Supplementary Information

An Ion-Selective Chemiresistive Platform as Demonstrated for the Detection of Nitrogen Species in Water

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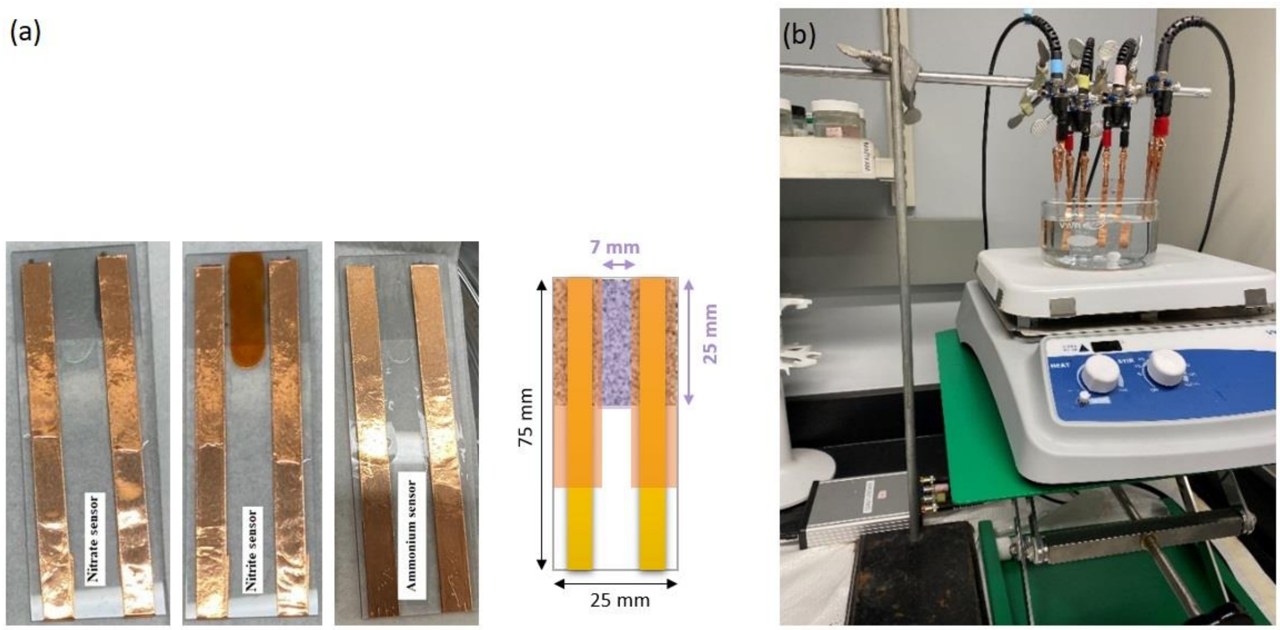
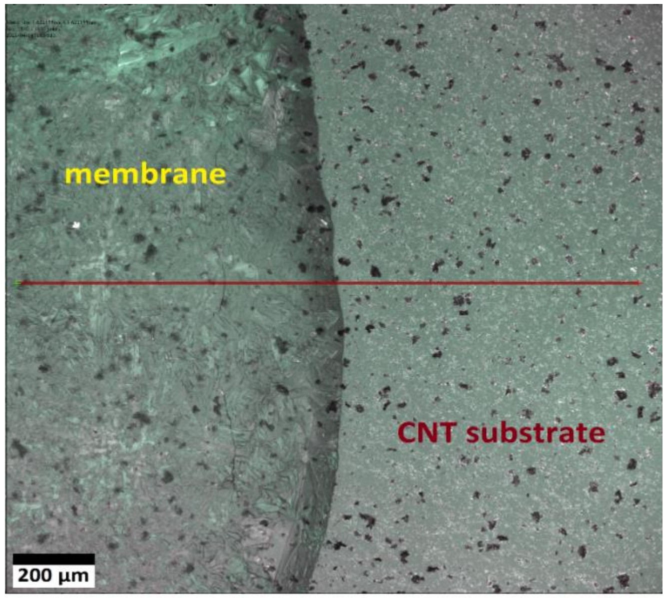


Figure S1. a) Images and dimensions of the fabricated sensors: nitrate sensor, nitrite sensor, ammonium sensor (from left to right). b) Experiment set-up: Installed sensors connected to an eDAQ device in a bowl of background solution which is constantly stirring on a stirrer and an adjustable support stand.



Height Step

	Angle / °	Distance / µm
Height Step 1	0.049992	38.716314

Figure S1. Measured membrane thickness of the fabricated sensor by Alicona Microscopy, distance between CNT substrate and membrane (Scale bar: 200 µm).

Table S1. Resistance table of the fabricated sensors in this study

	$R_{cured\ CNT\text{-}TPM}$ (kΩ)	$R_{Cu\ contacts}$ (kΩ)	R_{PDMS} (kΩ)	$R_{membrane}$ (kΩ)	$R_{conditioning}$ (kΩ)
Nitrate sensor (range)	**12.0-19.0**	**12.0-19.0**	**14.0-22.0**	**19.0-28.0**	**24.0-39.0**
Sensor 1	15.3	14.5	16.8	22.5	35.4
Sensor 2	12.6	12.1	14.3	19.4	24.3
Sensor 3	18.4	18.1	21.7	27.6	38.2
Sensor 4 (blank)	13.4	13.2	15.0	21.6	35.5
Nitrite sensor (range)	**13.0-19.0**	**12.0-18.0**	**14.0-22.0**	**18.0-27.0**	**25.0-43.0**
Sensor 1	13.4	12.9	14.4	17.8	25.0
Sensor 2	18.2	18.0	21.3	26.5	42.2
Sensor 3	15.5	15.4	18.2	24.4	38.7
Sensor 4 (blank)	17.1	16.5	18.7	22.9	36.2
Ammonium sensor (range)	**11.0-18.0**	**11.0-18.0**	**13.0-20.0**	**17.0-30.0**	**27.0-47.0**
Sensor 1	11.2	11.1	13.2	17.1	27.0
Sensor 2	14.2	13.9	14.5	18.3	28.8
Sensor 3	17.5	17.6	19.3	29.2	46.3

Sensor 4 (blank)	16.6	16.3	17.9	24.5	38.2

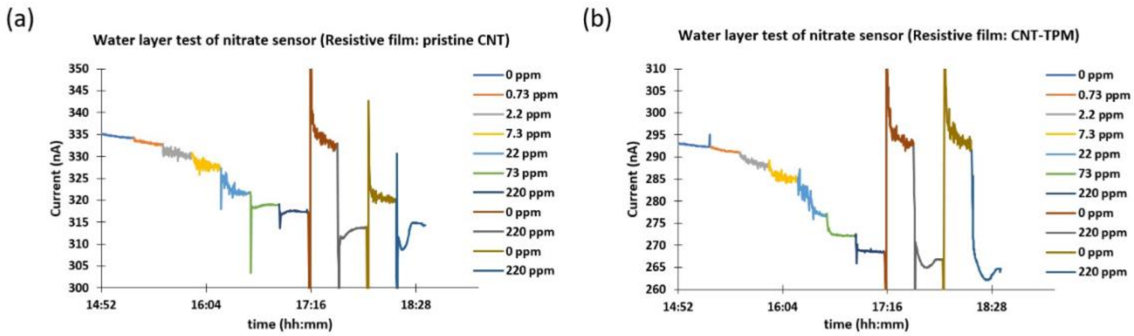


Figure S3. Water layer test. Sensor performance comparison between a) non-modified surface and b) optimized TPM modified surface.

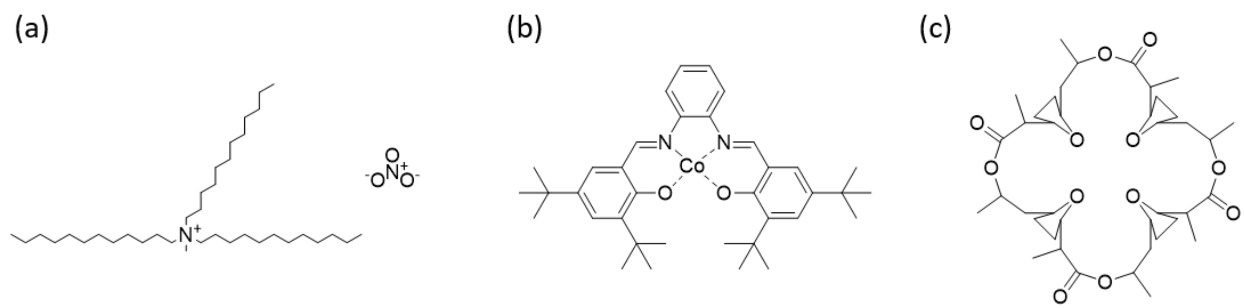


Figure S4. Ionophores structures. a) Nitrate ionophore: Tridodecylmethylammonium nitrate (TDMAN), b) Nitrite ionophore: Cobalt (II) tert-butyl salophen, C) Ammonium ionophore: Nonactin.

Table S2. Fitting parameters for calibration curves of each developed sensor.

Sensor	*Fitted equation*	*A*	*B (ppm^{-1})*	*m (ppm^{-1})*	*n*	*R^2*
Nitrate	Langmuir	14.1	0.06	-	-	0.99
Nitrite	Langmuir	28.6	0.19	-	-	0.98
Ammonium	Freundlich	-	-	6.7	4.5	0.95

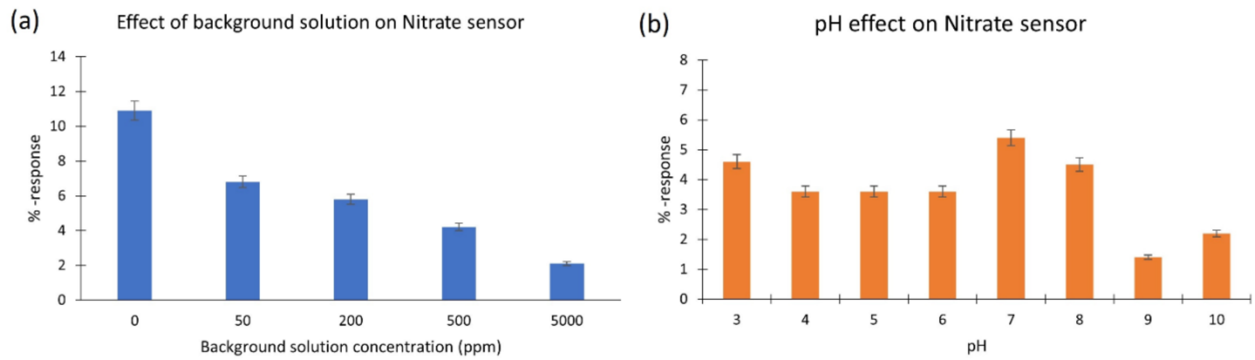


Figure S5. Effect of pH and background solution concentration on response of the nitrate sensor. 10 ppm of nitrate solution was added in all measurements, average response of three sensors.

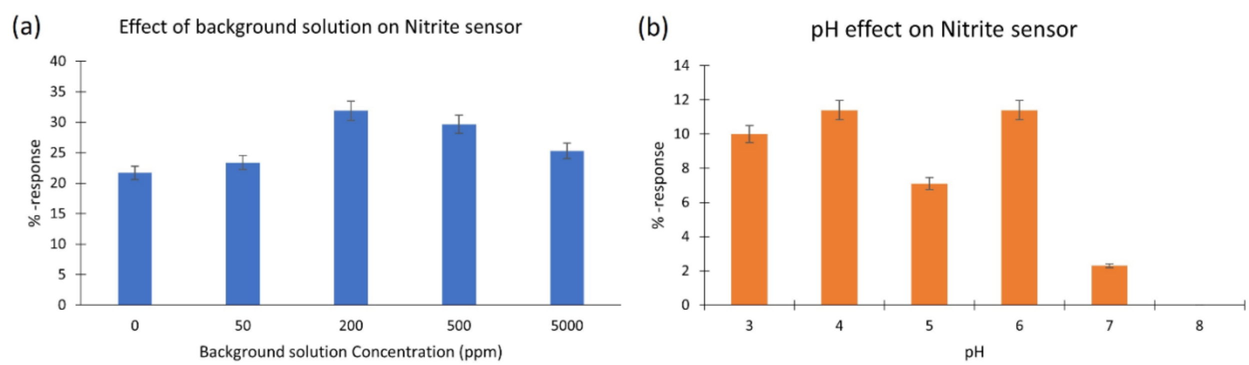
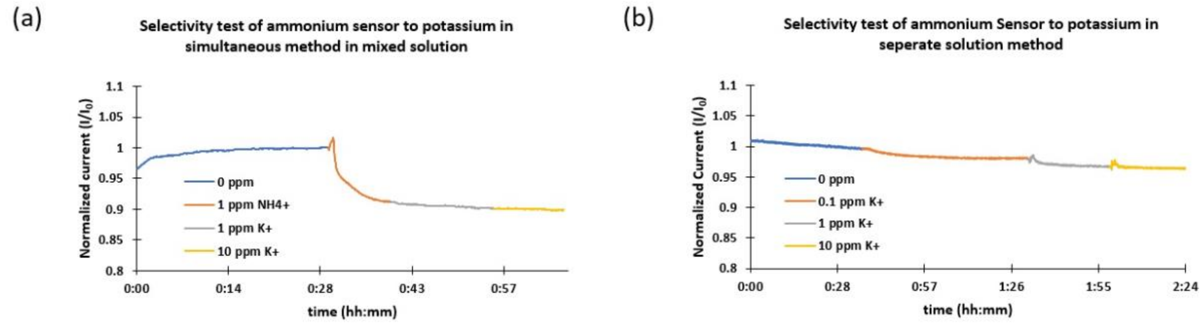
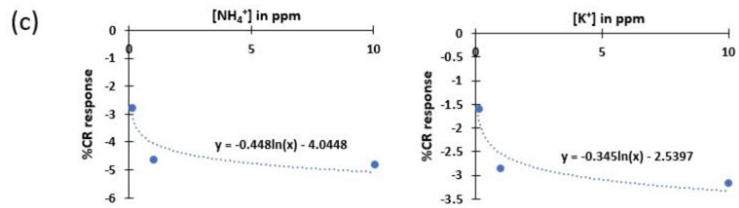
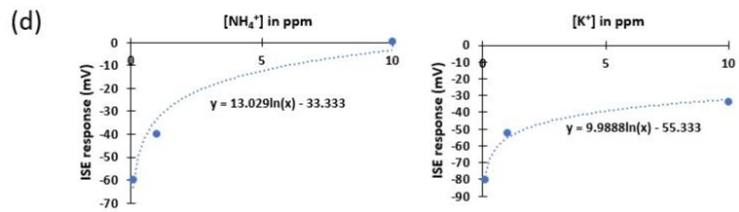


Figure S6. Effect of pH and background solution concentration on response of the nitrite sensor. 10 ppm of nitrite solution was added in all measurements, average response of three sensors.





%CR response	$[NH_4^+]$ in ppm	$[K^+]$ in ppm	$[K^+]/[NH_4^+]$
-2.73	0.053	1.74	32.83018868
-4.6	3.45	392.24	113.6927536
-4.8	5.4	700.36	129.6962963



ISE response (mV)	$[NH_4^+]$ in ppm	$[K^+]$ in ppm	$[K^+]/[NH_4^+]$
-61.02	0.13	0.62	4.7692308
-40.1	0.6	4.66	7.7666667
0.04	12.9	254.6	19.736434

Figure S7. Investigation of potassium interference on the developed ammonium-selective chemiresistive sensor. a) potassium interference in presence of ammonium ions in solution, b) potassium interference in absence of ammonium in solution, c) Comparison of chemiresistive response of ammonium sensor to ammonium ions and potassium ions at different concentrations by plotting their calibration curves d) Comparison of potentiometric response of ammonium sensor to ammonium ions and potassium ions at different concentrations by plotting their calibration curves.

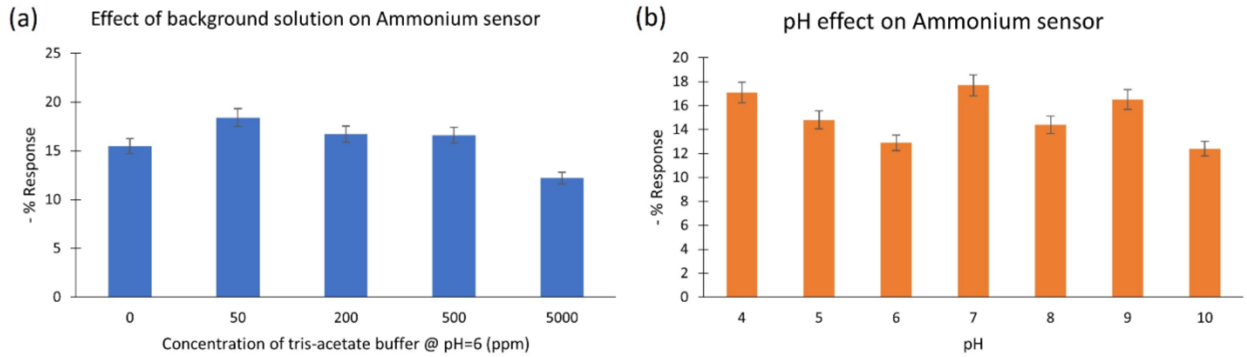


Figure S8. Effect of pH and background solution concentration on response of the ammonium sensor. 10 ppm of ammonium solution was added in all measurements, average response of three sensors.

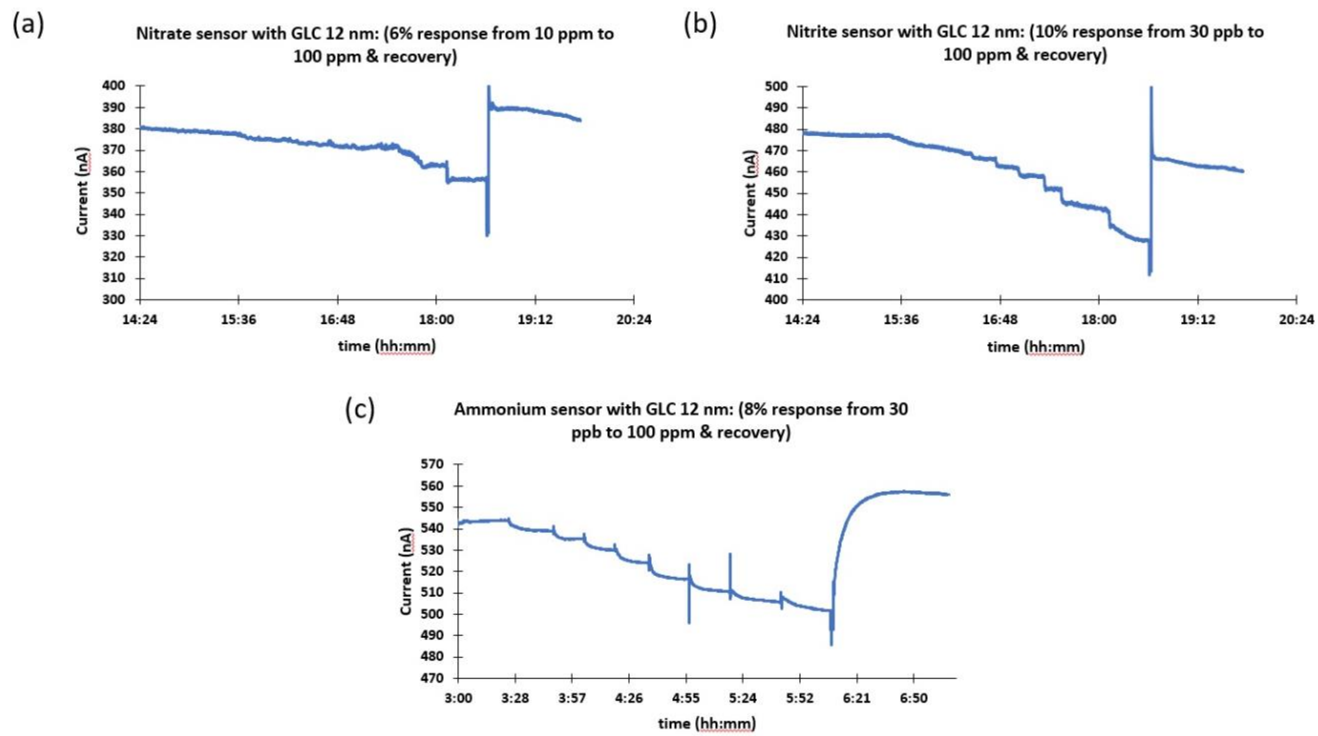


Figure S9. Responses of (a) nitrate, (b) nitrite and (c) ammonium sensors made of GLC sheets (thickness 12 nm). The sensors showed reversible responses with less sensitivity compared to CNT.

Table S3. Fabrication cost breakdown per sensor

Materials	Cost per sensor
Glass slide	50¢
Pencil 9B	<1¢
Carbon nanotube (CNT)	10¢
3-(Trimethoxysilyl)propyl methacrylate (TMP)	<1¢
Methanol	<1¢
Copper tape	20¢
PDMS	<1¢
Ionophore	30¢-40¢
Plasticizer	<1¢
PVC	<1¢
THF	<1¢
Total	**<$1.3**

Protocol for testing nitrate with Orion Aquamate 8000, UV-Vis spectrophotometer using the zinc reduction method

The detection range of the protocol used was 1-40 mg/L nitrate ion. Therefore, the samples with nitrate values higher than the upper limit were diluted using DI water. The reagent vial was filled with the 10 ml of the sample and the blank was measured. Nitrate no. 1 tablet was added and crushed followed by nitrate no. 2 tablet. Once, both the tablets were dissolved, the sample was incubated for 10 minutes, and measurement was performed.

Protocol for testing nitrite with Orion Aquamate 8000, UV-Vis spectrophotometer using the N-(1-Naphthyl)-ethylenediamine method

The measuring range of the protocol used was 0.01-0.5 mg/L nitrogen concentration. Therefore, the samples with nitrogen values higher than the upper limit were diluted using DI water. The reagent vial was filled with the 10 ml of the sample and the blank was measured. Nitrite tablet was added and crushed. Once the tablet was dissolved, the sample was incubated for 10 minutes, and measurement was performed.

Protocol for testing ammonium with Orion Aquamate 8000, UV-Vis spectrophotometer using the Indophenol Blue method

The measuring range of the protocol used was 0.02-1 mg/L nitrogen concentration. Therefore, the samples with nitrogen values higher than the upper limit were diluted using DI water. The reagent vial was filled with 10 ml of sample, and the blank was measured. Ammonium no. 1 tablet was added and crushed followed by ammonium no. 2 tablet. Once both the tablets were dissolved, the sample was incubated for 10 minutes, and the measurement was performed.

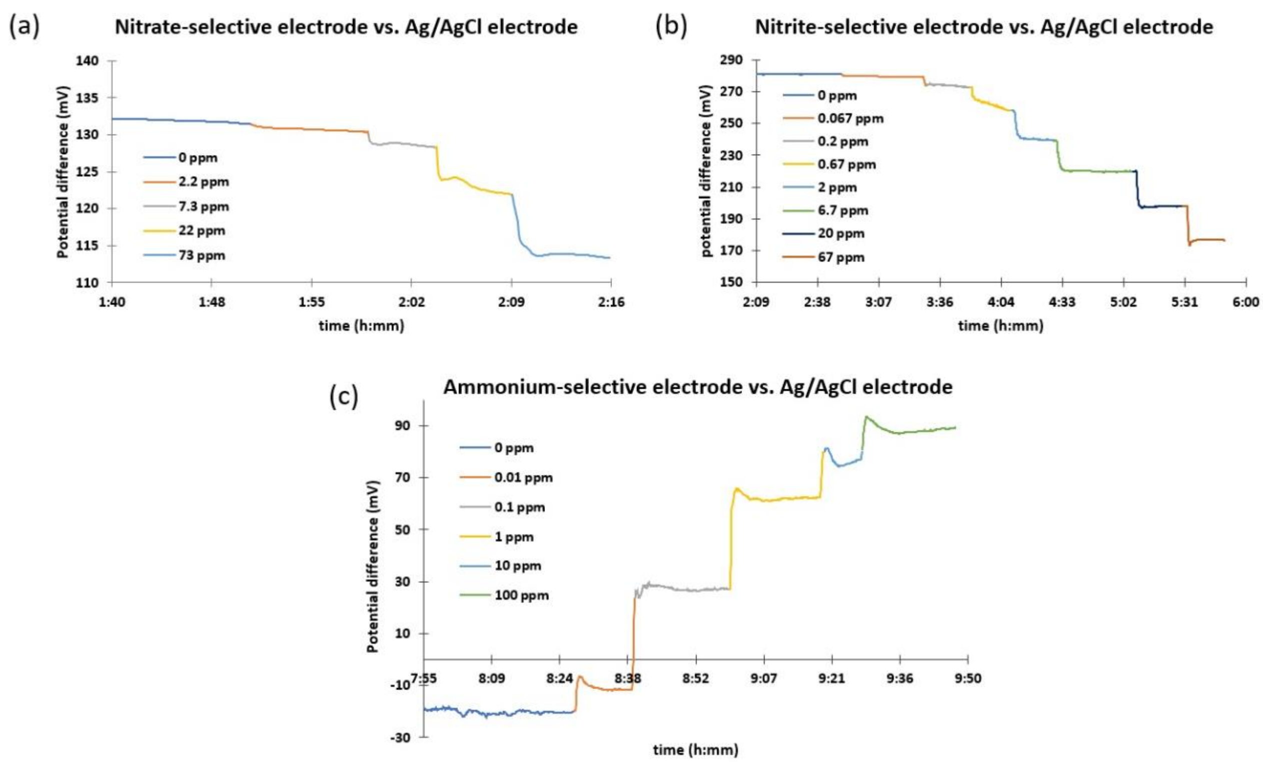


Figure S10. Potentiometric responses of (a) nitrate, (b) nitrite and (c) ammonium sensors when they used as ion-selective electrodes vs. a reference electrode.