Wireless Networked Sensors in Water for Heavy Metal Detection

2018 Crosscutting Research Project Review

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U.S. DEPARTMENT OF ENERGY

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Outline

1. Program Overview
2. Technologies
3. Technical Results
   - Initial results
   - Recent results
4. Summary

Program Objective

Objective: Develop wireless networked sensors using conformal nanomembrane based chemical field effect transistors (ChemFET) for heavy metal detection in water for energy sector.

Electrostatic self-assembly (ESA) + conformal nanomembrane ChemFET + wireless sensor network
→ *in situ* environmental monitoring

Key Expectations:

- Heavy metal selectivity: RCRA 8s (arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver)
- Heavy metal ion sensitivity: <0.01 ppm, with minimal cross-sensitivities
- Sensor element size: <(100 micron)^2
- Dynamic range: >40dB
- Frequency response: DC to >10kHz
- Operating temperature: -40°C to 100°C
- Multiplexing capability: >100 individual sensor elements
- Power supply: Battery or integrated energy harvesting device
- Transmission band: 2.4 GHz, IEEE 802.15.4 protocol; BLE protocol
- Packaging options: Patch, Conformal, Portable, and Flowable
- Operation mode: wake-up, measurement, data transfer, and low-power stand-by

Nano-CS Integrated RCRA 8 Sensor Probe

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Opportunity for Wireless Sensors for Heavy Metal Detection

To allow efficient monitoring of heavy metal levels for environmental surveillance in water for fossil energy sector, a precise, mobile and highly sensitive/selective/re-usable measuring instrument is required.

- ❑ Conventional chemical concentration sensing is typically done by taking soil or water samples on-site and transporting them back to a laboratory for analysis, or hand-carrying a sensor unit around an area and making, recording and mapping data.
- ❑ Multiple sensor devices can be configured in a small, lightweight and low cost array to analyze multiple sensor targets simultaneously. It can be used as an in-situ sensor attachable for permanent installation or portable inspection in a field.
- ❑ Such systems can be used to
  - detect and map multiple environmentally-hazardous chemical concentrations,
  - locate sources of pollution from analysis of concentration gradients, and
  - identify chemical concentrations potentially harmful to people and/or destructive to industry/agriculture.

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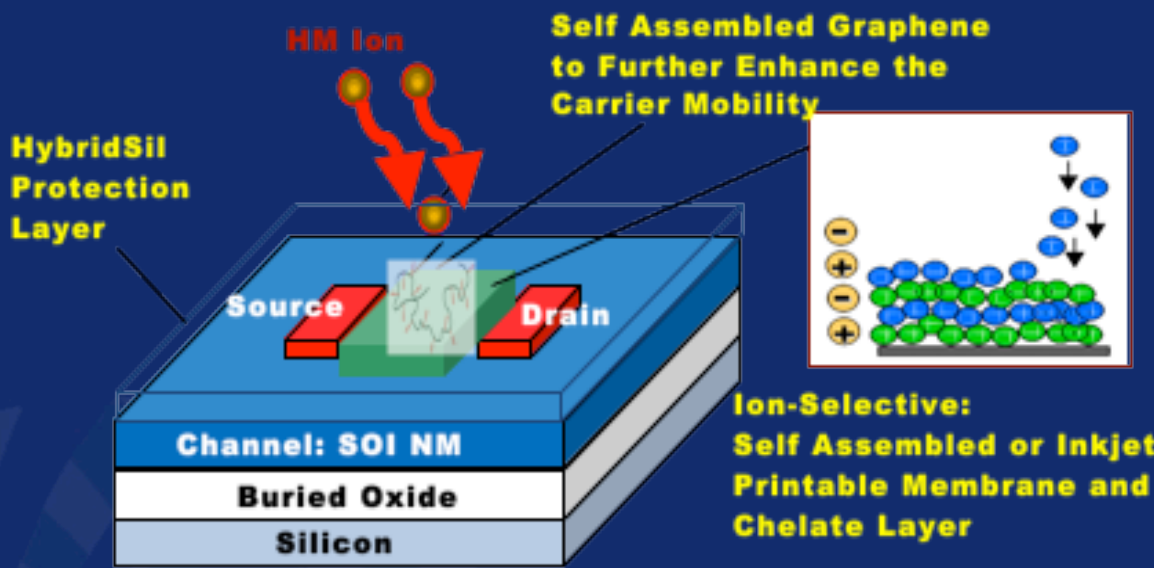
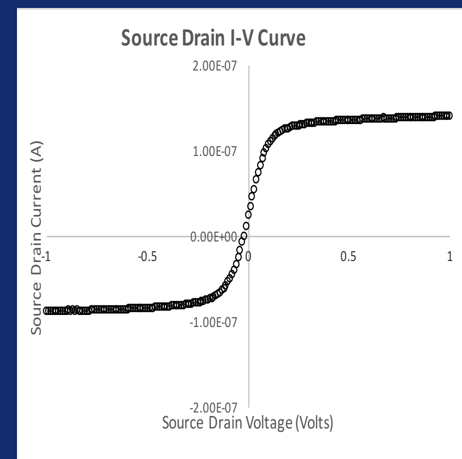
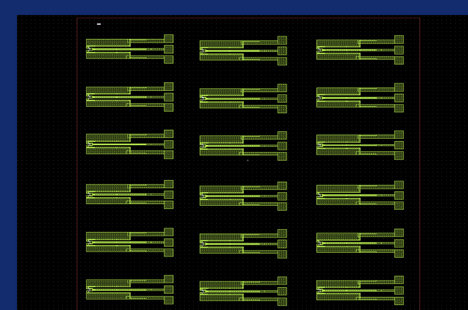
Nanomembrane ChemFET Sensor Configuration



Silicon NM Channel Processed from SOI Wafer



I-V characteristics of ChemFET

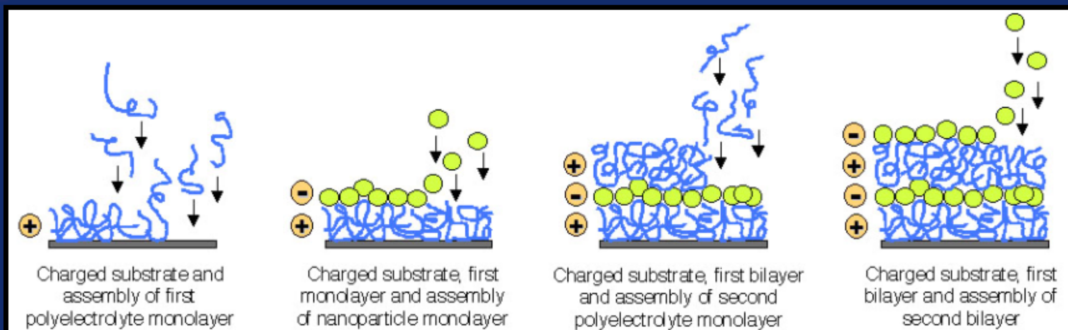


Mask Design

- ❑ High Carrier Mobility
- ❑ High Sensitivity
- ❑ High Selectivity

- ❑ Ultralightweight
- ❑ Ultraflexibility
- ❑ Array Configuration

Electrostatic Self-Assembly



Self Assembly Process:
- polymer/polymer
- polymer/particle
- particle/particle

- Conformal, homogeneous molecular layer by layer process
- Precise nanoscale control over thickness
- Excellent long-term environmental robustness
- Environmentally-friendly process
- Multifunction – conductors, polymers, semiconductors, ceramics

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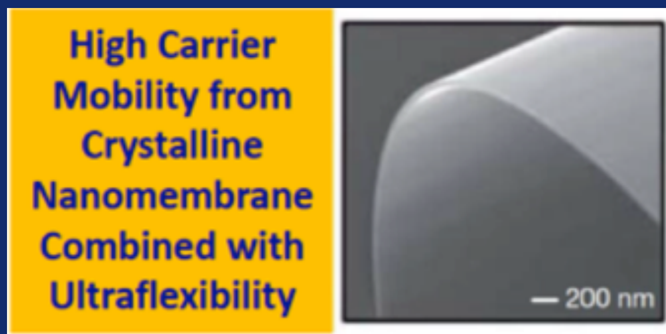
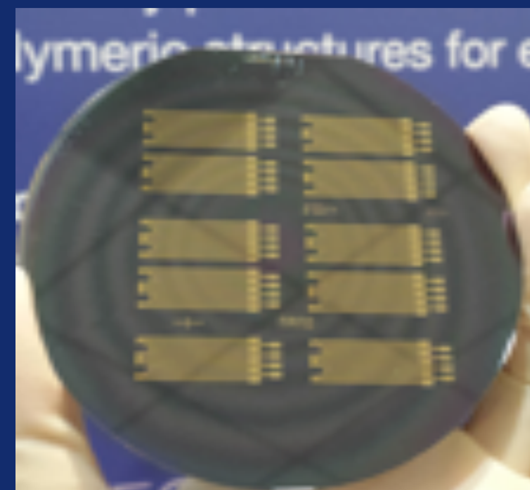
Partial Library of Demonstrated ESA Material Functions

Material Properties	Precursors	Measured Properties	Comments
Chemical Detection	Semiconductor nanocrystals	Chemical Sensitivity and Selectivity	Surface modification on nanocrsytals
Electrical Conductivity	Noble metal nanoclusters (Ag, Cu, Au, Pt)	0.1 – 1.0 Ω•m 10^{-4} Ω•cm	Mechanically flexible, optically transparent
Refractive Index	Polymers and polymer / nanocluster combinations	n = 1.2 to 1.8	Tailored Transparent stacks
Young's Modulus	Noble metal nanoclusters (Ag, Cu, Au, Pt), Carbon nanotubes	0.1 MPa – 1.0 Gpa	Mechanically flexible
Thermal conductivity	Polymers and nanoclusters	2 W/mK	20 W/mK feasible based on current work
Mechanical Robustness	Oxide nanoclusters (TiO_2, ZrO_2, Al_2O_3, SiO_2)	Good Taber abrasion and haze results	Nanohardness 1 GPa

Silicon Nanomembrane



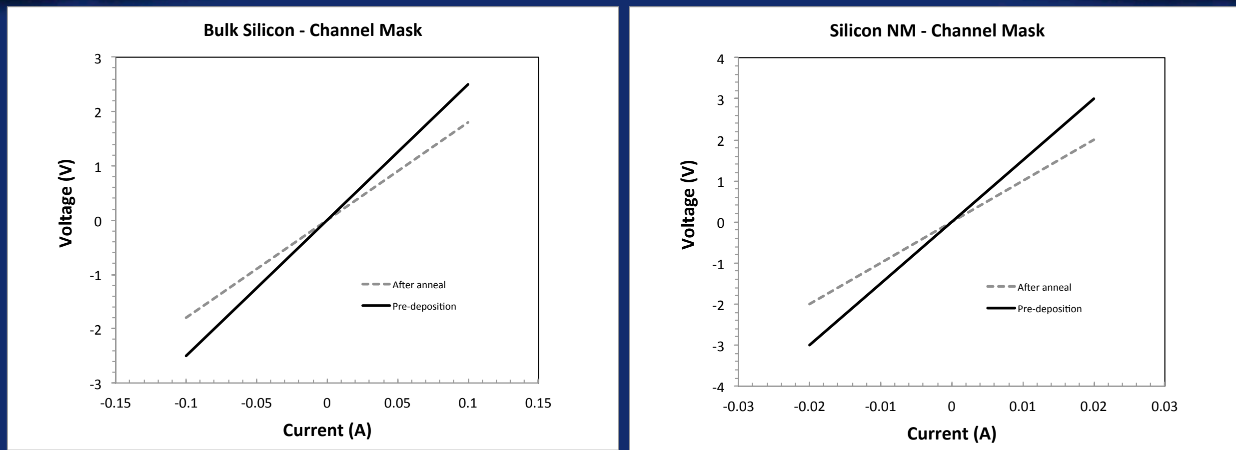
- Thin
- Flexible
- Can be strain engineered
- Transparent
- Transferable
- Bondable
- Stackable
- Conformable
- Patternable (wires, ribbons, tubes)



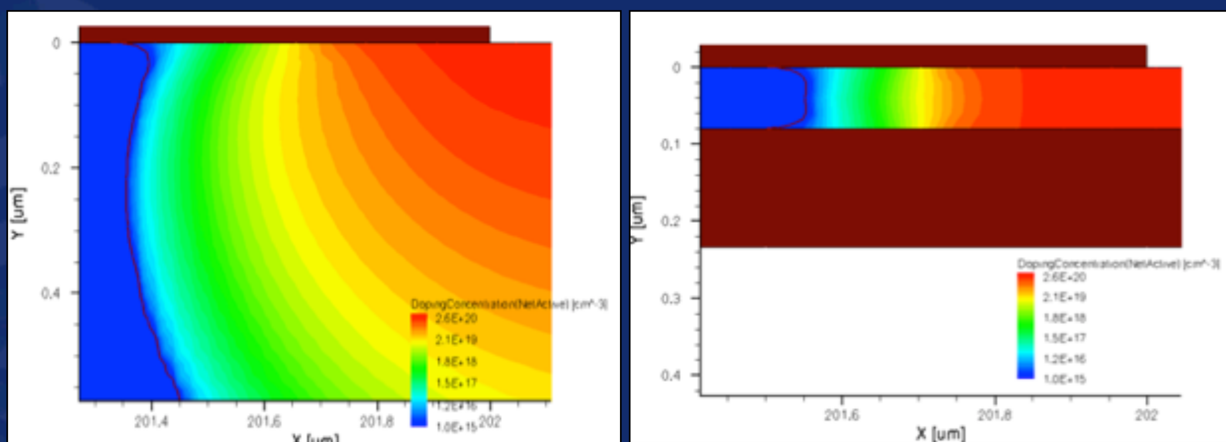
Nanomembrane–based ChemFET sensors

- 1974: Epitaxial $Ga_{1-x}Al_xAs$ (X>0.6) sacrificial layer for separating a $GaAs/Ga_{1-x}Al_xAs$ (x=0.3) from GaAs with HCl etchant
- 1987: Yablonocitch: spin on wax to strain film for efficient release, enable removal of high quality GaAs films as large as $0.8*2mm^2$ and as thin as 80nm
- 2004: Rogers: transferred membranes of Si from silicon-on-insulator (SOI) to fabricate Si flexible thin-film electronics
- 2012: NanoSonic: Si nanomembrane based flexible solar cells
- **2015: NanoSonic: Nanomembraned based ChemFET sensors**

Process Monitoring During Fabrication



I-V characteristics of bulk and nanostructures with oxide mask and channel length of 5 µm, the sensor operates in the linear region



Phosphorus doping profile at the channel-drain side for bulk Si (left) and SOI nanomembranes (right) after source and drain doping. Oxide mask shown in dark red and buried oxide in SOI in dark red

Standard Sensor Packages

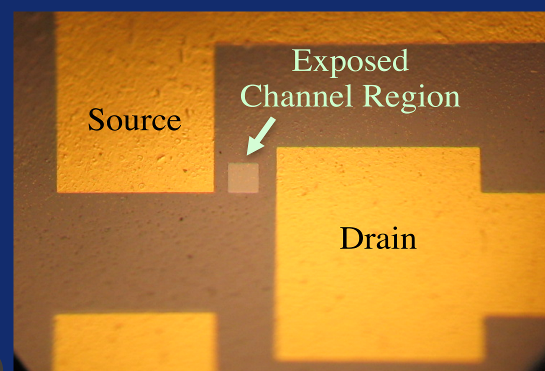
Standard Sensor Package Can be "Flowable" (Left), "Portable" (Center) and "Attachable" (Center Right) for Sensor Applications

Self-Assembly of Gold/Thiol Functionalization Layers


a)


b)

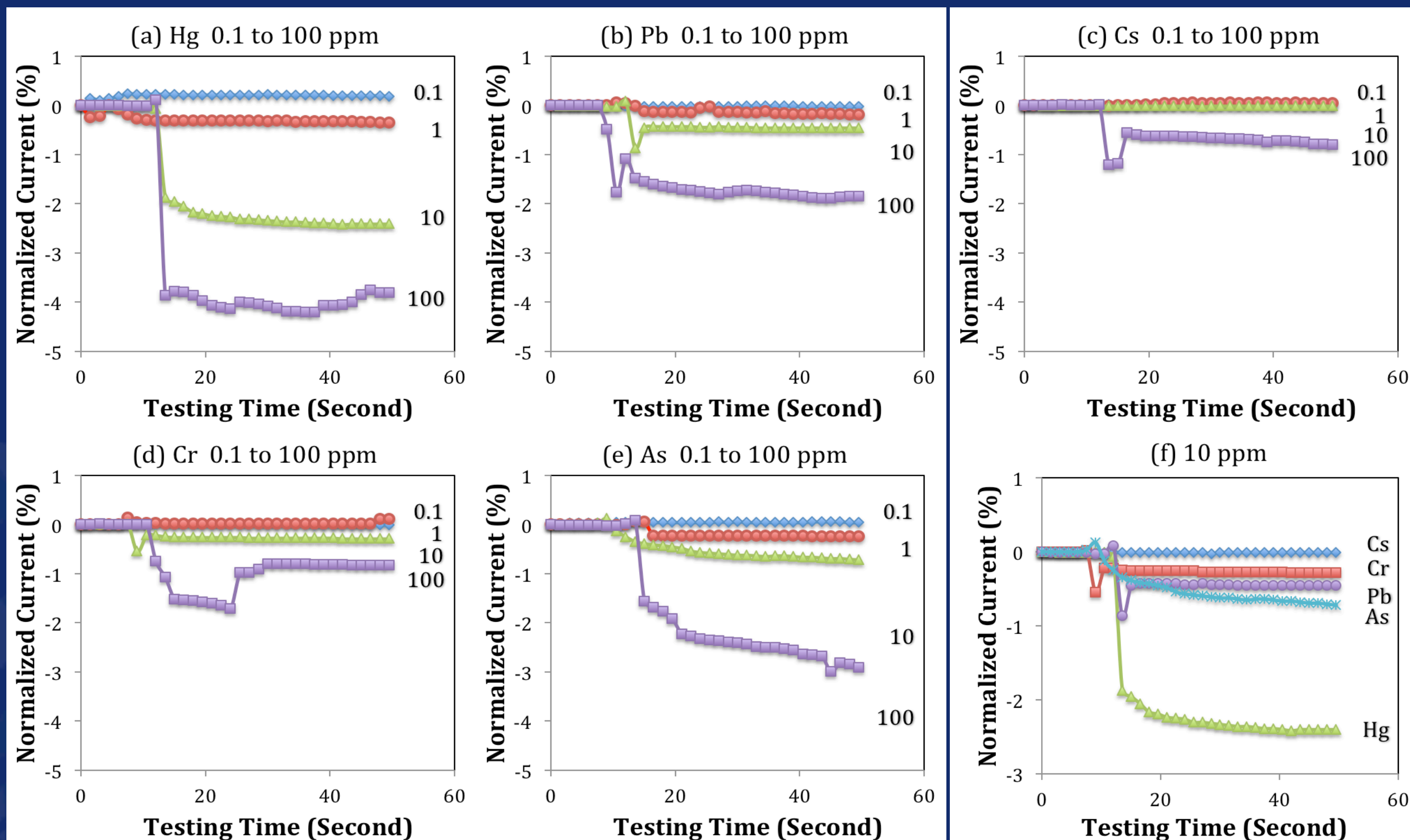

c)



d)

Hand dipping (a, b) and Robot (c) Set Up Used to Self-Assemble the Gold/Thiol Functionalization Layers. (d) Mircophotograph of a Completed Device with 9 Bilayers of Gold Nanoparticles in the 100 um by 100 um Channel Region.

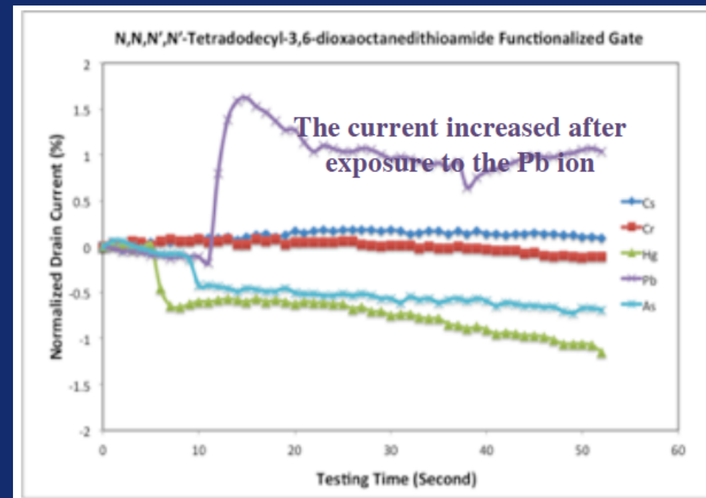
Initial Modification Example #1: Self-Assembled Au and Thioglycolic Acid-Functionalized ChemFET Sensor

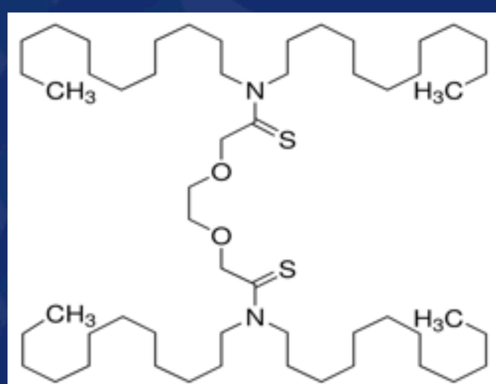


Testing results of the self assembled Au and thioglycolic acid functionalized ChemFET sensor after exposure to different concentrations of (a) Hg, (b) Pb, (c) Cs, (d) Cr, and (e) As ion solutions, as well as (f) different targets with the same concentration of 10ppm. The response for the Hg ion is significantly higher than for other ions.

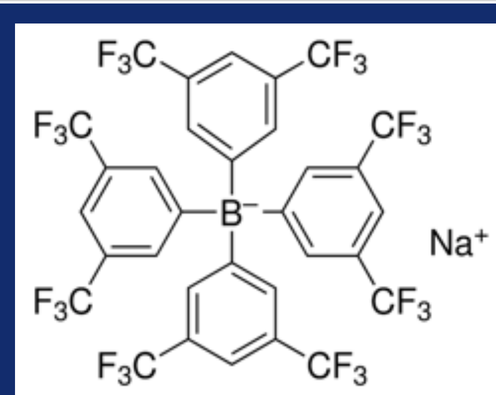
Initial Modification Example #2: : Sensor Modification for Lead Ion Selectivity

Chemical Name	Abbreviation	Wt%
tetrahydrofuran	THF	
polyvinylchloride	PVC	42.1
bis(2-ethylhexyl)sebacate	DOS	54.9
Sodium tetrakis(4-fluorophenyl)borate dihydrate	NaTFPB	0.44
N,N,N′,N′-Tetradodecyl-3,6-dioxaoctanedithioamide	ETH 5435	1.39
Tetrakis(4-chlorophenyl)borate tetradodecylammonium salt	ETH 500	1.15



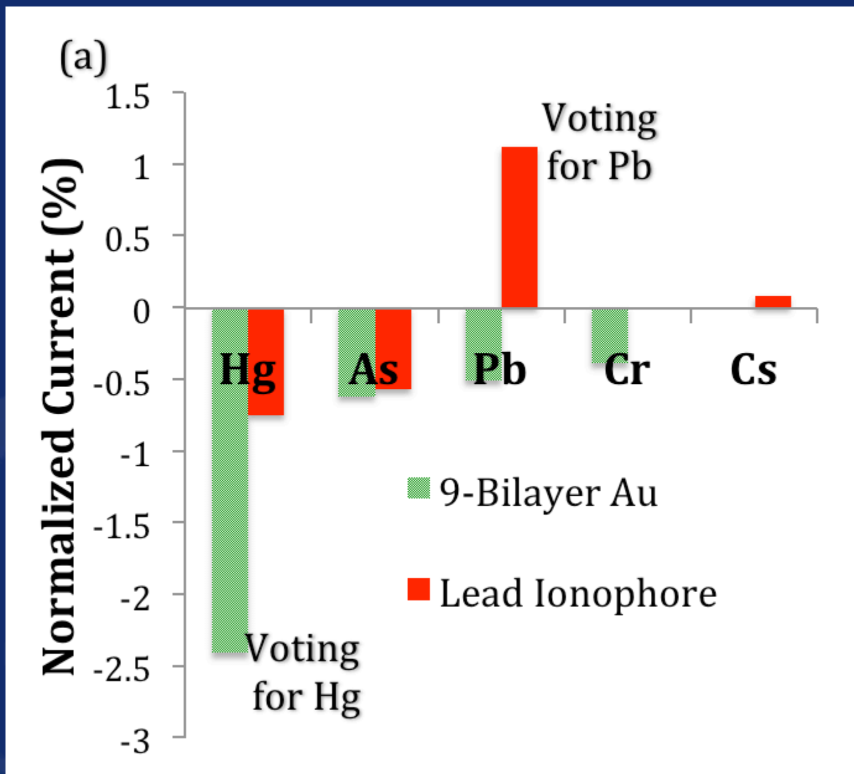


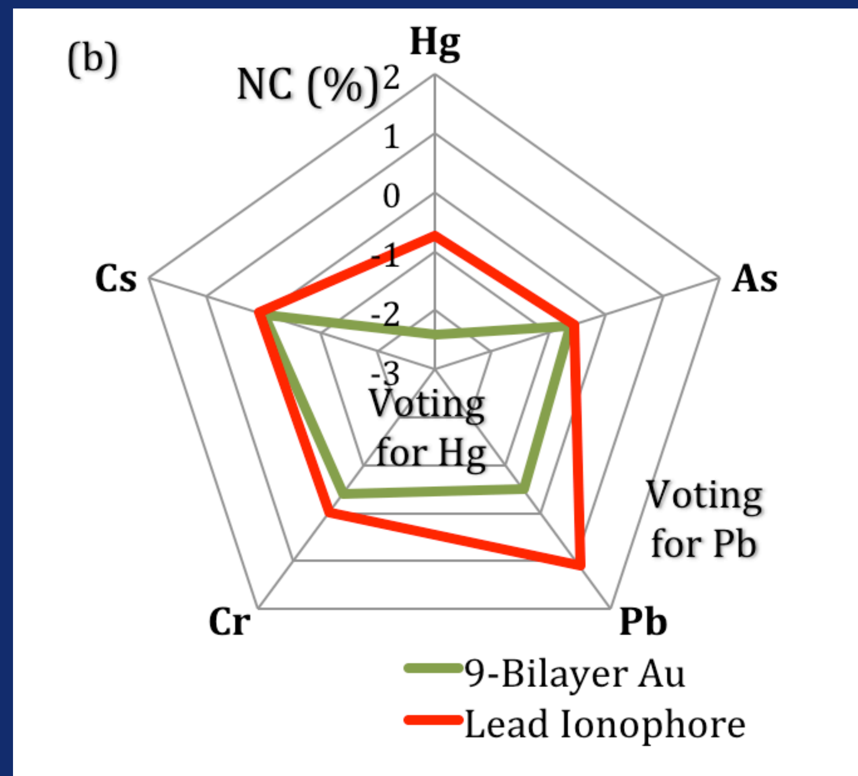
N,N,N′,N′-Tetradodecyl-3,6-dioxaoctanedithioamide



Sodium tetrakis(4-fluorophenyl)borate dihydrate

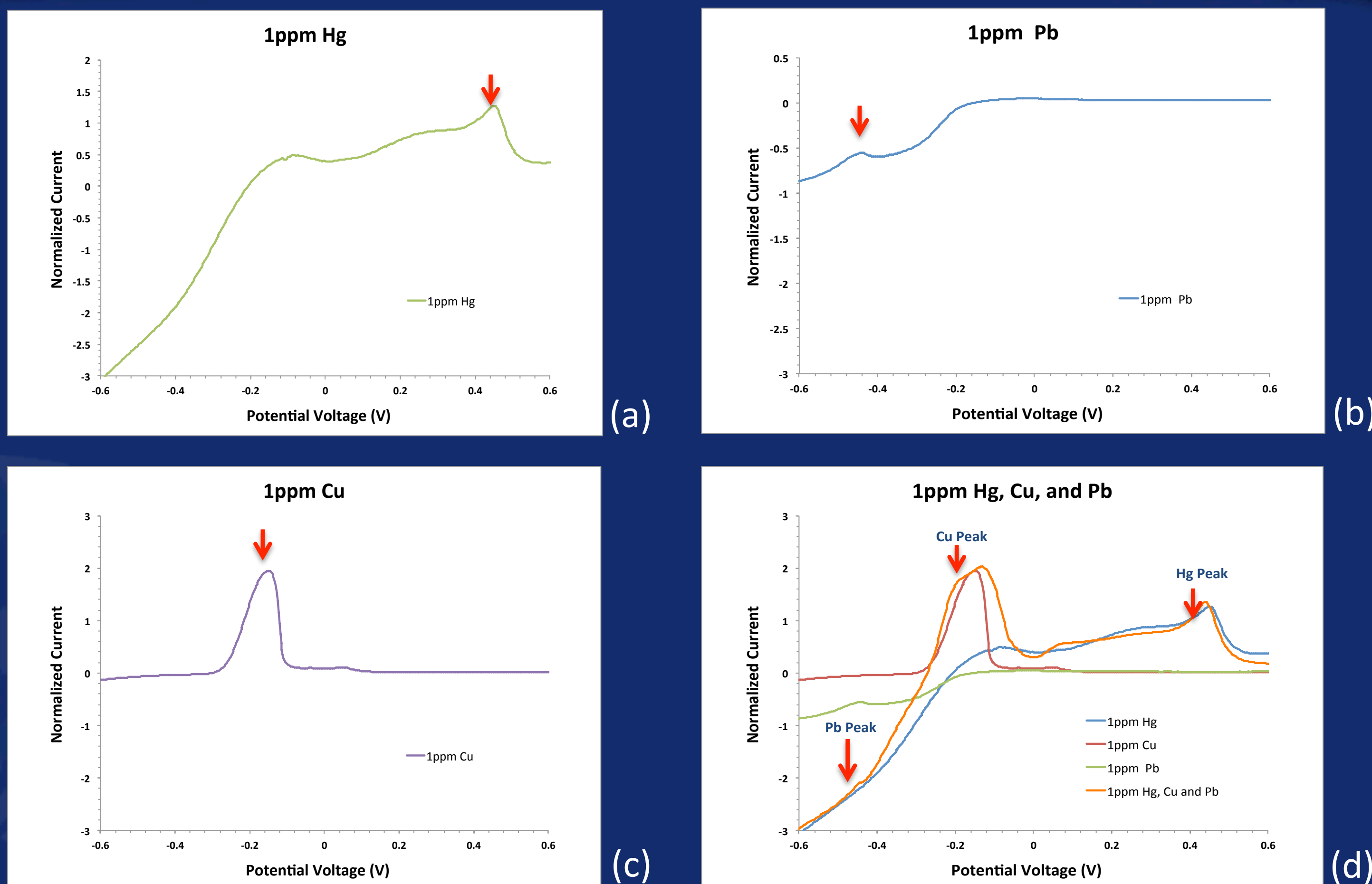
Multi-Target Selectivity Results for Self Assembled Au Sensor and Lead Ionophore Sensor





Cross sensitivity results with Bar Plot (a) and Radar Plot (b) for self assembled Au sensor and Lead ionophore sensor.

Stripping Voltammetry Enhanced ChemFET Sensor – Mixed Solution



Testing results of the stripping voltammetry enhanced ChemFET sensor with self assembled Au for 1ppm Hg (a), 1ppm Pb (b) and 1ppm Cu (c) and mixed solution of all three ions at 1ppm (d) respectively.

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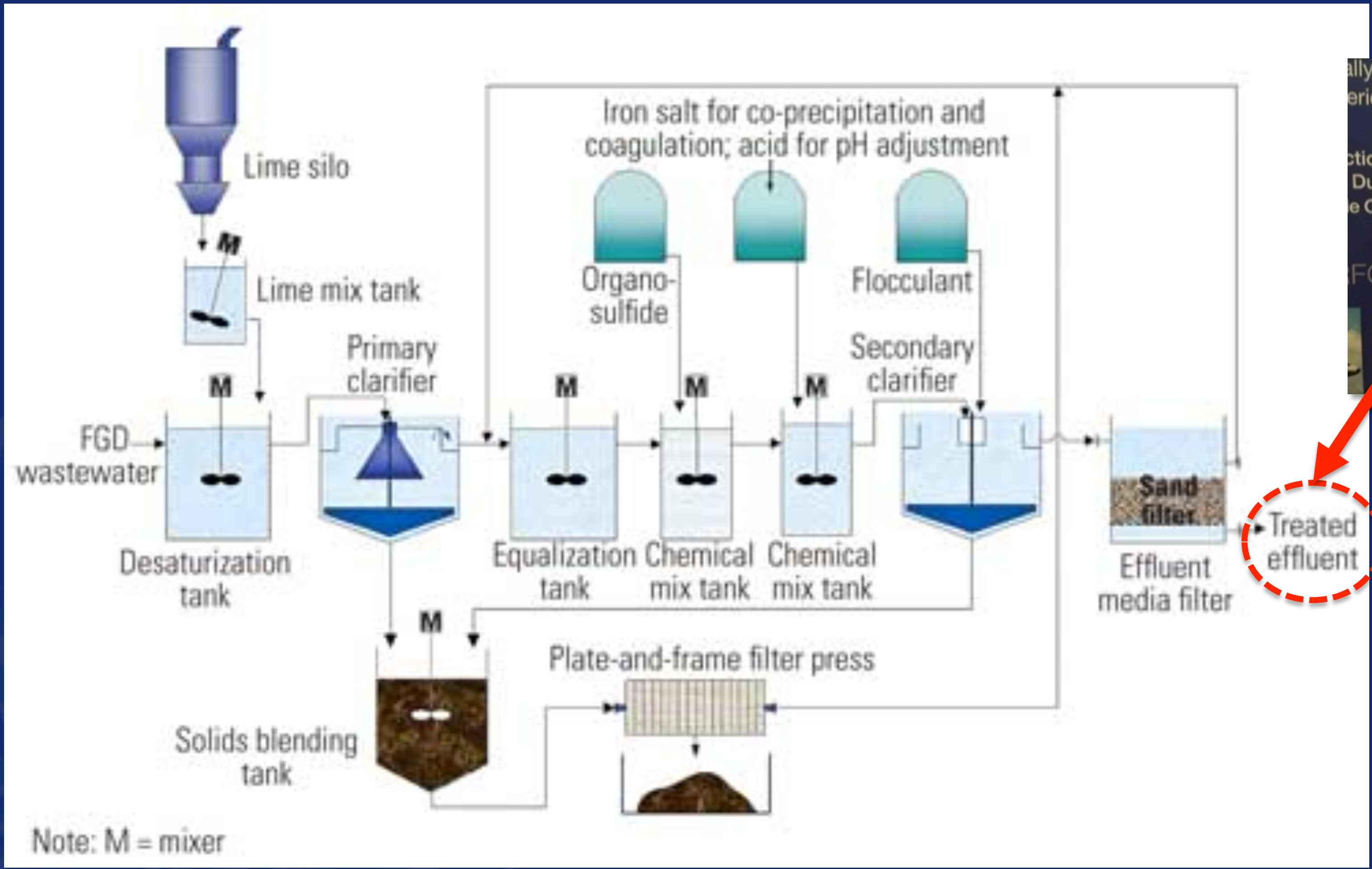
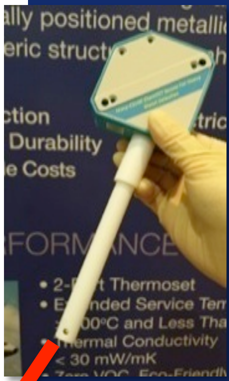
Example of Potential Use - Flue Gas Desulfurization (FGD) Wastewater Treatment





Potential use of RCRA 8 sensor to monitor the heavy metals of treated effluent for real-time close loop control

http://www.powermag.com/flue-gas-desulfurization-wastewater-treatment-primer/

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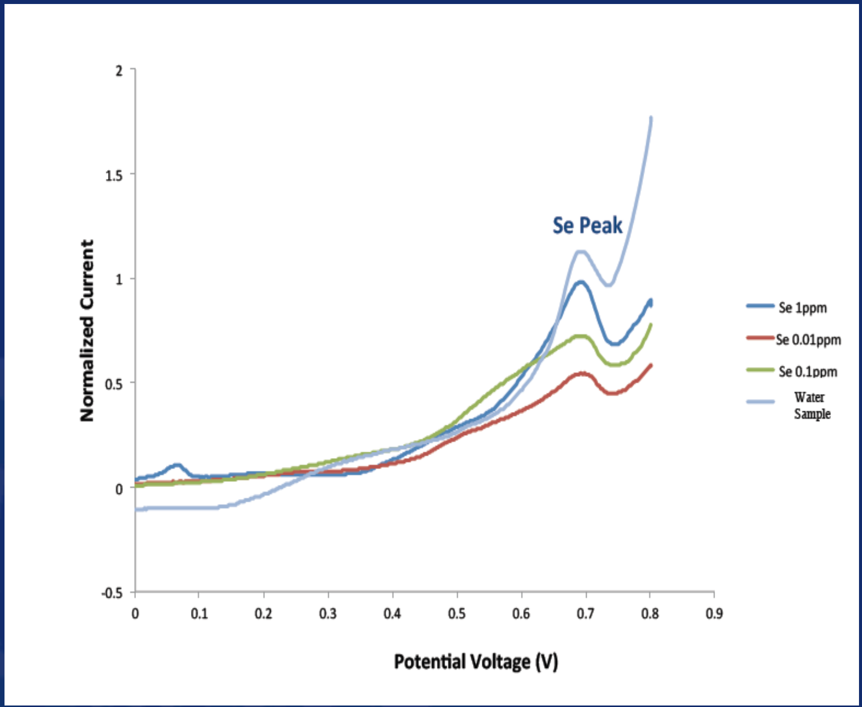
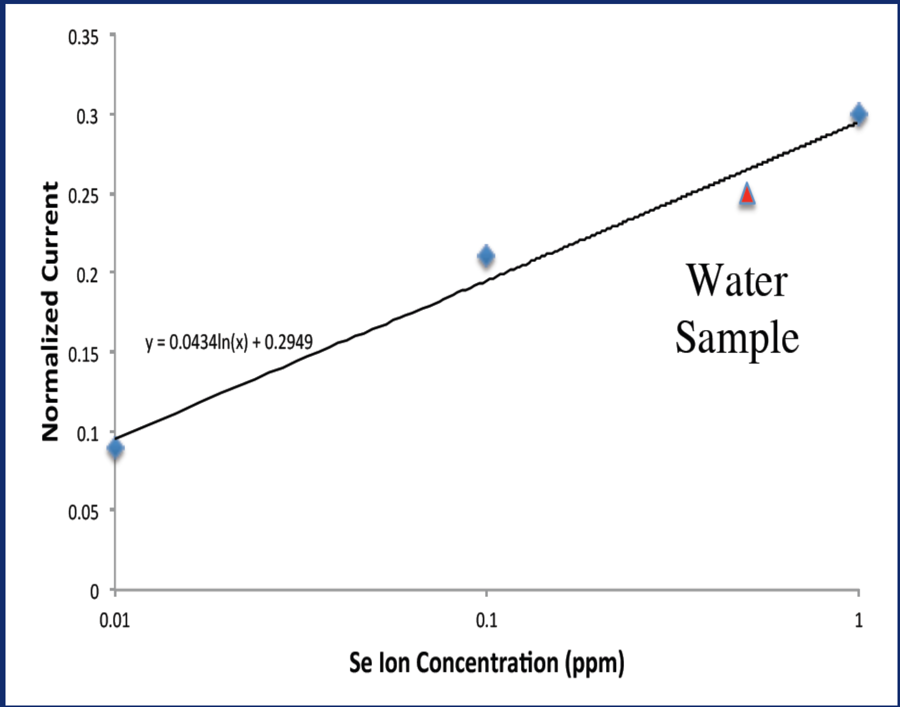
Stripping Voltammetry Enhanced ChemFET Sensor – Selenium Detection

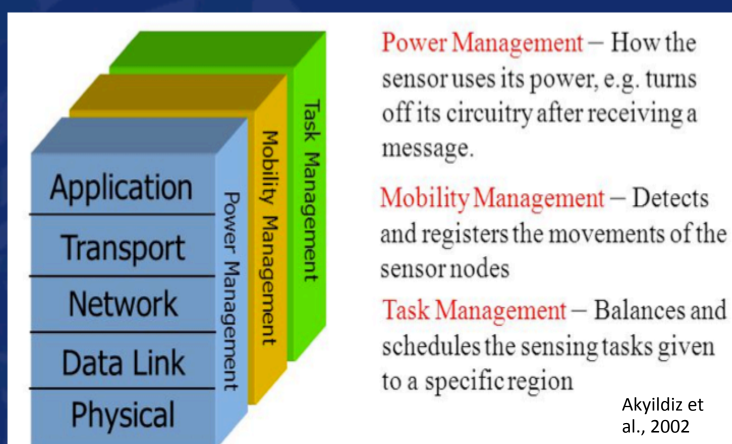




Testing results of a self assembled gold nanoparticles and selenium ionophore (in-house) functionalized chemical sensor in response to Se solutions. The selenium concentration from the sample is measured as 0.78ppm, which is in good agreement with the concentration level of 0.86ppm obtained from a third party laboratory

Wireless Sensor Modular Hardware

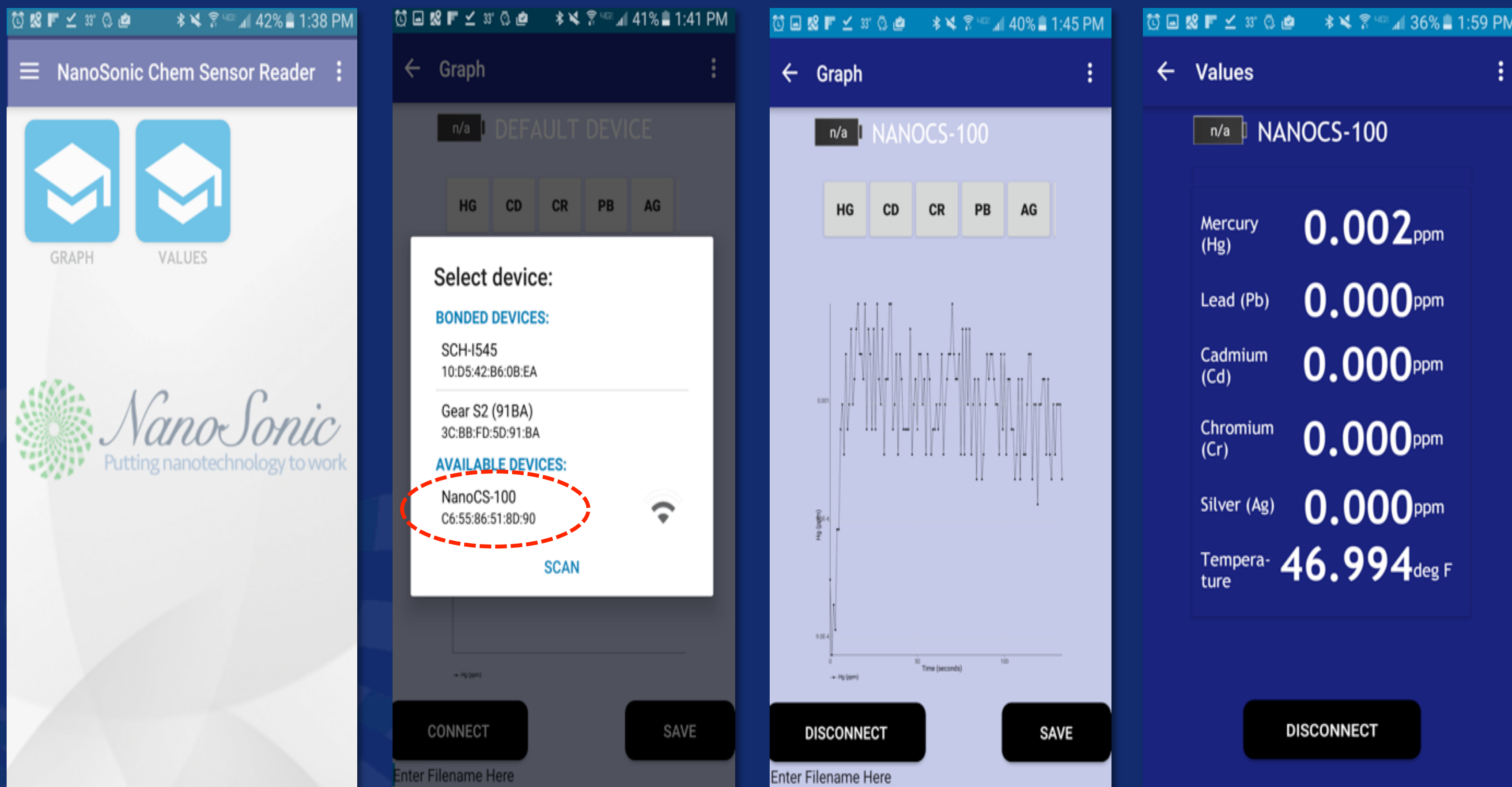
NanoSonic's Wireless Sensor Modular Hardware, "M" Shape Antenna Operates at 2.4 GHz band with 25 Possible Channels



WSN Protocol Stack

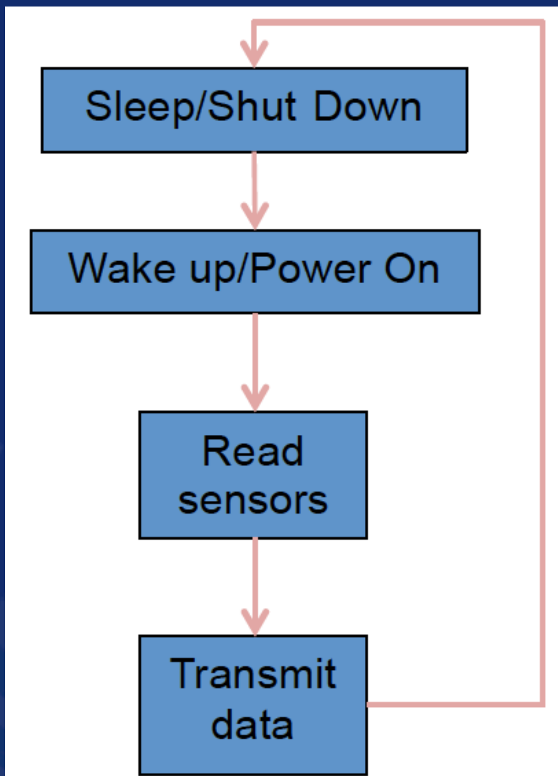
- ✓Sensing Unit
- ✓Processing Unit
- ✓Transceiver Unit
- ✓Power Unit
- ✓Location Finding System (optional)
- ✓Power Generator (optional)
- ✓Mobilizer (optional)

Tablet App to Read and Output Data



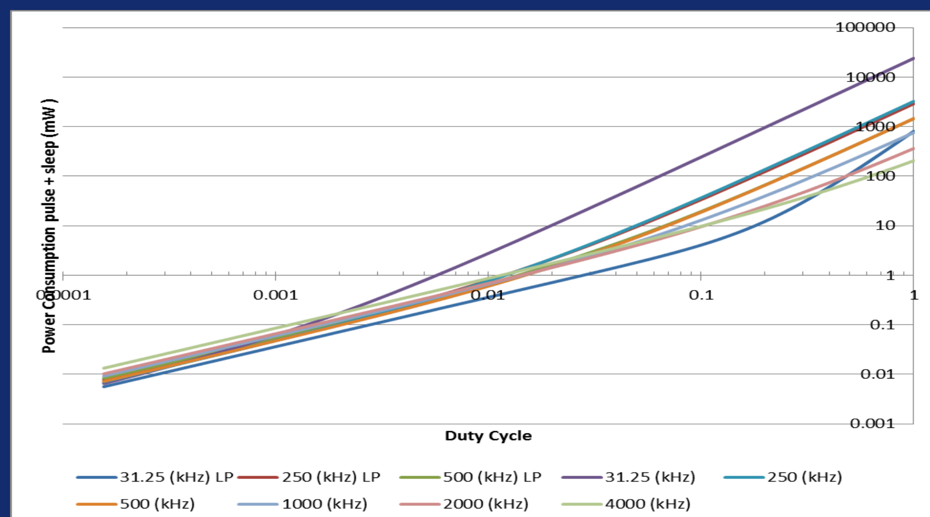
Low power tablet App with code to read, process and output the data wirelessly from the sensor to tablet.

Power Management of Wireless Sensor Network



Run time optimization for Power Consumption						
CLOCK	LP-INTO	HP-INTO	Sleep Time (ms)	Active Time (ms)	Current Sleep (mA)	Current Active (mA)
31.25 (kHz)	X		73000	30000	1.1	24.5
250 (kHz)	X		9600	3600	1.52	24.5
500 (kHz)	X		4800	1800	1.62	24.5
31.25 (kHz)		X	73000	30000	1.16	24.25
250 (kHz)		X	9200	4000	1.36	24.6
500 (kHz)		X	4800	1800	1.4	24.6
1000 (kHz)		X	2400	920	1.8	25
2000 (kHz)		X	1200	440	2	25
4000 (kHz)		X	560	240	2.6	26

Power-Availability Duty Cycle Allows for Extremely Low Average Power Consumption for Wireless Sensor Nodes.



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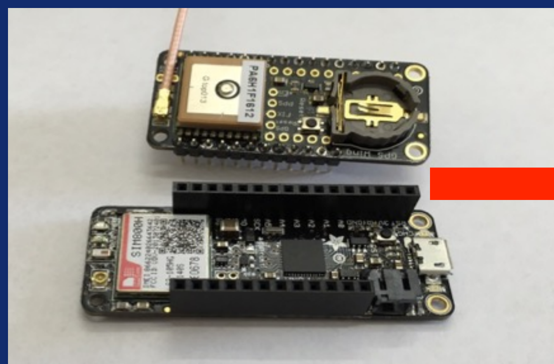
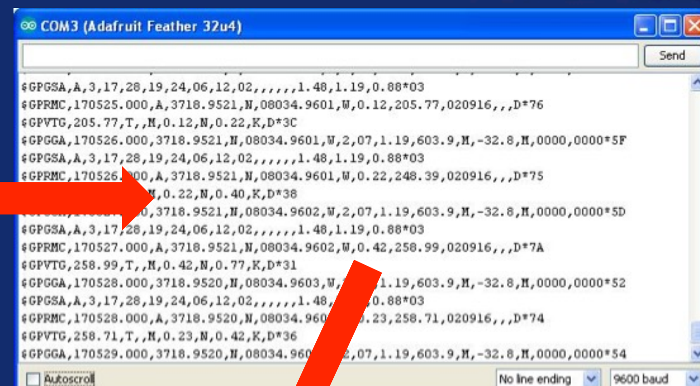
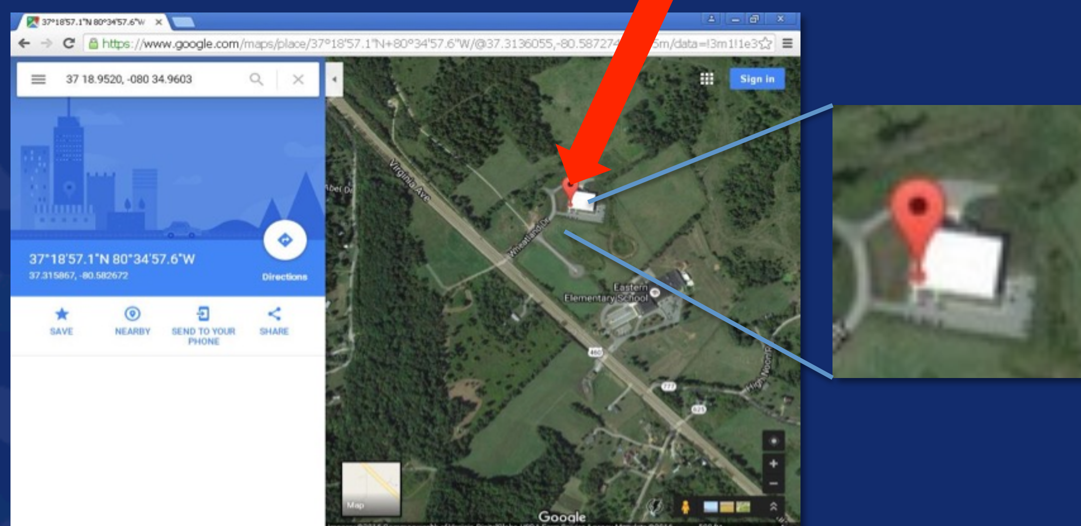
Demonstration of GPS Receiver to Determine Geographical Information



GPS hardware



Raw GPS data taken at the NanoSonic facility



Google maps image showing the location of the received coordinates

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Summary of NanoSonic's Integrated Sensor Probes

NanoSonic is developing a sensor probe that selectively measures the concentrations of all eight RCRA heavy metals in water with sensitivities better than 0.01 ppm.

Data can be transmitted wirelessly with multi-hop routing, or subsequently transmitted via the web.

Data refresh may be varied from seconds to days; rapid refresh means that emergencies can be detected.

Factor	NanoSonic Integrated RCRA 8 Probe	Current Testing Technology
• Price	Estimated $1000 initial probe unit price for continuous testing/monitoring	$100-$300+ per RCRA 8 test
• Field time hours	Siting and installation of probes only	Required for each sample taken
• Data availability	Near real-time (<10s)	Days to weeks from testing lab
• Alerts/warnings	Immediate	Not available until the next testing time
• Record keeping	Automatically transmit data wirelessly to a computer network	Requires periodic manual updates
• Remediation and litigation cost	Reduced due to immediate RCRA 8 data and alerts to concentration gradients	Higher due to lack of an alert/alarm capability

Acknowledgments

Thank You

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- NanoSonic DOE SBIR Team

Rick Claus, William Harrison, Hang Ruan, Echo Kang, Michelle Homer, Liz Gladwin
Lee Williams, Bill Rieger

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