Wireless Networked Sensors in Water for Heavy Metal Detection

2017 Crosscutting Research Project Review

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U.S. DEPARTMENT OF ENERGY

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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:

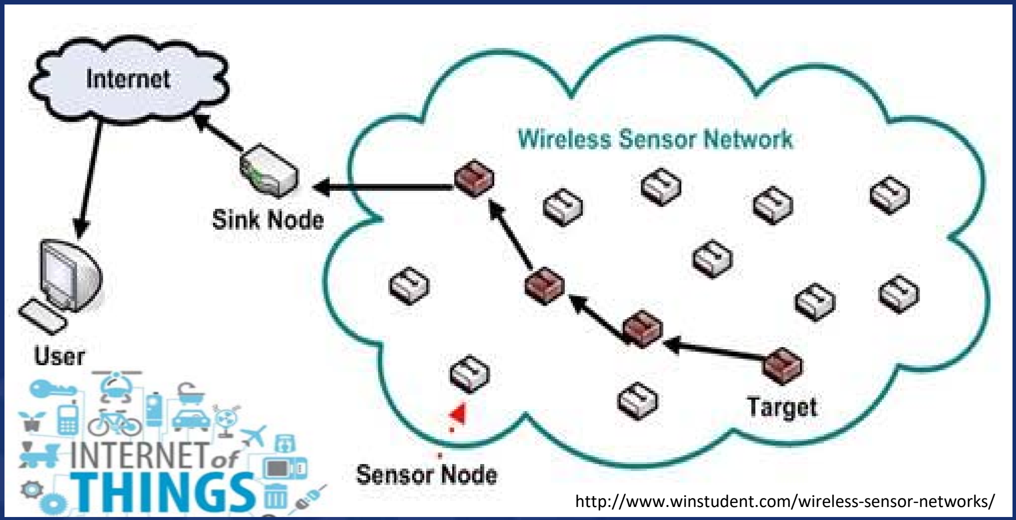
- Heavy metal selectivity: RCRA 8s (arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver)
- Heavy metal ion sensitivity: <0.01 ppm, with minimal cross-sensitivities
- Sensor element size: <(100 micron)^2
- Dynamic range: >40dB
- Frequency response: DC to >10kHz
- Operating temperature: -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

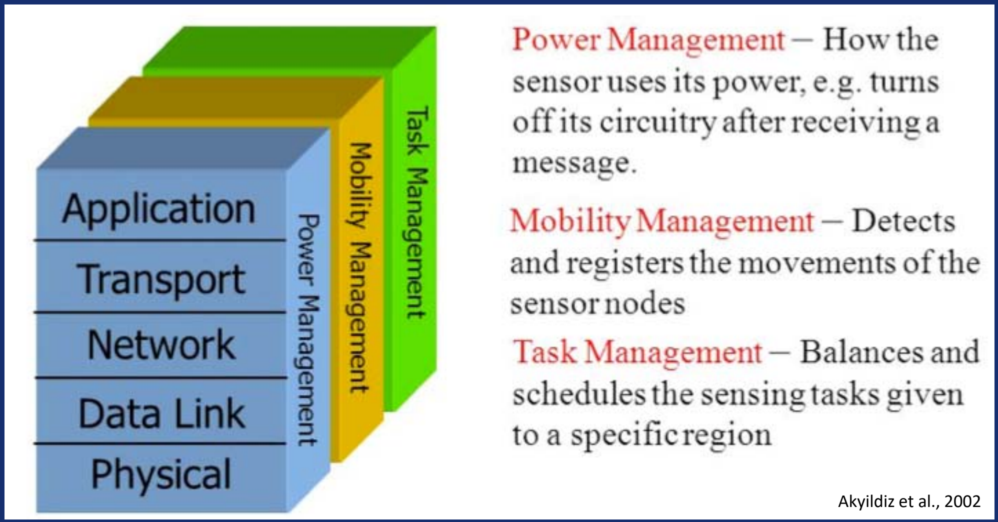
Outline

1. Program Overview
2. Technical Results
3. Summary

How to Build a Wireless Sensor Network?



WSN Communication Architecture



WSN Protocol Stack

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

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.

UAV as a transceiver

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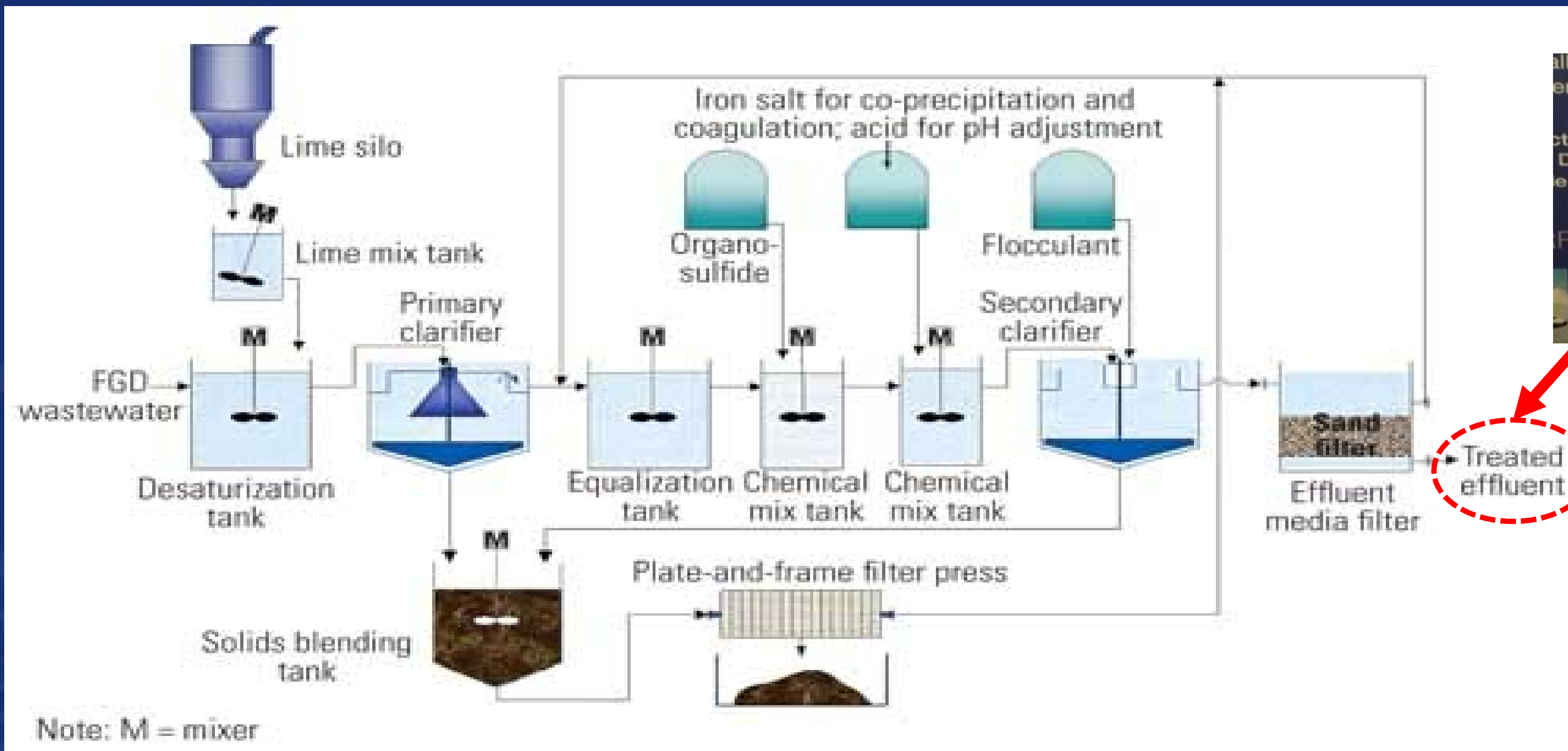
Advantages of NanoSonic's Integrated Sensor Probes

For power plant operators and other customers, NanoSonic's integrated sensor probes will

- ❑ reduce total RCRA 8 water analysis costs,
- ❑ reduce the number of hours of personnel field time required to obtain water samples,
- ❑ reduce the time required to obtain water quality data back from analysis laboratories,
- ❑ allow instantaneous alerts of significant increases in concentrations possibly indicative of unwanted events or failures,
- ❑ permit the automated record-keeping of historical water quality data, and
- ❑ potentially reduce the likelihood and cost of remediation efforts and litigation related to high concentrations

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

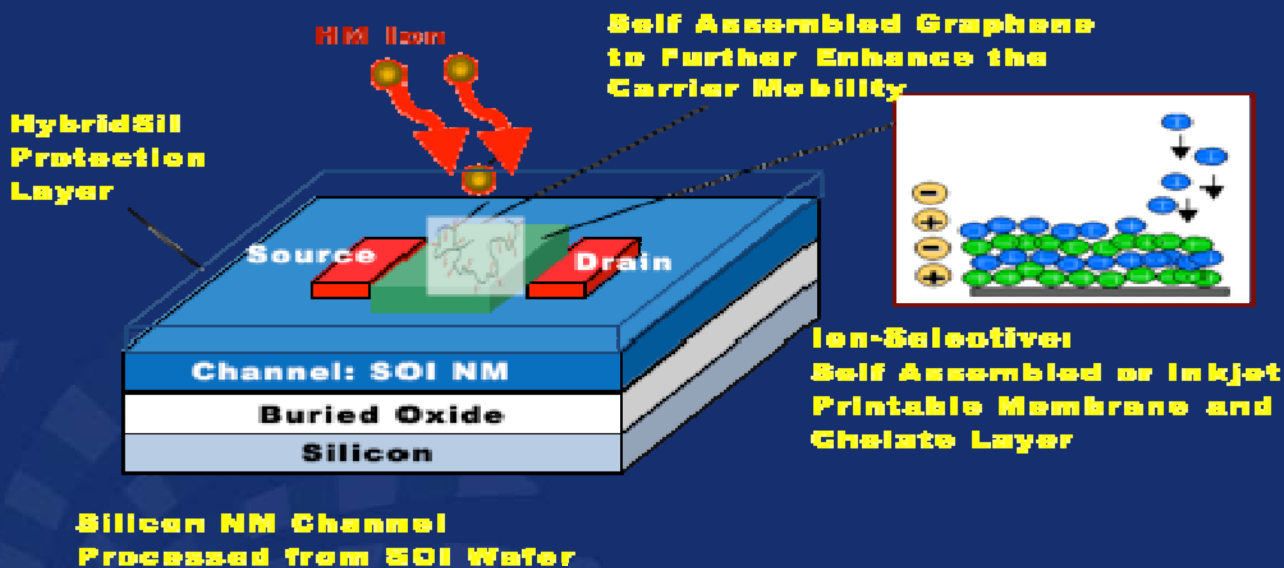
Example of Potential Use - Flue Gas Desulfurization (FGD) Wastewater Treatment

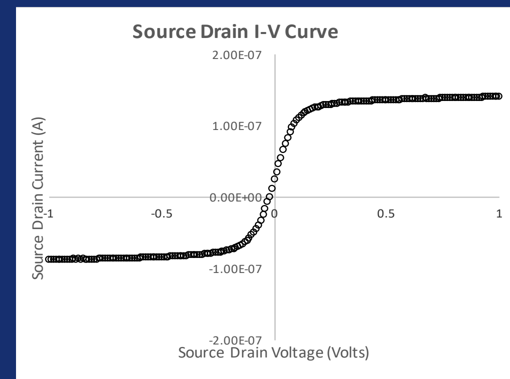


Potential use of RCRA 8 sensor to monitor the heavy metals of treated effluent for real-time close loop control

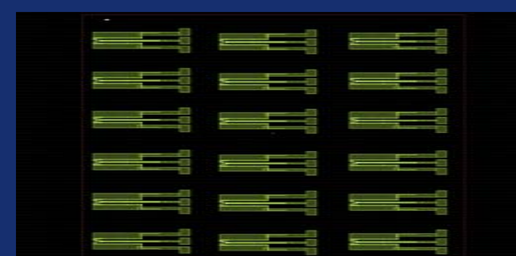
http://www.powermag.com/flue-gas-desulfurization-wastewater-treatment-primer/

Nanomembrane ChemFET Sensor Configuration





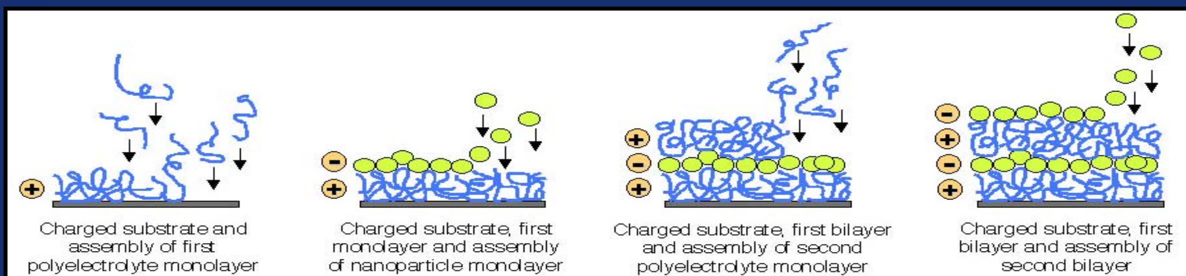
I-V characteristics of ChemFET



Mask Design

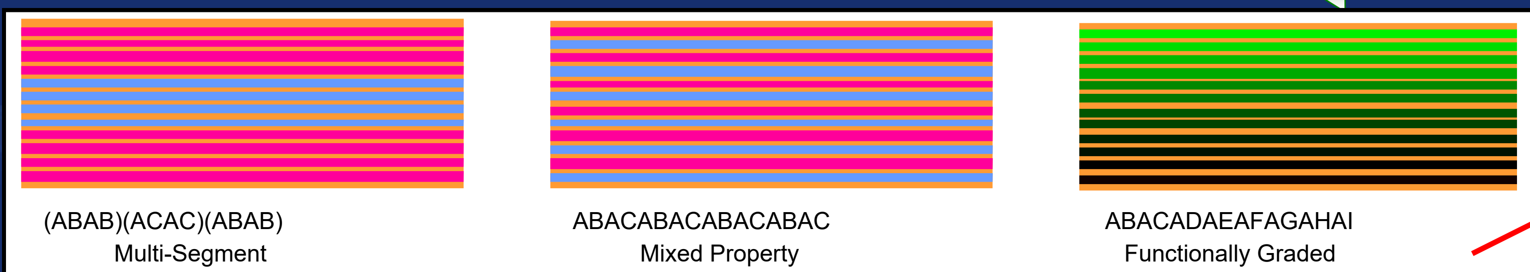
- ❑ High Carrier Mobility
- ❑ High Sensitivity
- ❑ High Selectivity
- ❑ Ultralightweight
- ❑ Ultraflexibility
- ❑ Array Configuration

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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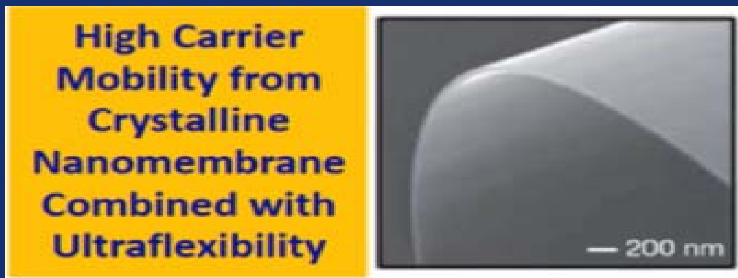
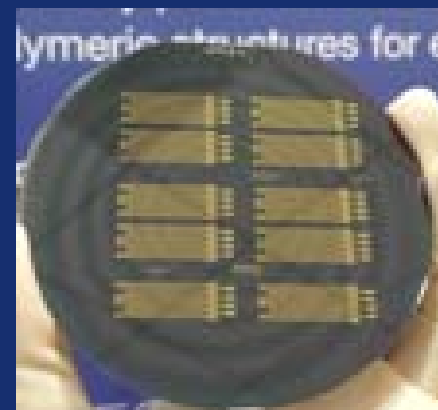
Silicon Nanomembrane



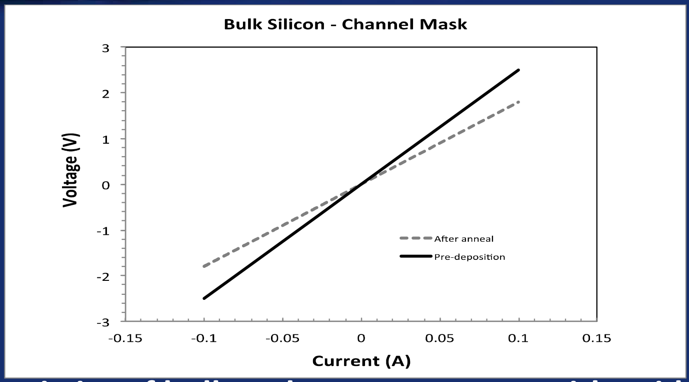
- Thin
- Flexible
- Can be strain engineered
- Transparent
- Transferable
- Bondable
- Stackable
- Conformable
- Patternable (wires, ribbons, tubes)

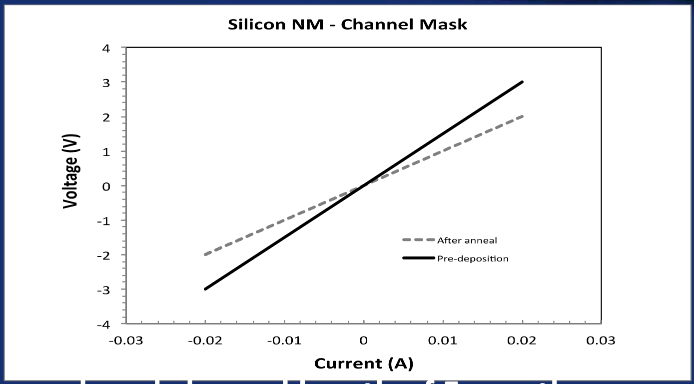


Nanomembrane–based ChemFET sensors

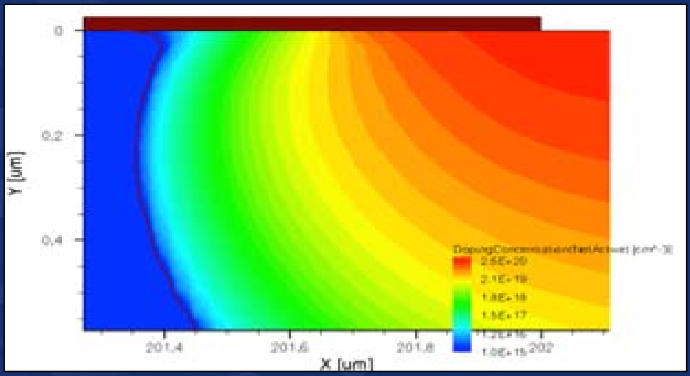
- 1974: Epitaxial $Ga_{1-x}Al_xAs$ (X>0.6) sacrificial layer for separating a $GaAs/Ga_{1-x}Al_xAs$ (x=0.3) from GaAs with HCl etchant
- 1987: Yablonocitch: spin on wax to strain film for efficient release, enable removal of high quality GaAs films as large as $0.8*2mm^2$ and as thin as 80nm
- 2004: 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**

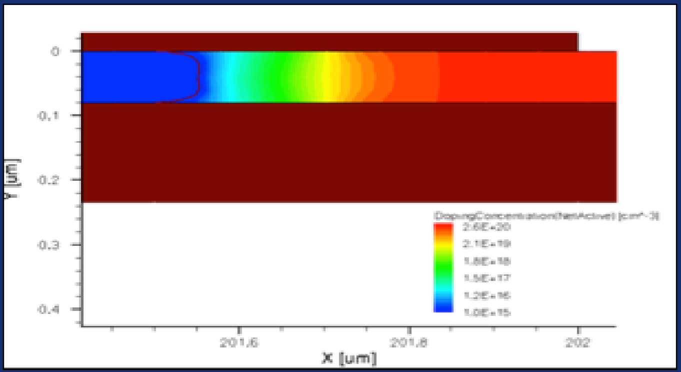
Process Monitoring During Fabrication





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



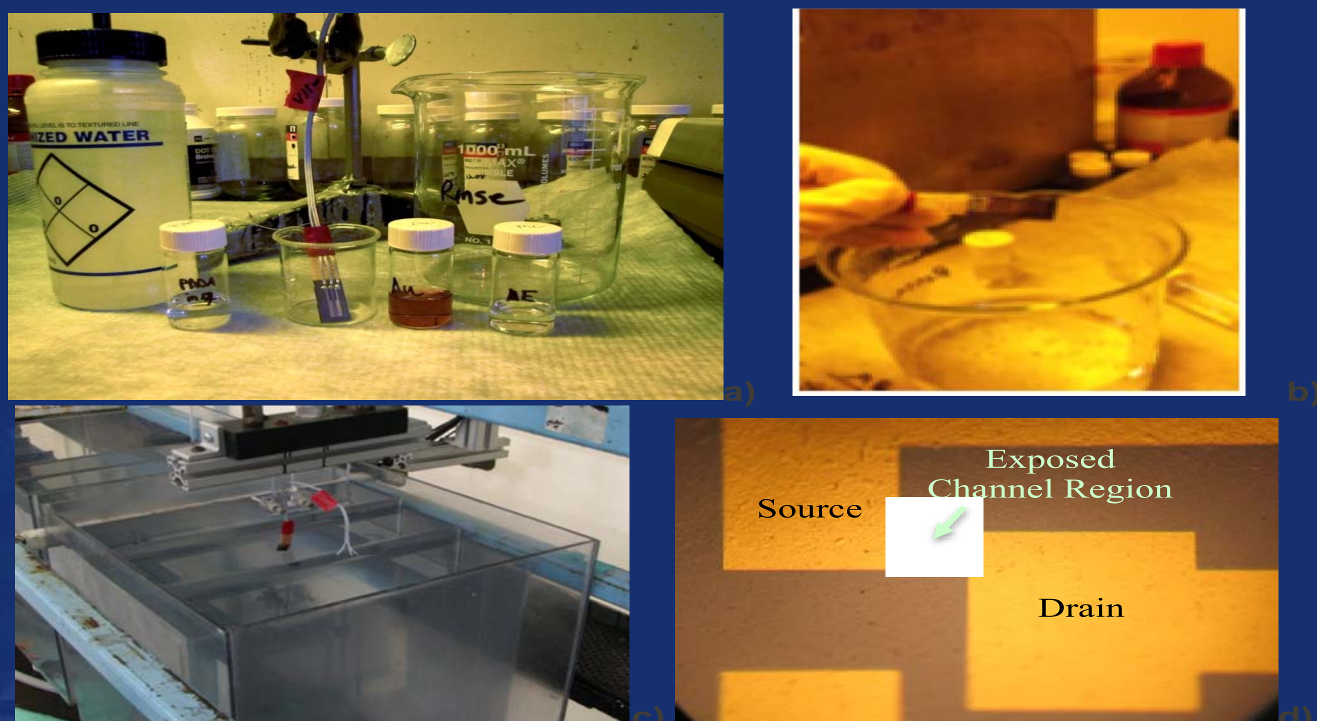


Phosphorus doping profile at the channel-drain side for bulk Si (left) and SOI nanomembranes (right) after source and drain doping. Oxide mask shown in dark red and buried oxide in SOI in dark red.

Standard Sensor Packages

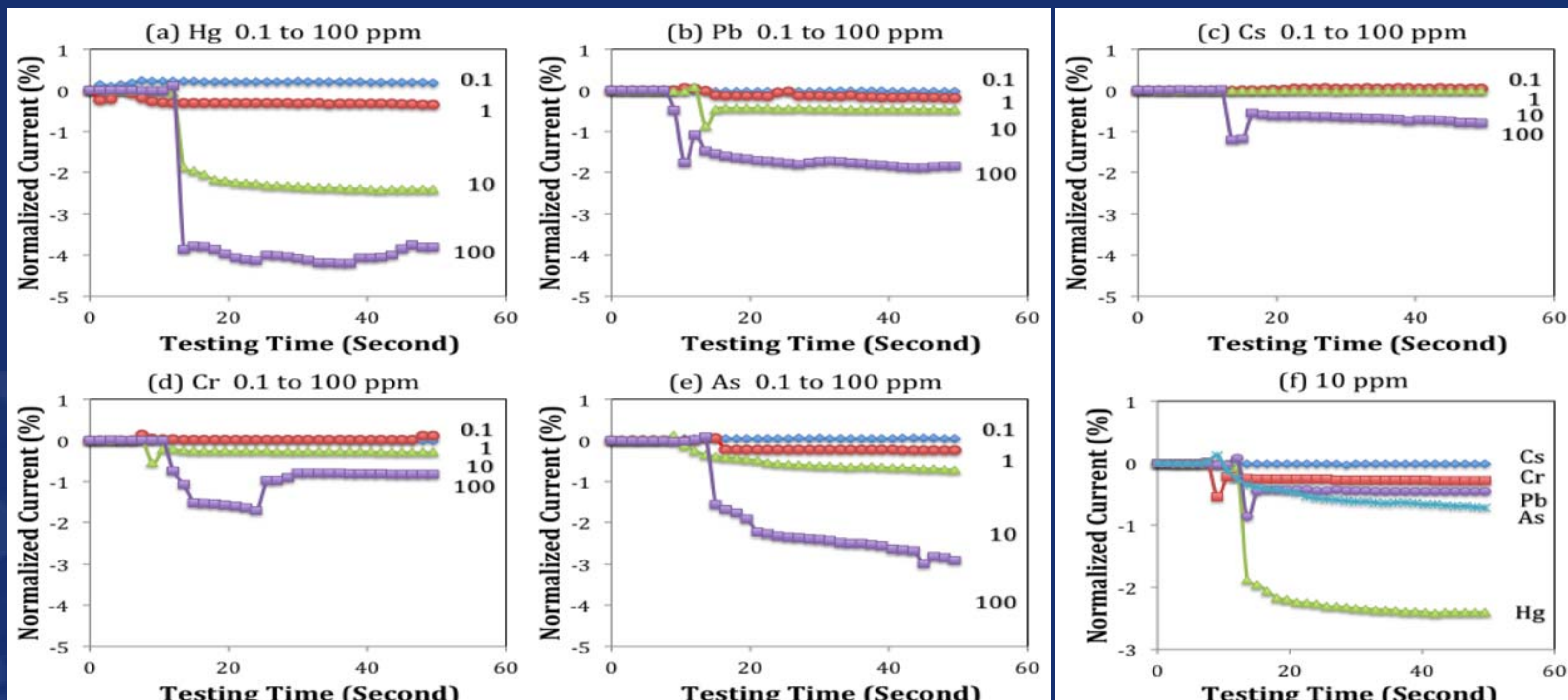
Standard Sensor Package Can be “Flowable” (Left), “Portable” (Center) and “Attachable” (Center Right) for Sensor Applications

Self-Assembly of Gold/Thiol Functionalization Layers



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.

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.

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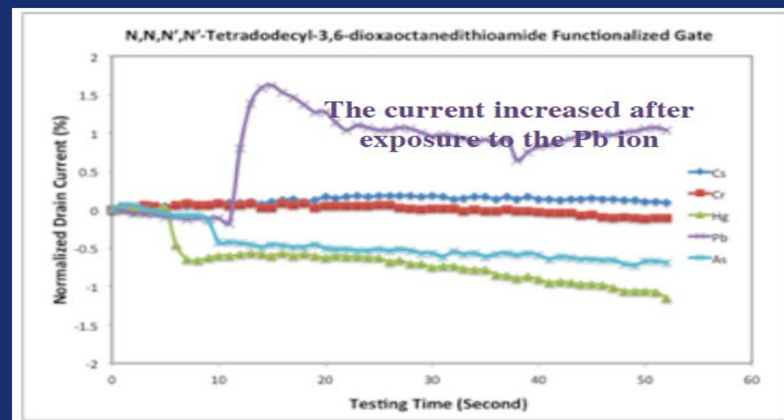
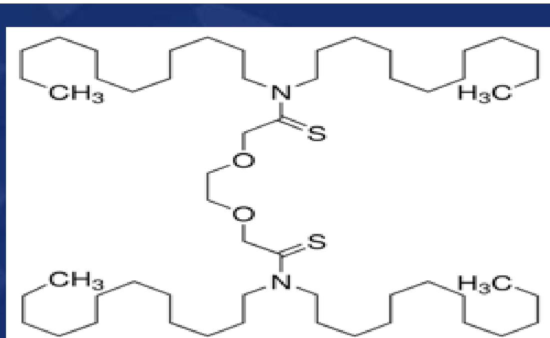
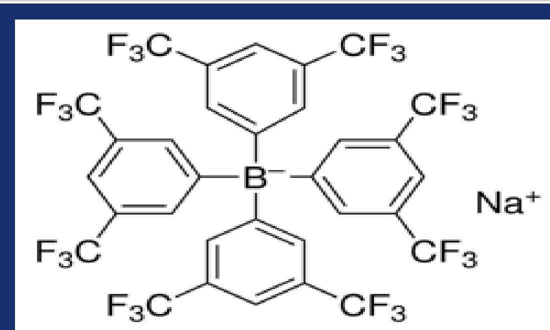
Modification Example #2: : Sensor Modification for Lead Ion Selectivity

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



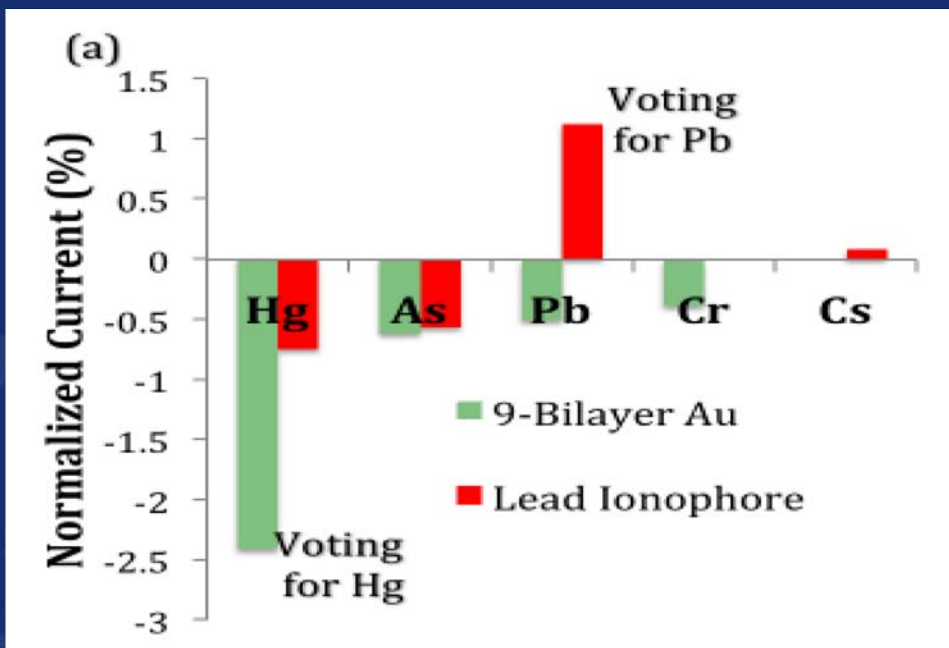


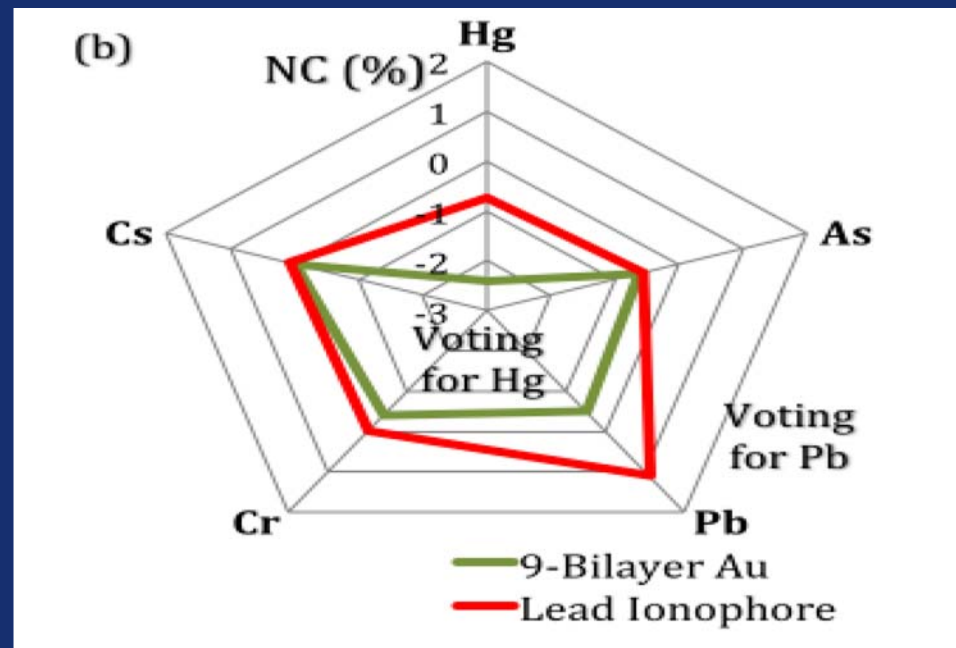
N,N,N′,N′-Tetradodecyl-3,6-dioxaoctanedithioamide



Sodium tetrakis(4-fluorophenyl)borate dihydrate

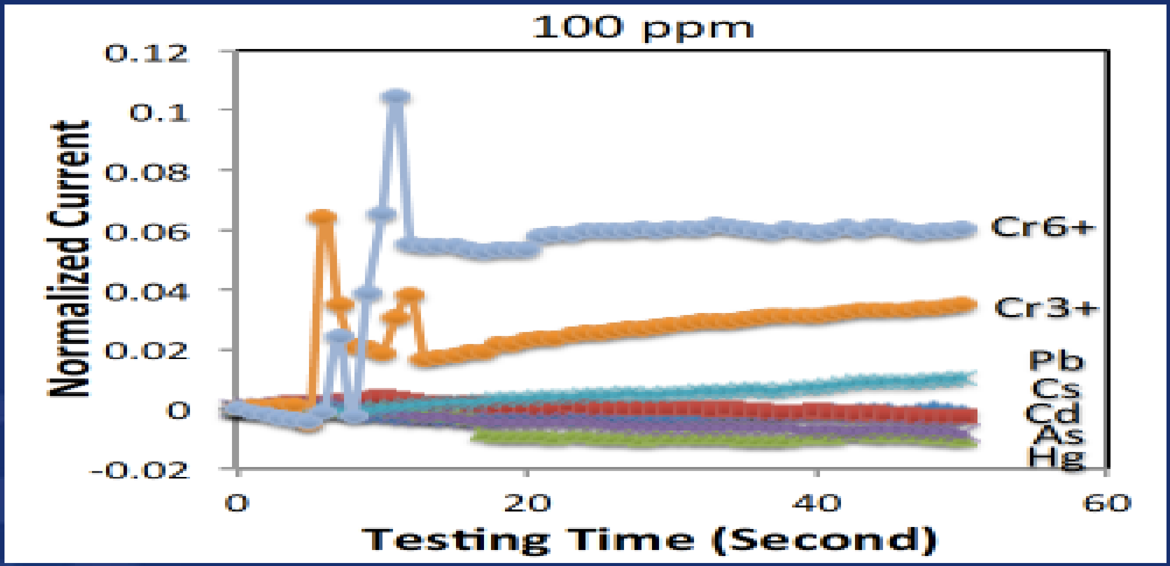
Multi-Target Selectivity Results for Self Assembled Au Sensor and Lead Ionophore Sensor





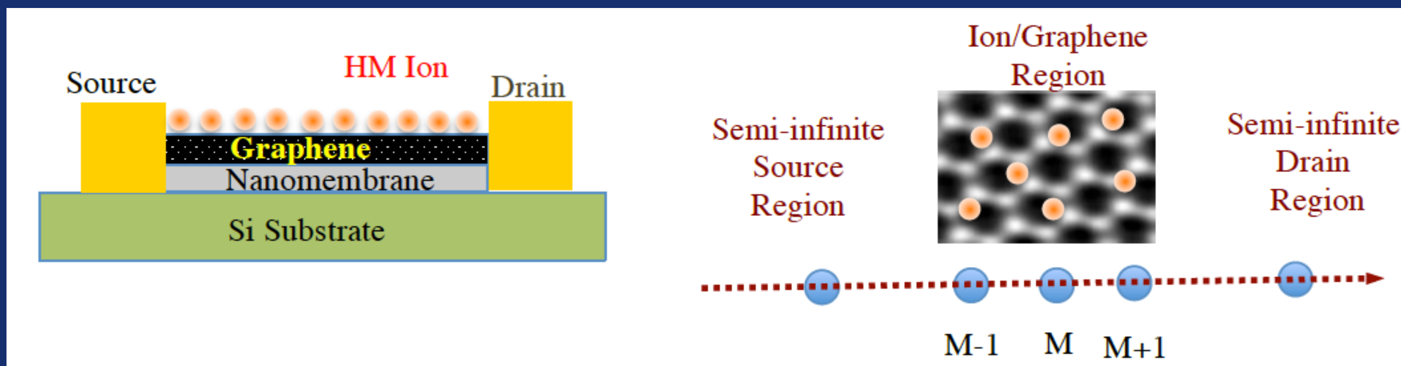
Cross sensitivity results with Bar Plot (a) and Radar Plot (b) for self assembled Au sensor and Lead ionophore sensor.

Modification Example #3: Hybrid ESA/Au and ETH 5435 Functionalization

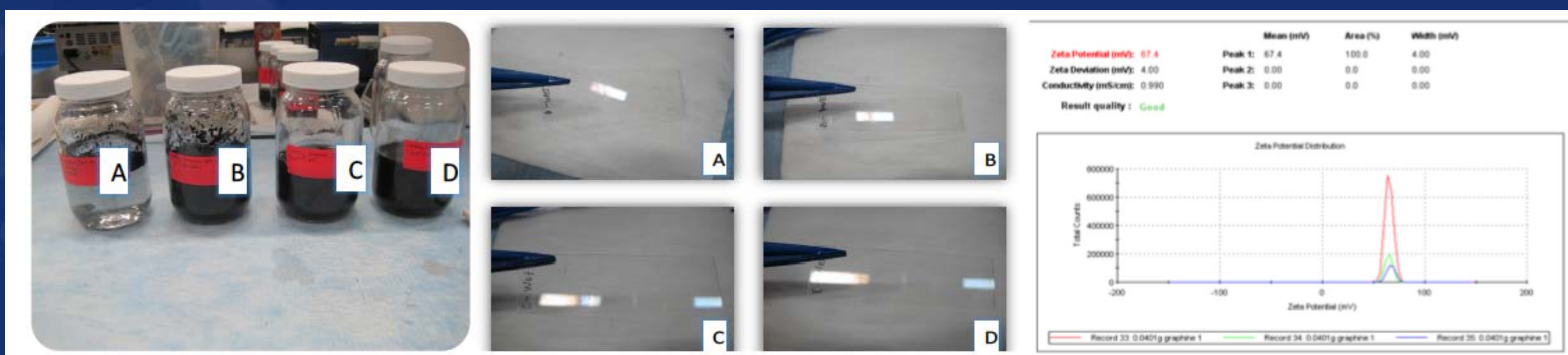


Time dependent response of the drain current for the hybrid ESA/Au and ETH 5435 functionalized ChemFET sensor. Noted that the responses for the Cr^{3+} and Cr^{6+}, with the normalized current change of 2.9% for Cr^{3+} and 5.9% for Cr^{6+}, are significantly higher than for other ions such as Cs, Cd, Hg, Pb and As.

Improvement #1: Self-Assembled Graphene for Nanomembrane-based ChemFET

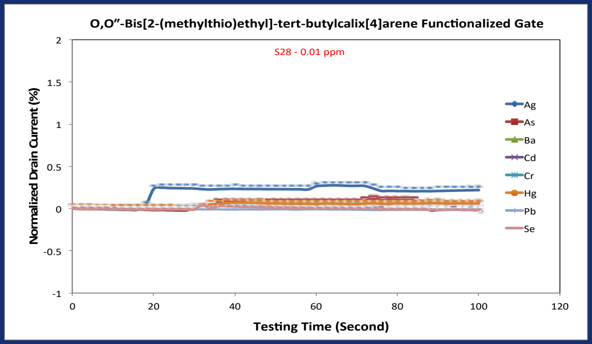


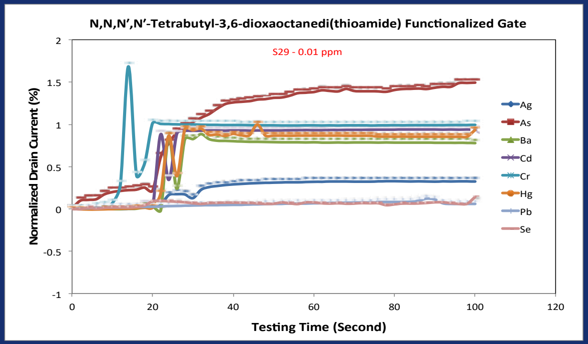
Structure of Graphene Enhanced ChemFET (left) and Quasi-1D nonequilibrium Green's function Model (right)

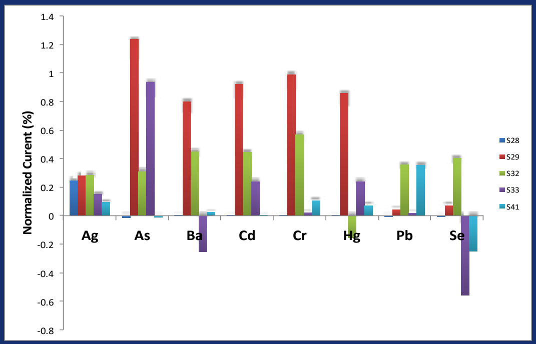


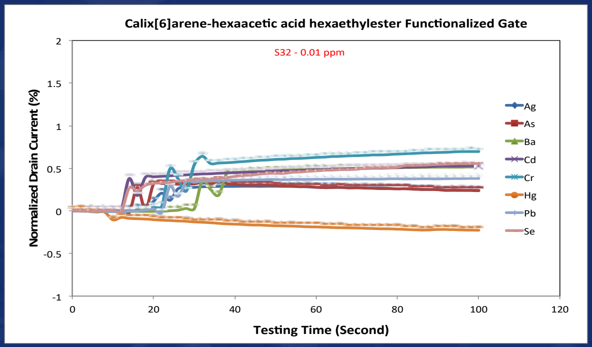
Graphene Precursors for Self Assembly

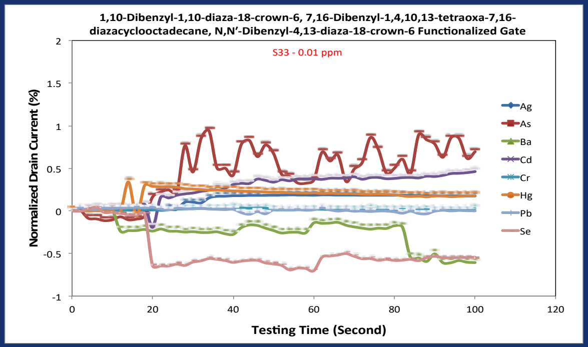
Multiple Selective Functionalizations on Graphene Improved Sensors

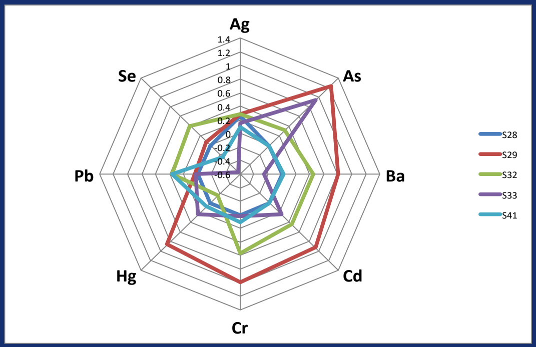












Multiple sensor elements in an array can be used to simultaneously detect all RCRA 8 heavy metal targets.

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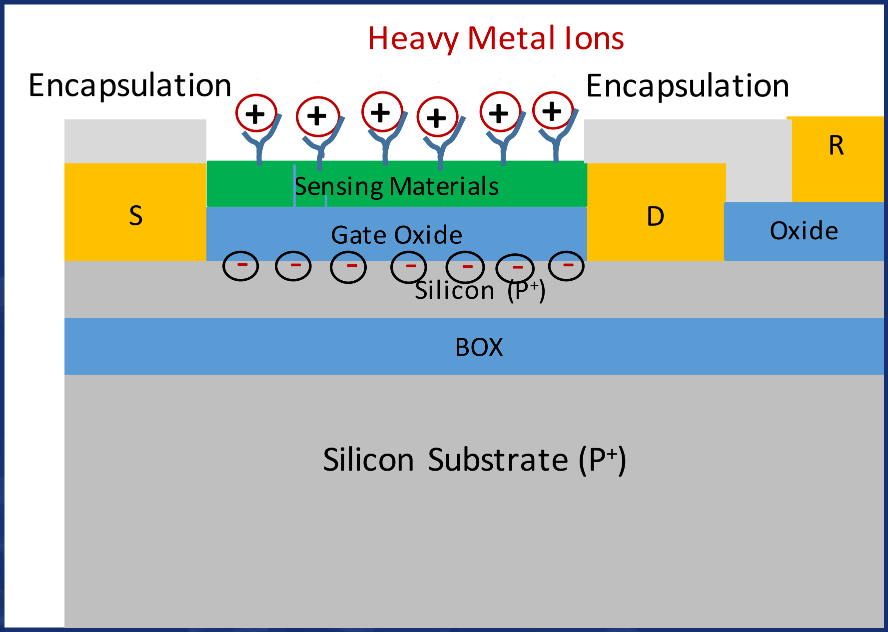
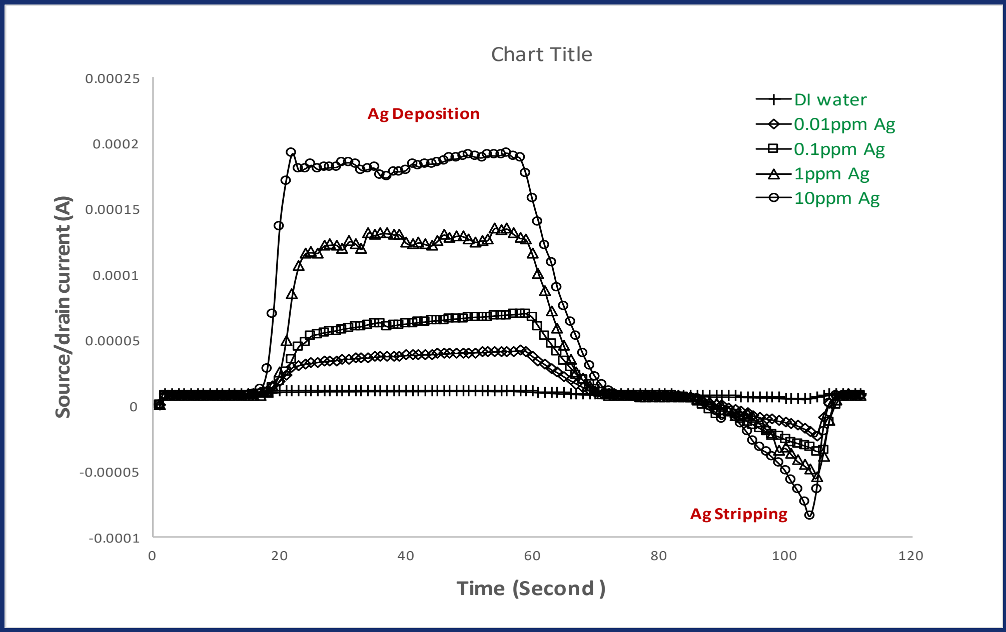
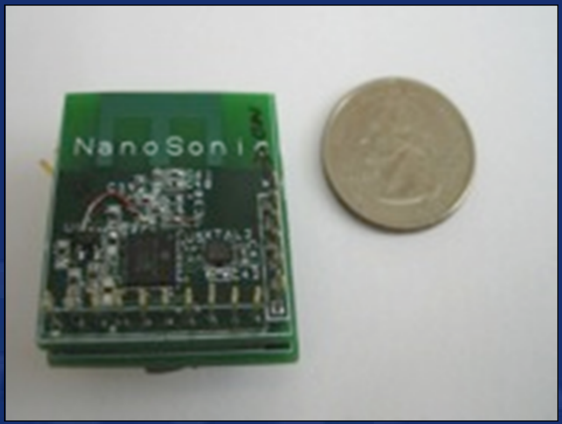
Improvement #2: Stripping Voltammetry Enhanced ChemFET Sensor

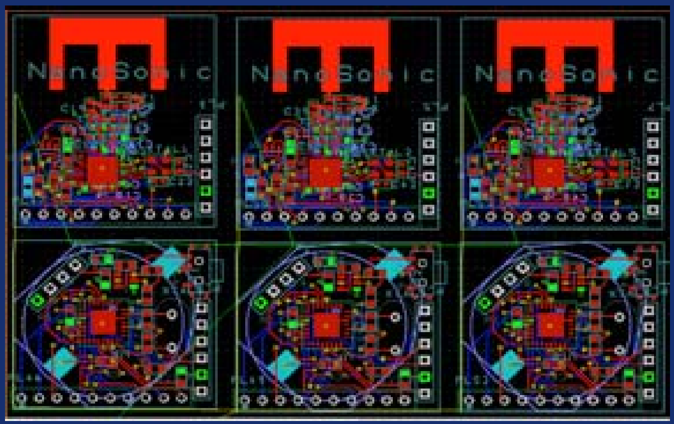




Self assembled Au/cysteine functionalized ChemFET sensor after exposure to different concentration of Ag ion solutions

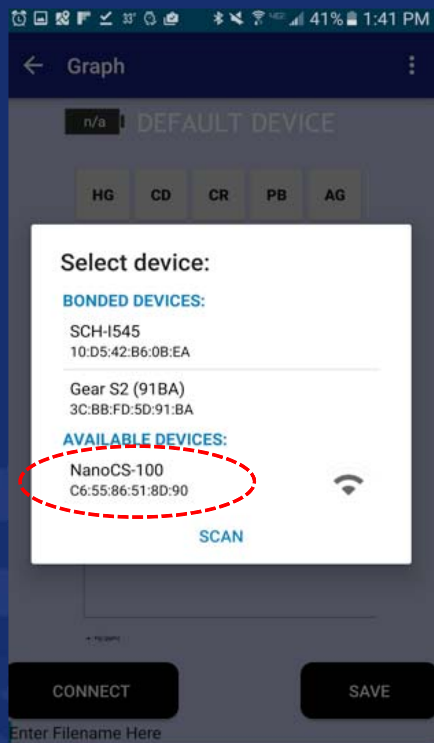
Wireless Sensor Modular Hardware

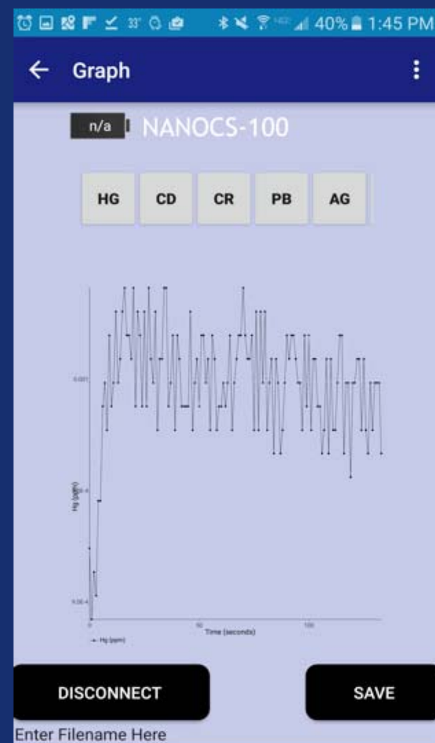




NanoSonic's Wireless Sensor Modular Hardware, "M" Shape Antenna Operates at 2.4 GHz band with 25 Possible Channels

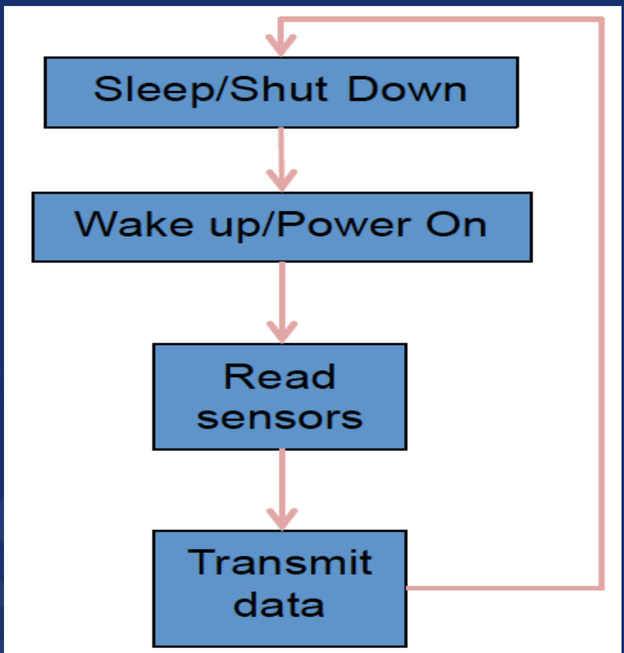
Tablet App to Read and Output Data



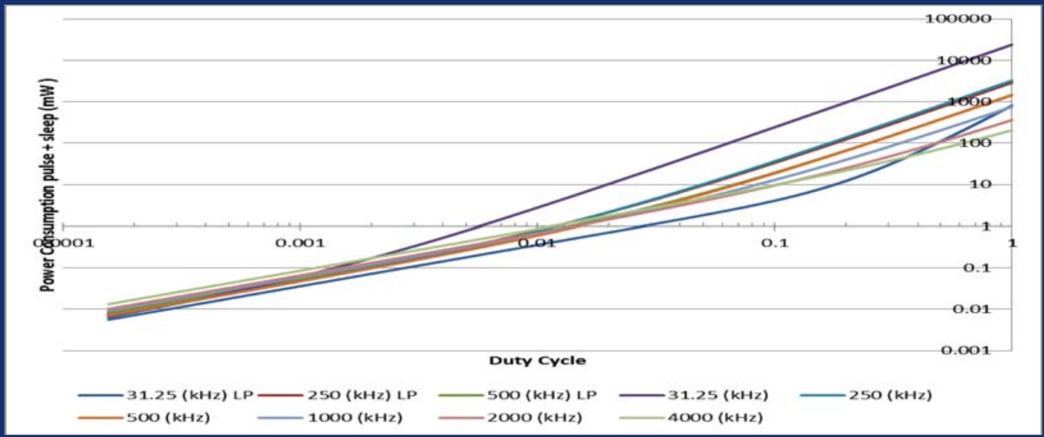


Low power tablet App with code to read, process and output the data wirelessly from the sensor to tablet.

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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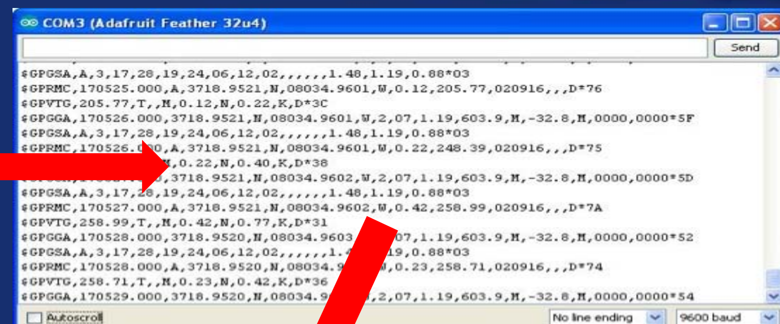
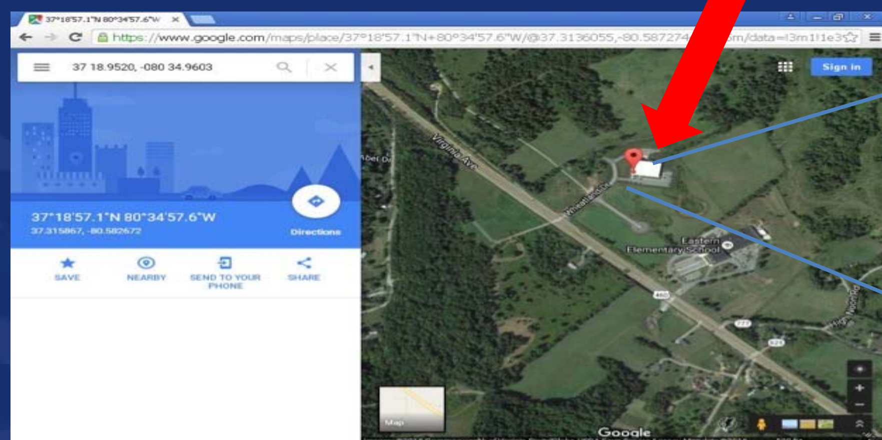
Demonstration of GPS Receiver to Determine Geographical Information

GPS hardware



Raw GPS data taken at the NanoSonic facility



Google maps image showing the location of the received coordinates

DOE SOW vs. Progress Status

	Phase II Program Task	Quarter 1	2	3	4	5	6	7	8	Projected Percent Complete	Actual Percent Complete
0	Kickoff meeting with TPOC	X								100%	100%
1	Develop improved understanding of sensor operation through analysis and testing	X	X	X	X					50%	60%
2	Further design polymer and semiconductor chemistries to improve sensor performance		X	X	X	X				50%	60%
3	Develop means to compensate for cross-sensitivity effects		X	X	X	X	X			20%	40%
4	Standardize sensor design and fabrication			X	X	X	X			0%	20%
5	Develop simple means of sensor calibration				X	X	X	X		0%	20%
6	Develop simple data acquisition interface				X	X	X			0%	20%
7	Use developed sensors through piggyback research tests with Phase II partners			X	X	X	X	X	X	0%	20%
8	Field Test Nano-CS RCRA 8 Sensor Probes at Steam-Electric Power Plants and Other Sites			X	X	X	X	X	X	0%	20%
9	Develop product transition plan with the manufacture partner				X	X	X	X	X	0%	10%

Program Summary

NanoSonic has developed 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.

NanoSonic is partnering with a water quality survey company, a major U.S. manufacturer of sensors and environmental controls, a regional Water Authority, and a major electric power company.

Phase II testing would be performed at regional power plants and other sites.

Acknowledgments

Thank You

- DOE – Dr. Jessica Mullen and Dr. Bob Romanosky

and

- NanoSonic DOE SBIR Team

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