Supplementary Material

Real-time *in situ* monitoring of nitrogen dynamics in wastewater treatment processes using wireless, solid-state, and ion-selective membrane (S-ISM) sensors

Yuankai Huang[1], Tianbao Wang[1], Zhiheng Xu[1], Emma Hughes[1], Fengyu Qian[2], Meredith Lee[1], Yingzheng Fan[1], Yu Lei[3], Christian Brückner[4], Baikun Li[1*]

[1] Department of Civil and Environmental Engineering, University of Connecticut, Storrs, Connecticut 06269, United States

[2] Department of Electrical and Computer Engineering, University of Connecticut, Storrs, Connecticut 06269, United States

[3] Department of Chemical and Biomolecular Engineering, University of Connecticut, Storrs, Connecticut 06269, United States

[4] Department of Chemistry, University of Connecticut, Storrs, Connecticut 06269, United States

(*corresponding author: baikun.li@uconn.edu; Phone: 860-486-2339)

Number of pages: 25

Number of tables: 2

Number of figures: 15

Table of Content

Fabrication procedures of gold ink:

Chemicals Required:

3.0 g Tetraoctyl ammonium bromide

0.864 g $AuCl_3.3H_2O$

0.76 g of Sodium borohydride ($NaBH_4$)

87.6 μL 1-Dodecane thiol

30 - 40 mL of Ethanol

160 mL of Toluene

RO water as needed

Procedure:

1. Clean all glassware with toluene and/or water before using and performing synthesis.

Set up a 500 mL clean round bottom flask with a magnetic stir bar and place above a magnetic stir plate.

2. To the flask add 160 mL of toluene and 3.0 g of tetraoctyl ammonium bromide and mix well.

3. Dissolve 0.864 g of $AuCl_3.3H_2O$ in 35.0 mL of water and add to the flask. Rinse the beaker with up to 5 mL water and also add to the flask.

4. Stir for 10 mins making sure that the two layers are mixing.

5. Remove the bottom aqueous layer - it should be clear. Use a pasture pipette or a thin-stem separating funnel only.

6. Add 87.6 μL of 1-dodecane thiol and stir for another 10 mins.

7. Weigh out 0.76 g of $NaBH_4$ in a beaker. Just before 10 min stirring is up, add 40 mL of water to dissolve it and immediately add the solution to the flask. Rinse the beaker with another 10 mL of water and add it to the flask.

8. Stir for 3 hours without bumping.

9. After reaction is complete, stop stirring and remove the bottom aqueous layer.

10. Rinse with 20-30 mL of water 3 times, removing the aqueous layer each time.

11. Rotavap off the solution under reduced pressure at 50 °C until all toluene is removed.

12. Add 30 mL of ethanol to the flask and sonicate briefly (few seconds).

13. Filter the nanoparticle solution through a frit. Rinse the particles with 30 mL of ethanol and 150 mL of water.

14. Let the particles air-dry on the frit for a day. Wrap the funnel in aluminum foil to reduce exposure to light.

To make printing ink:

Weigh out gold nanoparticles (Do not scrape the frit).

Dissolve in toluene (density = 0.867 g/mL) for concentration of 100 mg/mL.

Silver nanoparticles ink (SunTronic® Silver, Sigma-Aldrich) was used as silver ink.

Fabrication procedures of sensor arrays:

First, the gold nanoparticle ink was printed onto the Kapton film by ink-jet printer. Then the sensor arrays were heated to 200 °C for 3 min until the color of the gold layer lightened. Then the sensor arrays were rinsed with DI water and aligned before printing the silver layer. Finally the sensor arrays were heated to 150 °C for 10 min or until the color of the silver layer lightened.

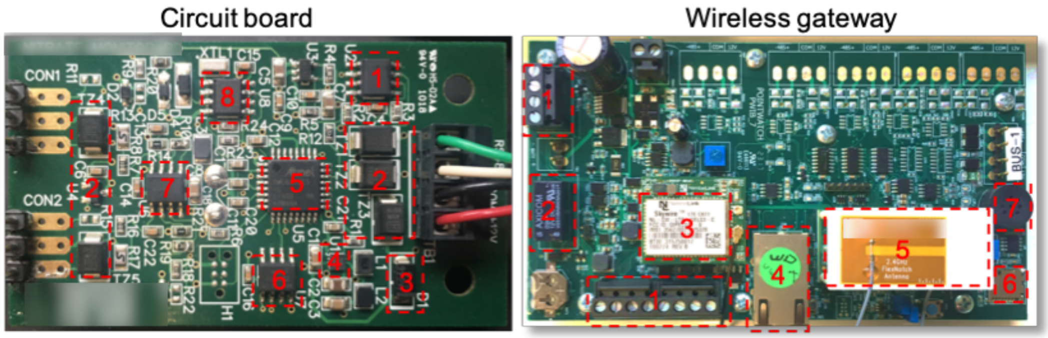

Figure S1 Details of the circuit board (left) and the wireless gateway (right) of the wireless S-ISM sensor assembly for 7-day field tests. (The circuit board: 1-Over voltage fault survivor; 2-Five diodes for circuit protection; 3-General-purpose rectifier; 4-Temperature sensor; 5-Microcontroller unit; 6-Flash memory; 7- Operational amplifier; 8- Clock & calendar unit. The wireless gateway: 1-General purpose input/output (GPIO) pots; 2-Backup battery; 3-Cellular transceiver; 4-Ethernet interface; 5-Portable computer with wireless service; 6-SD card; 7-Speaker).

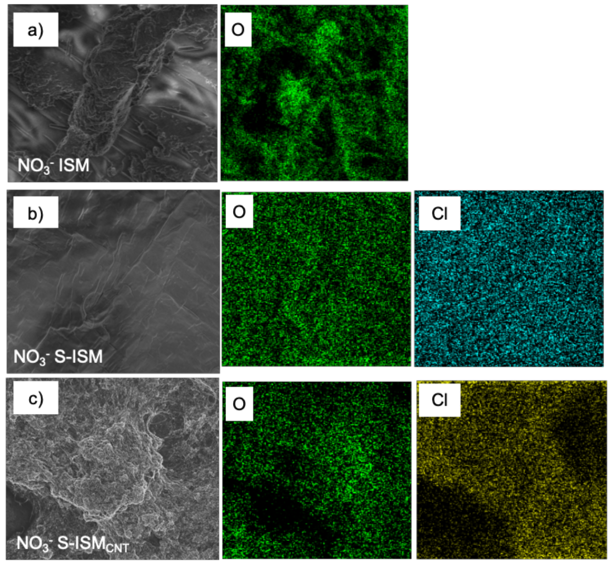

Figure S2 Enhancement of NO3- ISM by mixing with PVC to form S-ISM and mixing with PVC and CNT to form S-ISMCNT. a) The scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS) images of NO_3^- ISM (ionophore), atomic percentage (at. %) - C: 81.97, O: 15.28; b) The SEM and EDS images of S-ISM (ionophore mixed with PVC), atomic percentage (at. %) - C: 87.20, O: 11.13, Cl: 1.15; c) The SEM and EDS images of S-ISM_{CNT} (ionophore mixed with PVC and CNT), atomic percentage (at. %) - C: 84.05, O: 2.37, Cl: 0.86.

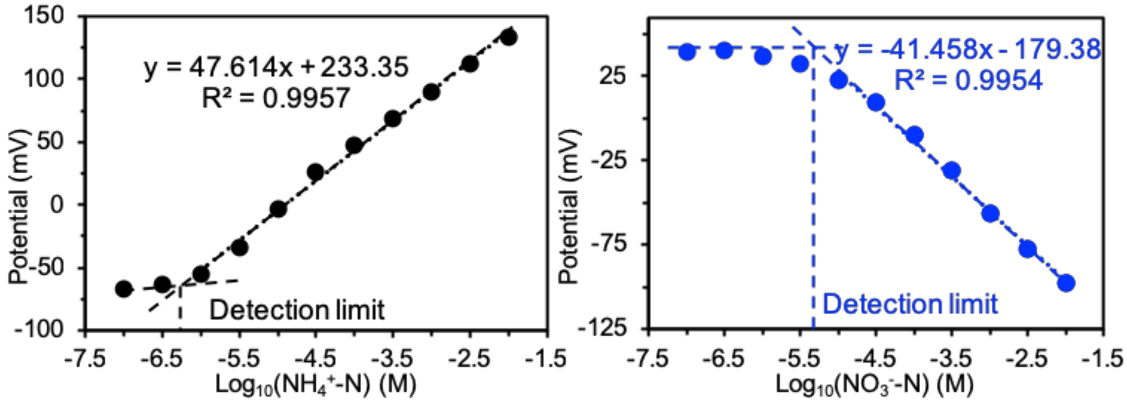

Figure S3 The detection limit (sensitivity) test for NH_4^+ and NO_3^- S-ISM sensors.

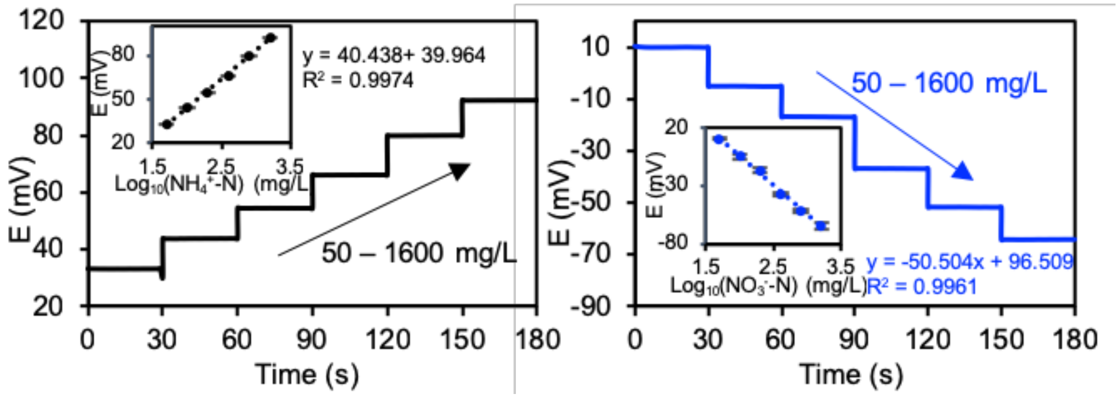

Figure S4 Calibration curves of NH_4^+ and NO_3^- S-ISM sensors from 50 to 1600 mg N/L.

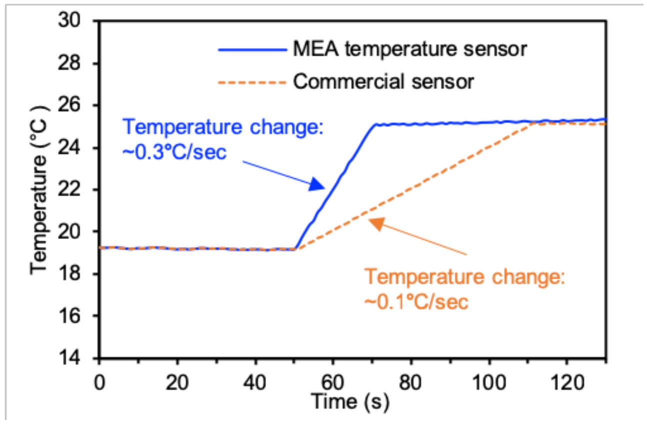

Figure S5 Comparison between a mm-sized temperature solid-state sensor and a commercial nitrogen sensor under temperature shocks.

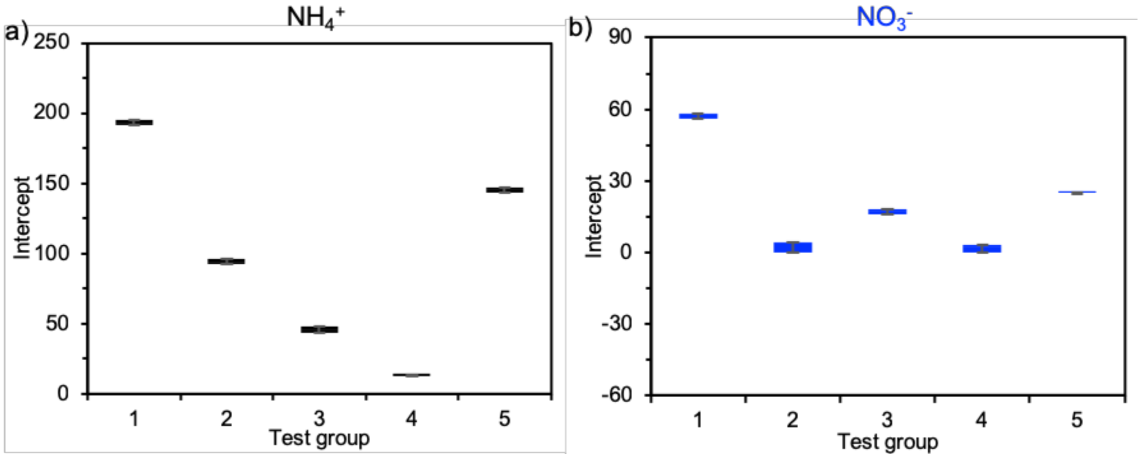

Figure S6 Intercept of calibration curves for five pieces of nitrogen S-ISM sensors (Left: NH_4^+ S-ISM sensors; Right: NO_3^- S-ISM sensors).

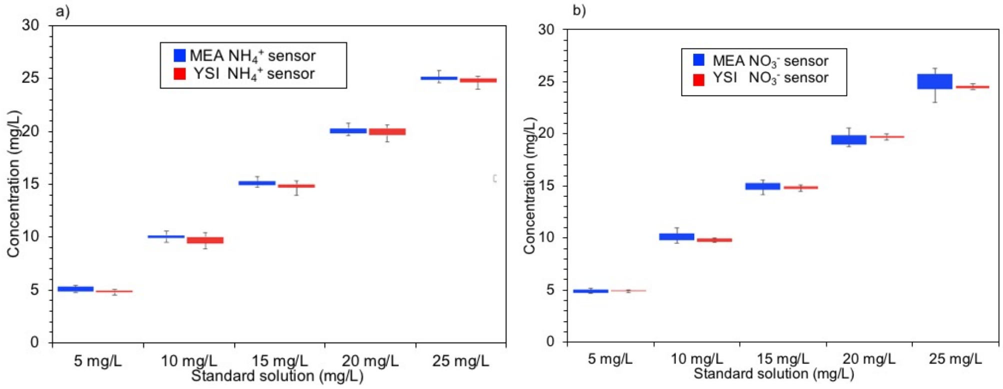

Figure S7 Comparison of nitrogen S-ISM sensors with commercial sensors at five different concentrations (5, 10, 15, 20 and 25 mg-N/L). a) NH_4^+ S-ISM sensor (Two-way analysis P value: 0.133, 0.125, 0.145, 0.451 and 0.265 for five pieces of S-ISM sensors. T-test P value: 0.134, 0.163, 0.0354, 0.150 and 0.0836 between S-ISM sensors and commercial sensors); b) NO_3^- S-ISM sensor (Two-way analysis P value: 0.125, 0.103, 0.590, 0.385 and 0.409 for five pieces of S-ISM sensors. T-test P value: 0.291, 0.101, 0.147, 0.294 and 0.070 between S-ISM sensors and commercial sensors).

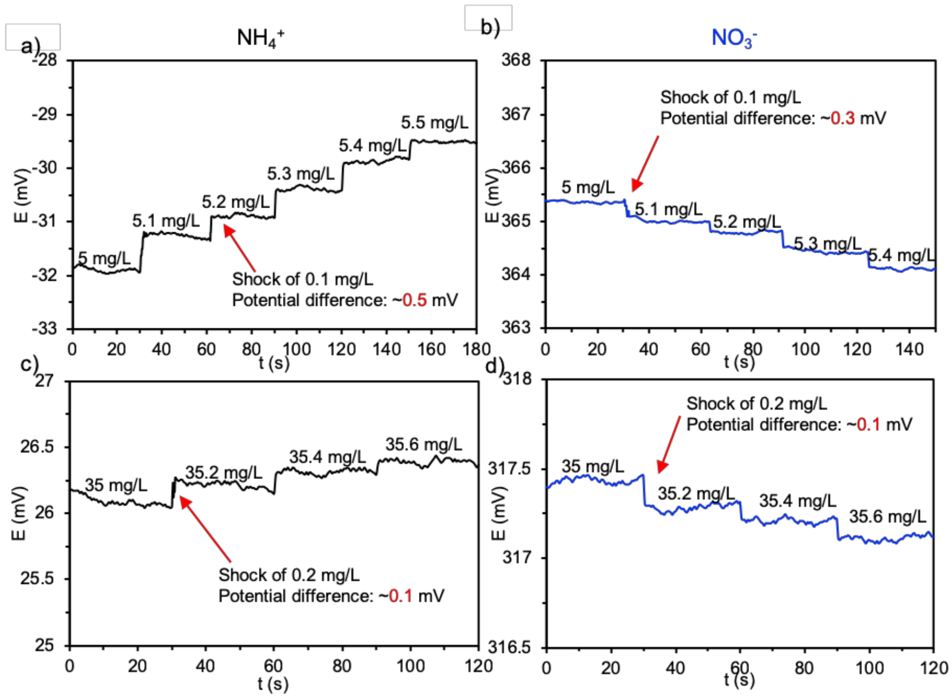

Figure S8 Resolution test of nitrogen S-ISM sensors at low (5 mg-N/L) and high (35 mg-N/L) concentrations. a) and b) the readings of the NH_4^+ and NO_3^- S-ISM sensors at low concentration; c) and d) the readings of the NH_4^+ and NO_3^- S-ISM sensors in high concentration.

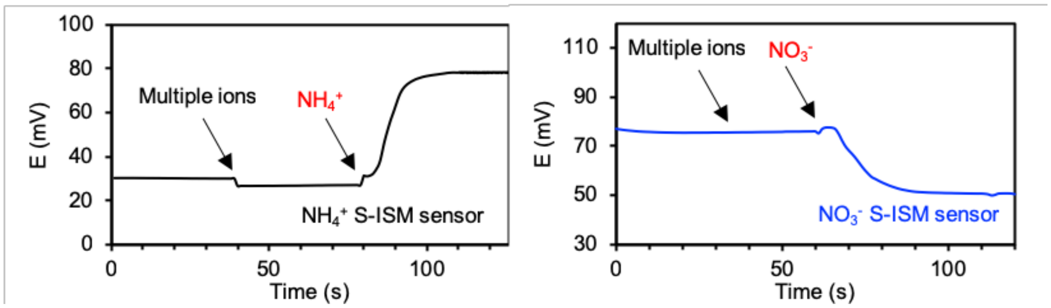

Figure S9 Selectivity tests of the nitrogen S-ISM sensors: shock tests using interference ions (added the ions simultaneously) and targeted ions for the nitrogen S-ISM sensors.

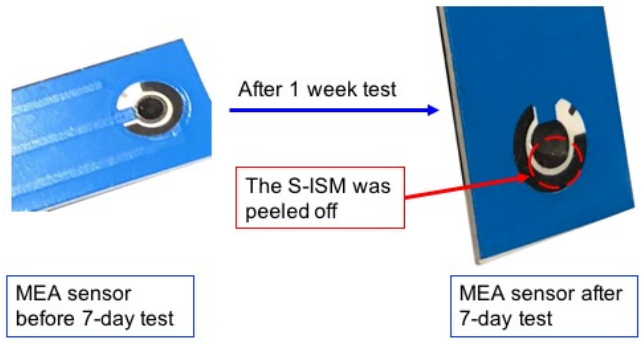

Figure S10 The S-ISM on the working electrode of a NO_3^- S-ISM sensor after submerged in real wastewater for 7 days.

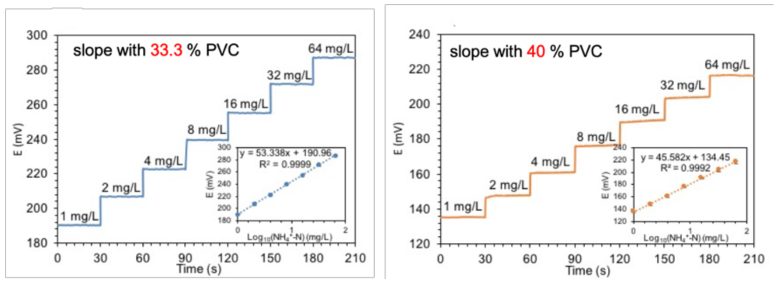

Figure S11 The comparison of sensitivities of NH_4^+ S-ISM sensors with the PVC ration of 33.3 % and 40 %.

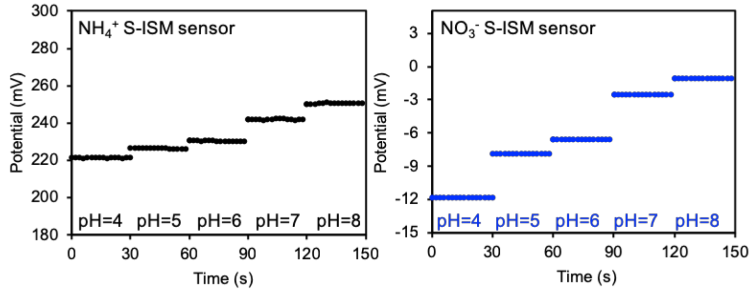

Figure S12 The pH interference at 20 mg N/L for nitrogen S-ISM sensors.

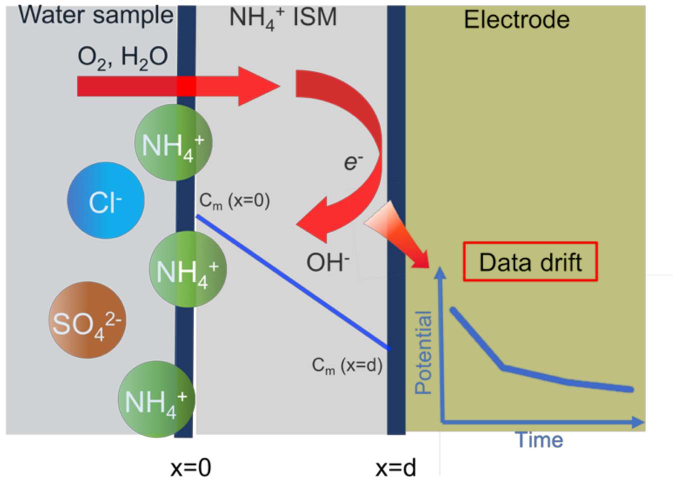

Figure S13 Schematic diagram of data drifting on the surface of a NH_4^+ S-ISM sensor.

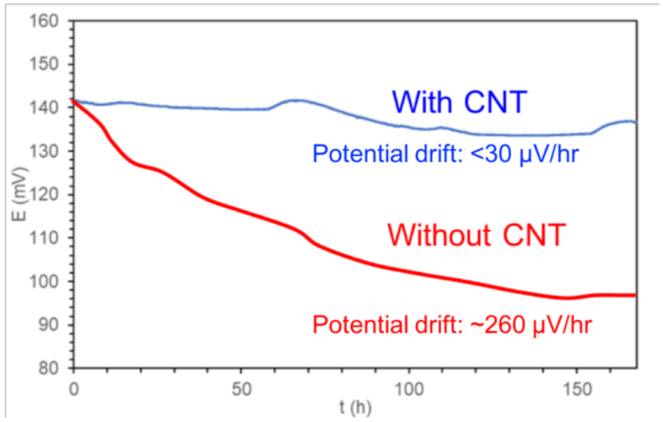

Figure S14 Alleviation of data drifting using a NH_4^+ S-ISM_{CNT} sensor.

Table S1 Comparison of energy consumption and nitrogen discharge in a wastewater treatment plant (WWTP) with and without wireless nitrogen sensing technology.

	With wireless monitor (real-time data access and proactive control)	Without wireless monitor (assumable 2-hr delay in data access and control)
Annual energy consumption in normal wastewater treatment status	5.86×10^{6} kWh	7.82×10^{6} kWh
Annual ammonium discharge in violent condition	5526.7 kg	7105.0 kg

Assumptions for energy consumption:

1) The treatment capacity of a WWTP: 2 million gallon per day ≈ 7.57×10^{6} L per day;
2) The electricity consumption for the wireless nitrogen monitoring system: 0.5 kWh;
3) The electricity consumption for the WWTP under normal operational status: 10 kBtu/gallon wastewater;
4) Real-time monitoring, control and adjustment for the WWTP with wireless nitrogen sensing technology;
5) Occurrence of lag-time monitoring, control and adjustment for the WWTP without wireless sensing technology: once per day.
6) Duration of electricity over-consumption in the WWTP without wireless nitrogen sensing technology: two-hour delay in response and operation per day.
7) Electricity over-consumption for the WWTP without wireless nitrogen sensing technology under normal operational status : 50 kBtu/gallon wastewater;

Calculation for energy consumption:

1) The electricity consumption for the WWTP with wireless monitor under normal status: the electricity consumption for the WWTP operation + the electricity consumption for the wireless nitrogen monitoring system = 10 kBtu/gallon × 2,000,000 gallon + 0.5 kWh = 2.93 kWh/gallon × 2,000,000 gallon+ 0.5 kWh ≈ 5.86×10^6 kWh.
2) The electricity consumption for the WWTP without wireless monitoring under normal status: the electricity consumption for the WWTP operation (22 hours per day) + the unnecessary electricity consumption (2 hours per day) = 10 kBtu/gallon × 2,000,000 gallon × 22/24 + 50 kBtu/gallon × 2,000,000 gallon × 2/24 = 2.93 kWh/gallon × 2,000,000 gallon × 22/24 + 14.65 kWh/gallon × 2,000,000 gallon × 2/24 ≈ 7.82×10^6 kWh.

Assumptions for nitrogen discharge:

1) The treatment capacity of a WWTP: 2 million gallon per day ≈ 7.57×10^6 L per day;
2) The ammonium concentration in the effluent discharge under normal status: 2 mg/L;
3) The ammonium concentration in the effluent discharge under violation: 50 mg/L;
4) Occurrence of nitrogen violation in effluent discharge for a WWTP: once per week.
5) Prompt capture of effluent violation for the WWTP with wireless nitrogen sensing technology;
6) Duration of effluent violation for the WWTP without wireless nitrogen sensing technology: Two-hour delay in response and operation per week to solve the effluent discharge violation.

Calculation for nitrogen discharge:

1) The annual ammonium discharge for a WWTP with wireless sensing technology under discharge violation: the amount of normal ammonium discharge during the whole week (168 hours per week) = 2 mg/L × 7.57×10^6 L/day × 365 day ≈ 5.5267×10^9 mg = 5526.7 kg.

2) The annual ammonium discharge for a WWTP without wireless sensing technology: the amount of normal ammonium discharge (166 hours per week) + the amount of violent ammonium discharge (2 hours per week) = 2 mg/L × 7.57×10^6 L/day × 365 day × 166/168 + 50 mg/L × 7.57×10^6 L/day × 365 day × 2/168 ≈ 7.1050×10^9 mg = 7105.0 kg.

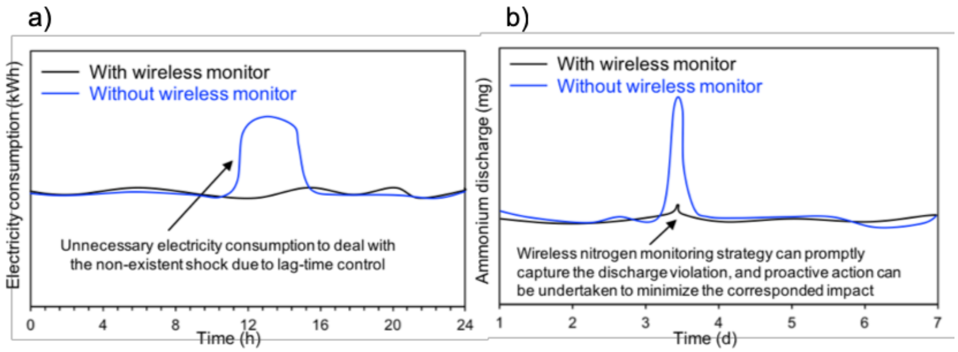

Figure S15 a) Comparison of energy consumption between a WWTP with wireless nitrogen sensing technology capable of real-time control and adjustment and the one without wireless nitrogen sensing technology causing 2-hr energy overconsumption due to lag-time control; b) Comparison of nitrogen discharge between a WWTP with wireless nitrogen sensing technology capable of promptly capturing effluent violation and the one without wireless nitrogen sensing technology causing 2-hr delay to solve effluent violation.

Table S2 The cost analysis for S-ISM and commercial nitrogen sensors.

Cost for each MEA sensor / $	Film	Nanoparticle ink	Circuit board (connect 4 sensors)	Gateway (connect 12 sensors)	Total
MEA S-ISM sensor	0.02	0.2	10	30	40.22
Cost for each commercial sensor / $	Multiparameter meter		Wires	Sensors	
Commercial sensor	1200		200	300	1700