Supporting Information

Experimental details

Fabrication of common ISEs: Glass carbon electrode (GCE, 3 mm diameter) was polished with 0.05 μm alumina powder and then washed ultrasonically in water and ethanol, respectively. The GN film modified GCE (GCE/GN) was prepared by spring 20 μL of GN suspension (10 mg/L) onto the electrode surface and dried under an infrared lamp.[1] For the fabrication of GCE/GN/K-ISM, a K-ISM solution containing 1% valinomycin (Sigma), 32.8% PVC, 66% *o*-NPOE and 0.2% KTFPB was deposited (~50 μm thickness) onto the GN film by dip-coating into a tetrahydrofuran solution. For the fabrication of GCE/GN/Ca-ISM, a Ca-ISM solution containing 1.0 wt% calcium ionophore ETH 129 (Sigma), 33.0 wt% PVC, 65.8 wt% *o*-NPOE, and 0.2 wt% KTFPB was deposited (~50 μm thickness) onto the GN film by dip-coating into a tetrahydrofuran solution.[2] For the fabrication of GCE/GN/H-ISM, a H-ISM solution containing 2.2 wt% hydrogen ionophore tridodecylamine (Sigma), 32.8 wt% PVC, 64.7 wt% *o*-NPOE, and 0.3 wt% KTFPB was deposited (~50 μm thickness) onto the GN film by dip-coating into a tetrahydrofuran solution. K-ISE without any intermediate layer (denoted as Pt/K-ISM) was obtained by covering the Pt electrode with the above K-ISM. All the membrane electrodes were left to dry for 24 h at room temperature (25 ± 2 °C) and then conditioned in 10^{-2} M solution of the primary analyte for at least one day before further measurements and also between the measurements.

Fabrication of CNTPE: The CNTP was prepared according to method proposed by Novell and coworkers.[3] Firstly, CNT ink was prepared by adding SWCNTs to a 10 mg/mL sodium dodecylbenzenesulfonate aqueous solution. Secondly, the ink is printed onto a filter paper (10 cm diameter, 0.01 cm thick paper disk, 10-20 μm fiber thickness) and the solvent evaporates. Thirdly, the prepared paper was rinsed with water several times in order to reduce the surfactant. After rinsing, the CNTP was air-dried at room temperature. The CNPTE was obtained by cutting the CNTP into the designed size (sensing area is 2 mm × 3 mm), followed by coating with insulating ink and assembling with plastic mask.

Figure S1. CV curves for GNPE in the absence of oxygen (dashed line) and in the presence of oxygen (solid line). Supporting electrolyte: 0.1 M KCl solution. Scan rate: 0.1 V s^{-1}.

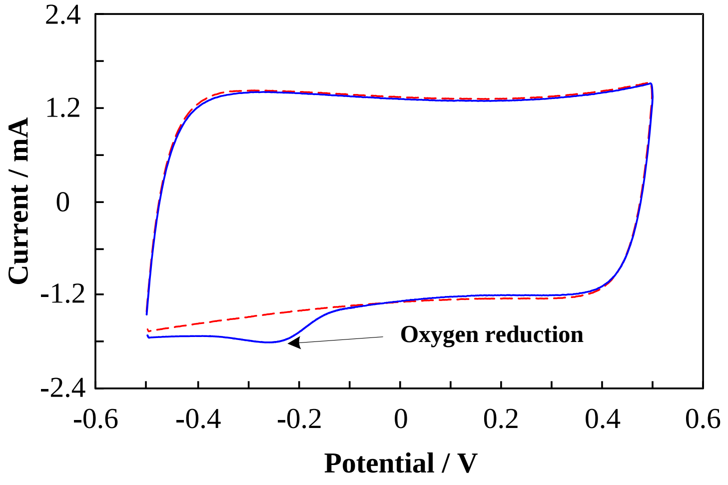

Figure S2. Impedance plots of Pt/K-ISM (blue) and GNPE/K-ISM (red) in 0.1 M KCl solution.

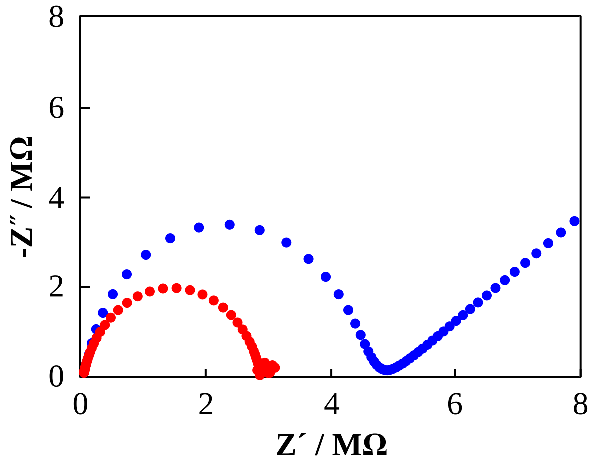

Figure S3. Chronopotentiograms for Pt/K-ISM (blue) and GNPE/K-ISM (red) recorded in 0.1 M KCl solution.

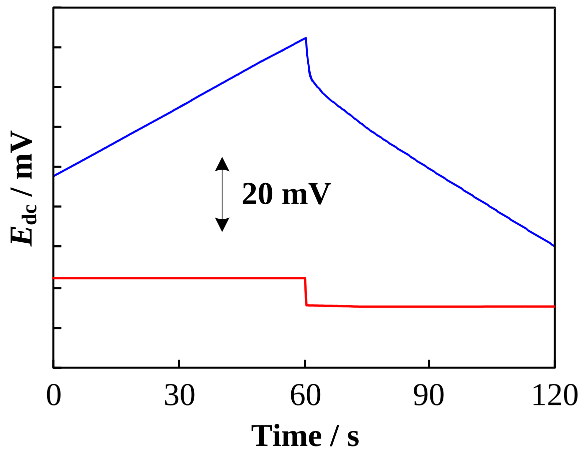

Figure S4. Water layer tests for Pt/K-ISM (blue) and GNPE/K-ISM (red) switched between 0.1 M NaCl and 0.1 M KCl solutions.

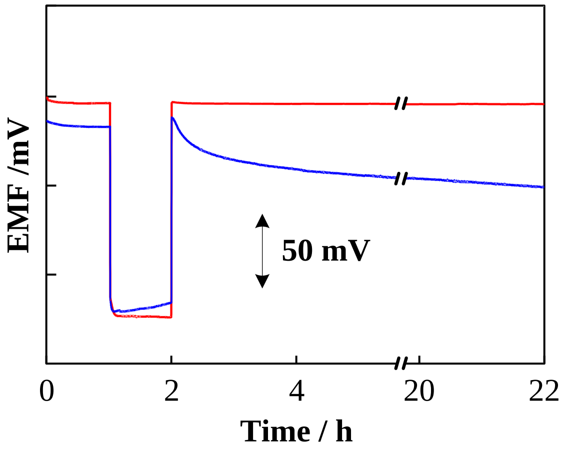

Figure S5. Optical images of a water droplet on GNOP (**A**) and GNP (**B**).

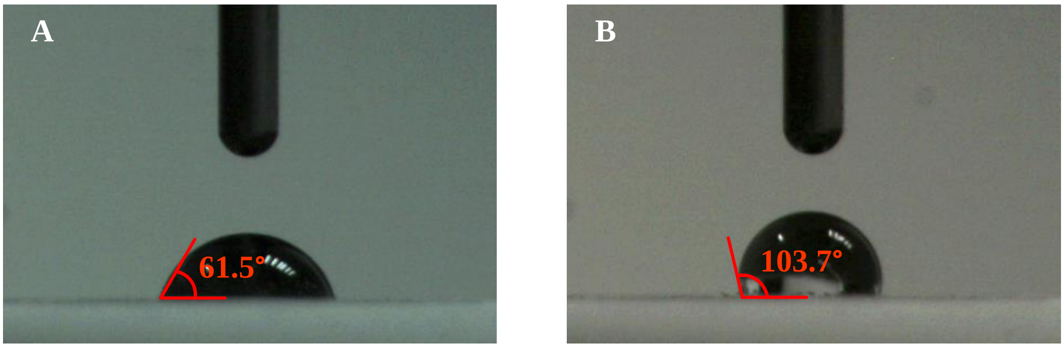

Figure S6. (**A**) Effect of light on the potential stability of H^+ sensing device, Ca^{2+} sensing device, and K^+ sensing device in 0.01 M KCl solution, 0.01 M $CaCl_2$ solution, and 0.05 M KCl solution, respectively. (**B**) Effect of O_2 and CO_2 on the potential stability of H^+ sensing device, Ca^{2+} sensing device, and K^+ sensing device in 0.01 M KCl solution, 0.01 M $CaCl_2$ solution, and 0.05 M KCl solution, respectively. (**C**) Redox interference test for H^+ sensing device, Ca^{2+} sensing device, and K^+ sensing device recorded in 0.01 M KCl solution with 10^{-4} M $FeCl_2/FeCl_3$, 0.01 M $CaCl_2$ solution with 10^{-4} M $FeCl_2/FeCl_3$, and 0.05 M KCl solution with 10^{-4} M $FeCl_2/FeCl_3$, respectively. (**D**) pH influence on the potential stability of Ca^{2+} sensing device and K^+ sensing device in 0.01 M $CaCl_2$ solution, and 0.01 M KCl solution, respectively.

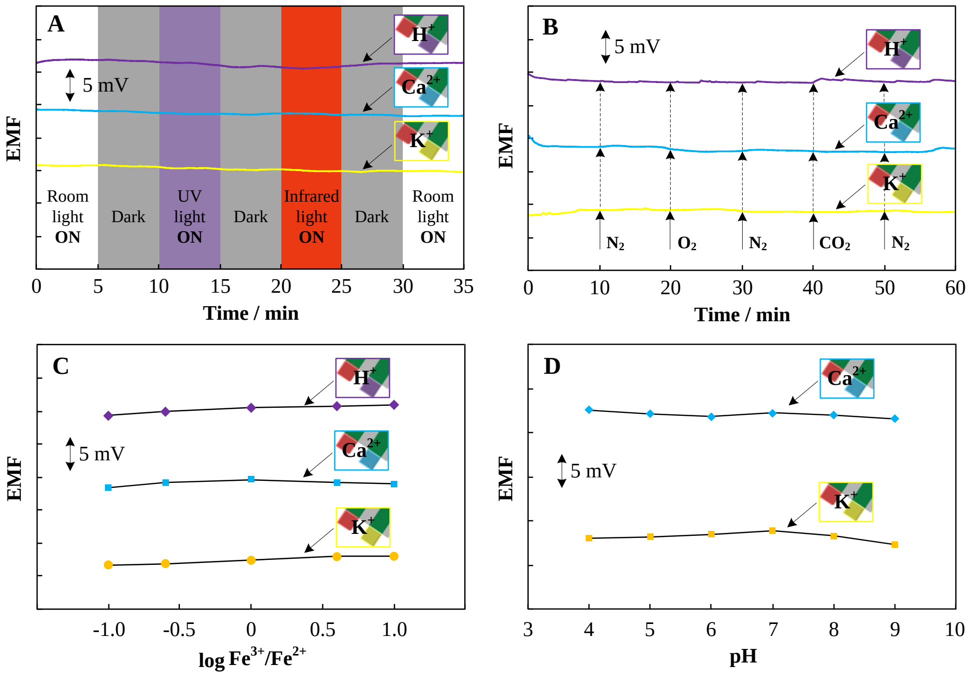

Table S1. Solution resistance (R_s), charge-transfer resistance (R_{ct}), and electronic contact resistance (R_e) obtained at GNPE in KCl solutions with different concentrations

electrolyte solution	R_e (Ω)[a]	R_{ct} (Ω)	R_s (Ω)[b]
0.01 M KCl	3.5 ± 0.3	33.6 ± 1.5	72.3 ± 1.8
0.05 M KCl	3.5 ± 0.2	10.3 ± 0.5	20.8 ± 0.7
0.1 M KCl	3.5 ± 0.3	8.6 ± 0.4	9.7 ± 0.3

[a] R_e was obtained by a multimeter.

[b] R_s was obtained by subtracting the sum (obtained from Nyquist plot) with R_e.

Table S2. Warburg resistance (Z_W) and interfacial constant phase element (CPE_I) obtained at GNPE in different electrolytes

electrolyte solution	Z_W[a]	CPE_I	
		Y_0[b]	n[c]
0.01 M KCl	0.0021	0.0019	0.7352
0.1 M KCl	0.04	0.0046	0.9736
0.01 M NaCl	0.0016	0.0047	0.6782
0.1 M NaCl	0.02	0.0103	0.8241
0.01 M LiCl	0.0019	0.0073	0.6394
0.1 M LiCl	0.03	0.0263	0.8163
0.01 M $NaClO_4$	0.0008	0.0022	0.6977
0.1 M $NaClO_4$	0.02	0.0096	0.8723

[a] Values for the Warburg resistance are given as $S \cdot s^{0.5}$ / cm^2. [b] Values of Y_0 are given as $S \cdot s^n$ / cm^2. [c] Adimensional.

Table S3. Analytical performance of the GNPE-based ISEs

Parameters	GNPE/K-ISM	GNPE/Ca-ISM	GNPE/H-ISM
sensitivity	59.0 ± 0.8 mV/decade	29.0 ± 0.4 mV/decade	59.0 ± 0.9 mV/decade
linear range	$10^{-5.8} - 10^{-1.0}$ M	$10^{-5.6} - 10^{-1.6}$ M	$10^{-9.8} - 10^{-3.9}$ M
detection limit	$10^{-6.0}$ M	$10^{-5.9}$ M	–
response time	12 − 35 s	15 − 38 s	10 – 40 s
standard potential (E^0)	403 ± 18 mV	209 ± 21 mV	467 ± 16 mV
intermediate term (20 h)	0.93 mV h^{-1}	1.18 mV h^{-1}	1.09 mV h^{-1}

Table S4. Selectivity Coefficients for K^+ ($\log K_{Kj}^{pot}$), Ca^{2+} ($\log K_{Caj}^{pot}$), and H^+ ($\log K_{Hj}^{pot}$) compared to the ones obtained at the ISEs using GN as transducer and GCE as substrate

ion *j*	GNPE/K-ISM	GCE/GN/K-ISM
Li^+	−3.1 ± 0.3	−3.5 ± 0.2
Na^+	−3.8 ± 0.4	−4.5 ± 0.3
Mg^{2+}	−4.2 ± 0.3	−4.4 ± 0.3
Ca^{2+}	−3.6 ± 0.3	−3.2 ± 0.2
NH_4^+	−2.3 ± 0.2	−2.1 ± 0.2
ion *j*	GNPE/Ca^{2+}-ISM	GCE/GN/Ca^{2+}-ISM
Li^+	−2.8 ± 0.3	−2.5 ± 0.3
Na^+	−3.1 ± 0.2	−2.8 ± 0.2
K^+	−2.6 ± 0.4	−2.4 ± 0.3
Mg^{2+}	−4.2 ± 0.4	−4.7 ± 0.4
NH_4^+	−2.9 ± 0.3	−3.2 ± 0.4
ion *j*	GNPE/H^+-ISM	GCE/GN/H^+-ISM
Li^+	−9.8 ± 0.6	−10.1 ± 0.5
Na^+	−10.3 ± 0.2	−10.2 ± 0.3
K^+	−10.2 ± 0.3	−9.9 ± 0.6
Mg^{2+}	−10.1 ± 0.2	−10.6 ± 0.3
Ca^{2+}	−9.9 ± 0.4	−9.7 ± 0.2
NH_4^+	−9.6 ± 0.2	−9.2 ± 0.1

Notes and references

1 J. F. Ping, Y. X. Wang, J. Wu and Y. B. Ying, *Electrochem. Commun.*, 2011, 13, 1529−1532.

2 J. F. Ping, Y. X. Wang, Y. B. Ying and J. Wu, *Anal. Chem.*, 2012, 84, 3473−3479.

3 M. Novell, M. Parrilla, G. A. Crespo, F. X. Rius and F. J. Andrade, *Anal. Chem.*, 2012, 84, 4695−4702.