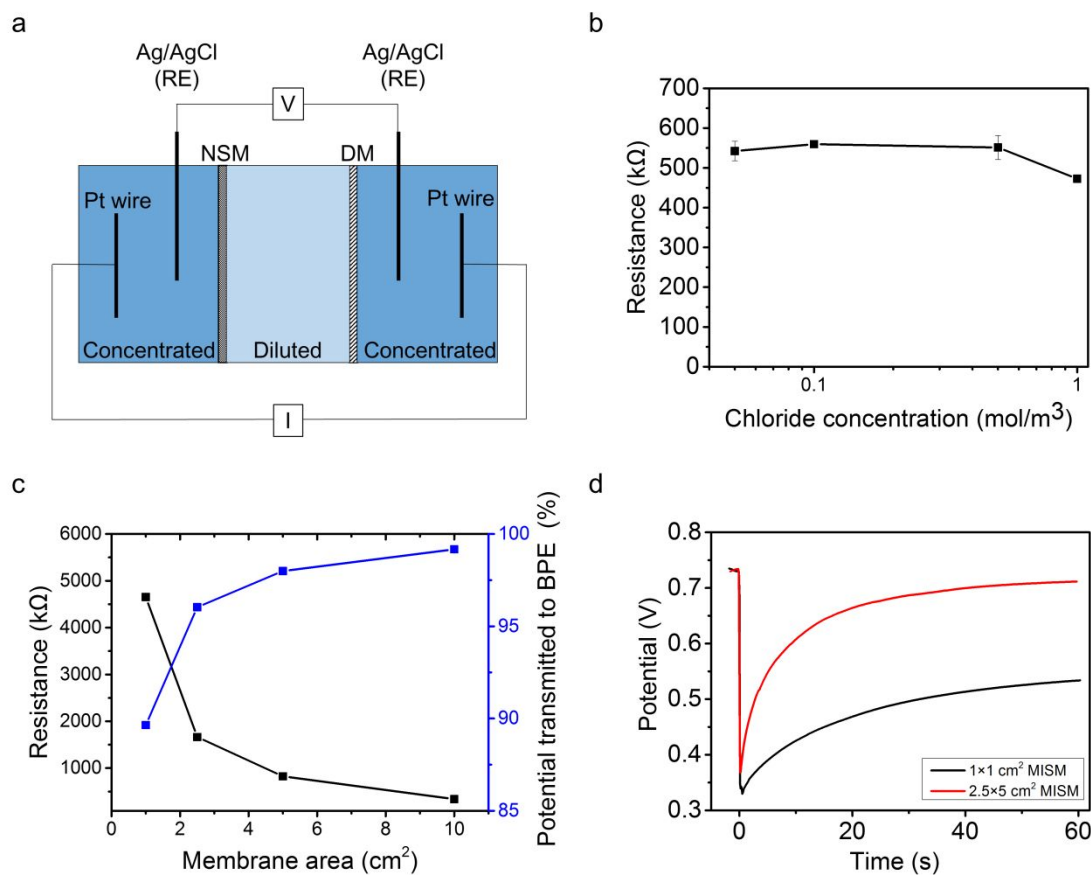
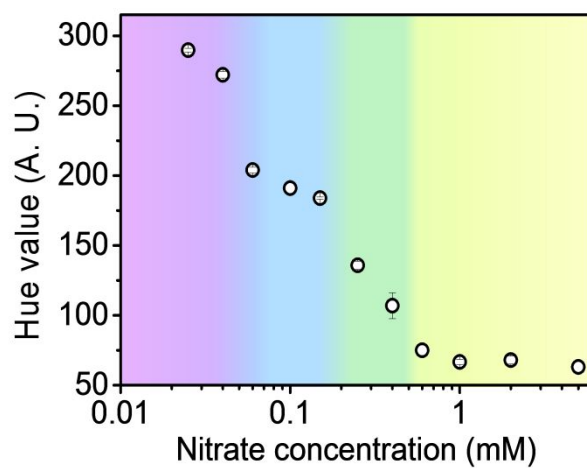


Figure S7. Resistance of MISM in various conditions. a. Scheme of membrane resistance measurement. Ag/AgCl reference electrodes were immersed in both chambers to record the potential difference. Constant current was applied to the MISM through Pt wires in the two chambers. The resistance of the MISM was calculated from the IR drop due to the current applied. b. Measured resistance for a series of chloride concentrations. c. Resistance and potential transmitted to the BPE for various membrane areas. d. Time-dependence of the potential for different MISM areas. The error bars in b., c. represent \pm SD ($n = 3$).

a



b

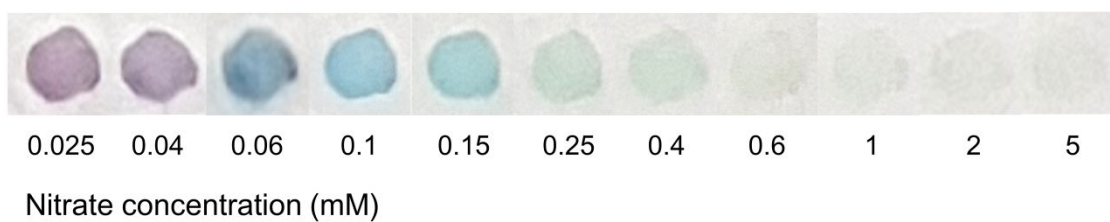


Figure S8. Hue value according to nitrate concentration and uncropped image of PANi. a. Hue values for a series of nitrate concentrations. The background indicates the color generated from BPE based potentiometric sensor. b. Colors of PANi generated from six-stack MISM in response to a series of nitrate concentrations. The cropped image is shown in Fig. 5c. The error bars in a. represent \pm SD ($n = 3$).

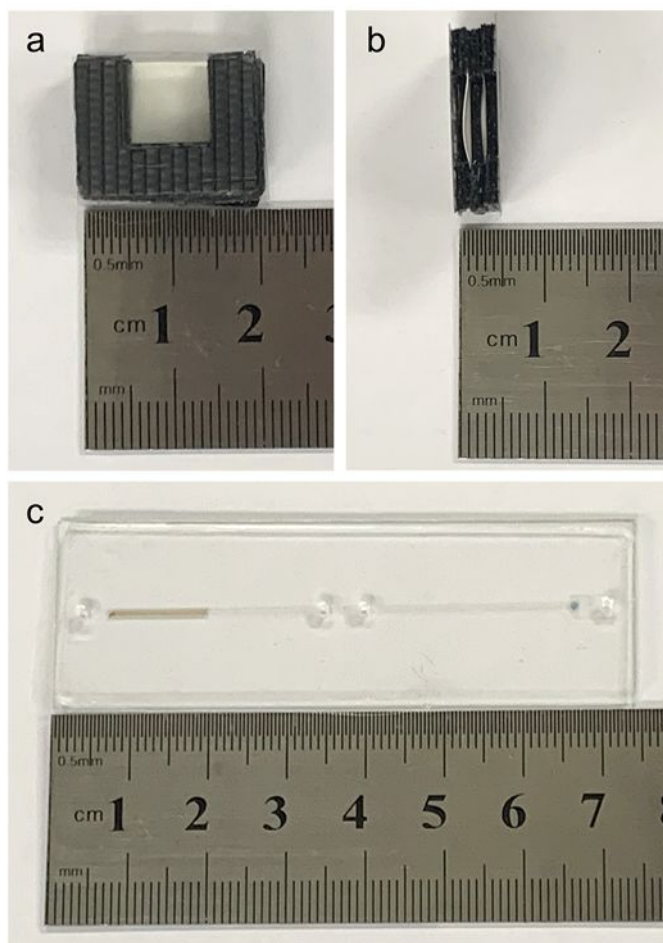


Figure S9. Photographs of a single stack MISM and BPE microchip. a. Front view of a single stack MISM. b. Top view of a single stack MISM c. Top view of a BPE microchip.

Table S1. Sensitivity of MISM as a function of the number of stacks. Nitrate concentrations from 0.02 mM to 5 mM were used to plot the trend line for sensitivity of each stack.

Number of stacks	Sensitivity (mV decade ⁻¹)	Sensitivity enhancement compared to single stack
1	57.1	1.00
2	116.2	2.03
3	159.9	2.80
4	215.5	3.77
5	270.5	4.73
6	320.8	5.62
7	388.1	6.80

Table S2. Absolute and relative error for 0.1 mM and 0.12 mM nitrate, for 1-stack and 2-stack. Each experiment includes 60 measurements.

Number of stacks	Nitrate concentration (mM)	Absolute error (mV)	Relative Error (%)
1	0.1	5.6	5.8
1	0.12	5.1	5.2
2	0.1	7.2	3.7
2	0.12	7.3	3.6

EXPERIMENTAL SECTION

Reagents and Apparatus

All chemicals were used without further purification. All aqueous solutions were prepared with ultrapure deionized water (18.2 MΩ) produced by NANO pure Diamond (Barnstead, NH, U.S.A.). Sodium nitrate, sodium chloride, sodium bicarbonate, sodium sulfate, potassium chloride, nitrate ionophore (VI), polyvinyl chloride, dibutyl phthalate, tetraoctylammonium chloride, calcium chloride, calcium ionophore (IV), sodium tetrphenylborate, 2-nitrophenyl octyl ether, silver wire (dia. 0.5 mm), platinum wire (dia. 0.5 mm) and aniline were purchased from Sigma Aldrich (St. Louis, MO, U.S.A.). Hydrochloric acid was purchased from Samchun Chemicals (South Korea). Ag/AgCl reference electrode was purchased from BASi (West Lafayette, IN, U.S.A.). We obtained poly(dimethylsiloxane) (PDMS) monomer and curing agent from Dow Corning (Midland, MI, U.S.A.), ITO coated glass from Techinstro (Yadav Nagar, Nagpur Maharashtra, India). Hexamethyldisilazane (HMDS), hydrogen peroxide (30% aq.), ethanol, acetone and sulfuric acid were obtained from J. T. Baker (Phillipsburg, NJ, U.S.A.). Photoresist (PR; AZ 4620) and developer (AZ 400K) were purchased from Merck (Kenilworth, NJ, U.S.A.). SU-8 was obtained from Microchem (Westborough, MA, U.S.A.). TIN etchant (TE-100) was purchased from Transene Company (Danvers, MA, U.S.A.). Anion exchange membrane (Selemon AMV) and cation exchange membrane (CMV) were products of Asahi Glass Co., Ltd. (Tokyo, Japan). Cellulose ester dialysis membranes with 1,000, 100, 10 kDa were purchased from Spectrum Laboratories (Rancho Dominguez, CA, U.S.A.). Potentiostat (CHI 604, CH Instrument) was used for electrochemical experiment.

Selectivity

The selectivity coefficients were calculated from equation (1).

$$K_{NO_3^-, B}^{pot} = \frac{\Delta \alpha_{NO_3^-}}{\alpha_B} \quad (1)$$

HCO₃⁻, SO₄²⁻, and Cl⁻ were selected as the interfering ions (B) and single stack MISM was used for selectivity measurements. The two end chambers were filled with reference electrolyte as described above. The middle chamber was filled with a mixture of NO₃⁻ and each of the corresponding interfering ion. The concentration of NO₃⁻ was fixed to 2.0 × 10⁻⁵ M and the concentrations of interfering ions were varied from 2.0 × 10⁻⁵ to 5.0 × 10⁻³ M where the potentials were obtained for each concentration of the interfering ions. Next, potentials were recorded for NO₃⁻ ions only of the same concentrations in the absence of any interfering ion. With these values, the selectivity coefficients were determined by the matched potential method. Interfering ions (= 2.0 × 10⁻⁵ – 5.0 × 10⁻³ M) were added to the reference solution (= 2.0 × 10⁻⁵ M) until the potential change from interfering ion reached the potential change caused by the primary ion. The selectivity of CSM based MISM was measured in a similar manner. Na⁺ and K⁺ were used as interfering ions.

Membrane charge density calculation

DM charge densities were calculated from Equation (2), as was previously reported.¹ The experimental setup used for the measurement of membrane charge density featured a chamber divided into two cells by the DM (Fig. S2a), and the potential difference was measured across the DM between dissimilar ion concentrations in two cells. (Fig. S2b, 2c, 2d) The membrane potential of 1,000, 100, 10-kDa DM was measured as a function of the diluted side concentration of KCl concentration with the optimized flow rate of the cells (Fig. S2e).

$$\left(\frac{F}{RT}\right)\Delta E = (1 - 2t_+^*) \ln r - \frac{2(r-1)}{r} t_+^* (1 - t_+^*) \left(\frac{\theta}{C_2}\right) \quad (2)$$

Here, ΔE is the membrane potential, t_+^* is the cation transport number, θ is the membrane charge density, and r is the high (C_1) to low (C_2) concentration ratio, which was set to 10. The measured potential was converted into membrane charge density using Equation (1) based on the obtained steady-state potential and cation transport number.

BPE-based colorimetric sensor fabrication

ITO-coated glass (7.5 cm × 2.5 cm) was washed with ethanol, acetone and deionized water for 10 min, respectively. Then it was baked at 100 °C for 5 min. HMDS was spin coated and baked at 110 °C for 1.5 min, and PR was spin coated and baked at 100 °C for 1.5 min. PR was illuminated with UV light (365 nm) for 20 s while being covered with a patterned mask fabricated in the shape of the BPE (rectangular, length 6 cm, width 0.1 cm). PR is dissolved in AZ 400K developer and baked at 120 °C for 15 min. The ITO was etched using etchant (TE-100) for 15 min at 80 °C. PR residues were removed by washing with acetone.

The mold for PDMS cover was fabricated as the followings. Silicon wafer was cleaned with piranha solution (H₂SO₄:H₂O₂ 3:1) for 20 min and dried at 200 °C for 2 min. After cooling, SU-8 was spin coated and baked at 65 °C for 2 min and at 95 °C for 7 min. UV light was illuminated on SU-8 for 20 s being covered with a patterned mask which was fabricated in the shape of the closed BPE channel (length 3.3 cm, width 400 μm, height 90 μm). SU-8 pattern was developed by treating with SU-8 remover for 2 min. The wafer was baked at 200 °C for 10 min, and at 65 °C for 5 min. Mixture of PDMS monomer and curing agent (10 : 1) was poured on the patterned wafer after attaching it onto a dish and baked at 60 °C for 2 h.

Ag/AgCl paste first is applied on one end of ITO (width 400 μm , length 2 cm, thickness 30 μm) and heated at 150 °C for 20 min, and PANi is electrodeposited on the other end of ITO. For PANi electrodeposition, the ITO electrode was covered with insulating tape with 0.1 cm in diameter, and constant voltage of 0.75 V (vs Ag/AgCl) was applied to the ITO until total charge reached 1.2×10^{-4} C in 0.5 M aniline and 1.0 M H_2SO_4 solution. After PANi deposition, polymerized PDMS from PDMS mold was cut into 7.5 cm \times 2.5 cm and aligned along with ITO patterned glass to be attached onto it. (Photographs of the BPE microchip is shown in Fig. S9).

For the MIS voltage measurement, two channels of the BPE chip were filled with 0.1 M HCl on the PANi and 0.1 M NaCl for the Ag/AgCl channels, respectively. During operation, Ag/AgCl wires connect the chip reservoirs and MIS edge chambers. After 10s, color of oxidized PANi was recorded with digital camera. For the next measurement, PANi was reduced by applying a reverse bias (-0.2 V) to the BPE with the potentiostat.

Hue value and pixel intensity calculation

Photograph of PANi on patterned ITO glass was taken with digital camera and central area with 0.9 mm in diameter was further analyzed as following.

First pixel values (R, G, B values) are obtained as an average of all pixels. Among the three, the maximum value (max) and the minimum value (min) are determined.

If max = R, then hue value = $60 \times ((G - B) \div (R - \text{min}))$

If max = G, then hue value = $60 \times (2.0 + (B - R) \div (G - \text{min}))$.

If max = B, then hue value = $60 \times (4.0 + (R - G) \div (B - \text{min}))$.

If the obtained hue value is negative, 360 is added. The average of the three R, G, and B values gives pixel intensity.

References

- (1) Yamamoto, K.; Ogawa, T.; Matsuda, M.; Iino, A.; Yakushiji, T.; Miyasaka, T.; Sakai, K. Membrane Potential and Charge Density of Hollow-Fiber Dialysis Membranes. *J. Memb. Sci.* **2010**, 355, 182–185.